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

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IT was shown in Part I (J., 1926, 2484) that the reaction between ethyl acetate and potassium phenoxide, in alcoholic solution, did not follow the usual bimolecular law, as required by the equation $C_6H_5 \cdot OK + CH_3 \cdot CO_2Et \longrightarrow C_6H_5 \cdot OEt + CH_3 \cdot CO_2K$, but was due to small amounts of potassium hydroxide produced by hydrolysis of the phenoxide by water present in the alcoholic solution. Alcoholysis of the phenoxide did not appear to be a cause of reaction.

A mathematical expression was deduced which gave satisfactory constants for the ester hydrolysis; the value of this constant, however, was the product of the velocity coefficient and an equilibrium constant, but it was not possible to determine these two factors separately with any degree of certainty.

Smith (J., 1927, 170) extended this work to the interaction of potassium *m*-tolyloxide and ethyl acetate in aqueous alcoholic solution, and obtained similar results. Numerous esters of the aliphatic series have now been studied, and in all cases, except for esters of oxalic acid, the reaction has been found to proceed as a result of hydrolysis of the phenoxide.

EXPERIMENTAL.

The following experiment is typical of the whole series. Time is expressed in minutes and concentrations in milliequivs. per litre.

Potassium phenoxide, $N/4$; ethyl propionate $N/4$; H_2O, 2%; Temp., 70°.

Time.	Titre.	x.	$a - x$.	$b - x$.	$Kk \times 10^6$.
0	20·0	0·0	500·0	1111	—
70	13·8	155·0	345·0	956	1·04
136	12·4	190·0	310·0	921	0·98
180	11·5	212·5	287·5	898	1·05
240	11·0	225·0	275·0	886	0·95
300	10·2	245·0	255·0	866	1·01
355	9·8	255·0	245·0	856	0·99
				Mean	1·00

In the following table are shown the values of the constants for various percentages of water for the esters examined, the concentration of the ester and phenoxide being $N/4$ in every case and the temperature 70°.

Water, %.	0·2	1·0	2·0	3·5	5·0	10·0	20·0
Ester.				$Kk \times 10^6$.			
$CH_3 \cdot CO_2Me$	1·26	1·79	1·25	—	—	0·67	0·57
$CH_3 \cdot CO_2Pr^a$	2·23	2·06	1·85	1·71	1·52	1·35	—
$CH_3 \cdot CO_2Bu^a$	—	—	1·56	—	1·45	0·98	—
$CH_3 \cdot CO_2Bu^\beta$	—	2·35	2·83	1·58	1·50	1·39	—
$CH_3 \cdot CO_2C_5H_{11}(iso)$	—	2·57	2·76	2·37	2·13	1·85	—
$C_2H_5 \cdot CO_2Me$	—	—	0·87	0·83	0·81	0·73	—
$C_2H_5 \cdot CO_2Et$	—	—	1·00	0·87	0·73	0·68	—
$C_2H_5 \cdot CO_2Pr^a$	—	2·57	1·04	0·84	—	0·77	—
$n\text{-}C_3H_7 \cdot CO_2Me$	—	—	0·62	0·62	0·52	0·47	0·56
$n\text{-}C_3H_7 \cdot CO_2Et$	—	—	0·61	0·64	0·55	0·43	0·30
$n\text{-}C_3H_7 \cdot CO_2Pr^a$	—	—	0·66	0·58	0·42	0·34	0·28
$n\text{-}C_3H_7 \cdot CO_2Bu^\beta$	—	0·51	0·47	0·44	0·31	0·23	0·24
$n\text{-}C_3H_7 \cdot CO_2C_5H_{11}(iso)$	---	—	-·-	—	- ·	1·17*	0·90

* $Kk \times 10^6 = 1·12$ at 15%.

Relative Activities of the Esters.—The values of Kk for the different esters do not appear to be strictly in order of the atomic weights. There is, however, a distinct decrease in the values of the constants from acetate to butyrate.

In conclusion, I should like to thank Dr. J. C. Crocker for his continued interest in the work.