# Reactions of acetaldehyde in the preparation of pentaerythritol

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On the basis of experimental material and theoretical mechanism of aldol condensation two systems of rate equations describing the first step of the reaction of formaldehyde with acetaldehyde giving rise to pentaerythritol have been made up. The first model is based on the "classical" assumption of constant concentration of carbanion while the second one is based on the assumption that the carbanion behaves as a nonanalyzed intermediate. Both procedures are almost equally precise for expressing the experimental material, but the second one immediately supplies the values of rate constants and, for this reason, it is more convenient for the study of mechanism. The relative values of pseudoconstants and constants obtained by either procedure are in good agreement with theoretical ideas concerning the relative rates of elementary steps in aldol condensation. Experimental data, rate relations, and the values of rate constants of the reaction of acetaldehyde yielding acetaldol have been also obtained in the scope of this work.

На основе экспериментальных данных и теоретического механизма альдольной конденсации были составлены две системы уравнений для скоростей, характеризующих первую стадию реакции формальдегида с ацетальдегидом, ведущей к образованию пентаэритрита. Первая модель исходила из »классического« предположения о постоянной концентрации карбаниона, вторая из предположения, что карбанион является промежуточным соединением. Оба метода приблизительно одинаково точно интерпретируют экспериментальные данные, однако второй прямо дает величины констант скоростей и, поэтому, более удобен для изучения механизма. Относительные значения псевдоконстант и констант, вычисленные этими двумя методами хорошо согласуются с теоретическими представлениями об относительных скоростях элементарных стадий альдольной конденсации. В ходе работы получены также экспериментальные данные, соотношения скоростей и величины констант скоростей для реакции превращения ацетальдегида в ацетальдоль.

The reactions of aldehydes in alkaline aqueous medium belong among fundamental procedures in organic chemistry and are widely used in industry. The

production of pentaerythritol is based on the reaction between formaldehyde and acetaldehyde in aqueous solution in the presence of a base according to the following summary equation

$$4HCHO + CH_3CHO + OH^- \rightarrow C(CH_2OH)_4 + HCOO^- \tag{1}$$

Eqn (1) is a rough description of gradual aldol condensation of three molecules of formaldehyde on the $\alpha$-carbon of acetaldehyde and final Cannizzaro reaction of the arising pentaerythrose with formaldehyde.

Besides this main reaction sequence other undesirable side reactions take place in this reaction medium. Formaldehyde turns into formoses, acetaldehyde into acetaldol and the present aldehydes react according to Cannizzaro mechanism. This reaction system is extraordinarily complicated from the view-point of mechanism and kinetics and has not been quantitatively satisfactorily described until now. The basic analysis and resulting mathematical model of the system have been presented in our preceding publication [1]. In this paper, we publish the quantitative results obtained by investigating the reactions of acetaldehyde.

### Analysis of the problem

The first step of the reactions giving rise to pentaerythritol is the aldol condensation of formaldehyde with acetaldehyde yielding $\beta$-hydroxypropionaldehyde (hydracrolein)

$$HCHO + CH_3CHO \rightarrow HOCH_2-CH_2-CHO \tag{2}$$
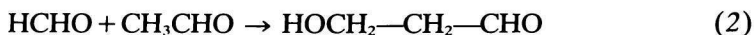
This reaction is made possible by the existence of the "acid" hydrogen on the $\alpha$-carbon of acetaldehyde and its mechanism belongs among the fundamental ones in organic chemistry. In general, it is assumed [2, 3] that the first step is the reaction of acetaldehyde with the present base giving carbanion which subsequently reacts with formaldehyde.

If we write A for acetaldehyde, $A^-$ for carbanion, B for base (usually $OH^-$), C for the second aldehyde (in our case formaldehyde), and $BH^+$ for the neutralized base (for instance water in the case of $OH^-$), the basic mechanism may be expressed as follows

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A^- + BH^+ \tag{3}$$

$$A^- + C \overset{k_3}{\rightarrow} A^-C \tag{4}$$

$$A^-C + H_2O \rightarrow \beta\text{-hydroxypropionaldehyde} + B \tag{5}$$

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Supposing that reaction (5) is very fast, the following rate equations can be derived for acetaldehyde, formaldehyde, and carbanion
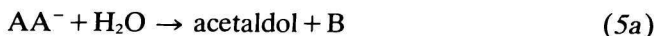
$$\frac{d[A]}{dt} = -k_1[A][B] + k_2[A^-][BH^+] \tag{6}$$

$$\frac{d[A^-]}{dt} = k_1[A][B] - k_2[A^-][BH^+] - k_3[A^-][C] \tag{7}$$

$$\frac{d[C]}{dt} = -k_3[A^-][C] \tag{8}$$

On the basis of this mechanism *Frost* and *Pearson* [2] derived the rate equation for the product of reaction (4) by using the assumption of a dynamic equilibrium concentration of carbanion

$$\frac{d[A^-C]}{dt} = \frac{k_1 k_3[A][B][C]}{k_3[C] + k_2[BH^+]} \tag{9}$$

However, not only formaldehyde but also acetaldehyde is available for reaction (4) in the preparation of pentaerythritol owing to which the undesirable side reaction proceeds parallelly and supplies the intermediate yielding acetaldol

$$A + A^- \xrightarrow{k_4} AA^- \tag{4a}$$

$$AA^- + H_2O \rightarrow \text{acetaldol} + B \tag{5a}$$

For this reason, the rate equations for acetaldehyde and carbanion are to be modified into the form

$$\frac{d[A]}{dt} = -k_1[A][B] + k_2[A^-][BH^+] - k_4[A][A^-] \tag{6a}$$

$$\frac{d[A^-]}{dt} = k_1[A][B] - k_2[A^-][BH^+] - k_3[A^-][C] - k_4[A][A^-] \tag{7a}$$

If we assume again a fast progress of reaction (5a) and dynamic equilibrium for the concentration of carbanion, we may rearrange and the following rate equations are obtained for acetaldehyde and formaldehyde

$$\frac{d[A]}{dt} = -k_1[A][B] \frac{k_3'[C] + 2k_4'[A]}{1 + k_3'[C] + k_4'[A]} \tag{10}$$

$$\frac{d[C]}{dt} = \frac{-k_1 k_3'[A][B][C]}{1 + k_3'[C] + k_4'[A]} \tag{11}$$

where

$$k_3' = \frac{k_3}{k_2[H_2O]} \qquad k_4' = \frac{k_4}{k_2[H_2O]} \qquad (12ab)$$

If we apply this mechanism and the above-mentioned assumptions to the reaction of acetaldehyde in the absence of other aldehyde giving rise to acetaldol, we can analogously obtain

$$\frac{d[A]}{dt} = \frac{-2k_1k_3'[A]^2[B]}{1 + k_4'[A]} \qquad (13)$$

The quantitative study of this complicated reaction system is not closed for the time being, nor do we know satisfactorily precise values of rate constants which could be used, *e.g.* for the mathematical model of a reactor for the production of pentaerythritol. The literature data concerning these problems are rather incoherent.

*Bell* and *McTigue* [4] investigated the kinetics of aldol condensation of acetaldehyde and formaldehyde in the presence of sodium hydroxide. They used a combination of dilatometry and spectrophotometry for investigating the progress of this reaction at 25 °C, but they did not succeed in transforming the results from volumetric units in concentration units. Later, *McTigue et al.* [5] reported in a short communication that they gave more precision to the preceding measurements by using the data obtained by measuring absorption in ultraviolet region. The aldolization of acetaldehyde itself was studied, only dilatometrically again, by *Bell* [6] and the results of his measurements are critically reviewed in monograph [2]. Nevertheless, they are not suited to direct application in rate equations. The results of a more thorough study based on direct kinetic measurements in the presence of NaOH at temperatures ranging from 0 °C to 25 °C were published by *Ogata et al.* [7]. They evaluated the decrease in total amount of aldehydes by the use of the sulfite method and calculated the instantaneous concentration of acetaldehyde on the basis of considerably simplified conditions so that their conclusions have a limited validity. *Vik* [8] was the first to analyze the acetaldehyde content by gas chromatography and chose the working conditions so that the condensation of acetaldehyde by itself was minimum. He used NaOH as a base, too.

The initial concentration of acetaldehyde in the measured mixtures was very low (0.001 mol dm$^{-3}$) while formaldehyde was present in great excess (0.1—4 mol dm$^{-3}$). For this reason, the rate equation could be simplified in the form

$$\frac{-d[A]}{dt} = k'[A][NaOH] \qquad (14)$$

As for the rate constants, only the values of $k'$[NaOH] are given as functions of the initial concentration of base and formaldehyde.

The technological aspects of the reaction of acetaldehyde giving rise to acetaldol are the topic of many publications, *e.g.* [9—14] which are, however, unfit for description of the process from the kinetic point of view.

The use of sodium hydroxide makes difficulties in evaluation of the relations obtained experimentally. The titration enables us to determine the total concentration of base in the reaction medium but not its effective concentration. The influence of formaldehyde and acetaldehyde functioning as weak acid cannot be revealed in this way. In the course of measurement, it varies with the change in their concentration, which also affects the value of the concentration term of base in the rate equation.

Calcium hydroxide does not have this drawback. It is added into the reaction mixture in the amount exceeding considerably the quantity necessary for obtaining its saturated solution. The rest remains in the form of suspension and the consumed quantity is continuously replaced by dissolution of other portions. Thus, if we use calcium hydroxide, we may consider, with certain approximation, the concentration of base to be constant and equal to the concentration of the saturated solution.

The real amount of $Ca(OH)_2$ dissolved in aqueous solution of aldehydes is much greater than the corresponding value of solubility in water. We used this fact for estimating the concentration of carbanion and for estimating the value of $k_2$ which cannot be determined from eqns (9) and (12).

## Experimental

### Chemicals

Calcium hydroxide (Lachema, Brno); $Ca(OH)_2$ — 96.3 mass % (acidometrically), calcium — 54.63 mass % (complexometrically), traces of silicon, magnesium, and copper (by emission spectroscopy).

Acetaldehyde (import from the USSR); content of acetaldehyde over 99.5 mass %.

Technical aqueous formaldehyde (Chemko, Strážske); content of formaldehyde 400 mg cm$^{-3}$, methanol 1.5 mass %.

### Working procedure

The reaction took place in a three-litre flask equipped with mechanical stirrer, thermometer, and outlet for sampling. The required temperature was maintained by external cooling or in the advanced stage of reaction by heating with a water bath. The calculated amount of diluting water was added into the lime milk prepared and analyzed beforehand and the suspension was under stirring heated to a temperature by a few degrees (3—5 °C) lower than the temperature required for the main course of reaction. Subsequently, the necessary amount of analyzed ca. 50 % aqueous solution of acetaldehyde was added. The

temperature rapidly rose under intensive stirring to the required value (in less than 1 min). The samples taken in regular time intervals were neutralized with formic acid and the content of acetaldehyde was determined. A constant quantity of formic acid was ready in the sampling vessel, owing to which the neutralization proceeded immediately. The time necessary for sampling was thus limited to pipetting a sample into the sampling vessel, which did not exceed 15 s. The content of calcium hydroxide in the samples taken parallelly was determined by titration.

The reaction of formaldehyde with acetaldehyde in the presence of $Ca(OH)_2$ was investigated by using the same procedure, but besides lime milk and diluting water, the calculated amount of technical aqueous formaldehyde was put into the flask and the solution was also quickly warmed to a temperature by a few degrees lower than the required value. Moreover, the content of formaldehyde in individual samples was determined colorimetrically.

The solubility of calcium hydroxide in aqueous solutions of acetaldehyde was measured in a 100 cm³ flask which was thermostated at 9 °C and equipped with a mechanical stirrer. The suspension of $Ca(OH)_2$ was kept in contact with the solution of acetaldehyde of required concentration for 30 min. At the beginning and end of measurement, the content of $Ca(OH)_2$ in filtrate was determined acidimetrically, after the solid phase was quickly filtered off. In addition, the content of $Ca^{2+}$ was determined complexometrically.

In all cases, the revolutions of the stirrer were held constant and the shape of this stirrer was also constant so that the hydrodynamic conditions of individual measurements were equal. The reproducibility of the measurements of aldehyde concentration was found to be on the level of $\pm$ 3.6 % (relatively) for repeated measurements.

## Analytical methods

The content of $Ca(OH)_2$ was determined potentiometrically after neutralization with excess 0.1 M-HCl by using reverse titration with 0.1 M-NaOH.

The content of calcium was determined complexometrically by means of Complexon III.

Acetaldehyde was determined with a gas chromatograph Mikrochrom 04 (made in Research Institute of Petrochemistry, Nováky) packed with Porapak Q and equipped with a flame ionization detector by using acetone as internal standard [15]. The accuracy of analysis was 1.5—2 relative %.

Formaldehyde was determined colorimetrically by measuring the absorbance at 500 nm with a colorimeter Spekol [15] after preceding reaction with phloroglucinol. The accuracy of analysis was 0.5—1.0 relative %.

## Results

### Condensation of acetaldehyde itself

The results of the measurement of acetaldehyde concentration as a function of time are given in Table 1. The first three measurements were performed at 40 °C whereas the last one

*Table 1*

Variation of acetaldehyde concentration (mol kg$^{-1}$) with time for the condensation of acetaldehyde itself in the presence of Ca(OH)$_2$ (0.444 mol kg$^{-1}$ of reaction mixture)

| t/min | Experiment | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| 0 | 0.741 | 0.370 | 0.185 | 0.743 |
| 1 | — | — | — | — |
| 2 | — | — | 0.127 | — |
| 3 | 0.179 | 0.153 | 0.083 | 0.463 |
| 4 | 0.133 | 0.099 | — | 0.448 |
| 5 | 0.096 | — | 0.071 | 0.381 |
| 6 | — | 0.071 | — | — |
| 7 | 0.093 | — | 0.061 | 0.335 |
| 8 | — | 0.049 | — | — |
| 9 | 0.018 | — | 0.050 | 0.316 |
| 10 | — | 0.038 | — | — |
| 11 | 0.016 | — | — | — |
| 12 | — | 0.032 | — | — |
| 13 | 0.004 | — | — | — |
| 16 | — | — | 0.036 | 0.241 |
| 17 | — | 0.023 | — | — |
| 18 | 0.003 | — | — | — |
| 21 | — | — | 0.028 | 0.187 |
| 26 | — | — | 0.025 | 0.176 |
| 27 | — | 0.017 | — | — |
| 31 | — | — | 0.021 | 0.131 |

No. *1—3* at 40 °C, No. *4* at 20 °C.

was carried out at 20 °C. The initial concentration of Ca(OH)$_2$ was equal in all cases, its value being 0.444 mol kg$^{-1}$ of reaction mixture.

The solubility of Ca(OH)$_2$ in aqueous solutions of acetaldehyde was determined in a short series of measurements at 9 °C. The low temperature was chosen in order to prevent a significant condensation of acetaldehyde. The results are listed in Table 2.

## Condensation of acetaldehyde with formaldehyde

This subject matter was studied in much more detail. The basic experimental program had the form of centrally planned experiment [16, 17] involving three independent variables, *i.e.* initial mole ratio formaldehyde/acetaldehyde, initial mole ratio Ca(OH)$_2$/acetaldehyde, and initial concentration of aldehydes in the reaction mixture.

Solubility of $Ca(OH)_2$ (g $dm^{-3}$) in aqueous solutions of acetaldehyde at 9 °C

| No. | Solution $c[CH_3CHO]$ | 0 min | | 30 min | |
|-----|-----------------------|-------|---|--------|---|
| | mol $dm^{-3}$ | $Ca(OH)_2$ | $Ca^{2+}$ | $Ca(OH)_2$ | $Ca^{2+}$ |
| 1 | 0.0 | 1.432 | 0.804 | not measured | |
| 2 | 0.5 | not measured | | 2.440 | 1.483 |
| 3 | 1.0 | 3.150 | 1.760 | 3.240 | 1.980 |
| 4 | 2.0 | 5.403 | 3.041 | 5.620 | 3.213 |

The data about input conditions of individual measurements are given in Table 3 and some time dependences of formaldehyde and acetaldehyde concentration are presented in Table 4. All measurements were carried out at 40 °C.

Table 3

Initial conditions for investigation of the condensation of formaldehyde with acetaldehyde at 40 °C

| No. | $\dfrac{c[HCHO]}{mol\ dm^{-3}}$ | $\dfrac{c[CH_3CHO]}{mol\ dm^{-3}}$ | $\dfrac{c[Ca(OH)_2]}{mol\ dm^{-3}}$ |
|-----|------|------|------|
| 1 | 2.215 | 0.481 | 0.289 |
| 2 | 2.687 | 0.146 | 0.088 |
| 3 | 2.294 | 0.499 | 0.898 |
| 4 | 2.714 | 0.147 | 0.265 |
| 5 | 3.610 | 0.785 | 0.471 |
| 6 | 4.322 | 0.235 | 0.141 |
| 7 | 3.625 | 0.824 | 1.483 |
| 8 | 4.376 | 0.238 | 0.428 |
| 9 | 2.687 | 0.861 | 1.033 |
| 10 | 3.538 | 0.178 | 0.214 |
| 11 | 3.356 | 0.292 | 0.137 |
| 12 | 3.431 | 0.298 | 0.576 |
| 13 | 2.424 | 0.211 | 0.253 |
| 14 | 4.387 | 0.382 | 0.458 |
| 15 | 3.389 | 0.295 | 0.354 |

## Discussion

In calculating the optimum values of rate constants, we proceeded as follows. First of all, we calculated the rate constants corresponding to the condensation of acetaldehyde itself from experimental results. Then we completed the missing

*Table 4*

Typical concentration course of formaldehyde and acetaldehyde at 40 °C ($c$/mol dm$^{-3}$)

| $t$/min | Experiment | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 2 | | 7 | | 9 | | 12 | | 13 | |
| | HCHO | CH$_3$CHO | HCHO | CH$_3$CHO | HCHO | CH$_3$CHO | HCHO | CH$_3$CHO | HCHO | CH$_3$CHO |
| 0 | 2.687 | 0.146 | 3.625 | 0.824 | 2.687 | 0.861 | 3.431 | 0.298 | 2.424 | 0.211 |
| 1 | 2.397 | 0.046 | — | 0.275 | 1.593 | 0.199 | 2.631 | 0.043 | 2.029 | 0.037 |
| 2 | 2.226 | 0.020 | 2.520 | 0.094 | 1.176 | 0.132 | 2.413 | 0.028 | 1.898 | 0.017 |
| 3 | 2.171 | 0.012 | — | 0.058 | 0.968 | 0.056 | 2.367 | 0.022 | 1.788 | 0.013 |
| 4 | — | — | 1.904 | 0.032 | — | — | — | — | — | — |
| 5 | 2.170 | 0.007 | — | 0.028 | 0.427 | 0.028 | 2.181 | 0.013 | 1.638 | 0.007 |
| 6 | — | — | 1.772 | 0.022 | — | — | — | — | — | — |
| 7 | 2.131 | 0.004 | — | — | — | — | — | 0.012 | — | — |
| 8 | — | — | 1.278 | 0.019 | — | — | — | — | — | — |
| 10 | — | — | 1.126 | 0.017 | — | — | — | — | — | — |
| 11 | — | — | — | — | 0.333 | 0.018 | — | — | — | — |

values of rate constants from the experimental results relative to the reaction of acetaldehyde with formaldehyde.

We processed two variants of calculation. In the first one, we chose the "classical" approach and assumed an equilibrium, though unknown, concentration of carbanion $A^-$ and the values of rate constants were calculated from eqns $(10-13)$.

However, this procedure is not fully justified. Carbanion $A^-$ behaves in the reaction sequence as a typical intermediate and its concentration might be constant in a longer time interval only in uncommon cases.

As for the second variant, we calculated the optimum values of rate constants directly from eqns $(6a)$, $(7a)$, and $(8)$ and used eqns $(6a)$ and $(15)$ for the evaluation of the condensation of acetaldehyde itself

$$\frac{d[A^-]}{dt} = k_1[A][B] - k_2[A^-][BH^+] - k_4[A][A^-] \qquad (15)$$

Of course, the calculated concentration function $[A^-] = f(t)$ cannot be confirmed experimentally. However, we limited the calculation of the optimum values of constants within the region where the sum of the calculated concentration of acetaldehyde and its carbanion is smaller or equal to the initial concentration of acetaldehyde determined experimentally. For this balance limitation, the calculation is real though it is without any analytical control of the course of $[A^-] = f(t)$.

The calculation procedure was as follows:

Variant 1

Eqn $(13)$ corresponding to the condensation of acetaldehyde itself was analytically integrated (on the assumption of a constant concentration of the hydroxyl ions) to obtain

$$\frac{1}{2k_1k_4'[OH^-]}\left(\frac{1}{a} - \frac{1}{a_0}\right) + \frac{1}{2k_1[OH^-]} \ln \frac{a_0}{a} = t \qquad (16)$$

where $a$ is the instantaneous concentration of acetaldehyde and $a_0$ is its initial concentration.

The experimental material presented in Table 1 was processed by means of eqn $(16)$ and linear regression and the optimum values of both coefficients were thus calculated. The sum of squared deviations of the calculated values of $a$ from the measured values is used as an object function. The known solubility of $Ca(OH)_2$ in water at 20 and 40 °C [18] was employed for determining the following optimum values

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| | $\dfrac{k_1[\text{OH}^-]}{\text{min}^{-1}}$ | $\dfrac{k_1}{\text{dm}^3\,\text{mol}^{-1}\,\text{min}^{-1}}$ | $\dfrac{k_4'}{\text{dm}^3\,\text{mol}^{-1}}$ |
|---|---|---|---|
| at 40 °C | 1.6701 | 43.879 | 0.5411 |
| at 20 °C | 0.6472 | 14.531 | 0.1155 |

The values of $k_4$ and $k_2$ cannot be calculated by this procedure. However, we obtained a good quantitative estimate by expressing the concentration of $A^-$ on the basis of the measured increased solubility of calcium hydroxide in acetaldehyde solutions. We assumed that the dissolved calcium hydroxide exceeding the value of the saturated aqueous solution reacted with acetaldehyde according to eqn (3). Then we could directly calculate the values of $k_2$ and $k_4$ from eqns (12b) and (17)

$$[\text{A}^-] = \frac{k_1[\text{A}][\text{OH}^-]}{k_2[\text{H}_2\text{O}] + k_4[\text{A}]} \qquad (17)$$

The result presented in Table 5 is only of orientating value because we coupled the solubility measurements of lime at 9 °C with the results of calculation for 40 °C. Notwithstanding, it is in good agreement with the theoretical ideas concerning the relative rates of individual simultaneous reactions. It appears that the most rapid reaction is the formation of carbanion from acetaldehyde while the inverse reaction is slower by two decimal orders and reaction (4a) is slower than the formation of carbanion.

After inserting the calculated values of $k_1[\text{OH}^-]$ and $k_4'$ into eqns (10) and (11), we calculated the optimum value of $k_3'$ by combining numerical integration with simple search procedure. The sum of squared deviations between the calculated and experimentally determined concentrations of acetaldehyde and formaldehyde in corresponding time moments was taken as optimality criterion. By repeating the calculation for different values of $k_3'$ we obtained the relationship SSD = f($k_3'$). We determined the optimum value of $k_3'$ from the minimum value of the sum of squared deviations by using graphical representation of the above-mentioned relationship. The optimum value of rate constants (more exactly pseudoconstants because of eqns (12a) and (12b) as well as the sum of squared deviations are given in Table 6.

Variant 2

The calculation according to the second variant, in which carbanion is regarded as an analytically noncontrolled intermediate, is more intricate because eqns (6a) and (15) or (6a), (7a), and (8) cannot be easily integrated in analytical form. Therefore we developed a procedure joining numerical integration with nonlinear

*Table 5*

Calculated concentration of the enolized acetaldehyde and the values of $k_2$ and $k_4$ at 40 °C

| Solution $c[CH_3CHO]$ mol dm$^{-3}$ | $c[Ca(OH)_2]$ mol dm$^{-3}$ after 30 min | $\dfrac{\Delta C}{\text{mol dm}^{-3}}$ | $\dfrac{[A^-]}{\text{mol dm}^{-3}}$ | $\dfrac{[A^-]}{[A]_0}$ 100 % | $\dfrac{k_2}{\text{min}^{-1}}$ | $\dfrac{k_4}{\text{min}^{-1}}$ |
|---|---|---|---|---|---|---|
| 0.0 | 0.0193 | — | — | — | — | — |
| 0.5 | 0.0329 | 0.0136 | 0.0272 | 5.44 | 0.4265 | 12.5078 |
| 1.0 | 0.0437 | 0.0244 | 0.0488 | 4.88 | 0.4062 | 11.6349 |
| 2.0 | 0.0768 | 0.0565 | 0.1130 | 5.65 | 0.2742 | 7.4708 |
| Average between 0.5 and 1.0 | | | | | 0.4164 | 12.0714 |

*Table 6*

Optimum values of rate constants and pseudoconstants and the sum of squared deviations between calculated and experimental values

|  | Variant 1 | Variant 2 |
|---|---|---|
| Rate constants |  |  |
| $k_1[OH^-]/min^{-1}$ | 1.6701 | 1.3388 |
| $k_2[H_2O]/min^{-1}$ | — | 8.5369 |
| $k_3/dm^3\ mol^{-1}\ min^{-1}$ | — | 5.6860 |
| $k_3'/dm^3\ mol^{-1}$ | 0.6543 | 0.6660 |
| $k_4/dm^3\ mol^{-1}\ min^{-1}$ | — | 9.3110 |
| $k_4'/dm^3\ mol^{-1}$ | 0.5411 | 1.0910 |
| Sum of squared deviations |  |  |
| for acetaldehyde/mol$^2$ dm$^{-6}$ | $14.116 \times 10^{-3}$ | $18.570 \times 10^{-3}$ |
| for formaldehyde/mol$^2$ dm$^{-6}$ | 13.775 | 15.830 |

iterative regression [19]. However, we modified the optimality criterion for acetaldehyde when compared with preceding variant. As for the analysis of a sample of reaction solution by gas chromatography, we can expect that the present enol decomposes and gives acetaldehyde and base after feeding and evaporation of the sample, owing to which the determined concentration of acetaldehyde really represents the sum of the effective concentrations of acetaldehyde and enol. Therefore we defined the object function as the sum of squared deviations of the experimental concentrations of acetaldehyde from the sum of calculated concentrations of acetaldehyde and enol

$$SSD = \Sigma\{[A]_{exp} - ([A]_{calc} + [A^-]_{calc})\}^2 \qquad (18)$$

The method of evaluation for formaldehyde was not changed.

The optimum values of constants as well as the corresponding values of optimality criterion are also given in Table 6. For comparison, we give the time course of acetaldehyde concentration found in experiment *2* and the corresponding values of concentration calculated according to both variants (Fig. 1).

As obvious, both variants express almost equally well the experimental results though the agreement with the calculated concentration course is for acetaldehyde better than for formaldehyde. That is comprehensible because mechanisms (*3—5*) describe only the first of aldol condensations of formaldehyde on the $\alpha$-carbon of acetaldehyde and the rate equation for fomaldehyde, *i.e.* (*8*) or (*11*), is therefore incomplete.

If we compare both variants of calculation with each other, we prefer variant 2 in spite of a slightly higher value of the sum of squared deviations. In contrast to variant 1 by which we obtain only the values of $k_1[OH^-]$, $k_3'$, and $k_4'$ because of
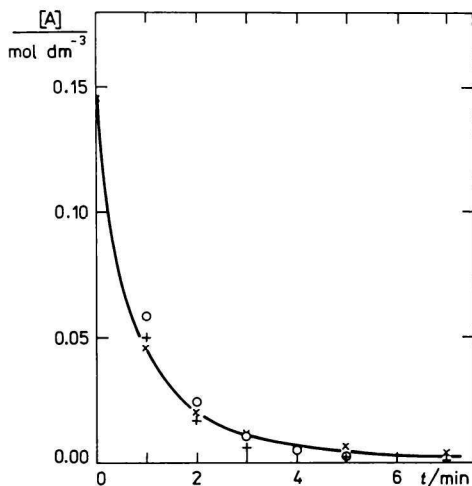
*Fig. 1.* Confrontation of experimental results with calculations for concentration course of acetaldehyde in experiment *2*.
× Experimental values; + values calculated according to variant 1; ○ values calculated according to variant 2.

mathematical limitation in the form of eqns (*10*) and (*11*), variant 2 also supplies the values of $k_2[H_2O]$, $k_3$, and $k_4$ and is therefore more valuable from the view-point of study and prospective confrontation of mechanisms.


## Conclusion

The first step in the reaction sequence occurring in the production of pentaery-thritol, *i.e.* the reaction of formaldehyde with acetaldehyde giving rise to $\beta$-hy-droxypropionaldehyde, is the step effectual for obtaining the optimum technical and economical parameters of production. The calculated values of rate constants and cohering rate relations are necessary basis for quantitative mathematical simulation of the whole reaction system and also throw light on the undesirable side reaction of acetaldehyde giving rise to acetaldol.


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