A combination of equations 46 and 48 leads to eq. 49

$$k_3\lambda = \ln\frac{A_0}{A} \qquad (49)$$

On assigning values to the constants A_0 and k_3, we may arbitrarily generate a test set of A values for various times t through use of equation 46. This test set of A values can be used to generate a test set of λ values through use of equation 49. Both sets of test values are independent of any equations derived in this paper and apply to the situation where the rate constants are in the ratio of $k_1:k_2:k_3 = 3:2:1$.

On assigning a value of 6.51 to k_3 and 0.03000 to A_0, values of λ and A were generated and are listed in Table I. Also listed in Table I, column 3, are the values of A later calculated using the values of k_1, k_2 and k_3 generated by the iterative procedure. The initial estimates of the three rate constants and the values given by the iterative procedure are summarized below Table I. The iteration was stopped when Δk_1 became smaller than 1% of the outstanding value of k_1. Three cycles through the iterative procedure were required in this test case. Close estimates of the rate constants were chosen as a measure of economy. The calculations were done by an IBM-704 electronic computer.

In the application to experimental data, initial estimates of k_1 were found by plotting A vs. λ and estimating the slope at $\lambda = 0$ in accordance with the equation 33. If k_3 is much smaller than both k_1 and k_2, equation 14 reduces to equation 50 for large values of λ

$$\lim_{\lambda\to\infty} A/B_0 = G_3 e^{-k_3\lambda} \qquad (50)$$

The logarithmic form of equation 50 is

$$\lim_{\lambda\to\infty}\left(\log\frac{A}{B_0}\right) = \log G_3 - \frac{k_3}{2.303}\lambda \qquad (51)$$

The initial estimates of k_3 were found by plotting $\log A$ vs. λ and estimating the slope at large values of λ. The initial estimates of k_2 were found by

TABLE I

FIT OF THE TEST DATA AS CALCULATED BY THE MACHINE ITERATION

A, mole min./l.	A, mole/l.	A_{calcd}, mole/l.	$A - A_{calcd}$, mole/l.
0.01437	0.02733	0.02732	0.000010
.03909	.02325	.02325	.000000
.06226	.01999	.01999	.000000
.08034	.01777	.01777	.000000
.09959	.01567	.01567	.000000
.11689	.01400	.01400	.000000
.12590	.01320	.01320	.000000
.15239	.01111	.01111	.000000
.20914	.007672	.007671	.000001
.26716	.005256	.005256	.000000
.33698	.003333	.003335	− .000002

k_i	Actual value	Initial estimate	Calcd. value
k_1	19.53	20.0	19.53
k_2	13.02	15.0	13.07
k_3	6.51	6.5	6.51

simply guessing the values, it being assumed that $k_3 < k_2 < k_1$.

Our experience is that the iterative procedure will not converge unless the estimate $^0k_3$ is within 100% of the actual value of k_3, whereas $^0k_2$ and $^0k_1$ can be at variance more than 300% from the actual values of k_1 and k_2. Furthermore, we observed that in duplicate runs, reproducible values for k_3 will result only if the reaction is carried out until the plot of $\log A$ vs. λ approaches linearity. This usually occurred at about 75% completion of the reaction.

The Kinetics of the Alkaline Hydrolysis of 1,3,5-Tricarbomethoxybenzene[1,2]

BY W. J. SVIRBELY AND JAY A. BLAUER

The three step alkaline hydrolysis of 1,3,5-tricarbomethoxybenzene has been studied in dioxane–water mixtures over a temperature range. The three rate constants have been determined using procedures developed for the determination of the rate constants for a three-step consecutive-competitive second-order reaction involving a symmetrical molecule where there may be interaction among the reaction sites. The various thermodynamic activation values have been calculated. The data have been examined statistically for their significance. It was observed that the k_2/k_3 ratio approached unity in the low dielectric media. The experimental observations can be explained on the basis of the formation of ion-pairs or aggregates.

Introduction

A recent[3] study of the alkaline hydrolysis of 1,3,5-tri-(4-carbomethoxyphenyl)-benzene showed

that under the conditions of the experiment, i.e. dielectric constant $\sim$9, the ratio of the rate con-

stants were $k_1:k_2:k_3 = 3:2:1$. It was postulated that such should be in the case of a symmetrical molecule where the reacting groups on the molecule are far enough apart so that interaction between the groups does not occur. In this research we shall report on our study of the alkaline hydrolysis of 1,3,5-tricarbomethoxybenzene, a triester whose structural formula is

COOCH₃

H₃COOC   COOCH₃
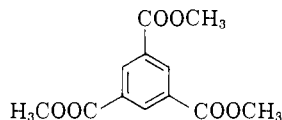
This triester is symmetrical so there is no ambiguity as to the rate constant for each step of the reaction. However, in this molecule the reacting groups are quite close compared to the situation existing in 1,3,5-tri-(4-carbomethoxyphenyl)-benzene. Consequently, interaction among the groups is anticipated and the statistical ratio of $3:2:1$ should not exist.

Furthermore, our first study on triester hydrolysis[3] indicated that the existence of ion-pairs was quite likely and that we may not be dealing with the usual alkaline hydrolysis of an ester ion involving ions of like charge sign. These conclusions have been supported by a recent study involving diester hydrolysis in our Laboratory.[4] If such were the case in the alkaline hydrolysis of 1,3,5-tricarbomethoxybenzene, the variation in the solvent composition should also have an effect on the rate constant ratios.

Therefore, in order to answer such questions, the alkaline hydrolysis of 1,3,5-tricarbomethoxybenzene was studied over a temperature range in dioxane–water mixtures of varying composition and dielectric constant.

Materials and Apparatus

Dioxane, water, sodium hydroxide solutions and hydrochloric acid solutions were prepared or purified as before.[3]

The triester was prepared by a procedure in the literature.[5] The m.p. was 144.8–145.8°. The saponification equivalent indicated a purity of more than 99.9%.

Anal.[6] C, 57.37; H, 5.10. Calcd., C: 57.14; H, 4.80.

Apparatus.—The apparatus used in this research has been described.[3]

Procedure.—The procedure has been described.[3] The starting concentrations of the triester and the sodium hydroxide were adjusted so that equivalent amounts were used (*i.e.*, $A_0 = 3B_0$, where A_0 and B_0 were the initial concentrations in mole/l. of hydroxide and triester, respectively). The temperature control of the bath was ± 0.05°. At some time during each run, the density of the solution was determined. This datum was used to transform weight data to volume data. Duplicate runs (occasionally triplicate runs) usually were made for each environmental condition.

The dielectric constants of all dioxane–water mixtures used were determined from data in the literature.[7]

Calculations and Discussion

Evaluation of Rate Constants.—The alkaline hydrolysis of the triester may be represented by
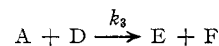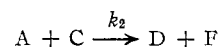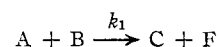
(4) W. J. Svirbely and A. D. Kuchta, *J. Phys. Chem.*, **65**, 1333 (1961).

(5) J. V. Karabinos, J. I. Wright and H. E. Hipsher, *J. Am. Chem. Soc.*, **68**, 906 (1946).

(6) We gratefully acknowledge our indebtedness to Prof. M. Kathryn Gerdeman for the analysis.

(7) G. C. Åkerlöf and O. A. Short, *J. Am. Chem. Soc.*, **58**, 1241 (1936).

the reactions

$$A + B \xrightarrow{k_1} C + F$$

$$A + C \xrightarrow{k_2} D + F$$

$$A + D \xrightarrow{k_3} E + F$$

In our reaction A,B,C,D,E and F are the hydroxyl ion, triester $[R\text{-}(COOCH_3)_3]$, monovalent ion of the triester, $[R\text{-}(COOCH_3)_2COO^-]$, divalent ion of the triester, $[R\text{-}(COOCH_3)(COO^-)_2]$, trivalent ion of the triester, $[R\text{-}(COO^-)_3]$ and methanol, respectively. R is the appropriate radical as seen by reference to the structural formula of the triester.

Table I shows a typical time–concentration set of data. The values of λ in the third column of Table I were obtained by a graphical integration of an A *vs.* t plot[8] in accordance with equation 6, ref. 8, namely

$$\lambda = \int_0^t A \, dt \qquad \text{R8-6}$$

The procedure for the calculation of the rate constants in Table I is described under Method 1, ref. 8. Different stages of the iterative process for run 47 are listed in Table I. In the case of run 48, a duplicate of run 47, the final values only of the rate constants are given.

TABLE I

DATE IN DIOXANE–WATER AT 5.82°; $D = 28.85$; $A_0 = 0.02090$ MOLE/L.; $B_0 = \frac{1}{3}A_0$; WT. % OF DIOXANE = 60.0, RUN 47

Time, min.	A (exptl.), mole/l.	λ, mole min./l.	A (calcd.), mole/l.	$(A_{exp} - A_{calcd})$
4.50	0.05140	0.0770	0.01586	−0.00046
8.67	.01422	.1383	.01404	+ .00018
12.67	.01335	.1932	.01307	+ .00028
17.75	.01253	.2587	.01226	+ .00027
22.67	.01181	.3187	.01168	+ .00013
27.08	.01139	.3698	.01125	+ .00014
32.00	.01092	.4248	.01083	+ .00009
36.00	.01054	.4678	.01053	+ .00001
46.33	.009780	.5729	.009859	− .00008
57.00	.009157	.6744	.009284	− .00013
69.00	.008594	.7815	.008741	− .00015
76.75	.008395	.8476	.008435	− .00004
90.00	.007891	.9554	.007976	− .00009
102.00	.007510	1.0481	.007618	− .00011
108.00	.007370	1.0928	.007456	− .00009
147.92	.006646	1.3750	.006567	+ .00008
198.00	.005883	1.6866	.005789	+ .00009
241.75	.005322	1.9317	.005284	+ .00004
270.25	.004960	2.0788	.005015	− .00006
326.25	.004518	2.3446	.004581	− .00006
418.00	.004075	2.7367	.004034	+ .00004
501.00	.003715	3.0599	.003647	+ .00007

| | Initial esti- | | | | | Run 47 Cycle 5 | Run 48 Cycle 5 |
k_i	mates	Cycle 1	Cycle 2	Cycle 3	Cycle 4	(final)	(final)
k_1	8.70	12.60	14.92	14.66	14.69	14.69	14.72
k_2	3.00	0.786	1.448	1.571	1.558	1.558	1.502
k_3	0.54	0.1676	0.1689	0.2760	0.2896	0.2899	0.2986

[a] Standard deviation of the concentration values is 0.00017 for Runs 47 and 48. [b] Duplicate Run #48 lists only the k's on the final cycle. Starting conditions and initial estimates were the same in Runs 47 and 48. [c] Rate constants units are l. mole⁻¹ min.⁻¹ in all tables.

The three rate constants of the reaction for each environmental condition are listed in Table II. It is appropriate at this point to compare the two methods of calculation developed in ref. 8 and tested

(8) W. J. Svirbely and J. A. Blauer, *ibid.*, **83**, 4115 (1961).

TABLE II
SUMMARY OF RATE CONSTANTS[a]

Runs	Temp., °C.	Dioxane, wt. %	D	A_0, mole/1.	k_1, 1./mole min.	k_2, 1./mole min.	k_3, 1./mole min.	k_3/k_2	k_2/k_3	k_1/k_3
47, 48	5.82	60	28.85	0.02090	14.71 ± 0.02[c]	1.53 ± 0.07	0.294 ± 0.005	9.61	5.20	50.0
23, 24	10.94	60	28.02	.02080	17.0 ± .5	2.10 ± .02	.414 ± .007	8.06	5.07	40.9
43, 44[b]	15.38	60	27.35	.02084	24.4 ± .7	3.30 ± .02	.643 ± .008	7.38	5.13	37.9
14, 15, 35	19.03	60	26.75	.02068	32.6 ± 1.1	4.19 ± .06	.846 ± .013	7.77	4.95	38.5
29, 30	23.67	60	26.05	.02067	40.8 ± 0.5	5.88 ± .02	1.126 ± .012	6.93	5.22	36.2
47, 48	5.82	60	28.85	.02090	14.71 ± 0.02	1.53 ± .07	0.294 ± .005	9.61	5.20	50.0
25, 26, 34	10.94	59.1	28.85	.02079	16.4 ± 1.2	2.12 ± .02	.380 ± .011	7.74	5.58	43.2
45, 46	15.20	58.3	28.85	.02079	25.7 ± 0.3	3.12 ± .04	.576 ± .014	8.24	5.42	44.7
16, 17	19.03	57.6	28.85	.02071	31.6 ± 1.2	4.10 ± .03	.740 ± .011	7.71	5.54	42.7
31, 32, 27	23.67	56.8	28.85	.02066	45.1 ± 3.9	5.57 ± .06	.993 ± .005	8.10	5.61	45.4
33[c]	23.67	56.8	28.85	.02071	35.2	8.48	1.98	4.15	4.28	17.8
41	10.94	62.7	26.05	.02094	16.0	2.24	0.463	7.14	4.84	34.6
18, 19[d]	19.03	80	11.05	.02072	25.1	10.03	9.56	2.50	1.05	2.63

[a] With the exception of the runs designated below, the calculations of the rate constants was accomplished by use of Method 1, ref. 8, using an I.B.M. 704 computer. [b] Runs 43 and 44 were calculated by use of Method 1, ref. 8 using a desk calculator. [c] 0.0992 M NaCl was added. [d] The calculation of the rate constants for runs 18, 19 was by method 2, ref. 8. The data of the runs were pooled for the calculation. [e] Variations listed for the k's are A.D.M. values.

in this work. Runs 18 and 19 could not be solved by Method 1, ref. 8. Since Method 1 will fail if any of the two rate constants are equal, it was suspected that the environmental conditions were such as to make a condition of indeterminacy exist. Method 2, ref. 8, was tested by making use of the data of run 24 and then applied to runs 18 and 19. The results are summarized in Table III.

TABLE III
A COMPARISON OF THE RATE CONSTANTS OF RUN No. 24 BY THE VARIOUS METHODS

	Method 1	Method 2
k_1	16.53	17.55
k_2	2.123	2.120
k_3	0.407	0.409

Both methods for the determination of rate constants are identical within experimental error.

In addition to the runs listed in Table II a number of runs were made at 30 and 40° in 53 to 60% dioxane–water mixtures. At these higher temperatures, the hydroxide-ion concentration dropped below 50% of its initial value by the time the first datum point was obtained, i.e. in about 4 minutes. As a result, the initial portion of the time–concentration curve for such runs could not be accurately drawn. Since the first step of the reaction is the most important step in this region, it is to be expected that any value of k_1 calculated from such data by the iterative procedure will be grossly in error. The data obtained at 30 and 40° were rejected. This rejection will be referred to again.

Standard deviation of the concentrations about the fitted curve were calculated[9] for each run by

$$S = \sqrt{\frac{(A - A_{\text{calcd}})^2}{n - 3}} \quad (1)$$

where A is the observed concentration value and (A_{calcd}) is the value calculated by equation 13, ref. 8, using the rate constants obtained for the run and the observed values of λ, and n is the number of datum points. Table I is representative of such calculations.

(9) W. J. Youden, "Statistical Methods for Chemists," John Wiley and Sons, Inc., New York, N. Y., 1943, page 42.

The concentrations of the various reacting species can be calculated by equations 2–5 which in turn are obtained by integration of the appropriate equations (8–12) of ref. 8.

$$B = B_0 e^{-k_1\lambda} \quad (2)$$

$$C = \frac{k_1 B_0}{k_2 - k_1} e^{-k_1\lambda} - \frac{k_1 B_0}{k_2 - k_1} e^{-k_2\lambda} \quad (3)$$

$$D = \frac{k_1 k_2 B_0}{(k_2 - k_1)(k_3 - k_1)} e^{-k_1\lambda} - \frac{k_1 k_2 B_0}{(k_2 - k_1)(k_3 - k_2)} e^{-k_2\lambda} + \frac{k_1 k_2 B_0}{(k_3 - k_2)(k_3 - k_1)} e^{-k_3} \quad (4)$$

$$E = \frac{k_2 k_3 B_0}{(k_2 - k_1)(k_3 - k_1)} (1 - e^{-k_1\lambda}) - \frac{k_1 k_3 B_0}{(k_2 - k_1)(k_3 - k_2)} (1 - e^{-k_2\lambda}) + \frac{k_1 k_2 B_0}{(k_3 - k_2)(k_3 - k_1)} (1 - e^{-k_3\lambda}) \quad (5)$$

The results of such calculations yield curves which in general are similar to those of Fig. 2, ref. 3.

Activation Energies.—Activation energies were calculated through use of the Arrhenius equation, namely

$$\log k = \log A - \frac{E}{2.303\ RT} \quad (6)$$

The data were treated by means of a least squares computation with weighting of the log k's[10] and a covariance analysis of the weighted data.[11] The results are shown in Table IV. In the nomenclature of statistics, the F of (++) for slope has the meaning that the values of the slopes could have occurred by chance alone with a probability of less than 1%. The application of the "t" test for significant differences between the activation energies in isocomposition and isodielectric media and for significant differences between E_1, E_2 and E_3 in both isodielectric and isocomposition media showed such differences to be statistically insignificant.[12] The application of the "t" test

(10) W. R. McBride and D. S. Villars, Anal. Chem., 26, 901 (1954)
(11) D. S. Villars, "Statistical Design and Analysis," W. C. Brown Co., Dubuque, Iowa, 1951, p. 159.
(12) A reexamination of the "t" test calculation[1] for significant difference between the energies of activation for the alkaline hydrolysis of 1,3,5-tri-(4-carbomethoxyphenyl)-benzene in isocomposition and

TABLE IV

SUMMARY OF THERMODYNAMIC DATA

| | Isocomposition (60% dioxane) | | | Isodielectric (D = 28.85) | | |
	Step 1	Step 2	Step 3	Step 1	Step 2	Step 3
E(cal./mole)	10,000	12,600	12,300	11,800	12,200	11,700
Standard deviation	570	310	430	940	240	330
F (for slope)	++	++	++	++	++	++
Log A	9.1	10.1	9.1	10.3	9.7	8.6
Standard deviation	0.43	0.23	0.28	0.70	0.18	0.25
ΔF^* (cal./mole at 23.67°)	17,600	18,700	19,700	17,500	18,800	19,800
ΔS^* (e.u. at 23.67°)	−26.8	−22.5	−26.8	−21.4	−24.3	−29.4

for significant differences between log A_2 and log A_1, log A_2 and log A_3 and log A_1 and log A_3 in both isodielectric and isocomposition media showed such differences to be statistically insignificant.

In a log k vs. $1/T$ plot, it is observed that the rejected data referred to earlier are not consistent with the linearity observed at temperatures below 25°. This is in agreement with our contention as to the inaccurate determination of k_1 at higher temperatures where the first step of the reaction is quite rapid. If k_1 is inaccurately determined, the values of k_2 and k_3 will be affected by the iterative procedure.

Thermodynamic Activation Values.—The free energy and the entropy of activation were calculated[13] by

$$\Delta F^* = 2.3 \, RT \left(\log \frac{RT}{Nh} - \log k \right) \qquad (7)$$

$$\Delta S^* = 2.3 \, R \left(\log A - \log \frac{eRT}{Nh} \right) \qquad (8)$$

The results, using the data obtained at 23.67°, are listed in Table IV.

Significance of the Differences Between the Rate Constants.—Since it has been established that the differences between the energies of activation and the frequency factors determined for the three steps of the reaction are not statistically significant, it becomes desirable to test the significance of the differences between the rate constants themselves.

Runs 25, 26 and 34 are triplicates and as such represent three independent determinations of the rate constants. By using the results of those runs, the standard deviations of the three rate constants were determined and were 1.64, 0.028 and 0.0142 for k_1, k_2 and k_3, respectively. The "t" test was then applied for significant differences between any two rate constants. It was found that the "t" test gave values represented by (+), (+) and (+++) for $(k_1 - k_2)$, $(k_1 - k_3)$ and $(k_2 - k_3)$, respectively. These values indicate that the differences between the rate constants could have occurred by chance alone with probabilities of less than 5, 0.5 and 0.1% respectively. Since the free energy of activation depends explicitly upon the values of the rate constants (equation 7), and having demonstrated that the differences between the rate constants is

isodielectric media gave a "t" value of (−), i.e., no significant difference. Therefore, on the basis of the "t" test, the difference in activation energies is *not* real. This is a reversal of our previous conclusion. The standard deviations of the energies of activation in cal./mole on recalculation become ±126 and ±122 instead of ±33 and ±37 as reported in Table IV.[*] The error did not affect the significance of the "F" test for slope.

(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.

statistically significant, it follows that the differences between the corresponding free energies of activation are statistically significant.

Salt Effects.—In order to augment a possible ionic strength effect on steps two and three of the reaction, a run was made precisely like runs 31, 32 and 37 except that 0.0992 mole/1. of sodium chloride was added. The results are listed under run 33 in Table II. There is a negative salt effect on the first step of the reaction but a very definite positive salt effect on both the second and third steps of the reaction.

Effect of Medium on the Rate Constants.—We have gathered together in Table V the rate constants obtained at a constant temperature but in media of varying composition. It is obvious that the first step of the reaction is decreasing with decreasing dielectric constant, but the second and third steps of the reaction are increasing with decreasing dielectric constant. In 80% dioxane–water mixtures at $D{\sim}11$, the rate constants for the second and third steps are almost equal, the ratio of k_2/k_3 being 1.05. This is in marked contrast with the results obtained for the alkaline hydrolysis of 1,3,5-tri-(4-carbomethoxyphenyl)-benzene which under similar environmental conditions gave the statistical ratio of $k_2/k_3 = 2$.

TABLE V

EFFECT OF MEDIUM AT 19.03°

Dioxane, wt. %	D	k_1	k_2	k_3
57.6	28.85	31.6 ± 1.2	4.10 ± 0.03	0.740 ± 0.011
60	26.75	32.6 ± 1.1	4.19 ± 0.06	0.846 ± 0.013
80	11.05	25.1	10.03	9.56

Discussion

While in higher dielectric media (D = 28.85) there is a marked difference between the values of k_2 and k_3 for this reaction, this difference disappears in low dielectric media (D = 11.05). Since the k_2/k_3 ratio is approaching unity, one may conclude that the mechanisms of the second and third steps of the reaction are becoming more nearly alike as the dioxane content of the medium is increased. The direction of the change of k_2 and k_3 with decrease in dielectric constant implies[4] that we are no longer dealing with reactions involving ions of like charge sign. However, at D = 28.85, the salt effect on k_2 and k_3 is in the direction which implies that the reaction could be between ions of like charge sign in both steps. The behavior observed here is similar to our observations for diester hydrolysis.[4] We explained our results before by ion-pairing. The studies reported here are consistent with such an explanation.