Monatshefte für Chemie 111, 841—849 (1980)

Monatshefte für Chemie

Kinetic Salt Effects in the Acid Hydrolysis of Potassium Ethyl Malonate in Water and in 50% Dioxane—Water Mixture

Fayez Y. Khalil* and **M. T. Hanna**

Chemistry Department, Faculty of Science, Alexandria University,
Alexandria, Egypt

(Received 7 April 1978. Accepted 11 October 1978)

The rates of the acid hydrolysis of potassium ethyl malonate in presence of KCl, NaCl, Li_2SO_4 and $MgSO_4$ in water and in 50% by weight of dioxane—water mixture were measured. The concentration of the added salts covered the range 0-1 *M*. A negative salt effect on the rate of the half-ester hydrolysis was observed. The applicability of *Brønsted*'s equation was tested and deviations found were explained as due among other reasons, to the operation of an ion-dipole type of interaction. The correlation between the hydration numbers as well as the radii of the cations of the added electrolytes and the reaction rate were discussed. The activation energy was found to increase with an increase of the concentration of electrolyte due to the relative changes in solvation of the transition state as a result of hydration of the electrolytes added. The thermodynamic properties of the activated complex were calculated and discussed as functions of the salt concentration. A remarkable linear compensation between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ was found.

(Keywords: Hydrolysis; Potassium ethyl malonate; Salt effect)

Der kinetische Salz-Effekt bei der sauren Hydrolyse von Kaliumethylmalonat in Wasser und in 50% Dioxan—Wasser

Es wurde die Kinetik der Hydrolyse von Kaliumethylmalonat in Gegenwart von KCl, NaCl, Li_2SO_4 und $MgSO_4$ (jeweils 0—1 *M*) in Wasser und in 50% (*w*/*w*) Dioxan—Wasser untersucht. Es wurde ein negativer Salz-Effekt bezüglich der Hydrolysegeschwindigkeit des Halbesters beobachtet. Es werden sowohl Korrelationen zwischen Hydratationszahlen bzw. Ionenradien und der Reaktionsgeschwindigkeit, als auch zwischen Aktivierungsenergie und Elektrolytkonzentration diskutiert. Die thermodynamischen Parameter werden als Funktion der Salzkonzentration untersucht.

0026-9247/80/0111/0841/$ 01.80

Introduction

Although an extensive study has been made on the kinetic salt effects on many reactions, only little work has been done on the effect of added electrolytes on the acid hydrolysis of dicarboxylic esters and almost no study was made on the acid hydrolysis of half-esters. To gain more insight into the medium effects on the latter type of reaction it is of interest to study the kinetic salt effects on the hydrolysis of potassium ethyl malonate by adding different types of electrolytes (covering wide ranges of concentration) to the reaction medium in which the relative quantities of the solvent components are kept constant. The measurements have been made both in pure water and 50% dioxane (*w*/*w*) in order to gather more information on the primary kinetic salt effects on the reaction rate, activation energy, activity of hydronium ions and other factors controlling the reaction in presence of salts.

Experimental

Materials. Potassium ethyl malonate was prepared according to the method described by *Nielsen*[1]. The ester was estimated to be 99% pure by complete hydrolysis with excess of potassium hydroxide and back titration with hydrochloric acid. The purification of dioxane was made using standard method[2]. AnalaR (May and Baker) inorganic salts were used without further purification.

Rate Measurements. The kinetic runs in presence of inorganic salts were followed in glass-stoppered flasks. Different amounts of the salts were weighed in several measuring flasks, then 25 ml of the acid mixed solvent (0.05 *M*-HCl) were added. The flasks were thoroughly shaken until the salts dissolved, then placed in a thermostat adjusted to ± 0.05° of the desired temperature. The rate was traced by titrating samples at different time intervals against a standard sodium hydroxide solution using a screened indicator consisting of 0.1% solution of methylene blue and neutral red in absolute ethanol. The infinity values were determined by titrating samples which had been heated at 65 °C in sealed ampoules for several days, until constant readings were obtained. The values were almost equal to the theoretical ones calculated on the basis of the concentrations of ester and sodium hydroxide used[3].

Results and Discussion

The first-order rate constants, k', in water as well as in a 50.05% (*w*/*w*) dioxane-water mixture at 30–45 °C in presence of different concentrations of potassium chloride covering the range 0–1 *M* were measured. The effect of changing the type of salt was studied also by measuring the rate using NaCl, Li_2SO_4 and $MgSO_4$. The rate constants at different temperatures and salt concentrations are collected in Tab. 1 and 2.

Table 1. *Observed rate constants for the acid hydrolysis of potassium ethyl malonate in presence of* KCl *in water and dioxane-water mixture*

[KCl]	$\sqrt{\mu}$	$k' \times 10^6/\text{min}^{-1}$					
		Aqueous medium			50.05% (*w/w*) dioxane		
M	total	30 °C	40 °C	45 °C	35 °C	40 °C	45 °C
0.00	0.25	84	171	272	55	85	126
0.04	0.32	66	166	257	48	77	118
0.10	0.40	56	155	251	46	72	114
0.30	0.60	47	143	244	41	68	110
0.40	0.68	—	—	—	32	56	97
0.70	0.87	38	115	192	—	—	—
1.00	1.03	32	105	168	—	—	—

Table 2. *Observed rate constants for the acid hydrolysis of potassium ethyl malonate in presence of different electrolytes in water at 40 °C*

[salt]	$k' \times 10^6/\text{min}^{-1}$		
M	NaCl	Li_2SO_4	$MgSO_4$
0.00	171	171	171
0.04	171	115	108
0.08	—	—	91
0.10	171	100	88
0.20	—	—	56
0.30	167	62	43
0.40	—	54	33
0.50	160	35	—
0.70	155	—	—
0.80	145	—	—

Effect of Ionic Strength on Rate

The *Brønsted* equation[4] necessitates that the plot of log k' against $\sqrt{\mu}$ (the square root of ionic strength) should give a straight line whose slope equals to $Z_A Z_B A'$, where Z_A and Z_B are the charges on the reactants A and B and $A' = 2\,A/2.303$ where A is the *Debye-Hückel* constant. The equation is valid only for dilute solutions where the ionic strength is small. Deviations are known to be observed as the ionic strength of the medium is increased, especially if ions of high valences are used[5]. In the present work, comprising higher ionic concentration of salts (0-1 M), the plots of log k' against $\sqrt{\mu}$ give straight lines at different temperatures with slopes that are less than the limiting ones predicted by the *Brønsted* formula. The values of these slopes amount to 0.3 and 0.4 for

KCl in water and 50.05% (*w/w*) dioxane, respectively, and 0.1, 0.6 and 0.7 for NaCl, Li_2SO_4 and $MgSO_4$ in water, respectively. Similar deviations were observed before in the case of the alkaline hydrolysis of half-esters of dicarboxylic acids[1,6] as well as some acid-catalyzed hydrolysis reactions[7]. Examination of Tab. 1 and 2 shows that the rate decreases with an increase of the salt concentration. The effect is, however, more evident in purely aqueous media than in organic solvent-water mixtures which is attributable to the large difference in the dielectric constants of the two media. The hydration number of the cation involved plays also an important role in the rate decrease. Since electrolyte hadration decreases the availability of "free" water molecules necessary for the reaction[8,9], the rate should decrease with increasing salt concentration and also with increasing hydration number of the respective cation. The order of increasing hydration number is $K^+ < Na^+ < Li^+ < Mg^{++}$, and it may be useful to mention the well-known values reported by *Harned* and *Owen*[10], namely, 4, 4, 6 and 15.5 for the hydration numbers of the above cations in respective order. It is to be concluded, therefore, that the effect of the magnesium salt is largest due to the highest hydration number of this ion. The rate-decreasing effect of ionic strength runs almost parallel to the increase in the value of the hydration number.

The above discussion deals with the applicability of the *Brønsted* equation in the sense that a linear relationship of log k' against $\sqrt{\mu}$, with a negative slope, is still preserved. However, the reason why the values of such slopes diverge from the limiting slopes predicted by the equation can be attributed to several factors. Firstly, the validity of the *Brønsted* equation is maintained only in dilute solutions[5], not exceeding 0.01 M. The slopes obtained in the present study give, therefore, the limiting values of the exponential decrease from the expected values. Moreover, the rate decrease at higher ionic strengths is also due to the decrease in the activity coefficients of the reactant ions (specially the H_3O^+) not taken into account by the *Debye-Hückel* theory. The latter effect will be dealt with later on. Secondly, the cation of the added electrolyte will have a diminishing effect on the negative charge of the COO^- group of the half-ester through formation of ion-pairs. However, this effect would be exerted only in solvent mixtures of low dielectric constants[11–13] and would increase with increasing concentration of the cation and decrease with increasing cation radius, as observed in the present investigation. Thus, at 40 °C in the presence of 0.7 M-NaCl and KCl, the rate constants are 155×10^{-6} min^{-1} and 115×10^{-6} min^{-1}, and the radii of Na^+ and K^+ ions are 0.95 Å and 1.33 Å, respectively[14]. The radii of the other ions under investigation are 0.60 and 0.65 Å for Li^+ and Mg^{+2} cations, respectively[14], following the same trend. Thirdly, the rate decrease due to the added salts is not precisely the one to be expected from an ionic strength effect since the same concentrations of, e.g., different uni-uni electrolytes produce different effects. Furthermore, if the present salt effect study conforms strictly to the *Brønsted* equation, a profound effect should have been observed at lower ionic strengths, with salt concentrations of NaCl below 0.01 *M*, which is not the case. As evident from Tab. 2 there is no effect of increasing salt concentration up to 0.1 *M*-NaCl.

The above observations firmly establish that the reaction considered differs largely from other typical ion—ion reactions in which more remarkable salt effects of uni-uni electrolytes are normally exhibited. The present reaction is, therefore, essentially an ion—dipole rather than an ion—ion interaction, although the half-ester anion has a charge center which would affect the rate[13, 15].

Effect of Ionic Strength on Activation Energy

The *Arrhenius* equation is strictly followed in this system, where linear plots of log k' against $1/T$ were obtained. The activation energy shown in Tab. 3 ranges from 15.4 kcal/mol in aqueous medium to 21.5 kcal/mol in 50.05% (w/w) dioxane in the range of salt studied. The point of interest is the variation of the activation energy in isocomposition media with change of added electrolyte concentration (Fig. 1).

Table 3. *Activation energies for the acid hydrolysis of potassium ethyl malonate at different concentrations of* KCl

(a) aqueous medium

[KCl], *M*	0.00	0.04	0.10	0.30	0.70	1.00
E, kcal/mol	15.36	17.28	18.97	20.47	20.73	21.43

(b) 50.05% (w/w) dioxane

[KCl], *M*	0.00	0.04	0.10	0.30	0.40
E, kcal/mol	15.63	17.28	17.95	20.19	21.50

The *E* value increases first sharply then gradually until it reaches a more or less constant value at higher salt concentrations. The trend is indicative of profound solvation changes in reactants and transition state, specially the latter, since it is the more polar entity[16]. The salt present, being relatively highly charged and therefore much more polar than the transition state, will be preferentially hydrated by water necessary for solvation of the latter. This effect will lead to a progressive elevation in the energy barrier of the reaction and hence the activation energy will increase. The process in which the activated complex is deprived of its water of solvation will continue until a point is reached in which the salt concentration is so high as to capture most of the free water molecules in the medium through solvation sheaths, then further addition of salt will not have a noticeable effect. Hence the activation energy will remain more or less constant with increasing salt concentration, as found experimentally. A similar trend, but lower in magnitude, was reported for the hydrolysis of sodium ethyl succinate and sodium ethyl glutarate in aqueous medium in a narrow range of salt concentration (0.01–0.1 M)[17].

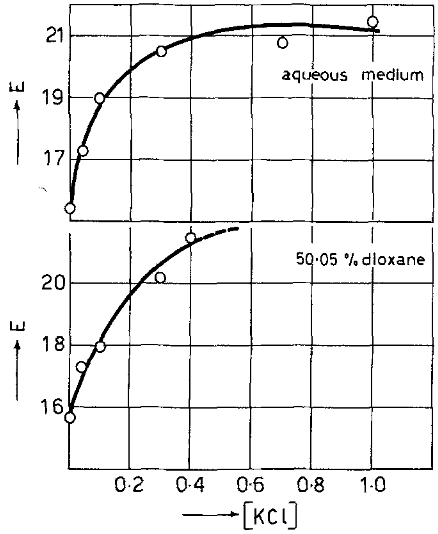

Fig. 1. Activation energy vs. electrolyte concentration

Ionic Strength and the Activity of Hydronium Ions

The effect of ionic strength on rate can also be discussed by considering the influence of concentration of the electrolytes added on the activity of H_3O^+ in the reaction medium. Since the values of such activities were not measured experimentally, they were obtained by estimating the corresponding activity coefficients $f_{H_3O^+}$ by the aid of the *Debye-Hückel* first approximation[4]:

$$-\ln f_{H_3O^+} = \frac{Z^2_{H_3O^+} A\sqrt{\mu}}{1 + \beta r_* \sqrt{\mu}}$$

Table 4. *Experimental values of rate constants as a function of ionic strength, activity coefficients and pH at 40 °C.* $A = 1.21256$, $\beta = 3323 \times 10^4$, [ester] $= 0.01\,M$ *and* [HCl] $= 0.05\,M$

Salt	[salt] M	μ salt	$\sqrt{\mu}$ total	$f_{H_3O^+}$	a_{H^+} $c_{H_3O^+} \cdot f_{H_3O^+}$	pH	$6 + \log k'$
KCl	0.00	0.00	0.25	0.798	0.040	1.398	2.232
	0.04	0.04	0.32	0.763	0.038	1.418	2.220
	0.10	0.10	0.40	0.731	0.037	1.437	2.190
	0.30	0.30	0.60	0.670	0.034	1.475	2.155
	0.70	0.70	0.87	0.617	0.031	1.511	2.060
	1.00	1.00	1.03	0.595	0.030	1.527	2.020

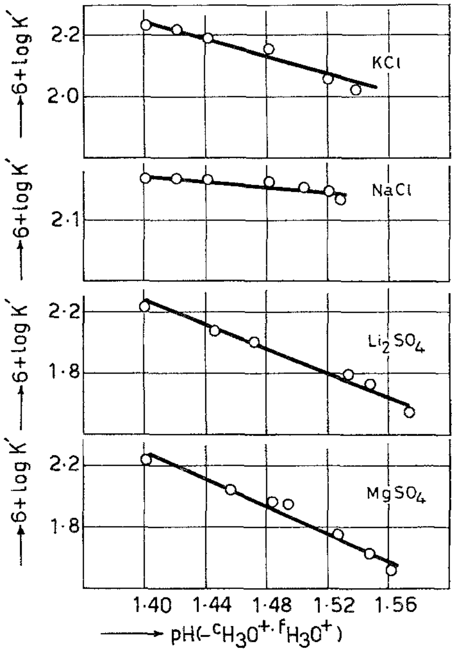

Fig. 2. $\log k'$ vs. pH for different electrolytes

The details of these data are listed in Tab. 4, where A and β are the *Debye-Hückel* constants, calculated according to the theory[4], the ionic strength μ being based on all ionic species present including the half-ester ion, and r_*, the distance of closest approach, was taken equal to the radius of the activated complex (4.1 Å) which was, in turn, evaluated from the slopes of the plots of $\log k'$ against $1/D$ (D being the dielectric constant) for the acid hydrolysis of potassium ethyl malonate in dioxane-water and acetone-water mixtures[18]. The concentration of hydronium ion $c_{H_3O^+}$, was taken as the stoichiometric concentration of added HCl. The table shows that the negative logarithm of the activity of the hydronium ion (i.e. *pH*) increases with the increase of the salt concentration. These results are supported by the findings of *Amis*[19] and *Harned*[20] in conjunction to rate measurements of the acid hydrolysis of methyl propionate and ethyl acetate. The reaction rate, as given in Tab. 4, shows an inverse trend to that of the change in *pH* of the medium. The plots of log k' against *pH* gave straight lines with negative slopes conforming in general to the theories of acid-base catalysis reported by *Euler* and *Olander*[21] (Fig. 2).

Ionic Strength and the Thermodynamic Parameters

The thermodynamic data of activation are calculated in the whole range of KCl concentration studied in water and 50.05% (*w*/*w*) dioxane. The values are compiled in Tab. 5. The free energy of activation, $\Delta F^{\ddagger}$, shows very poor dependence on the salt concentration. This is attributed to a large linear compensation between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, which shows a strong dependence on the salt concentration, where both parameters become more positive as the ionic strength is increased. The increasing value of the activation enthalpy shows that an additional amount of energy is expended in order to overcome the hydration energy of the salt present. Since the latter energy increases with

Table 5. *Thermodynamic parameters of activation at 40 °C*
(a) aqueous medium

Parameter	[salt] *M*					
	0.00	0.04	0.10	0.30	0.70	1.00
$\Delta F^{\ddagger}$, kcal/mol	26.20	26.22	26.26	26.31	26.44	26.51
$\Delta H^{\ddagger}$, kcal/mol	14.74	16.66	18.35	19.85	20.11	20.81
$-\Delta S^{\ddagger}$, cal/(mol deg)	36.62	30.55	25.27	20.64	20.22	18.22

(b) 50.05% (*w*/*w*) dioxane

Parameter	[salt] *M*				
	0.00	0.04	0.10	0.30	0.40
$\Delta F^{\ddagger}$, kcal/mol	26.63	26.70	26.73	26.77	26.89
$\Delta H^{\ddagger}$, kcal/mol	15.01	16.66	17.33	19.57	20.88
$-\Delta S^{\ddagger}$, cal/(mol deg)	37.14	32.07	30.03	23.00	19.21

increase of the salt concentration, a consequent increase in $\Delta H^{\ddagger}$ should be expected, as observed experimentally. The plot of $\Delta H^{\ddagger}$ against $\Delta S^{\ddagger}$ is a straight line whose slope gives an isokinetic temperature[22] of 333 K.

References

[1] *R. F. Nielsen.* J. Amer. Chem. Soc. **58**, 206 (1936).

[2] *A. I. Vogel,* A Text Book of Practical Organic Chemistry, 3rd ed. London: Longmans Green. 1959.

[3] *H. Sadek, F. Y. Khalil,* and *M. T. Hanna,* Z. physik. Chem. Neue Folge **73**, 77 (1970).

[4] *E. S. Amis,* Solvent Effect on Reaction Rates and Mechanisms. New York-London: Academic Press. 1966.

[5] *A. A. Frost* and *R. G. Pearson,* Kinetics and Mechanism, 2nd ed. New York: J. Wiley. 1961.

[6] *J. I. Hoppé* and *J. E. Prue,* J. Chem. Soc. **1957**, 1775.

[7] *F. A. Long, W. F. McDevit,* and *F. B. Dunkle,* J. Physic. Colloid Chem. **55**, 819 (1951).

[8] *M. A. Paul,* J. Amer. Chem. Soc. **76**, 3236 (1954).

[9] *F. A. Long* and *D. McIntyre,* J. Amer. Chem. Soc. **76**, 3243 (1954).

[10] *H. S. Harned* and *B. B. Owen,* The Physical Chemistry of Electrolytic Solutions, 3rd ed. New York: Reinhold Publishing Corporation. 1964.

[11] *W. J. Svirbely* and *P. A. Cunniff,* Canad. J. Chem. **40**, 1826 (1962).

[12] *G. Venkoba Rao* and *N. Venkatasubramanian,* Indian J. Chem. **10**, 178 (1972).

[13] *G. Venkoba Rao* and *N. Venkatasubramanian,* Proc. Indian Acad. Sci., Sect. A **LXXV**, 8 (1972).

[14] *R. A. Robinson* and *R. H. Stokes,* Electrolyte Solutions. London: Butterworths. 1955.

[15] *W. J. Broach* and *E. S. Amis,* J. Chem. Phys. **22**, 39 (1954).

[16] *S. Glasstone, K. J. Laidler,* and *H. Eyring,* The Theory of Rate Processes. New York: McGraw-Hill. 1941.

[17] *V. Holba* and *M. Rievaj,* Collect. Czech. Chem. Commun. **38**, 3283 (1973).

[18] *F. Y. Khalil, H. Sadek,* and *M. T. Hanna,* Mh. Chem. **108**, 469 (1977).

[19] *J. L. Hockersmith* and *E. S. Amis,* Anal. Chim. Acta. **9**, 101 (1953).

[20] *H. S. Harned* and *R. Pfanstiel,* J. Amer. Chem. Soc. **44**, 2193 (1922).

[21] *G. M. Schwab, H. S. Taylor,* and *R. Spence,* Catalysis. New York: D. Van Nostrand. 1937.

[22] *J. E. Leffler* and *E. Grunwald,* Rates and Equilibria of Organic Reactions. New York: J. Wiley. 1963.