

Studying Kinetics of the Dehydration Reaction of Acetaldehyde in Aqueous Solutions Using Polarographic Kinetic Currents

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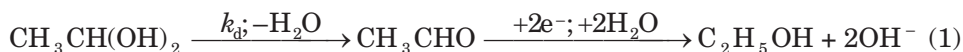
The well-known Koutecky's equation cannot be used to describe the polarographic kinetic currents of acetaldehyde in aqueous solutions since the diffusion contribution of the depolarizer from the bulk solution is not considered. The rate constants of dehydration reaction of acetaldehyde hydrate derived from Koutecky's equations are larger as compared with the data obtained by other (non-polarographic) methods. Koutecky's equation modified by us taking into account the diffusion contribution of the depolarizer from the bulk solution allows one to obtain the rate constants of the dehydration of acetaldehyde hydrate close to the ones found by non-polarographic methods.

In addition, we present a detailed consideration and analysis of the equilibrium constants of the hydration reaction of acetaldehyde found by different methods in order to choose the most reliable constant for kinetic calculations.

Key words: dehydration reaction, acetaldehyde, polarographic kinetic currents.

INTRODUCTION

Analogously to formaldehyde,¹ the polarographic kinetic current of acetaldehyde in aqueous solutions, detected by the direct current polarography (DCP), is caused by the preceding electrode chemical reaction of the dehydration of acetaldehyde hydrate (*gem*-diol):^{2,3}



where k_d is the rate constant of the dehydration reaction of acetaldehyde hydrate.

For the study of the kinetics of the chemical reaction (scheme (1)), the DCP technique can be regarded as the electrochemical trapping technique. In comparison with similar chemical techniques (for example, with the formation of semicarbazone or hydrazone), the advantage of the electrochemical trapping technique is that the rate constant of the corresponding chemical reaction can be evaluated only from one kinetic current measurement.

Unlike formaldehyde,¹ the DCP technique has not yet been applied for determination of the rate constant of the dehydration reaction of acetaldehyde hydrate. Perhaps, the reason is the large diffusion contribution of the depolarizer (as aldehyde form, see reaction (1)) from the bulk solution to the overall polarographic kinetic and diffusion currents. In this case, the usual Koutecky's equation^{4,5} (Eq. (2)) is not suitable for determination of the k_d value.^{1,6,7}

$$\sum \bar{i}_1^k / (\sum \bar{i}_1^d - \sum \bar{i}_1^k) = 0.886 [k_d(1+K_h)t_1 / (K_h)^2]^{0.5} \quad (2)$$

In Eq. (2) $\sum \bar{i}_1^k$ and $\sum \bar{i}_1^d$ are the average kinetic and diffusion limiting currents, respectively, t_1 is the drop time of the dropping mercury electrode, K_h is the equilibrium constant of the hydration reaction of acetaldehyde (Eq. 3).

$$K_h = [\text{CH}_3\text{CH}(\text{OH})_2] / [\text{CH}_3\text{CHO}] = k_h/k_d \quad (3)$$

Taking into account the diffusion contribution of the depolarizer (in the case of acetaldehyde it is CH_3CHO) from the bulk solution, we have modified Koutecky's equation (Eq. (2)):^{1,6,7}

$$\{\sum \bar{i}_1^k - [\sum i_1^d / (1+K_h)]\} / (\sum \bar{i}_1^d - \sum \bar{i}_1^k) = 0.886 [k_d(1+K_h)t_1 / (K_h)^2]^{0.5} \quad (4)$$

Use of Eq. (4) has allowed us to obtain the correct values of k_d for glyoxylic acid,⁶ pyruvic acid,⁷ ethyl pyruvate⁷ and formaldehyde.¹

In this work, the correct value of k_d has been derived for the dehydration reaction of a acetaldehyde hydrate from Eq. (4). Moreover, a detailed analysis of equilibrium constants, *i.e.*, K_h , found by different methods has been performed.

It should be noted that the estimation of K_h is necessary not only for determination of k_d by the polarographic method using Eq. (4) but also that

other methods could be used since the dehydration reaction of acetaldehyde hydrate is a reversible reaction of the pseudo-first-order.⁸

EQUILIBRIUM CONSTANTS OF THE HYDRATION REACTION OF ACETALDEHYDE

Table I presents the K_h values from the studies of Bell,⁹ Le Henaff,¹⁰ and Sorensen and Jencks,¹¹ and other data. Analogously to Ref. 11, the K_h values have been recalculated to 25 °C (Table I) on the basis of $\Delta_h H = -5.1$ kcal mol⁻¹ (cp. with Refs. 14,15,18,21,23,25,30).

Detailed analysis of K_h values derived from different works showed that the most reliable K_h values are 1.17–1.23, obtained by Sorensen and Jencks¹¹ from the rate constants using different methods (Table I). Taking this into account, we have selected the K_h values in the range of 1.06–1.28 (values in Table I without brackets) to use them in further calculations. The average value of K_h found by spectrophotometric measurements (7 values) and by nuclear magnetic resonance measurements (4 values) is $K_h = 1.19 \pm 0.05$.

Our recalculation of the data from Ref. 23 (Raman spectroscopic method) to $C_{H_2O} \approx 100\%$ and to 25 °C did not give the correct K_h value (Table I) because of the high concentration of acetaldehyde and hence a lower concentration of H₂O. These influences could be taken into account by introducing the activity coefficients which has not been done in Ref. 23.

In DCP, the kinetic current of sufficiently fast electrode chemical reactions cannot be used for precise determination of the equilibrium constants of these reactions. Therefore, instead of the DCP method, the linear sweep voltammetry has been applied by Valenta³¹ for determination of the K_h value of the hydration reaction of formaldehyde. However, Dirscheri and Bergmeyer,² as well as Barnes and Zuman,³ have used DCP for determination of K_h of acetaldehyde at pH = 7 (Table I) when the kinetic contribution in the total kinetic current is insignificant.

In Ref. 2, the influence of the height of the mercury reservoir (H_{Hg}) on the kinetic component of $\sum \bar{i}_1^k$ at pH = 7 has been neglected and the equation for K_h determination has been derived:

$$K_h = 1 - [((\sum \bar{i}_1^d)_1 - (\sum \bar{i}_1^d)_2) / ((\sum \bar{i}_1^k)_1 - (\sum \bar{i}_1^k)_2)] \quad (5)$$

where indexes »1« and »2« correspond to the values of $\sum \bar{i}_1^k$ and $\sum \bar{i}_1^d$ at different values of H_{Hg} . The values of $\sum \bar{i}_1^k$ have been measured and the $\sum \bar{i}_1^d$ values have been calculated from Ilcovic's equation. The K_h value found

TABLE I
Equilibrium constants of the acetaldehyde hydration in aqueous solution (25 °C)

K_h	(1.9)	(1.54)	1.21 ^a	(1.5)	(0.87)	1.22 ^a	(0.93)	(0.85)	1.06	1.06	1.20	1.17	1.23
Method ^b	S	S	S	S	S	S	S	S	S	S	S	S ^c	S ^d
Ref.	12	13	14	15	16	17	18	19	20	21	22	11	11
K_h	(0.3-0.7) ^{a,e}	(1.49)	1.23 ^{a,e}	1.22	1.22 ^a	(0.96) ^a	1.28 ^a	(1.50)	(1.49)	(0.99)	(2.13)	(0.9-2.6) ^a	
Method ^b	RS	NMR	NMR ^f	NMR	NMR	NMR	NMR	Ch	Ch	Ch	DCP	DCP	
Ref.	23	24	11, 25	26	27	28	29	26	9	30	2	3	

^a The K_h values have been recalculated by us and in Ref. 11 to 25 °C using $\Delta_r H = -5.1$ kcal mol⁻¹.

^b S, Spectrophotometry; RS, Raman spectroscopy; NMR, nuclear magnetic resonance; Ch, chemical; DCP, direct current polarography.

^c Spectrophotometry with kinetic measurements (injection and trapping techniques).

^d Spectrophotometry with kinetic measurements (temperature jump and trapping techniques).

^e Our recalculation and that of Ref. 11 from $K_h' = [\text{CH}_3\text{CH}(\text{OH})_2]/[\text{CH}_3\text{CHO}][\text{H}_2\text{O}]$ to K_h for $\approx 100\%$ H₂O.

^f Nuclear magnetic resonance with kinetic measurements.

from Eq. (5) (Table I) has been overstated, probably because of the non-buffer solutions used for the determination of the $\sum \bar{i}_1^k$ values (Table 4 in Ref. 2) when additional catalysis (autocatalysis) by OH^- ions takes place.³²

Neglect of the H_{Hg} influence on the kinetic component of $\sum \bar{i}_1^k$ at a low value of this component does not allow the use of Eq. (5) in different conditions. For example, at $\text{pH} \geq 9$, such assumption of the insignificant H_{Hg} influence on the $\sum \bar{i}_1^k$ is impossible and therefore Eq. (5) cannot be used for determination of the K_h value. In contrast to this, Eq. (4) and the similar equations,³³ but only for the freely dropping mercury electrode, do not demand fulfilment of the indicated limitation and therefore have an advantage over Eq. (5).

In Ref. 3, the K_h value has been calculated by equation (6) for the solution at $\text{pH} = 7$ when the kinetic contribution to $\sum \bar{i}_1^k$ can be neglected.

$$K_h = (\sum \bar{i}_1^d - \sum \bar{i}_1^k) / \sum \bar{i}_1^k \quad (6)$$

It was found³ that $K_h = 1.0$ (20 °C), which has been recalculated by us to 25 °C ($K_h = 0.9$) (Table I). $K_h = 1.09$ (25 °C) has been determined by us by Eq. (6) on the basis of data from Ref. 2 at $\text{pH} = 6.5\text{--}7.5$ (the $\sum \bar{i}_1^d$ value was calculated using Ilcovic's equation). These K_h values (especially the one obtained from Ref. 2) are close to the correct K_h value found from the other methods: $K_h = 1.19 \pm 0.05$ (25 °C) (Table I). This is a result of the insignificant influence of the kinetic contribution to $\sum \bar{i}_1^k$ at $\text{pH} = 7$. However, this influence could not be fully excluded and therefore these K_h values were lowered. An attempt³ to calculate the kinetic contribution led to a higher K_h value, equal to 2.6 (25 °C) (Table I). It should be noted that a correct calculation of the kinetic contribution to $\sum \bar{i}_1^k$ demands to know the K_h value and the rate constant of the dehydration reaction. This means that the independent determination of the K_h value is impossible in this way.

KINETICS OF THE DEHYDRATION REACTION OF ACETALDEHYDE HYDRATE

The kinetics of the dehydration reaction of acetaldehyde hydrate from DCP data (scheme (1)) has been studied by us using Eq. (4) in buffer solutions (general acid-base catalysis).¹¹

To determine the k_d values, we have used two $\sum \bar{i}_1^k$ vs. pH dependencies of the S-shaped form obtained by Dirsheri and Bergmeyer² and Barnes and Zuman.³ From Ref. 2 only the $\sum \bar{i}_1^k$ values extrapolated to zero time have been used. In Ref. 34, the dependence of $\sum \bar{i}_1^k$ vs. pH is significantly distinct

and for this reason and also because of the absence of the capillary characteristic, these data have not been used for the k_d determination.

The plots of $\sum \bar{i}_1^k$ vs. pH at $11 \leq \text{pH} \leq 7.5$ in Ref. 2 and at $12 \leq \text{pH} \leq 7.0$ in Ref. 3 at 20–25 °C reveal that $\sum \bar{i}_1^k$ values are pH independent. The upper plot corresponds to the diffusion limiting current,³ which has been confirmed by our calculations using Ilcovic's equation. In Ref. 2, the value of this current is slightly lower than that found from Ilcovic's equation.

In spite of the closeness of the acid dissociation constants of acetaldehyde hydrate and formaldehyde hydrate,³⁵ unlike formaldehyde,¹ the maximum on the upper plot of the $\sum \bar{i}_1^k$ vs. pH dependence has not been observed for acetaldehyde at 20–25 °C.^{2,3} This is caused by the considerably higher value of the rate constant of the dehydration reaction the acetaldehyde hydrate in catalysis by OH⁻ ions (see below). At a low temperature (2 °C), this maximum has been also detected for acetaldehyde.³

We have used the dependencies of $\sum \bar{i}_1^k$ on pH at 25 °C from Tables 1 in Ref. 2 and Ref. 3. These data are shown in Table II.

Analogously to Ref. 2, the diffusion coefficient of actetaldehyde $D = 1.31 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 25 °C (Ref. 36) has been used for the calculation of $\sum \bar{i}_1^d$ from Ilcovic's equation. As a result, the value of $\sum \bar{i}_1^d = 11.66 \mu\text{A}$ (based on the data of Ref. 2) and $\sum \bar{i}_1^d = 2.18 \mu\text{A}$ (from the data of Ref. 3).

Three K_h values have been used, in the estimation of k_d *i.e.*, 1.14; 1.19; 1.24 (the average K_h value is 1.19 ± 0.05 ; Table I). At the same time, only $K_h = 1.19$ has been used for the k_d calculations by Koutecky's equation (2) (data in brackets).

In Table II $k_d^{\text{H}_2\text{O}} = k_d(\text{pH} = 6.5\text{--}7.5)$ and $k_d^{\text{OH}} = k_d / [\text{OH}^-]$ (pH = 9–11) are shown at different pH. For all cases, the k_d values were found by the modified Koutecky's equation (4). The independence of $k_d^{\text{H}_2\text{O}}$ and k_d^{OH} on pH (Table II) reveals the predomination in these conditions of the H₂O and OH⁻ catalysis, respectively. The $k_d^{\text{H}_2\text{O}}$ and k_d^{OH} values are close to the corresponding values found by other (non-polarographic) methods (Table III). At the same time, the values of $k_d^{\text{H}_2\text{O}}$ and k_d^{OH} calculated by Koutecky's equation (2) are considerably higher, especially at pH = 6.5–7.5 where the kinetic contribution is low (Table II).

Error in the $k_d^{\text{H}_2\text{O}}$ determination is rather large (Table II) even in case of a small error in the K_h estimation because of the low kinetic contribution and hence the closeness of the $\sum \bar{i}_1^k$ and $\sum \bar{i}_1^d / (1 + K_h)$ values in Eq. (4). Therefore, the $k_d^{\text{H}_2\text{O}}$ value (Table II) has been found only approximately.

Fluctuation in the k_d^{OH} value determined from the data in Ref. 3 (Table II) has been caused by the scattering points on the $\sum \bar{i}_1^k$ vs. pH curve.

TABLE II

Determination of the rate constants of the dehydration of acetaldehyde hydrate from polarographic data and of the stationarity condition of the diffusion and chemical reactions (25 °C)^a

pH	$\sum \bar{i}_1^k$ from Ref. 2 $c_{Ac} = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ $t_1 = 0.755 \text{ s}$				$\sum \bar{i}_1^k$ from Ref. 3 $c_{Ac} = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$ $t_1 = 3.1 \text{ s}$		
	$\frac{\sum \bar{i}_1^k}{\mu A}$	$\frac{k_d^{OH} \times 10^{-4}}{(\text{mol dm}^{-3})^{-1} \text{ s}^{-1}}$	$\frac{k_d^{H_2O} \times 10^3}{\text{s}^{-1}}$	μ_D / μ_R	$\frac{\sum \bar{i}_1^k}{\mu A}$	$\frac{k_d^{OH} \times 10^{-4}}{(\text{mol dm}^{-3})^{-1} \text{ s}^{-1}}$	μ_D / μ_R
6.5	5.58	—	2.3 ± 1.4 (919)	1.4	—	—	—
7.5	5.58	—	2.3 ± 1.4 (919)	1.4	—	—	—
9.0	—	—	—	—	1.45	1.0 ± 0.1	3.1
9.45	—	—	—	—	1.70	2.0 ± 0.2	5.5
9.5	7.80	1.4 ± 0.1 (14)	—	3.1	—	—	—
9.7	8.25	1.6 ± 0.1 (13)	—	3.8	—	—	—
9.8	—	—	—	—	1.70	0.91 ± 0.07	5.5
10.15	—	—	—	—	1.80	0.85 ± 0.07	7.4
10.4	9.50	1.6 ± 0.1 (8.4)	—	6.8	—	—	—
10.45	—	—	—	—	1.85	0.64 ± 0.05	8.8
11.0	—	—	—	—	2.10	5.0 ± 0.3	34.4

The k_d^{OH} values for acetaldehyde (Table II) are about one order higher than those for formaldehyde.¹ This explains the absence of the maximum in acetaldehyde solutions of high pH on the curve of $\sum \bar{i}_1^k$ vs. pH at 20–25 °C, as indicated above.

In conclusion, we consider the availability of the stationarity of the diffusion and chemical reactions to be necessary⁷ for using Eq. (4) when the condition $\sum \bar{i}_1^d \gg \sum \bar{i}_1^k$ is not fulfilled.

This stationarity condition is determined by the correlation:³⁹

$$\mu_D / \mu_R \geq 3 \quad (7)$$

TABLE III

The rate constants of the dehydration reaction of acetaldehyde hydrate determined from non-polarographic data (25 °C)^a

$\frac{k_d^{\text{OH}} \times 10^{-4}}{(\text{mol dm}^{-3})^{-1} \text{s}^{-1}}$	3.6	1.2	1.7	—
$\frac{k_d^{\text{H}_2\text{O}} \times 10^3}{\text{s}^{-1}}$	3.6	4.1	5.1	3.4
Method ^b	T	C	S	Ch
Ref.	37	8	11	38

^a Our recalculation to $K_h = 1.19$.

^b T, thermal; C, calorimetry; S, spectrophotometry; Ch, chemical.

where μ_D and μ_R are the thickness of the diffusion and reaction layers, respectively. For the calculation of the μ_D/μ_R value in the case of appreciable diffusion contribution of the depolarizer, the following equation has been derived by us:⁷

$$\mu_D / \mu_R = 1.309 y K_h \quad (8)$$

where

$$y = \sum \bar{l}_1^k / (\sum \bar{l}_1^d - \sum \bar{l}_1^k) \quad (9)$$

The μ_D/μ_R values calculated by Eq. (8) are presented in Table II. As it can be seen, the condition (7) is carried out at pH between 9.0 and 11.0. This means that the stationarity of the diffusion and chemical reactions takes place and the Eq. (4) could be used for the k_d determination. At pH = 6.5–7.5 this stationarity is disturbed (Table II). This is, one of the reasons why the $k_d^{\text{H}_2\text{O}}$ value could be estimated only approximately.

CONCLUSIONS

From the 25 determinations of the equilibrium constants of the hydration reaction of acetaldehyde (K_h), the most reliable eleven values have been selected for the kinetic calculations with an average value of $K_h = 1.19 \pm 0.05$ at 25 °C.

On the basis of the modified Koutecky's equation,^{6,7} taking into account the diffusion contribution of the depolarizer from the bulk solution, the rate

constants of the dehydration reaction of acetaldehyde hydrate in the catalysis of OH^- ions (k_d^{OH}) and H_2O molecules ($k_d^{\text{H}_2\text{O}}$) have been determined using the polarographic kinetic currents. The found values of k_d^{OH} and $k_d^{\text{H}_2\text{O}}$ were close to those derived by other (non-polarographic) methods, while $k_d^{\text{H}_2\text{O}}$ was estimated only approximately.

The possibility of applying the modified Koutecky's equation for the calculation of the rate constants of the dehydration reaction of acetaldehyde at $\text{pH} \geq 9.0$ (k_d^{OH}) has been confirmed by the availability of the stationarity of the diffusion and chemical reactions.

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SAŽETAK

Studij kinetike dehidracije acetaldehida u vodenim otopinama s pomoću polarografskih kinetičkih struja

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Polarografske kinetičke struje acetaldehida u vodenim otopinama ne mogu se opisati poznatom jednadžbom Kouteckoga, jer se u njoj zanemaruje doprinos difuzije depolarizatora iz glavnine otopine. Konstante brzine dehidracije acetaldehid-hidrata izračunane jednadžbom Kouteckoga veće su od vrijednosti dobivenih nepolarografskim metodama. U ovom radu izvedena je modificirana jednadžba Kouteckoga, koja uključuje i utjecaj difuzije depolarizatora i omogućuje točnije računanje konstante brzine dehidracije acetaldehid-hidrata. Rezultati njezine primjene u skladu su s vrijednostima koje su dobivene nepolarografskim metodama. Osim toga, analizirane su konstante ravnoteže hidracije acetaldehida određene različitim metodama i preporučena je najpouzdanija konstanta koju treba rabiti za računanje kinetičkih parametara.