206. *The Reaction between Potassium* o-*Tolyloxide and Aliphatic Esters in Aqueous-alcoholic Solutions.*

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It has been shown by Gyngell (J., 1926, 2484) and Smith (J., 1927, 170) that, in reactions of the type studied in this research, the water in the aqueous alcohol hydrolyses the potassium salt to the free phenol and potassium hydroxide, and that the latter then hydrolyses the ester. The development of this hypothesis results in the following general expression for the velocity coefficient:

$$[Kk] = 1/t \, . \log_e\left[\left(\frac{a}{a-x}\right)^{\alpha} \cdot \left(\frac{b}{b-x}\right)^{\beta} \cdot \left(\frac{c}{c-x}\right)^{\gamma}\right] \quad . \quad . \quad . \quad . \quad (1)$$

where K is an equilibrium constant, k a velocity constant, x and t have their usual significance, and

$$\alpha = \frac{(d+a)}{(b-a)(c-a)}; \quad \beta = \frac{(d+b)}{(a-b)(c-b)}; \quad \gamma = \frac{(d+c)}{(a-c)(b-c)}$$

a, b, c, and d being the initial concentrations of ester, tolyloxide, water, and *o*-cresol, respectively.

Equation (1) is developed on the assumption that the free alkali concentration (y) is negligibly small compared with x. If, however, the effect of the term y on the tolyloxide concentration ($b - x - y$) is considered in the case when tolyloxide and ester are present in equivalent concentrations, then equation (1) takes the form

$$[Kk] = \frac{1}{t} \cdot \frac{d+c}{(c-a)^2}\left\{\log_e \frac{(a-x)}{(c-x)} \cdot \frac{c}{a}\right\} + \frac{1}{t}\left\{K + \frac{(d+a)}{(c-a)}\right\}\frac{x}{a(a-x)} \cdot \quad . \quad (2)$$

If the effect of the term y is neglected, the resulting equation is:

$$[Kk] = \frac{1}{t}\frac{d+c}{(c-a)^2}\left\{\log_e \frac{c}{a} \cdot \frac{(a-x)}{(c-x)}\right\} + \frac{1}{t}\frac{(d+a)}{(c-a)}\left\{\frac{x}{a(a-x)}\right\} \quad . \quad . \quad . \quad (3)$$

Equations (2) and (3) differ by the term $Kx/a(a-x)t$. Now K is of the order 10^{-4}, so appreciable error will not be introduced by the use of equation (3) unless (i) an ester of high velocity of saponification is used—ethyl formate was found to be a case in point—or (ii) a very highly hydrolysed phenoxide is employed. In cases (i) and (ii) the value of the composite velocity constant $[Kk]$ would decrease as the reaction proceeded.

If the effect of the alkali concentration y on the tolyloxide term ($b - x - y$) is considered in the case where the tolyloxide, ester, and water are non-equivalent and there is no initial excess of *o*-cresol, then

$$[Kk] = [A]/t + [B]/t$$

where the term $[A]/t$ is identical with the general equation (1) and

$$[B] = K\left[\frac{(b+c-2a)}{(b-a)(c-a)}\log_e\frac{a}{(a-x)} + \frac{1}{(a-b)}\log_e\frac{b}{(b-x)} + \frac{1}{(a-c)}\log_e\frac{c}{(c-x)}\right]$$

The value of $[B]$ at half reaction (time $t_{\frac{1}{2}}$), for the majority of the reactions studied in this work, was approximately

$$[B]_{t_{\frac{1}{2}}} = -\,0{\cdot}002 \times K/t_{\frac{1}{2}},\ i.e.,\ -\,2 \times 10^{-7}/t_{\frac{1}{2}} \text{ approx.}$$

In all but very fast reactions this term is negligible. The reaction between potassium *o*-tolyloxide and ethyl acetate proceeded smoothly, and values for the composite velocity constant were obtained which were within the limits of experimental error and in accordance with the theory indicated. A typical example is shown below, and the results are summarised in Table I.

Potassium *o*-tolyloxide = $N/4$. Ethyl acetate = $N/2$. Water = 10%. Initial excess *o*-cresol = $N/4$. Temp. = 60°.

t.	Titre.	*a*—*x*.	*b*—*x*.	*c*—*x*.	*x*.	10^6 *Kk*.	*t*.	Titre.	*a*—*x*.	*b*—*x*.	*c*—*x*.	*x*.	10^6 *Kk*.
0	20·0	500·0	250·0	5556	0	—	45	11·40	392·5	142·5	5448	107·5	1·52
5	18·20	477·5	227·5	5533	22·5	—	58	10·20	377·5	127·5	5433	122·5	1·42
15	15·80	447·5	197·5	5503	52·5	1·46	75	8·85	360·0	110·6	5417	139·4	1·52
25	14·05	425·6	175·6	5482	74·4	1·43	90	7·95	349·4	99·4	5405	150·6	1·40
35	12·60	407·5	157·5	5463	92·5	1·50	101	7·40	342·5	92·5	5398	157·5	1·45
												Mean	1·46

TABLE I.

Temp.	*b*.	*a*.	H_2O, %.	$Kk \times 10^6$.	Temp.	*b*.	*a*.	H_2O, %.	$Kk \times 10^6$.
50°	$N/2$	$N/2$	5·0	0·993	60°	$N/4$	$N/4$	2·5	1·96
,,	,,	,,	10·0	0·670	,,	$N/2$	$N/2$	5·0	1·67
55	$N/4$	$N/4$	2·68	1·57	,,	$N/4$	,,	5·0	1·66
,,	,,	$N/2$	2·5	1·53	,,	$N/8$	,,	5·0	1·66
,,	$N/2$	N	2·5	1·54	65	$N/4$	$N/4$	2·5	2·89
,,	,,	$N/2$	2·68	1·56	,,	$N/2$	$N/2$	5·0	2·60
,,	,,	,,	5·0	1·26	,,	$N/4$	,,	5·18	2·65
,,	,,	$N/4$	5·0	1·27	,,	,,	$N/4$	5·18	2·48
,,	,,	$N/8$	5·0	1·29	,,	$N/2$	,,	10·18	2·22
,,	$N/4$	$N/4$	5·0	1·16	,,	$N/4$	,,	10·0	2·09
,,	$N/2$	$N/2$	10·0	0·845	70	$N/2$	,,	12·5	4·02
60	,,	,,	2·5	1·95	,,	,,	,,	5·0	3·97
,,	$N/4$	,,	2·5	1·94	,,	,,	,,	10·0	3·17

The strong accelerating influence of water on the velocity is a marked feature of this reaction. The time for half reaction falls rapidly as the percentage of water is increased, but as Table II shows, the composite velocity constant *Kk* also decreases in value when the water content of the alcohol is increased.

TABLE II.

$N/4$-Potassium *o*-tolyloxide. $N/2$-Ethyl acetate.

	Temp. 60°.							Temp. 70°.				
H_2O, %	0·36	2·5	5·0	10·0	20·0	40·0	60·0	2·68	5·0	10·0	12·5	25·0
$Kk \times 10^6$	3·25	1·94	1·66	1·43	1·18	0·996	0·813	4·30	3·79	3·12	2·89	2·21

It was found, however, that although the velocity of reaction is greatly accelerated by increasing the water content of the solvent alcohol, the velocity is not strictly proportional to the concentration of water present, as Table III shows. This is explained by the fact that the solvent medium is considerably altered by the addition of more than 10% water.

TABLE III.

$N/4$-Potassium *o*-tolyloxide. $N/2$-Ethyl acetate. Temp. 60°.

H_2O, %	2·5	5·0	10·0	20·0	40·0	60·0
Amount of H_2O at 50% reaction	1,264	2,653	5,431	10,985	22,097	33,208
dx/dt at 50% reaction	0·9196	1·650	2·912	4·863	8·253	10·13
$10^4(dx/dt)/[H_2O]$ at 50% reaction	7·27	6·22	5·36	4·43	3·74	3·05

The reaction, however, will not proceed in the absence of water, and Smith's statement (J., 1927, 172) that the time for half reaction is infinite when the water content falls below half that of the concentration of ester and tolyloxide has now been confirmed. It is, in fact, possible to use this reaction to determine the water content of ethyl alcohol, by interpolating the reciprocal of time to half reaction against the water content, on a graph drawn from a series of reactions with known water content. This method is sufficiently accurate to measure 0·15% of water.

Temperature Coefficient.—This has been determined by application of the modified Arrhenius equation :

$$\log_e \frac{[Kk]_{t+10}}{[Kk]_t} = \frac{(Q_1 + Q_2)}{R}\left(\frac{1}{T} - \frac{1}{T + 10}\right)$$

The mean value for $(Q_1 + Q_2)$ calculated over the range 55—70° is 16,400. The ratio $[Kk]_{t+10}/[Kk]_t$ over the same range is 2·1.

Displacement Effect.—The reaction has been studied in mixed alcohols. The partial displacement of ethyl by methyl alcohol gave irregular results. The addition of up to 10% by volume of methyl alcohol raised the velocity of reaction; further addition up to 40% retarded it. On the other hand, displacement of ethyl alcohol by both *n*-propyl and *n*-butyl alcohol caused progressive acceleration of the reaction : the velocity was 1·9 times as fast in *n*-butyl as in ethyl alcohol. It is very doubtful whether this accelerating influence is due to increased alcoholysis. That slight alcoholysis may occur with ethyl alcohol as a solvent is probable, but it can be shown that if the composite velocity constant *Kk* is approximately proportional to the time to half reaction, then the extent to which alcoholysis is increased by the addition of a second alcohol is negligible. That the relationship $Kk \propto 1/t_{\frac{1}{2}}$ is approximately true for mixtures of ethyl with *n*-propyl and *n*-butyl alcohol is shown in Table IV. The proportionality does not hold for methyl alcohol.

TABLE IV.

N/4-*o*-Tolyloxide. N/2-Ethyl acetate. Water 5%. Temp. 60°.

Methyl alcohol.				n-*Propyl alcohol.*				n-*Butyl alcohol.*			
Second alcohol, %.	$10^6 Kk$.	$t_{\frac{1}{2}}$, mins.	$10^5 Kk \times t_{\frac{1}{2}}$.	Second alcohol, %.	$10^6 Kk$.	$t_{\frac{1}{2}}$, mins.	$10^5 Kk \times t_{\frac{1}{2}}$.	Second alcohol, %.	$10^6 Kk$.	$t_{\frac{1}{2}}$, mins.	$10^5 Kk \times t_{\frac{1}{2}}$.
0	1·66	28·0	4·65	2·5	1·73	25·5	4·41	5·0	1·77	25·5	4·51
5	1·96	23·5	4·61	5·0	1·77	25·0	4·42	10·0	2·02	22·5	4·54
10·0	2·07	23·5	4·86	10·0	1·84	24·0	4·42	40·0	2·37	19·0	4·50
20·0	1·98	23·0	4·55	20·0	1·92	23·0	4·42	80·0	2·83	15·5	4·40
40·0	2·11	24·5	5·17	40·0	2·14	21·0	4·49	100·0	3·09	14·0	4·43

There are indications that the acceleration in the presence of mixed alcohols is due to alcohol–cresol association. There is nothing to show, however, whether the velocity of saponification is either accelerated or retarded by the solvent employed, or whether there is any variation in the equilibrium constant.

Relative Ester Activity.—In general, the degree of activity falls off in a regular manner with increase in the molecular weight of the ester. Table V shows the comparative activities of the esters, ethyl acetate being taken as the standard.

TABLE V.

N/4-Potassium *o*-tolyloxide. N/2-Ester. 5% Water. Temp. 60°.

Ester.	$10^6 Kk$.	$\frac{[Kk]_{\text{ester}}}{[Kk]_{\text{EtOAc}}}$.	Ester.	$10^6 Kk$.	$\frac{[Kk]_{\text{ester}}}{[Kk]_{\text{EtOAc}}}$.
Ethyl formate	*ca.* 894·0	*ca.* 539·0	Propyl acetate	1·59	0·96
,, acetate	1·66	(1·00)	*n*-Butyl ,,	1·54	0·93
,, propionate	0·940	0·57	*iso*Butyl ,,	1·40	0·84
,, butyrate	0·507	0·30	*Phenyl ,,	0·094	0·057
Methyl acetate	2·35	1·42			

* With N/4-potassium phenoxide.

The reaction with ethyl formate was abnormally fast and it was impossible to obtain satisfactory constants. There is reason to believe that this is in part due to the presence of formic acid formed as result of partial hydrolysis of the ester by the water. Neither methyl nor *iso*butyl acetate, as compared with ethyl acetate, is quite regular in its degree of reactivity; as might be expected, the phenyl acetate–potassium phenoxide reaction is normal but extremely slow. This is due to the repression of the hydrolysis of potassium phenoxide by the phenol liberated by the saponification of the ester. Satisfactory constants were obtained by use of the formulæ, suitably modified. An example is given in Table VI.

TABLE VI.

N/4-Potassium phenoxide. *N*/2-Phenyl acetate. 5% Water. Temp. 60°.

t.	Titre.	*a*—*x*.	*b*—*x*.	*c*—*x*.	*x*.	10^7 *Kk*.	*t*.	Titre.	*a*—*x*.	*b*—*x*.	*c*—*x*.	*x*.	10^7 *Kk*.
0	30·0	500·0	250·0	2778	0	—	65	16·05	450·6	200·6	2728	49·1	1·01
10	17·85	473·2	223·2	2751	26·8	—	95	15·5	443·8	193·8	2721	56·2	0·96
20	17·05	463·1	213·1	2741	36·9	0·96	110	15·25	440·6	190·6	2718	59·4	0·86
35	16·70	458·8	208·8	2736	41·2	0·94	122	15·1	438·8	188·8	2716	61·2	0·91
												Mean	0·94

Evaluation of Equilibrium Constant, K, *and Velocity Constant,* k.—By carrying out a series of experiments with the same concentrations of reactants in each case, and gradually increasing the initial quantity of *o*-cresol until the velocity of reaction became very small, it was possible to estimate approximately the extent to which the potassium *o*-tolyloxide was hydrolysed. This was done by comparing the times to 10%, 20%, 30%, etc., reaction (measured in terms of the theoretical quantity of *o*-cresol present in the reaction mixture) with the experimental results obtained when no initial excess of *o*-cresol was added. In the latter circumstances the empirical results showed a small but regular displacement from those indicated theoretically, and the extent of the displacement was taken as an approximate measure of the extent of hydrolysis of the tolyloxide. The results obtained are shown below.

N/4-Potassium *o*-tolyloxide. *N*/2-Ethyl acetate. Temp. 60°.

Water, %.	Hydrolysis of KOC_6H_4Me, %.	*Kk* × 10^6.	*K* × 10^4.	*k* × 10^3.
5	4·9	1·66	2·28	7·28
10	6·4	1·43	1·98	7·23

Since the velocity constant is approximately the same with both 5% and 10% water solutions, it may be assumed that the variation of the equilibrium constant is the factor which causes the decrease in the values of the composite velocity constants with increase in the water concentration as noted in Table II.

EXPERIMENTAL.

Ethyl alcohol was dried by repeated refluxing over freshly burnt quicklime. Final drying by refluxing over fresh calcium turnings and also by Selman and Fletcher's method (*Trans. Faraday Soc.*, 1929, **25**, 432) offered no advantage. Methyl, *n*-propyl, and *n*-butyl alcohols were fractionated before treatment with quicklime. The esters were washed with dilute sodium carbonate solution, shaken vigorously with a saturated solution of calcium chloride to remove alcohol, dried for several days over freshly fused calcium chloride, and fractionated. Ethyl formate so treated developed traces of formic acid after a few days; it was therefore kept over chalk and distilled as required. Potassium *o*-tolyloxide was prepared in alcoholic solution by Robertson and Acree's method (*Amer. Chem. J.*, 1913, **49**, 474; see also Cox, J., 1918, **113**, 670). The solution was bright golden-yellow.

An ordinary gas-heated thermostat fitted with a mercury–toluene gas regulator of variable limit ± 0·05° was used. The reaction mixture was contained in Jena hard-glass tubes of approximately 12 c.c. capacity, fitted with rubber bungs. Ester solutions were prepared by weighing out the required amount of ester and diluting immediately with dry alcohol. The calculated quantity of water was then added, and finally the solution was diluted with dry alcohol to bring it to the exact normality required. 5 C.c. quantities of both tolyloxide and ester solutions were then pipetted separately into the reaction tubes. The most suitable indicator was found to be litmus. When the concentration of initially added *o*-cresol was high, the end-point was difficult to observe owing to slight fading; moreover, it was not very sharp when the reaction was nearing completion. All other indicators, except lacmoid, exhibited pronounced fading. The double tube method for the measurement of rapid reactions described by Smith (*loc. cit.*) was used for the ethyl formate reaction, but it did not give satisfactory results at the temperatures used in this work, for the ester was partially hydrolysed during the warming period, so satisfactory constants were not obtained.

The reaction products were examined by Cox's method of relative densities for formation of ether, but no trace was detected in any of the reactions; nor was any compound found other than those indicated by theory.

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