

Aldol condensation of butanal in alkaline medium

Comparison of kinetic models

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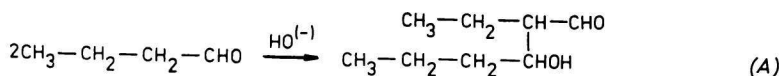
Kinetic measurements were evaluated and the conclusions were drawn for relative rates of particular steps of the aldol condensation of butanal. Four kinetic models are compared: a semiempirical model of the first-order reaction; a model based on the assumption of constant concentration of carbanion; a model according to which carbanion is an intermediate and its concentration varies with time; a model equal to the preceding one with further assumption of irreversible formation of carbanion. Such a system of equations and rate constants has been selected which depicts the experimental material best and is in agreement with the present theoretical ideas on the operating mechanism.

Обобщены кинетические измерения и сделаны выводы об относительных скоростях отдельных стадий альдольной конденсации бутанала. Были сравнены четыре кинетические модели: полуэмпирическая модель реакции I порядка; модель, исходящая из предположения постоянной концентрации карбаниона; модель, рассматривающая карбанион как интермедиат с концентрацией, меняющейся во времени; модель с таким же исходным предположением, как и у предыдущей, но с дополнительным предположением о необратимости образования карбаниона. Была выбрана система уравнений и констант скоростей, лучшим образом отражающая использованный экспериментальный материал и находящаяся в согласии с современными теоретическими представлениями о механизме процесса.

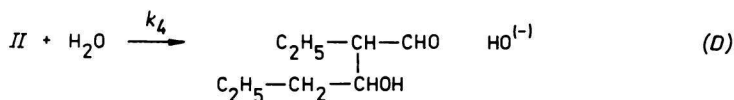
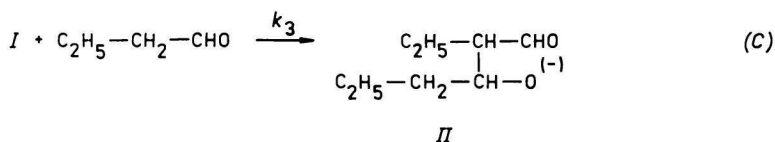
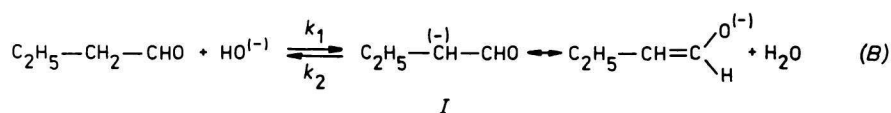
The condensation reactions of butanal in alkaline medium are of great importance in chemical industry. We meet them in the production of 2-ethylhexanol where they represent the major reaction course as well as in the production of 2,2-di(hydroxymethyl)-1-butanol (commercial name trimethylolpropane) where they appear as an undesirable side reaction which reduces the yield of the main product. Their mechanism is relatively well known but the pertinent kinetics has been studied in an insufficient degree.

It is widely assumed [1—4] that the aldol condensation of aldehydes in aqueous alkaline medium proceeds, in principle, in three steps. The first step is the reaction of aldehyde with the present base giving rise to carbanion, while the second step is the reaction of carbanion with free aldehyde. In the third step, the formed O-anion decomposes to yield the resulting product.

The summary chemical reaction



may be laid out into individual steps as follows



If we designate with indices 1 — butanal, 2 — $\overset{(-)}{\text{O}}\text{H}$, 3 — carbanion of butanal, 4 — water, 5 — intermediate (*II*) (O-anion), 6 — 2-ethyl-3-hydroxyhexanal (butyraldol), we may construct the following rate equations for the main reaction components

$$\frac{dC_1}{dt} = -k_1 C_1 C_2 + k_2 C_3 C_4 - k_3 C_1 C_3 \quad (1)$$

$$\frac{dC_2}{dt} = -k_1 C_1 C_2 + k_2 C_3 C_4 + k_4 C_4 C_5 \quad (2)$$

$$\frac{dC_3}{dt} = k_1 C_1 C_2 - k_2 C_3 C_4 - k_3 C_1 C_3 \quad (3)$$

In general, it is assumed that reaction (*D*), i.e. the decomposition of O-anion, is very fast [1, 2]. On the basis of this mechanism involving the assumption of equilibrium concentration of carbanion, *Frost and Pearson* [1] derived the rate equation for the product of reaction (*C*)

$$\frac{dC_5}{dt} = \frac{k_1 k_3 C_1^2 C_2}{k_2 C_4 + k_3 C_1} \quad (4)$$

As this product decomposes rapidly, eqn (4), as a matter of fact, describes the formation of the final product.

Analogously, we may derive the equation for the time change in the concentration of butanal. After small arrangements, we obtain under equal assumptions

$$\frac{dC_1}{dt} = \frac{-2k_1 k_3 C_1^2 C_2}{k_2 C_4 + k_3 C_1} \quad (5)$$

In practical analytical activity, it is much easier to investigate the course of butanal concentration than the course of concentration of the final product and, for this reason, eqn (5) is more convenient for kinetic evaluation. As a rule, this equation can be further simplified: When $k_3 C_1$ is much greater than $k_2 C_4$, eqn (5) assumes the simple form valid for a first-order reaction with respect to butanal

$$\frac{dC_1}{dt} = -k_1 C_1 C_2 \quad (6)$$

However, provided $k_2 C_4 \gg k_3 C_1$, we may in good approximation write

$$\frac{dC_1}{dt} = -k' C_1^2 C_2 \quad (7)$$

which means that the rate equation corresponds to a second-order reaction.

The concentration of the base should not change during experiments because its quantity bound in the first step is liberated again in the third step. By using the experimental dependence of butanal concentration on time and a convenient mathematical procedure, we are able to calculate the values of rate constants which express best the relationship $C_1 = f(t)$ for a chosen rate relation.

Though there are some technological publications about the aldol condensation of butanal in periodical and patent literature, the data concerning kinetic measurements are rare. *Tulisová* [5] measured this reaction in the temperature range 10–40 °C by using sodium hydroxide as a base. In these investigations, the initial concentrations of aldehyde were 0.042 and 0.083 mol dm⁻³ and those of the base 0.1 and 0.05 mol dm⁻³. The concentration of butanal in the course of reaction was investigated by gas chromatography, while the concentration of the base was determined alkalimetrically. The experimental results were consistent with eqn (6) of the first-order reaction but the dependence on the concentration of base was not in agreement with eqn (6) and was not unambiguous. Eqn (7) valid for a second-order reaction with respect to butanal did not evidently satisfy. Furthermore, the author analytically integrated eqn (5) arranged into the form

$$\frac{dC_1}{dt} = \frac{-2k_1k'_3C_1^2C_2}{1+k'_3C_1} \quad (8)$$

where

$$k'_3 = \frac{k_3}{k_2C_4} \quad (9)$$

and assuming a constant concentration of the base, she calculated the optimum values of rate constants k_1 and k'_3 by linear regression of integrated eqn (8) and expressed the temperature dependence of these constants as well.

The assumption of a constant concentration of carbanion is not, however, fully justified and was evidently used only for simplification of calculation. As for the mechanism of the aldol condensation, the rates of eqns (B) and (C) are comparable and carbanion behaves as a typical intermediate of two consecutive reactions. First of all, its concentration increases and after reaching the maximum value, it decreases again. Therefore it is more correct to calculate the optimum values of rate constants directly from eqns (1—3) though the concentration of carbanion cannot be immediately analyzed in this way.

We used the experimental data taken from paper [5] which concern the condensation of butanal in aqueous alkaline medium in the presence of NaOH for comparing four kinetic models.

1. The simple relationship for a first-order reaction based on eqn (6)

$$\frac{dC_1}{dt} = -kC_1 \quad (10)$$

where $k = f(C_2)$.

2. The relationship derived on the assumption of a constant concentration of carbanion and expressed by eqns (8) and (9).

3. The model derived from the mechanism of eqns (B—D) expressed by eqns (1) and (3) while the concentration of water and thus the expression k_2C_4 are approximately constant and the concentration of carbanion changes with time.

4. The model based on the assumption of irreversible formation of carbanion in eqn (B), i.e. $k_2 = 0$, described by the following equations

$$\frac{dC_1}{dt} = -k_1C_1C_2 - k_3C_1C_3 \quad (11)$$

$$\frac{dC_3}{dt} = k_1C_1C_2 - k_3C_1C_3 \quad (12)$$

In this case, we also take into account the change in carbanion concentration with time.

The method of calculation of the optimum values of rate constants and the choice of the criterion of closeness of the calculated values with respect to the experimental values published in paper [5] were as follows.

As for Model 1, we calculated the values of k for each experimental point after integration of eqn (10) and determined the mean value of $k^{(1)}$ for the corresponding experimental set. The sum of the squared deviations of butanal concentrations calculated by means of $k^{(1)}$ from the experimental values published in paper [5] was used as criterion of fit of calculation with experiment.

As for Model 2, we calculated the optimum values of rate constants by combining the numerical integration of eqn (8) (Runge—Kutta, the fourth degree) with iterative optimization procedure according to Marquardt [6]. The method of calculation is described in more detail in our paper [7]. The sum of the squared deviations of the calculated values from the values found experimentally in particular time points was used again as criterion of optimization and measure of fit of the time course calculated for butanal with respect to the experimental values. The mean concentration of base for a given set of measurements was inserted into equation instead of the term C_2 .

As for Model 3, we proceeded analogously and used the same optimization criterion, but we currently interpolated the base concentration during calculation on the basis of the experimental values determined earlier [5].

Since Model 4 was a certain simplification of Model 3, we used equal integration and optimization method including interpolation of the values of base concentration, but we tried to express the fit by a different optimization criterion. The experimental results presented in paper [5] were obtained by gas chromatographic analysis in which the carbanion did not evidently produce any response. Therefore, we might expect that during the flash evaporation of the sample shot into the feeder, a part or the whole quantity of carbanion should decompose back into butanal and the solid base. Thus the analysis gave information about the sum of the concentrations of butanal and its carbanion in the sample but not about concentration of free butanal. For this reason, we formulated the optimization criterion (OC) for this model as the sum of the squared deviations of the values of butanal concentrations determined analytically in paper [5] for the particular time points $(C_1)_{\text{exp}}$ from the sum of the calculated concentrations of butanal and its carbanion $(C_1)_{\text{calc}} + (C_3)_{\text{calc}}$

$$\text{OC} = \sum_1^N [(C_1)_{\text{exp}} - (C_1)_{\text{calc}} - (C_3)_{\text{calc}}]^2 \quad (13)$$

where N is the number of evaluated experimental points.

In this way we processed the data from paper [5] obtained at 20 °C, 30 °C, and 40 °C (the values obtained at 10 °C were very little consistent even at visual examination). We evaluated four sets with different initial concentrations of butanal and base for each temperature. All sets corresponding to one temperature were simultaneously processed by calculation (one exception concerned Model 1 where the values of $k^{(1)}$ were calculated separately for each set).

Results and discussion

The evaluation of Model 1 is given in Table 1. As obvious from the very low values of OC, the agreement of calculations with the experimental results is very good provided the pertinent values $k^{(1)} = kC_2$ are used in individual sets.

Table 1

Evaluation of Model 1

Measurement according to [5]	$\theta/^\circ\text{C}$	Initial concentrations			
		Butanal	NaOH	$k^{(1)} = k_1 C_2$	$OC \cdot 10^5$
		(mol dm ⁻³)	(mol dm ⁻³)	(min ⁻¹)	(mol dm ⁻³) ²
1	20	0.083	0.1	0.099	1.549
2	20	0.083	0.05	0.080	0.972
3	20	0.042	0.1	0.117	1.214
4	20	0.042	0.05	0.104	1.345
5	30	0.083	0.1	0.132	1.342
6	30	0.083	0.05	0.132	3.703
7	30	0.042	0.1	0.145	4.182
8	30	0.042	0.05	0.138	3.007
9	40	0.083	0.1	0.249	7.969
10	40	0.083	0.05	0.236	9.202
11	40	0.042	0.1	0.217	3.718
12	40	0.042	0.05	0.171	1.028

A comparison of the calculated values of $k^{(1)}$ with the data of paper [5] where these values were calculated from the slope of the equation

$$\ln \frac{C_1^0}{C_1} = kt \quad (14)$$

also shows a very good agreement. The average difference referred to the data according to [5] is 14.7 %.

The calculated rate pseudoconstants $k^{(1)}$ ought to be proportional to the base concentration in the sense of eqn (6). However, the data in Table 1 show that the values of $k^{(1)}$ are greater at higher initial concentrations of NaOH (except sets 5 and 6 where these values are equal) but the required proportionality does not exist. Of course, the values increase with temperature.

Thus Model 1 does not correctly express the whole experimental material though it can give a very good approximation to the experimental time dependence of the concentration of butanal provided the individual sets are evaluated separately. The dependence of $k^{(1)}$ on temperature (expressed in K) and base concentration (in mol dm⁻³) may be expressed in terms of an empirical relation which assumes after regression processing of the whole evaluated material the following form

$$k^{(1)} = -1.3574 + 4.9 \times 10^{-3} T + 0.323 C_2 \quad (15)$$

If we use this relationship in combination with eqn (10), we obtain the concentration courses of butanal with good closeness though the agreement with experiment is poorer than it is for separate choice of k for each set (Fig. 1). An attempt to express the temperature dependence by the Arrhenius equation results in too great deviations of calculation from experiment.

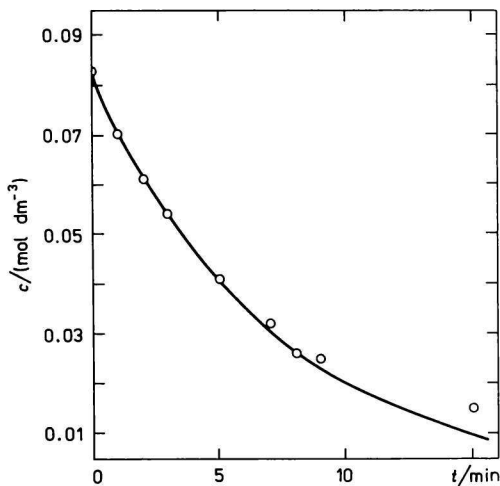


Fig. 1. Experimental values according to [5] and calculated values according to Model 1.

$\theta = 30\text{ }^{\circ}\text{C}$, $(\text{NaOH})_0 = 0.05\text{ mol dm}^{-3}$.

○ Experimental values according to [5].

— Course calculated according to Model 1.

If we calculate the optimum values of rate constants according to Model 2, we have to use eqn (8) and not eqn (5) in which some convergence problems and ambiguous results appear. The application of eqn (8) makes possible an iteration calculation of $k_1^{(2)}$ and $k_3^{(2)}$ but it does not give information about the value of $k_2^{(2)}$ and $k_2^{(2)}C_4$.

The pertinent results are presented in Table 2. The fit expressed by the values of OC is relatively good. An evaluation of the temperature dependence by means of the Arrhenius equation leads to the expressions

Table 2

Evaluation of Model 2

Measurement according to [5]	$k_1^{(2)}$	$k_3^{(2)}$	OC · 10 ³
	(dm ³ mol ⁻¹ min ⁻¹)	(dm ³ mol ⁻¹)	(mol dm ⁻³) ²
1— 4	2.1389	1.1568	0.603
5— 8	3.8018	2.8937	0.333
9—12	6.3270	11.848	0.937

$$k_1^{(2)} = 3.20 \times 10^7 \exp(-40.2/RT) \quad (16)$$

$$k_3^{(2)} = 6.96 \times 10^{15} \exp(-88.79/RT) \quad (17)$$

where the activation energy is given in kJ mol^{-1}

Comparisons with the data from paper [5] which were obtained from the basic relation by a different method show a good agreement for the values of k_1 with a mean deviation of 26.6 %. A poorer agreement is observed for the values of k_3 which are considerably higher in [5]. With respect to the method of processing, we consider our results to be more accurate.

As the concentration of water is approximately equal to 55.5 mol dm^{-3} , it ensues from eqn (9) that k_3 is much greater than k_2 , which is in harmony with the theoretical views on relative rates of individual steps of the aldol condensation. The formation of anion ought to be the most rapid while the subsequent reaction with free aldehyde should be more rapid than its reverse decomposition.

We achieved a very good agreement of calculation with experiment by using Model 3 in which carbanion was regarded as an intermediate the concentration of which is not constant in the course of time (Fig. 2). The optimum values of rate constants and the sum of the squared deviations are in Table 3. In calculating the value of $k_2^{(3)}$ we assumed that the concentration of water was practically constant and equal to 55.5 mol dm^{-3} . We expressed the temperature dependence of the values of these constants by the Arrhenius equation in the form

$$k_1^{(3)} = 1.78 \times 10^6 \exp(-32.92/RT) \quad (18)$$

$$k_2^{(3)} = 1.09 \times 10^8 \exp(-63.31/RT) \quad (19)$$

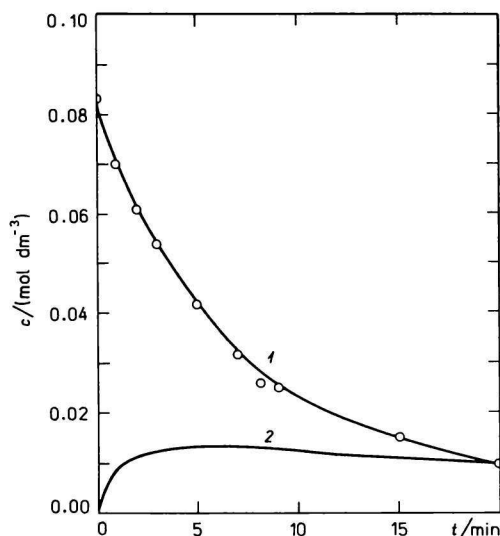


Fig. 2. Experimental values according to [5] and calculated values according to Model 3. $\theta = 30^\circ\text{C}$, $(\text{NaOH})_0 = 0.05 \text{ mol dm}^{-3}$. \circ Experimental values according to [5]. 1. Concentration of butanal according to Model 3; 2. concentration of carbanion according to Model 3.

Table 3

Evaluation of Model 3

Measurement according to [5]	$k_1^{(3)}$ (dm ³ mol ⁻¹ min ⁻¹)	$k_2^{(3)}$ (dm ³ mol ⁻¹ min ⁻¹)	$k_3^{(3)}$ (dm ³ mol ⁻¹ min ⁻¹)	$K = k_1/k_2$	$OC \cdot 10^3$ (mol dm ⁻³) ²
1— 4	2.331	$5.42 \times 10^{-}$	1.215	4317	0.597
5— 8	4.163	$1.50 \times 10^{-}$	4.686	2775	0.225
9—12	5.498	$2.83 \times 10^{-}$	7.265	1943	0.514

Table 4

Evaluation of Model 4

Measurement according to [5]	$k_1^{(4)}$ (dm ³ mol ⁻¹ min ⁻¹)	$k_3^{(4)}$ (dm ³ mol ⁻¹ min ⁻¹)	$OC \cdot 10^3$ (mol dm ⁻³) ²
1— 4	3.413	5.190	0.601
5— 8	4.543	9.283	0.666
9—12	5.110	21.702	0.368

$$k_3^{(3)} = 2.44 \times 10^{12} \exp(-68.71/RT) \quad (20)$$

A comparison of the values of rate constants with the mechanism of the reaction reveals a very important fact. The formation of carbanion according to eqn (B) is many times more rapid than its reverse decomposition into butanal and base and thus the equilibrium is very distinctly shifted to the right side. It is also obvious from the high value of equilibrium constant of eqn (B) which is also given in Table 3. The assumption of irreversible reaction (B) introduced by Model 4 should, therefore, not result in a misrepresentation of physicochemical reality and it ought to express the experimental material almost equally well as Model 3, of course, by using only two rate constants ($k_2 = 0$).

We applied the modified criterion of fit to Model 4 involving the assumption of the irreversible formation of carbanion. The calculated values of $k_1^{(4)}$ and $k_3^{(4)}$ are in Table 4 which also contains the data about the squared deviations of calculation from experiment at individual temperatures. A comparison of Table 3 and Table 4 shows clearly that the level of fit for Model 4 is only a little poorer than that for Model 3 though the concentration of butanal and carbanion calculated according to Model 4 are different owing to a different criterion of fit. After consumption of butanal, a certain portion of carbanion remains in the solution according to the model because it has no reaction partner, which, however, does not correspond to reality. Butanal always reacts up to complete consumption.

The values of rate constants according to Model 4 were smoothed again by the Arrhenius equation into the form

$$k_1^{(4)} = 2.01 \times 10^3 \exp(-15.49/RT) \quad (21)$$

$$k_3^{(4)} = 2.69 \times 10^{10} \exp(-54.65/RT) \quad (22)$$

The values of activation energy are given in kJ mol^{-1} .

Conclusion

The following realities result from the estimation of the compared models.

Simple Model 1 with empirical dependence of rate constant on temperature and concentration of base according to eqn (15) gives good results in practical application. The agreement of calculation with experiment is illustrated in Fig. 1. However, it is a semiempirical model which gives no deeper insight into the course of reaction and relative rates of particular steps.

Model 2 based on the assumption of a constant equilibrium concentration of carbanion gives a poorer agreement of calculation with experiment and besides k_1 , it does not bring the true values of rate constants.

This drawback does not occur with Model 3 on the basis of which the values of all three rate constants and the corresponding activation energies of individual partial reactions could be calculated. A relatively flat time course of the calculated concentration of carbanion is due to the fact that the reserve of carbanion rapidly produced by reaction (B) is consumed only slowly because the amount of butanal available for reaction (C) gets lower and lower. A comparison of calculation with experiment according to Model 3 is represented in Fig. 2. In this example, the concentration of carbanion reaches a flat maximum in the seventh minute and afterwards it slowly decreases. The relative values of rate constants are in agreement with theoretical ideas on the relative rates of individual steps of the aldol condensation.

As the reverse decomposition of carbanion is very slow, Model 4 assuming its irreversible formation also gives results with satisfactory accuracy. Notwithstanding, it is not realistic from the point of view of our knowledge of the mechanism of the proceeding reactions and, for this reason, its use does not lead to so exact description as the use of Model 3. This drawback is not compensated even by the fact that only two rate constants are necessary for its application and thus the model is relatively very simple.

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