

Parr bomb followed by Volhard titration; and the sulfur by Parr bomb, followed by gravimetric determination of BaSO₄.

Analytical Application. The quaternary salt employed was Hyamine 1622 (5), approximately 0.0055*M* solution. A typical standardization was performed as follows:

Dissolve 3.954 grams of potassium 2,4,5-trichlorobenzenesulfonate in water to 500 ml. of total solution. Titrate 5 ml. of this solution as detailed in the House and Darragh (3) modification of Epton's (2) procedure with 24.4 ml. of the quaternary solution.

Normality =

$$\frac{(\text{sample weight}) (1000)}{(\text{aliquot}) (\text{molecular weight})} = \frac{(\text{ml. Hyamine 1622})}{(24.4)}$$

$$\frac{(3.954) (1000)}{(100) (300) (24.4)} = 0.0054$$

DISCUSSION

The sulfonates were stable at least a year at room temperature, both in solid form and in water solution. The potassium salts were favored over sodium merely because the former were more fully described in the literature (4); as noted above, the former are less soluble in water.

The series of five sulfonates of ascending molecular weight was prepared to permit standardization at various desired points over the usual commercial range of water-soluble surfactants (3). In general agreement with others (1, 3), the present study shows the quaternary titration procedure to be inapplicable

to sulfonic acids of molecular weight about 250 and less.

ACKNOWLEDGMENT

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LITERATURE CITED

- (1) American Society for Testing Materials, Philadelphia, Pa., ASTM Standards, D 1681-59T, Pt. 10, p. 276, 1959.
- (2) Epton, S. R., *Trans. Faraday Soc.* **44**, 226 (1948).
- (3) House, R., Darragh, J. L., *ANAL. CHEM.* **26**, 1492 (1954).
- (4) Prager, B., et al., eds., "Beilsteins Handbuch der Organischen Chemie," IV ed., Vol. XI, Berlin, Springer, 1928.
- (5) Rohm and Haas Co., Philadelphia, Pa., *Tech. Bull. SAN-60*, 1954.

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A Classification Test for Alkyl Halides

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► Treatment of alkyl halides with sodium nitrite in a dimethylformamide solution containing urea yields the corresponding nitroparaffins of the primary and secondary compounds. After addition of aqueous sodium hydroxide and carbon tetrachloride, acid is added dropwise to produce the red nitrolic acid salt from the primary nitroalkane, a blue-green pseudonitrole from the secondary compound. The test distinguishes primary and secondary alkyl halides through octyl, and most cycloalkyl halides. It is not applicable to benzyl or allyl halides, cyclohexyl chloride, or most difunctional compounds. Sodium nitrite in dimethyl sulfoxide provides an even more sensitive test with some alkyl chlorides and many bromides and iodides. Unfortunately, an interfering color develops with tertiary bromides and iodides which makes the solution undesirable for general test purposes.

THE only tests included in the common organic qualitative analysis tests to classify alkyl halides are of limited utility. Alcoholic silver nitrate is primarily applicable only to chlorides and even then does not differentiate between primary and secondary chloroalkanes. The less common sodium iodide in acetone test gives a partial differentiation of primary, secondary, and tertiary alkyl bromides and chlorides but is useless with alkyl iodides.

Meyer, as a consequence of his re-

search on nitroles and pseudonitroles, proposed a sequence of reactions to classify alcohols (4). First, the alcohols were converted to the iodides using phosphorus and iodine. Next, the iodides were heated with silver nitrite to form the nitroparaffins. Finally, by nitrosation, the primary nitroalkanes were converted to reddish tan salts of nitrolic acids, the secondary nitroalkanes formed blue pseudonitroles, while the tertiary nitroalkanes were unchanged. This was called "the red, white, and blue test for alcohols." The simplicity of the nitrosation step has resulted in the continued use of this portion of the procedure as a classification test for nitroparaffins. The Meyer procedure has not been used as a classification test for alkyl halides in general because of the quantities of reagents needed and the limitation that only some of the more reactive halides, usually primary bromides or iodides (3), give satisfactory tests.

Kornblum (1) and his coworkers have recently reported that alkyl halides react with sodium nitrite in dimethylformamide or dimethyl sulfoxide solution to form nitroparaffins. In the present work, the procedure of Kornblum has been adapted together with the nitrosation reaction of Meyer to give a complete classification test for alkyl halides.

EXPERIMENTAL

Reagents. The compounds used in testing these procedures were gener-

ally samples of commercial products or the more highly purified compounds sold by chemical supply houses. A few unusual halides were available from other research in progress in the laboratory. No attempt was made to purify any of these samples further.

Special Solution. Dissolve 15 grams of sodium nitrite and 25 grams of urea in 500 ml. of dimethylformamide. Kornblum and his coworkers, in developing the procedure for preparation of nitroparaffins, inhibited a side reaction of oxidation by adding resorcinol or catechol (1). These compounds could not be used in the present work for they give a red color interference in the final step of acidification.

Procedure Using Dimethylformamide. Place 0.5 ml. of the alkyl halide and 1.5 ml. of a solution of sodium nitrite in dimethylformamide in a test tube. Allow alkyl iodide mixtures to stand for 20 minutes; place bromide and chloride mixtures in boiling water for 15 minutes. If the alkyl chloride has a boiling point below 100° C., it will distill and give no test unless a reflux condenser is attached to the test tube.

Next, add 1 ml. of 10% aqueous NaNO₂ and 2 ml. of 10% NaOH and mix well. Add 1 ml. of CCl₄ and then 1.5 ml. of 10% sulfuric acid drop by drop with shaking. If the aqueous solution turns tan, the halide is a primary type. The reaction mixture sometimes is brownish before adding sulfuric acid. To be a positive test, the color must become more intense on adding acid. (If there is still doubt regarding the tan color, confirmation can be obtained by adding acetic acid until the solution is acid. In a proper

primary halide test, the tan color should disappear or decrease markedly in acid solution but be regenerated when alkali is added.)

Add up to 3 ml. of 10% acetic acid drop by drop with shaking. Cease the addition if the carbon tetrachloride layer turns blue. If the CCl_4 layer develops a blue or blue-green color, the halide is a secondary type. If no color has developed, the halide is tertiary. (It is possible to use sulfuric acid only but acetic acid gives a buffered solution which does not become sufficiently acidic to yield free iodine from iodides.)

RESULTS AND DISCUSSION

The following discussion is concerned exclusively with the dimethylformamide test solution except when dimethylsulfoxide is specifically mentioned.

Primary Alkyl Halides. Proper tests were obtained with the following:

Chlorides	Bromides	Iodides
1-Chloropropane	Bromoethane	Iodomethane
1-Chlorobutane	1-Bromopropane	Iodoethane
1-Chloropentane	1-Bromobutane	1-Iodopropane
1-Chlorohexane	1-Bromo-2-methylpropane	1-Iodobutane
1-Chloroheptane	1-Bromopentane	1-Iodopentane
1-Chloro-octane	1-Bromo-3-methylbutane	1-Iodohexane
	1-Bromohexane	1-Iodoheptane
	1-Bromoheptane	1-Iodo-octane
	1-Bromo-octane	

No tests were obtained with 1-chlorodecane, 1-chlorooctadecane, 1-bromodecane, or 1-iododecane.

The approximate yields of nitroalkanes produced from representative alkyl halides were determined as follows: Standard solutions of 1-nitropropane in carbon tetrachloride were subjected to the entire test procedure. The colors obtained from these standards were compared with the tests from alkyl halides. The assumptions were necessarily made that the nitrosation step proceeded in identical yield with all nitroalkanes and that the resultant sodium salts of nitrolic acids were all of the same shade and intensity of color. These are gross assumptions and the

Table I. Typical Primary Halide Tests

Halide	Mmoles/ 0.5 Ml. of Alkyl Halide	Mmoles of NO_2 Compound	Yield, %
$n\text{-C}_4\text{H}_9\text{Cl}$	4.9	0.50	10
$n\text{-C}_8\text{H}_{17}\text{Cl}$	3.0	0.15	5
$n\text{-C}_{10}\text{H}_{21}\text{Cl}$	2.5	No color	Low
$n\text{-C}_3\text{H}_7\text{Br}$	5.5	0.50	9
$n\text{-C}_7\text{H}_{15}\text{Br}$	3.2	0.20	6
$n\text{-C}_9\text{H}_{17}\text{Br}$	2.9	0.12	4
$n\text{-C}_{10}\text{H}_{21}\text{Br}$	2.4	No color	Low
$n\text{-C}_4\text{H}_9\text{I}$	4.4	0.15	3.9
$n\text{-C}_6\text{H}_{13}\text{I}$	3.4	0.10	3
$n\text{-C}_7\text{H}_{15}\text{I}$	3.0	0.05	1.5
$n\text{-C}_9\text{H}_{17}\text{I}$	2.8	0.07	1.5

figures listed in Table I are of limited accuracy. Since the reactivity of molecules generally decreases with increasing molecular weight, these are probably minimum values.

To those unfamiliar with the test, the limit of detection is probably 0.10 mmole of nitroalkane. To one accustomed to the procedure, a quantity of 0.05 mmole can be discerned.

Secondary Alkyl Halides. Proper tests were obtained with the following:

Chlorides	Bromides	Iodides
2-Chloropropane	2-Bromopropane	2-Iodopropane
2-Chlorobutane	2-Bromobutane	2-Iodobutane
2-Chloropentane	2-Bromopentane	2-Iodo-octane
2-Chloroheptane	2-Bromooctane	
3-Chloroheptane		
4-Chloroheptane		
2-Chlorooctane		

No secondary alkyl halides of higher molecular weight are commercially

Mixture of Halides. The test has been applied to an equimolecular mixture of 1-bromopentane and 2-bromopentane. Both tests were obtained although weaker than usual because of the dilution of the components on mixing.

Cycloalkyl Halides. Satisfactory tests were obtained with cycloalkyl bromide and iodides as shown in Table III. However, it was necessary to use heat in the iodo-cyclohexane

test to obtain a reasonable conversion to the nitro derivative. Yields were again estimated using 2-nitropropane as a standard.

Kornblum (1) has reported that cyclohexyl halides do not give nitro-cycloalkanes by this procedure. Obviously the nitro compound is obtained when cyclohexyl bromide or iodide is used and although the yields are too low for preparative use, they are adequate for purposes of this test. From Kornblum's work (1), it may be predicted that cycloheptyl bromide and iodide will also give the test properly.

Table II. Typical Secondary Halide Tests

Halide	Mmoles/ 0.5 of Ml. of Alkyl Halide	Mmoles of NO_2 Com- pound	Yield, %
2-Chloro- propane	5.5	0.15	2.5
2-Chloro- octane	3.0	0.05	1.5
2-Bromo- propane	5.3	0.50	10
2-Bromo- octane	2.8	0.15	5
2-Iodopro- pane	5.0	0.30	6
2-Iodo-octane	2.7	0.05	2

Table III. Typical Cycloalkyl Halide Tests

Halide	Mmoles/0.5 Ml. of Cycloalkyl Halide	Mmoles of NO_2 Compound	Yield, %
Chlorocyclopentane	4.8	0.3	6
Chlorocyclohexane	4.1	No color	..
Bromocyclopentane	4.6	0.50	10
Bromocyclohexane	4.1	0.15	4
Iodocyclopentane	4.5	0.15	3
Iodocyclohexane	3.8	0.15	3

Benzyl and Allyl Halides. Benzyl and allyl halides give an interfering color which obscures any possible test. This is in agreement with Kornblum's investigations in which he found that only at low temperatures were the nitro compounds formed.

Dihalides. No test was obtained with dichloromethane, ethylene dihalides, or 1,3-dichloropropane. The only other commercially available higher dihalide, 1,5-diiodopentane, did give a weak but definite test (0.15 mmole of nitro compound obtained, 5% yield).

Difunctional Compounds. A positive test was obtained with only one halide derivative containing a second functional group, 3-chloro-1-propanol. Either no color or interfering colors were obtained with the following:

2-Chloroethanol
2,3-Dichloro-1-propanol
1-Chloro-2-propanone
Chloroacetic anhydride
Chloroacetic acid
2-Chloroethyl acetate
Ethyl 3-chloropropionate
2-Chloroacetamide
4-Chlorobutyronitrile
Epichlorohydrin
Bis(2-chloroethyl) ether

Procedure Using Dimethyl Sulfoxide. Sodium nitrite is more soluble in dimethyl sulfoxide than in dimethyl-

formamide and Kornblum has recommended (2) this solvent for formation of the nitroalkanes. Essentially, the procedure previously described was used except that a 10% solution of sodium nitrite in dimethyl sulfoxide was substituted for the dimethylformamide reagent.

Positive tests were obtained with all primary chloroalkanes through 1-chlorodecane. However, most of the red color develops on adding alkali to the original reaction mixture. Dropwise addition of sulfuric acid gives only a slight intensification of the color. The red color disappears in acid solution and is regenerated in basic media.

Secondary chloroalkanes generally give a deeper color using the dimethyl sulfoxide reagent in comparison to the dimethylformamide. An exception is chlorocyclopentane which gives only a faint test using the sulfoxide solution.

2-Chloro-2-methylpropane gives a negative test using the sulfoxide procedure. 2-Bromo-2-methylpropane and 2-iodo-2-methylpropane give a yellowish tan color when the sulfuric acid addition is made. This conflicts with the test for a primary halide.

CONCLUSIONS

This test should be applied only to

those compounds which give a positive test with alcoholic silver nitrate. With such compounds proper classification will be obtained with simple alkyl and cycloalkyl halides within the limits specified.

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LITERATURE CITED

- (1) Kornblum, N., Larson, H. O., Blackwood, R. K., Mooberry, D. D., Oliveto, E. P., Graham, G. E., *J. Am. Chem. Soc.* **78**, 1497 (1956).
- (2) Kornblum, N., Powers, J. W., *J. Org. Chem.* **22**, 455 (1957).
- (3) Kornblum, N., Taub, B., Ungnade, H. E., *J. Am. Chem. Soc.* **76**, 3209 (1954).
- (4) Meyer, V., Locher, J., *Ber.* **7**, 1510 (1874).

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Differential Colorimetric Determination of Nitrite and Nitrate Ions

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► Nitrite and nitrate ion in the ranges of 0 to 1.5 and 0 to 2.0 p.p.m., respectively, are determined colorimetrically by the formation of a red dye through the diazotization-coupling reaction. (4-Aminophenyl)trimethylammonium ion is used as the diazotizable amine and *N,N*-dimethyl-1-naphthylamine is used as the coupling agent. Nitrite ion is determined directly in acid solution. Nitrate ion is first reduced by zinc in ammoniacal solution of pH 10.8 in the presence of manganous hydroxide, and then determined by the same reaction as the nitrite ion. Nitrite ion is eliminated in the nitrate determination by exchanging the diazonium cation formed onto a nuclear sulfonic ion exchange resin (potassium form) prior to the reduction of nitrate ion. Removal of residual chlorine, which interferes in the nitrate determination, is accomplished through reaction with the same ion exchange resin, presumably through

chlorination of the resin. Residual chlorine and nitrite ion are not found together. Chloride, sulfate, and other commonly occurring substances do not interfere.

NITRITE ION can be determined colorimetrically by its well known selective diazotization-coupling reaction to form an azo dye (1, 3). Bray and co-workers (6) used this reaction for the determination of nitrate ion in soils after reduction to nitrite ion by zinc in acid solution in the presence of manganous ion. Middleton (5) has shown that the reduction is quantitative only in ammoniacal solution of pH 10.2 to 11.2 and at lower than room temperatures.

Methods used most often for the determination of nitrate ion in water are the phenoldisulfonic acid (1) and the brucine procedures (2). The phenoldisulfonic acid method is time consuming and subject to interference by chloride ion. The brucine method can

be used to determine nitrate ion if nitrite ion is absent; otherwise, nitrate is determined by difference. Both procedures produce yellow solutions which are difficult to compare visually.

The method described here can be used to determine nitrate and nitrite ions separately in the presence of each other. Nitrite ion is determined by the diazotization of (4-aminophenyl)trimethylammonium ion and subsequent coupling with *N,N*-dimethyl-1-naphthylamine. A bright red dye is produced which is excellent for visual or spectrophotometric purposes. Nitrate ion is determined by the same reaction following quantitative reduction to nitrite ion. When nitrate ion is determined separately in the presence of nitrite ion, the latter is first removed by diazotization of the (4-aminophenyl)trimethylammonium ion and exchange of the resulting dipositive cation onto a nuclear sulfonic ion exchange resin. The resin also serves to remove residual chlorine prior