CCCXXVII.—*The Alkaline Hydrolysis of Esters in Aqueous Alcoholic Solution. Part I. The Interaction of Phenoxides and Aliphatic Esters in Alcoholic Solution.*

By Eric Stephen Gyngell.

It was found by Creasy (unpublished work) that when sodium β-naphthoxide and ethyl acetate were allowed to react in alcoholic solution, β-naphthol and sodium acetate were the principal products, ethyl ether and naphthyl acetate being obtained in small quantity. These results were interpreted as showing that the reaction had taken place according to the equations,

$$(1)\ C_{10}H_7{\cdot}ONa + Et{\cdot}OH \rightleftharpoons C_{10}H_7{\cdot}OH + NaOEt,$$
$$(2)\ CH_3{\cdot}CO_2Et + NaOEt \longrightarrow CH_3{\cdot}CO_2Na + Et_2O.$$

Robertson and Acree (*Amer. Chem. J.*, 1913, **49**, 474) drew the similar conclusion that the reaction between sodium ethoxide and phenol did not proceed to completion in the formation of phenoxide. Cox (J., 1918, **113**, 666; 1920, **117**, 493), Haywood (J., 1922, **121**, 1904), and Segaller (J., 1913, **103**, 1104) have investigated reactions involving similar equilibria, without drawing any definite conclusion as to the importance or position of the equilibrium point. The velocity coefficients obtained by these workers show a slight decline in value as the reaction proceeds. This has been taken as evidence in favour of the view that slight alcoholysis has taken place. This decrease in value is not larger than that obtained by Hecht, Conrad, and Brückner (*Z. physikal. Chem.*, 1891, **7**, 274) in their researches on the reaction between sodium ethoxide and alkyl iodides in alcoholic solution. There is no possibility of alcoholysis in this reaction and the slight decrease in the value of the velocity coefficients may be due to hydrolysis of the ethoxide by water present in the solution. (See also, Walker and Kay, J., 1897, **78**, 489; Kreman, *Monatsh.*, 1905, **26**, 279; and Senter, J., 1915, **107**, 1070.)

It was noticed by Cajola (*Gazzetta*, 1900, **30**, i, 233) that the saponification of methyl acetate by various bases in absolute methyl alcohol was not strictly bimolecular, and that the reaction appeared to cease before all the ester had been used. This has been interpreted by Cashmore, McCombie, and Scarborough (J., 1923, **123**, 197) as due to the degree of ionisation of the bases employed and to the stability of certain complexes. It is postulated that the reaction $CH_3{\cdot}OH + MOH \rightleftharpoons CH_3{\cdot}OM + H_2O$ cannot adjust itself with sufficient speed for the main reaction to go to completion or for bimolecular laws to be obeyed.

In the present work, it was considered desirable to conduct a series of preliminary experiments with a view to elucidate the conditions obtaining in alcoholic solutions of phenoxides. These experiments were at first conducted on the usual lines for velocity of reaction measurements. At 70° in ordinary absolute alcohol solution and with *N*/2-solutions, the time for half-reaction was considerably more than 10 hours. It was also evident that the reaction did not obey the simple bimolecular law which should have been followed had the course of the reaction been mainly:

$$1.\ C_6H_5{\cdot}ONa + CH_3{\cdot}CO_2Et \longrightarrow C_6H_5{\cdot}OEt + CH_3{\cdot}CO_2Na.$$

As a result of alcoholysis, there was also the possibility of the following reaction:

$$2.\ CH_3{\cdot}CO_2Et + EtONa \longrightarrow Et_2O + CH_3{\cdot}CO_2Na.$$

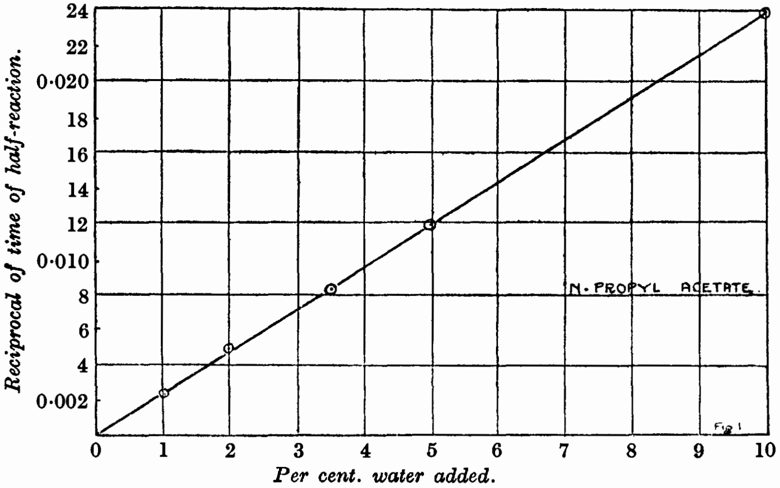
Conceivably both these reactions could take place at the same time, the extent depending somewhat upon the degree of alcoholysis of the phenoxide.

In general, the reaction yielded neither phenetole nor ether, and therefore did not proceed according to either of the above equations. Sodium acetate and phenol were, however, produced in quantity. In a few cases, notably with methyl and ethyl oxalates, anisole and phenetole, respectively, were produced in quantity, and the reaction proceeded much more rapidly than with esters of the acetic acid series. No phenyl ether was produced from malonic or succinic esters with the possible exception of dimethylmalonic esters.

The Rôle of Water in Alcohol.

Although elaborate precautions were taken to remove and exclude all traces of water from the ethyl alcohol used as solvent, its complete removal was found to be impracticable. In the purest alcohol obtainable, however, the reaction was very slow; but it was markedly accelerated by the water in less perfectly dried alcohol—even the 99·8% quality corresponds to a concentration of $N/10$ with regard to water.

FIG. 1.



By using very pure alcohol, it was hoped to show that the velocity of the reaction was zero in the absence of water. It was not possible, however, to demonstrate this directly by experiment, but by plotting the reciprocal of the time of half-reaction against the amounts of water added (Fig. 1), it was shown that the curve passed through the origin, thus indicating that the reaction would not proceed if the complete removal of water could be effected.

The form of the reaction curves suggested the intervention of an equilibrium. It was thought that an intermediate additive compound between the ester and the sodium phenoxide, similar to that produced in the formation of acetoacetic ester, might be formed, but no evidence could be obtained for this supposition. The postulation of a hydrolytic equilibrium, however, provided a satisfactory hypothesis, since it explained the form of the curves, and the effects of water in accelerating and of phenol in retarding the reaction. Thus, if the equilibrium and subsequent reaction are :

$$\underset{(c-x-y)}{C_6H_5{\cdot}OK} + \underset{(b-x-y)}{H_2O} \rightleftarrows \underset{(d+x+y)}{C_6H_5{\cdot}OH} + \underset{y}{KOH}.$$

$$\underset{(a-x)}{CH_3{\cdot}CO_2Et} + \underset{y}{KOH} \longrightarrow \underset{x}{CH_3{\cdot}CO_2K} + \underset{x}{EtOH}.$$

where a, b, c, and d are the initial concentrations of ester, water, phenoxide, and phenol, respectively, and x is the amount of potassium acetate formed and y is the amount of free potassium hydroxide present at time t; then the concentrations of the reacting molecules are as shown, and, for equilibrium,

$$K(c-x-y)(b-x-y) = (d+x+y)y \quad . \quad . \quad . \quad (1)$$

where K is the equilibrium constant. For the saponification of the ester,

$$dx/dt = k(a-x)y \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

k being the velocity coefficient. It must now be assumed that y is always very small compared with x, *i.e.*, that the alkali formed by hydrolysis is always at a negligibly small concentration. Combining (1) and (2) and eliminating y, we obtain

$$dx/dt = Kk(a-x)(b-x)(c-x)/(d+x) \quad . \quad . \quad (3)$$

which on integration yields

$$Kkt = \frac{d+a}{(b-a)(c-a)}\log_e\frac{a}{a-x} + \frac{d+b}{(a-b)(c-b)}\log_e\frac{b}{b-x} + \frac{d+c}{(a-c)(b-c)}\log_e\frac{c}{c-x} \quad (4)$$

Similarly, when the ester and phenoxide are present in equivalent amounts we obtain

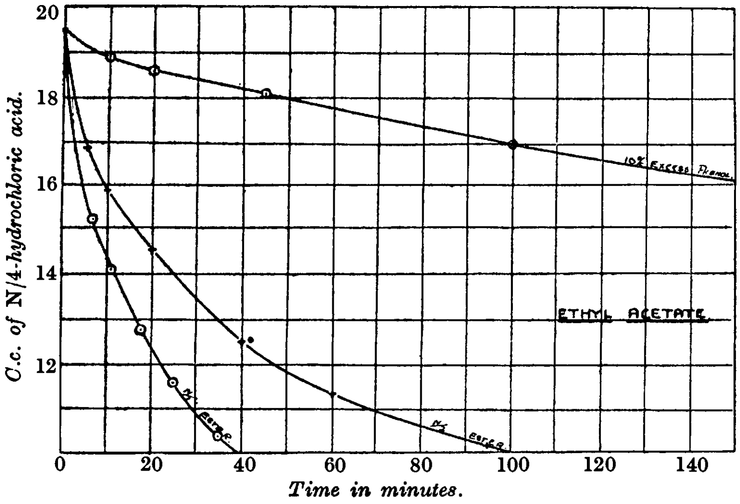
$$Kkt = \frac{d+b}{(b-a)^2}\log_e\frac{b(a-x)}{a(b-x)} + \frac{a+d}{b-a}\cdot\frac{x}{a(a-x)} \quad . \quad . \quad (5)$$

These formulæ were applied to the experiments performed with potassium phenoxide and ethyl acetate in alcoholic solution with satisfactory results. Formula (5) was, however, later modified to correct for the difference between the practical and the theoretical zero of the reaction. The formula used was

$$Kk(t_2 - t_1) = \frac{b}{(b-a)^2}\log_e\frac{(a-x_2)(b-x_1)}{(a-x_1)(b-x_2)} + \frac{1}{b-a}\left\{\frac{x_2}{a-x_2} - \frac{x_1}{a-x_1}\right\} \quad . \quad . \quad (6)$$

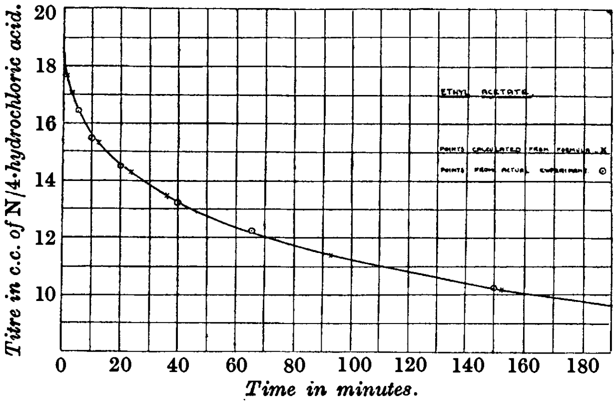
where the initial amount of phenol is zero. Actually it was found that the values of the coefficients obtained from this formula differed but little from those obtained from formula (5).

FIG. 2.



It will be seen that the velocity is proportional to the product (ester)(phenoxide)(water)/(phenol), and the effect of varying the concentration of the reactants is shown in Fig. 2. Fig. 3 shows

FIG. 3.



the experimental points and also the theoretical curve for a solution containing $N/2$-phenoxide and ester with 5% by volume of added water.

In a few cases it has been found possible to calculate the amount of water present in a solution containing no added water, and to use this calculated quantity for the determination of the velocity coefficients with satisfactory results.

EXPERIMENTAL.

Preparation of Potassium Phenoxide Solutions.—The phenoxide solutions employed were prepared by the method described by Robertson and Acree, except that it was impracticable to remove xylene from the metallic potassium by washing with absolute alcohol. Good potassium balls were therefore obtained practically free from incrustations. These balls were scraped clean under xylene, rapidly dried between filter-papers, and added to specially dried absolute alcohol under a reflux condenser. The condenser was fitted with a calcium chloride drying-tube, and the flask containing the alcohol was cooled by cold water. In this way it was found that phenoxide solutions could be prepared free from suspended matter, and showing scarcely any coloration even after standing for several weeks.

The ethoxide solution was titrated with standard acid, and the calculated amount of phenol was dissolved in alcohol and added to it; the whole was then diluted with alcohol to the required strength (usually N).

Purification of Alcohol.—The method employed consisted in refluxing alcohol with good, freshly-burnt quicklime for several days. It was thus possible to obtain alcohol of conductivity less than $0{\cdot}1 \times 10^{-6}$ at 25°. Loss of alcohol due to the wetting of the lime was reduced by using the lime successively for increasingly damp alcohol.

Preparation and Purification of Esters.—The esters were prepared by Fischer's method from pure materials. After purification in the usual way, they were carefully fractionated. Kahlbaum's esters were simply fractionated.

Phenol.—The best obtainable phenol was dried in a vacuum desiccator over sulphuric acid for several days, and it then distilled at a constant temperature.

Ester Solutions.—Purified ester was weighed out and diluted with the specially purified alcohol. The amount of water required was added at this stage, and the whole solution was diluted with absolute alcohol to make the N-solution. Thus for a reaction mixture to be $N/2$ with regard to both phenoxide and ester and to contain 5% of water by volume, the ester solution would be made N and would contain 10% by volume of water.

The reaction was found to proceed with suitable velocity at 70° and with potassium phenoxide and ethyl acetate concentrations of about $N/2$. Equal volumes (5 c.c.) of phenoxide and ester solutions were mixed in Jena glass tubes of about 13 or 14 c.c. capacity; these were then well corked and placed in the thermostat. Tubes were withdrawn at intervals, emptied into a beaker, rinsed with alcohol, and the liquid was titrated with standard acid. Some difficulty was found in obtaining an indicator giving a sharp end-point in phenolic solutions. Phenolphthalein and methyl-orange were valueless, but litmus and *p*-nitrophenol were the most satisfactory.

The following two tables show the velocity coefficients calculated from equation (6). The ethyl acetate and phenoxide were of equivalent strengths and the solutions contained 5% of water and no added water, respectively.

$a = c = 500;\ b = 2777{\cdot}7.$

t.	C.c. $N/2$-HCl.	x.	$a - x$.	$b - x$.	$kK \times 10^6$.
0	20	0	500·0	2777·7	—
10	15·6	110·0	390·0	2667·7	1·24
17	14·6	135·0	365·0	2642·7	1·21
25	13·6	160·0	340·0	2617·7	1·27
37	12·7	182·5	317·5	2595·2	1·19
50	11·2	202·5	297·5	2575·2	1·22
64	11·2	220·0	280·0	2557·7	1·23
112	9·7	257·5	242·5	2520·2	1·15
					Mean 1·22

$a = c = 500;\ b$ (calc.) $= 83{\cdot}3.$

t.	Titre.	x.	$a - x$.	$b - x$.	$kK \times 10^6$.
0	17·3	0	432·5	83·3	—
10	16·5	20·0	412·5	63·3	2·11
15	16·3	25·0	407·5	58·3	2·16
25	16·1	30·0	402·5	53·3	2·44
45	15·7	40·0	392·5	43·3	2·07
					Mean 2·19

The following table summarises the results of these and six other experiments and exhibits the effects of varying the initial concentrations of ethyl acetate, water, phenoxide, and phenol:

a.	b.	c.	d.	$kK \times 10^6$ (range).	$kK \times 10^6$ (mean).
500	2777·7	500	—	1·15—1·27	1·22
500	83·3	500	—	2·07—2·44	2·19
500	2777·7	122·5	—	0·92—1·12	1·02
500	2777·7	247·5	—	1·01—1·16	1·05
1000	2777·7	487·5	—	0·96—1·15	1·05
250	2777·7	487·5	—	0·88—1·19	1·00
487·5	2777·7	487·5	532·0	1·30—1·41	1·34
487·5	2777·7	487·5	212·7	1·12—1·50	1·38

Summary.

1. In alcoholic solution, the reaction between phenoxides and the esters studied does not follow the usual bimolecular law.

2. Normally the reaction does not go to completion, and the time–titration curves suggest an equilibrium reaction.

3. There is no evidence to show that the reaction proceeds according to the equation

$$C_6H_5{\cdot}OK + CH_3{\cdot}CO_2C_2H_5 \longrightarrow C_6H_5{\cdot}O{\cdot}C_2H_5 + CH_3{\cdot}CO_2K.$$

4. There is also no evidence in favour of the view that the reaction proceeds as a result of " alcoholysis " of the phenoxide.

5. The reaction proceeds as a result of hydrolysis of the phenoxide by water present in, or added to, the solution.

6. A mathematical expression has been deduced for the reaction and the velocity coefficients are shown to be satisfactory.

In conclusion, I should like to thank Dr. J. C. Crocker, for suggesting the research and for his unfailing interest in it, also the Department of Scientific and Industrial Research for a grant which made it possible for the work to be undertaken.

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[*Received, May* 31*st*, 1926.]