

ALKALINE HYDROLYSIS OF MONOMETHYL ESTERS OF MALEIC AND FUMARIC ACIDS

Peter KOMADEL, Vladislav HOLBA and Štefan TRUCHLIK, JR

*Department of Physical Chemistry,
Comenius University, 842 15 Bratislava*

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The kinetics of alkaline hydrolysis of maleic and fumaric acids monomethyl esters were studied as function of the temperature, ionic strength, and relative permittivity of the reaction medium. Electrostatic and nonelectrostatic contributions of the interaction energies of reacting species were calculated from the measured data and compared with the experimental activation energy values. The dependence of the rate constant on the temperature brings an evidence for the mutual compensation of the electrostatic and nonelectrostatic effects.

Alkaline hydrolysis of monoesters of dicarboxylic acids is a type of homogeneous reactions in solutions which enable one to obtain the kinetic parameters with an accuracy sufficient to make conclusions about the influence of the reaction medium. These reactions were studied earlier from the point of view of the kinetic salt effects¹, and it turned out that certain ions of the supporting electrolytes have a specific effect²⁻⁶. Several authors described the kinetics of alkaline hydrolysis of monoesters of dicarboxylic acids in mixed aqueous-nonaqueous solvents⁷⁻¹⁰. In studying the effect of supporting electrolytes and of nonaqueous cosolvents, it turned out that the nonelectrostatic portion of the activation energy is not negligible. The discrepancy between the experimental results and the theory of the primary salt effect can be attributed to the specific catalytic influence of certain cations, mainly Tl^+ and Ba^{2+} , which form a part of the activated complex². It seems desirable, therefore, to study this specific influence in cases where the possibility of a complex formation between the supporting electrolyte cation and the monoester anion is appreciably different. This applies to the monoesters of maleic and fumaric acids, which have a different space configuration. The alkaline hydrolysis of their monomethyl esters forms the subject of the present work.

EXPERIMENTAL

Monomethyl ester of maleic acid was prepared according to Spatz and Stone¹¹. Its sodium salt was obtained by neutralization of its methanolic solution with a methanolic solution of NaOH at 293–303 K, filtration, and evaporation in vacuum. The crystalline product was dried at 370 K.

Analysis gave 39.45% C, 3.30% H, 15.25% Na as compared with the theory for $C_5H_5NaO_4$ (152.1): 39.49% C, 3.31% H, 15.11% Na.

Monomethyl ester of fumaric acid was prepared according to the same authors¹¹ and its sodium salt was prepared analogously (neutralization temperature 313 K); the product was sucked off and another portion of it was obtained from the filtrate after partial evaporation. Analysis gave 39.65% C, 3.29% H, 15.28% Na as compared with the theory, 39.49% C, 3.31% H, and 15.11% Na.

The solution of sodium hydroxide (0.125 mol/dm^3) was freed from traces of carbonate⁷.

Kinetic Measurements

The reaction was followed conductometrically with the use of a semiautomatic bridge of the type BM 484 (Tesla Brno). 25 ml of the reaction mixture was prepared by adding 0.6–3.0 ml of 0.125M-NaOH to 22.0–24.4 ml of a tempered solution of a sodium salt of the monomethyl ester containing the base electrolyte or methanol. Redistilled water from which air had been removed by boiling was used, since the dissolved oxygen causes a lower reproducibility of the conductivity measurements¹². The reaction mixture thus prepared was placed in a conductometric glass cell of 25 ml holding capacity. The electrodes were from a platinum wire of 1 mm in diameter. The cell dimensions were chosen so that it was possible to compensate the capacitive component of the measured admittance. The electrodes were during the measurements dipped in the solution to prevent drying, which would affect their surface¹². The solution was thermostated to within $\pm 0.005 \text{ K}$. The temperature (from 290.50 to 323.09 K) was measured with Beckmann thermometers with a range of 5 K, which were calibrated by standard thermometers (Deutsches Amt für Messwesen und Wareprüfung der DDR).

The initial concentrations of the monoester and hydroxide were the same. For reactions of the second order with equal initial concentrations of the reactants c_0 we have the equation

$$kt = 1/(c_0 - x) - 1/c_0, \quad (1)$$

from which it is possible to derive a relation involving the conductivities G_{t_1} , G_{t_2} and G_∞ of the reaction system at $t = t_1$, $t = t_2$, and $t \rightarrow \infty$ (after the reaction is finished)

$$G_{t_1} - G_{t_2} = (t_2 G_{t_2} - t_1 G_{t_1}) c_0 k - (t_2 - t_1) G_\infty c_0 k. \quad (2)$$

The rate constant k can be calculated from the slope of the straight line obtained by plotting $G_{t_1} - G_{t_2}$ against $t_2 G_{t_2} - t_1 G_{t_1}$ on the assumption that the time interval $t_2 - t_1$ is constant. The latter was chosen as 0.4–0.9 times the reaction half-time $t_{1/2}$. The choice of the time interval in this range had no influence on the rate constant but only on its accuracy. The values of the rate constant k were calculated by the least squares method (the correlation coefficients of the linear dependences were not smaller than 0.9999) and the data given below are mean values from three independent measurements, their relative error being less than 0.9%.

RESULTS AND DISCUSSION

The rate constants of the alkaline hydrolysis of maleic and fumaric acids monomethyl esters are given in Table I for various temperatures and ionic strengths adjusted by the initial concentrations of the reactants. Analogous results are given in Table

II; in this case the ionic strength values were adjusted by additions of base electrolytes at a constant initial concentration of the reactants.

The product of the hydrolysis has a higher negative charge than the starting substance and the ionic strength is lowered during the reaction owing to consumption of OH^- ions. To take these facts into account, we calculated the contribution of the reactants to the ionic strength as $2.5c_0$, which corresponds to the reaction half-time. The dependence of the rate constant on the ionic strength was calculated as

$$\log k = \log k_0 + 2Az_A z_B \sqrt{I} / (1 + Ba \sqrt{I}), \quad (3)$$

TABLE I

Rate constants for alkaline hydrolysis of monomethyl esters of maleic and fumaric acids as functions of temperature and ionic strength. Equimolar initial concentrations of ester and NaOH

<i>T</i> K	$10^3 \cdot I$ mol dm ⁻³	$10^2 \cdot k$ dm ³ mol ⁻¹ s ⁻¹	<i>T</i> K	$10^3 \cdot I$ mol dm ⁻³	$10^2 \cdot k$ dm ³ mol ⁻¹ s ⁻¹
Maleic acid monomethyl ester (I)					
290.50	37.5	0.6761	314.42	37.5	4.221
292.42	37.5	0.7944	316.79	37.5	5.006
294.43	37.5	0.9310	318.36	37.5	5.582
296.35	37.5	1.098	320.82	37.5	6.597
298.46	37.5	1.294	323.09	7.5	6.211
300.23	37.5	1.481	323.09	10.0	6.383
302.07	37.5	1.716	323.09	12.5	6.587
304.07	37.5	1.994	323.09	17.5	6.792
306.41	37.5	2.383	323.09	22.5	7.072
308.68	37.5	2.822	323.09	25.0	7.251
310.61	37.5	3.224	323.09	30.0	7.428
312.86	37.5	3.632	323.09	37.5	7.696
Fumaric acid monomethyl ester (II)					
290.72	7.5	23.03	292.52	12.5	26.71
290.72	12.5	23.64	294.07	12.5	29.62
290.72	17.5	24.26	296.13	12.5	34.09
290.72	22.5	24.77	—	—	—

where A and B were taken from ref.¹³ with regard to the considered temperatures.

When the ionic strength was adjusted by changing the initial concentrations of the reactants (Table I), the dependences of $\log k$ on $\sqrt{I}/(1 + Ba\sqrt{I})$ were linear as in the case where the ionic strength was adjusted by additions of a uni-univalent base electrolyte (Table II). The values of Ba were chosen so that the slope of this dependence corresponded to its theoretical value, i.e., $2Az_Az_B$ for $z_A = z_B = -1$. From these values of Ba , the values of the distance of the closest approach, a , were calculated (Table III). In the case where the ionic strength was adjusted by the initial concentrations of the reactants, we obtained $a = 0.22$ nm and 1.10 nm for the monomethyl esters of maleic and fumaric acids, respectively. Although the found values of a cannot be considered as the true distance between the reacting ions, since Eq. (3) is based on an oversimplified model, they give an information about the dependence of the rate of the studied reaction on the ionic strength. The found values of a substantiate the experimental observation that the rate of alkaline hydrolysis of the monoester depends the more on the ionic strength the less distant is the attacked ester group from the ionic carboxyl group, which bears a negative charge¹⁰. The values of a found for the studied reactions in the presence of base electrolytes apparently reflect non-electrostatic effects. Since the cation was the same with all electrolytes used, the differences in the values of a can be attributed to the influence of anions of the base

TABLE II

Rate constants for alkaline hydrolysis of monomethyl maleate (k^I , $T = 323.09$ K, $c_{\text{est}}^0 = c_{\text{NaOH}}^0 = 7 \cdot 10^{-3}$ mol/dm³) and monomethyl fumarate (k^{II} , $T = 290.72$ K, $c_{\text{est}}^0 = c_{\text{NaOH}}^0 = 5 \cdot 10^{-3}$ mol/dm³) as functions of ionic strength adjusted by the base electrolyte concentration c_e

Base el. $10^3 \cdot c_e$ mol dm ⁻³	C ₆ H ₅ COONa		NaClO ₄		NaCl	
	$10^2 \cdot k^I$ dm ³ mol ⁻¹ s ⁻¹	$10^2 \cdot k^{II}$ dm ³ mol ⁻¹ s ⁻¹	$10^2 \cdot k^I$ dm ³ mol ⁻¹ s ⁻¹	$10^2 \cdot k^{II}$ dm ³ mol ⁻¹ s ⁻¹	$10^2 \cdot k^I$ dm ³ mol ⁻¹ s ⁻¹	$10^2 \cdot k^{II}$ dm ³ mol ⁻¹ s ⁻¹
0	6.792	23.64	6.792	23.64	6.792	23.64
2.5	6.904	23.96	6.927	24.07	6.927	24.05
5.0	7.047	24.24	7.027	24.38	7.066	24.57
7.5	7.162	24.59	7.110	24.81	7.192	24.89
10.0	7.201	24.96	7.152	25.31	7.284	25.35
15.0	7.367	25.56	7.346	26.03	7.429	26.01
20.0	—	—	7.387	26.42	—	—
30.0	—	—	7.650	27.42	—	—
40.0	—	—	7.904	28.12	—	—
50.0	—	—	8.124	28.89	—	—

electrolytes. A similar conclusion was made also in a study of the alkaline hydrolysis of terephthalic acid monomethyl ester⁶.

The dependences of the rate constants of alkaline hydrolysis of maleic (*I*) and fumaric (*II*) acids monomethyl esters on the ionic strength (adjusted with BaCl₂) are given in Table IV. These cannot be linearized by choosing the distance of closest approach *a* in Eq. (3) so as to obtain a straight line with a slope 2*A*. The reaction rate in the presence of barium chloride is higher than with other base electrolytes at equal ionic strength. The ratio of the rate constants in 0.005M-BaCl₂ and in the absence of a base electrolyte, k_{BaCl_2}/k , is for *I* equal to 1.54 and for *II* 1.13. A stronger influence of Ba²⁺ cations on the reaction of *I* can be attributed to the formation of a chelate of the monoester with Ba²⁺ ions, where the activated complex is stabilized similarly as in the case of hydrolysis of monoesters of saturated aliphatic dicarboxylic acids². In the reaction of the compound *II*, the formation of such a chelate is little

TABLE III

Distances of closest approach of ions during alkaline hydrolysis of monomethyl esters of maleic (*I*) and fumaric (*II*) acids

Base electr.	<i>I</i> <i>a</i> (nm)	<i>II</i> <i>a</i> (nm)
C ₆ H ₅ COONa	0.45	0.58
NaClO ₄	0.55	0.45
NaCl	0.32	0.30

TABLE IV

Rate constants for alkaline hydrolysis of monomethyl maleate (k^I , $T = 323.09$ K) and monomethyl fumarate (k^{II} , $T = 290.72$ K) as functions of ionic strength adjusted with barium chloride; $c_{\text{est}}^0 = c_{\text{NaOH}}^0 = 5 \cdot 10^{-3}$ mol/dm³

$10^3 \cdot c_{\text{BaCl}_2}$ mol dm ⁻³	$10^3 \cdot I$ mol dm ⁻³	$10^2 \cdot k^I$ dm ³ mol ⁻¹ s ⁻¹	$10^2 \cdot k^{II}$ dm ³ mol ⁻¹ s ⁻¹
0	12.5	6.587	23.64
1.67	17.5	8.467	25.08
3.33	22.5	9.406	26.06
5.00	27.5	10.157	26.65

probable for steric reason, hence the lower value of the ratio of k_{BaCl_2}/k . A similar effect of BaCl_2 on the rate of alkaline hydrolysis was observed with monoesters of *o*-phthalic, terephthalic, diphenic, and succinic acids, where the mentioned ratio decreased with increasing distance of the carboxyl groups, hence with decreasing tendency of chelate formation^{3-5,10}.

Extrapolated thermodynamic activation parameters were obtained from the temperature dependences of the rate constants extrapolated to zero ionic strength and are given in Table V. The steric factor P_0 was calculated from the extrapolated pre-exponential factor A_0 by dividing with the number of collisions $Z = 6.2 \cdot 10^9 \text{ dm}^3 \cdot \text{mol}^{-1} \text{ s}^{-1}$. The critical interionic distance was calculated from the equation

$$r_0 = -z_A z_B e^2 L / 4\pi\epsilon_0 \epsilon_r k \ln P_0, \quad (4)$$

TABLE V

Extrapolated activation parameters and critical interionic distances for alkaline hydrolysis of monomethyl maleate (I) and fumarate (II)

Ester	E_A^\ddagger kJ mol ⁻¹	A^0 dm ³ mol ⁻¹ s ⁻¹	P^0	ΔS_0^\ddagger J mol ⁻¹ K ⁻¹	r_0 nm
I	57.55	$1.021 \cdot 10^8$	$1.647 \cdot 10^{-2}$	-100.1	0.25
II	47.7	$7.45 \cdot 10^7$	$1.27 \cdot 10^{-2}$	-102	0.2

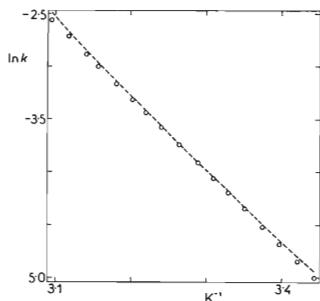


FIG. 1
Dependence of the logarithm of rate constant for alkaline hydrolysis of monomethyl maleate on reciprocal temperature calculated from Eq. (5). Points denote experimental values; $c_{\text{est}}^0 = c_{\text{NaOH}}^0 = 0.015 \text{ mol/dm}^3$

where L denotes Abegg's constant equal to $-(\partial \log \epsilon_r / \partial T)_p$, for water $L = 4.63 \cdot 10^{-3} \text{ K}^{-1}$, k is Boltzmann's constant, and other symbols have their usual significance. The relatively narrow interval of temperatures, in which the reaction of compound *II* was studied, was due to experimental difficulties. At higher temperatures, the reaction was too rapid to be measured and at temperatures lower than 290.5 K the thermostating was not accurate enough. The error of the activation energy thus found is $\pm 1.7 \text{ kJ/mol}$ and that of the activation entropy $\pm 5.7 \text{ J mol}^{-1} \text{ K}^{-1}$; the analogous values for compound *I* are $\pm 0.30 \text{ kJ/mol}$ and $\pm 1.0 \text{ K mol}^{-1} \text{ K}^{-1}$. For the reaction of compound *I*, the dependence of $\ln k$ on $1/T$ should reflect the change of the relative permittivity of water with temperature; the value of ϵ_r is namely 81.38 at 290.50 K and 70.45 at 323.09 K (the experimental temperature limits). As a result, the mentioned dependence should be curved (Fig. 1). The dependence of the activation energy on the temperature is in such a case given by the equation¹⁴

$$dE_A/dT = R/2 - (N_A z_A z_B e^2 / 4\pi \epsilon_0 \epsilon_r r_0) [L^2 T - (3/2) (2e^2 N_A I / \epsilon_0 \epsilon_r k)^{1/2} \cdot r_0 (LT - 1)^2]. \quad (5)$$

For a critical interionic distance of 0.25 nm, mean temperature of 306.80 K, $\epsilon_r = 75.54$, and ionic strength $3.75 \cdot 10^{-2} \text{ mol/dm}^3$, the temperature coefficient of the activation energy is according to the above equation equal to $267 \text{ J mol}^{-1} \text{ K}^{-1}$. Since, however, the experimental dependence of $\ln k$ on $1/T$ is exactly linear (correlation coefficient 0.99998), the dependence according to Eq. (5) must be compensated in some way. This leads to a negative temperature coefficient of the activation energy whose absolute value is equal to that calculated from Eq. (5). This compensation may be caused by the same effect as the negative temperature coefficient of the activation enthalpy reported earlier^{12,15-19}.

The interaction energy of two reacting ions whose distance is r can be divided into a nonelectrostatic, $\Phi_1(r)$, and an electrostatic one, $\Phi_2(r)$. Their values can be evaluated²⁰ for a critical interionic distance r_0 from the measured values of a_T and a_{ϵ_r} defined as

$$a_{\epsilon_r} = \partial \ln k / \partial (1/\epsilon_r), \quad (6)$$

$$a_T = \partial \ln k / \partial (1/T). \quad (7)$$

For a reaction of ions with equal sign of the charge, the inequality $a_T/a_{\epsilon_r} > T/\epsilon_r$ holds²⁰. The dependence of the rate constant for the alkaline hydrolysis of monomethyl maleate on the reciprocal relative permittivity of the reaction medium (controlled by the addition of methanol) from 56.95 to 73.12 at 313.15 K is not linear (Fig. 2). Therefore, the coefficient a_{ϵ_r} was evaluated from the slope of the tangent to the experimental curve in both end points. The analogous dependence for the reaction of monomethyl fumarate at $\epsilon_r = 60.54 - 79.99$ and 294.15 K is linear (Fig. 2). The values

of the coefficient a_T for both reactions were determined from the data in Table I. The coefficients a_{e_r} , a_T , electrostatic and nonelectrostatic contributions to the activation energies and other data are given in Table VI. The calculations involved the critical interionic distances r_0 given in Table V. It is apparent from Table VI that for the reaction of monomethyl maleate the sum of $N_A\Phi_1(r_0) + N_A\Phi_2(r_0)$ is higher than the extrapolated activation energy (Table V) in accord with the fact that oppositely charged ions take part in the reaction. With respect to the narrow temperature interval in which the hydrolysis of monomethyl fumarate was studied, the experimental error of the activation energy is higher than the difference between the terms $N_A[\Phi_1(r_0) + \Phi_2(r_0)]$ and E_A^0 . The ratio of a_T/a_{e_r} is for both studied reactions higher than the ratio of T/ϵ_r (Table VI, 5th and 6th column). Also, it follows from Table VI

TABLE VI

Electrostatic and nonelectrostatic quantities for alkaline hydrolysis of monomethyl maleate (I) and fumarate (II)

Ester	T K	ϵ_r^a	a_T	a_{e_r}	a_T/a_{e_r}	T/ϵ_r	$N_A\Phi_2(r_0)$ kJ mol ⁻¹	$N_A\Phi_1(r_0)$ kJ mol ⁻¹	$\Phi_1(r_0)/\Phi_2(r_0)$
I	313.15	56.95	-6 992	-250	27.97	5.50	48.40	9.73	4.97
I	313.15	73.12	-6 992	-520	13.45	4.28	50.55	7.58	6.67
II	294.15	70.27	-5 823	-554	10.52	4.19	39.45	8.96	4.40

^a Relative permittivity was changed by addition of methanol.

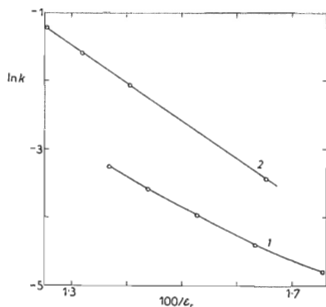


FIG. 2

Dependence of the logarithm of rate constant for alkaline hydrolysis of monomethyl maleate (curve 1) at 313.15 K and $c_{est}^0 = c_{NaOH}^0 = 0.015$ mol/dm³ and of monomethyl fumarate (curve 2) at 294.15 K and $c_{est}^0 = c_{NaOH}^0 = 0.005$ mol/dm³ on reciprocal relative permittivity in water-methanol mixtures

that the nonelectrostatic portion $\Phi_1(r_0)$ is for both reactions higher than the electrostatic one $\Phi_2(r_0)$. Similar results were obtained for many ionic reactions²¹, where the ratio of $\Phi_1(r_0)/\Phi_2(r_0)$ was in the interval from 2.9 to 10.9. A small value of the electrostatic contribution obtained from the equation involving the relative permittivity may be due to the fact that a macroscopic value is substituted for ϵ_r . In reality, the relative permittivity is in the vicinity of ions lowered as a result of normal saturation²². However, in the vicinity of univalent ions at the distances r_0 used (Table V), this decrease is relatively small²³. Hence, the large difference between the values of $\Phi_1(r_0)$ and $\Phi_2(r_0)$ cannot be attributed to normal saturation. The non-electrostatic contribution is apparently the result of strong repulsive interactions acting on small distances such as those between the reacting particles during the formation of an activated complex.

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