31. *The Interaction of Alkyl Iodides and Sodium* m-4-*Xylyloxide in Ethyl Alcohol.*

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In various investigations on the relative reactivities of the alkyl iodides with sodium alkoxides and phenoxides, it has been necessary to compare measurements of the reaction velocity at the same dilution, since the bimolecular constants vary with the initial concentration of the reactants. Acree and co-workers (J., 1914, **105**, 2582) attributed this to simultaneous reactions of the alkyl iodide with anions and un-ionised molecules of the electrolyte and, *e.g.*, for sodium phenoxide, they calculated separate constants (k_i and k_m respectively), independent of the dilution, from the equation $k = \alpha k_i + (1 - \alpha)k_m$, where k is the observed bimolecular coefficient and α the degree of dissociation.

The object of the present work was to extend the measurements to sodium *m*-4-xylyloxide at different temperatures, and thence to calculate the heats of activation. The results indicate that, in each reaction, the measured velocity depends almost entirely on the interaction of the alkyl iodide and xylyloxide ions, negligibly small values of k_m being derived from the above relation for dual catalysis.

EXPERIMENTAL.

Preparation of Materials.—The alkyl iodides (methyl, ethyl, *n*- and *iso*-propyl, *n*- and *iso*-butyl, and *n*-amyl), supplied by Messrs. B.D.H., were washed with dilute alkali and water, dried, and fractionally distilled shortly before use. Absolute alcohol was refluxed over freshly-burnt lime, fractionated, and kept in a dry atmosphere. Sodium *m*-4-xylyloxide was prepared in alcoholic solution from equivalent amounts of sodium ethoxide and the phenol (Kahlbaum).

Course of the Reactions.—Preliminary experiments, in which equimolecular quantities of methyl iodide (14·2 g.) and the sodium salt were allowed to react to completion in dry alcohol at 25°, afforded a 92% yield of the methyl ether after it had been salted out, extracted with light petroleum, and distilled (b. p. 192—194°).

Measurement of Reaction Velocity.—Equivalent solutions of the reactants were mixed and equal quantities (10 ml.) transferred to Jena-glass tubes which were stoppered and placed in a thermostat controlled to $\pm$ 0·05°. On attaining constant temperature, a tube was withdrawn, emptied into cold water, and the residual sodium *m*-4-xylyloxide determined by titration with hydrochloric acid, the procedure being carefully standardised to avoid indicator (azolitmin) errors. This was taken as the zero of similar measurements made after suitable intervals, and the bimolecular constant was calculated from the equation $k = (1/c_t - 1/c_0)/t$, where c_0 and c_t are the concentrations (g.-mols./l.) of xylyloxide at zero time and t mins. Values of k for each reaction were determined at two temperatures for initial concentrations ranging from 0·5 to 0·05N, some 70 series of measurements being made.

In Table I some typical results for three experiments are set out in detail, the remainder being summarised in Table II, where the velocity constant for each reaction is shown to increase progressively with the initial dilution. The corresponding degree of ionisation (α) of the sodium salt, also given, was determined as described below.

TABLE I.

Methyl iodide. Initial concn. = 0·493N. Temp. 28·15°. HCl, 0·1733N.			Ethyl iodide. Initial concn. = 0·192N. Temp. 53·80°. HCl, 0·0818N.			n-Propyl iodide. Initial concn. = 0·0948N. Temp. 63·00°. HCl, 0·0380N.		
t.	Titre (ml.).	100k.	t.	Titre (ml.).	100k.	t.	Titre (ml.).	100k.
0	22·79	—	0	18·53	—	0	21·00	—
15	20·21	2·15	10	16·25	9·28	10	19·16	12·0
30	18·14	2·16	20	14·49	9·21	20	17·46	12·7
40	16·97	2·17	30	13·00	9·35	35	15·58	12·5
55	15·63	2·11	40	11·88	9·23	55	13·65	12·3
70	14·46	2·08	50	10·93	9·18	65	12·80	12·4
Mean k = 2·13 × 10⁻².			Mean k = 9·25 × 10⁻².			Mean k = 12·4 × 10⁻².		

Mean $k = 2\cdot13 \times 10^{-2}$. Mean $k = 9\cdot25 \times 10^{-2}$. Mean $k = 12\cdot4 \times 10^{-2}$.

TABLE II.

Methyl iodide.

Temp. 28·15°.			Temp. 37·90°.		
Initial concn., N.	a.	100k (mean).	Initial concn., N.	a.	100k (mean).
0·493	0·151	2·13	0·488	0·151	5·93
0·247	0·209	2·59	0·244	0·208	7·80
0·197	0·229	2·87	0·195	0·227	8·47
0·123	0·273	3·52	0·122	0·269	9·88
0·0986	0·296	3·83	0·0976	0·293	10·6

Ethyl iodide.

Temp. 45·40°.			Temp. 53·80°.		
Initial concn., N.	a.	100k (mean).	Initial concn., N.	a.	100k (mean).
0·484	0·151	2·90	0·479	0·151	6·94
0·242	0·207	3·83	0·240	0·207	8·64
0·194	0·226	4·20	0·192	0·226	9·25
0·161	0·242	4·54	0·120	0·266	10·9
0·121	0·267	5·04	0·0958	0·289	11·7
0·0968	0·291	5·44			
0·0484	0·358	7·0			

n-Propyl iodide.

Temp. 53·80°.			Temp. 63·00°.		
0·479	0·151	2·98	0·474	0·151	7·2
0·240	0·207	3·63	0·284	0·190	8·37
0·192	0·226	3·92	0·142	0·249	10·6
0·0958	0·289	4·86	0·0948	0·287	12·4
0·0479	0·356	6·50	0·0474	0·354	19·1

isoPropyl iodide.

Temp. 58·10°.			Temp. 65·92°.		
0·286	0·189	3·12	0·283	0·189	7·09
0·238	0·206	3·36	0·189	0·224	8·26
0·119	0·265	4·30	0·142	0·248	9·17
0·0953	0·287	4·62	0·0944	0·287	10·5
0·0477	0·355	6·0	0·0472	0·353	14·4

n-Butyl iodide.

Temp. 50·00°.			Temp. 59·10°.		
0·289	0·190	2·03	0·286	0·189	5·11
0·192	0·225	2·29	0·190	0·225	5·95
0·144	0·249	2·46	0·143	0·248	6·47
0·0962	0·289	2·83	0·0952	0·287	7·48

isoButyl iodide.

Temp. 54·00°.			Temp. 65·00°.		
0·287	0·190	1·33	0·284	0·189	3·90
0·192	0·226	1·71	0·189	0·224	4·71
0·144	0·250	2·00	0·142	0·247	5·66
0·0958	0·289	2·37	0·0945	0·286	7·56

n-Amyl iodide.

Temp. 56·00°.					
0·287	0·190	3·69	0·143	0·248	4·62
0·191	0·224	4·14	0·0955	0·289	5·35

Temp. 65·00°.					
0·284	0·189	8·80	0·142	0·247	10·7
0·189	0·224	9·80	0·0945	0·286	12·5

Determination of the Degree of Ionisation of Sodium m-4-*Xylyloxide in Alcohol.*—Conductivity measurements were made at 25° and 35°, solutions being prepared by the successive dilution of a 0·5N-solution of the sodium salt with dry alcohol containing 5% of m-4-xylenol to counteract alcoholysis. The results are summarised in Table III, where κ is the specific conductivity of the solvent in reciprocal ohms, v the dilution in l./g.-equiv., and Λ_v the corresponding equivalent conductivity, the value at infinite dilution (Λ_∞) being derived by extrapolating the straight line obtained on plotting Λ_v against $\sqrt{1/v}$ for the lowest concentrations. The degree of ionisation ($\alpha = \Lambda_v/\Lambda_\infty$) at dilutions from 2 to 32 l. was determined for other temperatures (T) from values of the equivalent conductivity (Λ_T) calculated from the equation $\Lambda_T = \Lambda_{T_0} (1 + aT)$, where Λ_{T_0} is the value at 0° and a the temperature coefficient ascertained from the given data.

TABLE III.

Temp. 25·00°. $\kappa = 0\cdot32 \times 10^{-6}$.

v	2	4	8	16	32	64	128	256	512	1024	2048	4096	∞
Λ_v ...	5·595	7·74	10·12	12·72	15·78	18·94	22·21	25·29	27·88	30·50	32·61	34·02	37·1

Temp. 35·00°. $\kappa = 0\cdot24 \times 10^{-6}$.

v	2	4	8	16	32	64	128	256	512	1024	2048	4096	∞
Λ_v ...	6·475	8·89	11·54	14·54	17·86	21·69	25·91	29·55	32·75	35·62	37·84	39·55	43·1

DISCUSSION OF RESULTS.

Values of k_i *and* k_m.—On plotting values of the velocity constant (k) at different dilutions against the degree of ionisation (α) of the sodium salt (Table II), the points obtained for each iodide lie approximately on a straight line. The data may therefore be interpreted in terms of the dual hypothesis (see p. 141). In Table IV the separate constants have been calculated from values of k and α for each pair of dilutions, the results obtained for ethyl iodide at 45·40° being recorded in detail as typical of those averaged for the other iodides.

TABLE IV.

Ethyl iodide. Temp. 45·40°.

Concns., N.	k_i.	k_m.	Iodide.	Temp.	k_i (mean).	k_m (mean).	$k_i(=k/a)$ (mean).
0·242—0·194	0·193	−0·002	Methyl	28·15°	0·141	−0·005	0·127
0·242—0·161	0·201	−0·004		37·90	0·341	+0·009	0·370
0·242—0·121	0·198	−0·003	Ethyl	45·40	0·194	−0·002	0·187
0·242—0·097	0·191	−0·002		53·80	0·375	+0·011	0·410
0·194—0·161	0·210	−0·007	*n*-Propyl	53·80	0·155	+0·005	0·174
0·194—0·121	0·200	−0·004		63·00	0·371	+0·016	0·432
0·194—0·097	0·191	−0·001	*iso*Propyl	58·10	0·159	+0·001	0·163
0·161—0·121	0·194	−0·002		65·92	0·360	+0·003	0·370
0·161—0·097	0·185	+0·001	*n*-Butyl	50·00	0·084	+0·005	0·102
0·121—0·097	0·175	+0·005		59·10	0·246	+0·005	0·264
			*iso*Butyl	54·00	0·101	−0·007	0·077
Means	0·194	−0·002		65·00	0·340	−0·036	0·227
			n-Amyl	56·00	0·175	+0·003	0·188
				65·00	0·393	+0·013	0·443

In each reaction k_m is zero within the limits of experimental error. Moreover k_i, although almost independent of the dilution, is more nearly constant if calculated from the equation $k_i = k/\alpha$. This is shown by the following results for ethyl iodide at 45·40°, similarly concordant values being averaged for the other iodides in the last column of the above table.

Concn., N	0·484	0·242	0·194	0·161	0·121	0·097	
$k_i = k/a$	0·192	0·185	0·186	0·188	0·189	0·187	Mean 0·187

Heats of Activation, and the Relative Reactivities of the Alkyl Iodides.—In the following table the heats of activation (E, in kg.-cals./g.-mol.) have been determined from the temperature coefficients of $k_i(= k/\alpha)$ in the usual manner. The relative reactivities, r, calculated to *n*-propyl iodide ($k_i = 10\cdot0$) at 50° as standard, are in general agreement with values found by Segaller (J., 1913, **103**, 1154) using a constant initial concentration of sodium phenoxide.

Iodide.	E.	r.	Iodide.	E.	r.
Methyl	20·5	108	*n*-Butyl	22·4	8·8
Ethyl	19·5	24·5	*iso*Butyl	21·7	4·3
n-Propyl	21·7	(10·0)	*n*-Amyl	21·2	8·6
*iso*Propyl	23·4	5·7			

The Molecular Statistics of the Reactions.—Expressed in terms of the collision theory, the velocity constant for a bimolecular reaction is given by

$$k = \frac{N_0}{1000} \cdot \sigma_{1,2}{}^2 \left[8\pi RT\left(\frac{1}{M_1} + \frac{1}{M_2}\right)\right]^{\frac{1}{2}} \cdot e^{-E/RT}$$

where M_1 and M_2 are the molecular weights of the reactants, $\sigma_{1,2}$ is the sum of their molecular radii, and N_0 the Avogadro constant, the units of k being g.-mols./l./sec.

In the reaction of ethyl iodide and *m*-4-xylyloxide ions at 45·4°, for example, $\sigma_{1,2}$ = 5×10^{-8} cm. approx., M_1 = 156, M_2 = 121, and E = 19,500 calories; whence k_i = 6·04 $\times$ 10^{-3}, which is of the same order as the value $3\cdot12 \times 10^{-3}$ found experimentally, after conversion of time to seconds. The reaction may thus be classed with others involving an ion (cf. Moelwyn-Hughes, *Chem. Reviews*, 1932, **10**, 241) which usually proceed at a rate comparable with the calculated rate of activation, as distinct from the interactions of neutral molecules for which the observed velocity is frequently several powers of ten smaller than the predicted value.

Summary.

The bimolecular constants (k) for the reactions of alkyl iodides with sodium m-4-xylyloxide in ethyl alcohol increase with decreasing initial concentration of the reactants.

Measurements of the degree of dissociation (α) of the xylyloxide indicate that the observed velocities are due almost entirely to the xylyloxide ions, satisfactory constants (k_i), independent of the dilution, being derived from the equation $k = \alpha k_i$.

The reactivities of the n-alkyl iodides progressively decrease to a limiting value with increasing molecular weight.

The reactions proceed at a velocity comparable with that predicted by the theory of simple collisional activation.