CXLIII.—*The Reactivity of Alkyl Iodides with Sodium Benzyl Oxide. A Criticism.*

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THE reactivity of alkyl iodides with sodium benzyl oxide and the effect of temperature on such reactions were studied by Haywood (J., 1922, **121**, 1904), whose reaction mixture consisted of equal volumes of $N/5$-alcoholic solutions of sodium benzyl oxide and alkyl iodide. As the molecular ratio of ethyl alcohol to sodium benzyl oxide in such a mixture is about 170, it is extremely improbable that Haywood's velocity coefficients can be a measure of the rate of the reaction $C_6H_5 \cdot CH_2 \cdot ONa + RI = NaI + C_6H_5 \cdot CH_2 \cdot OR$. It is more likely that in such a mixture the concentration of sodium ethoxide is much greater than the concentration of sodium benzyl oxide, and that the velocity measured by Haywood was really that

of the reaction $C_2H_5\cdot ONa + RI = NaI + C_2H_5\cdot OR$. Although he remarked that alcoholysis " to a certain extent " is to be expected, Haywood apparently did not realise the probability that under the conditions of his experiments alcoholysis would be almost complete.

In order to put the matter to the test, the author mixed equal volumes of $N/5$-ethyl-alcoholic solutions of sodium ethoxide and ethyl iodide and compared the rate of the reaction in this mixture at 35° with the rate of the reaction in a mixture of equal volumes of $N/5$-ethyl-alcoholic solutions of sodium benzyl oxide and ethyl iodide. The velocity coefficients in the two experiments were practically identical. As there was a possibility that this result might have been due to coincidence, the reactivities of sodium benzyl oxide and sodium ethoxide being the same in ethyl-alcoholic solution, two further experiments were performed, in which *n*-butyl alcohol was used as solvent in the place of ethyl alcohol. Here again the velocity of the reaction in a mixture of equal volumes of $N/5$-butyl-alcoholic solutions of sodium butyl oxide and ethyl iodide was practically the same as the velocity in a mixture of equal volumes of $N/5$-butyl-alcoholic solutions of sodium benzyl oxide and ethyl iodide.

A final experiment was performed as a crucial test, the object of which was to isolate and examine the products of the reaction. A solution prepared by mixing equal volumes of $2N$-ethyl-alcoholic solutions of sodium benzyl oxide and ethyl iodide was fractionally distilled after sufficient time had elapsed for the completion of the reaction (at 35°). If in this experiment no ethyl benzyl ether had been formed, the sole reaction being that between sodium ethoxide and ethyl iodide, 14·8 g. of ethyl ether should have been formed. Actually 11 g. of liquid boiling below 45° were collected and from this 6 g. of pure ethyl ether were obtained by further fractionation. Thus it is clear that even in a normal ethyl-alcoholic solution of sodium benzyl oxide and ethyl iodide the main reaction is that represented by the equation

$$C_2H_5\cdot ONa + C_2H_5I = C_2H_5\cdot O\cdot C_2H_5 + NaI.$$

In Haywood's experiments, in which the concentrations were tenth-normal, the amount of ethyl benzyl ether formed must have been negligibly small.

Experimental.

The ethyl alcohol used in these experiments was commercial absolute alcohol, dried by digesting with lime and calcium. The ethyl iodide (Kahlbaum's) was purified just before use by washing with dilute alkali and water, drying over calcium chloride, and distilling from silver powder.

The benzyl alcohol (Kahlbaum's) was redistilled before use. The *n*-butyl alcohol was purified by distillation, after treatment with lime.

All the instruments used were standardised with reference to standard instruments.

During the velocity determinations the temperature, kept constant by means of a thermostat provided with an Ostwald toluene regulator and stirrer, did not vary more than 0·05°. In the preparation of the *N*/5-ethyl-alcoholic solution of sodium benzyl oxide, a weighed quantity of benzyl alcohol was mixed with a measured volume of a standard alcoholic solution of sodium ethoxide, containing an equivalent quantity of the ethoxide. The mixture was then diluted to the calculated volume with alcohol. The solution of sodium benzyl oxide in butyl alcohol was similarly prepared. The rates of reaction were measured in the manner described by Haywood.

Results.—The velocity coefficients are calculated from the formula $k = \frac{1}{t} \cdot \frac{x}{a-x} \cdot \frac{y}{C_0 a}$, in which x, y, t, a and C_0 have the same significance as in Haywood's paper.

N/40-Hydrochloric acid was used in the titrations.

1st Expt. Equal volumes of N/5-sodium benzyl oxide (in ethyl alcohol) and *N*/5-ethyl iodide (in ethyl alcohol).

Temp. 35°. Zero = 35·40 c.c. y = 38·45 c.c.

t.	$a-x$.	x.	$k \times 10^4$.
120	27·33	8·07	267
234	23·06	12·34	248
326	20·02	15·38	256
441	17·50	17·90	252
		Mean	256

2nd Expt. Equal volumes of *N*/5-sodium ethoxide (in ethyl alcohol) and *N*/5-ethyl iodide (in ethyl alcohol).

Temp. 35°. Zero = 35·40 c.c. y = 40·00 c.c.

t.	$a-x$.	x.	$k \times 10^4$.
45	32·00	3·40	267
101	28·75	6·65	259
248	22·50	12·90	261
319	20·45	14·95	259
		Mean	262

3rd Expt. Equal volumes of *N*/5-sodium benzyl oxide (in *n*-butyl alcohol) and *N*/5-ethyl iodide (in *n*-butyl alcohol).

Temp. 35°. Zero = 36·82 c.c. y = 39·84 c.c.

t.	$a-x$.	x.	$k \times 10^4$.
62	33·40	3·42	178 *
187	28·80	8·02	160
352	24·60	12·22	152
		Mean	156

4th Expt. Equal volumes of *N*/5-sodium *n*-butoxide (in *n*-butyl alcohol) and *N*/5-ethyl iodide (in *n*-butyl alcohol).

Temp. 35°. Zero = 36·9 c.c. y = 40·00 c.c.

t.	$a-x$.	x.	$k \times 10^4$.
90	32·32	4·58	169
150	29·95	6·95	166
273	26·35	10·55	158
419	23·10	13·80	153
		Mean	159

* Omitted in calculating the mean.

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