376. *The Relative Reactivities of the Aliphatic Iodides. The Interaction of Alkyl Iodides with Sodium Guaiacoxide in Ethyl-alcoholic Solution.*

By JOHN A. MITCHELL.

The reactions between sodium guaiacoxide and eight *n*-alkyl iodides in alcoholic solution are bimolecular in each case, but the dependence of the velocity coefficient upon initial concentration shows that the guaiacoxide reacts in virtue of its ion, the contribution of the undissociated molecule being negligible.

The reaction between velocity coefficient and temperature conforms to the Arrhenius equation.

The reactivities of the iodides decrease rapidly from methyl to butyl and then remain nearly constant.

IN the development of the theories of chemical reactivity, considerable research has been done on the reaction between phenoxides and alkyl iodides to yield ethers. Moelwyn-Hughes (*Ann. Reports*, **1935**, **32**, **103**) refers to reactions of the type $R_1ONa + R_2Cl \longrightarrow R_1OR_2 + NaCl$ as being chiefly ionic, involving R_1O' ions, and states that this has been justified by more reliable determinations of the degree of dissociation.

The experiments now described continue this line of investigation by a determination of the relative reactivities of the first eight *n*-alkyl iodides in their reactions with sodium guaiacoxide in ethyl alcohol. The following conclusions have been reached.

The mechanism of the reaction conforms with Acree and Shroder's equation for dual catalysis (J., 1914, **105**, 2582), *viz.*, $k = \alpha k_i + (1 - \alpha)k_m$, where k, referred to as k_0 in these experiments, represents the bimolecular velocity constant at the hypothetical time zero, at which time the exact value of α, the degree of dissociation of the sodium guaiacoxide, which behaves as a weak electrolyte, is known; k_i and k_m relate to the ion and the undissociated molecule respectively.

The reactions now considered are bimolecular (but see below). They conform closely to the Arrhenius equation, $k = Ze^{-E/RT}$, the graph connecting $\log k_i$ with $1/T$ being linear.

The reactivities of the *n*-alkyl iodides fall rapidly from methyl to butyl iodide and then remain more or less constant.

That the observed velocities are predominantly due to the interaction of the guaiacoxide ions with the alkyl iodide is inferred from the following results: (1) k_m is negligibly small; (2) for a constant concentration of ethyl iodide, k_0 increases as the guaiacoxide concentration decreases; (3) addition of a neutral salt, sodium iodide, produces a ' secondary salt ' effect; (4) the probability factor P in $k_i = PZe^{-E/RT}$ is of the magnitude usually associated with reactions in which one of the reacting species is an ion.

EXPERIMENTAL.

Separation of the Products.—A mixture of sodium guaiacoxide with rather more than the equivalent of methyl iodide, and 5% of guaiacol to prevent alcoholysis, was refluxed for many hours. The alcohol was distilled off, the guaiacol removed by sodium hydroxide solution, and the guaiacol methyl ether extracted by ether, fractionally distilled, and weighed. This method was repeated for other iodides and gave liquid products of definite b.p.: the yields and b.p.'s are given below.

Guaiacol ether.	Yield, %.	B.p.
Methyl	88·9	206—207° *
Ethyl	90·2	217—218
Propyl	84·2	227—230
Butyl	85·0	244—246°
Amyl	89·1	262—266
Hexyl	84·0	280—284

* Beilstein, 1923, Band 6, 771; B.P. 205,206.

Measurement of the Velocity Constant k_0.—The method in most respects was similar to that of Segaller (J., 1913, **103**, 1157) in regard to the purification of the alcohol, the storage of the alkyl iodides, the preparation of equivalent and non-equivalent mixtures, their immersion in a thermostat, and their titration at different intervals of time.

The bimolecular constant was calculated from the equation $k = (C_2 - C_1)/C_1C_2\ (t_1 - t_2)$, where C_1 and C_2 are the concentrations (g.-mols./l.) of the guaiacoxide at t_1 and t_2 minutes respectively. By extrapolating the graph of $1/y$ against t, where y is the titre in c.c., the hypothetical time zero was deduced. This is illustrated in Table I, which refers to the reaction with ethyl iodide at 17°, the concentration of both reagents being 0·1250N., and the titrating acid being 0·05N.

TABLE I.

t.	*y*.	*t*, corr.	$k \times 10^5$.
Hypothetical time zero	25	0	—
Working zero	23·4	10	5702
17	21·18	27	5571
40	18·88	50	5405
70	16·70	80	5181
105	14·80	115	4997
145	13·10	155	4887
178	12·10	188	4729

These values of k were plotted against the mean time intervals, and if the positions could be connected to form a smooth curve this was extrapolated to zero-time. If the positions were not sufficiently accurately defined, the means of the first four and of the last four values of k were plotted against the corresponding mean time intervals. These two points were joined by a straight line and produced to cut the ordinate to give k_0. This method was adopted for the data in Table I and gave $k_0 = 0·057$.

The values of k_0 were plotted against concentration of reaction mixture, and values at seven concentrations (0·04—0·20N.) obtained by interpolation. Table II shows the mean values of k_0/α, the figures in parentheses representing the extreme values.

TABLE II.

k_0/a at	45°.	55°.	62·7°.
CH_3I	1·182 (1·361—1·121)	3·03 (3·30—2·76)	5·43 (5·74—5·28)
	55°.	62·7°.	72°.
C_2H_5I	0·705 (0·756—0·660)	1·495 (1·565—1·416)	3·34 (3·54—3·14)
C_3H_7I	0·275 (0·295—0·261)	0·563 (0·580—0·549)	1·319 (1·380—1·267)
C_4H_9I	0·250 (0·274—0·231)	0·522 (0·573—0·491)	1·096 (1·212—1·026)
$C_5H_{11}I$	0·275 (0·301—0·257)	0·526 (0·554—0·497)	1·143 (1·180—1·107)
$C_6H_{13}I$	0·264 (0·277—0·249)	0·565 (0·580—0·545)	1·250 (1·304—1·212)
$C_7H_{15}I$	0·273 (0·296—0·257)	0·505 (0·519—0·490)	1·268 (1·302—1·248)
$C_8H_{17}I$	0·259 (0·283—0·246)	0·495 (0·538—0·474)	1·0565 (1·074—1·020)

Determination of the Degree of Ionisation of Sodium Guaiacoxide in Alcohol.—Conductivity measurements were made at 0°, 25°, 35°, and 62·7°. The graphs of log λ_v against $\sqrt[3]{c}$ at these temperatures were drawn, and the equivalent conductivity at infinite dilution (λ_∞) for the solution at 35° found by extrapolation to be 49·77. For the other three temperatures values of log λ_v at *equal* concentrations were obtained by interpolation, and these values were plotted against log λ_v at 35°, the linear parts of the graphs being extended until they cut the ordinate drawn from that point on the abscissa which represented log 49·77. These points of intersection were taken as the equivalent conductivities at infinite dilution for the three temperatures; thus, at 0°, 25°, and 62·7°, λ_∞ = 28·7, 43·11, and 65·46 respectively.

The degrees of dissociation (α) were calculated for these four temperatures, and those for 45° and 55° were obtained from the graphs of α against temperature at different concentrations and of α against concentration at the required temperatures (see following table).

Concn. (N.)	0·04	0·05	0·06	0·08	0·10	0·11	0·14	0·17	0·20	0·25
$\alpha_{45°}$	0·133	0·1207	0·1117	0·0988	0·090	0·087	0·0794	0·073	0·0678	
$\alpha_{55°}$	0·1266	0·1153	0·1065	0·0938	0·0855	0·0828	0·0753	0·0697	0·0648	0·0590
$\alpha_{62·7°}$	0·1211	0·1108	0·1024	0·0899	0·08203	0·0793	0·0727	0·0674	0·0626	
$\alpha_{72°}$	0·115	0·1051	0·0973	0·0852	0·0778	0·0753	0·0689	0·064	0·0599	

Discussion of Results.—Relative reactivities of the alkyl iodides. From the values of k_0 the relative reactivities were calculated, that of propyl iodide being taken as 10 in each case:

Temp.	Methyl.	Ethyl.	Propyl.	Butyl.	Amyl.	Hexyl.	Heptyl.	Octyl.
55·0°	110·0	25·6	10	9·08	10·0	9·61	9·92	9·41
62·7	96·5	26·6	10	9·28	9·34	10·10	8·97	8·79
72·0	86·8	25·3	10	8·31	8·67	9·48	9·61	8·01

The rapid fall of reactivity from methyl iodide to propyl iodide, followed by more or less constant values for the higher homologues, has also been found by Segaller (*loc. cit.*) and Hardwick (J., 1935, 144).

Values of k_{i} *and* k_{m}. The dual hypothesis was tested by evaluating k_{i} and k_{m} from Acree's equation (p. 1793); in every case k_{m} was very small compared with k_{i}. Further evidence that undissociated molecules did not appreciably contribute to the reaction was provided by two methods.

(1) The velocity constants showed little change in k_0 when the initial concentration of the iodide was varied but that of the guaiacoxide was kept constant (Table III, *a*), whereas in experiments of the converse type, k_0 increased with diminishing initial guaiacoxide concentration in such a manner as to give a linear graph when plotted against α for the appropriate guaiacoxide concentrations (Table III, *b*).

TABLE III.

(*a*) Temperature 55°. $[C_7H_7O_2Na]$ = 0·120N.

$[C_2H_5I]$	0·080	0·120	0·240
$k_0 \times 10^4$	559	570	581

(*b*) Temperature 55°. $[C_2H_5I]$ = 0·240N.

$[C_7H_7O_2Na]$	0·24	0·22	0·20	0·17	0·14	0·12	0·10	0·08	0·06	0·04
α	0·0600	0·0622	0·0648	0·0697	0·0753	0·0801	0·0855	0·0938	0·1065	0·1266
$k_0 \times 10^4$	459	469	482	505	544	581	632	694	793	957
$k_0 \times 10^4/\alpha$	7649	7541	7437	7246	7224	7254	7391	7399	7446	7558

(2) Addition of various weights of sodium iodide (2—8 g.) to 100 c.c. of a 0·12N-reaction mixture containing ethyl iodide at 55° led to diminution of the velocity constant by 28—45%. This would appear to be due to a secondary salt effect in which the dissociation of the sodium guaiacoxide was depressed by the increase in the concentration of the common sodium ion. Moreover, addition of guaiacol ethyl ether to an equivalent 0·12N-mixture at 55° produced only a negligible effect, decreasing k_0 from 0·057 to 0·0565.

Heats of activation. On the assumption that k_m is negligibly small, the ionic velocity coefficient (k_i) is equal to k_0/α. The mean values of k_i are set out in Table II, and from these were calculated the temperature coefficients, which were approximately 1·7—2·6 for 10°, and the heats of activation, which ranged from 18,101 to 20,708 cals./g.-mol. For the ethyl iodide reaction, E was 20,588, which agrees with Moelwyn-Hughes's value of 21,300 ± 700 (J., 1933, 1578).

The molecular statistics of the reactions. Substitution of k_0/α for k in the equation $k = PZe^{-E/RT}$ led to values for P of 0·04—2·96, which indicated that these reactions fall into line with those of normal specific velocity, tabulated by Moelwyn-Hughes (*Chem. Reviews*, 1932, **10**, 241), where one of the reacting species is an ion.

The author thanks Dr. J. C. Crocker for helpful criticism and advice, and also the Dixon Fund Committee and the Chemical Society for grants.

CHELSEA POLYTECHNIC, LONDON, S.W. 3.

[*Received, September 25th,* 1937.]