XXVIII.—*The Interaction of Potassium* m-*Tolyloxide with Aliphatic Esters in Aqueous–Alcoholic Solutions.*

By Ernest Lester Smith.

This research is an extension of the work of Gyngell (J., 1926, 2484; and private communication) on the interaction of potassium phenoxide with aliphatic esters in alcoholic solutions. The present reaction is shown to take the same course as the former : The water in the aqueous alcohol hydrolyses the potassium tolyloxide, with formation of cresol and potassium hydroxide; the latter then hydrolyses the ester. This hypothesis led to an expression for the velocity coefficient which was satisfactory within the limits of experimental error. Thus, we have

$$\underset{(c-x-y)}{CH_3{\cdot}C_6H_4{\cdot}OK} + \underset{(b-x-y)}{H_2O} \rightleftharpoons \underset{(d+x+y)}{CH_3{\cdot}C_6H_4{\cdot}OH} + \underset{y}{KOH}$$

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

where a, b, c, and d are the initial concentrations of ester, water, tolyloxide, and cresol, respectively, and x is the amount of potassium acetate formed and y the amount of free potassium hydroxide present at time t, the concentrations of the reacting molecules being as shown. For equilibrium

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

where K is the equilibrium constant. For the second reaction

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

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. Eliminating y, we obtain

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

which on integration yields

$$Kk(t_2-t_1) = \frac{(d+a)}{(b-a)(c-a)}\log_e\frac{(a-x_1)}{(a-x_2)} + \frac{(d+b)}{(a-b)(c-b)}\log_e\frac{(b-x_1)}{(b-x_2)} + \frac{(d+c)}{(a-c)(b-c)}\log_e\frac{(c-x_1)}{(c-x_2)} \quad . \quad . \quad . \quad . \quad (4)$$

t_1 and x_1 corresponding to the earliest determinable time and titre, respectively, and t_2 and x_2 to subsequent determinations.

Simplification can be effected for two special cases: (*a*) When ester and tolyloxide are present in equivalent proportions, *i.e.*, $a = c$,

$$Kk(t_2 - t_1) = \frac{(d+a)(x_2-x_1)}{(b-a)(a-x_1)(a-x_2)} + \frac{(d+b)}{(b-a)^2}\log_e\frac{(b-x_1)(a-x_2)}{(b-x_2)(a-x_1)} \quad (5)$$

and (*b*) when, in addition, water is in such large excess as to be virtually constant,

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

The reaction between potassium *m*-tolyloxide and ethyl acetate proceeded somewhat more rapidly than that with potassium phenoxide under the same conditions. On application of formula (5), with $x_1 = 0$, $t_1 = 0$, values were obtained for Kk which were sensibly constant. Further experiments, in which the concentrations of the reactants and also the temperature have been varied between wide limits, have yielded values for kK in which the maximum deviation from the mean usually lies between 2 and 5%; this can be ascribed to experimental error, since the deviations are irregular.

The following experiment is typical, time being expressed in minutes and concentrations in milliequivs. per litre.

TABLE I.

Potassium *m*-tolyloxide, *N*/2. Temperature 70°.
Ethyl acetate, *N*/2. Water = 10% of total.

Time.	Titre.	% Reaction.	x.	$a - x$.	$b - x$.	$Kk \times 10^6$.
0	20·0	—	—	500	5555	—
5	15·3	23·5	117·5	382·5	5438	—
19	11·75	41·2	206	294	5349	1·64
35	9·95	50·2	251	249	5304	1·65
41	9·6	52·0	260	240	5295	1·58
54	8·65	56·8	284	216	5271	1·64
87	7·25	63·8	319	181	5236	1·62
119	6·3	68·5	342·5	157·5	5213	1·63
125	6·25	68·8	344	156	5211	1·60
					Mean	1·62

The reaction is evidently similar to that investigated by Gyngell (*loc. cit.*). No trace of the *m*-tolyl ether could be detected among the products of reaction. Further, if it proceeded in any way different from that assumed, it is extremely unlikely that constant values for Kk would be obtained from the above formula. For example, it can be shown that any side reaction, occurring to the extent of 1—2% during the course of an experiment, would suffice to make Kk increase or decrease to the extent of about 10% during the run.

The reciprocal of the time for half-reaction was plotted against water concentration for several series of experiments. In each case, the curve was found to cut the water axis at a point corresponding to a water concentration of half that of the ester and tolyloxide, indicating that the time for half-reaction is infinite for water concentrations below this amount; this result is confirmed by the fact that reaction ceases when the water is entirely consumed.

Tables II, III, IV, and V show the values of Kk obtained with the four esters examined. In the last three tables, the concentration of both the ester and the tolyloxide was $N/4$.

TABLE II.

Reaction with ethyl acetate.

% Water.	Tolyloxide.	Ester.	$Kk \times 10^6$.	
0·27	$N/2$	$N/2$	2·55	
1	,,	,,	2·48	
2·5	,,	,,	2·31	
2·5	,,	,,	2·29	Excess cresol = $N/8$.
2·5	,,	,,	2·48	Excess cresol = $N/4$.
5·2	$N/4$	$N/4$	1·92	
5	,,	,,	1·21	Temp. 64·9°.
5	,,	,,	0·84	Temp. 60·1°.
5	$N/8$	$N/2$	1·70	
5	$N/4$	,,	1·82	
5	$N/2$	,,	2·00	
5	,,	N	1·97	
5	,,	$N/4$	1·98	
7·5	,,	$N/2$	1·85	
9	,,	,,	1·65	
10	,,	,,	1·62	
12	,,	,,	1·50	
15	,,	,,	1·37	
20	,,	,,	1·26	
30	,,	,,	1·17	
100	$N/8$	$N/8$	0·880	
100	,,	,,	0·0240	Temp. 30°.
100	,,	,,	0·0149	Temp. 25°.

TABLE III.

Reaction with *n*-butyl acetate.

% Water ...	1·1	2·7	5·0	7·7	10·0	20·0	30·0	45·0
$kK \times 10^6$ ...	1·23	1·22	1·08	1·04	1·041	0·783	0·652	0·525

TABLE IV.

Reaction with *n*-propyl acetate.

% Water	1	2·5	5	10	15	20
$kK \times 10^6$	2·10	1·90	1·67	1·445	1·265	1·13

TABLE V.

Reaction with methyl acetate.

% Water	1	2·5	5	7·5	10	15	25
$kK \times 10^6$	1·91	1·605	1·40	1·34	1·29	1·31	1·33

Relative Activity of the Esters.—It was to be expected that the values of kK for the different esters would be in the order of their molecular weights, since the esters employed are members of an homologous series. As shown by the tables, however, methyl acetate is abnormal for low percentages of water.

Evaluation of Equilibrium Constant.—The constants obtained are the product of an equilibrium constant and a velocity coefficient. It is obviously desirable to determine the magnitudes of these separately if possible. A method by which this might be achieved, for the reaction in aqueous solution, was the comparison of the rates of hydrolysis of an ester by potassium tolyloxide and by potassium hydroxide, respectively. In the second case, k can be obtained directly, and by substituting this in the value for kK from the first experiment, it is evident that K can be calculated.

Preliminary experiments indicated that the reaction between potassium hydroxide and ethyl acetate was half completed in about 1 minute in the concentrations used, *viz.*, $N/8$ at 30°. As it was desirable to carry out the experiment under these conditions, a special apparatus was designed for the purpose, which is described in the experimental section. The bimolecular coefficients obtained show a maximum deviation from the mean of only 2·5%. The results are as follows :

Concentrations, $N/8$ in aqueous solution. Temperature, 30°. $kK = 0{\cdot}024 \times 10^{-6}$; $k = 0{\cdot}0086$; therefore $K = 2{\cdot}80 \times 10^{-6}$.

A further method by which the value of the equilibrium constant in aqueous solution has been found is by electrometric measurement of the hydrogen-ion concentration in solutions of potassium *m*-tolyloxide. The *E.M.F.* between a hydrogen electrode, immersed in a $N/8$-solution of potassium *m*-tolyloxide, and a saturated calomel electrode was measured by a potentiometer in the usual way. As the p_H is largely affected by a slight excess of either *m*-cresol or potassium hydroxide in the solution, the following procedure was adopted : To the solution were added a few c.c. of potassium hydroxide solution, and the mixture titrated until acid, using a microburette. The curve showed two breaks as anticipated. The first corresponds to the point where cresol and alkali are present in equivalent amounts, and the second more pronounced break to the point where all the alkali has been neutralised. The position of the first break was fixed by a cusp on the first differential curve. K

could have been calculated from the voltage at the equivalent point, so found, but for various reasons it was considered preferable to make use of a comparison method. Accordingly, the experiment was repeated, adding $N/10$-potassium hydroxide to $N/8$-potassium chloride solution. The ionisation of the former can be considered the same in solutions of potassium chloride or tolyloxide of the same strength; the alkali concentration is therefore the same in the two solutions when the *E.M.F.* is the same. Hence K can readily be calculated. The results are as follows :

Percentage hydrolysis of potassium *m*-tolyloxide	2·8%.
Equilibrium constant, K,	$1{\cdot}6 \times 10^{-6}$.

These experiments were carried out at 14·5°. Applying the temperature coefficient to the value for K obtained by the previous (kinetic) method, the value at 14·5° is calculated to be $1{\cdot}55 \times 10^{-6}$.

Both these methods appear to be of general application for the determination of the hydrolysis constants of the salts of very weak acids. The dynamical method is probably the more accurate. This value cannot, however, be applied to alcoholic solutions with any certainty, owing to "solvent effect," and it has not been found possible to determine K for alcoholic solutions. The comparison of the rates of hydrolysis of an ester by potassium tolyloxide and by potassium hydroxide is of no value on account of the potassium hydroxide–ethoxide equilibrium, for which the value of the equilibrium constant is at present unknown. Electrometric methods are equally inapplicable.

It will be seen from the tables that in aqueous-alcoholic solutions the value of the composite constant kK decreases with increase in the water concentration. It is, however, impossible to state whether this is due to variation of the velocity coefficient, of the equilibrium constant, or of both.

Alcoholysis of Potassium m-*Tolyloxide.*—In aqueous–alcoholic solutions of potassium *m*-tolyloxide, it is very probable that a certain amount of potassium ethoxide is present in equilibrium with the other components. It can be shown that the extent of this alcoholysis must be very small, since otherwise a more complicated formula would be required in order to give satisfactorily constant values for kK.

Temperature Coefficients.—It can be shown that the value of Q in the Arrhenius equation is the sum of the values for the two reactions :

$$\log_e K_1/K_2 = Q_1(1/T - 1/T')/R$$

$$\log_e k_1/k_2 = Q_2(1/T - 1/T')/R$$

Adding,

$$\log_e k_1K_1/k_2K_2 = (Q_1 + Q_2)(1/T - 1/T')/R$$

The temperature coefficient in alcoholic solution with 5% of water has been measured with the following results :

TABLE VI.

Ethyl acetate, $N/4$. Potassium *m*-tolyloxide, $N/4$.

Temp.	$kK \times 10^6$.	$Q_1 + Q_2$.
60·1°	0·84	
64·9	1·21	17,000
70·0	1·76	16,900
		Mean 16,950

Ratio for 10° rise, 2·1.

The temperature coefficient in aqueous solution has also been measured :

TABLE VII.

Ethyl acetate, $N/8$. Potassium *m*-tolyloxide, $N/8$.

Temp.	$kK \times 10^6$.	$Q_1 + Q_2$.
25·1°	0·0149	
30·0	0·0240	17,200
70·0	0·880	18,500

Q_2, the value of Q for the hydrolysis of ethyl acetate by potassium hydroxide in aqueous solution, has been determined previously. Its value over the range 25—35° is 10,900 calories. If this number be subtracted from the value of $Q_1 + Q_2$ above, for the same range, the result will be Q_1. Hence $Q_1 = 6{,}300$ calories.

Reaction with Other Esters.—Gyngell (*loc. cit.*) has shown that certain esters, notably methyl and ethyl oxalates, react with potassium phenoxide differently from those of the methyl acetate series, giving rise to the corresponding phenyl ether in the same way as the alkyl iodides. The reaction between potassium *m*-tolyloxide and ethyl oxalate in dry alcoholic solution has been investigated. A liquid was obtained identical in properties with *m*-tolyl ether, prepared in the usual way.

Ethyl tartrate and ethyl and propyl formates have also been used. These esters react normally, but more than one hundred times as rapidly as ethyl acetate. After the water in the alcohol has been consumed, a very slow reaction appears to continue, with formation of the tolyl ether. In these cases, the yield was very small, rendering identification difficult.

Gyngell has suggested that the only esters with which this ether formation occurs are those in which no α-hydrogen atom is present. It is, however, difficult to understand how the mere absence of a group can cause a reaction to proceed, or how its presence can inhibit a reaction in which the group concerned takes no part. Moreover, formic and tartaric esters contain one α-hydrogen atom.

A fact much more likely to influence their reactivity is that these esters are all derived from relatively strong organic acids. This suggestion brings these esters into line with those of the common inorganic acids, which all appear to yield the ether readily and are all derived from very strong acids.

Reaction with Ethyl Monochloroacetate.—Monochloroacetic acid is one of the strongest organic acids, and, moreover, it has two α-hydrogen atoms. It therefore seemed of special interest to investigate the behaviour of its ethyl ester with potassium *m*-tolyloxide. The substances reacted very rapidly in dry alcoholic solution, but the main product proved to be a new ester, *ethyl* m-*tolyloxyacetate* :

$$CH_2Cl{\cdot}CO_2Et + C_7H_7{\cdot}OK \longrightarrow KCl + C_7H_7{\cdot}O{\cdot}CH_2{\cdot}CO_2Et.$$

At the same time, a small quantity of the tolyl ether appeared to be formed.

Ethyl *m*-tolyloxyacetate does not appear to have been described previously, although the corresponding acid and some of its other compounds are mentioned by Beilstein. The ester is a colourless, oily liquid with a peculiar characteristic smell; b. p. 264°, with slight decomposition.

EXPERIMENTAL.

Alcohol was dried by refluxing with quick-lime for a few days. During the earlier part of this work, alcohol so treated was deemed to be dry, but later the remaining water was estimated by a method devised by the author, which it is hoped to publish shortly.

Potassium *m*-tolyloxide was prepared in solution only; potassium metal, rapidly freed from oil between filter papers, was added to alcohol under reflux, and the equivalent of *m*-cresol then added. This method of preparing such compounds has been justified by Robertson and Acree (*Amer. Chem. J.*, 1913, **49**, 474) and by Cox (J., 1918, **113**, 670).

In all cases, the desired amount of water was added to the ester solutions, prepared as required. The reaction was carried out in a series of gas-heated thermostats regulated to ± 0·05° by means of mercury-filled thermo-regulators. The reaction vessels consisted of hard-glass test-tubes of about 15 c.c. capacity closed by rubber stoppers. In most cases, 5 c.c. of each solution were pipetted separately into each tube. After shaking, the tubes were transferred to the thermostat and withdrawn at suitable intervals of time, the contents being titrated with standard hydrochloric acid.

The Titration.—The accurate titration of the reaction mixture presents a problem of some difficulty. The mixture consists of alcohol, unchanged ester, free cresol, and potassium acetate and tolyloxide. The last two substances are salts of a strong base and a weak acid, so that both will be hydrolysed in solution, although to a different extent. In titrating the solution in the usual way, we are treating the potassium tolyloxide as an alkali and the potassium acetate as a neutral salt. Neither assumption is strictly correct. If a solution of the two salts, together with excess alkali, is titrated electrometrically, a curve will be obtained which shows three breaks, corresponding respectively to neutralisation of the free base, of that in the potassium tolyloxide, and of that in the potassium acetate. Consequently, the breaks cover a smaller range of p_H and are much less sharp than in an ordinary titration, and the choice of a suitable indicator is important. The problem is further complicated by the fact that the amount of potassium tolyloxide is decreasing, and potassium acetate increasing, throughout a run. It has been calculated that in a typical experiment the p_H value at the end-point varies from about 6 initially to 8 at three-quarter reaction, the end-point becoming progressively less sharp as the reaction proceeds. Since it is preferable to use the same indicator throughout, it is best to choose one which changes at p_H 7—8. This condition is satisfactorily fulfilled by litmus, provided that the bluish-violet colour is taken to indicate the end-point. These considerations are completely borne out in practice. Litmus is the only indicator, apart from lacmoid, which has been found satisfactory, others changing colour slowly and not at the true end-point.

Measurement of Rapid Reactions.—A simple apparatus was devised for this purpose consisting of a hard-glass boiling tube, with a smaller tube inside of about 12 c.c. capacity. The outer tube was closed by a rubber stopper to which was affixed a piece of stiff wire, bent at the end, which held the inner tube in position. 10 C.c. of one solution were delivered into the inner tube, and 10 c.c. of the other into the outer tube. After being heated in the thermostat for about 15 minutes, the apparatus was inverted once or twice to mix the solutions, then rapidly replaced in the thermostat. After the desired time, the contents were quickly poured into 20 c.c. of cold water containing nearly sufficient acid to neutralise the remaining alkali, the tubes rinsed out, and the titration was completed. By this means, the time error was probably not more than 2 or 3 seconds.

Summary.

1. The velocity of reaction between potassium *m*-tolyloxide and certain aliphatic esters in aqueous–alcoholic solutions has been investigated.

2. It is found that an equilibrium is established between potassium tolyloxide, water, cresol, and potassium hydroxide; the ester is hydrolysed by the last substance.

3. Constants are calculated which are the product of an equilibrium constant and a velocity coefficient.

4. The equilibrium constant in aqueous solution has been evaluated by two methods.

5. The temperature coefficient has been measured in both aqueous and alcoholic solutions.

6. It is found that esters of strong organic acids react very rapidly as above, and they also slowly form the corresponding *m*-tolyl ether.

7. A new ester, ethyl *m*-tolyloxyacetate, is described.

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