

Chapter 229

APPLICATIONS OF TETRAVALENT CERIUM COMPOUNDS

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Abbreviations

atm	atmosphere	HOPO	hydroxypyridonate
BNPP	bis-(<i>p</i> -nitrophenyl)phosphate	HTPA	1,3-amino-2-hydroxypropane- <i>N,N,N',N''</i> -tetraacetic acid
bpy	2,2'-bipyridine	HTXA	5-methyl-2-hydroxy-1,3-xylene- α,α -diamine- <i>N,N,N',N''</i> -tetraacetic acid
bpyO ₂	2,2'-bipyridine <i>N,N'</i> -oxide	<i>t</i> -PrOH	<i>iso</i> -propanol
Bu	butyl	Me	methyl
BZ	Belousov-Zhabotinsky	MMTr	monomethoxytrityl
CAN	ammonium hexanitratocerate(IV)	NBS	<i>N</i> -bromosuccinimide
CAS	ammonium cerium(IV) sulfate	NHPI	<i>N</i> -hydroxy phthalimide
CPC	pyridinium hexachlorocerate(IV)	PCB	polychlorobenzene
CPN	pyridinium hexanitratocerate(IV)	Phe	phenyl
CTAN	tetra- <i>n</i> -butylammonium hexanitratocerate(IV)	phen	1,10-phenanthroline, <i>o</i> -phenanthroline
CTEAN	triethylammonium hexanitratocerate(IV)	RT	room temperature
CTH	cerium(IV) trihydroxy hydroperoxide	SAP	superabsorbent polymer
DCM	dichloromethane	SDS	sodium dodecylsulfate
DMF	<i>N,N</i> -dimethylformamide	TBHP	<i>tert</i> -butyl hydroperoxide
DMP	dimethyl phosphate	TBMS	<i>tert</i> -butyldimethylsilyl
dmsO	dimethylsulfoxide (as ligand)	<i>t</i> -Boc	<i>tert</i> -butoxycarbonyl
DMSO	dimethylsulfoxide (as solvent)	tdpo	tris(dimethylamido)phosphine oxide
Et	ethyl	TEMPO	2,2,6,6-tetramethylpiperidinyl-1-oxyl
EXAFS	extended X-ray absorption fine structure	TFA	trifluoroacetic acid
FKM	Field, Kőrös, and Noyes	THF	tetrahydrofuran
Gy	gray (unit of absorbed dose)	THP	tetrahydropyranyl
HEPES	<i>N'</i> -(2-hydroxyethyl)piperazine- <i>N</i> -ethanesulfonic acid	tpo	triphenylphosphine oxide
H ₂ ETAM	<i>N,N'</i> -diethyl-2,3-dihydroxyterephthalamide	TRIS	tris(hydroxymethyl)methylamine
HNPP	2-hydroxypropyl (<i>p</i> -nitrophenyl) phosphate	TTCPP	tris[tetratratocerium(IV)]paraperiodate
		XANES	X-ray absorption near-edge structure

1. Introduction

Cerium is the most abundant element of the rare earths. On average the Earth's crust contains 66 ppm of cerium (=66 g per ton), a value that is very comparable with the abundance of copper (68 ppm) (Emsley, 1991). Few people know that there are on Earth larger resources of cerium than of other more popular elements like cobalt (29 ppm), lead (13 ppm), tin (2.1 ppm), silver (0.08 ppm) or gold (0.004 ppm). A special property of cerium is that it has a stable tetravalent oxidation state besides the trivalent state which is so common for the rare earths. Although the tetravalent oxidation state is also known for solid state compounds of praseodymium and terbium, cerium is the only rare-earth element that has a stable tetravalent oxidation state in solution. Many of the applications of cerium are based on the one-electron Ce⁴⁺/Ce³⁺ redox couple.

The aim of this chapter is to give an overview of the applications of tetravalent cerium compounds in solution; not only their well-known use as reagents in organic synthesis and as oxidizing agents for redox titrations (cerimetry), but also their role in oscillating reactions, their application in biochemical research will be covered, as well as more exotic applications. The message is that cerium(IV) reagents are not restricted to ammonium hexanitratocerate(IV), which is better known as ceric ammonium nitrate or as CAN for short. When reading the literature, one could get the impression that there are no other cerium(IV)-containing reagents besides CAN (Ho, 1973; Nair et al., 1997, 2004; Hwu and King, 2001). For this reason, this chapter gives a detailed description of the cerium(IV) salts that are used in organic reactions. However all organic reactions that can be mediated by cerium(IV) salts will not be described here. This would take up too much space, given that CAN is very often used as an oxidizing reagent. The interested reader will be given a feeling of what is possible with cerium(IV) reagents in organic synthesis. More examples can be found in earlier reviews (Ho, 1973; Kagan and Namy, 1986; Molander, 1992; Imamoto, 1994; Nair et al., 1997, 2004; Hwu and King, 2001). This review will not focus on applications of cerium dioxide (ceria), because its applications in heterogeneous catalysis have been reviewed elsewhere (Trovarelli, 2002). For an overview of applications of cerium in chemical technology, the reader is referred to a booklet written by Kilbourn (Kilbourn, 1992). Several chapters in this handbook have been devoted to different aspects of cerium. These include chapter 20 on valence changes (Jayaraman, 1979), chapter 43 on catalysis (Netzer and Bertel, 1982), chapter 57 on reagents for organic synthesis (Long, 1986), chapter 66 on photoemission (Lynch and Weaver, 1988), chapter 98 on low-temperature behavior of cerium compounds (Sereni, 1991), chapters 102 and 122 on redox reactions (Nash and Sullivan, 1991; Morss, 1994), chapters 103 and 127 on hydrolysis (Rizkalla and Chopin, 1991, 1994), chapter 105 on valence fluctuations (Loewenhaupt and Fischer, 1993), chapter 125 on oxides (Haire and Eyring, 1994), chapter 184 on ceria-containing three-way catalysts (Kašpar et al., 2000), and chapter 222 on DNA and RNA hydrolysis (Komiyama, 2005). The terms "*cerous*" and "*ceric*" are often used, respectively, for the cerium ion in its lower oxidation state (+3) and in its higher oxidation state (+4). The terms *cerium(III)* instead of *cerous*, and *cerium(IV)* instead of *ceric* will be consistently used in this review.

2. Redox properties of cerium(IV)

The characteristic oxidation state for the rare earth elements is +3 (Nash and Sullivan, 1991). The chemistry of the rare earths is largely determined by this oxidation state. There are only few examples of stable rare-earth ions in other oxidation states. One example is tetravalent cerium, cerium(IV). The stability of the +4 oxidation state can be attributed to the empty 4f-shell in the [Xe]4f⁰ electronic configuration of Ce⁴⁺.

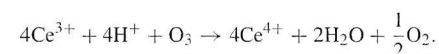
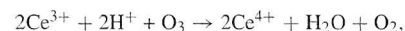
In acidic medium, cerium(IV) is a very strong one-electron oxidant and its oxidizing power is comparable to that of lead(IV) oxide or that of manganese(III) salts. The first detailed study of the redox potential of the Ce⁴⁺/Ce³⁺ couple under carefully controlled conditions in sulfuric acid was published by Kunz (1931). Noyes and Garner (1936) studied the redox potential of the same redox couple in nitric acid. The redox potential of the Ce⁴⁺/Ce³⁺ couple depends very much on the nature and the concentration of the acid. For instance, the redox potential is +1.28 V in 1 M HCl, +1.44 V in 1 M H₂SO₄, +1.61 V in 1 M HNO₃, +1.70 V in 1 M HClO₄, and it is as high as +1.87 V in 8 M HClO₄ (Smith and Getz, 1938; Wadsworth et al., 1957). The redox potential thus increases in the order hydrochloric acid < sulfuric acid < nitric acid < perchloric acid. Whereas the redox potential increases with increasing concentrations of perchloric acid, it decreases with increasing concentrations of nitric acid and sulfuric acid (Smith and Getz, 1938).

Fluoride ions forms very stable complexes with cerium(IV) and lowers the redox potential considerably. A cerium(IV) sulfate solution is not able to oxidize iodide to iodine when appreciable amounts of fluoride ions are present. The most important fluoro complex is hexafluorocerate(IV), [CeF₆]²⁻, which can be formed by addition of ammonium fluoride to a solution of cerium(IV). The behavior of cerium(IV) in presence of fluoride ions is markedly different from that of cerium(III). Addition of an ammonium fluoride solution to a solution containing cerium(III) results in the precipitation of gelatinous cerium(III) fluoride, CeF₃, which becomes powdery upon standing (Svehla, 1979). The use of cerium(IV) fluoride as a fluorinating agent is discussed in sections 5.16 and 6.7.

Cerium(III) can be oxidized to cerium(IV) electrolytically or by the use of strong oxidizing agents. Upon addition of a small excess of silver(II) oxide, AgO, to a cold solution of cerium(III) in a 3 to 5 M nitric acid solution, rapid oxidation of cerium(III) to cerium(IV) takes place. By simply diluting and warming the solution for a few minutes the excess of silver(II) is completely reduced by water (Lingane and Davis, 1956). The problem of oxidizing cerium(III) by metal-containing oxidizing agents is that the cerium solution gets contaminated by other metal ions. For some applications this is not a problem, but for other applications it is. A useful oxidizing agent for oxidation of cerium(III) in sulfuric acid medium is lead(IV) oxide (Gordon and Feibush, 1955). Neither PbO₂ nor PbSO₄, that are formed during the reaction, are soluble in sulfuric acid, so that both compounds can easily be removed by filtration. The oxidation of cerium(III) to cerium(IV) by persulfate is catalyzed by small amounts of silver(I) salts (Skarzewski, 1984). Milyukova et al. used a mixture of silver nitrate and ammonium persulfate to oxidize cerium(III) and berkelium(III) (Milyukova et al., 1977). The persulfate method is the most popular method for the chemical oxidation of cerium(III) to

cerium(IV). Potassium persulfate, K₂S₂O₈, or ammonium persulfate, (NH₄)₂S₂O₈, can be used as oxidizing reagents.

Nikitina and coworkers have studied the kinetics of the oxidation of cerium(III) by ozone in nitric acid solutions (Nikitina et al., 1980). It was observed that the oxidation of cerium(III) by ozone in 4 M HNO₃ at 25 °C required substantially more than two moles of cerium(III) per ozone molecule consumed. The kinetic data could only be explained by considering that the oxidation takes place by two different reactions, that occur simultaneously and that are of overall second order. The stoichiometry of the reaction of cerium(III) with ozone can be described by the following equations:



In general, cerium(III) cannot be oxidized to cerium(IV) by molecular oxygen. An exception is the oxidation of cerium β -diketonate complexes by O₂ (Christoffers and Werner, 2002; Christoffers et al., 2003a, 2003b; Rössle et al., 2005). Complex formation shifts the redox potential of the Ce⁴⁺/Ce³⁺ couple to less positive values. As discussed in section 10.2, aqueous solutions of cerium(IV) are metastable with respect to oxidation of water to oxygen gas. Under normal conditions this reaction will not occur due to the presence of a high kinetic barrier, and acidic solutions of cerium(IV) can be stored for quite a long time. However, cerium(IV) ions can decompose water in presence of a catalyst like platinum or ruthenium(IV) oxide.

Because of the high redox potential of the Ce⁴⁺/Ce³⁺ redox couple, the choice of the electrode is important, especially in electroanalytical studies. The kinetics of the Ce⁴⁺/Ce³⁺ redox reaction have been investigated using different types of electrodes: a stationary platinum disc electrode (Randle and Kuhn, 1983; Kuhn and Randle, 1985), a rotating platinum disc electrode (Greef and Aulich, 1968; Randle and Kuhn, 1986), a bubbling platinum electrode (Desideri, 1961), a platinized titanium electrode (Tzedakis and Savall, 1997), a gold electrode (Ferro and De Battisti, 2002), a glassy carbon electrode (Pletcher and Valdes, 1988a; Maeda et al., 1999; Vijayarathi et al., 2001), a conductive diamond electrode (Ferro and De Battisti, 2002), and a pyrolytic graphite electrode (Miller and Zittel, 1964). The bubbling platinum electrode is a thin platinum ring electrode renewed at regular intervals by gas bubbles, and can be used as an alternative for the dropping mercury electrode for polarographic systems with a high redox potential (Cozzi and Desideri, 1960).

The assignment of oxidation states in cerium compounds is not always an easy task. A well-known case is that of *cerocene*, bis(cyclooctatetraene)cerium, Ce(η^8 -C₈H₈)₂. This complex was originally formulated as a cerium(IV) compound with two (η^8 -C₈H₈)²⁻ anions (Greco et al., 1976). Later calculations indicated that the stoichiometry of *cerocene* is better described as [Ce³⁺{(η^8 -C₈H₈)₂}³⁻] (Neumann and Fulde, 1989). *Ab initio* calculations showed that *cerocene* is in fact a mixed valent compound, with a ground state consisting of 83% 4f¹_{e_{2u}} π^3 _{e_{2u}} (i.e. Ce³⁺) and 17% 4f⁰ π^4 _{e_{2u}} (i.e. Ce⁴⁺) (Dolg et al., 1991, 1995). X-ray absorption near-edge structure (XANES) data gave evidence that the ground state of *cerocene* was primarily Ce³⁺ (Edelstein et al., 1996). The layered cerium iodate Ce₂(IO₃)₆(OH_{0.44}) that can be prepared

by reaction of $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ with I_2O_5 at 180°C in aqueous medium in an autoclave is another example of a mixed valent cerium compound (Sykora et al., 2004). The best method to determine the oxidation state of cerium is by XANES, because this is a direct spectroscopic probe for the cerium oxidation state (Antonio et al., 1999). Both K-edge and L-edge Ce XANES has been used for solving problems about the valence of cerium (Antonio and Soderholm, 1994; Antonio et al., 1988, 1996, 1999; Edelstein et al., 1996; Bidoglio et al., 1992; Sham, 1983; Skanthakumar and Soderholm, 1996; Reidy and Swider, 1995; Sunstrom et al., 1993; Overbury et al., 1998; Beck et al., 1989). Other experimental methods like EPR, magnetic measurements, UV-VIS spectroscopy or cyclic voltammetry give less conclusive results.

Because the anionic ligands that are typically used for the synthesis of organolanthanide complexes, e.g. C_5H_5^- , $\text{C}_8\text{H}_8^{2-}$ or R^- , are strongly reducing, it remains a challenge to obtain organometallic cerium(IV) complexes. One of the few examples of such compounds is the cerium(IV) cyclopentadienyl *tert*-butoxide complex $(\text{C}_5\text{H}_5)_3\text{Ce}(\text{OCMe}_3)$ reported by Evans and coworkers (Evans et al., 1989b).

3. Oxidimetry (cerimetry)

3.1. Principles

Solutions of cerium(IV) have been often used as oxidizing titrants for redox titrations, because the reduction of Ce^{4+} to Ce^{3+} proceeds cleanly in acidic solutions. The titrimetric methods based on cerium(IV) are also known as *cerimetry* or *cerate oxidimetry*. The use of cerium(IV) salts as reagents for volumetric analysis was first proposed by Lange in the middle of the 19th century (Lange, 1861), but systematic studies started only about 70 years later (Willard and Young, 1928a, 1928b, 1928c, 1928d, 1928e, 1929a, 1929b). Potentiometric methods based on cerium(IV) sulfate as titrant were developed at the same time by Furman (Furman, 1928a, 1928b; Furman and Evans, 1929; Furman and Wallace Jr., 1930a, 1930b) and by Atanasiu (Atanasiu, 1927; Atanasiu and Stefanescu, 1928). A review on the earlier work of oxidimetry with cerium(IV) salts was written by Young (Young, 1952). The classic work of Kolthoff on volumetric analysis (Kolthoff et al., 1957) contains descriptions of detailed procedures for cerimetry. Several examples of cerimetry are described also in the well-known *Vogel's textbook of quantitative inorganic analysis* (Bassett et al., 1981). Standard solutions can be prepared from different cerium(IV) salts (see section 3.2), but most often cerium(IV) sulfate is chosen. Solutions of cerium(IV) sulfate can be used only in acidic medium (0.5 M H_3O^+ or higher concentrations), because at neutral or high pH values, cerium(IV) hydroxide (hydrated CeO_2) or other basic salts precipitate. Although the most popular reagent for oxidimetry is without doubt potassium permanganate, KMnO_4 , solutions of cerium(IV) sulfate offer several advantages. Firstly, cerium(IV) sulfate solutions are very stable over long periods of time. It is not necessary to take precautions to protect the standard solutions from light, and the solutions may be boiled without noticeable change in concentration. Acidic solutions of cerium(IV) sulfate are therefore more stable than permanganate solutions. Secondly, cerium(IV) is a one-electron acceptor, and a simple valence change takes place upon

reduction: $\text{Ce}^{4+} + \text{e}^- \rightleftharpoons \text{Ce}^{3+}$. The equivalent weight is therefore equal to the molecular weight. With potassium permanganate, a number of intermediate unstable oxidation states can be formed depending on the experimental conditions. Thirdly, cerium(IV) sulfate may be used as an oxidizing titrant in presence of high concentrations of hydrochloric acid, provided that the solutions are not boiled. In contrast, potassium permanganate cannot be used for titrations of the reducing agent in a hydrochloric acid solution, because chlorine gas is liberated. However, solutions of cerium(IV) in hydrochloric acid do not have a long-term stability (see below). Fourthly, cerium(IV) solutions at the commonly used concentration of 0.1 M are not too highly colored, so that there are no problems when reading the meniscus in burettes. Fifthly, the $\text{Ce}^{4+}/\text{Ce}^{3+}$ couple has a highly positive standard redox potential, so that cerium(IV) acts as an oxidant towards many reducing agents. Notice that a unique property of cerium(IV) salts is that they are together with silver(II) and cobalt(III) salts among the few stable oxidizing agents that have the cation as the primary active component (Furman and Evans, 1929). In most other strongly oxidizing agents, like perchlorate, bromate, periodate, bismuthate, persulfate, permanganate and dichromate, the active component is an anion. As mentioned in section 2, the redox potential of the $\text{Ce}^{4+}/\text{Ce}^{3+}$ couple is strongly dependent on the acidity of the solution and on the nature of the counter ion.

3.2. Standard solutions

An overview of the compounds used for the preparation of standard solutions of cerium(IV) is given in table 1. Ammonium hexanitratocerate(IV) is commercially available in primary-standard grade and can be used to prepare standard solutions of cerium(IV) by weight (Smith and Fly, 1949). The weighted amount of ammonium hexanitratocerate(IV) is dissolved in 1 M H_2SO_4 and used directly (Smith et al., 1936). It is recommended to dry primary-standard grade ammonium hexanitratocerate(IV) at 85°C before use. Cerium(IV) dissolved in sulfuric acid is indefinitely stable. Solutions of cerium(IV) in nitric acid or in perchloric acid undergo slow photochemical decomposition. Solutions of cerium(IV) in hydrochloric acid are slowly oxidized. When the less expensive ammonium hexanitratocerate(IV) of reagent-grade or another cerium(IV) compound is used to prepare the cerium(IV) solution, the resulting solutions have to be standardized with a primary standard.

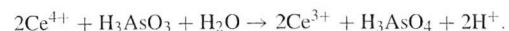
When a cerium(IV) solution is prepared by dissolving ammonium hexanitratocerate(IV) in sulfuric acid, both sulfate and nitrate ions are present. In many cases, the nitrate ions do not interfere in the analysis. When the presence of nitrate ions is undesirable, the ammonium

Table 1
Cerium(IV) compounds used for the preparation of standard solutions

Name	Formula	Formula weight (g/mol)
Ammonium hexanitratocerate(IV)	$(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$	548.23
Ammonium cerium(IV) sulfate	$(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$	632.56
Cerium(IV) sulfate	$\text{Ce}(\text{SO}_4)_2$	333.25
Cerium(IV) hydrogen sulfate	$\text{Ce}(\text{HSO}_4)_4$	502.13
Cerium(IV) hydroxide	$\text{Ce}(\text{OH})_4$	208.15

hexanitratocerate(IV) solution is evaporated almost to dryness with an excess of concentrated sulfuric acid. The resulting cerium(IV) sulfate is redissolved in a molar sulfuric acid solution. Alternatively, cerium(IV) is precipitated from the ammonium hexanitratocerate(IV) solution by addition of an aqueous ammonia solution, and after washing with water to remove the adsorbed nitrate ions the precipitate is redissolved in sulfuric acid. A standard cerium(IV) solution can be prepared also from $\text{Ce}(\text{HSO}_4)_4$ as the starting material (Zielen, 1969). For titrations in nitric acid or in hydrochloric acid solution, ammonium hexanitratocerate(IV) is chosen as the titrant (Rao et al., 1962). For redox titrations in non-aqueous media, the use of a solution of ammonium hexanitratocerate(IV) in glacial acetic acid has been suggested (Hinsvark and Stone, 1956). The authors preferred acetic acid because it is readily available in pure form and because it dissolves most oxygen-containing organic compounds. However, the solution has only a moderate stability and should be standardized every day. The oxidations have to be carried out in presence of perchloric acid, because otherwise they are too slow. Studies have shown that the solvent also participates in the reaction.

Arsenic(III) oxide, As_2O_3 , is the preferred reagent for the standardization of cerium(IV) solutions (Bassett et al., 1981). Because the reaction is very slow at ambient temperatures, it must be catalyzed by addition of small amounts of osmium tetroxide, OsO_4 , ruthenium tetroxide, RuO_4 , or less preferably iodine monochloride, ICl . Ruthenium tetroxide is less toxic and less expensive than osmium tetroxide (Keatch, 1961). Arsenic(III) oxide is dissolved in a sodium hydroxide solution, and the solution is acidified with a dilute sulfuric acid solution. After adding the catalyst and the redox indicator, the solution is titrated with the cerium(IV) solution to the first sharp color change from orange-red to very pale blue. The relevant reaction is:



Other primary standards for the standardization of cerium(IV) solutions are pure iron or sodium oxalate. For the standardization of cerium(IV) against sodium oxalate, a hot solution of hydrochloric or sulfuric acid is used.

In coulometric titrations, cerium(IV) is generated *in situ* by electrolysis. Pastor et al. (1982) studied the anodic generation of cerium(IV). The formal redox potential of the $\text{Ce}^{4+}/\text{Ce}^{3+}$ system decreases as concentration of potassium acetate in the solution increases.

3.3. End-point determination and redox indicators

The end-point of titrations with cerium(IV) solutions can be detected visually (without or with use of a redox indicator) or potentiometrically. Whereas the intense purple color of a permanganate solution allows an easy visual detection of the end point, the yellow-orange color of cerium(IV) solutions is often not intense enough to act as an indicator. Only in a limited number of cases, for instance when oxalic acid or hydrogen peroxide is the analyte, can the titration be made without a redox indicator, provided that the concentrations of the analyte are not too low and that an appropriate blank correction is made. It is easier to detect the end point in hot solutions than in cold solutions, because of an intensification of the yellow color of the cerium(IV) ion with a rise in temperature. A large blank correction is required

when the titrant serves as its own indicator. On the other hand, end points can readily be determined potentiometrically by measuring the potential of the cell containing the analyte solution during the titration.

The preferred redox indicator for titrations with cerium(IV) is *ferroin*, which is in fact the tris(1,10-phenanthroline)iron(II) complex, $[\text{Fe}(\text{phen})_3]^{2+}$ (Walden et al., 1931, 1933). Ferroin itself has a deep red color, whereas its oxidized form (*ferrin*), $[\text{Fe}(\text{phen})_3]^{3+}$, is pale blue to colorless. The transition potential is +1.10 V in 1 M sulfuric acid. Ferroin is a very good redox indicator, because its reaction is rapid and reversible, because the color change is very pronounced, and because ferroin solutions are easy to prepare and stable up to 60 °C. Several redox indicators based on 1,10-phenanthroline derivatives have been reported. Walden and coworkers (Walden et al., 1934) prepared the iron(II) complex of 5-nitro-1,10-phenanthroline (*nitroferroin*), which has a transition potential of +1.25 V. Nitroferroin is more stable than ferroin, but is not very useful for oxidations with cerium(IV) sulfate in sulfuric acid solution, because a significant excess of the titrant is required to oxidize the indicator. However, nitroferroin is useful for titrations with cerium(IV) ions in perchloric acid or in nitric acid solution, where the oxidation potential of the $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox couple is higher. The oxidation potential of iron(II) phenanthroline complexes can be systematically varied between +0.84 V and +1.10 V by the number and position of methyl substituents on the 1,10-phenanthroline core (Brandt and Smith, 1949). The kinetics of the oxidation of ferroin by cerium(IV) have been studied by Dulz and Sutin (1963). The rate constant of the oxidation reaction increased with increasing sulfuric acid concentrations. Iron(II) complexes of 2,2'-bipyridine are less suitable as redox indicator than those of 1,10-phenanthroline, because of the poor stability of the complexes of 2,2'-bipyridine in acidic medium (Walden et al., 1931, 1933). However, tris(2,2'-bipyridine)ruthenium(II) dichloride can be applied as indicator for titrations with cerium(IV) in perchloric or nitric acid solution, because of the high transition potential (+1.25 V) and because the ruthenium(II) complex is more stable than the corresponding iron(II) complex (Steigman et al., 1942). A useful alternative indicator for ferroin in sulfuric acid solution is *N*-phenylanthranilic acid (*o*-diphenylaminocarboxylic acid) (Syrokonskii and Stiepin, 1936). This indicator is pink in the oxidized form and colorless in the reduced form. Bányai et al. (1965) proposed eriochrome blue as a redox indicator for cerimetry. Chlorpromazine hydrochloride was introduced as an indicator for microtitrations with 0.0005–0.001 N cerium(IV) solutions (Kum-Tatt and Tong, 1962).

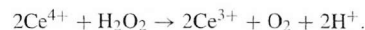
3.4. Applications

Most of the procedures for oxidimetry with potassium permanganate work also with cerium(IV) solutions (Kolthoff et al., 1957). As mentioned in section 3.1, the latter have some advantages over permanganate solutions. For instance, cerium(IV) can be used for the titration of iron(II) ions in presence of chloride, contrary to permanganate. Methods have been developed for the titration of many metals and metalloids: antimony (Willard and Young, 1933; Furman, 1932), arsenic (Furman, 1932; Gleu, 1933; Smith and Fritz, 1948), mercury (Willard and Young, 1930d), thallium (Willard and Young, 1930a), rhenium (Geilmann and Wrigge, 1935), tellurium (Willard and Young, 1930c), tin (Bassett and Stumpf, 1934), vanadium (Willard and Young, 1929a), iron (Willard and Young, 1928b), copper (Birbaum

and Edmonds, 1940; Baker and Gibbs, 1943, 1946), molybdenum (Furman and Murray, 1936), titanium (Claassen and Visser, 1941) and uranium (Birnbaum and Edmonds, 1940; Fritz et al., 1954; Furman and Schoonover, 1931; Ewing and Wilson, 1931). It is evident from the publication year of the references that all these procedures are quite old. They have been published in a time when instrumental analysis methods were not widely available. Many of the older titration methods have been replaced by more modern analytical methods, although the procedures themselves remain useful.

In some applications, the oxidation of the analyte by cerium(IV) is very slow. In this case, an alkali iodide can be added as a catalyst. Ce^{4+} is able to oxidize I^- very fast to I_2 , and iodine acts as the redox active species in the titration reaction. The iodide ions that are formed are regenerated by oxidization by Ce^{4+} . A typical example is the iodide-catalyzed oxidation of arsenic(III) by cerium(IV) (Yates and Thomas, 1956).

An analytical application of cerimetry that is still in use is the determination of *hydrogen peroxide* by titration with a 0.1 M cerium(IV) sulfate solution to the pale blue end point of a ferroin indicator (Hurdis and Romeyn, 1954). The reaction is:



The method is applicable to solutions that contain 1 to 30 wt.% H_2O_2 . Samples with a higher concentration should be diluted prior to analysis. Other peroxides in the solution do not interfere. Takahashi and Sakurai (1962) determined H_2O_2 coulometrically with electro-generated cerium(IV).

Cerium(IV) solutions have been used intensively in the past for the determination of organic compounds. A review of these methods has been written by Ashworth (1964, 1965). Cerium(IV) oxidizes most organic compounds to carbon dioxide and water, although the oxidation is sometimes stopped at an intermediate stage. For instance, formic acid is the stable end product of different polycarboxylic acids and hydroxycarboxylic acids under certain conditions. The organic compounds can be titrated in an acidic aqueous solution, although ethanol or acetic acid can be added for solubilizing purposes. Acetonitrile has also been used as a solvent for titrations with cerium(IV). Maleic, fumaric, benzoic, phthalic and salicylic acid are completely oxidized to carbon dioxide and water by cerium(IV) sulfate, so that these acids can be titrated by cerium(IV) sulfate (Sharma and Mehrotra, 1954b). On the other hand, acetic and succinic acid are not oxidized by cerium(IV) sulfate, even not in solutions with a high sulfuric acid concentration. By choosing an appropriate sample treatment, it is also possible to oxidize formic, glycolic, malic, malonic and tartaric acid by cerium(IV) sulfate (Sharma and Mehrotra, 1954a). Oxidation of formic acid by pure cerium(IV) sulfate is negligible (Willard and Young, 1930b), but by using chromium(III) sulfate as a catalyst, formic acid can be quantitatively oxidized (Sharma and Mehrotra, 1955). Koch and Strong (1969) described a procedure for the determination of oxalate in urine by cerimetry.

4. Cerium-catalyzed Belousov-Zhabotinsky reactions

4.1. Historical background

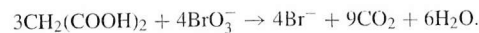
Most chemical reactions proceed continuously from a starting point to an end point. However, *oscillating reactions* change their state in a rhythmic way, when they are proceeding to their end point (Franck, 1978). This type of reactions is characterized for instance by a periodic color change. The Russian biophysicist *Boris Pavlovich Belousov* (1883–1970) has attempted to model catalysis in the Krebs cycle by using cerium(IV) as the catalyst instead of metalloenzymes, when, purely by accident, he observed in 1951 that the color of a solution of citric acid, bromate, and of a cerium(IV) salt in diluted sulfuric acid oscillated between yellow and colorless. However, due to resistance among the chemistry community he encountered difficulties during several years problems for publishing his work. Finally, it appeared in an obscure journal (Belousov, 1959). An English translation of Belousov's seminal paper can be found in a book authored by Field and Burger (1985). The resistance of the chemical community to accept chemical oscillations can be explained by the fact that it was commonly thought that it would be contrary to the second law of thermodynamics for a chemical reaction to oscillate. Chemical reactions should approach the thermodynamic equilibrium monotonically. It was thought that Belousov's observations were caused by an insufficient stirring of the solution. Belousov used the redox indicator ferroin to intensify the color change during oscillations. As mentioned in section 3.3, ferroin is red in reduced solution and blue in oxidized form, providing a more easily visible variation than the pale yellow to colorless change of the cerium(IV)/cerium(III) system. Another Russian biophysicist, *Anatol Markovich Zhabotinsky* (1938–) refined Belousov's reaction, replacing citric acid by malonic acid and discovering that when a thin, homogenous layer of the solution is left undisturbed, fascinating geometric patterns such as concentric circles and Archimedean spirals propagate across the medium. Therefore, the reaction oscillates both in space and time; it is a so-called *spatio-temporal oscillator*. Despite initial problems to convince referees and journal editors, Zhabotinsky was ultimately able to publish several papers concerning what would become known as the *Belousov-Zhabotinsky* reaction (Zhabotinsky, 1964a, 1964b; Zaikin and Zhabotinsky, 1970). The *Belousov-Zhabotinsky* reaction is also spelled as the *Belousov-Zhabotinskii* reaction, or written as BZ reaction for short. In 1980, twenty years after Belousov's death, the Lenin Prize was awarded to Belousov (posthumously), Zhabotinsky, Krinsky and Ivantinsky for their work on oscillating reactions. The discovery of the oscillating reaction by Belousov has been described by Winfree (1984). The acceptance of oscillating reactions by the chemical community was made possible not only by the research of Zhabotinsky, but also by the work of Prigogine on the thermodynamics of systems far from the state of thermodynamics equilibrium (Prigogine, 1962; Nicolis and Prigogine, 1977). The Belousov-Zhabotinsky reaction is widely used as a model system for the study of non-linear phenomena in chemical kinetics. The theory that deals with such non-linear phenomena is known as "*catastrophe theory*" (Okiniski, 1992).

The Belousov-Zhabotinsky reaction is an example of a class of processes, in which the chemical compositions exhibit regular periodic variations in time or space. These periodic

variations can be made visible by a sequence of color changes. Many chemical oscillators (including the BZ reaction) contain the bromate ions as an essential component, and are also referred to as *bromate-driven oscillators* (Ruoff et al., 1988). The reactions related to a bromate-driven oscillator involve bromination and oxidation of an organic compound by bromate in acidic solution. In some systems a catalyst is used, although also uncatalyzed bromate oscillators have been described (Kuhnert and Linde, 1977). Bromate-driven oscillators where a metal ion or a metal complex is present as a catalyst are known as "*classical systems*" (Noyes, 1980). The term *Belousov-Zhabotinsky reaction* is today not restricted to the original chemical system, but is used for any metal-ion-catalyzed, bromate-driven oscillating system. The Belousov-Zhabotinsky reaction is a homogenous chemical oscillator, because the reaction products are all dissolved in one liquid phase.

4.2. Mechanism

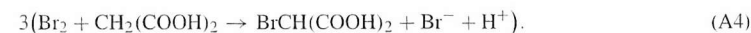
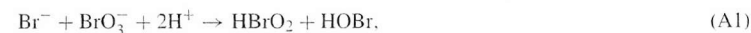
Most studies of the Belousov-Zhabotinsky reaction use malonic acid as the organic acid. The BZ reaction is based on an autocatalytic system, with reaction steps coupled in such a way that the products formed by one reaction slow down another reaction or make another reaction possible. In this way, reactions can experience positive or negative feed-back. The oscillations can only take place because the system is far away from equilibrium; otherwise equilibrium would be established very quickly. Oscillating chemical reactions are always very complex and involve a large number of chemical species, which can be classified as reactants, products or intermediates. In a classic chemical reaction, the concentration of the reactants steadily decreases and the concentration of the products steadily increases, while the intermediates are present at a low, relatively constant concentration. In an oscillating reaction, the concentration of the reactants also steadily decreases, but the concentrations of the intermediates shows oscillatory behavior. The oscillations in concentration can be very large. For instance, in the BZ reaction, the bromide ion concentration varies between 10^{-11} M and 10^{-6} M (Field and Schneider, 1989). The color changes are due to differences in the ratio of the concentrations of the oxidized and reduced forms of the cerium catalyst and of the redox indicator. Field, Körös and Noyes (Field et al., 1972; Noyes et al., 1972) proposed a detailed mechanistic model for the oscillating behavior of the Belousov-Zhabotinsky reaction (*FKN model*). The overall reaction occurring is the cerium-catalyzed oxidation of malonic acid by bromate ions in dilute sulfuric acid. The bromate ions are reduced to bromide ions, while the malonic acid is oxidized to carbon dioxide and water. In the course of the reaction, bromide ions and malonic acids are slowly consumed and their concentrations monotonically decrease. The overall reaction can be written as:



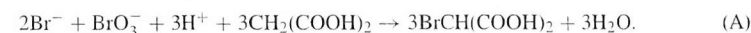
This equation cannot explain the most striking feature of the BZ reaction, namely the periodic changes in the color of the solution when the reaction proceeds. The equation does not explain the role played by the cerium catalyst or by the bromide ions that are added before the start of the reaction. A careful examination of the reaction mechanism is therefore necessary. Three processes are of importance: Process A: consumption of bromide ions; Process B: formation

of cerium(IV) ions; Process C: formation of bromide ions upon consumption of cerium(IV) ions. In these processes, the following reactions take place (Ruoff et al., 1988; Jacobs and Epstein, 1976):

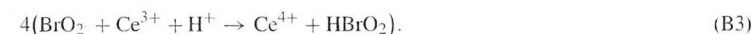
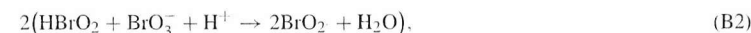
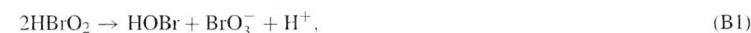
Process A:



The overall reaction for process A is:



Process B:



The overall reaction for process B is:



Process C:

Process C is the reaction of bromomalonic acid with cerium(IV). The detailed mechanism of this process is not known yet. Zhabotinsky (1964a, 1964b) made the first suggestion for the overall reaction in process C:



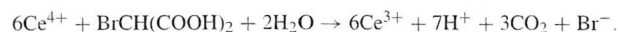
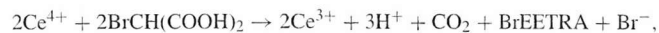
In the FKN model, process C is usually written in the following form:



Processes A and B are fundamentally different. Process A involves ions, and the steps are two-electron transfers (oxygen-atom transfer). The dominant reaction is the reaction between bromide (Br^-) and bromate (BrO_3^-) ions, followed by the bromination of malonic acid. Intermediates are hypobromous acid (HOBr) and bromous acid (HBrO_2). Process B involves radicals and one-electron transfers, whereby cerium(III) is oxidized to cerium(IV). The bromide ion concentration determines which process is dominant at a particular time. Process A occurs when the bromide concentration rises above a certain critical concentration, while

process B takes place when the bromide concentration is lower than the critical concentration. The oscillations occur because process A consumes bromide ions and leads to conditions at which process B becomes favorable. On the other hand, process B indirectly generates bromide ions, so that the system returns to the condition where it is controlled by process A. The critical bromide ion concentration is $[\text{Br}^-]_{\text{crit}} = 5 \times 10^{-6} [\text{BrO}_3^-]$ (Noyes et al., 1972; Gyenge et al., 1977, 1978). During process A, the system is said to be in its *reduced state*, while during process B the system is considered to be in its *oxidized state*. Process B is an example of an *autocatalytic process*, because HBrO_2 formed in reaction B3 is a reactant in reactions B1 and B2. It should be noticed that although the FKN model explains the basic mechanism of the Belousov-Zhabotinsky reaction, many of the details of the reaction still remain unclear. For instance, there is still no agreement about the exact stoichiometry and the reaction mechanism of process C. Edelson, Field and Noyes (Edelson et al., 1975, 1979) published a more detailed description of Belousov-Zhabotinsky reaction than the original FKN model, with over 20 steps. Calculations based on this model can account for the long induction time before the oscillations begin.

Originally, it was assumed that the other products in process C included formic acid (Field et al., 1972), but this assumption was later abandoned (Field, 1975). Oslovovitch et al. (1998) investigated the reaction of bromomalonic acid with cerium(IV) (process C). They detected bromethentetracarboxylic acid (BrEETRA), $(\text{HOOC})_2\text{C}=\text{CBrCOOH}$, as a reaction product, and proposed the following stoichiometries for process C:



The first reaction dominates at low cerium(IV) concentrations, i.e. as in the cerium-catalyzed BZ reaction. The second reaction dominates when cerium(IV) is present in large excess. Nagygyory et al. (1999) postulated the occurrence of carbene intermediates in the reactions between cerium(IV) and malonic acid or bromomalonic acid. These authors also consider two different reactions, depending on the concentration of cerium(IV). Process C has two functions (Field and Boyd, 1985). The first function is the transformation of some reaction products of process B into a species which inhibits process B, by competing with reaction B1 for HBrO_2 . The second function is to reinitialize the system by reducing cerium(IV) to cerium(III) after process B has stopped.

The formation of peroxy malonyl radicals in the reaction of cerium with malonic acid in acidic medium was experimentally established by Neumann et al. (1995). Malonyl radicals were observed in the reaction mixture (Brusa et al., 1985; Försterling and Noszticzius, 1989; Försterling et al., 1990). The presence of malonyl radicals is evident from the detection of ethanetetracarboxylic acid (recombination product of two alkyl malonyl radicals) and malonyl malonate (recombination product of an alkyl and a carboxylato malonyl radical) (Gao et al., 1994; Sirimungkala et al., 1996). Försterling et al. (1990) proposed that the oscillations are controlled by malonyl radicals instead of bromide ions. Noszticzius et al. (1984) suggested control of the oscillations by Br_2 . Field and Försterling (1986) published a revised set of rate constants for the reactions involved in the FKN mechanism. One conclusion was that HBrO_2

is considerably more stable than previously thought. There has been debate about how bromide ions are produced in the reaction (Ruoff et al., 1988). According to the FKN mechanism, bromide ions are generated by reaction between cerium(IV) and bromomalonic acid. This assumption was supported by the fact that the oscillations start only after the concentration of bromomalonic acid is above a certain critical value. There is however evidence for the production of bromide ions from other sources than bromomalonic acid. Varga et al. (1985) have demonstrated by isotope tracer experiments with ^{82}Br -labeled bromomalonic acid that a large fraction of the bromide ions produced in process C comes from reduction products of BrO_3^- , like HOBr , and not from bromomalonic acid. High performance liquid chromatography is a valuable experimental tool for the study of the Belousov-Zhabotinsky reaction (Hegedus et al., 2001). At different moments during the reaction, samples can be withdrawn from the reaction mixture and analyzed. This allows the characterization of different intermediates and measurements of their concentrations. It is difficult to measure the concentration of bromine in solution, because Br_2 rapidly reacts with malonic acid to form bromomalonic acid. The reaction occurs via the enol form of malonic acid, rather than via the diacid form (Sirimungkala et al., 1999).

The important role of the bromide ion in the metal-catalyzed BZ reaction is emphasized in the *Oregonator* model, which is a simplified version of the FKN model (Field and Noyes, 1974; Ruoff et al., 1988; Field and Schneider, 1989). The Oregonator is so-called because Noyes's group works at the University of Oregon. This oscillator is characterized by five steps:



here, X stands for HBrO_2 , Y for Br^- , Z for 2Ce^{4+} , A for BrO_3^- and P for HOBr . The concentration of A is often kept constant in the model, so that X, Y and Z are the only kinetically active species. These dynamic variables correspond to reaction intermediates. In Eq (O5), f is an expendable stoichiometric factor. Oscillations occur only for $0.5 \leq f \leq 1 + 2^{1/2}$. It is a good assumption that f is close to 1 (Noyes and Jwo, 1975). The Oregonator was developed because the equations in the initial FKN model were too complex for numerical analysis by the computers of that time. The Oregonator can be written in the form of a set of differential equations with only three variables. The individual steps in the Oregonator are not balanced chemical equations, but they summarize well what is happening in the system.

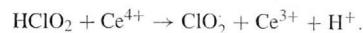
The oscillations in the Belousov-Zhabotinsky reaction occur over a wide range of initial concentrations of the reagents (table 2). Citric acid or malonic acid are not the only possible choices for the organic compounds. The only condition seems to be that the compound should contain one or more active methylene (CH_2) groups, that can be brominated or that active methylene groups can be formed easily by an oxidation reaction (Zhabotinsky,

Table 2
Ranges of initial concentrations in the Belousov-Zhabotinsky reaction

Reagent	Concentration range (mol/L)	Typical concentration (mol/L)
malonic acid	0.125-0.50	0.275
sodium bromate	0.03-0.625	0.625
sulfuric acid	0.5-2.5	1.5
(NH ₄) ₂ [Ce(NO ₃) ₆]	0.0001-0.01	0.002
ferroin	0.0006	0.0006

1964a). This condition is important, because the organic substrate should be easily brominated. Examples of such organic compounds include methylmalonic acid, ethylmalonic acid, benzylmalonic acid, maleic acid, malic acid, gallic acid, acetone, acetylacetone, acetyl acid and acetone dicarboxylic acid. No oscillatory reaction is observed for oxalic acid, tartronic acid, 3-hydroxypropionic acid, succinic acid and pyruvic acid (Kasperek and Bruce, 1971). Instead of ammonium hexanitratocerate(IV), (NH₄)₂[Ce(NO₃)₆], also ammonium tetrasulfatocerate(IV), (NH₄)₄[Ce(SO₄)₄], can be used as the cerium(IV) salt. The Ce⁴⁺/Ce³⁺ redox couple in the catalytic cycle can be replaced for instance by the Mn³⁺/Mn²⁺, the [Fe(phen)₃]³⁺/[Fe(phen)₃]²⁺ (ferriin/ferroin), the [Ru(bpy)₃]³⁺/[Ru(bpy)₃]²⁺, or the [Ru(phen)₃]³⁺/[Ru(phen)₃]²⁺ redox couples. A common feature of the catalytic system is that they are all one-electron redox systems with a redox potential between +1.0 V and +1.5 V. The actual choice of the reagent and concentration conditions has an influence on the oscillation characteristics: the induction period, the oscillation period, the peak potential and the total oscillation time. Generally, the induction period increases with increasing concentrations of bromate and malonic acid, whereas the oscillation period decreases with increasing concentrations of these reagents (Than et al., 2001). Typical periods are between 20 seconds and 2 minutes, but the period can be as long as 15 to 20 minutes (Shakhashiri, 1985). The oscillation period is not constant during the reaction and gradually increases toward the end of the reaction. BZ reactions with short oscillation periods can last for about 20 minutes before the oscillations stop, but BZ reactions with long oscillation periods can repeat their cycles for more than 8 hours.

Zhabotinsky (1964b) noticed that the oscillating reaction is completely inhibited by traces of chloride ions. This inhibition was also observed by Janjic et al. (1974) for systems where the dicarboxylic acid is replaced by acetylacetone. Jacobs and Epstein (1976) reported that the inhibition of the concentration oscillation by trace amounts of chloride ions is only of temporary duration, provided that the initial chloride concentration is below a threshold value. High concentrations of chloride ions suppress the oscillations completely. The inhibition is caused by the oxidation of chloride ions to chlorous acid, which then reduces cerium(IV) to cerium(III).



This reduction prevents the oscillations. When chlorous acid has been completely oxidized to chlorate, oscillations resume. The ultimate fate of any chloride in the system is thus oxidation

to chlorate, which has no effect on the oscillations. The overall reaction of chloride oxidation is:



Addition of iodide and the pseudohalide azide (N₃⁻) had a similar effect as addition of chloride, whereas addition of nitrate, sulfate or perchlorate ions had no effect. The oscillation period after the initial state was found to be identical with that of the unperturbed system. When the amount of chloride added is less than the amount of cerium(IV) present initially, no observable inhibition is expected. This system is more sensitive to addition of chloride after the oscillating reaction has started than to initial addition of chloride ions; smaller amounts of chloride ions are required to induce inhibition or to suppress the oscillations completely. Because of this inhibitory effect, the glass vessels used to prepare the solutions for a Belousov-Zhabotinsky experiment should be clean and free of chloride ions. Moreover, in the preparation of the ferroin indicator solution 1,10-phenanthroline must be used in its free base form and not in the form of the hydrochloride salt. If one wants to monitor the periodic changes in the chemical potential of the solution, one must use a reference electrode that does not leak chloride ions. Conventional calomel electrodes or silver/silver chloride electrodes are not suitable, but double-junction version of these electrodes are adequate.

The effect of oxygen on the BZ reaction has been investigated by several authors (Barkin et al., 1978; Bar-Eli and Haddad, 1979; Treindl and Fabian, 1980; Ruoff, 1982; Ganapathisubramanian and Noyes, 1982; Menzinger and Jankowski, 1986; Li and Li, 1988; Ruoff and Noyes, 1989; Jwo and Noyes, 1975; Sevcik and Adamacikova, 1988; Wang et al., 1996; Petrascu et al., 1999). The rate of the reduction of cerium(IV) by malonic acid is increased in presence of molecular oxygen (Barkin et al., 1978). Oxygen accelerates the release of bromide during oxidation of a mixture of bromomalonic acid and malonic acid by cerium(IV) (Jwo and Noyes, 1975). Introduction of oxygen in the reaction mixture increases the complexity of the oscillations and reduces their duration (Wang et al., 1996). The same authors attributed the influence of the stirring rate on the reaction to differences in dissolved oxygen. At low cerium concentrations, the effect of oxygen is an abrupt drop of the cerium(IV) concentration (Petrascu et al., 1999). The nature of the organic substrate influences the effect of oxygen, and this effect is most pronounced in the autocatalytic oxidation of cerium(III) by bromate ions (Treindl et al., 1997). This can be attributed to the scavenging of BrO₂ radicals by malonyl and peroxy malonyl radicals.

Whereas the Belousov-Zhabotinsky reaction with methylmalonic and with ethylmalonic acid shows oscillatory behavior under the conditions that gives oscillatory behavior for malonic acid, no oscillations are observed for benzylmalonic acid under the same conditions (Cavasino et al., 1999). Interestingly, oscillatory behavior was observed for the benzylmalonic acid system after addition of the cationic surfactant cetyltrimethylammonium nitrate. Addition of the surfactant also shortened the induction period for the reactions with methylmalonic and ethylmalonic acid. The oscillation period was affected as well by the surfactant. Pojman et al. (1992) reported that upon addition of acrylonitrile monomer to the reaction mixture of the Belousov-Zhabotinsky reaction, polymerization did not occur continuously, but in a step-wise manner, in phase with the oscillations in the cerium(IV) concentration. The addition of

other types of monomers like styrene or methacrylate has an inhibiting effect on the oscillations. Temperature has a pronounced effect on the BZ reaction. An increase in temperature generally leads to an increase in the frequency of the oscillations (Nagy et al., 1996).

Belousov originally studied only temporal oscillations in a well-stirred solution, but the formation of spatial patterns in an unstirred solution is also very interesting. If the reaction begins at a given point, the concentration of intermediates will propagate outward by diffusion and this diffusion process will initiate the reaction in the adjacent regions. The propagation of the spatial patterns is known as a *trigger wave*. Periodically, the reaction will reinitiate at the nucleation point. This results in successive bands (in a test tube) or in concentric rings (in a Petri dish). Nagy-Ungvarai and coworkers (Nagy-Ungvarai et al., 1989a, 1989b) investigated the wave profiles of the cerium-catalyzed BZ reaction in detail. The shape of the wave profiles – from very sharp to very broad wave fronts – depends on the initial composition of the system. The cerium waves are slower than the waves in the ferroin- or ruthenium-catalyzed systems, and the velocity depends on the catalyst concentration. The chemical waves are accompanied by changes in the local refractive index and density of the solution (Kasuya et al., 2005). Rotating spiral waves have been the subject of several theoretical and experimental studies (Winfree, 1973; Keener and Tyson, 1986; Mikhailov and Krinskii, 1983; Müller et al., 1987; Agladze and Krinskii, 1982; Jahnke et al., 1989; Nagy-Ungvarai et al., 1990). Gao et al. (1996) studied the cerium-catalyzed BZ reaction by magnetic resonance imaging (MRI). The imaging process is based on the fact that the proton relaxation times T_1 and T_2 for paramagnetic cerium(III) are shorter than for diamagnetic cerium(IV). The MRI contrast is determined by the ratio of relaxation times of cerium(III) and cerium(IV). For cerium, contrast produced by T_1 weighting is comparable to that produced by T_2 weighting. In the MRI images, a bright background is related to an excess of cerium(III), whereas a dark background is related to an excess of cerium(IV). The authors noticed that the cerium-catalyzed Belousov–Zhabotinsky reaction is much more difficult to visualize by MRI than the manganese- or ruthenium-catalyzed reactions. Ruoff (1994) showed that oscillatory photoluminescence due to oscillations in the cerium(III) concentration could be detected in the cerium-catalyzed BZ reaction. No chemiluminescence was observed. Monolayers of the dioctadecylester of luminescent $[\text{Ru}(\text{bpy})_3]^{2+}$ spread on the surface of a Belousov–Zhabotinsky reaction mixture have been used as a photosensitive redox indicator for the organization of the spatio-temporal structures in the subphase (Yoneyama et al., 1994a, 1994b; Yoneyama, 1995). The quality of the monolayer depends very much on the anions that are present in the aqueous subphase. Perchlorate ions have been found to give the most rigid packing in the monolayer, with the formation of crystalline microdomains. The presence of perchlorate ions in the subphase also lead to a higher luminescence intensity of the monolayer. The reaction has also been studied calorimetrically (Körös et al., 1979; Roelofs, 1988; Lamprecht, 1992; Fuijeda and Zhang, 1995).

4.3. Demonstration experiments

The Belousov–Zhabotinsky reaction and other oscillating reactions can be used for very fascinating chemical demonstrations. Detailed experimental descriptions of several oscillat-

ing reactions, including the classic Belousov–Zhabotinsky reaction and modified Belousov–Zhabotinsky reactions are given by Shkhashiri (1985). Jahnke and Winfree (1991) compared the different recipes for the BZ reaction. In the classic reaction, a clear colorless solution (containing potassium bromate) and a pale yellow solution (containing malonic acid and potassium bromide) are mixed producing an amber solution, which becomes colorless after about one minute. Then a yellow solution (containing ammonium hexanitratocerate(IV)) is added, followed by a small amount of a red solution (containing ferroin), producing a green solution. The color of the solution gradually changes over a period of one minute from green to blue, then to violet and finally to red. The color then suddenly returns to green, and the cycle is repeated more than twenty times. The color changes are more complex than the simple red-to-blue color change of the ferroin redox indicator. There are also the color changes related to the cerium ions: cerium(III) is colorless, while cerium(IV) is yellow. The color changes can be monitored spectrophotometrically. After some time the oscillations disappear and the stationary state (equilibrium) is reached.

The oscillations in most demonstration experiments produce periodic color changes. However, other properties of the solution, like the electrical potential, oscillate as well. This is due to changes in the concentrations of the redox active species. The electrical potential changes can be observed by measuring the potential of a platinum electrode versus a reference electrode. The voltage oscillates in phase with the color changes. The range of oscillations in the classic Belousov–Zhabotinsky reaction is about 200 mV. If the solution is poured in a petri dish and left unstirred, mosaic patterns appear as spatial oscillations.

5. Cerium(IV) reagents

5.1. Ammonium hexanitratocerate(IV) (CAN)

Ammonium hexanitratocerate(IV) is undoubtedly the most important cerium(IV) reagent for organic synthesis. A search in Chemical Abstracts (January 2006) resulted in more than 51 000 organic reactions in which ammonium hexanitratocerate(IV) was used as a reagent! The compound is commercially available from several chemical suppliers. Besides ammonium hexanitratocerate(IV), many other names are used for this reagent. Examples include ceric ammonium nitrate, ammonium ceric nitrate, cerium ammonium nitrate, cerium diammonium hexantrate, cerium(IV) ammonium nitrate, diammonium cerium hexantrate, diammonium hexanitratocerate and nitric acid ammonium cerium(+4) salt. However, most organic chemists know this compound as ceric ammonium nitrate or CAN for short. Likewise, the formula of CAN is written as $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$, $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ or $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, $\text{Ce}(\text{NO}_3)_4 \cdot 2\text{NH}_4\text{NO}_3$ or $[\text{Ce}(\text{NH}_4)_2](\text{NO}_3)_6$. The first form is the most correct one, because it reflects that the cerium(IV) ion is surrounded by six nitrate groups and that the ammonium ions are counter ions to compensate for the negative charge of the hexanitratocerate(IV) unit.

The compound can be prepared by dissolving cerium(IV) oxide or cerium(IV) hydroxide in concentrated nitric acid (Smith et al., 1936). The resulting solution is evaporated close to dryness, and ammonium nitrate is added. Nitric acid is added to the solution, and this solution

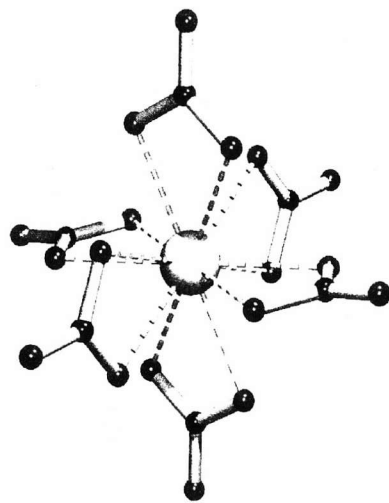


Fig. 1. First coordination sphere of cerium(IV) in ammonium hexanitratocerate(IV). The coordination number of cerium is twelve. The average Ce-O distance is 2.508 ± 0.007 Å (Beineke and Delgaudio, 1968).

is evaporated until crystals start to appear. Ammonium hexanitratocerate(IV) will crystallize from this concentrated solution. Although in some works the addition of a stoichiometric amount of ammonium is suggested (Smith et al., 1936), other papers advise to add a slight excess of ammonium nitrate (Smith, 1967). The complex can be precipitated from an aqueous solution by addition of concentrated nitric acid. The compound can be recrystallized from a dilute aqueous nitric acid solution. Crystals free of nitric acid can be obtained by drying at 100°C (Smith et al., 1936).

Ammonium hexanitratocerate(IV) occurs as small, orange-red, monoclinic crystals. Its crystal structure has been determined by Beineke and Delgaudio (1968) (figs. 1 and 2). The structure is composed of discrete ammonium cations and hexanitratocerate(IV) anions. In the hexanitratocerate(IV) cations, six bidentate nitrate groups bind to the cerium(IV) ion. The approximate symmetry of the complex is T_h . The hexanitratocerate(IV) anion is one of the few examples of a complex with coordination number twelve. The structure is held together by a three-dimensional network of hydrogen bonds. Each hexanitratocerate(IV) ion is involved in twelve hydrogen bonds. The hexanitratocerate(IV) ion is a relatively stable entity in solution (Larsen and Brown, 1964; Miller and Irish, 1967; Karraker, 1968), where it exists mainly as free ammonium ions and hexanitrated cerium(IV) species. The structure of the latter in solution is similar to that in the solid state. This is also evident from the lack of hydrolysis of the salt to insoluble cerium(IV) compounds; this is

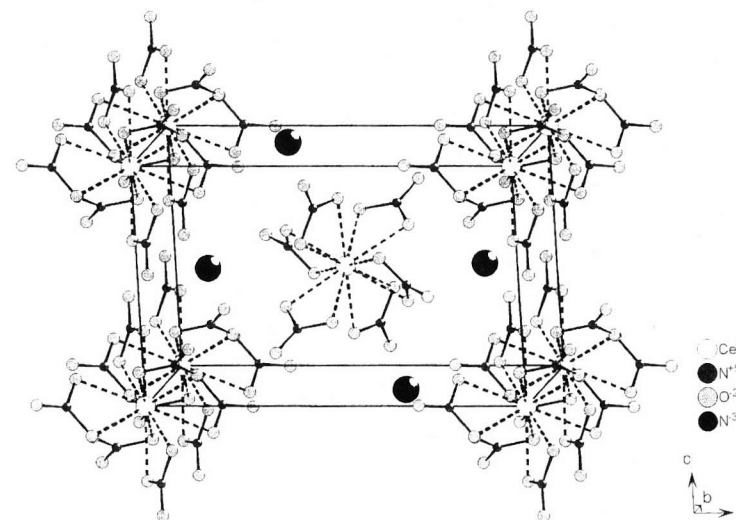


Fig. 2. Crystal structure of ammonium hexanitratocerate(IV). The atomic coordinates are those reported by Beineke and Delgaudio (1968).

in contrast to the behavior of ammonium cerium(IV) nitrate. $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ is the only compound that precipitates out a saturated solution in the ternary $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6] - \text{HNO}_3 - \text{H}_2\text{O}$ system. Blaustein and Gryder (1957) report that the $[\text{Ce}(\text{NO}_3)_6]^{2-}$ ion forms dimers or polymers in 5 M nitric acid.

Ammonium hexanitratocerate(IV) is very well soluble in water; its solubility is 141 g per 100 mL at 25°C . Meyer and Jacoby (1901) mention that a saturated aqueous solution of ammonium hexanitratocerate(IV) contains at 0°C , 25°C and 50°C respectively 55.74, 59.51 and 65.55 wt.% of $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$. The reagent is also soluble in polar organic solvents like methanol, ethanol, acetonitrile, and DMF. Often these solvents are mixed with water, in order to increase the solubility of the reagent. Acetic acid is a useful solvent for performing reactions with CAN, but the solubility of CAN in acetic acid is only 8×10^{-3} M at room temperature (Bacocchi et al., 1977). Ammonium hexanitratocerate(IV) is only very sparingly soluble in apolar solvents.

To overcome the solubility problems in apolar solvents, some authors added surfactants or phase transfer reagents to the aqueous reaction medium in which the cerium(IV) salt is dissolved, so that organic substrate could be solubilized inside micelles or that the surfactant acts as a phase transfer agent (Skarzewski, 1980; Skarzewski and Młochowski, 1985; Skarzewski and Cichacz, 1984; Pletcher and Valdes, 1987; Dehmlow and Makrandi, 1986; Bacocchi et al., 1988a). The yields of the reactions depend very much on the type of surfac-

tant used (Skarzewski and Cichacz, 1984), the best results being obtained with the anionic surfactant sodium dodecylsulfate (SDS). Pletcher and Valdes (1987) used tetrabutylammonium nitrate or tributylphosphate to transfer CAN to the organic phase in a biphasic system consisting of aqueous nitric acid and 1,2-chloroethane. The yields depended very much on the organic substrate and on the phase transfer agent. For instance tributylphosphate worked better for the oxidation of anthracene to anthraquinone, while tetrabutylammonium nitrate gave better yields for the oxidation of naphthalene to naphthoquinone. An uncommon phase transfer reagent is the lipophilic 4,4'-dialkoxy-2,2'-bipyridine 1,1'-dioxide (Skarzewski, 1980), but the reaction yields observed for this reagent are poor. Baciocchi et al. (1988a) added tetrabutylammonium bromide to the biphasic water/dichloromethane system to transfer CAN from the aqueous phase to the organic phase.

Different solvents can be used for reactions with ammonium hexanitratocerate(IV) as reagent. The most popular solvents are (in decreasing order of importance) water, acetonitrile, dichloromethane, THF and methanol. Often mixtures of these solvents are used. Solvents of less importance are DMF, toluene, diethyl ether, ethanol, pyridine, acetone, benzene, ethyl acetate, hexane, acetic acid, chloroform, dioxane, DMSO, carbon tetrachloride and 1,2-dichloroethane. Other solvents have found only marginal use for this type of reactions. One report describes CAN-mediated oxidation reactions in a mixture of dichloromethane and an imidazolium ionic liquid (Bar et al., 2003). Methanol is a better solvent than ethanol for CAN (Cho and Romero, 1995); whereas methanol reacts only very slowly with CAN, the reaction between ethanol and CAN is fast. It should be mentioned that in many reactions in apolar solvents, CAN is used as a suspension; thus under heterogeneous reaction conditions. Also reactions of CAN in acetic acid are often done under heterogeneous conditions. It was observed that for heterogeneous reactions of CAN in acetic acid, the nitrate/acetate ratio in the reactions mixture depends on the amount of solid CAN dispersed in acetic acid; as the amount of undissolved CAN increases, the nitrate/acetate ratio increases significantly (Baciocchi et al., 1977).

Ammonium hexanitratocerate(IV) is a very versatile reagent and can be used for many types of organic reactions (see further). However, it is not an ideal reagent. Disadvantages are the poor solubility in apolar solvents and the fact that many reactions are not specific. Side products are often formed.

5.2. Ammonium cerium(IV) sulfate (CAS)

Given the popularity of ammonium cerium(IV) sulfate for preparing standard solutions for redox titrations (cerimetry), it is surprising that it has been used only in very few cases as an oxidizing reagent in organic synthesis. This can partially be explained by the lower solubility of the ammonium sulfate cerium(IV) in polar organic solvents. This reagent is commercially available as a dihydrate, $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$. It is also known under the names ammonium tetrasulfatocerate(IV) and ceric ammonium sulfate (CAS). There is a major difference between CAS and ammonium hexanitratocerate(IV) (CAN). Whereas CAN is a complex salt with anionic hexanitratocerate(IV) complexes, dimeric units with bridging sulfate groups are present in CAS. The crystal structure of $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ has been reported by Shan and Huang (figs. 3 and 4) (Shan and Huang, 1998). $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ is not the

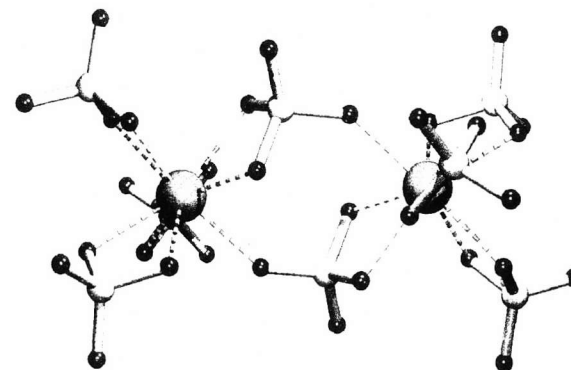


Fig. 3. Coordination sphere of cerium(IV) ammonium sulfate (Shan and Huang, 1998).

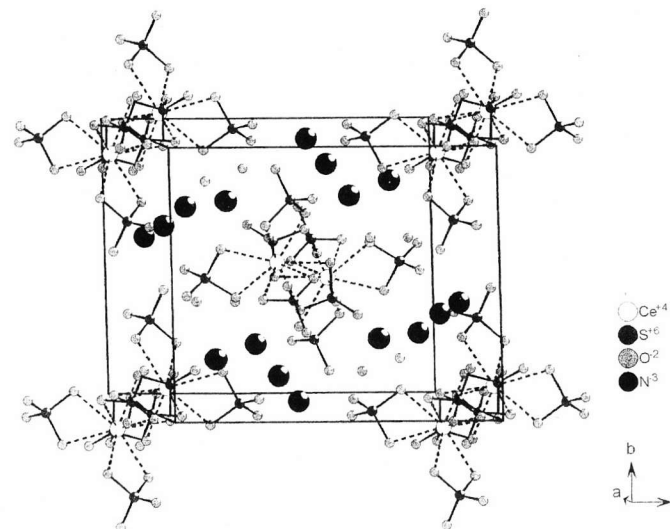


Fig. 4. Crystal structure cerium(IV) ammonium sulfate. The atomic coordinates are those of Shan and Huang (1998).

only compound in the ternary system $\text{NH}_4(\text{SO}_4)_2\text{-Ce}(\text{SO}_4)_2\text{-H}_2\text{O}$. Other compounds include $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4$, $(\text{NH}_4)_2\text{Ce}(\text{SO}_4)_3\cdot 2\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{Ce}(\text{SO}_4)_3\cdot 3\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{Ce}(\text{SO}_4)_5\cdot 3\text{H}_2\text{O}$, $(\text{NH}_4)_8\text{Ce}(\text{SO}_4)_6\cdot 3\text{H}_2\text{O}$, $(\text{NH}_4)_8\text{Ce}(\text{SO}_4)_6\cdot 5\text{H}_2\text{O}$ and $(\text{NH}_4)_{10}\text{Ce}(\text{SO}_4)_7\cdot 3\text{H}_2\text{O}$ (Golovnya and Pospelova, 1961; Golovnya et al., 1960).

Mehta et al. (1976) reported on the use of this reagent for the Baeyer-Villiger oxidation of polycyclic ketones like 1,3-bishomocubanone and 1,4-bishomocubanone into lactones. Ammonium tetrasulfatocerate(IV) dissolved in a mixture of dilute sulfuric acid and acetonitrile was applied as a reagent to transform polycyclic aromatic compounds into quinones (Periasamy and Bhatt, 1977a, 1977b). Skarzewski (1984) oxidized polycyclic aromatics with this reagent in a two-phase system with sodium dodecyl sulfate as a surfactant. CAS could be used in catalytic amounts if an excess of ammonium persulfate was present to steadily reconvert cerium(III) in cerium(IV).

5.3. Cerium(IV) sulfate tetrahydrate

The reactivity of cerium(IV) sulfate tetrahydrate, $\text{Ce}(\text{SO}_4)_2\cdot 4\text{H}_2\text{O}$, is comparable to that of ammonium tetrasulfatocerate(IV), but the former compound has a lower solubility in water. It has been suggested that cerium(IV) sulfate exists in sulfuric acid solutions either as $\text{H}_4[\text{Ce}(\text{SO}_4)_4]$ or as the hydrolysis products $\text{H}_4[\text{CeO}_x(\text{SO}_4)_{4-x}]$ (Jones and Soper, 1935). When the sulfuric acid concentration is below 0.5 M basic sulfates can precipitate. At this concentration cerium(IV) exists predominantly in solution as $\text{H}_3[\text{Ce}(\text{OH})(\text{SO}_4)_3]$. Further decrease of the sulfuric acid concentration leads to transformation of $\text{H}_3[\text{Ce}(\text{OH})(\text{SO}_4)_3]$ into $\text{H}_2[\text{Ce}(\text{OH})_2(\text{SO}_4)_2]$ and finally into $\text{H}[\text{Ce}(\text{OH})_3(\text{SO}_4)]$. Hardwick and Robertson (1951) suggested that in 1 M sulfuric acid solutions the cerium(IV) ion associates with sulfate ions to form successively $[\text{Ce}(\text{SO}_4)]^{2+}$, $[\text{Ce}(\text{SO}_4)_2]$ and $[\text{Ce}(\text{SO}_4)_3]^{2-}$. The most abundant species in solution is $[\text{Ce}(\text{SO}_4)_3]^{2-}$. The findings of these authors are in disagreement with those of Jones and Soper (Jones and Soper, 1935), who found no evidence of binding of protons or hydroxyl groups to the cerium complexes. The solubility of cerium(IV) sulfate in sulfuric acid has been studied by Paulenova and coworkers (Paulenova et al., 2002). The crystal structure of cerium(IV) sulfate tetrahydrate has been reported by Lindgren (fig. 5) (Lindgren, 1977) and that of anhydrous cerium(IV) sulfate by Rogachev and coworkers (fig. 6) (Rogachev et al., 1974). From the figures, it is evident that the cerium ion is part of a 3D polymeric network. This explains the lower solubility of these cerium(IV) sulfate salts in water. Brockhaus used cerium(IV) sulfate for the oxidation of catechol to *ortho*-benzoquinone (Brockhaus, 1968). Weinstock et al. (1988) generated malonyl radicals from dimethylmalonate with cerium(IV) sulfate and let this reactive species react with thiophene and furans. These heterocycles undergo reaction at the C_2 position with malonyl radicals. Finally, cerium(IV) sulfate in presence of iodine cleaves 2-alkylcycloalkanones to keto esters (He et al., 1999).

5.4. Cerium(IV) acetate

Cerium(IV) acetate, $\text{Ce}(\text{CH}_3\text{COO})_4$ or $\text{Ce}(\text{OAc})_4$, has been synthesized by oxidation of cerium(III) acetate by ozone in presence of nitrate ions (Hay and Kochi, 1968):

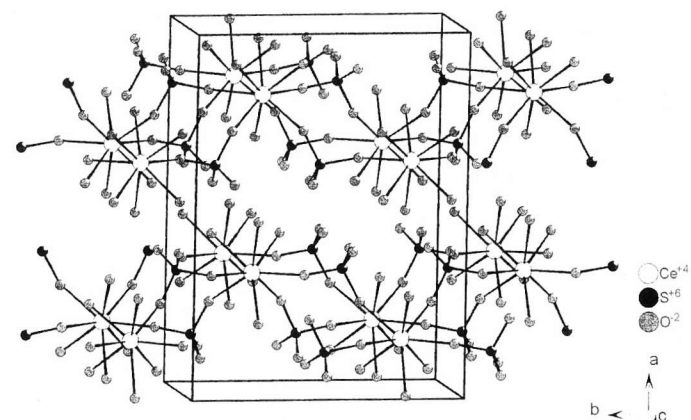
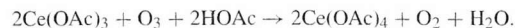


Fig. 5. Crystal structure of cerium(IV) sulfate tetrahydrate. The atomic coordinates are those given by Lindgren (1977).

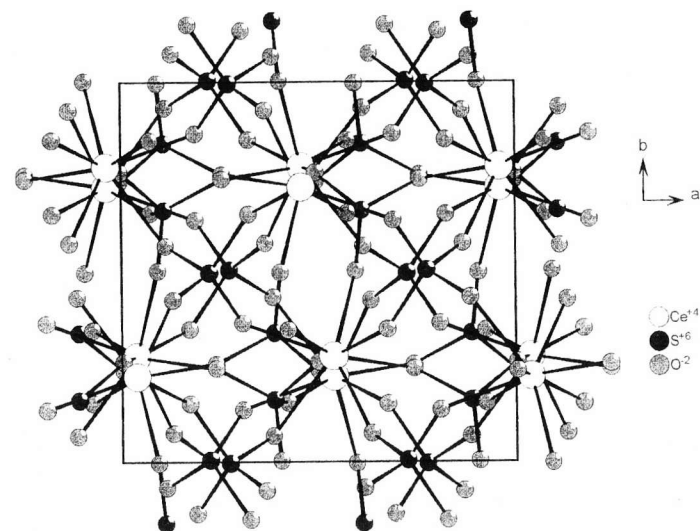


Fig. 6. Crystal structure of anhydrous cerium(IV) sulfate. The atomic coordinates are those reported by Rogachev et al. (1974).

The role of the nitrate ions is to prevent polymerization of cerium(III) acetate in glacial acetic acid/acetic anhydride solution, and to enhance the solubility of cerium(III) acetate in this medium. The yield of cerium(IV) acetate depended on the amount of nitrate ions present; the best results were obtained when 3.5 mol% of cerium(III) nitrate was added to cerium(III) acetate. Cerium(IV) acetate is soluble in aqueous solutions of strong acids, but is only slightly soluble in acetic acid and in benzene. A mixture of acetic acid and acetic anhydride can be used as a recrystallization solvent. The compound is hygroscopic and is also reported to be light sensitive. A solvate of cerium(IV) acetate with acetic acid is more soluble in organic solvents than the pure cerium(IV) acetate. When dissolved in glacial acetic acid that contains 10% potassium acetate, it can be used for the transformation of alkenes into lactones (Heiba and Dessau, 1971). Cerium(IV) acetate was used as a reagent for free-radical aromatic nitromethylations (Kurz and Ngoviwatchai, 1981).

5.5. Cerium(IV) trifluoroacetate

Cerium(IV) trifluoroacetate, $\text{Ce}(\text{CF}_3\text{COO})_4$, can be prepared by reaction of cerium(IV) hydroxide with trifluoroacetic acid (TFA). First a basic salt with composition $\text{Ce}(\text{OH})_2(\text{CF}_3\text{COO})_2$ or $\text{CeO}(\text{CF}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ is formed, which can be transformed into the desired product by further treatment with trifluoroacetic acid and the corresponding anhydride (Norman et al., 1973). This reagent is moisture sensitive and undergoes hydrolysis upon exposure to humid air. It can be dissolved in trifluoroacetic acid in presence of lithium trifluoroacetate. It is assumed that the cerium(IV) ion is present in these solutions under the form of an anionic complex. The solutions are stable in the absence of light. The presence of lithium trifluoroacetate has the advantage that it allows dissolution of larger quantities of aromatic compounds. Cerium(IV) trifluoroacetate is insoluble in chloroform, dichloromethane and benzene, but it can be solubilized in coordinating solvents like acetone, 1,2-dimethoxyethane, DMSO and acetonitrile. It has been used for the oxidation of electron rich hydrocarbons like mesitylene. Marrocco and Brilmyer (1983) describe the use of cerium(IV) trifluoroacetate for the oxidation of *m*-phenoxyltoluene to *m*-phenyloxybenzaldehyde.

5.6. Cerium(IV) perchlorate

Although the redox potential of the $\text{Ce}^{4+}/\text{Ce}^{3+}$ couple reaches the high value of +1.87 V in 8 M HClO_4 (Smith and Getz, 1938; Wadsworth et al., 1957), cerium(IV) perchlorate has not been often used as a reagent for organic reactions. When it is used, this is mostly under the form of an aqueous perchloric acid solution. The lack of interest in cerium(IV) perchlorate in comparison to ammonium hexanitratocerate(IV) can partially be explained by the fact that the former is more difficult to handle than other cerium(IV) salts. Perchlorates can be hazardous chemicals (for instance grinding of the solid compound can lead to an explosion) and this is also true for cerium(IV) perchlorate. Metal perchlorates are often very hygroscopic, because the perchlorate anion is a weakly coordinating anion. In aqueous solutions, perchlorate ions are not coordinated to the cerium(IV) ion. This lack of complex formation, causes hydrolysis of cerium(IV), even in strongly acidic solutions. In an aqueous perchloric acid solution of cerium(IV) perchlorate, different species are present. They include hydrated Ce^{4+} ,

the hydrolyzed species $[\text{Ce}(\text{OH})]^{3+}$ and $[\text{Ce}(\text{OH})_2]^{2+}$, and the dimeric species $[\text{Ce}-\text{O}-\text{Ce}]^{6+}$ (Sherrill et al., 1943; Heidt and Smith, 1948; Baker et al., 1960). The tendency to form dimers increases at increasing cerium(IV) concentrations. Although there is agreement that hydrolysis products and dimeric species co-exist in solution, there is still discussion about which hydrolyzed species are actually present and about the exact values of the equilibrium constants.

Standardized solutions of cerium(IV) perchlorate can be prepared starting from ammonium hexanitratocerate(IV) (Daugherty and Taylor, 1972). Under this firm, cerium(IV) is reduced to cerium(III) by hydrogen peroxide, and cerium(III) is precipitated by oxalic acid. Cerium(III) oxalate is ignited to form cerium dioxide, which is subsequently dissolved in hydrogen peroxide, and the latter is destroyed by boiling. Finally, cerium(III) is electrolytically oxidized to cerium(IV).

5.7. Cerium(IV) methanesulfonate

Solutions of cerium(IV) methanesulfonate, $\text{Ce}(\text{CH}_3\text{SO}_3)_4$, in aqueous methanesulfonic acid are most conveniently obtained by electrochemical oxidation of the corresponding cerium(III) methanesulfonate solution (Kreh et al., 1987, 1989; Kreh, 1988). A solution of cerium(III) in aqueous methanesulfonic acid can be prepared by adding the acid to a stirred suspension of cerium(III) carbonate in water. The behavior of solutions of cerium(III) and cerium(IV) methanesulfonate have been discussed in section 8. Because cerium(IV) has a lower solubility than cerium(III) in methanesulfonic acid, a solid cerium(IV) compound precipitates from concentrated cerium(III) methanesulfonate solution in dilute methanesulfonic acid during electrochemical oxidation. The stoichiometry of this solid compound is $\text{Ce}(\text{CH}_3\text{SO}_3)_2(\text{OH})_2 \cdot \text{H}_2\text{O}$ and its solubility in water is high, up to 1.7 M. The salt can be used for preparing solutions of cerium(IV) methanesulfonate in aqueous methanesulfonic acid. $\text{Ce}(\text{CH}_3\text{SO}_3)_2(\text{OH})_2 \cdot \text{H}_2\text{O}$ can be used for oxidation reactions as a solution in water or as a suspension in aqueous methanesulfonic acid. Both methods give similar results in most cases, although sometimes the suspension method works better. The use of slurries of this solid oxidant generates the more soluble cerium(III) methanesulfonate upon reduction. Other names that are used for cerium(IV) methanesulfonate are ceric mesylate and ceric methanesulfonate.

5.8. Cerium(IV) triflate

The rare-earth salts of trifluoromethanesulfonic acid (triflic acid) are popular reagents for lanthanide-mediated organic reactions. Especially scandium(III) triflate, $\text{Sc}(\text{CF}_3\text{SO}_3)_3$, and ytterbium(III) triflate, $\text{Yb}(\text{CF}_3\text{SO}_3)_3$, are often used as mild Lewis acids for reactions in water (Kobayashi et al., 2002). It is therefore surprising that only very few studies of cerium(IV)-mediated reactions describe the use of cerium(IV) triflate, $\text{Ce}(\text{CF}_3\text{SO}_3)_4$ or $\text{Ce}(\text{OTf})_4$, as a reagent. This salt was first reported by Kreh et al. (1987), who prepared a solution of cerium(IV) in aqueous triflic acid by electrochemical oxidation of a cerium(III) triflate solution. They illustrated the use of this reagent for oxidation of alkylaromatic and polycyclic aromatic compounds. Imamoto et al. (1990) prepared cerium(IV) triflate by reaction

of cerium(IV) carbonate with triflic acid. These authors noticed that "wet" cerium(IV) carbonate has to be used; dry cerium(IV) carbonate did not react. Cerium(IV) carbonate can be prepared by mixing aqueous solutions of potassium carbonate and ammonium hexanitratocerate(VI). Attempts to prepare cerium(IV) triflate by reaction of cerium(IV) hydroxide or cerium(IV) oxide were unsuccessful. The compound could be obtained as a bright yellow hygroscopic solid with composition $\text{Ce}(\text{CF}_3\text{SO}_3)_4 \cdot 1.5\text{H}_2\text{O}$, which decomposes above 120 °C into cerium(III) triflate. It is soluble in water, ethanol, tetrahydrofuran, 1,2-dimethoxyethane and 1,4-dioxane. Commercial cerium(IV) triflate hydrate, $\text{Ce}(\text{CF}_3\text{SO}_3)_4 \cdot n\text{H}_2\text{O}$, contains 2 to 5 moles of water (available from Aldrich). By using triflic anhydride (TfOTf) as a dehydrating agent, it is possible to obtain anhydrous cerium(IV) triflate in the form of a pale yellow powder (Berthet et al., 2000):



The reaction can be carried out at room temperature. In contrast to the hydrated form, the anhydrous form is stable against reduction: no decomposition was observed after 15 hours of heating at 100 °C. Cerium(IV) triflate is soluble in coordinating solvents like pyridine, tetrahydrofuran and diethyl ether; stable Lewis base adducts are formed. Although no crystal structure of anhydrous cerium(IV) triflate has been determined yet, it is assumed that this compound forms a polymeric structure with bridging triflate groups.

Cerium(IV) triflate has been used for epoxide ring opening (Iranpoor et al., 1998, 2002, 2003), benzylic oxidations of aromatics (Laali et al., 2001), oxidation of α -methylpyrrole (Thyran and Lightner, 1996), esterification (Iranpoor and Shekarriz, 1999a), iodofunctionalization of alkenes (Iranpoor and Shekarriz, 2000), the synthesis of biaryls (Iranpoor and Shekarriz, 1999b), and the deprotection of trityl ethers (Khalafi-Nezhad and Alamdari, 2001) and *tert*-butyldimethylsilyl ethers (Bartoli et al., 2002). Studies on the oxidation of benzylic compounds by cerium(IV) triflate (Laali et al., 2001), showed that the water content has a marked influence on the oxidation ability; the optimal water content is between 14 and 22 wt.% water. Commercial samples were found to have a lower oxidation power than freshly prepared samples. This behavior could be traced back to a lower water content in the commercial samples (11 to 13 wt.%). However, rehydration of the commercial samples did not lead to an activity as high as that of the initial samples. These studies show that the performance of cerium(IV) triflate as an oxidizing reagent depends very much on the preparation method. On the other hand, less unwanted side products are obtained than with ammonium hexanitratocerate(IV).

5.9. Hydrophobic cerium(IV) reagents

Although ammonium hexanitratocerate(IV) is a good reagent for many organic transformations in aqueous solutions or in polar organic solvents, it is much less suitable for use in non-polar organic solvents due to its poor solubility in these solvents. Several authors have tried to overcome these solubility problems by replacing the ammonium group by tertiary or quaternary ammonium ions. These ions are more hydrophobic (more lipophilic) than the ammonium ion, and its can be expected that the resulting cerium(IV) reagents dissolve as ion-pairs in apolar solvents.

Dehmlow and Makrandi (1986) prepared tetra-*n*-butylammonium hexanitratocerate(IV), $[(n\text{-Bu})_4\text{N}]_2[\text{Ce}(\text{NO}_3)_6]$, for use as an oxidant in solvents like dichloromethane. Here tetra-*n*-butylammonium acted as a phase reagent to transfer the hexanitratocerate(IV) anion into the organic phase. This reagent has been explored further by other authors for direct use in dichloromethane (Muathen, 1991; Chen and Mariano, 2000; Zhang et al., 2003a, 2003b, 2004; Zhang and Flowers II, 2004) and it is known as CTAN. Mishra et al. (2001) developed cetyltrimethylammonium hexanitratocerate(IV), $[(\text{C}_{16}\text{H}_{33})\text{N}(\text{CH}_3)_3]_2[\text{Ce}(\text{NO}_3)_6]$, which is soluble in both polar and apolar solvents due to its amphiphilic nature. It has been reported to be soluble in water, methanol, ethanol, chloroform, dioxane, benzene, tetrahydrofuran, acetic acid, acetonitrile, ethylacetate, DMF, DMSO, 1-octanol and *iso*-octanol. An example of a cerium(IV) reagent with a tertiary ammonium counter ion is triethylammonium hexanitratocerate(IV), $[\text{Et}_3\text{NH}]_2[\text{Ce}(\text{NO}_3)_6]$ (Firouzabadi and Iranpoor, 1983). These authors report the formula of this compound as $[\text{Ce}(\text{Et}_3\text{NH})_2](\text{NO}_3)_6$, which is misleading. The reagent is soluble in dichloromethane, alcohols, acetone, acetonitrile and water. It is also known as CTEAN, after ceric triethylammonium nitrate. A closely related reagent, that has not been studied in detail yet, is pyridinium hexanitratocerate(IV) (referred to as CPN) (Iranpoor and Owji, 1991).

5.10. Pyridinium hexachlorocerate(IV) (CPC)

Pyridinium hexachlorocerate(IV), $(\text{C}_5\text{H}_6\text{N})_2[\text{CeCl}_6]$, has been known for a long time (Grant and James, 1915), but Bradley and coworkers described a reliable method for the synthesis of this compound in 1956 (Bradley et al., 1956a). For the preparation, cerium(IV) hydroxide is freshly synthesized by addition of an excess of an aqueous sodium hydroxide solution (containing some bromine) to a solution of cerium(IV) ammonium sulfate. The carefully washed cerium(IV) hydroxide precipitate is then suspended in absolute ethanol, and dry hydrogen chloride is bubbled through the solution. The solution is filtrated, and pyridine is added to the filtrate. After further treatment of the solution with hydrogen chloride, the bright yellow $(\text{C}_5\text{H}_6\text{N})_2[\text{CeCl}_6]$ complex can be obtained by crystallization from the solution. Pyridinium hexachlorocerate(IV) is also known as dipyridinium hexachloride or cerium(IV) pyridinium chloride, and is referred to as CPC. The compound is stable in boiling ethanol, but not in boiling methanol (Maini et al., 1978). In boiling acetonitrile, the formation of chlorine gas is observed (Maini et al., 1978). CPC was originally used as a starting material for the synthesis of cerium(IV) alkoxides (Bradley et al., 1956a), and it is a reagent for the side-chain oxidation of highly substituted methylbenzenes (Maini et al., 1978). The pyridinium ions can be replaced by quaternary ammonium ions. Such compounds have not been reported as cerium(IV) reagents, although the synthesis of tetraethylammonium hexachlorocerate(IV), $(\text{NEt}_4)_2[\text{CeCl}_6]$ has been described (Barry et al., 1981). It is prepared by refluxing a solution of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ and tetraethylammonium chloride in thionyl chloride, which acts as an anhydrous oxidative chlorinating medium. The authors claim that this is a general method for the preparation of hexachlorocerate(IV) complexes with different counter ions, such as quaternary ammonium ions, but also quaternary phosphonium ions.

Notice that chloro complexes of cerium(IV) are much less stable than the corresponding nitrate or sulfato complexes, due to the oxidation of the chlorides to molecular chlorine by cerium(IV). For instance, cerium(IV) chloride, CeCl_4 , is an unstable compound.

However, hexachlorocerate(IV) salts have a much higher stability, as is illustrated by pyridinium hexachlorocerate(IV). This complex can be dried without decomposition at 120 °C in vacuo (Bradley et al., 1956a). The CeCl_4 moiety can also be stabilized by adduct formation with neutral ligands. Examples include $[\text{CeCl}_4(\text{dmsO})_3]$ (Brezina, 1971), $[\text{CeCl}_4(\text{tppo})_2]$ (Brezina, 1971), $[\text{CeCl}_4(\text{bpyO}_2)_2]$ (Brezina, 1973) and $[\text{CeCl}_4(\text{tdpo})_2]$ (du Preez et al., 1978; Barry et al., 1978), where dmsO = dimethylsulfoxide, tppo = triphenylphosphine oxide, bpyO_2 = 2,2'-bipyridine-*N,N'*-dioxide and tdpo = tris(dimethylamino)phosphine oxide.

5.11. Cerium(IV) trihydroxy hydroperoxide (CTH)

Cerium(IV) trihydroxy hydroperoxide (CTH), $\text{Ce}(\text{OH})_3\text{O}_2\text{H}$, was developed as a mild oxidation agent (Firouzabadi and Iranpoor, 1984). It can be synthesized by addition of a concentrated ammonia solution to a concentrated solution of cerium(III) chloride in water, followed by addition of hydrogen peroxide (30%). Other names for this orange-red reagent are ceric trihydroxy hydroperoxide and cerium(IV) hydroxide peroxide. The interesting feature of this reagent is that it can simply be regenerated after reaction by treatment of the solid with a concentrated solution of hydrogen peroxide (30%). The reagent has been tested for the oxidation of organic compounds in dry benzene. Since the reagent does not dissolve in benzene, reactions are heterogeneous. CTH is very efficient for the oxidation of benzyl alcohol to benzaldehyde. Benzhydrol is qualitatively oxidized to benzophenone. Hydroquinone and catechol are easily oxidized to the corresponding quinones. Aromatic thiols are converted to disulfides. For most reactions, two to three equivalents of CTH are used with respect to the organic substrate.

Other compounds that contain cerium(IV) and the peroxide group have been reported in the past, but these compounds have not found use as reagent for organic reactions. In 1885, a hydrated cerium(IV) peroxide was prepared by Cleve (Cleve, 1885). Job (1899a, 1899b) and Meloche (1915a, 1915b) reported procedures for the preparation of cerium(IV) peroxy carbonates. Warren (1964) investigated cerium(IV) peroxy acetate, $\text{Ce}_2(\text{O}_2)_3(\text{CH}_3\text{COO})_2$. This compound precipitates as an amorphous solid from an aqueous solution containing acetic acid, sodium acetate, cerium(III) nitrate, and hydrogen peroxide. However, cerium(IV) peroxy acetate is unstable and loses oxygen and acetic acid on standing at room temperature.

5.12. Cerium(IV) periodate

Hydrated cerium(IV) periodate, $\text{CeHIO}_6 \cdot 4\text{H}_2\text{O}$, was obtained as a yellow solid by reaction between $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ and H_5IO_6 in aqueous solutions at low pH (Levason and Oldroyd, 1996). This compound, which is insoluble in water, is able to oxidize benzyl alcohol to benzaldehyde in dichloromethane with tetramethylammonium periodate as co-oxidant, but the yields are only moderate (Griffith et al., 1996).

5.13. Tris[tetrinitratoceria(IV)] paraperiodate (TTCPP)

Tris[tetrinitratoceria(IV)] paraperiodate, $[\text{Ce}(\text{NO}_3)_3]_3 \cdot \text{H}_2\text{IO}_6$ (TTCPP for short) was developed as a reagent for oxidation reactions in aprotic organic solvents under neutral conditions (Firouzabadi et al., 1984d). TTCPP is sometimes also formulated as $[\text{Ce}(\text{NO}_3)_3]_3 \cdot \text{HIO}_6$

(Heravi et al., 1999). Heterogeneous reaction conditions are chosen for this compound. The reagent was prepared by addition of a solution of ammonium hexanitratocerate(IV) to a solution of potassium periodate, KIO_4 , in water. TTCPP is a very efficient oxidant for the cleavage of 1,2-diols to aldehydes. It also works well for the common oxidation reactions for which tetravalent cerium is used, like oxidation of benzyl alcohol to benzaldehyde and the oxidation of thiols to disulfides. Whereas triphenylphosphine is resistant towards oxidation by CAN, it is quantitatively converted to triphenylphosphine oxide by TTCPP. Other applications of tris[tetrinitratoceria(IV)] paraperiodate include the regioselective and stereoselective ring opening of epoxides (Iranpoor and Zardaloo, 1994), the tetrahydropyranlation of alcohols (Oskooie et al., 1998), and the oxidative deprotection of trimethylsilyl ethers to the corresponding carbonyl compounds (Firouzabadi and Shiriny, 1996a).

5.14. Bis[tetrinitratoceria(IV)] chromate and dinitratoceria(IV) chromate dihydrate

Bis[tetrinitratoceria(IV)] chromate, $[\text{Ce}(\text{NO}_3)_3]_2\text{CrO}_4$, was introduced as a mild oxidizing agent by Firouzabadi et al. (1984a). It is obtained as an orange-yellow compound by mixing a solution of potassium dichromate and ammonium hexanitratocerate(IV) in water. The compound is quite stable up to 190 °C. The reagent was developed for oxidation reactions in aprotic organic solvents. Bis[tetrinitratoceria(IV)] chromate worked well for oxidizing organic compounds in refluxing benzene, but not in refluxing dichloromethane. In contrast to tris[tetrinitratoceria(IV)] paraperiodate, bis[tetrinitratoceria(IV)] chromate cannot oxidize triphenylphosphine. The reagent has been used for the oxidation of thiols to disulfides (Firouzabadi et al., 1984b), the tetrahydropyranlation of alcohols (Oskooie et al., 1998), and oxidation of trimethylsilyl ethers to the corresponding carbonyl compounds (Firouzabadi and Shiriny, 1996b).

Dinitratoceria(IV) chromate dihydrate, $[\text{Ce}(\text{NO}_3)_3]_2\text{CrO}_4 \cdot 2\text{H}_2\text{O}$, was presented as a more economical alternative to bis[tetrinitratoceria(IV)] chromate because of the smaller cerium(IV)/chromium(VI) ratio (Firouzabadi et al., 1984c). It has been tested for the oxidation of different organic compounds like benzyl alcohols, secondary alcohols, and thiols in benzene, but in general the yields are lower than for bis[tetrinitratoceria(IV)] chromate. Later it was reported that this reagent gave unsatisfying results for the oxidative deprotection of trimethylsilyl ethers (Firouzabadi and Shiriny, 1996a, 1996b).

5.15. Cerium(IV) alkoxides

The first detailed accounts on the synthesis of cerium(IV) alkoxides have been published by Bradley and coworkers (Bradley et al., 1956a, 1956b, 1957). The cerium(IV) alkoxides of methanol, ethanol, *n*-propanol, *n*-butanol, *n*-pentanol, *iso*-butanol and *neo*-pentanol were prepared by passing ammonia gas through a solution of pyridinium hexachlorocerate(IV) and the corresponding alcohol in benzene (Bradley et al., 1956a). With *iso*-propanol, not the pure cerium(IV) isopropoxide was obtained, but an *iso*-propanol solvate. This compound was used to prepare other cerium(IV) alkoxides by alcohol interchange. Most of the cerium(IV) alkoxides are bright yellow solids that are extremely sensitive to hydrolysis. Upon heating the compounds melt without decomposition. However, the cerium(IV) *neo*-pentoxide is volatile so

that it could be sublimed. Later, cerium(IV) *iso*-propoxide (Bradley et al., 1956b) and the cerium(IV) alkoxides of several tertiary alcohols (Bradley et al., 1957) were also found to be volatile. The non-volatile cerium(IV) alkoxides are assumed to have a oligomeric or polymeric structure. Cerium(IV) methoxide and cerium(IV) ethoxide are insoluble in benzene or toluene. Gradeff and coworkers (Gradeff et al., 1985, 1986) reported procedures for the synthesis of cerium(IV) alkoxides from the readily available ammonium hexanitratocerate(IV), rather than from pyridinium hexachlorocerate(IV) (that has to be synthesized separately). Evans et al. (1989a) prepared a series of cerium(IV) *tert*-butoxides and cerium(IV) *tert*-butoxides by reaction between ammonium hexanitratocerate(IV) and sodium *iso*-butoxide. The stoichiometry of the complexes depended on the reaction conditions (solvent, molar ratio between reagents). The bulky *tert*-butoxide ligand allows stabilization of the complexes and causes an increase in solubility. Due to their susceptibility to hydrolysis, the cerium(IV) alkoxides are not used as reagents in organic synthesis, but they are very useful starting materials for the synthesis of cerium(IV) coordination compounds and organocerium(IV) compounds.

5.16. Cerium(IV) fluoride

Cerium(IV) fluoride or cerium tetrafluoride, CeF₄, can be prepared by reaction of cerium(III) fluoride with elemental fluorine at 450 to 500 °C (Cunningham et al., 1954; Wartenburg, 1940; Kim et al., 2003). It is also formed by reaction of xenon tetrafluoride, XeF₄, with cerium(III) fluoride at 200–400 °C (Spitsyn et al., 1974) or by stepwise reaction of xenon difluoride, XeF₂, with cerium(III) fluoride at 177 °C, 236 °C and 295 °C (Kiselev et al., 1985). Interestingly, reaction of CeO₂ with elemental fluorine does not yield CeF₄, but CeF₃ (Takashima et al., 1992). CeF₄ has a higher thermal stability than fluorides of other tetravalent lanthanides and actinides, but will eventually decompose with the release of gaseous fluorine (Kaiser et al., 1972; Gibson and Haire, 1988a, 1988b; Rau et al., 2001). Lanza and Fragala (1998) published a theoretical study on the molecular geometry, vibrational frequencies and bond dissociation energies of CeF₄. Cerium(IV) fluoride is a solid fluorinating agent, which has been used for the fluorination of benzene (Hudson et al., 1969) and benzotrifluoride (Hudson and Pedler, 1970) (see section 6.7). It was found that cerium(IV) fluoride could be regenerated *in situ* in the fluorination reactor by passing fluorine gas over the cerium(III) fluoride that was formed upon fluorination of benzene. It is also able to fluorinate ethylene (Asovich et al., 1994).

5.17. Cerium dioxide

Cerium dioxide (ceria) is a well-known heterogeneous catalyst. It is a key component in important industrial processes like fluid catalytic cracking and in the three-way catalyst in automobile exhaust systems. CeO₂ is also applied for the oxidative destruction of organic compounds in waste water and for removal of soot particles in diesel engine exhaust gases. The interested reader is referred to a book edited by Trovarelli (Trovarelli, 2002). In section 10.2 the use of cerium dioxide as photocatalyst for the decomposition of water is described. CeO₂ nanoparticles are catalyst for the photooxidation of toluene (Hernandez-Alonso et al., 2004). It can be expected that cerium dioxide, especially in the form of nanoparticles, has potential for application as reagents for organic transformations.

5.18. Supported cerium(IV) reagents

Supported reagents and catalysts offer the advantage of easy separation of excess reagent or catalyst from the products by simple filtration. Fischer and Henderson (1985) introduced ammonium hexanitratocerate(IV) coated on silica gel as a reagent for convenient oxidation of hydroquinones to quinones. The cerium(IV)/SiO₂ oxidizing agents with 10% to 20% ammonium hexanitratocerate(IV) was prepared by addition of dichloromethane, followed by silica gel to an efficiently stirred solution of ammonium hexanitratocerate(IV) in methanol. Evaporation of the solvents gave a free-flowing yellow powder. This supported reagent has been used for the deprotection of benzaldehyde diacetates to benzaldehydes (Cotelle and Catteau, 1992), for the removal of trityl and silyl protecting groups (Hwu et al., 2000), and for the removal of the *tert*-butoxycarbonyl (*t*-Boc) group (Hwu et al., 2002). Chawla and Mittal (1985) used silica gel-supported ammonium hexanitratocerate(IV) for the oxidative nitration of naphthalene, anthracene and phenanthrene. The adsorption of the cerium(IV) salt on silica gel reduced its oxidizing power so that mononitro derivatives could be obtained as the main product, whereas solutions of ammonium hexanitratocerate(IV) yield considerable amounts of dinitro derivatives or of the corresponding quinones. The authors use a quite uncommon reaction technique. They adsorb the polycyclic aromatic compound and the cerium(IV) salt separately on silica gel in an acetonitrile solution. The solvent is evaporated and the silica gel is dried. The dried powders are thoroughly mixed, added on top of a column packed with silica gel and eluted by a petroleum/benzene mixture. The mixture reacts in the column and the reaction product is collected in the eluate. Sulfides could be oxidized fast and in excellent yields to the corresponding sulfoxides by ammonium hexanitratocerate(IV) supported on hydrated silica gel in dichloromethane (Ali et al., 1998). Ammonium hexanitratocerate(IV) supported on silica gel in refluxing carbon tetrachloride or tetrachloroethylene have a low activity for the oxidation of cyclododecanol to cyclododecanone (Nishiguchi and Asano, 1989). Cerium(IV) sulfate supported on silica gel is an efficient catalyst for the acylation of alcohols by esters (Nishiguchi and Taya, 1990), such as ethyl formate or ethyl acetate which were used both as reagents and solvents. Microwave irradiation accelerates the oxidation of benzyl alcohols by ammonium hexanitratocerate(IV) supported on silica gel (Heravi et al., 2004).

Clay supported bis[trinitratocerium(IV)] chromate and tris[trinitratocerium(IV)] paraperiodate (on montmorillonite K-10 clay) have been used for the oxidative deprotection of tetrahydropyranyl ethers to the corresponding carbonyl compounds in dichloromethane (Heravi et al., 1999). The authors mention as advantages of the methodology the mild conditions, quite fast reaction times and good to high yields. Aghapoor et al. (2002) reported that for the cleavage of semicarbazones to the corresponding carbonyl compounds under solventless conditions (and with microwave irradiation) ammonium hexanitratocerate(IV) supported on wet alumina is a superior reagent in comparison with the same salt supported on montmorillonite K-10 clay or on silica gel.

There are only very few examples of polymer-supported cerium(IV) salts. Kanemoto et al. (1984) used ammonium hexanitratocerate(IV) impregnated in Nafion[®] as a catalyst for the oxidation of alcohols with *tert*-butylhydroperoxide. Nafion[®] is Dupont's brand name for a perfluorinated copolymer with sulfonate groups. This supported catalyst is also active for the oxidation of alcohols (Yamato and Shinoda, 2002) and of polyaromatic compounds (Yamato et

al., 2000) by sodium bromate. Poly(vinylpyridine) supported cerium(IV) nitrate has been used for the catalytic ring opening of epoxides (Tamani et al., 1993). This reagent can be considered as the solid analogue of pyridinium hexanitratocerate(IV). The pyridine group of the polymer becomes protonated under the reaction conditions used for the preparation of the reagent.

Hatanaka and coworkers prepared a CAN catalyst supported on activated charcoal (Hatanaka et al., 1983). The catalyst can be prepared by adding activated charcoal (3.0 g) to a solution of ammonium hexanitratocerate(IV) (0.82 g) in water (100 mL) with stirring. After 10 minutes, the solid compound is collected by filtration and dried in vacuo. The CAN-charcoal catalyst is effective for the oxidation of benzyl alcohols and acyloins to the corresponding carbonyl compounds.

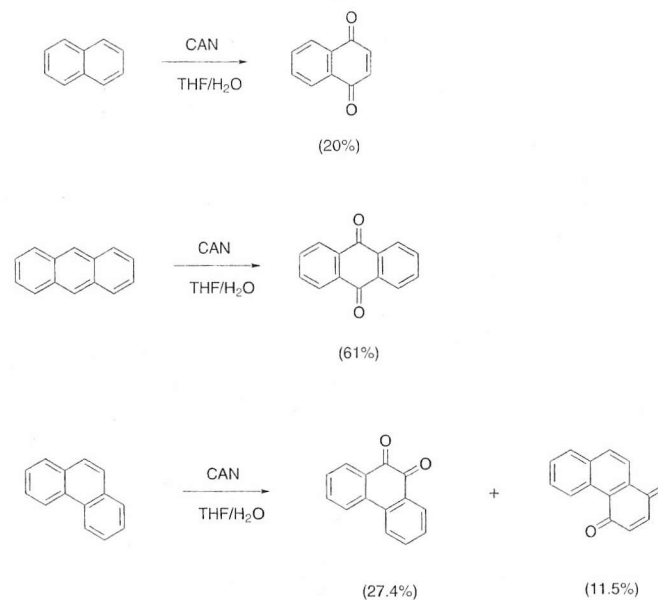
5.19. Other cerium(IV) compounds

Weakley-type polyoxometalate $\text{Na}_6\text{H}_2[\text{CeW}_{10}\text{O}_{36}]$ can be solubilized in apolar organic solvents by exchanging the counter ions for *N*-hexadecylpyridinium ions (Shiozaki et al., 1996). However, the corresponding compounds with tetraalkylammonium cations could not be obtained in acceptable purity. The reagent has been used for the oxidation of benzyl alcohols and secondary alcohols with hydrogen peroxide as oxidant. Ammonium decatungstocerate(IV), $(\text{NH}_4)_8[\text{CeW}_{10}\text{O}_{36}] \cdot 20\text{H}_2\text{O}$ can convert oxiranes into the corresponding thiiranes in the presence of ammonium thiocyanate and thiourea (Mirkhani et al., 2002). Cerium(IV) nitrates are not used as such, but cerium(III) nitrate hexahydrate, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, is a precursor for electrochemically generated cerium(IV) at a rather low anodic potential (1.4 V) (Cho and Romero, 1995). Therefore it can be used for organic electrosynthesis in solvents like acetonitrile. Cerium(III) nitrate is also used for the generation of the active cerium(IV) species in the CerOx process (see section 11.5). Tetranitratobis(triphenylphosphine oxide)cerium(IV) can be synthesized by mixing a solution of ammonium hexanitratocerate(IV) in acetone with a solution of triphenylphosphine oxide in acetone (Mazhar-ul-Haque et al., 1971). Ammonium nitrate will precipitate in acetone, and the cerium(IV) complex can be recovered by removal of the solvent. Tetravalent cerium forms stable tetrakis complexes with β -diketonate ligands (Allard, 1976; Baxter et al., 1998; Binnemans, 2005), but these compounds have not yet found use as reagents in cerium-mediated organic reactions.

6. Stoichiometric cerium(IV)-mediated reactions

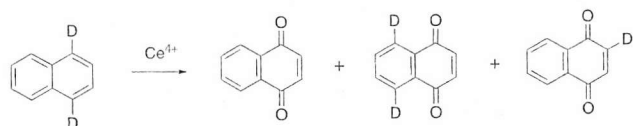
6.1. Oxidation of hydrocarbons

Polynuclear aromatic systems are oxidized to the corresponding quinones by ammonium hexanitratocerate(IV) in aqueous THF under mild conditions (25–60 °C) (scheme 1) (Ho et al., 1973). Water is the source of oxygen in the oxidation process. The yields are reasonable, but not very high, and the reaction is only useful for symmetric molecules like naphthalene and anthracene. Substituted and asymmetric substrates give often an intractable mixture of oxidation products (Balanikas et al., 1988). A problem associated with the use of ammonium hexanitratocerate(IV) is that nitration of the aromatic ring can also occur. Cerium(IV) ammonium

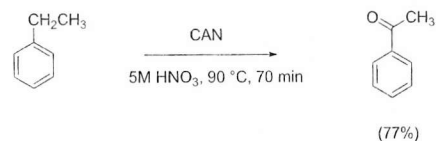
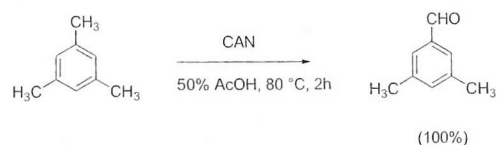


Scheme 1.

sulfate dissolved in a mixture of acetonitrile and 4 M aqueous sulfuric acid has been used as an alternative reaction medium for this reaction, leading to higher yields than with CAN in aqueous THF (Periasamy and Bhatt, 1977a). For instance, naphthoquinone could be obtained in 90 to 95% yield by this method. Six moles of cerium(IV) ammonium sulfate are required for the oxidation of one mole of naphthalene to 1,4-naphthoquinone. Kinetic experiments have shown that the initial step in the reaction is the formation of a 1 : 1 complex between cerium(IV) and naphthalene (Bhatt and Periasamy, 1993). This complex slowly decomposes to afford the naphthalene radical cation that is converted by fast further reaction steps into the 1,4-naphthoquinone. Periasamy and Bhatt observed a 1,2-shift in the oxidation of naphthalene and its derivatives (Periasamy and Bhatt, 1977b). For instance, the oxidation of deuterium-labeled naphthalene gave a mixture of three products (scheme 2). These results show that deuterium migrates to some extent from the 1- to the 2-position. Similar migration has been observed for phenyl or bromine substituents in oxidation of substituted naphthalenes. Later work has shown that this shift can arise from involvement of radical cations (Bhat et al., 1979; Bhatt and Periasamy, 1994). Rindone and Scolastico (1971) studied the reaction mechanism of the oxidation of anthracene by CAN in acetonitrile, methanol and acetic acid. The oxidation reaction occurs via an initial anthracene radical cation. The trinuclear aromatic compounds anthrone,



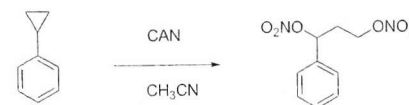
Scheme 2.



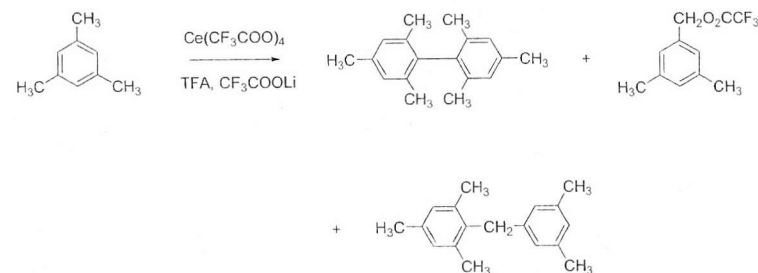
Scheme 3.

xanthen and thioxanthen were oxidized by CAN in methanol to anthraquinone, xanthone and thioxanthone, respectively (Rindone and Scolastico, 1975). Phenazine is oxidized in methanol to the corresponding mono-*N*-oxide. No reaction was observed for phenazine in acetic acid.

In an aqueous acidic medium (perchloric, nitric or acetic acid), ammonium hexanitratocerate(IV) readily oxidizes a single aromatic methyl group to an aldehyde group in very high yields (scheme 3) (Syper, 1966; Laing, 1968). Toluene is first oxidized to benzyl alcohol, and benzyl alcohol is further oxidized to benzaldehyde (Young and Trahanovsky, 1967). Dust and Gill (1970) report that the major primary reaction product of the oxidation of methylbenzenes by CAN in dilute nitric acid solution is a benzyl nitrate ester, which is subsequently hydrolyzed to the corresponding benzyl alcohol. Finally the benzyl alcohol is oxidized to the aldehyde. Reaction temperatures higher than 60 °C have to be avoided, because otherwise further oxidation of the aldehyde into the carboxylic acid occurs. The presence of electron-withdrawing groups (e.g. nitro or chloro groups) on the aromatic ring diminishes the yields. However, a second methyl group can be oxidized only under much more drastic reaction conditions. The benzylic CH_2 group of alkyl-substituted benzenes is oxidized to a ketone function (Syper, 1966). Methylbenzenes with a strongly electron-donating group like a methoxy, amino or hydroxy group tend to polymerize (Young and Trahanovsky, 1967). Tzedakis and Savall (1992) investigated the kinetics of the oxidation of 4-methoxytoluene to 4-methoxybenzaldehyde by cerium(IV) sulfate in aqueous sulfuric



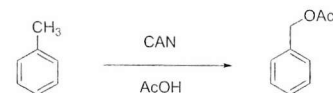
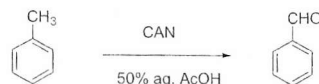
Scheme 4.



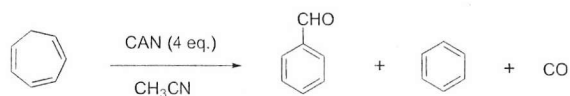
Scheme 5.

acid. Naphthalenes with a methyl group in the 1-position are oxidized to the corresponding naphthaldehydes by CAN in aqueous acetic acid at 80 °C (Sydnes et al., 1985). Arylcyclopropanes are cleaved by CAN to dinitrates in acetonitrile and to a mixture of dinitrates and nitrate acetates in acetic acid as solvent (Young, 1968). The major product of the reaction of cyclopropylbenzene with CAN in acetonitrile or in acetonitrile/methanol mixed solvents is 1-phenylpropane-1,3-diyl dinitrate (scheme 4) (Wang and Tanko, 1998). Cerium(IV) trifluoroacetate dissolved in trifluoroacetic acid containing lithium trifluoroacetate oxidizes mesitylene to a mixture of products (scheme 5) (Norman et al., 1973). Also other electron-rich aromatic hydrocarbons react under these conditions, but benzene is unreactive. Cerium(IV) triflate has been proposed as an alternative to ammonium hexanitratocerate(IV) for the oxidation of alkylbenzenes under very mild conditions (Imamoto et al., 1990). The choice of the solvent is an important parameter controlling the reactivity of alkylbenzenes in presence of cerium(IV) salts (scheme 6). In general, carbonyl compounds are obtained in acidic aqueous medium. However, benzylic acetates are formed in glacial acetic acid (Baclocchi et al., 1986; Trahanovsky and Young, 1966), and ethers in alcoholic solvents (Della Cort et al., 1983). Nitrates are formed by reaction of methylbenzenes with CAN in acetonitrile under photolytic conditions (Baclocchi et al., 1984a). In the absence of solvent, toluene is oxidized by CAN to benzaldehyde, but *ortho*-xylene gives 2-methylbenzyl nitrate.

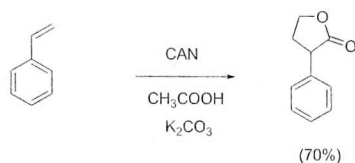
1,3,5-Cycloheptatriene is rapidly oxidized at 90 °C by 4 equivalents of ammonium hexanitratocerate(IV) in aqueous acetic acid to a mixture of benzaldehyde, benzene and carbon monoxide (scheme 7) (Trahanovsky et al., 1969d). The reaction works also in other solvents like acetonitrile and water. There is evidence that the tropylium ion is an intermediate in this



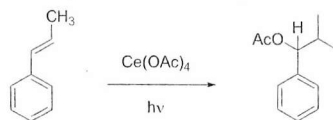
Scheme 6.



Scheme 7.



Scheme 8.



Scheme 9.

reaction. In anhydrous acetonitrile, the oxygen of the benzaldehyde produced comes from the nitrate ion of ammonium hexanitratocerate(IV).

The reaction of styrene with cerium(IV) acetate in glacial acetic acid containing 10% potassium acetate at 110 °C for 20 hours gives a lactone (scheme 8) (Heiba and Dessau, 1971). The reaction works with ammonium hexanitratocerate(IV) as well. The photochemical reaction of *trans*- β -methylstyrene gives an ester as the major product (scheme 9).

6.2. Oxidation of alcohols and phenols

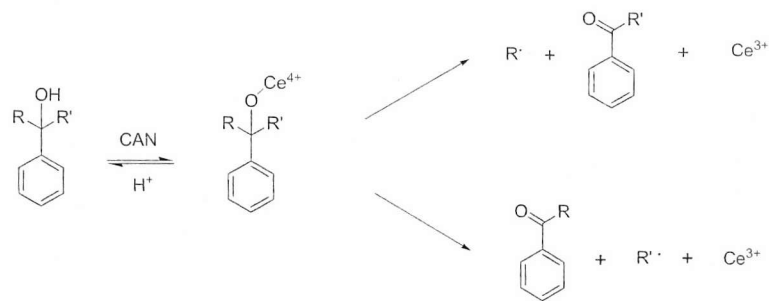
Depending on the structure of the alcohol, different types of reaction products can be formed by the reaction between an alcohol and a cerium(IV) salt (Ho, 1973; Trahanovsky, 1973). The alcohol can undergo direct oxidation, fragmentation or a combination of both processes. Benzyl alcohols and hydroxymethylcyclopropanol are oxidized in high yields to the corresponding aldehydes (scheme 10) (Trahanovsky et al., 1967; Young and Trahanovsky, 1969). These reactions are good synthetic routes for the preparation of these aldehydes, because the aldehydes are less easily oxidized by cerium(IV) than the alcohols. The fact that benzyl alcohols and hydroxymethylpropanol do not undergo oxidative cleavage can be rationalized by the low stability of the phenyl and cyclopropyl radicals. The presence of stable carbon radicals is indeed a condition for oxidative cleavage to occur.

Oxidation of benzyl alcohols is generally performed with ammonium hexanitratocerate(IV) (2.1. equivalents) in water or in aqueous acetic acid. Primary alcohols are in general resistant to oxidation by cerium(IV) reagents, although cyclic ethers can be formed (see below). Ethanol can be oxidized to acetaldehyde and acetic acid (Briois et al., 2005). Secondary alcohols are oxidized to the corresponding ketones (although slower than benzylic alcohols). Tertiary alcohols are fragmented by oxidative cleavage to give ketones with the formation of radicals (scheme 11) (Trahanovsky and Macaulay, 1973). Vicinal diols (1,2-diols) undergo oxidative cleavage (Trahanovsky et al., 1969c; Hintz and Johnson, 1967). Duke and coworkers showed that this oxidation takes place via the disproportionation of a coordination complex formed between the 1,2-diol and cerium(IV) (Duke and Forist, 1949; Duke and Bremer, 1951). The mechanism involves probably the formation of a monodentate cerium(IV) complex, followed by a one electron-cleavage to form an intermediate radical (Trahanovsky et al., 1973) which can be trapped by addition of acrylamide (Trahanovsky et al., 1969c). Mino and coworkers studied the oxidation of 2,3-dimethylbutane-2,3-diol (pinacol) to acetone by cerium(IV) sulfate in water (Mino et al., 1959).

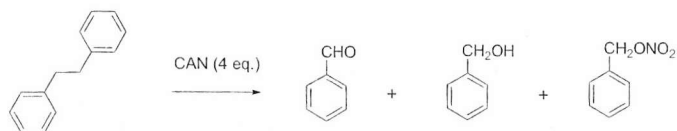
1,2-Diarylethanols give only products of oxidative cleavage (Nave and Trahanovsky, 1968, 1971; Trahanovsky and Brixius, 1973). For instance, 1,2-diphenylethanol is oxidized by 4 equivalents of CAN to a mixture of benzaldehyde, benzyl alcohol and benzyl nitrate (scheme 12) (Trahanovsky and Brixius, 1973). A radical cation intermediate is involved.



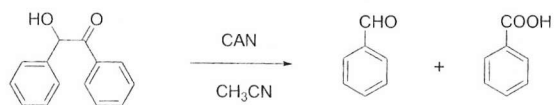
Scheme 10.



Scheme 11.



Scheme 12.



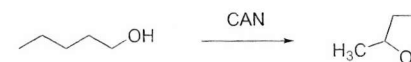
Scheme 13.

Phenylarylmethanols are transformed by cerium(IV) into a mixture of benzaldehyde and an alkyl phenyl ketone (Trahanovsky and Cramer, 1971). The ratio of the yield of benzaldehyde to the yield of ketone depends largely on the alkyl group. Ketone formation is predominant for methylphenylmethanol, whereas *iso*-propylmethanol and *tert*-butylmethanol undergo mainly oxidative cleavage. For ethylphenylketone, oxidative cleavage and ketone formation are of equal importance. These results can be explained by the high stability of the *iso*-propyl and *tert*-butyl free radicals. Benzoin is split by ammonium hexanitratocerate(IV) into an aryl aldehyde and an aryl radical. The radical is oxidized further to an arenecarboxylic acid (Ho, 1972). For instance benzoin itself is split into benzaldehyde and benzoic acid (scheme 13).

Cyclopropanol (Schaafsma et al., 1966) and cyclobutanol (Meyer and Roček, 1972) undergo rapid oxidative cleavage, due to the release of the strain energy of the aliphatic ring. Chain opening is a typical reaction of strained cycloalkanol in presence of one-electron oxidants. A mixture of reaction products is formed, and the actual composition of the reaction



Scheme 14.

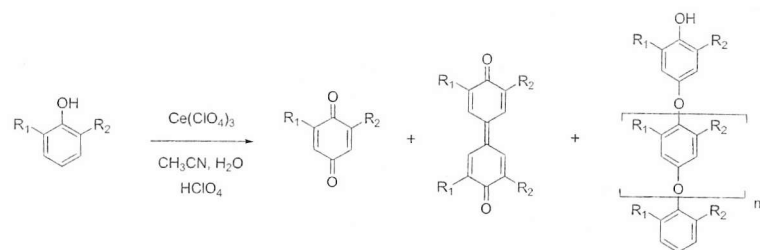


Scheme 15.

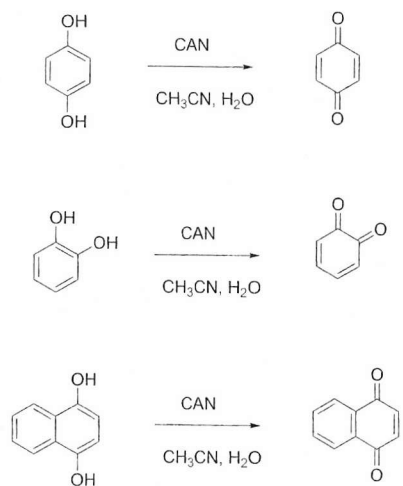
mixture depends on the reaction conditions, which can be optimized in order to obtain one major component. For instance, succinaldehyde is the only product observed upon oxidation of cyclobutanol with ammonium hexanitratocerate(IV) in acetonitrile in presence of molecular oxygen (Meyer and Roček, 1972). Cyclopentanol and cyclohexanol are oxidized by cerium(IV) sulfate to cyclopentanone, resp. cyclohexanone (Hintz and Johnson, 1967). Although adamantan-2-ol is initially oxidized by ammonium hexanitratocerate(IV) to adamantanone, it is subsequently transformed into a lactone by a Baeyer-Villiger oxidation reaction (scheme 14) (Soucy et al., 1972). The main reaction for bicyclic alcohols like bicyclo[2.2.1]-2-heptanol and bicyclo[2.2.2]-2-octanol is oxidative cleavage (Trahanovsky et al., 1969b).

Certain primary alcohols that possess a δ -hydrogen undergo an intramolecular cyclization into a tetrahydrofuran derivative via alkoxy δ -hydrogen abstraction and subsequent ring closure. For instance, *n*-pentanol reacts with ammonium hexanitratocerate(IV) to afford 2-methyltetrahydrofuran (scheme 15) (Trahanovsky et al., 1969a). This reaction has been further investigated by Doyle and coworkers (Doyle et al., 1975), who were also able to oxidize 5-phenyl-1-pentanol and 4-phenyl-1-butanol into 2-benzyltetrahydrofuran and 2-phenyltetrahydrofuran, respectively.

Simple phenols undergo oxidation and oxidative coupling reactions in presence of cerium(IV) salts (scheme 16). 2,6-dimethylphenols are oxidized to 4,4'-diphenoquinone and 1,4-benzoquinone derivatives by cerium(IV) perchlorate in aqueous or aqueous-acetonitrile solutions of perchloric acid at room temperature (Ignaczak and Dziegieć, 1992). The oxidation of 2,6-diisopropylphenol, 2-*tert*-butyl-6-methylphenol, 2,6-diphenylphenol and 2,6-dichlorophenol proceeds under the same experimental conditions to the corresponding 4,4'-diphenoquinones and oligomeric poly(1,4-phenylene) oxides (Domagała et al., 1998). 2,6-difluorophenol and 2,3,5,6-tetrafluorophenol give a high yield of the poly(1,4-phenylene) oxides (Prawicki and Dziegieć, 1996; Grzejdzia and Dziegieć, 1997), whereas 2,6-di-*tert*-butylphenol gives a high yield of the 4,4'-diphenoquinone (Ignaczak and Dziegieć, 1992). These differences in reactivity can be attributed to the stabilization of cation radicals in acidic phenols (those with fluoro or chloro substituents) or radicals (in phenols with branched alkyl groups).



Scheme 16.



Scheme 17.

6.3. Oxidation of hydroquinones and catechols

Hydroquinones (1,4-dihydroxybenzenes) and catechols (1,2-dihydroxybenzenes) are easily oxidized by ammonium hexanitratocerate(IV) to quinones (scheme 17) (Ho et al., 1972; Ho, 1973). However, the reaction conditions are critical, since it is not easy to avoid over-oxidation and the formation of side-products. The reactivity of ammonium hexanitratocerate(IV) can be reduced by coating the salt on silica gel (Fischer and Henderson, 1985), or by using the dual oxidant system CAN-NaBrO₃ (Ho, 1979). Brockhaus (1968) reported on the oxidation of catechol to *ortho*-benzoquinone by cerium(IV) sulfate in a chloroform/sulfuric acid biphasic

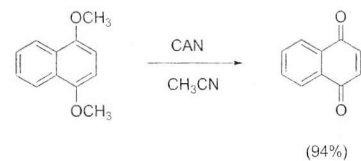
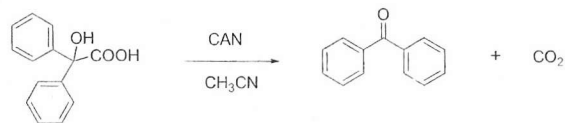
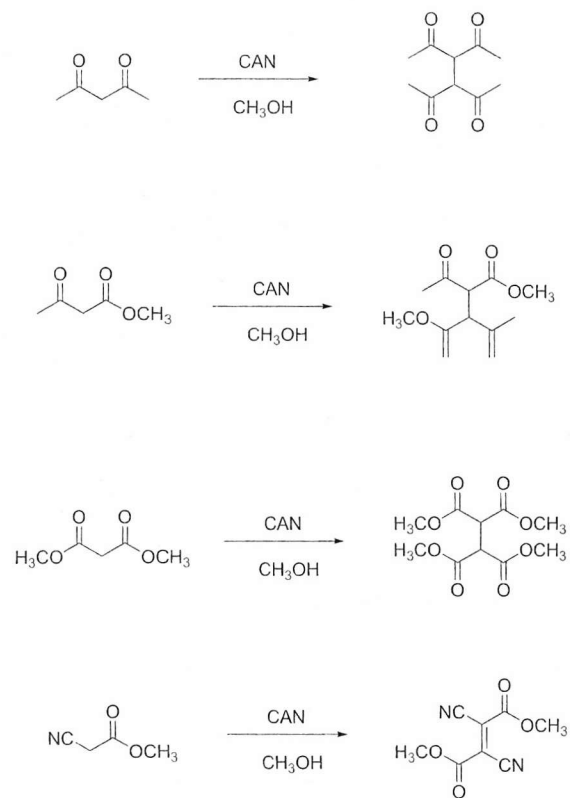
system. The oxidation of hydroquinones by ammonium hexanitratocerate(IV) can also be carried out in the solid state by grinding the substrate and cerium(IV) salt together with pestle and mortar, followed by keeping the mixture for several days in a closed vial (Morey and Saá, 1993). The oxidation reaction was found to be not very dependent on temperature, but it could be appreciably accelerated by ultrasonic irradiation or by shaking the reaction mixture. Brown-red vapors of nitrogen dioxide gas are formed during the reaction, which acts as a gaseous oxidant. Therefore, the best results for the oxidation of hydroquinones to quinones were obtained by keeping the reaction mixture in closed vials. In open vessels, or when the solid reaction mixture was flushed with a gentle stream of argon to remove nitrogen dioxide, only low reaction yields were obtained, even in presence of an excess of CAN. Catalytic amounts of CAN were sufficient when potassium bromate was used as a second solid oxidant. No reaction was observed with potassium chlorate or potassium iodate as the second oxidant, and potassium bromate alone cannot oxidize the hydroquinones.

6.4. Oxidation of carbonyl compounds

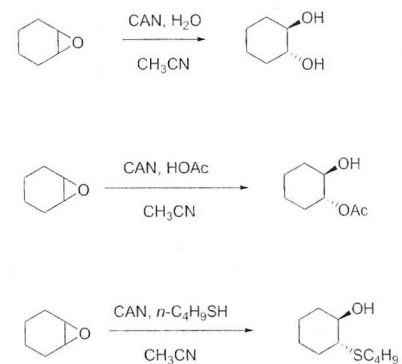
Polycyclic ketones undergo Baeyer–Villiger oxidation with ammonium hexanitratocerate(IV) or cerium(IV) ammonium sulfate to afford lactones (Soucy et al., 1972; Mehta et al., 1976). The Baeyer–Villiger oxidation of adamantanone to the corresponding lactone is shown above in scheme 14. Camphorquinone is oxidized to a complex mixture of oxidation products (Danieli and Palmisano, 1976). Simple aliphatic ketones are not oxidized by cerium(IV) in the absence of a catalyst. In presence of ruthenium(III) chloride, cerium(IV) sulfate oxidizes 2-butanone to acetic acid and formic acid, and 3-pentanone to a mixture of propionic acid, acetic acid and formic acid (Singh et al., 1980).

β -dicarbonyl and β -cyanocarbonyl compounds undergo oxidative dimerization in presence of ammonium hexanitratocerate(IV) (scheme 18) (Cho and Romero, 1995). For instance, 2,4-pentanedione is dimerized in methanol into 1,1,2,2-ethane tetraacetyl. The reaction can also be carried out by cerium(IV)-mediated electrosynthesis.

Oxalic and malonic acids, as well as α -hydroxy acids, easily react with cerium(IV) salts (Sheldon and Kochi, 1968). Simple alkanolic acids are much more resistant to attack by cerium(IV) salts. However, silver(I) salts catalyze the thermal decarboxylation of alkanolic acids by ammonium hexanitratocerate(IV) (Nagori et al., 1981). Cerium(IV) carboxylates can be decomposed by either a thermal or a photochemical reaction (Sheldon and Kochi, 1968). Alkyl radicals are released by the decarboxylation reaction, which yields alkanes, alkenes, esters and carbon dioxide. The oxidation of substituted benzoic acids by cerium(IV) salts affords the corresponding benzoic acids in quantitative yield (scheme 19) (Hanna and Sarac, 1977). Trahanovsky and coworkers reported that phenylacetic acid is decarboxylated by reaction with ammonium hexanitratocerate(IV) in aqueous acetonitrile containing nitric acid (Trahanovsky et al., 1974). The reaction products are benzyl alcohol, benzaldehyde, benzyl nitrate and carbon dioxide. The reaction is also applicable to substituted phenylacetic acids. The decarboxylation is a one-electron process and radicals are formed as intermediates. The rate-determining step is the decomposition of the phenylacetic acid/cerium(IV) complex into a benzyl radical and carbon dioxide.



Scheme 20.



Scheme 21.

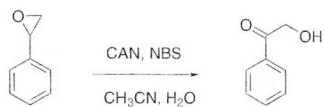
6.5. Ethers and epoxides

Hydroquinones dimethyl ethers undergo oxidative demethylation with ammonium hexanitratocerate(IV) to afford quinones (scheme 20) (Jacob et al., 1976). The reaction is fast in acetonitrile, even at room temperature. However, dimerization is a competitive side reaction for some substrates.

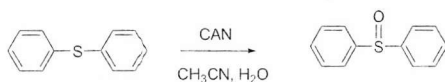
Ammonium hexanitratocerate(IV) can be used as a catalyst for the ring opening of epoxides in presence of water, thiols or acetic acid (scheme 21) (Iranpoor et al., 1991). Epoxides react in presence of an excess of nitrate ions and a catalytic amount of ammonium hexanitratocerate(IV) in acetonitrile to β -nitrate alcohols (Iranpoor and Salehi, 1995). A combination of ammonium hexanitratocerate(IV) and *N*-bromosuccinimide (NBS) transforms epoxides into α -hydroxy ketones (scheme 22) (Surendra et al., 2005). Aziridines give α -aminoketones under the same conditions.

6.6. Sulfur-containing compounds

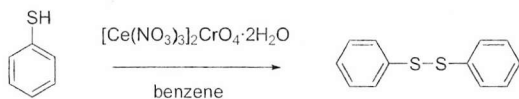
Diarylsulfides are oxidized in high yield by ammonium hexanitratocerate(IV) to the corresponding sulfoxides, without over-oxidation to sulfones (scheme 23) (Ho and Wong, 1972).



Scheme 22.



Scheme 23.

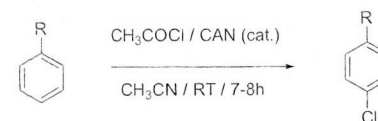


Scheme 24.

The reaction is generally carried out in aqueous acetonitrile at room temperature, and is complete within a few minutes. However, the synthetic method is not suitable for the oxidation of dialkyl sulfides containing α -hydrogen atoms, probably due to a Pummerer-type rearrangement of the resulting sulfoxides. Dialkylsulfides can be oxidized to the sulfoxides by CAN under phase transfer conditions (Baclocchi et al., 1988a). Thiols can be selectively oxidized to disulfides by dinitratoceric(IV) chromate dihydrate, $[\text{Ce}(\text{NO}_3)_3]_2\text{CrO}_4 \cdot 2\text{H}_2\text{O}$, in benzene (scheme 24) (Firouzabadi et al., 1984c). Aldehydes react with one equivalent of ethanedithiol and a catalytic amount of CAN in chloroform to 1,3-dithiolanes (Mandal and Roy, 1995). This thioacetalization can be used to protect an aldehyde function.

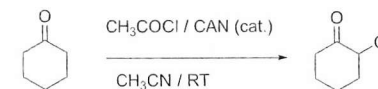
6.7. Halogenation reactions

Cerium(IV) fluoride is suitable for the fluorination of benzene (Hudson et al., 1969). The reaction was carried out by passing benzene vapor over heated cerium(IV) fluoride at temperatures between 250 °C and 480 °C. Below 400 °C little fluorination takes place, but above 410 °C the reaction rate increases rapidly. The reaction leads to a mixture of fluorinated compounds. For instance, the following products were isolated from the reaction mixture after fluorination at 480 °C: fluorobenzene, 1,3-difluorobenzene, 1,4-difluorobenzene, 1,2,4-trifluorobenzene, 1,2,4,5-tetrafluorobenzene, 1,2,3,4-tetrafluorobenzene and different fluorinated cyclohexenes and cyclohexadienes. Benzotrifluoride (trifluoromethylbenzene) was also fluorinated by the same procedure (Hudson and Pedler, 1970). Asovich et al. (1994) describe the use of cerium(IV) fluoride for the fluorination of ethylene. The extent of fluorination depends on the temperature; the higher the temperature, the more fluorine atoms are bound to the ethylene molecule. The composition of the mixture formed by reaction between ethylene



R = activating group

Scheme 25.



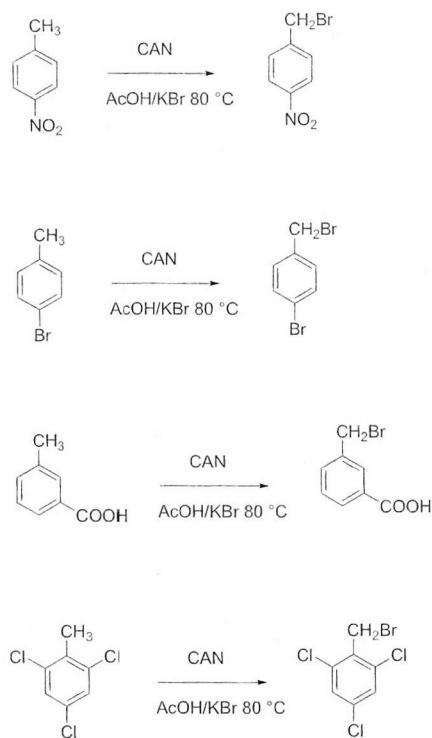
Scheme 26.

and CeF_4 at 370 °C is $\text{CF}_2\text{HCH}_2\text{F}$ (1%), $\text{CF}_3\text{CH}_2\text{F}$ (9%), CF_2HCF_3 (1%) and $\text{CF}_2\text{HCF}_2\text{H}$ (89%). No formation of hexafluoroethane was observed.

Acetyl chloride in presence of a catalytic amount of ammonium hexanitratocerate(IV) efficiently chlorinates activated aromatic compounds at room temperature (scheme 25) (Roy et al., 2003a), while deactivated aromatic compounds do not react. The same reagent can be used for the α -chlorination of ketones (scheme 26) (Roy et al., 2003b), but only monochlorination takes place, even in presence of a large excess of acetyl chloride.

Treatment of methylbenzenes containing electron-withdrawing substituents (COOH, NO_2 , Br) with ammonium hexanitratocerate(IV) in a mixture of acetic acid and potassium bromide at 80 °C allows bromination of the methyl group (Baclocchi et al., 1984b) (scheme 27). Benzyl bromides were also prepared by reaction of *para*-substituted toluenes with ammonium hexanitratocerate(IV) in aqueous solutions containing trifluoroacetic acid and sodium bromide (Maknon'kov et al., 1986).

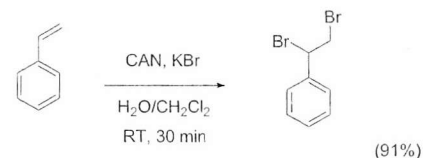
Nair et al. (2001) describe the bromination of alkenes using a mixture of ammonium hexanitratocerate(IV) and potassium bromide in a two-phase system consisting of water and dichloromethane. For instance, styrene is transformed by this reaction system in excellent yield at room temperature into 1,2-dibromo-phenyl ethane (scheme 28). It is assumed that the bromide ion is first oxidized by CAN to the bromine radical, which subsequently undergoes addition to the double bond to produce a benzylic radical. Trapping of another bromine radical results in the formation of the 1,2-dibromide. The method is not only applicable to substituted styrenes, but also to alkenes and α,β -unsaturated carbonyl compounds. However, the choice of the solvent is of prime importance: the reaction only occurs in the water/dichloromethane two-phase system. In other solvents, like aqueous solutions of methanol or acetonitrile, a variety of products such as phenacyl bromides and nitratobromides are formed (scheme 29). The nitro bromides are formed exclusively when the reaction is carried out in a deoxygenated atmosphere. In the two-phase system water/dichloromethane, side reactions are avoided be-



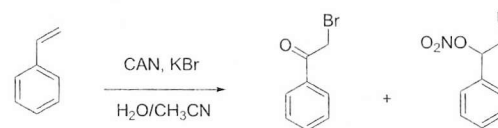
Scheme 27.

cause the bromine radicals and the alkene are mainly in the organic phase, whereas the cerium(IV) salt remains in the aqueous phase. 1,3-Dibromides can be synthesized by the reaction of cyclopropanes with ammonium hexanitratocerate(IV) and potassium bromide in the water/dichloromethane two-phase system (Nair et al., 2003).

The aromatic ring of electron-rich aromatics can be brominated by a system composed of lithium bromide as the bromine source and ammonium(IV) hexanitratocerate as the oxidant, and with acetonitrile as solvent (scheme 30) (Roy et al., 2001a). The electrophilic Br^+ is generated *in situ* by reaction between lithium bromide and CAN. The reaction is regioselective in the sense that the *para*-isomer is preferentially formed. Aromatic amines like aniline and *para*-toluidine did not show reaction under the given conditions. Naphthalene could be transformed in very high yield to 1-bromo-naphthalene. Roy and coworkers reported that *trans*- α,β -unsaturated aromatic acids undergo oxidative halodecarboxylation in presence of a



Scheme 28.



Scheme 29.

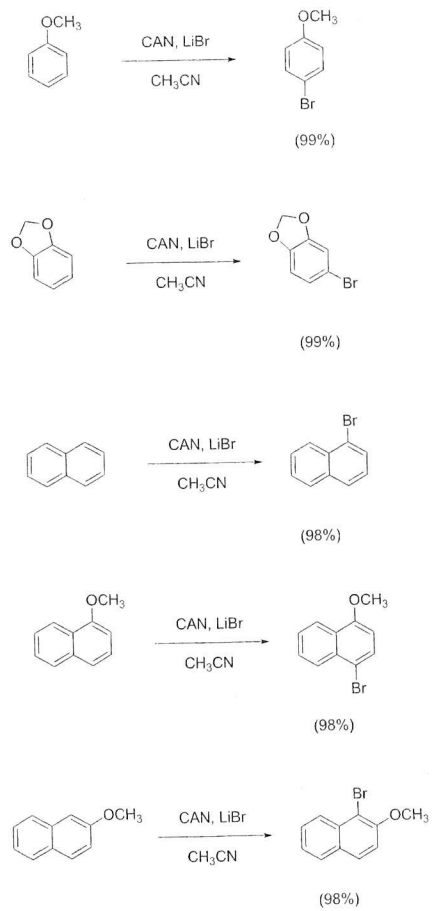
mixture of lithium bromide (or lithium chloride) and ammonium hexanitratocerate(IV) (Roy et al., 2001b). In aqueous acetonitrile, the reaction transforms *trans*- α,β -unsaturated aromatic acids into *trans*- β -halo styrenes (vinyl halides) (scheme 31). The solvent was an aqueous acetonitrile solution. The reaction yield increases with increasing water content, the maximum yield being obtained for a 10 : 1 acetonitrile:water mixture.

Sugiyama (1981) suggested ammonium hexanitratocerate(IV) as a reagent for the iodination of polymethylbenzenes, polymethoxybenzenes and naphthalene with tetrabutylammonium iodide, alkali iodides (LiI, NaI, KI) and molecular iodine as iodinating reagents (schemes 32 and 33). Ammonium hexanitratocerate(IV) was needed in stoichiometric amounts for the iodination with tetrabutylammonium iodide or alkali iodides, whereas catalytic amounts were sufficient in the case of iodination with molecular iodine.

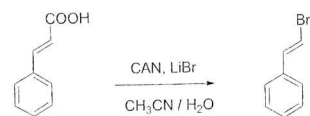
The regioselective synthesis of α -iodo ketones is achieved in good yields by CAN in presence of iodine. The more highly substituted α -iodo ketones are preferentially formed (scheme 34) (Horiuchi and Kiji, 1988). In a study of the iodination of 1,3,5-trimethylbenzene (mesitylene) and 1,2,3,4,5-tetramethylbenzene (durene) by CAN/I_2 , it was shown that the reactive intermediate is most likely the I^+ ion and that the reaction can be considered as an electrophilic aromatic substitution reaction (Galli, 1991).

Asakura and Robins described a mild procedure for the regioselective halogenation of uracil derivatives at the C-5 position with ammonium hexanitratocerate(IV) and elemental iodine, lithium halides or hydrochloric acid (scheme 35) (Asakura and Robins, 1988, 1990). The solvent for this type of reactions is methanol or acetonitrile. The reaction is very useful for the conversion of (protected) uracil nucleosides into (protected) 5-halouracil nucleosides. 4-Iodopyrazoles can be prepared by iodination of *N*-H and *N*-benzylpyrazoles with elemental iodine in presence of ammonium hexanitratocerate(IV) (scheme 36) (Rodríguez-Franco et al., 2001). The reaction works well, even with electron-withdrawing groups. Firouzabadi and coworkers reported that micellar solutions of sodium dodecyl sulfate catalyze the regio-

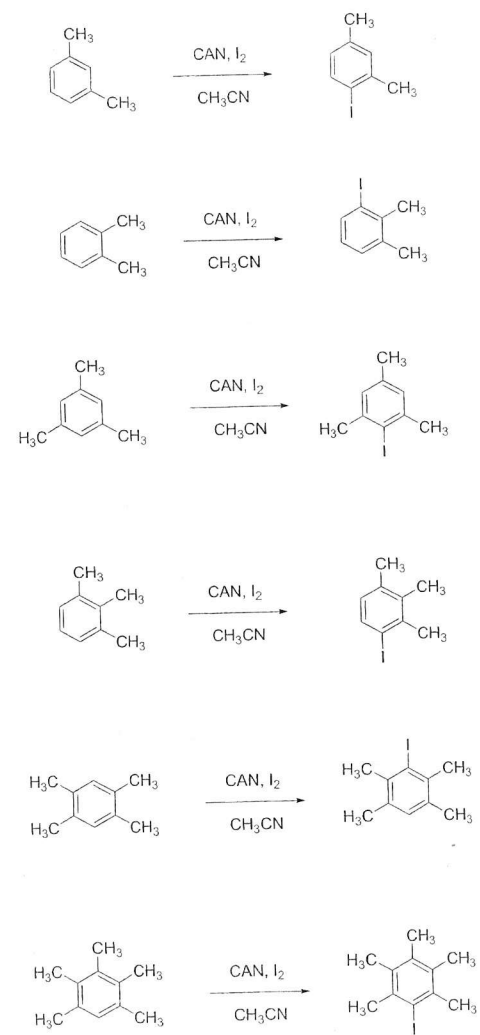
K. BINNEMANS



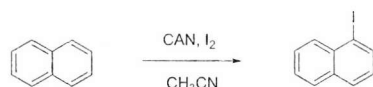
Scheme 30.



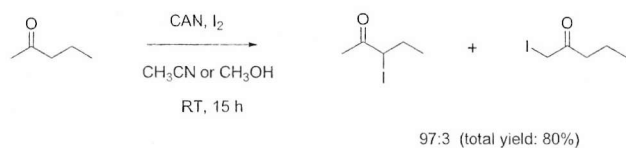
Scheme 31.



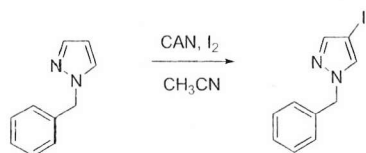
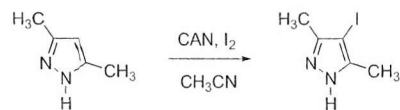
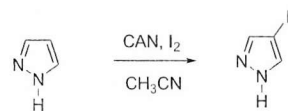
Scheme 32.



Scheme 33.

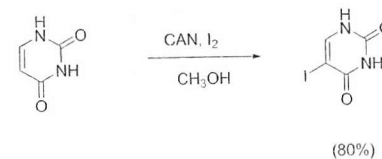
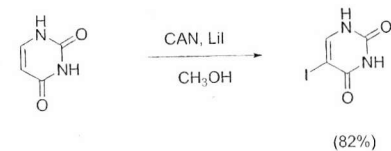
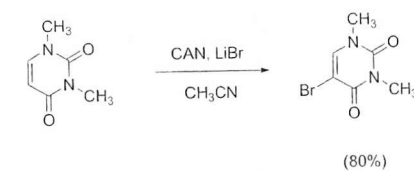
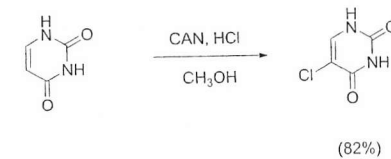
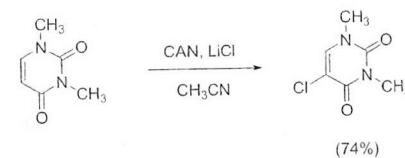


Scheme 34.

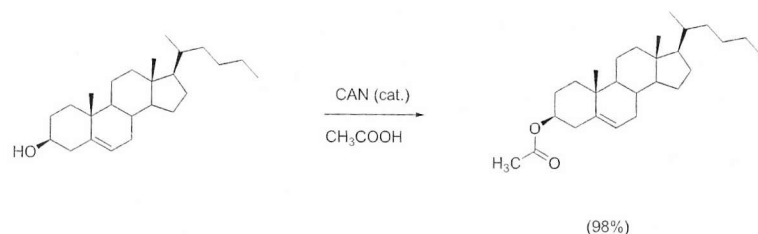


Scheme 35.

selective iodination of aromatic compounds with sodium iodide in presence of cerium(IV) trihydroxy hydroperoxide at room temperature (Firouzabadi et al., 2005). For instance, anisole could be transformed into 4-iodoanisole in 97% yield. In general, monosubstituted benzenes, 1,2-disubstituted benzenes and 1,3-disubstituted benzenes are regioselectively iodinated in the 4-position. Naphthalene was transformed into 1-iodonaphthalene. The presence of the mi-



Scheme 36.



Scheme 37.

celles is essential as shown by very low yields in acetonitrile or in dichloromethane only. It is proposed that within the micelles the reactants are in closer contact than in the bulk solvent phase.

Benzene and monosubstituted benzene derivatives could be radiolabeled with iodide-131 by reaction of the substrate with iodine-131 in presence of cerium(IV) triflate (Mennicke et al., 2000). The reaction was carried out in trifluoroacetic acid as solvent. Cerium(IV) is however not soluble in this solvent.

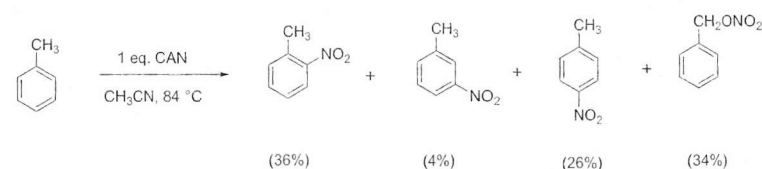
6.8. Esterification reactions

Ammonium hexanitratocerate(IV) is an efficient catalyst for fast esterification of carboxylic acids and alcohols under mild conditions (Goswami and Chowdhury, 2000). The reaction can be carried out under solventless conditions, or in chloroform. The reaction works with primary and secondary alcohols, and with aliphatic carboxylic acids. No reaction was observed for tertiary alcohols or for aromatic acids. The method is of interest because it is also applicable to the esterification of alcohols based on steroids and on other natural products (scheme 37). Pan and coworkers described the esterification of phenylacetic acids and *cis*-oleic acid with simple primary and secondary alcohols in presence of an excess of CAN at room temperature (Pan et al., 2003). The alcohol acted as solvent. Ammonium hexanitratocerate(IV) does catalyze not only the esterification of carboxylic acid, but also the transesterification with another alcohol (Stefane et al., 2002).

6.9. Nitration

Aromatic nitration or nitration in the benzylic position are often side reactions of oxidation reactions with ammonium hexanitratocerate(IV). In fact these unwanted reactions are one of the main drives to develop cerium(IV) reagents other than ammonium hexanitratocerate(IV). However, in some cases ammonium hexanitratocerate(IV) can be turned into a useful nitration reagent. A major parameter that governs the chemoselectivity of CAN is the solvent.

Benzene, alkylbenzenes and phenolic ethers react with CAN in acetonitrile to give nitration of the aromatic ring and, if α -hydrogen atoms are present, also products of side-chain substitution (Dinçtürk and Ridd, 1982a, 1982b). With many substrates, for instance with toluene,

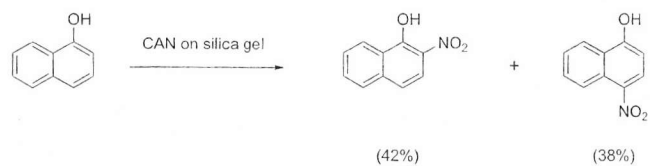


Scheme 38.

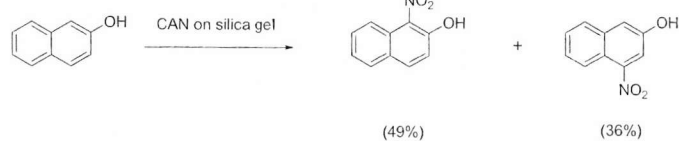
benzyl nitrates are formed by the side-chain reaction, while in other cases, for instance with ethylbenzene, an amide is formed (Dinçtürk and Ridd, 1982a). The side-chain substitution seems to occur through the intermediate formation of an aromatic radical cation, while the nitronium ion is involved in the nitration of the aromatic ring. Addition of water to acetonitrile suppresses the nitration of the aromatic ring, but not the side-chain substitution (Dinçtürk and Ridd, 1982b). No nitration of the aromatic ring occurs when the solvent is acetic acid. The product distribution of the reaction of toluene with CAN in acetonitrile is shown in scheme 38. Whereas the reactivities relative to benzene for nitration by ammonium hexanitratocerate(IV) in acetonitrile are very similar to those for nitration by nitric acid in acetonitrile, a large discrepancy is observed for anisole. Anisole reacts 298 times faster than benzene with HNO_3 , but it reacts 4899 times faster than benzene with CAN. Another difference is the product composition: with CAN 36.5% of the *ortho*-isomer and 63.5% of the *para*-isomer is formed, whereas with HNO_3 65.9% of the product mixture consists of the *ortho*-isomer and 34.1% of the *para*-isomer. It was assumed that these differences arose from the fact that anisole interacts more strongly with CAN at the time that the nitronium ion is formed. However, the detailed mechanism is not known yet. Benzyl nitrates are obtained in high yield by the photochemical reaction between CAN and methylbenzenes in acetonitrile (Baclocchi et al., 1984a).

Mononitration of 1-hydroxynaphthalene could be obtained by use of ammonium hexanitratocerate(IV) supported on silica gel in acetonitrile (Chawla and Mittal, 1985) (scheme 39). The same reaction with CAN in acetic acid give the 2,4- and 4,6-dinitro derivatives. By the same method, 2-hydroxynaphthalene is converted into 1-nitro-2-hydroxynaphthalene and 4-nitro-2-hydroxynaphthalene (scheme 40). The 1-alkoxynaphthalenes can be mononitrated regioselectively in the 4-position (scheme 41). The lower reactivity of CAN supported on silica gel is also evident from the fact that naphthalene derivatives are not oxidized into 1,4-naphthoquinones. The authors noticed that no reaction could be observed when ammonium hexanitratocerate(IV) was replaced by a mixture of ammonium nitrate and ammonium cerium(IV) nitrate. Silica supported CAN has also been used for the nitration of methoxybenzenes (Grenier et al., 1999) and less electron rich aromatic compounds like benzene, toluene, chlorobenzene and bromobenzene (Mellor et al., 2000) (scheme 42). For the less electron rich aromatics, dichloromethane is used as solvent instead of acetonitrile. In most cases, the yields are good to excellent.

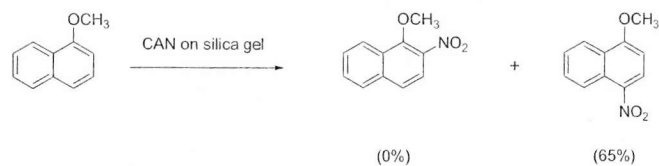
Mellor et al. (1997, 2000) found that when well-dried CAN supported on silica gel, sulfuric acid supported on silica gel, and naphthalene were stirred at room temperature in dichloromethane in presence of tetrabutylammonium nitrite, 1-nitronaphthalene was rapidly



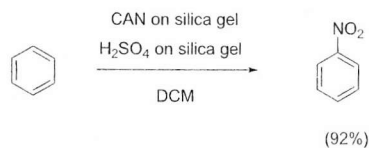
Scheme 39.



Scheme 40.

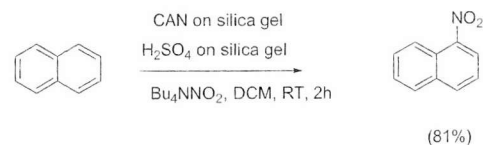


Scheme 41.

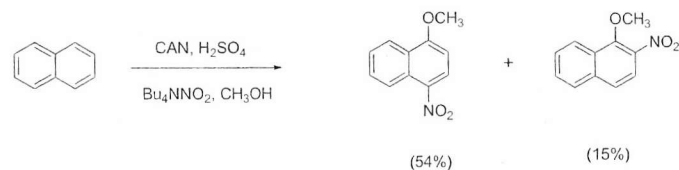


Scheme 42.

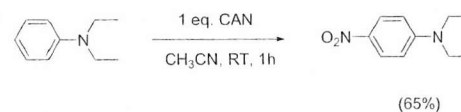
formed and could be isolated in good yield (scheme 43). The authors discovered that when naphthalene is treated with CAN, sulfuric acid and tetrabutylammonium nitrite in methanol, 1-methoxy-4-nitronaphthalene and 1-methoxy-2-nitronaphthalene could be obtained (scheme 44). When CAN is replaced by other nitrates like potassium nitrate or tetrabutylammonium nitrate, no nitration was observed.



Scheme 43.



Scheme 44.

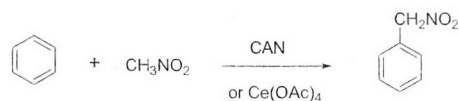


Scheme 45.

Ammonium hexanitratocerate(IV) can be used for the nitration of *N,N*-dialkylanilines in acetonitrile at room temperature to give *N,N*-dialkyl-4-nitroanilines in moderate yields, but with a good regioselectivity (Yang et al., 2005) (scheme 45).

A careful choice of the reaction conditions are of importance. The highest yields were observed when 1 equivalent of CAN was used, while no reaction was observed when the substrate was treated with 2 equivalents of CAN. The reaction only proceeds in aprotic solvents like acetonitrile in which CAN can be solubilized. No reaction was observed in dichloromethane, carbon tetrachloride or tetrahydrofuran, whereas the use of water, methanol or even mixtures of these solvents with acetonitrile yielded *N,N,N',N'*-tetraalkylbenzidines as the result of a coupling reaction. In fact the coupling of *N,N*-dialkylanilines by CAN (2 eq. for 1 eq. of substrate) in water is an efficient method for the synthesis of *N,N,N',N'*-tetraalkylbenzidines (Xi et al., 2005). The yields of the nitration reactions were low when a chlorine substituent was present on the phenyl ring; at the same time partial dealkylation of the amine group was observed. The reaction did not proceed when the aromatic ring contained two methyl groups in *meta*-position.

Free-radical aromatic nitromethylation is promoted by different cerium(IV) salts (Kurz and Ngoviwatchai, 1981). The reaction is carried out by refluxing a mixture of an aromatic compound, nitromethane, and a cerium(IV) salt in acetic acid (scheme 46). The mechanism in-



Scheme 46.

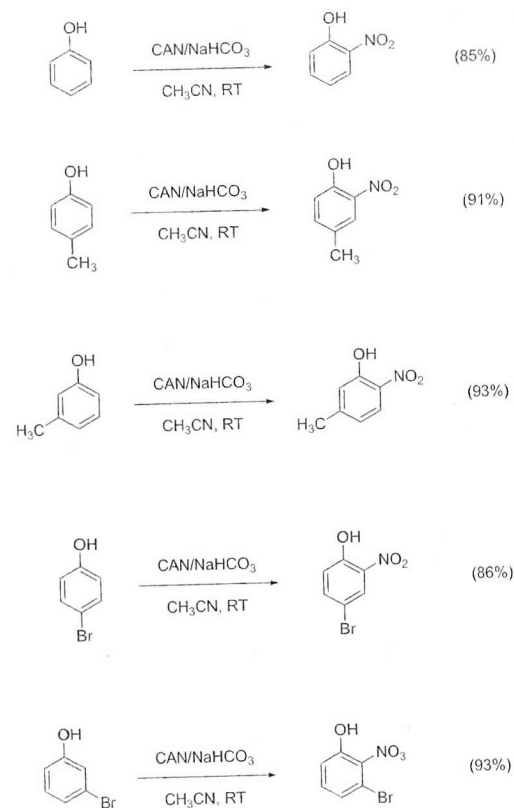
volves the generation of nitromethyl radicals by the oxidative deprotonation of nitromethane, and their subsequent substitution on the aromatic compound. The best cerium(IV) reagents for this reaction are ammonium hexanitratocerate(IV) and cerium(IV) acetate. However, both reagents have their advantages and disadvantages. The advantages of CAN are its commercial availability at a reasonable price and the good reaction yield (based on the conversion of the substrate). A disadvantage is that different byproducts are formed. For instance, nitromethylation of benzene not only gave the desired nitromethylated product, but also large amounts of benzaldehyde and benzyl acetate. Nitromethylation of toluene resulted in the formation of benzaldehyde, isomeric nitrotoluenes and toluenealdehydes, and methylbenzyl acetate as byproducts. Advantages of cerium(IV) acetate are the short reaction times, the color change occurring upon cerium(IV) reduction, which allows convenient monitoring of the reaction, and the lack of byproduct formation. Disadvantages are the fact that this salt is not commercially available and that it is rather light-sensitive. However, these disadvantages can be circumvented by preparing cerium(IV) acetate prior to its use and using it immediately without isolation.

Phenols that possess at least one unsubstituted *ortho*-position undergo fast, regioselective *ortho*-nitration with ammonium hexanitratocerate(IV) in presence of NaHCO_3 at room temperature to yield *ortho*-nitro phenols in high yield (schemes 47 and 48) (Sathunuru et al., 2003). Phenols with ring activating groups (OCH_3 , CH_3) and moderately ring deactivating groups (Cl , Br , CHO , CO_2Me) undergo nitration. However, phenols with strongly deactivating groups (CN , NO_2) or 2,6-disubstituted phenols could not be nitrated by $\text{CAN}/\text{NaHCO}_3$ in acetonitrile. The reaction has been extended to the nitration of hydroxy heterocycles (Sathunuru and Biehl, 2004) (scheme 49).

6.10. Functionalization of alkenes

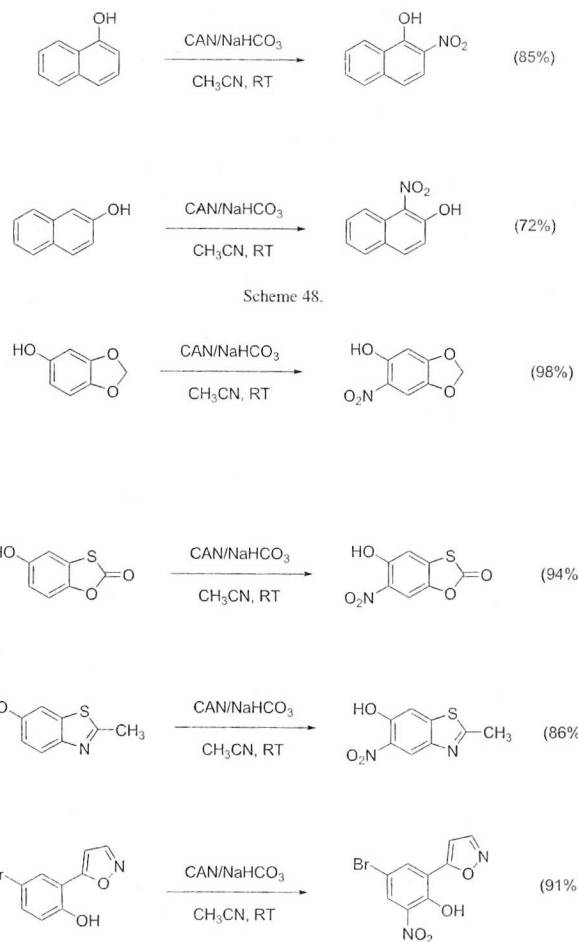
Cerium(IV) salts are very useful reagents for the functionalization of alkenes. In this section, only a few representative examples are shown. More examples can be found in reviews written by Nair and coworkers (Nair et al., 2002, 2004). The halogenation of alkenes with CAN has been described in section 6.7. Alkenes react with carboxylic acids in presence of cerium(IV) sulfate to yield carboxylic esters (scheme 50) (Horiuchi et al., 2003). The addition reaction follows Markovnikov's rule. The carboxylic acid also acts as solvent. This reaction provides a simple method for the preparation of carboxylic esters from alkenes.

Styrenes react with CAN and ammonium thiocyanate in methanol (Nair et al., 2000a). In presence of air (oxygen) phenacyl thiocyanates are formed, whereas in argon atmosphere bis(thiocyanates) are obtained (scheme 51). A similar reaction with potassium selenocyanate in methanol affords phenacyl selenocyanates and bis(selenocyanates) (scheme 52) (Nair et



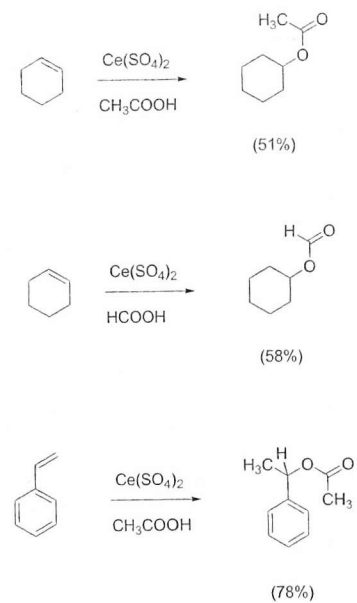
Scheme 47.

al., 2002). The reactions also work with indoles as substrates. Reaction of styrenes with CAN and sodium azide in methanol under oxygen atmosphere gives phenacyl azides (scheme 53) (Nair et al., 2000a). When sodium iodide is present besides sodium azide, azidoiodides are formed (Nair et al., 2000b). Replacement of methanol as solvent by acetonitrile, will result in the formation of other products: an alkene in presence of CAN and sodium azide will then be transformed into α -azido- β -nitroalkanes (scheme 54) (Trahanovsky and Robbins, 1971). It should be noticed that in absence of an alkene, the azide ion is very fast oxidized into nitrogen gas by CAN.

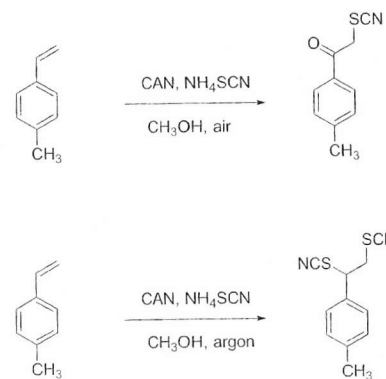


Scheme 49.

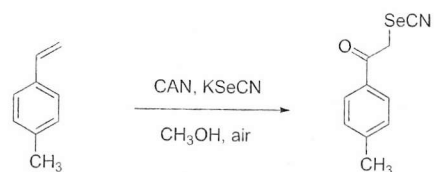
Depending on the solvent, different reaction products form when alkenes react with iodine in presence of cerium(IV) triflate: 1,2-hydroxy iodides in water, 1,2-alkoxy iodides in alcohols and 1,2-acetoxy iodides in acetic acid (Iranpoor and Shekarriz, 2000). Treatment of a mixture of styrene and sodium *p*-toluene sulfinate in anhydrous acetonitrile with CAN af-



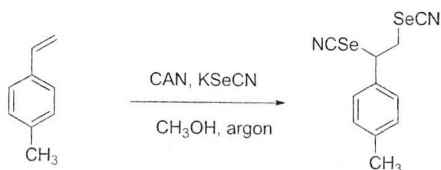
Scheme 50.



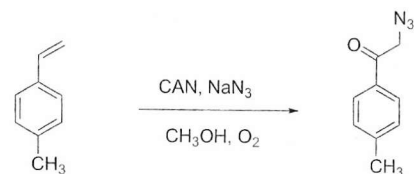
Scheme 51.



Scheme 52.



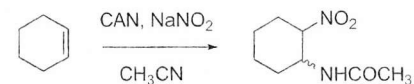
Scheme 53.



Scheme 54.

fords α -sulfonyl- β -nitro compounds (Nair et al., 2003). Nitroacetamidation of alkenes led to a mixture of ammonium hexanitratocerate(IV) and sodium nitrite in acetonitrile (scheme 55) (Reddy et al., 1995). Acetonitrile is not just a solvent, but also a reagent in this reaction.

Cerium-mediated reactions are also useful for the synthesis of heterocyclic compounds. 3-Acetylisoxazole derivatives are formed by reaction between alkenes and acetone in presence of CAN (scheme 56) (Itoh et al., 2002; Itoh and Horiuchi, 2004). When acetone is replaced



Scheme 55.



Scheme 56.

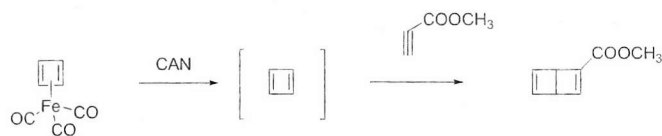
by acetophenone, 3-benzoylisoxazole derivatives are obtained. The reaction also works with alkynes. Baciocchi and Ruzziconi (1986) investigated the addition of different ketones as well as ethyl acetoacetate to 1,3-butadiene in presence of CAN. A mixture of 1,2- and 1,4-adducts was obtained.

6.11. Removal of protecting groups

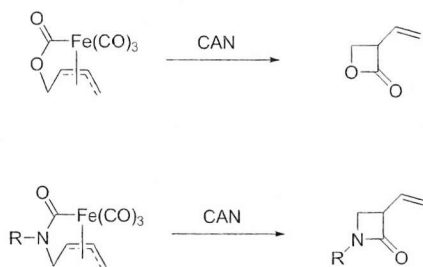
Ammonium hexanitratocerate(IV) is becoming more and more popular for the removal of protecting groups, especially on amino acids and nucleic acids (Hwu and King, 2001). The *tert*-butoxycarbonyl group (*t*-Boc) is often used for the protection of primary amines of amino acids in peptide synthesis. This group can also protect alcohols and thiols. CAN is able to remove this protecting group under neutral conditions, by heating the protected compounds with 0.2 equivalents of CAN in acetonitrile (Hwu et al., 1996a). This deprotection methodology is applicable to substrates with acid sensitive groups. Other protecting groups that can be removed by CAN include the triphenylmethyl (trityl) and the monomethoxytrityl (MMTr) protecting groups (Hwu et al., 1996b), as well as the *tert*-butyldimethylsilyl (TBDMS) group (Hwu and King, 2001). CAN impregnated on silica gel is effective for the removal of triisopropylsilyl protecting groups (Hwu and King, 2001). Bull and coworkers described the debenzoylation of *N*-benzyl tertiary amines with ammonium hexanitratocerate(IV) (Bull et al., 2000). Deprotection of tetrahydropyranyl (THP) and tetrahydrofuranyl (THF) ethers to the corresponding alcohols could be carried out by a catalytic amount of CAN (3 mol%) in a acetonitrile/borate buffer at pH 8 (Marko et al., 1999).

6.12. Splitting of organometallic compounds

Although cyclobutadiene itself is unknown, it can be liberated as an intermediate by oxidative degradation of the organometallic compound cyclobutadiene tricarbonyliron by ammonium hexanitratocerate(IV) (Watts et al., 1965; Paquette and Kelly, 1969). The transient intermediate can be trapped by a dienophile (scheme 57). When the oxidation is carried out in presence of a CAN solution saturated with lithium chloride, *trans*-3,4,-dichloro-cyclobutene is formed (Emerson et al., 1965). Because tricarbonyliron complexes are often used as reagents or intermediates in organic synthesis, the possibility to remove the $\text{Fe}(\text{CO})_3$ group by decomplexation



Scheme 57.



Scheme 58.

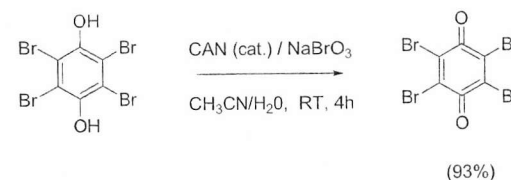
with ammonium hexanitratocerate(IV) is a very useful synthetic methodology (Levy, 1994). π -allyltricarbonyliron lactones and lactams can be obtained from a variety of precursors and they allow the regioselective synthesis of lactones and lactams (scheme 58). The stereochemistry of the organometallic compounds controls the stereochemistry of the product.

7. Indirect and catalytic reactions with cerium(IV) ions

7.1. Oxidations by bromate ions

Inspired by the Belousov-Zhabotinskii reaction, where cerium(III) is reoxidized by bromate ions, Ho developed a dual oxidant system consisting of ammonium hexanitratocerate(IV) and sodium bromate for the oxidation of arylmethanols (benzylic alcohols) to the corresponding aldehydes (Ho, 1978). The method has also been successfully used for the oxidation of hydroquinones to quinones (scheme 59) and for the oxidation of sulfides to sulfoxides (Ho, 1979).

Sodium bromate in presence of CAN or CAS is an effective reagent for the oxidation of secondary alcohols into the corresponding ketones (Tomioka et al., 1982; Kanemoto et al., 1986). For instance cyclododecanol is oxidized in 98% yield to cyclododecanone, and borneol is oxidized in 77% yield into camphor. Primary alcohols are not affected, so that this is a useful methodology for the oxidation of secondary alcohols in presence of primary ones. The presence of a double bond in the substrate, even at a position far way from the sec-



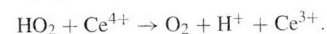
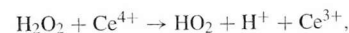
Scheme 59.

ondary alcohol group inhibits the reaction. Primary 1,4-diols react to yield γ -lactones. Sodium bromate does not dissolve in aqueous acetonitrile, so that the reaction mixture is a heterogeneous system. Ammonium hexanitratocerate(IV) and cerium(IV) ammonium sulfate are equally active as catalyst. Cerium(IV) impregnated on a perfluorinated sulfonic acid (Nafion) has been used as a supported catalyst for the oxidation of alcohols (Kanemoto et al., 1989; Yamato and Shinoda, 2002) and of polyaromatic compounds (Yamato et al., 2000) by sodium bromate.

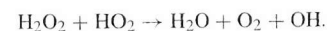
Alkyl and silyl ethers undergo oxidative cleavage to form the corresponding carbonyl compound by reaction with a molar equivalent of sodium bromate in presence of a catalytic amount of ammonium hexanitratocerate(IV) (Olah et al., 1980). For instance cyclohexyl methyl ether is transformed into cyclohexanone. Primary alkyl ethers were found to react slower than secondary alkyl ethers under similar reaction conditions. Ganin and Amer investigated the CAN-catalyzed oxidation of alkylbenzenes with potassium bromate (Ganin and Amer, 1995), whereas Shi and coworkers reported on the CeO_2 -catalyzed oxidation of alkylbenzenes with sodium bromate into aldehydes and ketones (Shi et al., 1999). α -Methylpyrroles can be converted to α -formyl pyrroles by sodium bromate in aqueous methanol, in presence of a catalytic quantity (1%) of CAN (Bobal and Lightner, 2001).

7.2. Oxidations by peroxides

Hydrogen peroxide is often used as an environmentally friendly oxidant (Sanderson, 2000). Although hydrogen peroxide can be decomposed catalytically by different redox active transition metal ions and complexes, the decomposition of hydrogen peroxide by cerium(IV) is not a catalytic process. It occurs spontaneously in the pH range from 0 to 1.4 if an excess of hydrogen peroxide is avoided. Hydrogen peroxide is oxidized to oxygen and Ce^{4+} is reduced to Ce^{3+} . Unlike $\text{Fe}^{3+}/\text{Fe}^{2+}$, the $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox couple is not able to decompose hydrogen peroxide catalytically. The relevant reactions are (Baer and Stein, 1953):



The following reaction does not seem to take place, even in presence of a large excess of hydrogen peroxide:



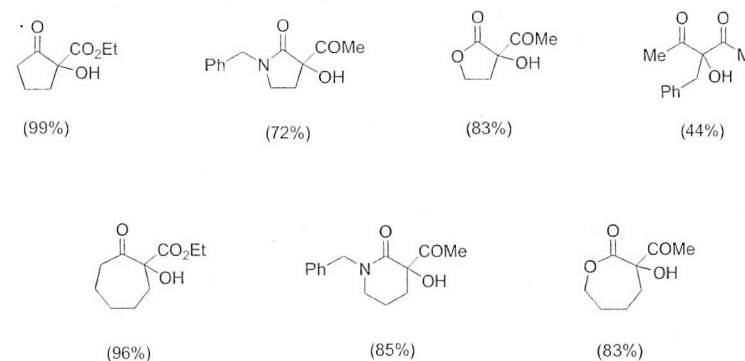
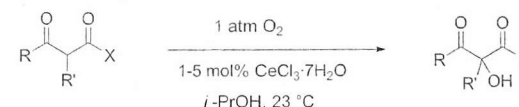
The fast reaction between cerium(IV) sulfate and hydrogen peroxide is useful to determine the concentration of hydrogen peroxide in solution by cerimetric titrations (see section 3). However, the decomposition of hydrogen peroxide by cerium(IV) in perchloric acid solution is slow at pH values above 0.7 (Baer and Stein, 1953; Ardon and Stein, 1956), at which colloid polymeric cerium(IV) complexes are formed. These are able to interact with hydrogen peroxide to afford colored complexes that are only slowly decomposed. At very low pH values, the polymeric complexes are not formed and decomposition of hydrogen peroxide is fast.

Auty and coworkers showed that 4-*tert*-butyltoluene can be oxidized in acetic acid into 4-*tert*-butylbenzaldehyde by 35% aqueous hydrogen peroxide in a process catalyzed by cerium(III) and bromide ions (Auty et al., 1997). The different reaction steps are benzylic bromination, hydrolysis of the bromide to the benzylic alcohol and the fast oxidation of the benzylic alcohol to the aldehyde by bromine. The role of cerium(III) is not clear yet. It is assumed that cerium(IV) is formed during the first step; experimental evidence for the occurrence of cerium(IV) was given by the absorption spectrum of the reaction mixture. The reaction does not work when sodium bromide is replaced by sodium chloride or sodium iodide. The polyoxometalate $[\text{CeW}_{10}\text{O}_{36}]^{8-}$ with hydrogen peroxide as co-oxidant is able to oxidize benzyl alcohol to benzaldehyde and secondary alcohols into ketones, but it seems that the active catalytic species is $[\text{W}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2]^{2-}$ and not a cerium(IV) compound (Griffith et al., 1996). $[\text{CeW}_{10}\text{O}_{36}]^{8-}$ with *N*-hexadecylpyridinium counter ions was used for the oxidation of benzyl and secondary alcohols by hydrogen peroxide under biphasic reaction conditions with chloroform as the organic solvent (Shiozaki et al., 1996). No reaction mechanism has been reported. Hydrogen peroxide can be used to control the oxidizing capability of cerium(IV) salts, so that over-oxidation can be avoided (Chawla and Sharma, 1990; Chakrabarty et al., 1993). The control of the oxophilicity can be attributed to the formation of cerium(IV) peroxo complexes, which are less oxidizing than for instance ammonium hexanitratocerate(IV). Differences in product distribution were observed when oxidative couplings of phenol by CAN were carried out in presence and absence of hydrogen peroxide.

Krohn and Vitz (2000) used *tert*-butyl hydroperoxide (TBHP) with catalytic amounts of CAN for the oxidation of hydroquinones and hydroquinone monomethyl ethers to quinones. TBHP is a cheap and convenient oxygen source (Sherrington, 1988). It will not oxidize organic substrates in the absence of a catalyst. High regioselectivity can be obtained by a careful choice of a catalyst. Cerium(IV) impregnated on Nafion[®] is an example of a supported catalyst for the oxidation of alcohols by *tert*-butyl hydroperoxide (Kanemoto et al., 1984, 1989).

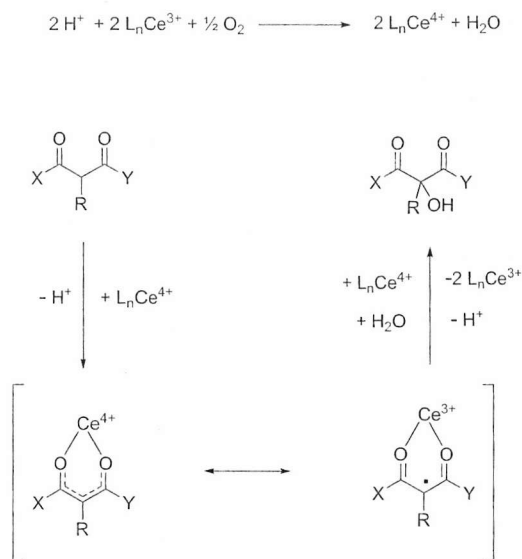
7.3. Oxidations by molecular oxygen

Cerium(III) chloride heptahydrate has been used by Christoffers and coworkers as a catalyst for the α -hydroxylation of β -dicarbonyl compounds by molecular oxygen (Christoffers and Werner, 2002; Christoffers et al., 2003a). The reaction is useful for the hydroxylation of cyclic β -dicarbonyl compounds, but many side reactions occur with acyclic β -dicarbonyl (scheme 60). The byproducts include α -chlorinated β -dicarbonyl compounds. In the proposed reaction mechanism, cerium(III) coordinates to a β -dicarbonyl ligand (scheme 61). The coordinated cerium(III) (L_nCe^{3+} in scheme 61) is oxidized by molecular oxygen to cerium(IV).



Scheme 60.

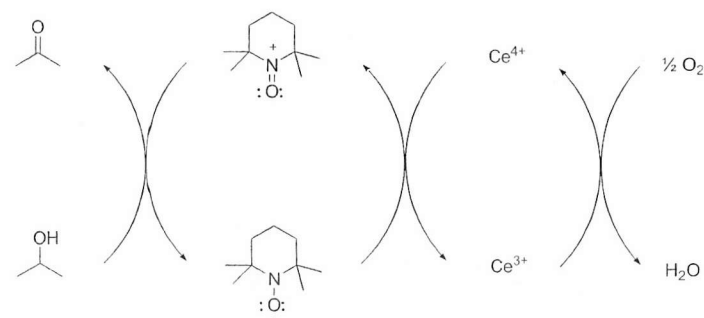
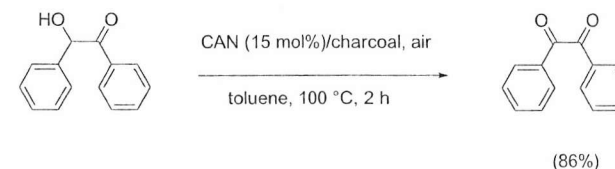
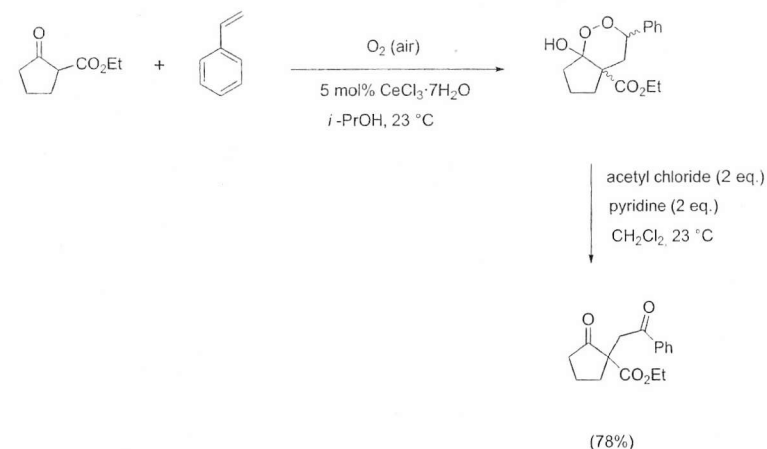
By an intramolecular electron transfer (ligand-to-metal charge transfer), cerium(IV) is transformed back into cerium(III), while at the same time an unpaired electron is generated on the β -dicarbonyl ligand. This radical species is further oxidized by a second cerium(IV) ion and hydrated. During the reaction, two moles of protons are released, so that the reaction mixtures become more and more acidic when the reaction proceeds. The reaction can be considered as a form of water activation. It is assumed that molecular oxygen is able to oxidize cerium(III) to cerium(IV), because coordination of β -dicarbonyl compounds to cerium(III) reduces the redox potential of the $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox couple. The solvent plays an important role in the reaction, because the solubility of molecular oxygen in the solvent is crucial. The optimal solvents were found to be DMF or *iso*-propanol. The reaction can be run at room temperature. For some substrates, the reaction can be run with air, but in most cases pure oxygen gas (1 atm) gave superior results. Oxygen has to be bubbled through the reaction solution; a static oxygen atmosphere gave irreproducible results, probably due to lowering of the partial oxygen pressure about the liquid phase by partial evaporation of the solvent. $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ was chosen as the source of cerium, because it is one of the cheapest cerium salts. However, it has been replaced in some experiments by $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ or $\text{Ce}(\text{OAc})_3 \cdot \text{H}_2\text{O}$. The cerium salts were used in catalytic amounts (less than 5 mol%) and after the reaction they were removed by filtration through SiO_2 .



The methodology has been extended to C–C coupling reactions of alkenes and β -dicarbonyl compounds with air as the oxidant and with $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ as the catalyst (Christoffers et al., 2003b; Rössle et al., 2005). The reactions yield diastereoisomeric mixtures of hydroxyperoxides, which disproportionate in presence of acetyl chloride/pyridine by Kornblum–DeLaMare fragmentation into dioxo esters (scheme 62). These dioxo derivatives have a 1,4-dicarbonyl structural motif. This reaction has been explored with styrene and substituted alkenes as the alkene substrate.

Yamada and coworkers (Yamada et al., 1993) reported on the cyclization reaction of mono-substituted alkenes with β -ketoesters, in presence of molecular oxygen and catalytic amounts of CAN. The reaction yielded substituted 1,2-dioxan-3-ols. CAN supported on charcoal (CAN-charcoal) is a catalyst for the air oxidation of benzyl alcohols to benzaldehydes and α -hydroxyketones (acyloins) into α -diketones (Hatanaka et al., 1983) (scheme 63).

Kim and Jung (2003) oxidized benzylic and allylic alcohols by molecular oxygen in presence of catalytic amounts of 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO) and CAN (scheme 64). Molecular oxygen is reduced to water by oxidation of Ce^{3+} to Ce^{4+} . The nitroxyl radical of TEMPO is oxidized to the *N*-oxoammonium cation by Ce^{4+} . The *N*-oxoammonium cation then oxidizes the alcohol to a carbonyl compound. The reactions were carried out in refluxing acetonitrile and molecular oxygen was bubbled through the reaction mixture. The amount of CAN varied between 10 and 20 mol%, and the amount of TEMPO



was 10 mol%. Both primary and secondary benzyl alcohol gave good reaction yields, but the latter reacted much faster than the primary ones. Allylic alcohols gave good yields after prolonged reaction periods, but the presence of sterically demanding groups reduced the yields. Aliphatic alcohols like cyclohexanol showed no reactivity. The reactions are slow at room temperature. TEMPO can be replaced by *N*-hydroxy phthalimide (NHPI) (Kim and Rajagopal, 2004). Both diarylsulfides and dialkylsulfides can be oxidized to the corresponding sulfoxides by molecular oxygen in presence of catalytic amounts of CAN (Riley and Correa, 1986).

8. Cerium-mediated electrosynthesis

Electrochemical synthesis (electrosynthesis) is being used for a long time by the chemical industry for the manufacture of inorganic chemicals like chlorine, sodium hydroxide, sodium hypochlorite, fluorine, potassium peroxydisulfate, potassium permanganate, and perchloric acid. Electrosynthesis could be a method for the environmentally benign manufacture of organic compounds on an industrial scale, establishing a "green" alternative to conventional processing methods (Scott, 1995). There are many advantages associated with electrochemical synthesis methods. They are applicable to a wide range of substrates and are often highly selective, only a limited amount of side products being formed. Moreover, toxic reagents can be avoided. As a result, much less waste is generated by electrochemical processes than by conventional chemical processes. Electrons are relatively cheap reagents; they are much cheaper than commonly used redox agents like chromate and peroxide (but not cheaper than air or nitric acid). The conditions in electrochemical processes are close to ambient temperature and pressure. Finally, electrochemical technology is well developed. Electrolytic cells are readily available for both batch and continuous processes. They can be integrated with other production units in a complex production process. However, there are still some limitations in electrochemical technology that hampers the widespread use of electrochemical synthesis of organic compounds on an industrial scale. In *direct electrosynthesis*, the maximum rate of chemical change per unit area of electrode (the current density) is proportional to the concentration of the reactant in solution. An electrochemical process can become economically feasible only if the current density of the process is high, and this requires a high concentration of the reactants in the electrolyte solution. The preferred medium in commercial electrolysis processes is an aqueous electrolyte, because of the less complex electrochemistry than in non-aqueous media, the easier pH control, the cost-effectiveness and less problems due to solvent loss. Unfortunately, many organic compounds have a very low solubility in aqueous media. A strategy to overcome this difficulty is *indirect electrosynthesis*, where a *redox mediator* (a redox couple soluble in water) is used to transfer the electrons between the electrode and the reactant (Clarke et al., 1975). The redox mediator is continuously generated in its active oxidation state at the electrode and allowed to react with the organic substrate away from the electrode, either *in-cell* or *ex-cell*. In an *in-cell method*, the electrochemical reaction between the redox mediator and the organic substrate takes place in the electrolytic cell, where also the used redox mediator is regenerated. In an *ex-cell method*, the reaction occurs in a chemical reactor that is separated from the electrolytic cell. Following the reaction,

the electrolyte containing the used redox mediator is separated from the product phase, and the electrolyte solution is returned to the electrolytic cell for regeneration of the redox mediator. An advantage of the *ex-cell* method is that direct contact between the organic phase and the electrode is avoided, so that deactivation of the electrode (for instance by product deposition or by side reactions) is limited. Many indirect redox process uses multiphase conditions. The redox mediator can be transferred to the organic phase by a phase-transfer catalyst. Because the redox species are recycled, only small amounts of the redox reagents have to be used and there is no stoichiometric by-product stream from the redox reagent. Examples of popular redox mediators are Co^{3+} , Mn^{3+} and also Ce^{4+} . The interest of the chemical industry in cerium(IV)-mediated organic electrosynthesis can be explained by the need for fast and selective oxidation of toluene or xylenes to benzaldehydes and of (poly)aromatic compounds to quinones. Naphthoquinones are well-known intermediates for organic dyes. Aldehydes are used in perfumes or as intermediates for pharmaceuticals.

Several authors have explored the use of Ce^{4+} as a redox mediator in organic electrosynthesis, but they have been facing different types of problems. The main difficulty was to create a cerium solution that is concentrated enough to make the electrochemical regeneration process efficient. Oehr investigated cerium sulfate in dilute sulfuric acid for the electrooxidation of naphthalene to 1,4-naphthoquinone (Oehr, 1982a, 1982b). Unfortunately, both cerium(III) and cerium(IV) sulfates have a low solubility in dilute sulfuric acid. This leads to large volumes of solution for oxidizing small amounts of organic substrate. As a result the current efficiencies are low and the reaction vessels need to be prohibitively large to accommodate the large volumes of electrolyte. Oehr also used a cerium sulfate slurry to overcome the low solubility, but this is impractical in process technology. Rennie (1972) overcame the solubility problems of the cerium salts by working in nitric acid, but in this case significant quantities of nitrated by-products were formed. Ibl and coworkers (Ibl et al., 1979; Kramer et al., 1980) used cerium salts in perchloric acid for the electrosynthesis of substituted benzaldehydes. Although the process was very interesting from an economical point of view, explosion hazards related to the mixing of perchloric acid and organic compounds have probably limited further developments. Other authors (Torii et al., 1982) turned to the use of non-aqueous solvents for the oxidation reaction and electrochemical regeneration of ammonium hexanitratocerate(IV). Methanol turned out to be a suitable solvent for the oxidation of *p*-methoxytoluene to *p*-methoxybenzaldehyde, but cerium(IV) is not very stable in methanol. Cho and Romero (1995) proposed to use cerium(III) nitrate hexahydrate as a precursor for electrochemically generated cerium(IV). The advantage of this salt is that it has a lower redox potential than other cerium salts, so that an anodic potential of 1.4 V is sufficient to oxidize cerium(III) into cerium(IV). This low potential also allows the use of acetonitrile as solvent. Research has been conducted for increasing the solubility of cerium salts in the systems used for oxidation of organic compounds. Higher cerium concentrations have the advantage that the solution containing the redox mediator can oxidize a larger amount of organic substrate before regeneration is necessary.

Kreh et al. discovered that cerium(III) and cerium(IV) have a high solubility in aqueous methanesulfonic acid (Kreh and Spotnitz, 1987a, 1987c; Kreh et al., 1989; Spotnitz et al., 1990). When the concentration of methanesulfonic acid is between 1.5 and 9 molar the sol-

ubility of the cerium salt is at least 0.2 mol/L. For instance, in 2 M methanesulfonic acid, the solubility of cerium(III) is about 2.3 mol/L. The solubility of cerium(IV) decreases with increasing methanesulfonic acid concentration. The solubility of cerium(IV) in aqueous methanesulfonic acid is lower than the solubility of cerium(III), but the solubility of cerium(IV) depends very much on the concentration of methanesulfonic acid. At low concentrations of methanesulfonic acid, the solubility of cerium(IV) is limited (only about 0.1 mol/L cerium(IV) dissolves in 1 M methanesulfonic acid), but increases sharply with increasing acid concentration (about 1 mol/L cerium(IV) dissolves in 4 M methanesulfonic acid). Notice this major difference: the solubility of cerium(IV) increases with increasing methanesulfonic acid concentration, whereas the solubility of cerium(III) decreases (Spotnitz et al., 1990). The lower solubility of cerium(IV) in comparison to cerium(III) can result in precipitation of a cerium(IV) salt upon oxidation of cerium(III) to cerium(IV). The precipitated cerium(IV) salt is still effective for oxidizing organic substrates, although slurries are more difficult to handle than homogenous solutions. Advantages reported for methanesulfonic acid include low cost, safety, low nucleophilicity, stability to anodic oxidation and oxidation by cerium(IV), and a high solubility of cerium(III) and cerium(IV) (Kreh et al., 1989). The latter feature enables the use of high current density for fast anodic regeneration of cerium(IV) and allows faster reactions with the organic substrates. Regeneration of cerium(IV) takes place at current densities as high as 4000 A m^{-2} , with a current efficiency higher than 90%. It should be noticed that while Ce^{3+} is oxidized to Ce^{4+} at the anode, protons are reduced to hydrogen gas at the cathode. Therefore, the acidity of the solution decreases as the regeneration process proceeds. Cerium(IV) methanesulfonate that is electrochemically generated from cerium(III) methanesulfonate has been used as a redox mediator for the oxidizing of several types of organic compounds. Examples of substrates include toluene, xylenes, chlorotoluenes, ethylbenzene, styrene, naphthalene and anthracene. These oxidation reactions have been discussed more in detail in section 6. Pilot plant projects based on this method have been constructed for the synthesis of anthraquinone, aminoanthraquinone and *p*-tolualdehyde. It is also possible to replace methanesulfonic acid by trifluoromethanesulfonic acid (triflic acid), but the latter acid is more expensive (Kreh and Spotnitz, 1987b).

Although the process described by Kreh et al. was a major improvement in comparison with earlier processes, it is still not energy efficient enough to be of economical interest. Harrison (1993) developed an integrated process to improve the speed and efficiency of the indirect cerium-mediated electrosynthesis of oxidized aromatic compounds like 1,4-naphthoquinone in aqueous methanesulfonic acid. Naphthalene is dissolved in a water immiscible solvent like benzene, chlorobenzene, 1,2-dichloroethane or dichloromethane. The reaction rate depends on the degree of mixing of the two phases. Turbulence in the reaction mixture can be created by a static mixer. However, too fast mixing of the two immiscible solvents can lead to formation of emulsions. Following the reaction, Ce^{3+} is reoxidized to Ce^{4+} in an electrolytic cell under turbulent flow conditions, where the cerium solution is allowed to flow at large velocities past the anode. The cell was designed so that the anode area is greatly reduced, and that the anode and cathode compartments need not to be separated by an ion exchange membrane. The reaction conditions were improved to such an extent that the process could be run continuously. The electrosynthesis of naphthoquinone and tetrahydroanthraquinone

was scaled up to a 100 ton per year pilot-plant (Harrison and Théorêt, 1999). Mahdavi et al. (2002) described a method for the purification of a solution of the spent redox mediator before electroregeneration.

As mentioned above, hydrogen gas is produced at the cathode during the regeneration process. It would be desirable to produce simultaneously with the regeneration of the redox mediator in the oxidized form another redox mediator in the reduced form. This reduced mediator could then perform a reductive electrochemical reaction. Harrison (1997) describes a setup for simultaneously generating Ce^{4+} at the anode and Ti^{3+} at the cathode. The trivalent titanium was subsequently used for reactions such as the reduction of a nitro group into an amino group.

In addition to the interest in cerium-mediated electrosynthesis on an industrial scale, more fundamental studies have been performed. Morita et al. (1993) compared cerium sulfate and cerium perchlorate salt as redox mediators for the oxidation of alkylbenzenes to aromatic aldehydes. Cerium(IV) perchlorate has a higher oxidizing power than cerium(IV) sulfate. Therefore, cerium sulfate could be used to oxidize the easily oxidizable *p*-methylanisole, but not *p*-xylene. On the other hand, the redox mediator should be not too powerful. Therefore cerium(IV) sulfate is more suitable for the oxidation of *p*-methylanisole than cerium(IV) perchlorate. Cerium(IV) *p*-toluenesulfonate is slightly more reactive than cerium *p*-methoxybenzenesulfonate as redox mediator for the oxidation of alcohols, diols and alkylarenes (Purgato et al., 2000; Purgato and Romero, 2002). Cerium(IV) *p*-hydroxybenzenesulfonate is unsuitable as redox mediator, because of electrochemical oxidation of the ligand (Purgato et al., 2000). Cho and coworkers found that the behavior of β -dicarbonyl compounds in electrochemical oxidation reaction with Ce^{4+} depends on the nature of the cerium salt (Cho and Romero, 1988; Cho et al., 1999; Aleixo et al., 2000). When cerium nitrate was used, dimers were formed, whereas upon use of cerium methanesulfonate fragmentation products were obtained. With cerium methanesulfonate as the redox mediator, 2,4-pentanedione is transformed into acetic acid, 1,3-diphenyl-1,3-pentanedione into benzoic acid, 1,3-cyclohexanedione into glutaric acid, methyl acetoacetate into acetic acid and methanol, and dimethyl malonate yields methanol (Cho and Romero, 1988). Because of the low current densities, the reactions were slow. For instance, it took 48 hours to convert 2 mmol of 1,3-diphenyl-1,3-pentanedione into benzoic acid (initial current: 58 mA). No reaction was observed for methyl cyanoacetate and malononitrile. Indian researchers optimized the electrochemical oxidation of anthracene, naphthalene, benzene (Vijayarathi et al., 1999) and *p*-xylene (Jayaraman et al., 1998) in methanesulfonic acid. Studies of the $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox couple in methanesulfonic acid by cyclic voltammetry showed that the redox mediator Ce^{4+} can be employed in solutions of widely different acid strength, cerium concentrations and temperatures (Devadoss et al., 2003). In this respect the $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox couple is superior to the $\text{Mn}^{3+}/\text{Mn}^{2+}$ and $\text{Co}^{3+}/\text{Co}^{2+}$ redox couples. Ag^+ ions catalyze the oxidation of toluene to benzaldehyde by the redox mediator Ce^{4+} (Jow and Chou, 1988). Because of the formation of silver(II) oxide on the surface of the anode, the current efficiency for regeneration of Ce^{4+} increases. Ag^+ ions have thus also a catalytic effect on the regeneration of the redox mediator.

Because organic electrosynthesis with a redox mediator is often performed in multiphase systems (see above), knowledge about the extractability of the Ce^{4+} redox mediator from

the aqueous to the organic phase is very important. Pletcher and Valdes (1988a) showed that Ce^{4+} , but not Ce^{3+} , can be transferred from aqueous acid solutions to organic solvents by tetrabutylammonium or tributylphosphate as phase transfer catalysts. Extraction of Ce^{4+} to organic solvents is efficient from a nitric acid solution, but extraction is much less efficient from sulfuric acid and from perchloric acid solutions. Dichloromethane was found to be the only suitable organic solvent for extractions with tetrabutylammonium salts. With tributylphosphate as extractant, *n*-hexane is a better solvent than dichloromethane. However, extraction with tributylphosphate is less efficient than extraction with tetrabutylammonium. The electrochemical oxidation of cerium(III) to cerium(IV) in emulsions of aqueous nitric acid and water-immiscible organic solvents have been studied (Pletcher and Valdes, 1988b). A problem associated with the anodic oxidation of cerium in an undivided cell is the cathodic reduction of cerium(IV) to cerium(III). The problem can be solved by a proper choice of the phase catalyst and the organic phase, because in this case cerium(IV) is transferred immediately after its formation from the aqueous phase to the organic phase and is thus protected from cathodic reduction. The authors conclude that the best choice for the organic phase for oxidations with emulsions in an undivided cell is hexane/tributylphosphate or heptane/tributylphosphate. The oxidation of anthracene and naphthalene to the corresponding quinones was fast and good yields were obtained. The oxidation of toluenes to benzaldehydes in emulsions was less successful and the results largely depended on the substituents on the toluenes. Not only was the yield low, but many side products were formed as well. Better results were obtained for the oxidation of xylenes. These data illustrate that cerium(IV)-mediated electrochemical oxidations in organic/aqueous emulsions only work well under precise conditions, and that the choice of the reaction medium is of prime importance. For the direct anodic oxidation of cerium(III) to cerium(IV) in an aqueous solution, a divided cell has to be used to avoid reduction of the electrogenerated cerium(IV) at the cathode. This study also illustrated that divided cells are often much more convenient to work with.

The maximum rate of electrochemical regeneration of cerium(IV) is obtained with the concentration of cerium(III) at saturation level. When the cerium(III) ion does not interfere with the cerium(IV)-mediated reaction, it is advisable to add more cerium(III) salts to the reaction mixture than the amount that can be oxidized to cerium(IV). The concentration of cerium(IV) that can be reached is limited by the solubility of cerium(IV) in the reaction solvent, and the cerium(IV) solubility is often lower than the cerium(III) solubility. Tzedakis and Savall (1992) showed that the concentration of cerium(III) has no significant influence on the oxidation of 4-methoxytoluene to 4-methoxybenzaldehyde.

9. Initiation of radical polymerization reactions

Cerium(IV) ions are widely used as initiators for *radical polymerizations* of vinyl monomers (acrylamide, acrylonitrile, methyl methacrylate, vinyl acetate, ...). In order to act as an initiator, a reductant has to be added to the solutions containing the monomer and a cerium(IV) salt. Free radicals are produced by the oxidation of the reductant by cerium(IV) and these free radicals can initiate the polymerization reaction. Table 3 gives an overview of the different

Table 3
Overview of radical polymerization reactions initiated by cerium(IV)

Monomer	Reductant	Reference
acrylamide	acetoacetanilide	(Dong et al., 1994)
acrylamide	amino tri(methylene phosphonic acid)	(Öz and Akar, 2000)
acrylamide	4,4'-azobis(4-cyano pentanol)	(Tunca et al., 1989; Erim et al., 1992)
acrylamide	2-chloroethanol	(Gupta and Behari, 1986)
acrylamide	ethylenediamine tetraacetic acid	(Hsu et al., 1992)
acrylamide	lactic acid	(Misra and Khatib, 1982)
acrylamide	methionine	(Dinçer et al., 1997)
acrylic acid	amino tri(methylene phosphonic acid)	(Öz and Akar, 2000)
acrylonitrile	2-amino ethanethiol	(Lenka and Nayak, 1982)
acrylonitrile	amino tri(methylene phosphonic acid)	(Öz and Akar, 2000)
acrylonitrile	cysteine	(Lenka and Nayak, 1982)
acrylonitrile	glucose	(Padhi and Singh, 1983; Panda and Singh, 1995)
acrylonitrile	<i>N</i> -acetylglycine	(Patra and Singh, 1994a, 1994b)
acrylonitrile	propane-1,2-diol	(Mohanty et al., 1979)
acrylonitrile	sorbitol	(Mohanty et al., 1980)
acrylonitrile	thioacetamide	(Lenka and Nayak, 1982)
acrylonitrile	thioglycolic acid	(Lenka and Nayak, 1982)
acrylonitrile	thiourea	(Rout et al., 1977; Lenka and Nayak, 1982)
alkylcyanoacrylates	dextran	(Chauvierre et al., 2003)
ethyl acrylate	ethanol	(Reddy et al., 2006)
ethyl acrylate	methyl ethyl ketone	(Reddy et al., 2005)
ethyl acrylate	<i>n</i> -propanol	(Reddy et al., 2006)
methyl methacrylate	cellobiose	(Fernández and Guzmán, 1991)
methyl methacrylate	diethanol amine	(Pramanick, 1979)
methyl methacrylate	diethylamine	(Pramanick, 1979)
methyl methacrylate	ethanol amine	(Pramanick, 1979)
methyl methacrylate	ethylene diamine	(Pramanick, 1979)
methyl methacrylate	isobutanol	(Fernández and Guzmán, 1989a)
methyl methacrylate	isopropanol	Fernández and Guzmán, 1989a, 1989b; Fernández et al., 1989)
methyl methacrylate	maltose	(Fernández and Guzmán, 1991)
methyl methacrylate	methanol	(Coutinho et al., 1986)
methyl methacrylate	triethanol amine	(Pramanick, 1979)
methyl methacrylate	triethylamine	(Pramanick, 1979)
methyl methacrylate	water	(Pramanick and Sarkar, 1976)
methyl methacrylate	thiourea	(Pramanick and Chatterjee, 1981)
<i>N,N'</i> -methylenebis(acrylamide)	thiourea	(Paulrajan et al., 1983)
styrene	ethanol	(Kaeriyama, 1969)
styrene	cyclohexanone	(Kaeriyama, 1969)
styrene	dodecyl poly(ethylene oxide)	(Coutinho and Martins, 1991, 1992; Coutinho and Furtado, 1992)
vinyl acetate	amino tri(methylene phosphonic acid)	(Öz and Akar, 2000)

monomers that can be polymerized by radical polymerization by cerium(IV) ions, as well as an overview of the reductants used to generate the radicals.

When the reductant in the system is a polymer itself, the cerium(IV) mediated polymerization reactions allows one to graft another polymer onto the redox active polymer. A *graft copolymer* is a polymer in which a polymer chain of one polymer is chemically bonded to a polymer molecule of another monomer. The two components are known as the *backbone polymer* (or *substrate polymer*) and the *side-chain polymer* (or *rib polymer*). A graft copolymer differs from a block copolymer, because in the latter the addition takes place at one end of the substrate polymer, whereas this is not the case for a graft copolymer. In both cases the final product cannot be considered as a true copolymer because there is no random distribution of the monomers. The final polymeric products of both block and graft copolymerization look as if two polymers have been linked together. The experimental conditions of graft polymerization can be tuned so that a smaller or larger portion of the polymer that is intended to become the side chain is actually bonded to the polymer backbone. This ungrafted fraction of the side-chain polymer is called *homopolymer*. The term *homopolymer* is often used for the fraction of the side-chain polymer that can be extracted by a suitable solvent. Graft polymerization can be used to modify the substrate polymer and improve its properties. No phase separation of the two polymers is possible by the grafting process, because by grafting the polymer side chain is covalently linked to the backbone. Phase separation is a problem that often occurs in the case of physical blending. The grafting process can be influenced by the choice of the experimental conditions (Bhattacharyya and Maldas, 1984). The temperature has a large effect on the extent of grafting. In general the grafting yield increases with increasing temperature until a limiting value is reached. Further increase of the temperature beyond this limit causes an increased extent of radical termination and thus leads to a reduction of the grafting yield. The extent of grafting also increases with an increase of the Ce^{4+} concentration up to a certain limit; beyond the limit it levels off and even decreases with a further increase of the concentration of the initiator. The grafting yield increases with time, but tends to level off after some time. The influence of the monomer concentration on the yield is less obvious. In some cases an increase in monomer concentration has a positive effect, while it has a negative effect in other cases. It is often observed that more homopolymer is formed at high monomer concentrations.

Very often the redox active polymers that are used as backbone polymer are biopolymers like cellulose, which contains many oxidizable hydroxyl groups (Mino and Kaizerman, 1958; McDowall et al., 1984). Table 4 summarizes the different biopolymers and vinyl monomers used for graft polymerization. The graft polymerization process is a very complex chemical process, and all details are not understood yet. The formation of free radicals on these biopolymers can be demonstrated by electron spin resonance (Deshmukh and Singh, 1987). It is believed that the mechanism by which cerium(IV) generates the free radicals involves the formation of a complex between the cerium(IV) salt and the hydroxyl groups of the biopolymer. This complex subsequently disproportionates, with formation of a cerium(III) ion, a proton, and a free radical on the biopolymer chain. The presence of 1,2-diols in the substrate are of great importance for the graft polymerization with cerium(IV) salts (Hintz, 1966). A problem associated with this process is that the grafting yield is rather low. Okieimen and Ebhoaye

Table 4
Overview of studies of graft copolymerization initiated by ceric(IV) ions

Substrate	Monomer	Reference
agar	methacrylamide	(Athawale and Padwaldeai, 1999)
alginate acid	glycidyl methacrylate	(Vijayakumar et al., 1985)
amylopectin	acrylamide	(Rath and Singh, 1998)
amylopectin	hydroxyethyl methacrylate/methyl methacrylate	(Gurruchaga et al., 1992a, 1992b)
amylopectin	hydroxypropyl methacrylate/methyl methacrylate	(Gurruchaga et al., 1992a, 1992b)
amylopectin	hydroxyethyl methacrylate/ethyl methacrylate	(Gurruchaga et al., 1992a, 1992b)
amylopectin	hydroxypropyl methacrylate/ethyl methacrylate	(Gurruchaga et al., 1992a, 1992b)
amylose	acrylamide	(Karmakar and Singh, 1998)
amylose	butyl acrylate	(Vázquez et al., 1987a, 1987b)
amylose	butyl methacrylate	(Goñi et al., 1992)
amylose	ethyl acrylate	(Goñi et al., 1992)
amylose	ethyl methacrylate	(Goñi et al., 1992)
amylose	2-hydroxypropyl methacrylate/butyl acrylate	(Pascual et al., 1996)
amylose	2-hydroxypropyl methacrylate/ethyl acrylate	(Pascual et al., 1996)
amylose	2-hydroxypropyl methacrylate/methyl acrylate	(Pascual et al., 1996)
amylose	methyl acrylate	(Goñi et al., 1992)
carboxymethyl cellulose	acrylamide	(Biswal and Singh, 2004)
carboxymethyl cellulose	acrylonitrile	(Okieimen, 1998)
carboxymethyl cellulose	ethyl acrylate	(Okieimen, 1998; Okieimen and Ogbeifun, 1996)
carboxymethyl cellulose	methyl acrylate	(Okieimen, 1998; Okieimen and Ogbeifun, 1996)
carboxymethyl cellulose	ethyl methacrylate	(Okieimen, 1998; Okieimen and Ogbeifun, 1996)
carboxymethyl cellulose	methyl methacrylate	(Okieimen, 1998)
carboxymethyl cellulose	acrylamide	(Cao et al., 2002)
carboxymethyl cellulose	acrylonitrile	(Nera-Pacheco et al., 1993)
cassava starch	acrylonitrile	(Sharma et al., 2003)
<i>cassia tora</i> gum	methyl methacrylate	(Sakia and Ali, 1999)
α -cellulose	acrylamide	(Gupta and Khandekar, 2006)
cellulose	acrylamide/methyl methacrylate comonomer	(Gupta and Khandekar, 2002)

continued on next page

Table 4, continued

Substrate	Monomer	Reference
cellulose	acrylic acid	(Casinos, 1994; Okteimen, 1987; Vitta et al., 1986; Vitta et al., 1989; Okteimen and Ebroaye, 1986)
cellulose	acrylonitrile	(Gupta and Sahoo, 2001a; Gupta and Sahoo, 2001b; Rao and Kapur, 1969; Fanta et al., 1969; Hebeish and Mehta, 1968; Okteimen and Ebroaye, 1986)
cellulose	ethyl acrylate	(Gupta et al., 2002)
cellulose	ethyl methacrylate	(Gupta and Sahoo, 2001a)
cellulose	glycidyl methacrylate	(Navarro et al., 1999; Shukla and Athalye, 1994)
cellulose	hydroxyethyl methacrylate	(Shukla et al., 1991)
cellulose	methyl acrylate	(Fernández et al., 1990b, 1992; Graczyk, 1986; Vitta et al., 1989; Misra et al., 1993)
cellulose	methyl methacrylate	(Ogiwara et al., 1970; Ogiwara and Kubota, 1970)
cellulose	methyl methacrylate	(Barbucci et al., 1989)
cellulose	<i>N</i> -acryloyl-6-caproic acid	(Barbucci et al., 1989)
cellulose	<i>N</i> -acryloyl glycine	(Gupta and Khandekar, 2003)
cellulose	<i>N</i> -isopropylacrylamide	(Huang and Chandramouhi, 1968; Shukla et al., 1993)
cellulose	styrene	(Fernández et al., 1990b, 1992)
cellulose	vinyl acetate	(Fernández et al., 1990a, 1990c, 1991)
cellulose	vinyl acetate/methyl acrylate	(Guthrie, 1962)
cellulose	vinyl chloride	(Fang and Al-Afaeq, 2002)
cellulose (delignified)	acrylonitrile	(Kondo et al., 1989; Gupta and Sahoo, 2001b)
cellulose (regenerate film)	methyl methacrylate	
cellulose-thiocarbamate	acrylonitrile	(Nagieb and El-Gammal, 1986)
cellulose-thiocarbamate	ethyl acrylate	(Nagieb and El-Gammal, 1986)
β -chitin	methyl methacrylate	(Ren and Tokura, 1994)
chitin	methyl methacrylate	(Ren et al., 1993)
chitin	vinyl acetate	(Don et al., 2002)
chitosan	ethyl methacrylate	(Fares and Al-Ta'ani, 2003)

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Table 4, continued

Substrate	Monomer	Reference
chitosan	eugenol	(Jung et al., 2006)
chitosan	<i>N,N</i> -dimethyl- <i>N</i> -methacryloxyethyl- <i>N</i> -(3-sulfo)propyl	(Zhang et al., 2003b)
chitosan	ammonium	(Yilmaz et al., 1998)
chitosan	4-vinylpyridine	(Brauer and Termini, 1973)
collagen	methyl acrylate	(Brauer and Termini, 1973)
collagen	methyl methacrylate	(Ge et al., 2005)
corn starch	methyl acrylate	(Theappa and Pandey, 1982)
cotton	styrene	(Mostafa, 2005)
cotton yarn	methacrylamide	(Kantouch et al., 1971)
cotton yarn	acrylonitrile	(Kantouch et al., 1971)
cyanoethylated cotton	methyl methacrylate	(McCormick and Park, 1985)
cyanoethylated cotton	acrylamide/ <i>N</i> -(1,1-dimethyl-3-oxobutyl)acrylamide	(Wang et al., 2002)
dextran	<i>N</i> -isopropylacrylamide	(Onishi et al., 1978; Onishi, 1980)
dextran	methyl methacrylate	(Okteimen and Egharevba, 1992)
dextran	methyl acrylate	(Li et al., 1989)
dextrin	butyl acrylate	(Vázquez et al., 1995)
gelatin	2-hydroxyethyl methacrylate/butyl acrylate	(Kumaraswamy et al., 1980)
gelatin	methyl methacrylate	(Fanta et al., 1982, 2003)
gelatin	methyl methacrylate	(Thimma et al., 2003)
gelatin	acrylonitrile	(Chowdhury et al., 2001)
gelatinized wheat starch	acrylonitrile	(El-Shimawy and El-Kalyoubi, 1985; Fanta et al., 1982)
guar gum	methyl methacrylate	(Fanta et al., 1982)
guar gum	acrylonitrile	(Okteimen et al., 1987)
hemicellulose	methyl acrylate	(Okteimen and Idehen, 1987)
hemicellulose	methyl methacrylate	(Okteimen and Idehen, 1987)
holocellulose (bleached)	acrylonitrile	(Okteimen and Idehen, 1987)
holocellulose (bleached)	methyl methacrylate	(Okteimen and Idehen, 1987)
holocellulose (thiolated)	acrylonitrile	(Okteimen and Idehen, 1987)
holocellulose (thiolated)	methyl methacrylate	(Okteimen and Idehen, 1987)
hydroxypropyl guar gum	acrylamide	(Nayak and Singh, 2001)
pure fiber	acrylonitrile	(Das et al., 1990; Nayak et al., 1991; Patra and Singh, 1994a, 1994b)

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Table 4, continued

Substrate	Monomer	Reference
jute fiber	methyl methacrylate	(Chauthan et al., 2000; Patra and Singh, 1994a, 1994b)
kenaf fibers	acrylonitrile	(Eromosele and Agbo, 1999)
Kundoor mucilage	acrylamide	(Mishra and Bajpai, 2005)
lignin	acrylamide	(Meister et al., 1984)
maize starch	acrylic acid	(Athawale and Lete, 1998)
maize starch	methacrylonitrile	(Athawale and Lete, 2000)
mercaptochitin	methyl methacrylate	(Kurita et al., 2002)
methylcellulose	acrylic acid	(Eromosele et al., 2002)
mucilage (from <i>Plantago psyllium</i>)	acrylonitrile	(Mishra et al., 2002, 2003)
nitrocellulose	(Sudhakar et al., 1979)	
ovalbumin	acrylamide	(Imai and Iwakura, 1967)
ovalbumin	methyl methacrylate	(Imai and Iwakura, 1967)
paper	glycidyl acrylate	(Riande et al., 1970)
paper	methyl acrylate	(Ruande et al., 1970)
pineapple leaf fiber	acrylonitrile	(Samal and Bhuyan, 1994)
pine lignin	acrylamide	(Meister and Patel, 1985)
poly(ether urethane)	acrylic acid	(Feng et al., 1985)
poly(ethylene terephthalate) fiber	2-(methacryloyloxyethyl)phosphorylcholine	(Chansook and Klaikamjornwong, 2003)
poly(urethane) (segmented)	2-(methacryloyloxy)ethyl-2-(trimethylammonium)methyl phosphate	(Korematsu et al., 2002)
poly(urethane) (segmented)	phosphate	(Tomita et al., 1999)
poly(vinyl alcohol)	acrylic acid	(Fang et al., 1992)
poly(vinyl alcohol)	acrylonitrile	(Jana et al., 2000; Jin and Huang, 1988)
poly(vinyl alcohol)	hydroxyethyl methacrylate	(Jin and Huang, 1988)
poly(vinyl alcohol)	methyl acrylate	(Chowdhury and Pal, 1999)
poly(vinyl alcohol)	methacrylic acid	(Belakova et al., 2004)
poly(vinyl alcohol)	methacryloxyethyl trimethylammonium chloride	(Zheng et al., 2005)
poly(vinyl alcohol)	methyl methacrylate	(Chowdhury and Banerjee, 1998)
poly(vinyl alcohol)	acrylonitrile	(Lufor et al., 2001)
sago starch	glycidyl methacrylate	(Han et al., 2004)
sago starch	methyl acrylate	(Rahman et al., 2000)
sago starch	methyl methacrylate	(Fakhri-Pirazi et al., 2001)

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Table 4, continued

Substrate	Monomer	Reference
sago starch	styrene	(Janarthanan et al., 2003)
sericin	acrylonitrile	(Cho and Ahn, 1976b)
silk	acrylamide	(Cho and Ahn, 1976a)
silk	acrylonitrile	(Cho and Ahn, 1976a)
silk	methacrylamide	(Shim and Kim, 1969)
silk	methyl methacrylate	(Mohanty et al., 1983)
silk	tetrahydrofurfuryl acrylate	(El-Molla et al., 2001)
sisal	ethyl acrylate	(Barkakaty and Robson, 1979)
sisal	methyl acrylate	(Barkakaty and Robson, 1979)
sisal	methyl methacrylate	(Barkakaty and Robson, 1979)
sisal	acrylamide	(Tripathy et al., 1999)
sodium alginate	acrylamide	(Shah et al., 1995)
sodium alginate	methyl acrylate	(Shah et al., 1995)
sodium alginate	methyl methacrylate	(Patel et al., 1999)
sodium alginate (partially carboxymethylated)	methyl acrylate	(Athawale and Mumbui, 1998; Willett and Finkenstadt, 2006)
starch	acrylamide	(Okieimen et al., 1989)
starch	acrylic acid	(Reyes et al., 1973; Pourjavadi and Zohuriaan-Mehr, 2002; Bazuaye et al., 1988; Nagaty et al., 1980)
starch	acrylonitrile	(Abbott and James, 1981)
starch	2-butenyl acrylate	(Athawale and Kathi, 1997)
starch	butyl methacrylate	(Okieimen and Egharevba, 1989)
starch	ethyl acrylate	(Athawale and Kathi, 1997)
starch	ethyl methacrylate	(Fanta et al., 1970)
starch	2-hydroxy-3-methacryloyloxypropyltrimethylammonium chloride	
starch	ammonium chloride	
starch	methylacrylic acid	(Belakova et al., 2004)
starch	methyl acrylate	(Patil and Fanta, 1993; Liu et al., 1993)
starch	methyl methacrylate	(Athawale and Kathi, 1997)
starch	<i>N</i> -tert-butylacrylamide	(Fares et al., 2003)
starch	acrylonitrile	(Fanta et al., 2003)
starch-coated polyethylene film	acrylonitrile	(Vora et al., 1995)
styrene-maleic acid copolymer	acrylonitrile	

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Table 4. continued

Substrate	Monomer	Reference
wood pulp	acrylonitrile	(Lepoutre and Hui, 1975)
wood pulp	methyl methacrylate	(Hecker De Carvalho and Rudin, 1984)
wool fiber	acrylic acid	(Misra et al., 1980)
wool fiber	allyl methacrylate	(Abdel-Hay et al., 1982)
wool fiber	methyl methacrylate	(Kantouch et al., 1971; Misra et al., 1980; Shukla and Sharma, 1987)
wool fiber	vinyl acetate	(Misra et al., 1979)
wool (reduced)	acrylic acid	(Misra et al., 1981)
wool (reduced)	ethylacrylate	(Misra et al., 1980)

(1986) reported that on average less than five molecules of the side chain polymer are grafted onto one cellulose molecule. Another problem is that large quantities of the homopolymer are often formed. According to Okieimen (1998) the graft polymer formation on carboxymethyl-cellulose occurs preferentially by combination of the growing homopolymer chains with radicals formed on the backbone polymer rather than by the addition of monomer to the radicals formed on the backbone polymer. The extent of grafting depends on the physical state of the cellulose: the grafting mainly takes place in the amorphous region of the cellulose. The grafting of vinyl monomers on cellulose is usually carried out in aqueous medium, which is acidified to prevent hydrolysis of the cerium(IV) salt. Radical polymerizations are generally performed under an inert atmosphere, because oxygen has an inhibitory role on the reaction (oxygen is a radical scavenger).

The graft copolymerization of acrylonitrile, acrylamide or acrylic acid on starch or related biopolymers is of great importance for the preparation of superabsorbent polymers (Po, 1994). *Superabsorbent polymers* (SAPs) are a group of materials that can absorb over one hundred times their weight in liquids and do not easily release the absorbed fluids under pressure. The possibility of SAPs to retain water relies on the formation of a hydrogel. The superabsorbent polymers have been discovered by researchers at the National Center for Agricultural Utilization Research of the United States Department of Agriculture in 1973. Applications for these polymers were originally focused in the agriculture/horticulture markets where they were used as hydrogels to retain moisture in the surrounding soil during growing and transportation. These applications are still of prime importance. However, the popularity of superabsorbent polymers increased dramatically since they are being used as active material in disposable diapers. Other related applications include adult incontinence products and feminine hygiene products. In industry, SAPs are being used in packaging materials and for disposal of liquid waste. The original superabsorbent polymers were saponified starch-graft polyacrylonitrile copolymers, and they became known under the trivial name "*Super Sturper*". Ammonium hexanitratocerate(IV) has been used as an initiator with 0.1 mole of cerium(IV) ions in 1 N nitric acid. Optimal results are obtained when starch was gelatinized by heating in water at 80°C for an hour prior to the reaction. The graft polymerization occurs at around 30°C and atmospheric pressure. The starch chains are broken down by the gelatinization. This gives and increased reactivity with acrylonitrile monomers and a higher molecular weight product. After graft polymerization, the cyano groups have to be saponified to carboxylate or amide groups. The saponification reaction takes place at 95°C and atmospheric pressure with a ratio of alkali to acrylonitrile of 0.6–0.8 to 1. Washing with water removes excess salts produced during saponification. Although acrylonitrile was used initially, acrylic acid is presently often the preferred monomer, because it is non-toxic. Several starch sources can be used. Examples include corn, potato, and rice starches. The final product looks like flakes of dried, colorless gelatin.

Ceric(IV)-mediated graft polymerization can also be used to prepare inorganic-organic hybrid materials. Rao et al. (1981) grafted methyl methacrylate and acrylonitrile on mica. Murugan and Ramakrishna (2004) grafted glycidylmethacrylate on a demineralized bone matrix, while Wang et al. (2005) grafted *N*-isopropylacrylamide on hydroxylated glass coated with 3-aminopropyltriethoxysilane.

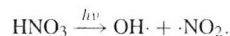
10. Miscellaneous reactions

10.1. Generation of nitrate free radicals

Martin and coworkers showed that nitrate free radicals can be generated efficiently at room temperature by flash photolysis of a solution of ammonium hexanitratocerate(IV) in a 6 M aqueous nitric acid solution. Upon irradiation with light quanta between 280 and 400 nm (Martin et al., 1963, 1964). Although there was the opinion that these nitrate free radicals arose from the direct photolysis of undissociated nitric acid solvent molecules (Hayon and Saito, 1965), Martin and Glass (Glass and Martin, 1970; Martin and Glass, 1970) were convinced that the cerium(IV) ion was directly involved in the generation of the radicals. It has been suggested that the $\text{NO}_3\cdot$ radicals are formed by an intramolecular electron-transfer process in the excited cerium(IV) complex (Wine et al., 1988; Glass and Martin, 1970):

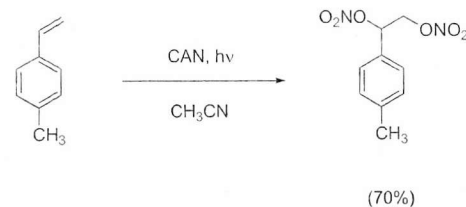


It has been shown later that under the same experimental conditions as those used for the photolysis of ammonium hexanitratocerate(IV), nitric acid is decomposed in hydroxyl radicals and nitrogen dioxide (Vione et al., 2001):



The quantum yield for the generation of the nitrate free radical by photolysis of CAN in presence of nitric acid is quite high at 360 nm. It ranges from 51% for 0.1 M HNO_3 to 88% for 1 M HNO_3 (Herrmann et al., 1991). The nitration of naphthalene with photochemically generated nitrate free radicals in an aqueous nitric acid solution has been investigated as part of an environmental study on the reactivity of polyaromatic compounds in the hydrosphere (Vione et al., 2005). The main product was 1-nitronaphthalene, with 2-nitronaphthalene being a byproduct. However, it was found that the formation rate of both 1-nitronaphthalene and 2-nitronaphthalene are higher in the dark than under UV irradiation, which suggests that the nitrate free radical mediated nitration is an unimportant pathway for naphthalene nitration in aqueous solutions. No nitronaphthalenes were formed in the dark in presence of nitric acid alone.

The $\text{NO}_3\cdot$ radicals can also be generated by flash photolysis of CAN in acetonitrile (Del Giacco et al., 1993). These photochemically produced nitrate free radicals have been used to study the one-electron oxidation of methylbenzenes. Depending on the oxidation potential of the substrate, radical cations or benzyl-type neutral radicals were formed. Formation of radical cations was observed for most of the methylbenzene derivatives that were studied, whereas formation of the benzyl radical was observed with toluene and with *ortho*- and *meta*-xylene. This reaction is not useful for synthetic applications. The reactivity of propellane C-C bonds towards free nitrate radicals photochemically generated from ammonium hexanitratocerate(IV) in acetonitrile was studied from both theoretical and experimental points of view (Fokin et al., 2000). Baciocchi and coworkers reported that the photochemical reaction of CAN in acetonitrile with cyclohexene, 1-octene and styrene derivatives leads to the formation of 1,2-dinitrate adducts in high yields (scheme 65) (Baciocchi et al., 1988b).



Scheme 65.

10.2. Decomposition of water

Because of the strongly oxidizing power of cerium(IV) ions, aqueous solutions of cerium(IV) are metastable with regard to the oxidation of water to oxygen gas. However, the kinetics of this reaction is very slow so that acidic aqueous solution of cerium(IV) can be stored for a long time without appreciable reduction of cerium(IV) to cerium(III). The reaction is only observed in presence of a catalyst, although it should be noticed that the wall of a glass vessel can show catalytic activity. The slowness of the reaction in the absence of a catalyst can be explained by the fact the oxidation of water to oxygen ($2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$) is a four-electron process. Because it is very difficult to get the four electrons at the same place at the same time, this reaction has a high overpotential (although the E_0 value is not higher than +1.23 V) (Mills, 1989).

Grant and Payne (1961) report that the decomposition of water by cerium(IV) is catalyzed heterogeneously at the surface of a glass vessel and by precipitated material in the solution. Grant (1964) also observed reduction of cerium(IV) by water upon heating a solution of cerium(IV) sulfate in sulfuric acid. Cerium(IV) containing solids and added silver(I) and mercury(II) ions were found to catalyze the redox reaction. However added copper(II) retarded the reaction. The silver(I) catalyzed oxidation of water with cerium(IV) in aqueous perchloric solutions was studied in detail by Indrayan and coworkers (Indrayan et al., 1982). Bruce and coworkers (King et al., 2005) showed that RuO_2 nanoparticles supported on mesoporous silica are very active in catalyzing the oxidation of water by cerium(IV) in sulfuric acid solution.

Cerium(IV) undergoes photochemical reduction in water, whereby water is oxidized to oxygen gas (Baur, 1908; Weiss and Porret, 1937; Heidt and Smith, 1948; Sworski, 1957). On the other hand, cerium(III) ions undergo photochemical oxidation, resulting in the formation of hydrogen gas (Heidt and McMillan, 1954). Because cerium(IV) can oxidize water in the dark, and cerium(III) can reduce water only in light, an experimental set-up can be designed in such a way that an aqueous solution of cerium(IV) and cerium(III) can produce pure oxygen in the dark and almost pure hydrogen or a mixture of oxygen and hydrogen in light (Heidt and McMillan, 1953). Because cerium(III) can only absorb UV light, the efficiency of the photoreduction of water is low. As mentioned above, the oxidation of water by cerium(IV) can be mediated by different catalysts. Cerium dioxide is a promising photocatalyst for the splitting of water into oxygen (Bamwenda and Arakawa, 2000, 2001; Bamwenda

et al., 2001). The oxygen is formed when a suspension of CeO_2 in an aqueous Ce^{4+} solution is illuminated by UV irradiation. When the energy of the absorbed radiation is larger than the band-gap of cerium dioxide, an electron-hole pair is created in the material. Electrons can be removed from the cerium oxide by surface-adsorbed Ce^{4+} ions, reducing them to Ce^{3+} . Simultaneously, surface-adsorbed water molecules are oxidized by the holes to oxygen in a four-electron exchange process. The role of Ce^{4+} is thus to act as an electron acceptor to remove the photogenerated electrons from the conduction band. The Ce^{3+} ions can be oxidized to Ce^{4+} in a photochemical process that involves the direct photoexcitation of the Ce^{3+} ion, which is followed by the reduction of protons or water to hydrogen gas. Alternatively, Ce^{4+} can be regenerated by reaction of Ce^{3+} on the surface with holes. Other semiconductor materials like WO_3 or TiO_2 show photocatalytic behavior as well. Research efforts are made towards the use of cerium dioxide for the overall splitting of water into oxygen and hydrogen, because this could be a means of solar energy conversion.

10.3. Hydrolysis of phosphodiester and DNA

Cerium(IV) complexes are used as very efficient non-enzymatic reagents for the hydrolysis of phosphodiester and the phosphodiester backbone of DNA (Ott and Krämer, 1999; Franklin, 2001; Mancin et al., 2005; Komiyama et al., 1999; Komiyama, 2005; Sreedhara Cowan, 2001). DNA is very resistant to spontaneous (uncatalyzed) hydrolysis. It has been estimated that the half-life of a single phosphodiester P-O bond at pH 7 and 25 °C is about 200 million years (Kim and Chin, 1992; Williams et al., 1999)! Although such hydrolytic inertness is a great advantage for the preservation of the genetic code, it makes DNA manipulation (expression, duplication, repair of damage) difficult. Nature solves this problem by the use of a variety of hydrolytic enzymes, like the nucleases. Many of these enzymes are metalloenzymes that contain a calcium(II), magnesium(II) or zinc(II) ion in the active site. Other studies have shown that transition metal ions, and especially the rare-earth ions, effectively accelerate the hydrolysis of phosphate esters (Takasaki and Chin, 1994; Komiyama et al., 1994a, 1995; Komiyama, 2005; Roigk et al., 1998).

The extremely high resistance of DNA towards hydrolysis makes it very difficult to study the mechanism of the hydrolysis reaction. Therefore, DNA is replaced in many studies by more reactive compounds with a phosphodiester bond (chart 1). Bis-(*p*-nitrophenyl)phosphate (BNPP) is a very popular model compound for the study of the hydrolytic cleavage by nucleases. Hydrolysis of the diphosphate ester yields two equivalents of a yellow nitrophenolate product, the formation of which can be monitored by spectrophotometry ($\lambda_{\text{max}} =$

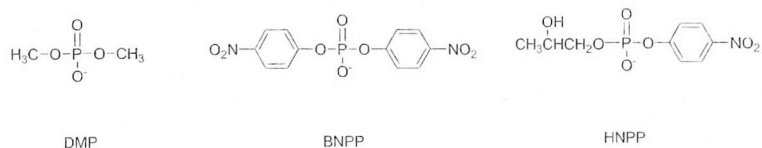
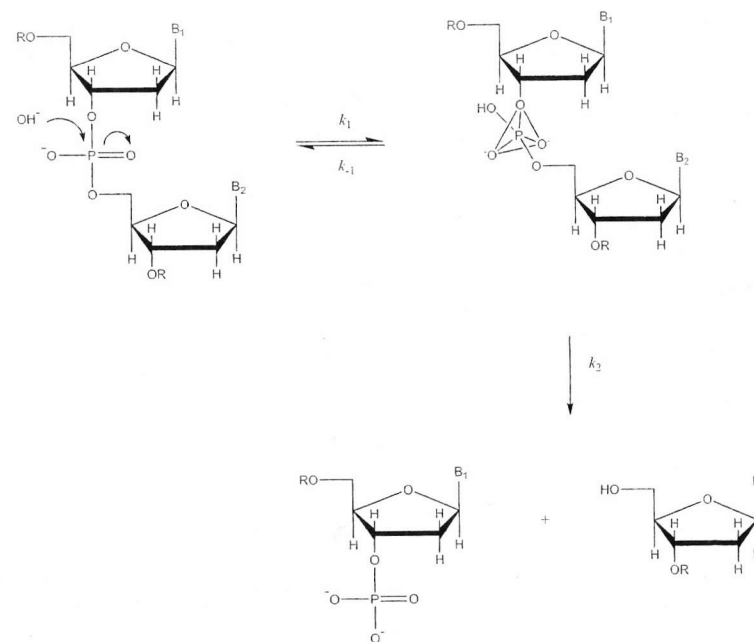


Chart 1. Model compounds for the study of phosphodiester hydrolysis.



400 nm). Other model compounds are dimethyl phosphate (DMP), and 2-hydroxypropyl (*p*-nitrophenyl) phosphate (HNPP) (chart 1). Supercoiled DNA is a more reactive form of DNA that can also be used in the study of hydrolytic cleavage, because it is activated by strain and other factors.

The presently accepted mechanism for the hydrolysis of the phosphodiester backbone of DNA involves the nucleophilic attack of the phosphorus atom by the oxygen atom of water or a hydroxide ion to give a five-coordinate phosphate intermediate (Hegg and Burstyn, 1998; Komiyama and Sumaoka, 1998; Komiyama et al., 1999) (scheme 66). This attack is followed by cleavage, leaving ROH and $\text{ROPO}_3(\text{H}_2)$ termini. In metal-assisted hydrolysis, the metal activates, as a Lewis acid, the phosphate group for attack by the nucleophile, increases the leaving group ability of the alcohol, or activates a metal-coordinated water molecule as a nucleophile (Mancin et al., 2005). Multinuclear complexes are often more active than mononuclear complexes. This is in agreement with the finding that many natural metallonucleases make use of the cooperative action of two or more metal ions. A high charge-to-ionic size diameter seems to be necessary for efficient catalysis of phosphodiester hydrolysis.

The Ce^{4+} ion has been found to enhance the rate of BNPP hydrolysis by a factor of more than 10^{10} and the rate of DNA hydrolysis by a factor of more than 10^{11} (Rammo et al., 1996; Komiya, 1999; Moss and Ragunathan, 1998; Sumaoka et al., 1998a). These rates are 20 to 1000 times faster than the rates of hydrolysis catalyzed by trivalent lanthanide ions. In fact, the Ce^{4+} ion is of all metal ions the best catalyst for DNA hydrolysis. It should be noticed that the trivalent lanthanide ions are better catalysts for the hydrolysis of RNA than Ce^{4+} (Komiya et al., 2005). The rate of DNA hydrolysis is almost constant in the pH range from 2.5 to pH 8.5. The nature of the nucleic acid bases does not influence the hydrolysis rate. At pH 7 and 50 °C, the half-life of the phosphodiester of DNA is reduced to a few hours (Komiya et al., 1994a, 1995). Some other substrates are hydrolyzed very fast: at pH 7 and 30 °C, the half-lives of the 3,5-cyclic monophosphates of adenosine and guanosine in presence of 0.1 M ammonium hexanitratocerate(IV) are as short as 7 and 16 seconds, respectively (Sumaoka et al., 1994). Cerium(III) becomes a more efficient catalyst for phosphodiester hydrolysis in presence of molecular oxygen, due to the oxidation of cerium(III) to cerium(IV) (Komiya et al., 1995). The activity of cerium(IV) is independent of the presence of molecular oxygen. Despite the redox activity of cerium(IV), the hydrolysis of phosphodiester by cerium(IV) takes place through a purely hydrolytic pathway, rather than through an oxidative pathway (Moss and Ragunathan, 1998). No oxidative cleavage of the deoxyribose units occurs. In a study to determine whether the P-O or the C-O bond is cleaved during phosphodiester hydrolysis, it was found that dimethylphosphate is cleaved by cerium(IV) with 91% P-O scission (Moss and Morales-Rojas, 1999). Phosphomonoesters are faster hydrolyzed by cerium(IV) than phosphodiester (Miyama et al., 1997). The selectivity of cerium(IV) for hydrolysis of phosphomonoesters over phosphodiester can be increased by using concentrated buffer solutions of tris(hydroxymethyl)methylamine (TRIS) or *N'*-(2-hydroxyethyl)piperazine-*N*-ethanesulfonic acid (HEPES). This selectivity is useful for selective removal of the terminal monophosphate from a dinucleotide.

Core-level photoelectron spectra of the 2*p* orbitals of the phosphorus atom in diphenyl phosphate (DPP) show that the binding energy of the orbitals is much greater in the cerium(IV)-DPP complexes than in the complexes formed with the trivalent lanthanide ions (Shigekawa et al., 1996). This indicates that cerium(IV) is more effective in electron-withdrawal from the phosphate than the trivalent lanthanide ions. The electron-withdrawing effect results in a higher electrophilicity of the phosphodiester linkage. The active role of the cerium 4*f* orbitals in the hydrolysis of phosphodiester was investigated by EXAFS and XANES (Shigekawa et al., 1999). It was observed that upon complex formation of cerium(IV) with DPP, 0.67 electrons are present in the 4*f* orbitals. Because one expects empty 4*f* orbitals for cerium(IV) (Ce^{4+} has no 4*f* electrons), these results show that electron density was transferred from the environment to cerium(IV). Most trivalent lanthanide ions cannot accept electrons (their divalent state is too unstable). There is evidence that the orbitals of the phosphodiester linkage mix with the 4*f* orbitals of cerium(IV) to form new hybrid orbitals (Komiya et al., 1999). This mixing is possible because the 4*f* orbitals of cerium(IV) are lower in energy than the 4*f* orbitals of the lanthanide(III) ions. These two factors, electron-withdrawal from the phosphate by cerium(IV) and the formation of hybrid orbitals, activate the phosphodiester linkage greatly for nucleophilic attack. The phosphate

group is actually attacked by a hydroxide ion coordinated to one or two cerium(IV) ions. The most active catalytic species is $[Ce_2(OH)_4]^{4+}$. The phosphodiester is thus coordinated by two cerium(IV) in a bimetallic complex. The cerium(IV) hydroxo cluster stabilizes the negatively charged transition state of DNA hydrolysis, and the pentacoordinate intermediate is efficiently formed. The water bound to cerium(IV) acts as an acid catalyst in the breakdown of this pentacoordinate intermediate, which is the rate-limiting step in the catalytic process. A comparison of the catalytic activity of different cerium(IV) hydroxo species in aqueous acetonitrile solutions was made by Maldonado and Yatsimirsky (2005). The catalytic activity was found to increase with increasing positive charge of the hydroxo species: $[Ce_4(OH)_{15}]^+ < [Ce_4(OH)_{14}]^{2+} < [Ce_4(OH)_{13}]^{3+}$. The $[Ce_4(OH)_{15}]^+$ complex occurs at pH > 7, $[Ce_4(OH)_{13}]^{3+}$ below pH 5 and $[Ce_4(OH)_{14}]^{2+}$ at intermediate pH values.

The activity of cerium for DNA hydrolysis can be enhanced further by one order of magnitude by addition of a praseodymium(III) salt ($Ce^{4+} : Pr^{3+}$ ratio is 2) (Tikeda et al., 1996). The two metal ions form a mixed hydroxo cluster, which is the active catalytic species. The function of praseodymium(III) is to provide metal-bound water to act as the acid catalyst in the cleavage of the intermediate (Komiya et al., 1999). Cooperative effects were also observed for the ternary system cerium(IV)-lanthanide(III)-dextran (Sumaoka et al., 1994, 1997, 1998b).

Most of the studies of the cerium(IV) catalyzed hydrolysis of phosphodiester are performed under acidic conditions. For instance, Moss and Ragunathan (1998) investigated the hydrolysis of dimethyl phosphate by ammonium hexanitratocerate(IV) at pH 1.8. Above pH 4, the formation and precipitation of cerium(IV) hydroxide gels hinders kinetic studies under physiological conditions. Complexation of the cerium(IV) ions could solve this problem. However stable cerium(IV) have a much lower activity than the free ion, probably because of the reduction of the overall charge of the complex and because of the saturation of the coordination sphere. An exception is the cerium(IV)-EDTA complex, that has a high activity for hydrolysis of DNA (Igawa et al., 2000). The catalytic activity of the cerium(IV)-EDTA complex is increased in presence of amines like ethylenediamine and spermine (Sumaoka et al., 2001). The degree of polymerization of DNA is crucial for the catalytic activity: the cerium(IV)-EDTA complex hydrolyzes oligonucleotides longer than tetranucleotides under physiological conditions, but not dinucleotides or trinucleotides (Igawa et al., 2000). The cerium(IV) EDTA complex hydrolyses single-stranded DNA far more efficiently than double-stranded DNA (Kitamura et al., 2003). By using this selectivity, gap-sites in DNA are preferentially hydrolyzed (Kitamura and Komiya, 2002). Unfortunately, this gap-site selective DNA hydrolysis is rather slow. Co-catalysts were designed to accelerate the selective hydrolysis at the gap site. Examples are oligoamine-acridine conjugates (Yamamoto et al., 2003). Komiya and coworkers tried to overcome the cerium hydroxo gel formation at physiological pH by forming a weak complex of cerium(IV) and γ -cyclodextrin (Sumaoka et al., 1994). Yan and coworkers investigated the catalytic activity of a cerium(IV) complex of ligands that can be considered as EDTA-bridged β -dimers (Yan et al., 2002). Cyclodextrins are able to bind a variety of hydrophobic substrates. The hydrophobic binding sites strongly contribute to the catalytic activity towards hydrolysis of BNPP. It was estimated that the cyclodextrin accelerates the reaction by a factor of 520 in comparison to the rate observed for the cerium(IV)

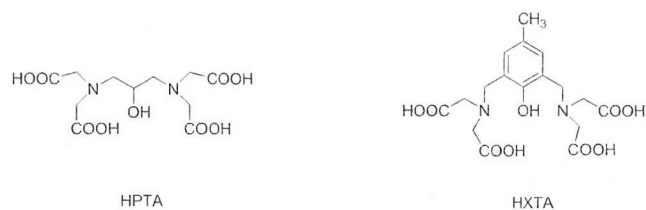


Chart 2. Aminopolycarboxylate ligands for cerium(IV).

complex of the dimethyl ester of EDTA. A remarkably fast cleavage of BNPP was observed by cerium(IV) complexes in an aqueous micellar solution (Bracken et al., 1997). The micelles were formed by the nonionic surfactant Brij-35 (a polyoxyethylene monolauryl ether). Ligands were palmitic acid, *N*-octanoyl-*N*-methyl-*D*-glucamine and 4-(1-hexadecynyl)-2,6-pyridinedicarboxylic acid. A complex composed of algae polysaccharides and cerium(IV) was found to be able to split supercoiled DNA into its linear form (Wang et al., 2005).

Cerium(IV)-containing systems that are able to catalyze sequence-specific hydrolysis of DNA are prototypes of artificial restriction enzymes. Site-selective DNA hydrolysis was achieved by attaching cerium(IV) complexes to sequence-recognizing antisense deoxy-oligonucleotides (Komiyama et al., 1994b; Komiyama, 1995). Komiyama used a system consisting of a ligand with an iminodiacetate group for cerium(IV) binding appended to a 19-mer DNA oligonucleotide for DNA recognition. A single strand 40-residue DNA was selectively cleaved at the linkage between residue 30 and residue 31 (Komiyama, 1995). There is no evidence for the self-digestion of the cerium(IV)-oligomer conjugate. Taking into account the fact that DNA is preferentially hydrolyzed at gap structures (see above), selective DNA hydrolysis can be obtained by forming gap structures in predetermined positions in substrate DNA (Chen et al., 2004). This gap formation can be obtained either by using two oligonucleotide additives that bear a monophosphate group at the termini through various linkers (Chen et al., 2004), by two oligonucleotides bearing ethylenediamine-*N,N,N',N'*-tetraacetate groups (Komiyama et al., 2005), or by one oligonucleotide additive bearing two monophosphate groups (Chen and Komiyama, 2005). The one-additive system is simpler and more convenient. Moreover, it has a higher stability so that it can be used at higher reaction temperatures.

The dicerium(IV) complex of 1,3-amino-2-hydroxypropane-*N,N,N',N'*-tetraacetate (HTPA) is capable of double-strand cleavage of plasmid DNA (Branum and Que, 1999). This is in contrast with the behavior of cerium(IV)-EDTA which favors single-strand cleavage of DNA. Another complex able of double-strand hydrolysis is the dicerium(IV) complex of 5-methyl-2-hydroxy-1,3-xylene- α,α' -diamine-*N,N,N',N'*-tetraacetic acid (HXTA) (chart 2) (Branum et al., 2001). Progress to site-selective two-strand hydrolysis of double-stranded DNA was made by Komiyama and coworkers (Yamamoto et al., 2004). They formed gap-like structures at pre-designed sites in double-stranded DNA by using invasion of two

pseudo-complementary peptide nucleic acid additives. The cerium(IV)-EDTA complex divides the double-stranded DNA into the desired two fragments.

The hydrolysis of phosphonic acid esters in Brij-35 micelles by cerium(IV) was investigated by Moss and Ragunathan (1999). The phosphonic esters differ from the phosphodiester by the presence of only one ester bond and by a direct bond between phosphorus and the carbon atom of an alkyl or aryl group. Cerium(IV) ions also accelerate the hydrolysis of these diesters (Moss and Morales-Rojas, 2001; Moss et al., 2004). The phosphonoformate diesters show structural similarities with the phosphodiester. Whereas zirconium(IV) and hafnium(IV) hydrolyze mainly the P-OR bond, cerium(IV) and thorium(IV) hydrolyze principally the C-OR bond in the phosphonoformate diesters. This chemoselective ester hydrolysis was not observed for the phosphodiester compounds.

10.4. Hydrolysis of peptides

The Ce^{4+} ion is one of the most active catalysts for peptide hydrolysis. Its activity is much higher than that of the trivalent lanthanide ions and other transition metal ions. In particular, Ce^{4+} is far superior to other tetravalent ions like Zr^{4+} or Hf^{4+} . Yashiro et al. (1994) reported that dipeptides and tripeptides were efficiently hydrolyzed under neutral conditions by the γ -cyclodextrin complex of cerium(IV). Komiyama and coworkers (Takarada et al., 2000) studied the catalytic hydrolysis of oligopeptides by cerium(IV) salts. The hydrolysis is fast, especially when the oligopeptides contain no metal-coordinating side-chains. The hydrolysis rates of the dipeptides, tripeptides and tetrapeptides is similar. The hydrolysis reaction was performed at pH 7 and 50 °C and under these conditions, the half-life of the amide bond was only a few hours. The authors found that ammonium hexanitratocerate(IV) is more active than other cerium(IV) compounds like ammonium cerium(IV) sulfate, cerium(IV) sulfate and cerium(IV) hydroxide. The lower reactivity of ammonium cerium(IV) sulfate is ascribed to the competitive inhibition by sulfate ions, while the low reactivity of cerium(IV) sulfate and cerium(IV) hydroxide can be explained by their poor solubility in water. However, in the reaction mixtures at the given reaction conditions, most of the cerium(IV) consists in a gel of cerium(IV) hydroxides. No oxidative cleavage has been observed.

11. Various applications

11.1. TLC stains

The most typical way of visualizing a developed TLC (Thin Layer Chromatography) plate is by examining it under UV light to observe the quenching of the luminescence of the phosphor in the alumina or silica gel layer by chromophoric groups of the organic compound. Unfortunately, many compounds do not have chromophoric groups. In this case, the spots on a TLC plate must be visualized by other means, typically by treating with a vapor or solution which reacts with residues on the plate to produce an image. Various staining solutions are based on cerium(IV) salts (Stahl, 1965; Touchstone, 1982; Touchstone and Dobbins, 1978). Cerium molybdate is prepared by dissolving cerium(IV)

sulfate and ammonium heptamolybdate in dilute sulfuric acid. Ammonium hexanitratocerate(IV) can be used instead of cerium(IV) sulfate. Cerium molybdate reagent is also known as "Hanessian's Stain" or "Blue stain". It is a general purpose stain, but it is very good for visualizing hydroxy groups. The stain requires heating to make the spots visible on the TLC plate. A stain prepared by dissolving cerium(IV) sulfate in dilute sulfuric acid is useful for alkaloids.

11.2. Test reagents

An application that has now become obsolete, but which is worth to be mentioned, is the use of cerium(IV) solutions as a test reagent for alcohols (Duke and Smith, 1940; Feigl, 1954), which form red 1 : 1 complexes upon coordination to cerium(IV) (Young and Trahanovsky, 1969). The reagent is either a solution of 400 g of $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ in 1 liter of 2 M HNO_3 , or a solution of 0.5 M $\text{Ce}(\text{ClO}_4)_4$ in 2 M HClO_4 . One ml of this test solution is diluted with 2 ml water or dioxane. The unknown material is dissolved in as little water or dioxane as possible, and one drop of this solution is added to the diluted test solution. A color change from yellow to red indicates the presence of primary, secondary or tertiary alcohols. Aldehydes, ketones, acids, esters and hydrocarbons do not interfere. Aliphatic amines could induce a raise in pH, leading to precipitation of cerium(IV) hydroxides. Aromatic phenols and amines interfere by the formation of colored complexes. Compounds that are easily oxidized may reduce the test reagent. The formation constant of cerium(IV) with different types of alcohols have been determined in aqueous acetonitrile containing 0.5 M nitric acid (Young and Trahanovsky, 1969). When ammonium hexanitratocerate(IV) is used as the source of cerium(IV) it is found that the nitrate ions are competing with the alcohol molecules for coordination to cerium(IV).

11.3. CAN as etchant

Solutions of ammonium hexanitratocerate(IV) in dilute perchloric acid or in dilute nitric acid are being widely used as etchants for the preparation of printed circuit boards, and in the semiconductor and microelectronics industry (Basceri et al., 2004). They are also used for cleaning surfaces prior to soldering (GFS Chemicals product catalog). They are particularly useful for etching nichrome, monel, stainless steel and many other ferrous and non-ferrous alloys (Acocella and David, 1988).

11.4. Ceric-cerous sulfate dosimeter

The *ceric-cerous sulfate dosimeter* is a chemical dosimeter acting either as a routine dosimeter or as a reference standard dosimeter for the measurement of high dose levels (Matthews, 1982). A routine dosimeter is used in radiation processing facilities for dose mapping. A reference standard dosimeter is used to calibrate radiation fields and routine dosimeters. The dosimeter is based on the reduction of cerium(IV) to cerium(III) in an aqueous solution by radiation (Matthews, 1971). Doses in the range 0.5 to 50 kGy can be determined by conventional spectrophotometric analysis in the ultraviolet region, or by measuring the difference in the electrochemical potential between the irradiated and non-irradiated solutions in an electrochemical potentiometer (Matthews, 1972; Church et al., 1976). As most dosimeters, the

ceric-cerous sulfate dosimeter does not exhibit a strict linear relationship between readout signal and absorbed dose. This means that it is not possible to define a single calibration factor for this type of dosimeter, and a curved calibration function has to be used instead. A new method to read out the dosimeter is via measurement of the NMR relaxation rate (Bäck et al., 2002). Applications of this type of dosimeters are found in the fields of food irradiation or radiation sterilization of medical devices to measure the amount of γ -radiation that the product has received in the irradiation facility.

11.5. CerOxTM process

The *CerOxTM* is a cerium-catalyzed electrochemical oxidation process for the destruction of organic hazardous wastes (Nelson, 2002; Surma et al., 1998, 1999; Steward, 1998). Applications of the process include the destruction of polychlorobenzenes (PCBs), dioxins, tetrachloroethylene, and a variety of chlorinated pesticides and herbicides. Non-chlorinated organic waste compounds like amines and phenols can also be destroyed by this technique. The *CerOxTM* process was originally developed by the Pacific Northwest National Laboratory and has been commercialized by *CerOx Corporation* (www.cerox.com). The oxidation reactions convert the organic material primarily into carbon dioxide and water, whereas carbon bound chlorine is converted to chlorine gas. Other heteroatoms such as nitrogen, phosphorus and sulfur are oxidized to respectively nitric, phosphoric and sulfuric acid. The chlorine gas that is formed by the oxidation of the chlorinated organic compounds is removed from the exhaust gas stream before venting. The *CerOxTM* process is performed in a series of enclosed tanks and pipes to avoid contamination of the environment. The electrolyte in the cathodic part is 4 M nitric acid. The organic waste materials are injected into the oxidizing electrolyte through an ultrasonic mixer (sonicator) that emulsifies the organic phase into the aqueous phase. The oxidative destruction of the organic waste by cerium(IV) takes place at 90 to 95 °C. The active cerium(IV) oxidant is regenerated from the reduced cerium(III) by reoxidation at the anode in the electrochemical cell. At the same time, nitrous acid, HNO_2 , is formed by reduction of nitric acid at the cathode. However nitrous acid disproportionates in solution to produce nitric acid and nitric oxide, NO. The gaseous NO is oxidized with atmospheric oxygen to NO_2 , which is redissolved in water to produce nitric acid. In this way much of the nitric acid consumed by the cathode reaction can be recycled. A schematic presentation of the liquid phase treatment in the *CerOxTM* process is shown in fig. 7. From time to time the cerium-containing electrolyte has to be replaced because of accumulation of inorganic salts in the electrolyte. In large systems, the removal process is done continuously. The anodic processes (waste destruction) are separated from the cathodic processes by a Nafion[®] membrane. The membrane allows the free passage of protons between the two cell compartments, but it is impermeable to anions. The electrodes are made of titanium, but the anode surface is covered with a layer of electroplated platinum metal. The electrolyte in the anodic part of the electrochemical cell is cerium nitrate (1.5 M) in 3.5 M nitric acid solution. Typically 2/3 of the cerium is present in the form of cerium(IV) and 1/3 in the form of cerium(III). This ratio provides a high enough cerium(IV) concentration for oxidation of the organic compounds, but makes the concentration potential for the anodic oxidation of cerium(III) not too high. The technology presented

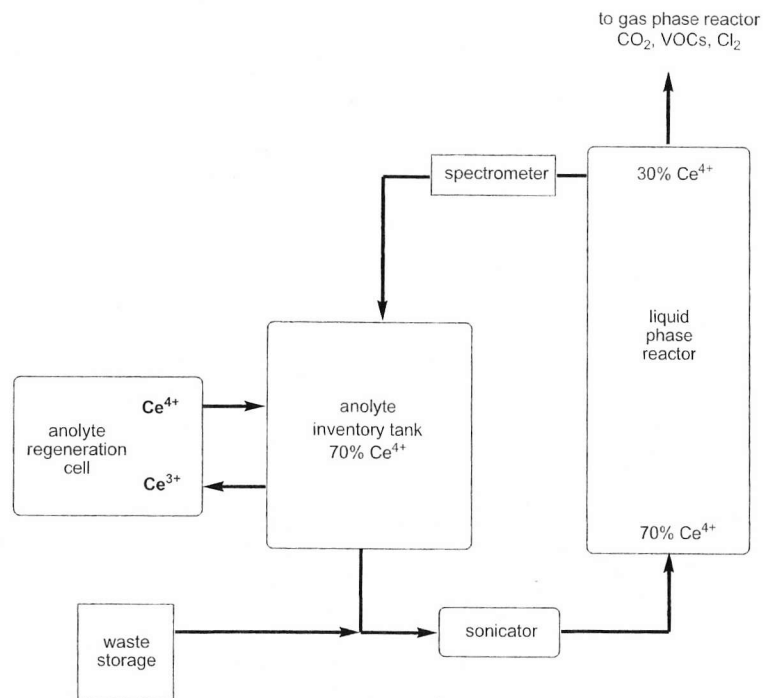


Figure 7. Liquid phase treatment in the CeO_x^{TM} process.

here is in many ways similar to the cerium-mediated electrosynthesis process discussed in section 8, but with the main difference that in the present case the process is intended for the destruction of organic compounds, not for their synthesis.

11.6. Model for tetravalent plutonium

The coordination chemistry of tetravalent cerium is in many aspects very similar to the coordination chemistry of tetravalent plutonium. The ionic radius of Ce^{4+} (0.94 Å) is within the experimental error identical to the ionic radius of Pu^{4+} (Shannon and Prewitt, 1969). Due to the similarity in the charge-to-ionic size ratio, the complex formation constants of tetravalent cerium are essentially the same as those of tetravalent plutonium. Complex formation causes for the two metal systems the same shift of the M^{4+}/M^{3+} redox potential. Cerium(IV) complexes are therefore good models for predicting the coordination chemistry

of plutonium(IV) (Gorden et al., 2003). Working with plutonium(IV) itself is difficult and expensive, because of the safety precautions that are necessary when handling this highly radioactive and chemotoxic material and because of the limited availability of plutonium in comparison with cerium. A good knowledge of the coordination chemistry of plutonium is however necessary to develop sequestering agents that are specific for the removal of plutonium(IV). Such sequestering agents are useful for environmental remediation and for chelation therapy (removal of plutonium from the human body after accidental uptake). The knowledge of plutonium chemistry is also of interest for the development of selective extraction agents. However, due to the very similar aqueous coordination chemistry of cerium(IV) and plutonium(IV) it is very difficult to separate cerium from plutonium. This is an important issue, because fission products in spent nuclear fuel rods contain often large quantities of rare earths. Pioneering work in the field of actinide specific sequestering agents has been done by Raymond and coworkers (Raymond and Smith, 1981; Raymond et al., 1984; Zhu et al., 1988; Gorden et al., 2003). An overview of ligands that form very stable complexes with cerium(IV) and that have been used as model compounds for plutonium(IV) is shown in chart 3.

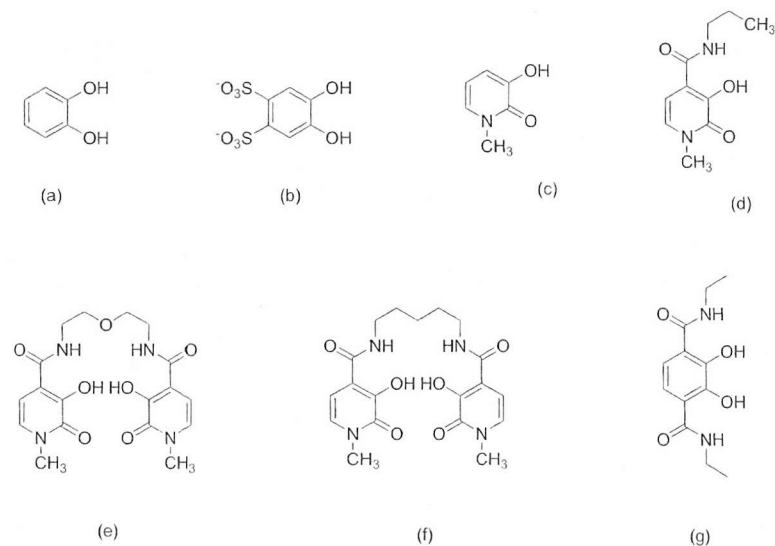


Chart 3. Ligands used for complex formation with cerium(IV) in model studies of plutonium(IV) coordination chemistry: (a) 1,2-dihydroxybenzene (catechol); (b) 3,5-disulfonate-1,2-dihydroxybenzene (triron); (c) 1-methyl-3-hydroxy-2(1H)-pyridinone (Me-3,2-HOPO); (d) PR-Me-3,2-HOPO; (e) 5LO-Me-3,2-HOPO; (f) 5LI-Me-3,2-HOPO (g) N,N' -diethyl-2,3-dihydroxyterephthalamide (H_2E7AM). The nomenclature of the HOPO ligands is that of Raymond and coworkers (Xu et al., 2000).

The first model compound studied was the cerium(IV) tetrakis(catecholate) complex, $\text{Na}_4[\text{Ce}(\text{O}_2\text{C}_6\text{H}_4)_4] \cdot 21\text{H}_2\text{O}$. A crystallographic study revealed that this diamagnetic bright red compound is indeed cerium(IV) tetrakis(catecholate), and not cerium(IV) tris(catecholate)-(semiquinone) complex (Sofen et al., 1978, 1979). The cerium(IV) ion is eight coordinate and the coordination polyhedron is very close to an ideal trigonal-faced dodecahedron. Electrochemical studies revealed that the formation constant of the cerium(IV) tetrakis(catecholate) complex is 10^{36} -fold larger than the formation constant of the corresponding cerium(III) complex! In general, catecholate and its derivatives form very stable complexes with metal ions in their high oxidation states, provided that the pH is high enough to fully deprotonate the ligand. Ligands such as catechol which form stable complexes with cerium(IV) lower the redox potential of the $\text{Ce}^{4+}/\text{Ce}^{3+}$ significantly. A model compound related to the cerium(IV) catecholate complex is the tetrakis(tironato)cerate(IV) complex (Haddad and Raymond, 1986). Tironate is 3,5-disulfonatecatecholate. In the crystal structure of $\text{Na}_{12}[\text{Ce}(\text{C}_6\text{H}_2\text{O}_2(\text{SO}_3)_2)_4] \cdot 9\text{H}_2\text{O} \cdot 6\text{C}_3\text{H}_7\text{NO}$, the coordination polyhedron of cerium(IV) is a highly distorted dodecahedron ($\text{C}_3\text{H}_7\text{NO}$ stands for dimethylformamide). The complex lacks any symmetry.

Several cerium(IV) complexes of various bidentate and tetradentate hydroxypyridinone (HOPO) complexes have been studied as model compounds for plutonium(IV) complexes (Xu et al., 2000). Bidentate HOPO monoanions are isoelectronic with catecholate dianions and they display a similar complex formation behavior towards cerium(IV) ions. However, HOPO ligands are more acidic and form stable complexes with cerium(IV) at lower pH values than catechol. The tetradentate ligands form more stable complexes than the corresponding bidentate ligands. New types of chelators for cerium(IV) and plutonium(IV) are the 2,3-dihydroxyterephthalamides (Gramer and Raymond, 2004; Xu et al., 2004). Some authors have made comparisons between the coordination chemistry and the redox behavior of cerium and berkelium (Lebedev et al., 1975; Milyukova et al., 1980; Yakovlev et al., 1982).

12. Conclusions and outlook

It is evident that cerium(IV) salts are very versatile reagents for a myriad of organic reactions. The unique reactivity is mainly based on the fact that Ce^{4+} is a strong one-electron oxidant and it is thus able to generate radicals and radical cations, promoting radical reactions. Some cerium(IV)-mediated organic reactions are difficult to achieve with other reagents, although manganese(III) can often replace cerium(IV) in oxidation reactions. Of special usefulness is the ability of cerium(IV) salts to initiate radical polymerization of vinylic monomers. This has been exploited in different applications related to the modification of biopolymers. A major disadvantage of cerium(IV) salts for use as a stoichiometric reagents in organic reactions is their high molecular weight. For instance, the molecular weight of ammonium hexanitratocerate(IV) is 548.23 g/mol. Moreover, since the $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox couple is a one-electron redox system, large amounts of cerium(IV) reagents are required to transform one mole of substrate into the desired product. There is thus a need to develop synthetic procedures that are based

on cheap, widely available low-molecular weight oxidants (air, molecular oxygen, hydrogen peroxide, *tert*-butylhydroperoxide, etc.) and that make use of catalytic amounts of cerium(IV) salts. The electrochemical regeneration of cerium(IV) offers interesting perspectives when stoichiometric amounts of cerium(IV) are still needed.

The dominance of ammonium hexanitratocerate(IV) among cerium(IV) reagent is evident. Although this reagent is a very useful one and gives access to synthetic transformations that cannot be made with other cerium(IV) compounds, it should be realized that this reagent has its limitations. For instance, unwanted side reactions may occur. It is surprising that all the other cerium(IV) salts remain underdeveloped. The exploration of the applicability of the whole variety of cerium(IV) salts to organic reactions remains a challenge, but very interesting results are to be expected. It is also desirable that further studies focus on reaction mechanisms and optimization of the experimental conditions, rather than on a simple screening of a large variety of substrates. A better understanding of the reasons why side reactions occur could lead to much higher yields. Because relatively few crystal structures of cerium(IV) compounds have been investigated, the coordination chemistry of cerium(IV) still offers a playground for coordination chemists and inorganic chemists.

This review shows that cerium(IV) salts can be used for applications other than reagents in organic synthesis. Whereas some applications like cerium(IV) salts as oxidizing agents in redox titrations (cerimetry) are one of the oldest applications of rare earths and are now of less importance, other applications still needs to be further developed. From an industrial point of view, cerium-mediated electrosynthesis of fine chemicals offers great opportunities. Closely related to this application is the treatment of industrial organic waste streams by electrochemically generated cerium(IV). The ability of cerium to decompose water into oxygen and hydrogen could solve partially the energy problem in the future. An artificial photosynthetic system based on the $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox couple provides a means for solar energy conversion. However, there is still a long way to go before the yields of the water splitting reaction will reach acceptable values.

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Chapter 230

SAMARIUM (II) BASED REDUCTANTS

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