247.   *The Chemical Kinetics of the Interaction of the Alkyl Iodides with Sodium Eugenoxide in Ethyl Alcohol.*

By Sidney S. Woolf.

THE kinetics of the reactions of alkyl iodides with various reagents, in particular the phenoxides, have been extensively studied. In early researches the observation that the bimolecular velocity constants in these reactions varied with initial concentrations was dealt with on empirical lines. The introduction of the " dual catalysis " hypothesis, however, led to an explanation of the reaction mechanism on the basis that ions and undissociated molecules of the phenoxide both played their part. By Acree's equation, viz., $k_{\text{obs.}} = k_i\alpha + k_m(1 - \alpha)$, it is possible to split the observed velocity constant into separate constants for ions and molecules (k_i and k_m respectively), α being the apparent degree of dissociation, and k_i and k_m being independent of the dilution. Recent extensions of kinetic theory have made it possible to classify the alkyl iodide–phenoxide reactions as " normal," *i.e.*, substantially free from factors reducing the perfect efficiency of activating collisions.

In the present work, the phenol studied was eugenol, and the rates of reaction in ethyl alcoholic solution of sodium eugenoxide with eight alkyl iodides in equivalent proportion were observed over as large a range of temperature and initial concentration as practicable. The bimolecular nature of the reactions was established, and the heats of activation and relative reactivities of the alkyl iodides in the individual reactions were ascertained.

The measured velocities depend almost entirely on the interaction of the alkyl iodide with eugenoxide ions, the values of k_m derived from the Acree equation being negligible.

A preliminary study was also made of the behaviour of the reactants when originally present in non-equivalent proportions; also, to investigate the unexplained fall in constant usually noticed in such reactions, some experiments were carried out in which resultants were added to the original equivalent reaction mixtures.

EXPERIMENTAL.

Preparation of Materials.—The alkyl iodides (methyl, ethyl, *n*- and *iso*-propyl, *n*- and *iso*-butyl, and *n*- and *iso*-amyl) as supplied by Messrs. British Drug Houses nearly always contained free iodine. They were washed with dilute alkali solution and water, dried over anhydrous calcium chloride, fractionally distilled, and stored over freshly ignited silver powder. In no case was there any sign of subsequent discoloration, although some specimens were kept for several years.

Commercial absolute alcohol was refluxed on a water-bath for 20—30 hours with freshly-burnt lime, and was fractionated, giving alcohol of a satisfactory quality, as established by con-ductivity measurements.

Eugenol (B.D.H.) was fractionated, the fraction of b. p. 249—251° being retained. It was stored in glass-stoppered amber-glass bottles, and each batch remained colourless over its period of use (less than 3 months).

Alcoholic sodium ethoxide solutions, prepared by dissolving clean sodium in absolute alcohol, were standardised by titration with standard hydrochloric acid, litmus being used as indicator. Sodium eugenoxide solutions were prepared by mixing eugenol with the calculated volume of alcoholic sodium ethoxide. A 10% excess over the stoicheiometric quantity of eugenol was used throughout in order to inhibit alcoholysis.

Course of the Reaction.—It was shown by quantitative isolation and identification of ethers that the reactions are represented by the equation

$$RI + ONa \cdot C_6H_3(OMe) \cdot CH_2 \cdot CH:CH_2 \longrightarrow NaI + OR \cdot C_6H_3(OMe) \cdot CH_2 \cdot CH:CH_2.$$
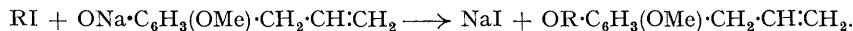
The methyl ether of eugenol (b. p. 248—250°) was prepared from methyl iodide and sodium eugenoxide; and its bromination produced 4-bromo-5-βγ-dibromopropylveratrole (m. p. 78·5—79°) (cf. *Ber.*, 1895, **28**, 2082). The ethyl ether was obtained in 93% yield from the reaction of ethyl iodide with sodium eugenoxide.

Measurement of Reaction Velocity.—Equivalent solutions of the reactants were mixed, and 10 ml. quantities were pipetted into hard-glass test-tubes which were closed with rubber bungs and transferred to a thermostat bath, controlled to ± 0·05°. On attaining constant temperature (10 mins.), a tube was withdrawn, emptied into cold water, and the unchanged sodium eugen-oxide titrated with standard hydrochloric acid, litmus being the indicator. Similar measure-ments were made at suitable intervals until " half-reaction " was reached.

The bimolecular equation $k = (1/t) \cdot (1/C_t - 1/C_0)$ was applied, concentrations being expressed in g.-mols./l., and time in minutes, but as values of k so obtained decreased during an experiment (mainly owing to accumulation of resultants), a graphical method was adopted in order to deter-mine velocity constants at zero time. All observed values of $1/C$ were plotted against t, and the best straight line drawn through these points, and extrapolated back to the value of $1/C$ at zero reaction $(1/C_0)$. The corresponding time t_0 was taken as the " hypothetical time-zero," and this appears in Table I as a number of minutes prior to the arbitrarily chosen time-zero used in the experiment. The fall in constant is thus eliminated.

All results were corrected for expansion, the coefficient of expansion of ethyl alcohol being used.

Values of k were obtained for each of the eight alkyl iodides at three different temperatures, and at initial dilutions extending over the range $V = 4$ to $V = 20$ l./g.-mol.

The results of a typical experiment are given in full (Table I), and values for the remainder are summarised in Table II, the progressive increase in k with initial dilution being evident.

In order to correlate the results obtained at different temperatures and dilutions, it was desir-able to deduce the values of velocity constants at common " round-number " dilutions. Over the range studied it was found that k varied linearly with V, and this observation was used to obtain values of k at $V = 4$, 6, 8, 10, 12, 14, and 16 l./g.-mol. for each iodide at the working temperatures.

TABLE I.

Methyl iodide at 42·5°.

Concn. of each reactant before mixing at 15° = $N/4$. Dilution (V) of each reactant in mixture at 42·5° = 8·23. Acid = 0·0505N-HCl. Hypothetical zero time = -21 mins.

t	0	5	10	15	20	30	45	70	
Titre (ml.)	20·2	19·2	18·4	17·7	17·0	15·9	14·3	12·5	
$k \times 10^4$	856	884	887	883	888	873	883	862	Mean 877

Temp. correction factor : 1·0287; k (corr. for temperature) = 903×10^{-4}.

TABLE II.

C_0' = Concentration of each reactant before mixing.

C_0'.	100k.	C_0'.	100k.	C_0'.	100k.	C_0'.	100k.	C_0'.	100k.	C_0'.	100k.
		Methyl iodide.						*Ethyl iodide.*			
42·5°.		50°.		55°.		50°.		57·5°.		68°.	
$N/2$	7·41	$3N/8$	15·14	$N/2$	21·8	$N/2$	3·56	$N/2$	7·02	$N/4$	20·9
$N/4$	9·03	$N/4$	17·10	$3N/8$	22·5	$N/4$	4·78	$3N/8$	7·39	$3N/16$	23·3
$3N/16$	9·86	$3N/16$	19·59	$N/4$	27·3	$3N/16$	5·29	$N/4$	8·72	$N/8$	29·8
$N/8$	12·66	$N/8$	24·25	$3N/16$	30·1	$N/8$	6·56	$3N/16$	9·35		
		$N/10$	31·52	$N/8$	36·9			$N/8$	12·43		
		n-Propyl iodide.						*n-Butyl iodide.*			
57·5°.		68°.		75°.		57·5°.		68°.		75°.	
$N/2$	2·55	$N/2$	6·71	$3N/8$	13·28	$N/2$	2·38	$N/2$	5·93	$N/2$	10·63
$3N/8$	2·84	$3N/8$	7·30	$N/4$	15·09	$3N/8$	2·59	$N/4$	7·70	$N/4$	13·49
$5N/16$	2·97	$N/4$	8·40	$3N/16$	17·10	$N/4$	3·01	$N/8$	11·40	$3N/16$	15·62
$N/4$	3·16	$3N/16$	9·83	$N/8$	21·04			$N/10$	13·19	$N/8$	19·34
		$N/8$	12·46	$N/10$	24·12					$N/10$	21·46
		n-Amyl iodide.						*isoPropyl iodide.*			
57·5°.		68°.		75°.		57·5°.		68°.		75°.	
$N/2$	2·26	$3N/8$	6·06	$N/2$	10·13	$N/2$	1·83	$N/2$	4·96	$N/2$	9·23
$3N/8$	2·49	$N/4$	7·07	$N/4$	12·54	$3N/8$	2·04	$N/4$	6·34	$N/4$	11·48
$N/4$	2·88	$3N/16$	8·20	$3N/16$	14·03	$N/4$	2·45	$3N/16$	7·33	$3N/16$	12·96
		$N/8$	10·02	$N/8$	17·42			$N/8$	9·35	$N/8$	16·68
				$N/10$	19·97					$N/10$	18·91
		isoButyl iodide.						*isoAmyl iodide.*			
57·5°.		68°.		75°.		57·5°.		68°.		75°.	
$N/2$	0·86	$N/2$	2·23	$N/2$	3·27	$N/2$	1·31	$N/2$	2·91	$N/2$	4·99
$3N/8$	0·96	$3N/8$	2·52	$N/4$	4·47	$3N/8$	1·46	$3N/8$	3·20	$N/4$	6·83
$N/4$	1·12	$N/4$	2·68	$3N/16$	5·52	$N/4$	1·69	$N/4$	4·08	$3N/16$	8·11
		$3N/16$	3·26	$N/8$	7·59			$3N/16$	4·90	$N/8$	11·05
		$N/8$	4·37	$N/10$	9·84			$N/8$	6·80	$N/10$	12·75

Determination of the Apparent Degree of Dissociation of Sodium Eugenoxide in Absolute Alcohol.
—Conductivity measurements were made at 25°, 35°, and 50°, solutions being prepared by successive dilutions of a 0·25N-solution of sodium eugenoxide in alcohol with a 0·05N-solution of eugenol in alcohol (to counteract alcoholysis). The results are summarised in Table III, where κ is the specific conductivity of the solvent in reciprocal ohms and μ_v the corresponding molecular conductivity, the value at infinite dilution μ_∞ being obtained by extrapolation of the most dilute readings when μ_v was plotted against $\sqrt{1/v}$.

TABLE III.

V.	4.	8.	16.	32.	64.	128.	256.	512.	1024.	2048.	∞.
				Temp. 25°; $\kappa = 0.93 \times 10^{-6}$.							
μ_v	2·707	3·854	5·303	7·129	9·479	12·31	15·74	19·72	24·27	27·65	36
				Temp. 35°; $\kappa = 1.0 \times 10^{-6}$.							
μ_v	2·861	4·019	5·492	7·326	9·863	12·77	16·47	20·91	25·95	30·45	41
				Temp. 50°; $\kappa = 1.1 \times 10^{-6}$.							
μ_v	3·417	4·705	6·362	8·589	11·42	14·99	19·68	25·45	31·96	38·09	51

From the molecular conductivities at 25°, 35°, and 50° so obtained, those for $V = 4, 8, 16$, and ∞ at the various temperatures ranging from 42·5° to 75° were calculated from the expression $\mu_t = \mu_0(1 + \beta t)$. Then, from $\alpha = \mu_v/\mu_\infty$, values for α were obtained. As a check on this, values of α at 25°, 35°, and 50° were calculated from the actual values of μ observed, and extrapolated mathematically to the working temperatures by the empirical relationship $\alpha_t = \alpha_0(1 - \gamma t)$. The means of the satisfactorily concordant values of α obtained by these two methods were used in subsequent calculations.

The values of α obtained gave approximate concordance with Ostwald's dilution law over the range studied, and were accordingly plotted against $\sqrt{v}$ in order to obtain α for the intermediate dilutions ($V = 6, 10, 12$, and 14). In Table IV values of α at " round number " dilutions and at the working temperatures are summarised.

TABLE IV.

V.	42·5°.	50°.	55°.	57·5°.	68°.	75°.	V.	42·5°.	50°.	55°.	57·5°.	68°.	75°.
4	0·069	0·066	0·065	0·064	0·062	0·060	12	0·114	0·109	0·105	0·103	0·097	0·093
6	0·083	0·079	0·077	0·076	0·073	0·070	14	0·122	0·117	0·113	0·111	0·104	0·100
8	0·095	0·091	0·088	0·087	0·082	0·079	16	0·130	0·124	0·120	0·118	0·110	0·106
10	0·105	0·100	0·097	0·095	0·090	0·086							

DISCUSSION OF RESULTS.

Application of Theory of Dual Catalysis.—When the values of k at the various temperatures and dilutions were plotted against the corresponding values of α, a series of straight lines was obtained for each iodide, all of which passed through the origin within experimental error, *i.e.*, as mentioned above, k_m is negligible, and the slope of the lines $(k_i - k_m)$ reduces to k_i. Acree's equation therefore becomes $k = k_i\alpha$, and k_i $(= k/\alpha)$ is the characteristic velocity constant for a given iodide and temperature, the dilution factor having thus been eliminated. This is confirmed by substituting the values of k and α for a given iodide and temperature in the original Acree equation, and solving the pairs of simultaneous equations for each dilution for k_i and k_m; *e.g.*, for n-propyl iodide at 75°, the mean values of k_i and k_m are 1·90 and $-0·001$ respectively, whilst the mean of the corresponding values of k/α $(= k_i)$ is 1·91.

In Table V are summarised, for experiments carried out at 75°, the interpolated values of k at " round-number " dilutions, and the values of k_i obtained by dividing these by the appropriate values of α (Table IV), and Table VI summarises the mean values of k_i obtained in this way, for all iodides and temperatures.

TABLE V.

$V=$		4.	6.	8.	10.	12.	14.	16.	Mean k_i.
n-Propyl iodide	$100k$	11·9	13·4	14·8	16·2	17·6	19·0	20·4	
	k_i	1·98	1·91	1·87	1·88	1·89	1·90	1·92	1·91
n-Butyl iodide	$100k$	10·4	11·8	13·1	14·4	15·8	17·1	18·4	
	k_i	1·73	1·69	1·66	1·68	1·70	1·71	1·73	1·70
n-Amyl iodide	$100k$	9·8	11·0	12·2	13·4	14·6	15·7	16·8	
	k_i	1·63	1·57	1·54	1·56	1·57	1·57	1·58	1·57
*iso*Propyl iodide	$100k$	9·0	10·1	11·2	12·4	13·6	14·7	15·8	
	k_i	1·50	1·44	1·42	1·44	1·46	1·47	1·49	1·46
*iso*Butyl iodide	$100k$	3·4	4·0	4·6	5·2	5·8	6·5	7·1	
	k_i	0·57	0·57	0·58	0·60	0·62	0·65	0·67	0·61
*iso*Amyl iodide	$100k$	5·1	6·0	6·8	7·7	8·6	9·4	10·3	
	k_i	0·85	0·85	0·86	0·89	0·92	0·94	0·97	0·90

TABLE VI.

Iodide.	75°.	68°.	57·5°.	55°.	50°.	42·5°.	Iodide.	75°.	68°.	57·5°.
Methyl	—	—	—	3·00	1·90	0·95	n-Amyl	1·57	0·87	0·33
Ethyl	—	2·50	1·00	—	0·52	—	*iso*Propyl	1·46	0·78	0·29
n-Propyl	1·91	1·04	0·38	—	—	—	*iso*Butyl	0·61	0·34	0·136
n-Butyl	1·70	0·94	0·35	—	—	—	*iso*Amyl	0·90	0·51	0·203

Temperature Coefficients, Critical Increments, and Relative Reactivities.—When the observed values of $\log k_i$ are plotted against the reciprocal of the absolute temperature, the Arrhenius

straight-line law is obeyed.   The corresponding equation $\log k_1 - \log k_2 = A(1/T_2 - 1/T_1)$ was therefore used to obtain values for 50° for those iodides which had not been measured at this temperature, which was adopted because it had been used by former workers and because the extrapolation involved was short.   Table VII shows the values (averaged over the temperatures used) of the temperature coefficient (k_{t+10}/k_t), which approximate to the normal value of 2·5.   The table also shows the values of E (in kg.-cals./ g.-mol.), calculated from $E = 2\cdot303AR$, and the relative reactivities (r) of the alkyl iodides at 50° (n-propyl iodide $= 10\cdot0$).

TABLE VII.

Iodide.	Temp. coeff.	E.	r.	Iodide.	Temp. coeff.	E.	r.
Methyl	2·51	18·9	104	n-Amyl	2·45	20·3	8·9
Ethyl	2·37	19·0	28·6	isoPropyl	2·54	21·1	7·5
n-Propyl	2·53	21·0	10·0	isoButyl	2·38	19·6	3·7
n-Butyl	2·48	20·6	9·3	isoAmyl	2·36	19·4	5·6

The relative reactivities show satisfactory agreement with those recorded by other workers for similar reactions.   As usual, methyl iodide is some 10 times and ethyl iodide 2—3 times as reactive as propyl iodide, and with further ascent of the homologous series the reactivity lessens, tending towards a limiting value.   The *iso*-iodides are less reactive than the corresponding n-iodides, and the anomalous behaviour of *iso*butyl iodide, reported by earlier workers, is again in evidence.

Mechanism of the Reaction from the Aspect of Collision Theory.—In Table VIII, typical values of k_t are compared with values calculated from the modified Lewis equation

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

where M_1 and M_2 are the molecular weights of the reactants, $\sigma_{1,2}$ is the sum of their molecular radii, N the Avogadro constant, E the " critical increment " in cals./g.-mol., and k the velocity constant in l./g.-mol.-sec.

The ratio $k_{t,\,\text{obs.}}/k_{t,\,\text{calc.}}$ can be identified with P, the probability factor in Hinshelwood's equation $k = PZe^{-E/RT}$, where Z is the collision frequency, and the order of these figures indicates that the interactions under investigation are " normal," a factor of 10 or 0·1 being not unusual in this sense.

TABLE VIII.

Iodide.	Temp.	$10^3 k_t$, calc.	$10^3 k_t$, obs.	P.	Iodide.	Temp.	$10^3 k_t$, calc.	$10^3 k_t$, obs.	P.
Methyl	50°	22·7	31·7	1·4	isoButyl	75°	66·5	10·2	0·2
Ethyl	50	18·8	8·7	0·5	isoButyl	50	7·2	1·1	0·2
n-Propyl	75	8·9	31·8	3·6	n-Amyl	68	12·9	14·5	1·1
n-Propyl	50	0·8	3·0	3·7	isoAmyl	57·5	19·2	3·4	0·2
isoPropyl	68	4·0	13·0	3·2				Mean	1·6

Non-equivalent Reactions.—The results of a few " non-equivalent " experiments with n-propyl iodide are tabulated below, together with corresponding " equivalent " reactions for comparison.

Original concentration of reactant in mixture.			Original concentration of reactant in mixture.		
Sodium eugenoxide.	n-Propyl iodide.	$10^4 k$ (obs.).	Sodium eugenoxide.	n-Propyl iodide.	$10^4 k$ (obs.).
$N/4$	$N/4$	671	$3N/16$	$3N/16$	730
$N/4$	$N/8$	757	$N/8$	$N/4$	793
$3N/32$	$3N/32$	983	$N/8$	$N/8$	840
$N/16$	$N/16$	1246	$N/8$	$N/16$	961

The general conclusion that excess or deficiency of " phenoxide " lowers or raises the constant respectively is thus confirmed.   The inference that " phenoxide " concentration is the prevailing influence in these " non-equivalent " experiments falls in line with the dual catalysis viewpoint, but the lowering of the constant observed with excess of alkyl iodide in some cases (including the present) is not yet clearly understood.

SUMMARY AND CONCLUSIONS.

(1) The reactions of sodium eugenoxide with eight alkyl iodides in absolute ethyl alcohol have been studied kinetically at various concentrations and temperatures. The fundamental reaction is essentially bimolecular, but of a special type, the constant for a given iodide and temperature increasing with dilution.

(2) The apparent degrees of ionisation of sodium eugenoxide in absolute alcohol were determined from conductivity experiments, and application of the theory of " dual catalysis " to the observed velocity constants shows that the reaction is due almost exclusively to interaction of eugenoxide ions with the alkyl iodides, the reactivity of un-ionised molecules of sodium eugenoxide being negligible. Characteristic velocity constants for the ionic reactions were obtained, and found to be independent of initial concentration in equivalent reactions.

(3) The temperature coefficient of the reactions was *ca.* 2·5 for 10° rise. The logarithms of the velocity constants varied linearly with the reciprocal of the absolute temperature, and the Arrhenius " critical increments " were calculated to be 19,000—21,000 cals./g.-mol.

(4) The mechanism of the reactions was investigated from the aspect of the modern collision theory as applied to reactions in solution, and they were found to be " normal " in type, the probability factor P in the standard equation $k = PZe^{-E/RT}$ being of the order of unity.

(5) The relative reactivities of the alkyl iodides were closely comparable with earlier values for similar reactions.