oxidized electropolished single crystal copper surfaces have been studied.

2. The adsorption isotherms were determined with a quartz beam vacuum microbalance of high sensitivity. The surfaces studied are believed to be good approximations to flat, clean, undistorted single crystals.

3. The heats of adsorption were found to vary in a unique manner with the coverage, uniformity and crystallography of the surfaces.

4. The physical significance of these studies has been evaluated qualitatively within the frame of established theoretical understanding of adsorption phenomena on single crystal metal surfaces. The approximations and assumptions inherent in such treatments now available considerably limit their quantitative application.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Kinetics of the Alkaline Hydrolysis of Monoethyl Malonate Ion[1]

BY W. J. SVIRBELY AND IRVING L. MADOR

The alkaline hydrolysis of monoethyl malonate ion has been studied previously.[2,3] Ritchie's studies were carried out over a temperature range of 0 to 25° in water, ethanol and a 50% ethanol–water mixture. The reaction was found to be of the second order. Ritchie, however, neglected salt effects. Westheimer, Jones and Lad investigated the reaction at 0° in water and in an 80% ethanol–water mixture. They observed a positive salt effect. Neither of the above investigations provides sufficient data for testing the various theories dealing with ionic reaction rates.

The purpose of this research was to reinvestigate the reaction

$$C_2H_5O_2CCH_2CO_2^{-1} + OH^{-1} \longrightarrow CH_2(CO_2)_2^{-2} + C_2H_5OH \quad (1)$$

in order: (1) to determine systematically the influence of the dielectric constant of the solvent upon the rate; (2) to obtain the various thermodynamic quantities of activation; (3) to test the applicability of the theories dealing with electrostatic effects on ionic reaction rates. Accordingly, the above reaction has been studied over a temperature range of 5 to 35° in two isocomposition media, water and 27.57 wt. % dioxane in water; and in three isodielectric dioxane–water media corresponding to dielectric constants of 50, 55 and 60; and at 25° in three isodielectric mixtures of *t*-butyl alcohol–water also corresponding to the dielectric constants of 50, 55 and 60.

Materials and Apparatus

Potassium Ethyl Malonate.—A technical grade of diethyl malonate was fractionally distilled under reduced pressure and the middle cut was collected. One mole of the distilled diethyl ester was dissolved in three times its volume of ethanol. Four-tenths of a mole of potassium hydroxide, also in alcoholic solution, was added slowly with stirring to the diethyl ester solution. The resulting semi-solid mass, which consisted mainly of potassium ethyl malonate and dipotassium malonate, was digested for 24 hours at 70°, cooled and filtered. The salts were washed with ether, dissolved in absolute ethanol and fractionally precipitated with ether. The first 10% of material to crystallize was discarded. The next 80% proved to be potassium ethyl malonate. Saponification analysis indicated a purity of 100 ± 0.1%.

Dioxane.—Commercial dioxane was purified by a standard procedure.[4]

***t*-Butyl Alcohol.**—Eastman Kodak Co. best-grade *t*-butyl alcohol was dried over anhydrous calcium sulfate and fractionally distilled. The center portion, boiling at 82.2°, was collected.

Water.—Boiled, distilled water was used in preparing all solutions.

Sodium Hydroxide.—Carbonate-free sodium hydroxide was used in the preparation of the standard alkali solutions. The solutions were standardized against a National Bureau of Standards standard sample of potassium acid phthalate.

The rate measurements were carried out in a thermostat held within ±0.02°. The thermometer was calibrated against a similar one which had been certified by the National Bureau of Standards.

A stopwatch, which had been calibrated against the National Bureau of Standards time signals, was used to observe the times of sampling.

A 20-ml., jacketed pipet was used for withdrawing samples. Water was circulated from the bath through the jacket. All pipets and burets were calibrated.

The reactions were carried out in glass-stoppered, alkali resistant flasks. Titrations were carried out in glass-stoppered, Pyrex flasks. All flasks were provided with a side arm through which nitrogen was passed. An atmosphere of nitrogen was thus kept over all solutions to prevent absorption of carbon dioxide.

Standard alkali solutions in stock bottles and in burets were protected from atmospheric carbon dioxide by Ascarite tubes. An automatic delivery arrangement permitted direct transfer from stock bottle to buret.

Experimental Method

In preparing a reaction mixture, the following procedure was used: (1) a sample of potassium ethyl malonate was weighed in a small vial; (2) the volume of standard sodium hydroxide (0.04253 *N*) calculated to contain an amount of alkali equivalent to the malonate sample was run into the reaction flask from a buret; (3) if a high ionic strength was required, a weighed sample of sodium chloride was added to the reaction flask; (4) when a mixed

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[1] (a) Abstracted from a thesis submitted by Irving L. Mador to the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (b) Presented in part at the Atlantic City Meeting of the American Chemical Society, September, 1949.

[2] M. Ritchie, *J. Chem. Soc.*, **139**, 3112 (1931).

[3] F. H. Westheimer, W. A. Jones and R. A. Lad, *J. Chem. Phys.*, **10**, 478 (1942).

[4] L. F. Fieser, "Experiments in Organic Chemistry," 2nd edition, D. C. Heath and Co., New York, N. Y., 1941, p. 368.

solvent was employed, the appropriate volume of organic solvent required to bring the mixture to the desired dielectric constant was added from a buret; (5) the reaction flask with its contents was placed in the thermostat and allowed to come to temperature equilibrium; (6) the vial containing the potassium ethyl malonate was dropped into the reaction flask and the flask was swirled to hasten solution of the sample.

At suitable time intervals, samples were withdrawn by a pipet and released into a weighed excess of standard hydrochloric acid (0.02843 *N*). This weight was corrected to vacuum and converted to volume, assuming the density of the acid to be the same as that of water. Since the hydrochloric acid was standardized by a similar procedure making the same assumption, no error was introduced by the fact that its density would actually be slightly different from that of water. The solution was back-titrated with standard sodium hydroxide (0.00785 *N*) to an end-point at a *p*H of 9.0. A mixed indicator of phenolphthalein and thymol blue was used.[5] The volume of standard alkali was corrected by a blank depending on the final total volume of the solution. Through use of data obtained in the above fashion, the normality of each sample was calculated.

The wt. % of dioxane[6a] and of *t*-butyl alcohol[6b] corresponding to any specified dielectric constant at each temperature in a water mixture was taken from the work of Åkerlöf.

The densities of dioxane and of *t*-butyl alcohol were taken from the literature.[7,8] These values were used in transforming weight data to volume data.

Calculations and Discussion

Evaluation of Rate Constants.—Table I gives the time–concentration data at 5.37° for the reaction in water only. The *k*'s were calculated by use of the equation for a second order reaction where both reactants have the same concentration in moles per liter, namely

$$\frac{1}{C_2} - \frac{1}{C_1} = k(t_2 - t_1) \qquad (2)$$

A pair of consecutive samples for a run was used in each calculation of *k*.

The ionic strength for this reaction can be expressed by the equation

$$\mu = x + 2C_0 \qquad (3)$$

where x is equal to the amount of material in moles per liter which has reacted and C_0 is the initial concentration of a reactant. (Both reactants were present initially in equal concentrations.) If a uni-univalent electrolyte is added, then the ionic strength is expressed by the equation

$$\mu = x + 2C_0 + S \qquad (4)$$

where S is equal to the concentration of salt in moles per liter. Since each value of *k* corresponds to an ionic strength range, the mean value of the ionic strength for two consecutive samples is given in the third column of Table I.

The values of the limiting velocity constant ($k°$) at $\sqrt{\mu} = 0$ were obtained by means of the equation[9]

$$\ln k = \ln k° + \frac{2Z_AZ_BA\sqrt{\mu}}{1 + \beta a_i\sqrt{\mu}} \qquad (5)$$

TABLE I

DATA IN WATER AT 5.37°, *D* 86.12

Time, min.	Normality	$\sqrt{\mu_{\text{mean}}}$	*k*, liter/mole-min.	*k*°, liter/mole-min.
	Run 1 Initial *N* 0.01499			
5.25	0.01436	....	...	...
23.08	.01342	0.1763	0.274	0.200
59.72	.01184	.1798	.271	.197
141.72	.009357	.1853	.273	.197
	Run 2 Initial *N* 0.01656			
31.03	0.01430	....	...	...
63.48	.01265	0.1903	0.281	0.202
129.08	.01026	.1955	.282	.201
192.07	.008643	.2005	.289	.205
	Run 3 Initial *N* 0.01507, NaCl *N* 0.1709			
8.55	0.01411	....	...	...
32.10	.01258	.04503	0.364	0.200
83.03	.01019	.4524	.366	.201
241.53	.006376	.4558	.370	.202
	Run 4 Initial *N* 0.01588, NaCl *N* 0.3278			
5.93	0.01506	....	...	...
33.05	.01298	0.6011	0.393	0.195
76.05	.01064	.6030	.393	.195
139.10	.008402	.6050	.397	.196
			k° av.	0.199

On substituting the proper values of all constants, equation 5 becomes

$$\log k° = \log k - \frac{3.647 \times 10^6\sqrt{\mu}}{(DT)^{3/2} + 5.028 \times 10^9 a_iDT\sqrt{\mu}} \qquad (6)$$

By trial and error, a value of a_i was determined by use of equation 6 which gave the most consistent values of *k*° from the *k* values over a large ionic strength range. In water and in the dioxane–water mixtures, the same value of a_i, *i. e.*, 4.8 Å., was found to fulfill the above criterion. In the case of *t*-butyl alcohol–water mixtures, the best value of a_i was 4.3 Å. The last column of Table I lists the *k*° values in water at 5.37° obtained from the data at various ionic strengths.

The average values of the limiting velocity constant (*k*°) for all of the runs obtained by the above method are given in Table II.

The advisability of using velocity constants based on mole fraction concentrations instead of volume concentrations has been pointed out by Scatchard.[10] For a second-order reaction taking place in a pure solvent, the rate constant (k_c) in terms of volume concentrations can be changed

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[5] F. Welcher, "Chemical Solutions," D. Van Nostrand Co., Inc., New York, N. Y., 1942, p. 177.

[6] (a) G. C. Åkerlöf, THIS JOURNAL, **58**, 1241 (1936); (b) **54**, 4125 (1932).

[7] F. Hovorka, R. A. Schaefer and D. Dreisbach, *ibid.*, **58**, 2264 (1936).

[8] J. Timmermans and Y. Delcourt, *J. chim. phys.*, **31**, 82 (1934).

[9] (a) G. Scatchard, *Chem. Revs.*, **10**, 229 (1932); (b) E. S. Amis, "Kinetics of Chemical Change in Solution," The Macmillan Co., New York, N. Y., 1949, Chapter IV.

[10] G. Scatchard, *J. Chem. Phys.*, **7**, 657 (1939); *Ann. N. Y. Acad. Sci.*, **39**, 341 (1940).

TABLE II

SUMMARY OF RATE CONSTANTS BASED ON VOLUME CONCENTRATIONS IN LITERS/MOLE-MIN.

Temp., °C. →	Dioxane-water								t-Butyl alcohol-water
	5.37		15.01		25.08		34.94		25.08°
Solvent	$k°$	k $\sqrt{\mu} = 0.2$	$k°$	k $\sqrt{\mu} = 0.2$	$k°$	k $\sqrt{\mu} = 0.2$	$k°$	k $\sqrt{\mu} = 0.2$	$k°$
H_2O	0.199	0.281	0.403	0.572	0.807	1.153	1.53	2.20	0.807
DC 60	.1142	.201	.244	.419	.513	0.859	1.002	1.64	.547
DC 55	.0963	.182	.209	.384	.441	.788	0.877	1.53	.484
DC 50	.0808	.167	.177	.354	.374	.725	.755	1.421	.448
27.57 wt. %	.1142	.201	.222	.397	.431	.781	.789	1.454	

The above temperatures were actual temperatures used. Throughout the paper these values are referred to as 5, 15, 25 and 35°.

to the rate constant (k_N) in terms of mole fractions by use of the equation

$$k_N = 1000 d k_0 / M \qquad (7)$$

where d is the density and M is the molecular weight of the solvent. For mixed solvents, the equation is

$$k_N = 1000\, \Sigma n\, k_0 / V \qquad (8)$$

where Σn is the total number of moles of solvent and V is the volume of the solution in milliliters. The rate constants at zero ionic strength listed in Table II were corrected to mole fraction rate constants and the results are given in Table III.

TABLE III

SUMMARY OF RATE CONSTANTS BASED ON MOLE FRACTION CONCENTRATIONS AT ZERO IONIC STRENGTH

Temp., °C. →	Dioxane-water				t-Butyl alcohol-H_2O
	5.37	15.01	25.08	34.94	25.08°
Solvent	k_N^0	k_N^0	k_N^0	k_N^0	k_N^0
H_2O	11.04	22.3	44.7	84.3	44.7
DC 60	5.00	11.01	24.1	47.9	23.9
DC 55	4.00	8.95	19.7	39.8	19.8
DC 50	3.18	7.17	15.6	32.4	17.0
27.57 wt. %	5.00	9.71	18.8	34.3	

Reference to Tables II and III shows agreement between the rate constants obtained in dioxane–water and in t-butyl alcohol–water media at the higher dielectrics when mole fraction concentration units are used. Such an agreement is not obtained on using volume concentration units. These results thus favor Scatchard's argument.

Order and Salt Effects.—Experiments were carried out in which the ester:alkali ratio was two to one, and two to three. The $k°$ values obtained in these experiments were in agreement with the values obtained in experiments where the ratio was one to one, showing a true second order reaction.

Figure 1 shows a plot of log k against $\sqrt{\mu}$ for part of our data. The positive primary salt effect observed is characteristic of a reaction between ions of like charge. The average values of $k°$ (shown as filled circles) are consistent with an extrapolation of the k values to zero ionic strength. It is evident that the distance of extrapolation is too great for the accurate graphical evaluation of $k°$. Limiting slopes (dotted lines), equal to $3.647 \times 10^6/(DT)^{3/2}$, have been drawn at the $k°$ points. It is evident that the limiting law, namely

$$\log k° = \log k - [3.647 \times 10^6 \sqrt{\mu}/(DT)^{3/2}] \qquad (9)$$

is applicable for only a small ionic strength range.

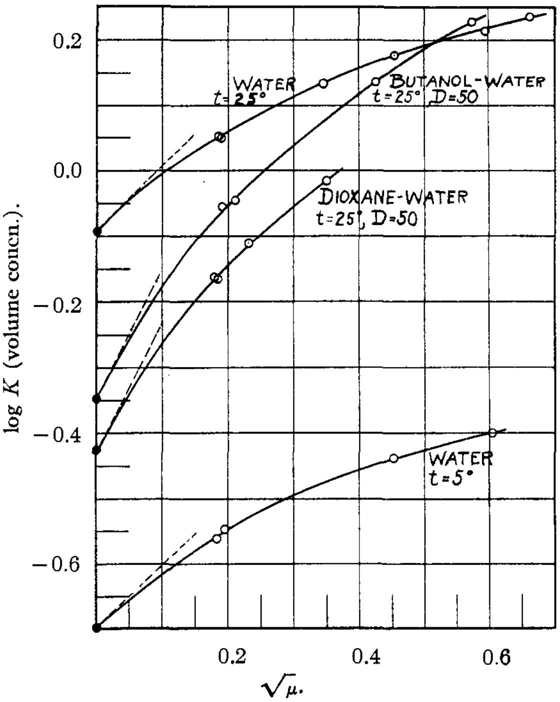

Fig. 1.—Influence of ionic strength on the rate of the alkaline hydrolysis of monoethyl malonate ion.

Activation Energies at Zero Ionic Strength.—Activation energies in water and in dioxane–water mixtures were calculated in the temperature intervals, 5–15°, 15–25° and 25–35°, by means of the integrated Arrhenius equation

$$\log \frac{k_2°}{k_1°} = \frac{E°}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (10)$$

The results were constant over the temperature range investigated within the precision of the measurements (± 1% of $k°$ values). The mean activation energies, based on volume concentration and on mole fraction $k°$'s are listed in the second and third columns of Table IV.

TABLE IV

ACTIVATION ENERGIES IN DIOXANE–WATER MIXTURES AT 25°

	Experimental				Calcd. by eq. 13
Solvent	$E°$ (kcal.) vol. concn. $\sqrt{\mu} = 0$	$E°$ (kcal.) mole fract. $\sqrt{\mu} = 0$	E (kcal.) vol. concn. $\sqrt{\mu} = 0.2$	$(E° - E_{\sqrt{\mu}=0.2})$ (cal.) vol. concn.	$(E° - E_{\sqrt{\mu}=0.2})$ (cal.) vol. concn.
H_2O	11.75 ± 0.08	11.72 ± 0.09	11.86 ± 0.10	−100	−110
D.C. 60	12.52 .12	13.02 .30	12.10 .12	400	420
D.C. 55	12.73 .08	13.24 .22	12.26 .08	500	470
D.C. 50	12.88 .20	13.39 .21	12.35 .20	500	530
27.57 wt. %	11.15 .12	11.10 .11	11.41 .16	−300	−260

It is apparent from these data that $E°_{\text{isodielectric}} > E^{x}_{\text{isocomposition}}$. This is in accord with theory[11] for a reaction between ions of like sign. The equation, derived[11] by Svirbely and Warner, namely

$$E°_{\text{isocomposition}} = E^{x}_{\text{isodielectric}} + 2.303RT^2\left(\frac{\partial \log k°}{\partial D}\right)_T \frac{dD}{dT} \quad (11)$$

was tested. In Fig. 2, log $k°$ values are plotted against $100/D$ on both a volume concentration and a mole fraction scale. From each graph, the value of $(\partial \log k°/\partial(1/D))_T$ was obtained at a dielectric constant corresponding to that of the isocomposition media. Since

$$\left(\frac{\partial \log k°}{\partial D}\right)_T = \frac{-1}{D^2}\left(\frac{\partial \log k°}{\partial 1/D}\right)_T$$

and since values of dD/dT are obtainable in the literature[6a] for dioxane–water mixtures, values of $E°_{\text{I.C}} - E°_{\text{I.D.}}$ can be calculated at any specified temperature by means of equation 11. The results, based on both concentration scales, are given as $(E°_{\text{I.C.}} - E°_{\text{I.D.}})_{\text{calcd.}}$ in Table V (Rows 1 and 3). In obtaining the data recorded as $(E°_{\text{I.C.}} - E°_{\text{I.D.}})_{\text{Exp.}}$ in Table V (Rows 2 and 4), the value of $E°_{\text{I.D.}}$ was determined at a dielectric value corresponding to that of the isocomposition media. In the case of water as the isocomposition media, this procedure corresponds to the extrapolation of an $E°_{\text{I.D.}}$ *versus* $1/D$ plot to a $1/D$ value of the same magnitude as actually exists in water at 25°. For the 27.57 wt. % mixture, the desired $E°_{\text{I.D.}}$ value could be interpolated from the experimental data.

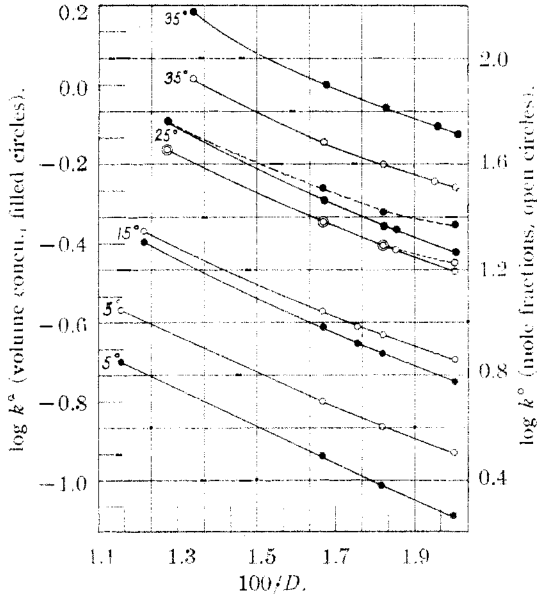

Fig. 2.—Influence of dielectric constant on the reaction rate at zero ionic strength. Solid and dotted curves represent data in dioxane–water and butanol–water media, respectively.

TABLE V

ACTIVATION ENERGY DIFFERENCES IN CALORIES AT 25° IN ISOCOMPOSITION AND ISODIELECTRIC MEDIA

		Isocomposition media	
	Concn. scale	Water	27.57 wt. % dioxane-water
$(E°_{\text{I.C.}} - E°_{\text{I.D.}})_{\text{calcd.}}$	Volume	−1480	−1640
$(E°_{\text{I.C.}} - E°_{\text{I.D.}})_{\text{exptl.}}$	Volume	− 360	−1590
$(E°_{\text{I.C.}} - E°_{\text{I.D.}})_{\text{calcd.}}$	Mole fraction	−2290	−2130
$(E°_{\text{I.C.}} - E°_{\text{I.D.}})_{\text{exptl.}}$	Mole fraction	− 870	−2140
$(E°_{\text{I.C.}} - E°_{\text{I.D.}})_{\text{calcd.}}$	Volume	−1000	
$(E°_{\text{I.C.}} - E°_{\text{I.D.}})_{\text{calcd.}}$	Mole fraction	−1300	

The agreement between the experimental and calculated values of $(E°_{\text{I.C.}} - E°_{\text{I.D.}})$ is excellent for the 27.57 wt. % mixture. It is not satisfactory when water is the isocomposition media. Better agreement is obtained in the latter case if one assumes that the value of

$$\left(\frac{\partial \log k°}{\partial 1/D}\right)_T$$

is constant and that the slope obtained at the lower dielectrics is the true value. A recalculation of $(E°_{\text{I.C.}} - E°_{\text{I.D.}})$ for water now leads to the results in the last two rows of Table V for the two different concentration scales.

Reference to Table IV shows that the conversion of $k°$ values from volume concentrations to mole fraction units has little effect on the activation energies in isocomposition media. This is in agreement with previous work on the ammonium cyanate reaction.[12] However, there is considerable difference in the activation energies based on the two different concentration scales in isodielectric media. It should be noted, however, that the agreement between the values

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(11) W. J. Svirbely and J. C. Warner, THIS JOURNAL, **57**, 1883 (1935).

(12) W. J. Svirbely and S. Peterson, *ibid.*, **65**, 166 (1943).

of activation energy obtained by using these two concentration scales in isocomposition media may have no real significance. The conversion factors used in converting the $k°$ values from volume concentration to mole fraction units change in isocomposition media with temperature only to the extent that the densities change. In isodielectric media, the composition, and thus the conversion factor, changes markedly with temperature.

Effect of Solvent on the Rate at Zero Ionic Strength.—Scatchard's theory[9a] of the effect of solvent, in so far as the dielectric constant is concerned, yields the relation

$$\left(\frac{\partial \log k°}{\partial\, 1/D}\right)_T = \frac{-e^2 Z_A Z_B}{2.303 r T k} \qquad (12)$$

For a reaction between ions of like sign, a plot of log $k°$ against $1/D$ should be a straight line with a negative slope. By means of equation 12 and the experimental slope obtained from such a plot (Fig. 2), it is possible to calculate r, the radius of the complex. Such results are summarized in Table VI. In the calculations, the slopes of the curves at the points corresponding to the dielectric constants of water and of 27.57 wt. % of dioxane–water mixtures were used. The order of magnitude of the radii are not unreasonable. The mode of change of the radii with temperature for both concentration scales is anomalous in as much as the radii decrease with increasing temperature in water but increase with increasing temperature in 27.57 wt. % dioxane–water mixtures.

As mentioned above, from theory the plot of log $k°$ *vs.* $1/D$ should be linear. The lines connecting the points at dielectrics 50, 55 and 60 in dioxane–water mixtures are relatively straight. When the lines are extended to include the water data, considerable curvature results, particularly at the higher temperatures. Such behavior is not compatible with the concept of salting out since in a mixture of water with a solvent of low dielectric constant the molecules of water should be preferentially oriented around the ions. Any change in the nature of the solvation should thus take place at the lower dielectrics. On the other hand, the behavior of the *t*-butyl alcohol–water curves (Fig. 2) could be explained by the salting out concept. We are unable to explain the increase in the curvature of these plots at the higher temperatures.

Effect of Ionic Strength on Activation Energies.—By use of equation 6 and the $k°$ values of Table II, values of k at $\sqrt{\mu} = 0.2$ have been calculated. These results are also given in Table II. For a few cases, the calculated values of k were checked with graphical values obtained from a log k *vs.* $\sqrt{\mu}$ plot. The agreement is good.

Experimental activation energies at $\sqrt{\mu} = 0.2$ were calculated by use of equation 10. The results are given in the 4th column of Table IV. On differentiating equation 6 with respect to temperature and multiplying throughout by $2.303RT^2$, one obtains[11] an equation relating the energies of activation at a fixed ionic strength and at zero ionic strength, namely

$$E_\mu = E° - 8.398 \times 10^6 \sqrt{\mu}\, RT^2 \left[\frac{3/2(DT)^{1/2} + 5.028 \times 10^9 a_1\sqrt{\mu}}{(DT)^{3/2} + 5.028 \times 10^9 a_i\sqrt{\mu}DT}\right]\left[D + T\frac{\mathrm{d}D}{\mathrm{d}T}\right] \qquad (13)$$

By use of equation 13, $(E° - E_{\sqrt{\mu}=0.2})_{\text{calcd.}}$ values were obtained and are recorded in the last column of Table IV. The values of $(E° - E_{\sqrt{\mu}=0.2})_{\text{exptl.}}$, recorded in the fifth column of Table IV, were obtained by subtracting the appropriate values of the activation energies listed in Table IV. The agreement between theory and experiment is better than could have been anticipated. Furthermore, it is observed that $E\mu > E°$ is isocomposition media, while $E\mu < E°$ is isodielectric media. These observations are in accord with theory[11] for a reaction between ions of like sign.

TABLE VI

RADIUS OF THE INTERMEDIATE COMPLEX IN Å.

	Water		27.57 wt. % dioxane-water	
Temp., °C.	Vol. concn.	Mole fraction concn.	Vol. concn.	Mole fraction concn.
5.37	4.61	2.92	5.83	4.34
15.01	4.33	2.83	5.90	4.60
25.08	4.01	2.59	5.92	4.56
34.94	2.87	1.95	6.81	4.91

Thermodynamic Activation Values.—The free energy and the entropy of activation at zero ionic strength, based on both volume concentration and mole fraction units, were calculated at 25° in dioxane–water mixtures by use of the equations[13]

$$\Delta F° = 2.3RT\,(\log\,(RT/Nh) - \log k°) \qquad (14)$$

$$\Delta S° = 2.3R\,(\log A - \log\,(eRT/Nh)) \qquad (15)$$

These values, as well as the values of the energies of activation and the Arrhenius frequency factor (log A) are given in Table VII. The various thermodynamic quantities of activation may be evaluated at zero ionic strength and at infinite dielectric constant by use of equations obtained by La Mer,[14] namely

$$\Delta F° = \Delta F_0 + \Delta F_D \qquad (16)$$

$$E° = \Delta E_0 + \Delta E_D \qquad (17)$$

$$\Delta S° = \Delta S_0 + \Delta S_D \qquad (18)$$

$$\Delta F_D = \frac{Z_A Z_B e^2 N}{D(r_A + r_B)} \qquad (19)$$

$$\Delta E_D = \Delta F_D\left(1 + \frac{T}{D}\frac{\partial D}{\partial T}\right) \qquad (20)$$

$$\Delta S_D = \frac{\Delta F_D}{D}\frac{\partial D}{\partial T} \qquad (21)$$

In calculating the values of ΔF_D by means of equation 19 the values of $(r_A + r_B)$ for water and 27.57 wt. % dioxane–water mixtures were taken from Table VI. The values of $(r_A + r_B)$ for the

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[13] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 195-199.

[14] V. K. La Mer, *J. Franklin Inst.*, **225**, 709 (1938).

TABLE VII

SUMMARY OF THERMODYNAMIC ACTIVATION DATA IN DIOXANE–WATER MIXTURES AT 25°

					$D = \infty$			
Solvent	log A exptl.	$E°$ exptl. cal.	$\Delta F°$ eq. 14 cal.	$\Delta S_{\ne}°$ eq. 15 (cal./°/mole)	ΔF_0 eq. 16 (cal.)	ΔE_0 eq. 17 (cal.)	ΔS_0 eq. 18 (cal./°/mole)	$r_A + r_B$, Å.
			Volume concentrations, $\sqrt{\mu} = 0$					
H_2O	8.509	11,750	20,000	−29.7	18,940	12,160	−24.8	4.01
					19,280	12,030	−26.3	5.92
DC 60	8.876	12,520	20,270	−28.0	19,330	11,590	−28.0	5.92
DC 55	8.964	12,730	20,350	−27.6	19,330	11,710	−27.6	5.92
DC 50	9.002	12,880	20,450	−27.5	19,330	11,760	−27.5	5.92
27.57 wt. %	7.797	11,150	20,370	−33.0	19,330	11,760	−27.5	5.92
			Mole fraction concentrations, $\sqrt{\mu} = 0$					
H_2O	10.231	11,720	17,620	−21.8	15,990	12,360	−14.1	2.59
					16,690	12,080	−17.4	4.56
DC 60	10.914	13,020	17,990	−18.7	16,770	11,810	−18.7	4.56
DC 55	10.988	13,240	18,100	−18.4	16,780	11,920	−18.4	4.56
DC 50	10.993	13,390	18,250	−18.4	16,790	11,940	−18.4	4.56
27.57 wt. %	9.401	11,100	18,130	−25.6	16,780	11,870	−18.4	4.56
			Volume concentrations, $\sqrt{\mu} = 0$					
						eq. 22	eq. 23	
H_2O	8.745	11,860	19,790	−28.6	....	12,000	−26.6	5.92

isodielectric mixtures were assumed to be the same as for the 27.57 wt. % mixture.[15] The results of the calculations are summarized in Table VII. The values of ΔF_0, ΔE_0 and ΔS_0 should be independent of solution composition. This is the case within experimental error in the isodielectric mixtures and the 27.57 wt. % mixture. However, the constancy in these thermodynamic quantities is not upheld when water is the solvent. By using the same value of $(r_A + r_B)$ when water is the solvent as was used in the other mixtures, the thermodynamic quantities obtained in water as the solvent are brought into better agreement with the values obtained in the other mixtures. This is also shown in Table VII.

At a fixed ionic strength, equations 17 and 18 become[14]

$$E_\mu = \Delta E_0 + \Delta E_D + \Delta E_{IN} \qquad (22)$$

$$\Delta S_\mu = \Delta S_0 + \Delta S_D + \Delta S_{IN} \qquad (23)$$

The contribution of the ionic atmosphere to the energy and entropy of activation in water may be calculated by the equations[16]

$$\Delta E_{IN}/2.3RT = 0.52\, Z_A Z_B \sqrt{\mu} \qquad (24)$$

$$\Delta S_{IN}/2.3R = 1.53\, Z_A Z_B \sqrt{\mu} \qquad (25)$$

The values of ΔE_0 and ΔS_0 obtained by use of equations 22 through 25 are listed in the last row of Table VII. It is apparent that the contribution of the ionic atmosphere to the energy and entropy of activation is satisfactorily accounted for by equations 24 and 25.

Comparison with Collision Theory.—In the absence of salt effects, the Christiansen–Scatchard equation[9a] may take[14] the form

$$\log k° = \log k_\infty - \frac{Z_A Z_B e^2 N}{2.3RDT} \frac{1}{(r_A + r_B)} \qquad (26)$$

In equation 26, log k_∞ signifies the rate constant extrapolated to infinite dielectric constant. Using La Mer's[16] method for testing the collision theory in terms of the thermodynamic theory, one calculates σ_0, the distance of nearest approach between the centers of the reactants for an effective collision between uncharged gas molecules, by means of the equation[17]

$$\log \sigma_0 = {}^1/_2 \log k_\infty - 13.933 + (\Delta E_0/2730) \qquad (27)$$

the log k_∞ values being obtained through use of equation 26, $(r_A + r_B = 5.92$ Å.). The σ_0 values obtained through use of equation 27 varied from 0.048 to 0.032 Å. in the water–dioxane mixtures. It is evident that the collision theory is not in satisfactory agreement with the thermodynamic treatment.

Concentration Scales.—For the comparison of rate constants at a given dielectric constant and temperature, but in different media, mole fraction units are necessary. This is shown by comparison of the data in the *t*-butyl alcohol–water and dioxane–water media. For the experimental activation energy and the thermodynamic quantities, while the numerical values are dependent on the concentration scale employed, in both cases the values are not unreasonable. In these cases the data do not show that mole fraction units are preferable as they would appear to be on theoretical grounds.

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[15] Reference to Fig. 2 shows that the slope of each curve is essentially the same in the dielectric range which includes the 27.57 wt. % mixture and the three isodielectric mixtures. This implies constancy in the $(r_A + r_A)$ values.

[16] E. S. Amis and V. K. La Mer, THIS JOURNAL, 61, 905 (1939).

[17] A. Chatenever and C. V. King, *ibid.*, 71, 3587 (1949). Our equation 27 differs from equation 14 of this reference in the term 13.933. This is because the molecular weights of our reactants are 131 and 17.

Summary

1. The kinetics of the alkaline hydrolysis of potassium ethyl malonate has been studied over a temperature range 5 to 35° in two isocomposition media, water and 27.57 wt. % dioxane in water; in three isodielectric dioxane–water mixtures corresponding to dielectric constants of 50, 55 and 60; and at 25° in three isodielectric *t*-butyl alcohol–water mixtures at the above dielectric values.

2. A positive primary salt effect has been found, which is in accord with the mechanism postulated for the reaction.

3. The distance of closest approach of the reacting ions is shown to be 4.8 Å. in water and in the dioxane–water mixtures. It is shown to be 4.3 Å. in the *t*-butyl alcohol–water mixtures.

4. A comparison is made between the use of volume concentration and mole fraction units for the expression of rate constants.

5. The energy of activation at zero ionic strength is greater in isodielectric media than in isocomposition media which is in accord with theory for a reaction between ions of like sign. Comparisons are made with theoretical calculations.

6. The effect of ionic strength upon the energy of activation is in excellent agreement with theory.

7. The influence of dielectric constant upon the rate constants is in good agreement with the Scatchard–Christiansen theory in dioxane–water mixtures.

8. Various thermodynamic activation values have been calculated. It is shown that the free energy of activation, energy of activation, and the entropy of activation, if calculated for $D = \infty$, are independent of solution composition.

9. It is shown that the simple collision theory and the thermodynamic treatment of La Mer are not in agreement for this reaction.

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Hydrolysis of Ethyl Silicate*

BY R. AELION, A. LOEBEL AND F. EIRICH

The hydrolysis of ethyl silicate is used in industrial applications as a convenient process for obtaining an adhesive type of silica. Hydrolysis will occur readily in the presence of acidic or basic catalysts, but due to the immiscibility of water and ethyl silicate, a mutual solvent is often used to obtain homogeneous reaction. A great deal of attention has been focussed on the development of the most convenient methods of obtaining the right degree of conversion of ethyl silicate to silica. For example, diagrams of solubilities of ternary mixtures of water, ethyl silicate and mutual solvent have been determined,[1] and special commercial processes for hydrolysis have been developed.[2] Quantitative information on the rate of hydrolysis of ethyl silicate in acidic and basic media and on the stability of hydrolysis products to gel formation is, however, still very scant.[3] The purpose of the work described in this paper was the collection of quantitative information regarding the rate of ethyl silicate hydrolysis, and the formulation of a possible reaction mechanism.

The over-all hydrolysis of ethyl silicate and the subsequent dehydration of the product formed may be formulated as

$$n\mathrm{Si(OC_2H_5)_4} + 4n\mathrm{H_2O} \longrightarrow n\mathrm{Si(OH)_4} + 4n\mathrm{C_2H_5OH} \qquad (1a)$$

$$n\mathrm{Si(OH)_4} \longrightarrow \mathrm{(SiO_2)}_n + 2n\mathrm{H_2O} \qquad (1b)$$

Depending on conditions, one or both of these consecutive reactions may only go to partial completion, leaving ethoxy or hydroxyl groups unreacted. The changes with time in the following quantities were experimentally determined: (1) The total loss of water, L_T, equal to the difference between the water taken up by the hydrolysis and the water regenerated by dehydration. (2) The production of alcohol, L_H, equivalent to the amount of water used in the hydrolysis reaction. (3) The degree of conversion of monomer.

Expressing L_T and L_H in moles per mole of ethyl silicate, a simple equation relates these two quantities at any stage of the reaction

$$L_T = L_H - aL_H/2 \qquad (2)$$

where a is the degree of completion of the dehydration reaction.

By determination of L_H and L_T the rate and extent of both reactions and therefore the number of unreacted ethoxy and hydroxyl groups can be calculated. The average composition of the polyethoxysiloxanes formed is then obtained by evaluating the degree of conversion of the monomer.

Experimental

Titration with Karl Fischer reagent[4] allows the instantaneous determinations of water content. This method

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[*] Taken in part from a thesis in preparation by M. Arnold Loebel for presentation to the Graduate School of the Polytechnic Institute of Brooklyn for the degree of Doctor of Philosophy in Chemistry.

(1) H. D. Cogan and C. A. Setterstrom, *Chem. Eng. News*, **24**, 2499 (1946); *Ind. Eng. Chem.*, **39**, 1364 (1947).

(2) C. Shaw and J. E. Hackford, *Ind. Chem.*, **21**, 130 (1945); **22**, 61 (1946); **22**, 1230 (1946).

(3) G. King, *J. Oil and Colour Chem. Assoc.*, **13**, 116 (1930).

(4) J. Mitchell and D. M. Smith, "Chemical Analysis," Vol. 5, Aquametry, Interscience Publishers, New York, N. Y., 1948, Chap. 4.