TABLE I

τ AS A FUNCTION OF K AND α

$1/K \downarrow$	$\alpha \rightarrow 0.9$	0.8	0.7	0.6	0.5	0.4	0.3	0.2
1.4	0.1105	0.2470	0.4212	0.6475	0.9710	1.438	2.223	3.800
1.5	.1110	.2500	.4286	.6667	1.000	1.500	2.3333	4.000
1.6	.1117	.2530	.4370	.6845	1.033	1.560	2.442	4.205
1.7	.1121	.2560	.4450	.7010	1.064	1.620	2.550	4.405
1.8		.2590	.4523	.7177	1.0985	1.682		
1.9		.2615	.4604	.7343	1.128	1.743		
2.0		.2642	.4669	.7494	1.1609	1.802		

If $P > q$, then

$$\int \frac{x^P \mathrm{d}x}{ax^q - 1} = \frac{1}{a(P - q + 1)} x^{P-q+1} + \frac{1}{a} \int \frac{x^{P-q}}{ax^q - 1} \mathrm{d}x \tag{26}$$

The integral on the right side of equation 26 is of the general form

$$\int \frac{x^s \mathrm{d}x}{ax^\eta - b}$$

where $\eta > S$. The solution[4] for this general integral is

$$\int \frac{x^s \mathrm{d}x}{ax^\eta - b} = \frac{1}{b} \left(\frac{b}{a}\right)^{s + 1/\eta} \int \frac{y^s \mathrm{d}y}{y^\eta - 1} \text{ with } y = \sqrt[\eta]{\frac{a}{b}}\, x \tag{27}$$

$$\int \frac{y^s \mathrm{d}y}{y^\eta - 1} = \frac{1}{\eta} \ln (y - 1) + \frac{(1 - j)(-1)^{s+1}}{\eta} \ln (y + 1) + \frac{2}{\eta} \sum_{\nu=1}^{r-1} \left[R_\nu \cos \frac{2\nu(s + 1)\pi}{\eta} - S_\nu \sin \frac{2\nu(s + 1)\pi}{\eta}\right] + C$$

with

$\eta = 2r - j;\ j = 0 \text{ or } 1;\ \eta > 2;\ s = 0,1 \cdots \eta - 1$

$$R_\nu = \frac{1}{2} \ln \left[y^2 - 2y \cos \frac{2\nu\pi}{\eta} + 1\right];$$

$$S_\nu = \text{arc tg} \left[\frac{y - \cos \frac{2\nu\pi}{\eta}}{\sin \frac{2\nu\pi}{\eta}}\right] \tag{28}$$

Tables of calculated values can be prepared for Case II in an analogous manner to Case I.

Case III. Solution Only.—For $K = 2/3$, *i.e.*, $k_1 = 3/2\, k_2$

$$\tau = \left(\frac{1}{\alpha} - 1\right) \text{ and } \alpha = \beta^{1/3} \tag{29}$$

The application of the data in Table I will be demonstrated in a later paper.

COLLEGE PARK, MARYLAND

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

The Kinetics of the Alkaline Hydrolysis of 1,3,5-Tri-(4-carbomethoxyphenyl)-benzene[1]

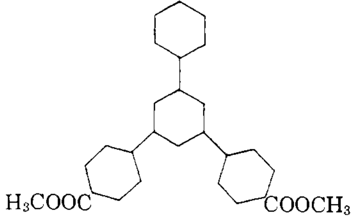
BY W. J. SVIRBELY AND HAROLD E. WEISBERG

RECEIVED JULY 28, 1958

The compounds 1,3,5-tri-(4-carbomethoxyphenyl)-benzene, (4-carbomethoxyphenyl) (4-carbomethoxy-β-methyl-styryl) ketone, 1,3,5-tri-(4-carboxyphenyl)-benzene and 1,3-di-(4-carboxyphenyl)-5-(4-carbomethoxyphenyl)-benzene disodium salt have been prepared. The three step alkaline hydrolysis of 1,3,5-tri-(4-carbomethoxyphenyl)-benzene has been studied in dioxane–water mixtures over a temperature range. The three rate constants have been determined in isocomposition and isodielectric media using a procedure developed for the determination of the rate constants for a three-step consecutive-competitive second-order reaction involving a symmetrical molecule where there is no interaction among the reaction sites. The rate constant of the third step was also determined independently by the alkaline hydrolysis of the monoester ion and it was in good agreement with the result obtained in the three-step case. The various thermodynamic activation values have been calculated in isocomposition and isodielectric media. The data have been examined statistically for their significance and a statistical adjustment of data analysis supports the conclusion that the rate constants are in the statistical ratio $k_1:k_2:k_3 = 3:2:1$. We concluded that not only are the succeeding steps of the reaction independent of each other but that each step behaves like a dipole–dipole reaction probably because of ion-association effects in our low dielectric media.

Introduction

Recently,[2] the kinetics of three-step competitive-consecutive second-order reactions was investigated mathematically in terms of general variables which in principle would apply to any reaction of that kinetic type. However, the labor involved in making the computations so that the resulting tables would be generally applicable was too involved. So, for the sake of convenience and instruction, the resulting equation was solved for the case of a reaction where $k_2 = 2k_3$ in which k_2 and k_3 are the rate constants for the second and third steps of the three-step reaction. In this paper we shall report on an application of the above analysis to the alkaline hydrolysis of 1,3,5-tri-(4-carbomethoxyphenyl)-benzene, a triester whose structural formula is



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[1] (a) Abstracted from a thesis submitted by Harold E. Weisberg 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 Chicago Meeting of the American Chemical Society, September, 1958.

[2] W. J. Svirbely, THIS JOURNAL, **81**, 255 (1959).

Preliminary Discussion

Assuming the validity of a mathematical relation[3,4] between the rate constants involved in the alkaline hydrolysis of a symmetrical diester, we can write analogous relationships for the case of a symmetrical triester, namely

$$\frac{k_1}{k_2} = \frac{3}{2}\, e^{\epsilon^2/\mathfrak{D}\kappa T r} \tag{1}$$

and

$$\frac{k_2}{k_3} = 2\, e^{\epsilon^2/\mathfrak{D}\kappa T r} \tag{2}$$

in which k_1, k_2 and k_3 are the rate constants for steps 1, 2 and 3, respectively, in the reaction

$$\begin{aligned} &A + B \longrightarrow C + E \\ &A + C \longrightarrow D + E \\ &A + D \longrightarrow F + E \end{aligned} \tag{3}$$

where κ is Boltzmann's constant, $\mathfrak{D}$ is the dielectric constant of the solvent, ϵ is the electronic charge and r is the distance between the site of the charge on the ester ion and the point of attack of the hydroxyl ion. In our reaction A, B, C, D, F and E are the hydroxyl ion, triester [R-(COOR')$_3$], monovalent ion of the triester [R-(COOR')$_2$-COO$^-$], divalent ion of the triester [R-(COOR')-(COO$^-$)$_2$], trivalent ion of the triester [R-(COO$^-$)$_3$] and methanol, respectively. R and R' are the appropriate radicals as seen by reference to the structural formula of the triester.

Reference to equations 1 and 2 shows that as r increases the k_1/k_2 and k_2/k_3 ratios should approach the statistical values of 3/2 and 2, respectively. A scale drawing of our triester gave a value of r equal to 13.1 Å. If this value of r is large enough so that $k_2/k_3 = 2$, then equations 16, 17 and Table I of reference 2 would apply, regardless of the k_1/k_2 ratio. However, the symmetry of the triester makes the presumption of the condition $k_2/k_3 = 2$ tantamount to assuming also the collateral presumption of $k_1/k_2 = 3/2$, in which case equation 29 of reference 2 would apply, namely

$$\tau = \frac{1}{\alpha} - 1 \tag{4}$$

where $\alpha = A/A_0$, $\tau = B_0k_1t$ and $A_0 = 3B_0$. On substituting these definitions into equation 4, one obtains

$$\frac{A_0 - A}{A_0A} = \frac{k_2}{2}\,t \tag{5}$$

Thus we have the simple result that for a symmetrical triester in which the ester groups are far enough separated so as not to interact in any way, it should be possible to calculate from the data for a single run, all three rate constants by means of a plot of $(A_0 - A)/A_0A$ *vs.* t. The result should be a straight line of slope $k_1/3$, $k_2/2$ or k_3. It would be necessary only to set up the run in such a way that the initial concentrations were equivalent and to measure the decrease in hydroxyl ion concentration with time. The correctness of the over-all analysis can be checked by making an independent study of the last step of the reaction and comparing the rate constant obtained with the value resulting from the study of the over-all reaction carried out under the same environmental conditions.

TABLE I

DATA IN DIOXANE–WATER AT 34.98°; D = 9.07; A_0 = 9.345 × 10^{-3} MOLE/L.

Time (min.)	$A \times 10^3$, mole/l.	τ_0	α_0 (r_0 = 1.50)	$-\left(\frac{\partial \tau}{\partial \alpha}\right)_r$ (r_0 = 1.50)	$\left(\frac{\partial \tau}{\partial r}\right)_\alpha$
4.00	9.218				
10.13	8.376				
16.00	7.819	0.19180	0.8367	1.430	0.0180
21.33	7.209	.28031	.7790	1.640	.0382
27.70	6.693	.38609	.7162	1.945	.0733
34.20	6.227	.49403	.6675	2.232	.1103
47.45	5.465	.71406	.5825	2.955	.2025
70.33	4.492	1.09400	.4790	4.340	.3820
96.27	3.823	1.52476	.3955	6.395	.6180
142.68	2.849	2.29545	.3040	11.400	1.068
153.40	2.717	2.47346	.2890	13.740	1.170
219.40	2.018	3.56946	.2208	18.220	1.740

Materials and Apparatus

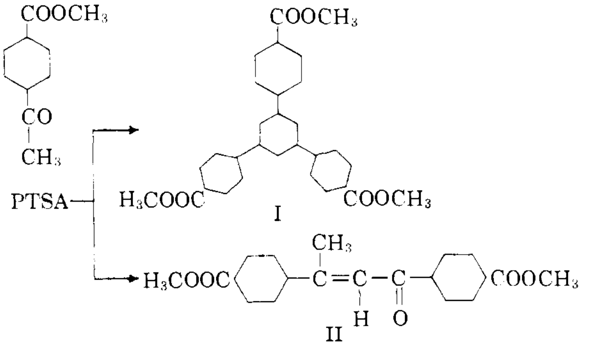
Dioxane.—Commercial dioxane was purified by a standard procedure.[5] It was continuously refluxed over sodium under a nitrogen atmosphere and some was freshly distilled off prior to each run.

Water.—Freshly distilled water through which nitrogen was bubbled for 24 hr. before use 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.

Hydrochloric Acid.—The acid solutions were standardized against the sodium hydroxide solutions. Phenolphthalein was used as the indicator throughout this research.

1,3,5-Tri-(4-carbomethoxyphenyl)-benzene.[6]—In the preparation of the triester a modification of the method developed by Pratt and his co-workers[7] for preparing 1,3,5-tri-(4-tolyl)-benzene was used. Starting with methyl *p*-acetylbenzoate, the reaction can be represented by



The procedure was as follows. A solution of 3.90 g. of *p*-toluenesulfonic acid monohydrate (0.02 mole) in 40 ml. of toluene was refluxed in a 250-ml. round bottom flask fitted with a Dean-Stark trap and condenser until all the water of hydration was removed. At this point, 10 g. of methyl *p*-

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(3) C. K. Ingold, *J. Chem. Soc.*, 1375 (1930).

(4) F. H. Westheimer and M. W. Shookhoff, THIS JOURNAL, **62**, 269 (1940).

(5) L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath & Co., New York, N. Y., 1941, p. 368.

(6) We gratefully acknowledge our indebtedness for the following: (a) The methyl *p*-acetylbenzoate for preparing the triester was a grant from the Monsanto Chemical Co. and was furnished by Mr. George F. Deebel. (b) The synthesis of the triester was performed by Dr. Mortimer J. Kamlet, Naval Ordnance Laboratory, White Oaks, Maryland. At his request, we are describing the synthesis in this paper. (c) Analyses of all compounds reported are due to Prof. Kathryn Gerdeman.

(7) G. Weiss, Thesis, University of Maryland, 1951.

acetylbenzoate was added and refluxing continued. Three additional 10.0 g. of the benzoate were added at two day intervals (0.225 mole total) and refluxing was continued for a total of ten days. The solution was cooled to 60° and 150 ml. of boiling methanol was added whereupon a solid separated which now was filtered off. Fractional precipitation from the mother liquor gave more solid. Two recrystallizations of the crude solid from ethyl acetate gave pale yellow crystals (A_1), (m.p. 241–242.5° uncor.). A third recrystallization from dioxane yielded white needles of the triester I (m.p. 244.5–245° cor.). The mother liquors from the original filtrations on further concentration yielded a yellow compound (B_1) which on two recrystallizations from methanol gave yellow needles of (4-carbomethoxyphenyl) (4-carbomethoxy-β-methyl-styryl) ketone (II) (m.p. 133.5–134.5° cor.). The procedure later was modified to increase the yield of compound I by adding methyl *p*-acetylbenzoate to compound II.

Calcd. for $C_{30}H_{24}O_6$ (I): C, 75.00; H, 5.00; O–CH_3, 19.38. Found: C, 75.00; H, 4.92; O–CH_3, 19.72. Calcd. for $C_{20}H_{18}O_5$ (II): C, 71.00; H, 5.33; O–CH_3, 18.34. Found: C, 71.37; H, 5.26; O–CH_3, 18.60.

In order to verify the distinction between compounds I and II and to prove the identity of I, additional tests were performed as follows: (1) dilute aqueous $KMnO_4$ solution had no action on a dioxane–water solution of I but oxidized II rapidly; (2) saponification equivalent in isopropyl alcohol for I gave 19.36% O–CH_3 and for II gave 18.30%; (3) the solution resulting from the saponification equivalent determination of I was acidified. A white crystalline solid was precipitated. The solid was recrystallized twice from dioxane (m.p. 325–325.5° cor.).

Calcd. for $C_{27}H_{18}O_6$ (III): C, 73.98; H, 4.11. Found: C, 73.99; H, 4.41. That compound III was 1,3,5-tri-(4-carboxyphenyl)-benzene was further verified by titration with standard sodium hydroxide. Equivalent weight was 145.8 (theory 146.0); (4) infrared spectra[8] determined on compressed pellets of substances I and II in KBr showed characteristic absorption bands for I and II at 1726, 1280 and 1096 cm.$^{-1}$ attributable[9] to aromatic ester groups. However, only the spectrum of II showed another band at 1685 cm.$^{-1}$ attributable[9] to the α,β-unsaturated carbonyl group.

From the saponification equivalent of I, it is estimated that the purity of this triester was 99.9 ± 0.1%.

1,3-Di-(4-carboxyphenyl)-5-(4-carbomethoxyphenyl)-benzene, Disodium Salt (IV).—3.0 g. (0.00624 mole) of I was dissolved in 250 ml. of dioxane and 20 ml. of water. 0.2875 g. (0.01248 mole) of sodium metal was dissolved in 35 ml. of methanol. At room temperature and with stirring the sodium methoxide solution was added dropwise to the ester solution. Two hundred and fifty ml. of dioxane was added and on standing overnight, a white crystalline precipitate settled out. The residue on filtration was washed with dioxane and extracted with methanol in a Soxhlet assembly for 8 hr. The extract was evaporated to dryness and the resulting residue was recrystallized twice from a methanol–water mixture. Saponification analysis was equivalent to 6.20% methoxyl. This corresponds to 99.2% purity based on IV above.

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

A chronometer which could be read easily to one second and which had been calibrated against the National Bureau of Standards time signals was used to observe times of sampling.

Procedure.—The reactions were carried out in a glass apparatus in which an atmosphere of nitrogen was continuously maintained. The required amount of dioxane to give the desired solvent mixture (based on amount of water present in the sodium hydroxide solution added later) and a weighed amount of triester were placed in the reaction vessel. The stoppered flask was placed in the bath until solution of the triester had occurred. The required amount (remember $A_0 = 3B_0$) of sodium hydroxide solution (*ca.* 0.05 *N*) was placed in a special water-jacketted buret protected by an Ascarite tube. A Magmix was placed in a long polyethylene bag and lowered into the bath. The ester solution was stirred rapidly with the magmix pellet and the sodium hydroxide solution was allowed to run in. Stirring was continued for one minute and then a special sampling pipet was inserted. Each sample was delivered into a measured amount of standard acid (*ca.* 0.01 *N*) contained in an erlenmeyer flask equipped with a side tube through which nitrogen was passed. Excess acid was titrated with standard sodium hydroxide (*ca.* 0.01 *N*) using phenolphthalein as the indicator. All reaction samples and standardizations were finished in a final volume of about 35 ml. to facilitate the applications of blank corrections.

The weight per cent. of dioxane[10] corresponding to any specified dielectric constant at each temperature in a dioxane–water mixture and the densities of the solutions[11] were taken from the literature. These latter values were used in transforming weight data to volume data.

Calculations and Discussion

Solubility.—Solubility studies of the triester were made at 35° in various dioxane–water solutions. The upper limit of the dielectric value to be used was set at about 9 because of the solubility limitations of the triester.

Evaluation of Rate Constants.—Table I shows a typical time–concentration set of data for run 5. In all cases the rate constant k_3 was taken as the calculated slope of the least squares best fit straight line determined by the coördinates $(t, (A_0 - A)/A_0A)$ in accordance with equation 5. The slope, its standard deviation and the $t_{\text{intercept}}$ were calculated by standard statistical procedures.[12] The results are summarized in Table II. Figure 1 shows typical plots of experimental data with the least squares lines superimposed thereon. Theoretically these lines should intersect the origin. We attribute the $t_{\text{intercepts}}$ to the small but finite time of mixing of the reagents. As shown in Fig. 2, there is a substantial induction period in the formation of the species D and F. The concentrations of the various reacting species were calculated by equations 6–10 which in turn were obtained by integra-

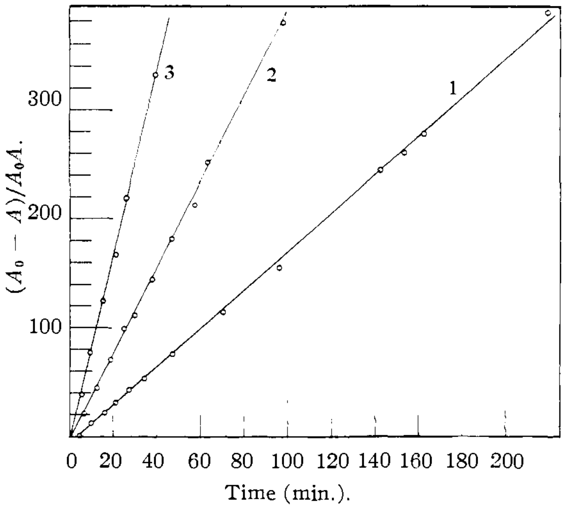

Fig. 1.—Typical plots of rate data: 1, run 5 at 34.98°; 2, run 11 at 45.46°; 3, run 16 at 56.12°.

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[8] Infrared spectra were obtained by Dr. Asa Leifer. We gratefully acknowledge his assistance.

[9] N. B. Colthup, *J. Op. Soc. Am.*, **40**, 397 (1950).

[10] G. C. Åkerlöf and O. A. Short, THIS JOURNAL, **58**, 1241 (1936).

[11] H. S. Harned and B. B. Owens, "Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950, p. 546.

[12] W. J. Youden, "Statistical Methods for Chemists," John Wiley and Sons, Inc., New York, N. Y., 1951, Ch. 5.

TABLE II

SUMMARY OF RATE CONSTANTS

Run	Medium	t, °C.	Wt. % dioxane	D	$A_0 \times 10^3$, mole/l.	k_1	k_2 l. mole^{-1} min.$^{-1}$	k_3	t_{intercep}
5	Isocomposition	34.98	82.0	9.07	9.345	5.34	3.56	1.78 ± 0.02	4.45
6	Isocomposition	34.98	82.0	9.07	9.345	5.37	3.58	1.79 ± .03	3.84
8	Isocomposition	34.98	82.0	9.07	4.874	5.40	3.60	1.80 ± .06	0.75
9	Isocomposition	34.98	82.0	9.07	4.874	5.43	3.62	1.81 ± .07	0.21
					Av. k's	5.36	3.57	1.79	
11	Isocomposition	45.46	82.0	8.62	9.095	11.82	7.88	3.94 ± .04	0.88
12	Isocomposition	45.46	82.0	8.62	9.095	11.76	7.84	3.92 ± .02	1.64
13	Isocomposition	45.46	82.0	8.62	9.095	11.70	7.80	3.90 ± .01	0.22
					Av. k's	11.75	7.84	3.92	
16	Isocomposition	56.12	82.0	8.15	8.988	25.11	16.74	8.37 ± .10	0.26
19	Isocomposition	56.12	82.0	8.15	8.990[b]			8.14 ± .03	
	Isodielectric	34.98	82.0	9.07	See c				
14	Isodielectric	45.46	81.1	9.08	9.578	11.97	7.98	3.99 ± .03	2.86
15	Isodielectric	45.46	81.1	9.08	9.578	11.97	7.98	3.99 ± .03	0.55
					Av. k's	11.97	7.98	3.99	
17	Isodielectric	56.12	80.1	9.06	9.976	26.34	17.56	8.78 ± .12	0.30
18	Isodielectric	56.12	80.1	9.06	9.976	25.16	17.44	8.72 ± .02	−0.18
					Av. k's	26.25	17.50	8.75	

[a] k_1 and k_2 were obtained from k_3 by multiplication with the statistical factors. [b] The reactant in this run was the monoester IV and k_3 was experimentally determined. In all of the other runs, the reactant was the triester. [c] The values of the k's at 34.98° are the same in both isodielectric and isocomposition media.

tion of the appropriate rate equations 1–4, reference 2.

$$A = \frac{2A_0}{A_0k_2t + 2} \tag{6}$$

$$B = \frac{8}{3}\,\frac{A_0}{(A_0k_2\,t + 2)^3} \tag{7}$$

$$C = \frac{4A_0}{(A_0k_2t + 2)^2} - \frac{8A_0}{(A_0k_2t + 2)^3} \tag{8}$$

$$D = \frac{8A_0}{(A_0k_2t + 2)^3} - \frac{8A_0}{(A_0k_2t + 2)^2} + \frac{2A_0}{(A_0k_2t + 2)} \tag{9}$$

$$F = \frac{A_0}{3} - \frac{2A_0}{(A_0k_2t + 2)} + \frac{4A_0}{(A_0k_2t + 2)^2} - \frac{8A_0}{(A_0k_2t + 2)^3} \tag{10}$$

For run 19 which was an independent determination of k_3 using the monoester IV (*i.e.*, D species), the calculation of the slope and intercept was made as above. We take the fact that since this independent determination of k_3 checked the value of k_3 obtained in a three-step reaction carried out under the same environmental conditions (run 16) within 3% as: (1) proof of the correctness of the over-all analysis; (2) further proof of the identity of compound IV.

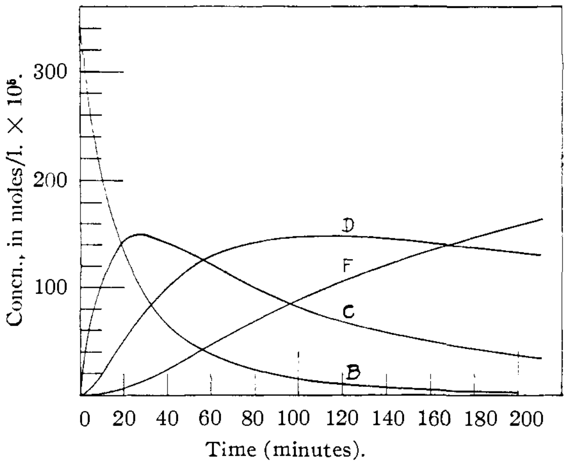

Fig. 2.—Time concn. plot of the various species in a three-step reaction.

The use of Table I, reference 2, would permit an alternative method of calculating the k_1/k_2 ratio provided that $k_2 = 2k_3$. One could use the time ratio method demonstrated by Frost and Schwemer.[13] These investigators have shown that the ratio of times for certain fractions of reactant remaining will be a function only of K (*i.e.*, k_2/k_1 in our case). In applying their procedure one would calculate values of various time ratios for specific values of $1/K$ calculated from the data in Table I, reference 2. Then on applying these calculated results to the experimental data the procedure would be to obtain several independent values of K from various experimental time ratios and to inspect them for constancy. After obtaining K, reference then would be made to Table I, reference 2, where for several values of the % of reaction τ could be determined. Having determined τ, k_1 could be evaluated using the experimental values of t and B_0 since $\tau = B_0k_1t$. From the values of K and k_1, the evaluation of k_2 and k_3 follows. In using this method of calculation, however, the times for specific percentages of reaction must be read from a time–concentration curve. Since this curve is one manually fitted to the experimental data, its pre-

TABLE III

COMPARISON OF VARIOUS METHODS FOR CALCULATING $1/K$ AND k_1 FOR RUN 5

	k_1	$1/K$
Straight line method	5.33 ± 0.02	1.50 (assumed)
Time-ratio method	5.91 ± .07	1.79 ± 0.11
Deming's method	5.34 ± .13	1.52 ± .08

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(13) A. A. Frost and W. C. Schwemer, THIS JOURNAL, **74**, 1268 (1952).

cise location is a matter of considerable subjective variation. Table III summarizes the results on application of this procedure to run 5.

Based on our experience, it was believed that an objective procedure would be much more satisfactory than the subjective procedure outlined above. Such an analysis was located.[14,15] This least squares method makes it unnecessary first to obtain corresponding values of α and t. By properly defining a condition function and its derivatives, one may enter directly the table (Table I, reference 2) relating the parameters and emerge with values of $1/K$ and k_1. The method is developed in the Appendix and some of the pertinent calculations are listed for run 5 in Table I. The results were in accord with values obtained in the simplified straight line least squares method described previously. Table III summarizes the final calculations. The somewhat lower precision measures of the Deming method are probably more reliable than those obtained by either of the other methods. However, the concordance demonstrated in Table III for run 5 made it seem not worthwhile to treat all runs by the Deming method. It is apparent that within the error limits of the present work, it is completely justifiable to make the assumption that $1/K = 1.50$.

Salt Effects.—The stoichiometric ionic strength of this reaction in terms of the reacting species can be expressed by

$$u = A + C + 3D + 6F \tag{11}$$

On substituting equation 6–10 into equation 11 the stoichiometric ionic strength at any time t becomes

$$u = 2A_0 - \frac{4A_0}{(A_0k_2t + 2)} + \frac{4A_0}{(A_0k_2t + 2)^2} \tag{12}$$

Normally, one would expect the alkaline hydrolysis of an ester-ion to exhibit an increase in the rate constant with an increase in ionic strength.[16,17] Use of equation 12 shows that the stoichiometric ionic strength of the solution increased as the products of the reaction accumulated. In run 5 for 100% reaction this increase in ionic strength would be twofold (*i.e.*, from 0.0093 to 0.0186). However, within the experimental error no increase in the rate constants was observed as was indicated by the constancy of the rate constant ratios. This behavior is similar to what was observed in the malonate ion–OH^- reaction[17] when no added inert electrolyte was present.

In order to augment a possible ionic strength effect on steps two and three of our reaction, a run was made precisely like run 5 except that potassium iodide (0.1 mole/l.) was added to the reaction mixture. Figure 3 shows a $(A_0 - A)/A_0A$ *vs.* t plot of the results. The plot is linear over the bulk of the reaction range and has a slope of 1.37 (*i.e.*, $k_3 = 1.37$). This would indicate a negative primary salt effect, a conclusion not only at variance with theory for a reaction between ions of like charge sign but also at variance with other observations involving the alkaline hydrolysis of an ester ion.[16,17] Recalling that our runs were made in very low dielectric constant media (*i.e.*, $D \sim 9$), the existance of ion pairs is quite likely[18] and so we may not be dealing with the usual alkaline hydrolysis of an ester ion involving ions of like charge sign.

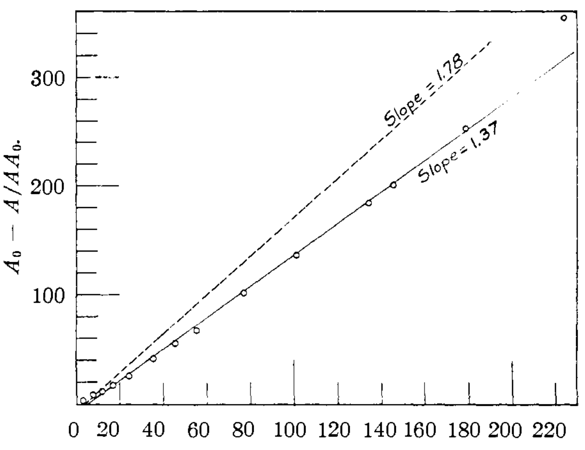

Fig. 3.—Effect of KI on the rate. Dotted line is run 5 without KI; solid line is a similar run with KI.

Activation Energies.—Activation energies in isodielectric and isocomposition media were calculated through use of the linear form of the Arrhenius equation, namely

$$\log k = \log A - \frac{E}{2.303RT} \tag{13}$$

The data were treated by a least squares computation with weighting[19] and a covariance analysis of the weighted data.[20] The results are shown in Table IV.

TABLE IV

ACTIVATION ENERGIES AND SIGNIFICANCE TESTS

	Isocomposition	Isodielectric
E_a (cal./mole)	14,740 ± 33	15,180 ± 37
F (for slope)	++	++
"t" test for significant difference	++	

In the nomenclature of statistics, the F and "t" significance test noted in Table IV (*i.e.*, ++) has the meaning that the values of the slopes and differences between them could have occurred by chance alone with a probability of less than 1%. Thus, we conclude: (1) the difference between the activation energies in isocomposition and isodielectric media is real: (2) that $E_{\text{I.D.}} > E_{\text{I.C.}}$ in each step of the reaction: (3) that both $E_{\text{I.D.}}$ and $E_{\text{I.C.}}$ are the same for each step of the reaction.

If we recall that the fundamental assumption upon which our rate law is based is the complete independence of and lack of interaction between the reaction sites, it therefore follows that the kinetic behavior should be consistent for each step. This statement is supported by the equality in the en-

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(14) We are indebted to Dr. E. A. Mason, Institute of Molecular Physics, University of Maryland, for pointing out the utility of this method and indicating the method of application.

(15) W. E. Deming, "Statistical Adjustment of Data," John Wiley and Sons, Inc., New York, N. Y., 1943.

(16) L. Pekkarinen, *Ann. Acad. Sci. Fenn.*, **AII**, 62 (1954).

(17) W. J. Svirbely and I. Mador, THIS JOURNAL, **72**, 5699 (1950).

(18) R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 1019 (1933); C. A. Kraus and R. M. Fuoss, *ibid.*, **55**, 21 (1933).

(19) W. R. McBride and D. S. Villars, *Anal. Chem.*, **26**, 901 (1954).

(20) D. S. Villars, "Statistical Design and Analysis," Wm. C. Brown Co., Dubuque, Iowa, 1951, p. 159.

TABLE V

SUMMARY OF THERMODYNAMIC ACTIVATION DATA AT 45.56°

	Isocomposition				Isodielectric			
	log A min.$^{-1}$	ΔF, cal.	ΔS, e.u.	E_a, cal.	log A, min.$^{-1}$	ΔF, cal.	ΔS, e.u.	E_a, cal.
Step 1	11.18	19,730	−17.63	14,740	11.48	19,720	−16.26	15,180
Step 2	11.00	19,980	−18.46	14,740	11.30	19,970	−17.08	15,180
Step 3	10.70	20,420	−19.83	14,740	11.00	20,410	−18.46	15,180

ergy of activation for each step. Thus, steps two and three of the reaction would not involve ester ions but entities which act like uncharged particles. The anomalous salt effect referred to above also supports the above argument.

Furthermore, although it has been shown[21] that at zero ionic strength $E^0_{\text{I.D.}} > E^0_{\text{I.C.}}$ for a reaction between ions of like charge sign, it also has been shown that $E^0_{\text{I.D.}} > E^0_{\text{I.C.}}$ for a dipole–dipole reaction.[22] It is true that these statements require k^0's, and one cannot be certain that the experimental relationship between $E_{\text{I.C.}}$ and $E_{\text{I.D.}}$ which we report would not be reversed at zero ionic strength. However, we believe that the true ionic strength of our reaction medium is much smaller than what one calculates by equation 12. In that event $E_{\text{I.D.}} > E_{\text{I.C.}}$ supports a dipole–dipole reaction mechanism for each step in the three-step reaction in our low dielectric media.

Effect of Dielectric Constant on the Rate Constant.—Although the dielectric range covered was small, nevertheless reference to Table II shows that at a fixed temperature an increase in dielectric constant increased the rate constant. This cannot be a specific solvent effect since the composition and nature of the solvent particles differed but slightly. Our observation is in accord with many experimental results involving the alkaline hydrolysis of ester ions and of carboxylic esters.[16,15,23] Theory based on k^0's predicts such behavior for reactions between two dipolar molecules,[24] between ions of like charge sign[25] and between ion–dipolar molecules.[22] However, based on the same arguments as presented above, we again favor a dipole–dipole reaction mechanism for each step of the reaction.

Thermodynamic Activation Values.—The free energy and the entropy of activation were calculated by means of the equations[26]

$$\Delta F^{\ddagger} = 2.3RT\left(\log\frac{RT}{Nh} - \log k\right) \qquad (14)$$

$$\Delta S^{\ddagger} = 2.3R\left(\log A - \log\frac{eRT}{Nh}\right) \qquad (15)$$

These values, as well as the Arrhenius frequency factors (log A) are given in Table V for each step of the reaction in both isocomposition and isodielectric media. The lower probability of formation of the activated complexes in the second and third steps of the reaction, and hence the smaller specific rate constants, is reflected in the larger negative entropies of activation. The increase in the rate constants with increasing dielectric constant in any step of the reaction in going from an isocomposition to an isodielectric medium can be seen to be the result of a smaller negative entropy of activation (about 8%) which apparently is large enough to overcome the effect of a higher energy of activation. Since the energies of activation of all three steps are identical in a given medium while the entropies of activation differ, it is evident that the free energies of activation determine the rates of the various steps of the reaction.

Rate Constant Ratios from Ingold's Formula.—Referring to equations 2 and 3 and substituting in the values of r = 13.1 Å. $\mathfrak{D}$ = 9.07, T = 318 and the appropriate values for the other constants one calculates that k_1/k_2 = 115 and k_2/k_3 = 352. Considering the fact that our kinetics actually yielded the statistical factors of 3/2 and 2 for k_1/k_2 and k_2/k_3, respectively, we must conclude that Ingold's equation is inadequate in this instance. Even if one accepts the suggestion[4] that the equation is properly applicable only at zero ionic strength the situation is not improved.

Appendix

Table I, reference 2, is set up in terms of $1/K$ and τ for various values of α, where $\tau = B_0k_1t$, $\alpha = A/A_0$. For convenience let $1/K = r$ and let $k_1 = k$. Then $\tau = \tau\ (r, \alpha)$. Trial values of r and k are chosen, say r_0 and k_0. Let

$$r = r_0 - r' \qquad (16)$$

$$k = k_0 - k' \qquad (17)$$

We are interested in setting up normal equations for computing the small correction terms r' and k'. We assume that there is no error in t but only in α. We therefore set up a condition function in α alone, namely

$$F = \frac{A}{A_0} - \alpha \qquad (18)$$

The condition functions for F_0, $(F_r)_0$ and $(F_k)_0$ become

$$F_0 = \left(\frac{A}{A_0}\right)_{\text{exp}} - \alpha_0 \qquad (19)$$

$$(Fr)_0 = \left(\frac{\partial\tau}{\partial r}\right)_\alpha \Big/ \left(\frac{\partial\tau}{\partial\alpha}\right)_r \qquad (20)$$

$$(Fk)_0 = -B_0t \Big/ \left(\frac{\partial\tau}{\partial\alpha}\right)_r \qquad (21)$$

These terms are to be evaluated for each experimental value of t at the trial values of r_0 and k_0. In the evaluation the following procedure was used: (1) in a run, for each of the time–concentration data the corresponding values of $\alpha = A/A_0$ and $\tau_0 = B_0k_0t$ were calculated. Interpolation[27] of the

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

[22] E. S. Amis and G. F. Jaffe, *J. Chem. Phys.*, **10**, 598 (1942).

[23] W. J. Svirbely and B. W. Lewis, *J. Phys. Chem.*, **56**, 1006 (1952).

[24] K. J. Laidler and H. Eyring, *Ann. N. Y. Acad. Sci.*, **39**, 303 (1940).

[25] G. Scatchard, *Chem. Revs.*, **X**, 229 (1932).

[26] 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.

[27] For this purpose we used the "Tables of Lagrangian Interpolation Coefficients," Columbia University Press, New York, N. Y., 1943. A graphical procedure also can be used but the procedure is less objective.

data in Table I, reference 2, at the trial value of r_0 permits one to obtain for each value of τ_0 a corresponding value of α_0. The calculation of F_0 then follows: (2) for each value of α in Table I, reference 2, the values of $(\partial\tau/\partial r)_\alpha$ were evaluated[28] at the trial value of r_0. Using the interpolation tables one gets from these figures (*i.e.*, α, $\partial\tau/\partial r$ values) a value of $(\partial\tau/\partial r)_\alpha$ for each value of α_0 obtained in (1) above: (3) at the trial value of r_0 one gets from the data in Table I, reference 2, the values[28] of $(\partial\tau/\partial\alpha)_r$ for each value of α. Using the interpolation tables one gets from these figures (*i.e.*, τ, $\partial\tau/\partial\alpha$ values) a value of $(\partial\tau/\partial\alpha)_{r_0}$ for each value of τ_0 obtained in (1) above; (4) calculations of $(F_r)_0$ and $(F_k)_0$ follow in accordance to their definitions.

The normal equations for computing the small correction terms and k' are written with detached coefficients as

$$\begin{array}{ccc} r' & k' & 1 \\ \Sigma(F_r)^2_0 & \Sigma(F_r)_0(F_k)_0 & \Sigma(F_r)_0F_0 \\ & \Sigma(F_k)^2_0 & \Sigma(F_k)_0F_0 \end{array} \qquad (22)$$

Through use of the tabular scheme in Deming (p. 158) one can calculate the values of r' and k'. Standard deviation from the measurements and the standard error of the parameters readily are obtained using the figures in the tabular scheme.

In treating the data of run 5, we selected $r_0 = 1.50$ and $k_0 = 5.331$ as our trial values. In calculating τ_0 at each experimental point the value of t used was defined as

$$t = t_{\text{exp}} - t_{\text{intercept}}$$

where $t_{\text{intercept}}$ was the time axis intercept of our straight line plot. For run 5, $t_{\text{intercept}}$ was 4.45 min. Some of the essential calculated results are given in Table I. r' and k' turned out to be 0.015 and 0.07, respectively, and the standard estimated errors in r and k were 0.08 and 0.13, respectively.

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[28] For this purpose we used the "Tables of Coefficients for Obtaining the First Derivatives Without Differences," National Bureau of Standards, Applied Mathematics Series, 2, 1948.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FLORIDA STATE UNIVERSITY AND RESEARCH INCORPORATED]

On the Solvent Isotope Effect of Deuterium in Aqueous Acid Solutions

BY E. LEE PURLEE[1]

RECEIVED MARCH 26, 1958

The Gross–Butler theory for the solvent isotope effect of deuterium on acid-catalyzed reaction rates in D_2O–H_2O mixtures is re-examined. New values for the thermodynamic activity function, $Q'(n)$, for proton and deuteron at 25° are derived from experimental data by using the correct value for the isotopic exchange equilibrium constant for D_2O–H_2O and by taking into account the apparent difference in free energy between (Cl^-) in D_2O and (Cl^-) in H_2O. An independent check of the $Q'(n)$-function at 25° is obtained by applying the rule of the geometric mean to the distribution of hydrogen isotopes between lyonium ion and water. Values for the thermodynamic activity function, $Q'(n)$, are calculated for application at temperatures other than 25°, and it is demonstrated that equilibrium constants and reaction rates observed at 0, 15, 18, 30 and 35° are well predicted by the Gross–Butler theory when values of the $Q'(n)$-function corresponding to the appropriate temperatures are used. The nature of deviations from the Gross–Butler rate equation is briefly discussed. It is noted that the acid-catalyzed inversion of sucrose and the acid-catalyzed hydrolysis of methyl acetate and ethyl formate show significant deviations from the theory. The complete failure of the Gross–Butler rate equation to predict the rates for the acid-catalyzed mutarotation of glucose indicates that this reaction does not proceed *via* a pre-equilibrium mechanism.

The Gross–Butler Theory

The theory for the solvent isotope effect of deuterium on reaction rates and equilibria in aqueous acid solutions was originally proposed by Gross and co-workers[2–4] in 1936. Shortly thereafter, Butler and co-workers[5–7] further developed the theory.[8] It has been employed by various investigators as a diagnostic aid in the elucidation of reaction mechanisms. Recently, Purlee and Taft[9] applied the theory to the acid-catalyzed hydration of olefins and Pritchard and Long[10] applied it to the acid-catalyzed hydrolysis of ethylene oxide and some of its derivatives.

Butler and his associates[6,7] derived functions relating the activities of protons and deuterons in D_2O–H_2O mixtures to proton activities in H_2O from experimental and theoretical values of equilibrium constants between the various isotopic species in acidified D_2O–H_2O mixtures. Since the value of one of the theoretical equilibrium constants (*i.e.*, K of eq. 2) used by Nelson and Butler has been shown to be incorrect[7,11,12] and since the value of a second equilibrium constant (L of eq. 4) derived indirectly from experimental data is open to serious question,[13,14] it is of importance to re-examine the treatment of available data.

The Gross–Butler Rate Equation.—As previously discussed,[9] this equation applies to acid-catalyzed reactions involving a proton transfer preliminary to the rate-determining step. However, in order to avoid the assumption that lyonium ion activities

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[1] Department of Chemistry, Florida State University. Requests for reprints should be sent to the author at P. O. Box 206, Tallahassee, Florida.

[2] Ph. Gross, H. Steiner and F. Krauss, *Trans. Faraday Soc.*, **32**, 877 (1936).

[3] Ph. Gross and A. Wischen, *ibid.*, **32**, 879 (1936).

[4] Ph. Gross, H. Steiner and H. Suess, *ibid.*, **32**, 883 (1936).

[5] J. C. Hornel and J. A. V. Butler, *J. Chem. Soc.*, 1361 (1936).

[6] W. J. C. Orr and J. A. V. Butler, *ibid.*, 330 (1937).

[7] W. E. Nelson and J. A. V. Butler, *ibid.*, 958 (1938).

[8] The theory has been referred to as that of Nelson and Butler (*cf.* ref. 9 and 10). If names are to be associated with the theory, that of Gross should indeed be included.

[9] E. L. Purlee and R. W. Taft, Jr., THIS JOURNAL, **78**, 5807 (1956).

[10] J. G. Pritchard and F. A. Long, *ibid.*, **78**, 6008 (1956).

[11] B. Topley and H. Eyring, *J. Chem. Phys.*, **2**, 220 (1934).

[12] H. C. Urey, *J. Chem. Soc.*, 562 (1947).

[13] G. Schwarzenbach, *Z. Elektrochem.*, **44**, 302 (1938).

[14] G. Schwarzenbach, A. Epprecht and H. Erlenmeyer *Helv. Chim. Acta*, **19**, 1292 (1936).