KINETIC STUDIES IN ESTER HYDROLYSIS

Part VIII. The Alkaline Hydrolysis of Ethyl Acetate in Acetone-Water Mixtures

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Received October 21, 1958

IN earlier parts of this series published in these *Proceedings*, the reaction in these solvent mixtures were studied over a large range of compositions. While it was clear that the reaction is an ion dipole one, certain discrepancies could not escape attention. While the trend of the reaction appeared to conform to normal expectations over the range of dielectric constants, abnormal features appeared to be unavoidable in the region of small additions of the organic solvent to water, particularly a reversal of the rate-constants in relation to the dielectric constant. A fuller study of these observations (5) appeared necessary and the present report deals with this abnormal region. A similar trend had also been noticed by Tommila and his associates, 1952.

DISCUSSION OF RESULTS

The experimental procedure adopted in the present studies involved a control of temperature and of composition as well as of analytical procedure which by standard statistical considerations can lead one to regard a difference in activation energy (Arrhenius) of the order of 300 calories as being outside the limits of experimental error. The values of the rate constants and the Arrhenius parameters for the reaction at three different temperatures are presented in Table I below. The range in temperatures had to be restricted by the low boiling point of the organic solvent and the need for a reasonable rate of reaction consistent with the accuracy aimed at. For fuller evaluation of the position of maximum rate and the drift in the position with temperature, it will be convenient to use the graphical representation in Fig. 1.

In all cases, rate constants as well as the Arrhenius parameters tend to rise progressively for small additions of organic solvent reaching a maximum in the region where the mole fraction of the acetone is between 0·015 and 0·021. Thereafter, the apparent influence of the solvent follows the normal expectations for an ion-dipole reaction. An examination of Fig. 1 further shows that increase of temperature enhances the abnormalities while retaining the general features. An examination of the Arrhenius parameters

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shows that, within the limits of experimental error, the activation energy increases linearly with the mole fraction of added acetone in the initial stages

TABLE I

All rate constants are in units of moles./litre/seconds^{-1}

Mole fraction of acetone	k_2 values			E K. Calories	$\log_{10}$ PZ
	30° C.	35° C.	40° C.		
0	0·1617	0·1862	0·2817	10·530	6·75
0·00497	0·1628	0·1929	0·2891	10·880	7·01
0·01009	0·1657	0·1974	0·2967	11·050	7·14
0·01538	0·1674	0·2053	0·3059	11·430	7·41
0·02084	0·1645	0·2018	0·3094	11·970	7·81
0·02646*	0·1589	0·1889	0·2890	11·340	7·33

* The value of the Arrhenius parameters for this solvent composition differs frcm the values reported in Part IV. This is partly due to the greater accuracy of temperature control as well as analytical technique.
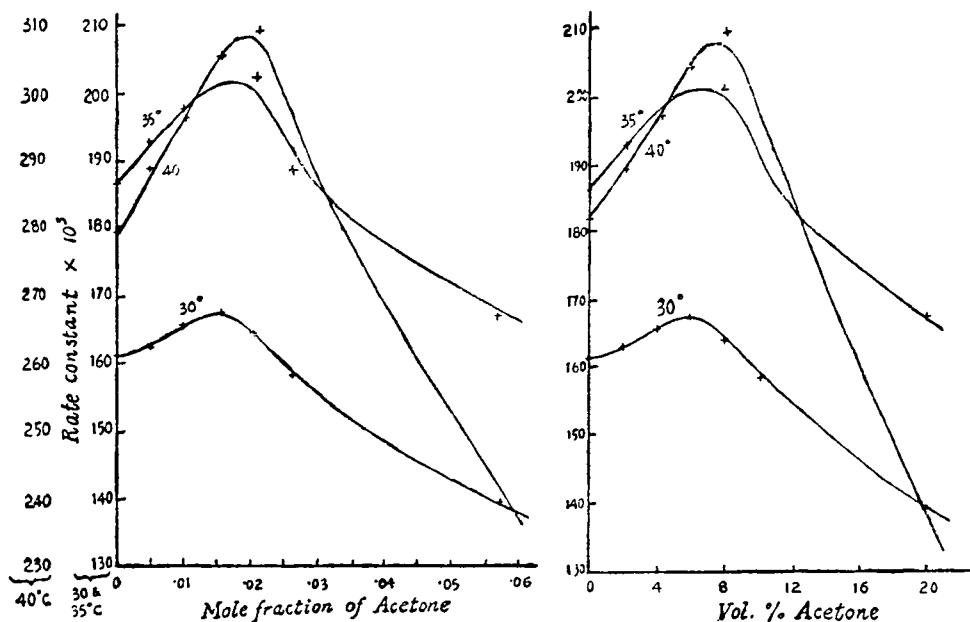

FIG. 1

before reaching a maximum value with a change in the slope thereafter (Fig. 2). The absence of any mechanistic change is clearly shown by the close parallelism between the frequency factor and Arrhenius activation energy (Fig. 3).
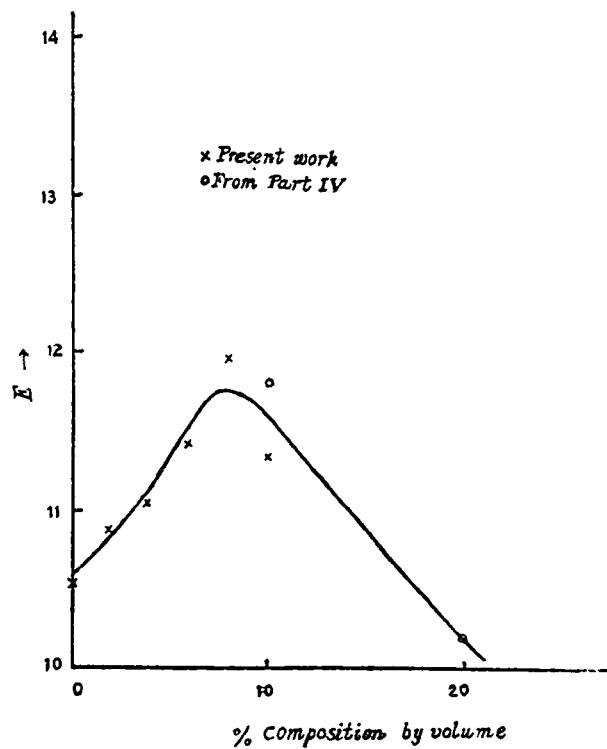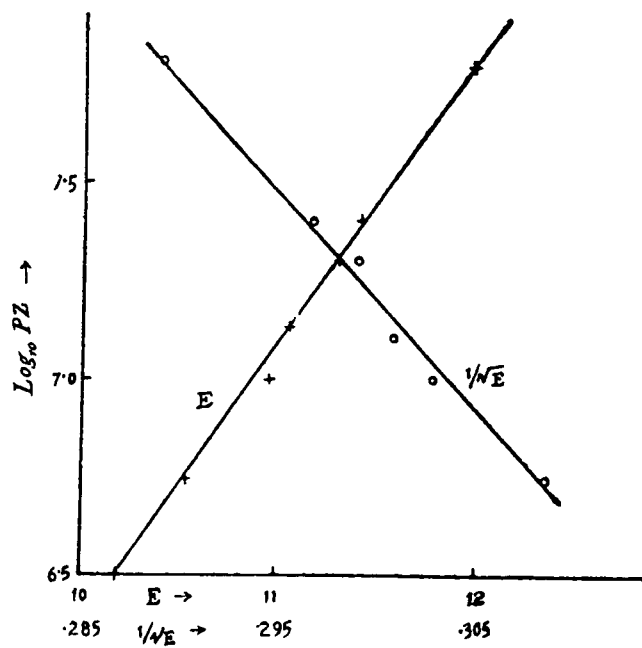
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FIG. 2

FIG. 3

A study of the physical properties of the mixtures of these two solvents clearly reveals the non-ideal behaviour of the binary system and this aspect is more fully considered in a separate communication. The last two columns of the table represent essentially composite quantities, not all of which can be readily computed. Following Fairclough and Hinshelwood (1938),[3] the entropy of activation which is included in the frequency factor of the rate equation may be considered to be related to the square-root of the activation energy and this too is noticed even where the rate constant is apparently abnormal (Fig. 3). The Arrhenius activation energy incorporates also a function of the dielectric constant of the medium but in the region of compositions used here no data are available and measurements are in progress in these laboratories to fill the gap.

Though it is generally considered that the slowest step in any postulated mechanism is the rate determining one and the measured rate constant is a measure of this part, it has to be recognised that all the terms in the rate equation are essentially composite involving all the steps. The accepted mechanism of ester hydrolysis involving hydroxyl ion catalysis involves in the first instance of a complex of the ester with the hydroxyl ion followed by interaction with solvent molecules leading to the products. Small additions of acetone can modify one or both the stages. The interacting ion is initially solvated, and as Ackermann (1957)[1] has shown, water molecules are disposed tetrahedrally round the hydroxyl ion. In the absence of evidence to the contrary, one may presume that small additions of acetone do not lead to any different reacting entity. The change in liquid structure brought about by this addition of acetone, however, alters the effective concentration of the hydrated hydroxyl ion and this should, in its turn, modify the entropy of activation. Apparently, this is balanced by the possibility of the solvation of the hydroxyl by acetone and the consequent increase in the size of the solvated ion increases the frequency of encounter.

As an ion-dipole reaction, even small changes in dielectric constant may be expected to be a dominant factor since the reaction rate constant may be ordinarily expressed by a relation of the type,

$$\ln k = \ln k_0 - f(1/D).$$

For small additions of organic solvent, changes in dielectric constant are relatively small and the normal influence of this factor is more than offset by structural changes in the environment.

While a study of catalysis by other species was not taken up, the earlier observations of Dawson (1927)[2] together with theoretical expectations on the

role of a common ionic species made it worth while to study the influence of added potassium acetate in the different solvent mixtures. Only a single concentration was tried and an upward trend in the rate was noticeable in all cases (Table II). At the same time the position of maximum velocity in relation to solvent composition shifted to a smaller proportion of the organic solvent.

TABLE II

Influence of added potassium acetate on reaction rate

Concentration of salt: 0·0444 M

Composition of solvent: Vol. % acetone	$100\ k_2$		
	30° C.	35° C.	40° C.
0	16·42	21·42	29·14
2	17·15	22·36	30·85
4	17·33	22·79	31·41
6	16·89	21·74	29·91
8	16·37	20·62	28·90
10	15·83	19·43	28·35

The pronounced catalytic effect of acetanions as well as the increase in dielectric constant in solutions of electrolytes appear to be more important than any possible mass law effect by the presence of a common ion. There does not appear to be any trend to suggest any complications of a first order kinetics that may be expected for base catalysed alkyl-oxygen fission. Under the conditions of experiment, normal acyl-oxygen fission with a transition state involving the association of the hydroxyl ion with the ester represents the course of the kinetics.

EXPERIMENTAL

Materials used.—All the solvents used were purified by methods described in earlier parts. Conductivity water was used, freshly prepared each time. The ester was purified by standard methods and fresh samples were used for each experiment. The potassium acetate used was a Merck extra-pure quality preparation and adequate precautions had to be taken to avoid

TABLE III

(Temperature of hydrolysis: 30° C.)

Volume % Acetone	Concentration of OH'	Concentration of Ester		Titre values for 5 ml. of reaction mixture				
0	0·02634 N	0·02584 M	t sec.	92·0	271·9	477·5	751·9	1440·0
			V, ml.	5·75	10·75	13·30	15·10	17·10
2	0·02365 N	0·02246 M	t sec.	92·4	313·0	510·8	684·1	966·1
			V, ml.	5·90	10·85	12·95	14·15	15·30
4	0·02420 N	0·02306 M	t sec.	77·7	226·6	402·5	597·0	838·0
			V, ml.	6·10	11·05	14·10	15·85	17·40
6	0·02400 N	0·02450 M	t sec.	83·2	257·6	456·0	679·6	1058·0
			V, ml.	5·75	10·70	13·20	14·85	16·25
8	0·02350 N	0·02486 M	t sec.	84·0	258·7	415·6	601·2	925·2
			V, ml.	6·10	10·90	13·10	14·60	16·05
10	0·02399 N	0·02752 M	t sec.	75·7	297·1	416·3	604·3	778·5
			V ml.	6·70	12·95	15·75	17·65	18·70

TABLE IV

(Temperature of hydrolysis: 35° C.)

Volume % Acetone	Concentration of			Titre values of aliquots				
	OH'	Ester						
0	0.02634 N	0.01981 M	t sec. V, ml.	128.5 3.60	398.5 8.70	711.2 10.15	1010.0 11.90	1372.0 12.50
2	0.02665 N	0.02284 M	t sec. V, ml.	94.5 3.00	358.9 9.50	593.4 11.65	891.9 13.05	1272.0 13.95
4	0.02704 N	0.02105 M	t sec. V, ml.	95.2 2.50	192.4 7.20	681.9 11.25	809.8 11.65	1186.2 12.55
6	0.02770 N	0.02375 M	t sec. V, ml.	97.2 3.00	326.0 9.10	664.6 12.15	1110.0 13.40	1328.0 14.05
8	0.02770 N	0.02171 M	t sec. V, ml.	107.8 2.85	296.8 7.85	540.4 10.35	769.6 11.55	973.5 12.20
10	0.02704 N	0.02416 M	t sec. V, ml.	118.6 4.10	380.5 9.95	639.9 12.25	908.6 13.45	1309.0 14.45

TABLE V

(Temperature of hydrolysis: 40° C.)

Volume % Acetone	Concentration of			Titre value of aliquots				
	OH'	Ester						
0	0·02845 N	0·02529 M	*t* sec.	86·7	275·6	465·9	836·9	1197·7
			V, ml.	6·40	12·55	14·80	16·60	17·35
2	0·02845 N	0·02462 M	*t* sec.	87·90	286·7	520·7	934·3	1286·2
			V, ml.	6·70	12·95	15·45	16·90	17·70
4	0·02715 N	0·02733 M	*t* sec.	80·20	278·4	475·1	763·9	1004·1
			V, ml.	7·00	13·70	16·20	17·75	18·45
6	0·02717 N	0·02334 M	*t* sec.	93·20	256·5	453·6	782·3	1223·4
			V, ml.	7·00	12·15	14·50	16·10	16·95
8	0·02629 N	0·02432 M	*t* sec.	78·60	248·4	424·1	675·0	883·0
			V, ml.	6·95	13·05	15·40	16·95	17·65
10	0·02589 N	0·02305 M	*t* sec.	72·10	217·1	365·4	549·8	743·0
			V, ml.	6·10	11·60	13·95	15·45	16·35

TABLE VI

The alkaline hydrolysis of ethyl acetate in the presence of potassium acetate

(Concentration of acetanions: 0·0444 M)

Volume % Acetone	Concentration of OH'	Concentration of Ester	Temp. °C		Titre values for aliquot parts			
0	0·025656 N	0·026204 M	30	t sec. V, ml.	117·3 4·85	326·1 10·25	533·0 12·65	785·2 14·40
	0·02592 N	0·02535 M	35	t sec. V, ml.	107·0 5·10	319·0 10·85	506·8 13·05	793·6 14·75
	0·02627 N	0·02322 M	40	t sec. V, ml.	79·90 6·70	274·00 12·50	420·3 14·20	712·0 15·80
2	0·02655 N	0·02589 M	30	t sec. V, ml.	337·30 11·24	506·20 13·35	762·20 15·15	984·2 15·85
	0·02656 N	0·02246 M	35	t sec. V, ml.	111·8 4·40	322·8 10·05	589·1 12·75	815·4 13·90
	0·02702 N	0·02435 M	40	t sec. V, ml.	74·35 6·00	225·2 11·44	377·4 13·65	558·2 14·95
4	0·02613 N	0·02181 M	30	t sec. V, ml.	276·0 8·90	503·4 11·80	693·0 13·15	999·4 14·35
	0·02526 N	0·02578 M	35	t sec. V, ml.	79·4 4·50	284·7 10·90	476·4 13·20	707·6 14·65
	0·02729 N	0·02522 M	40	t sec. V, ml.	87·8 6·70	261·0 11·70	443·6 13·60	747·3 15·00
6	0·02502 N	0·02578 M	30	t sec. V, ml.	74·2 4·80	216·7 9·50	410·5 12·85	593·4 14·60
	0·02526 N	0·02365 M	35	t sec. V, ml.	119·9 4·90	316·3 9·95	560·2 12·60	836·4 14·00
	0·02724 N	0·02609 M	40	t sec. V, ml.	82·2 9·55	252·1 15·55	481·6 18·15	853·6 19·55

errors through the hygroscopic nature of the compound. The physical characteristics used conformed to the following constant values in each sample prepared:

Ethyl Acetate: B.P., 77·1–77·2° C.
n_D^{30}, 1·3690
Density$_4^{25}$, 0·9010.

Acetone: B.P., 56·1–56·2° C.
n_D^{30}, 1·3530
Density$_4^{25}$, 0·7860.

Measurements.—The reaction was carried out in tested Jena glass bottles with negligible evaporation losses at the temperatures used over several weeks. Calibrated stoppered measuring flasks were used in preparing standard solutions and in determining concentrations, corrections were applied for the expansion of the solutions. Refractive indices were determined with a Pulfrich refractometer while densities were determined with pycnometers making due allowance for buoyancy corrections. The reactions were carried out in an accurate thermostat where temperatures were electronically controlled to 0·01° C.

Aliquot parts of the reaction mixture were analysed from time to time using an electrometric titration method employing the Serfass Electron Ray Titration Unit Assembly with two platinum electrodes.

Typical runs are presented in Tables III, IV, V and VI.

In Tables III, IV and V the concentration of the acid used for chilling the reaction was about twice that of the base.

SUMMARY

The alkaline hydrolysis of ethyl acetate in water containing small additions. of acetone have shown that the earlier expectations of abnormal trend in the rate of reaction were correct. The absence of mechanistic change is indicated by the continuity in the curve for correlation of the two Arrhenius parameters. Any explanation has to be in relation to the structure of the environment of the reacting species and the requirement of the properly hydrated reacting ion.

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