Mechanism of Substitution at a Saturated Carbon Atom. Part XLVIII. Kinetics of the Interaction of Iodide Ions with Simple Alkyl Iodides in Acetone.*

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Kinetic experiments on the second-order reactions of iodine exchange between lithium iodide and four simple alkyl iodides in acetone are reported. In the one case of *tert.*-butyl iodide the bimolecular substitution is accompanied by a probably unimolecular side-reaction, in an amount which is kinetically appreciable, but not too large to permit evaluation and correction. Salt conditions are standardised, and rate constants and parameters of the Arrhenius equation are determined.

NEARLY all previous investigations of the rate of iodine exchange between alkali-metal iodides and alkyl iodides relate to the reaction in solvent methyl or ethyl alcohol, which, owing to its tendency to enter into solvolytic reactions, is unsuitable as a medium for the halogen exchanges of tertiary and certain other alkyl halides. This type of medium was used by Seelig and Hull for the exchanges of *n*- and *iso*-propyl iodide (*J. Amer. Chem. Soc.*, 1942, **64**, 940), by McKay for those of a number of primary, secondary, and tertiary alkyl iodides (*ibid.*, 1943, **65**, 702), by Neimen and Protsenko for ethyl iodide (*Doklady Akad. Nauk S.S.S.R.*, 1950, **71**, 327), by May, Daudel, Schotsky, Sarraf, and Vobauré for ethyl and allyl iodide (*Compt. rend.*, 1951, **232**, 727; 1952, **235**, 935; *J. Chim. phys.*, 1952, **49**, 64),

* Part XLVII, preceding paper.

by Van Stratten, Nickolls, and Winkler for 1-methylhexyl and several *cyclo*alkyl iodides (*Canad. J. Chem.*, 1951, **29**, 372), and by Kuhn, Stilman, Purlee, and Reibsomer for benzyl iodides (*J. Amer. Chem. Soc.*, 1953, **75**, 3579; 1954, **76**, 1796). McKay's work was designed as a study of the effect of alkyl structure : it included some examination of the temperature coefficients of reaction rate, but not with sufficient extension to enable individual Arrhenius parameters to be quoted, though it is mentioned that the primary alkyl iodides gave energies of activation near 19, and the secondary values near 20·5 kcal./mole.

As to the kinetics of the exchange in non-hydroxylic solvents, Hughes, Juliusberger, Masterman, Topley, and Weiss examined the reaction between 1-methylheptyl iodide and sodium radio-iodide in solvent acetone (*J.*, 1935, 1525) and May, Daudel, Schotsky, Sarraf, and Vobauré studied analogous reactions of ethyl and allyl iodide in solvent acetonitrile (*locc. cit.*). However, no systematic work concerning structural effects on the kinetics of this exchange reaction in non-hydroxylic solvents has yet been reported.

As in the work described in the accompanying papers, so in the present study of halogen exchange between sodium radio-iodide and alkyl iodides, anhydrous acetone was used as solvent. The series of alkyl iodides employed was less complete than in the investigation of some other Finkelstein substitutions, but it was sufficient to show the main trends. Methyl iodide excluded itself by the rapidity of its reaction, but rate data have been obtained for the other members of the α-methylated branched-homologous series, ethyl, *iso*propyl, and *tert.*-butyl iodide, and also for the end members of the β-methylated series, ethyl and *neo*pentyl iodide.

The reactions were conducted in ampoules, one for each measurement of the extent of exchange. Each measurement involved separating the sodium iodide from the organic iodide, and noting the loss of radioactivity from the former. The separations were effected either by evaporation, or by partition between ether and water.

The exchange with *tert.*-butyl iodide was accompanied by a side reaction, which could be minimised, but not wholly eliminated, by conducting all manipulations under nitrogen and in dim light, and by using blackened ampoules for the kinetic runs. The main part of this residual side reaction is believed to be a unimolecular olefin elimination. It resulted in the appearance in the solution of hydrogen iodide was well as of a small amount of iodine. These substances must very quickly come into radioactive equilibrium with the sodium iodide; but in the separation, as conducted by evaporation, of the *tert.*-butyl iodide from the sodium iodide, hydrogen iodide and iodine are removed with the *tert.*-butyl iodide, which therefore becomes credited with too large an uptake of radioactivity from the sodium iodide. A correction for this additional exchange, resulting from the side reaction, was made as follows : A series of blank determinations was carried out, in each of which an ampoule, charged only with a solution of *tert.*-butyl iodide in acetone, was left at the temperature, and for approximately the length of time, of a determination of the exchange resulting from the reaction with sodium iodide. To the product of such a blank run, sodium radio-iodide was added; and then it was immediately separated by the evaporation method, and its radioactivity was measured. The loss of radioactivity was that due to the side reaction only, and the rate of such loss represented the negative correction to be applied to the total rate of loss as measured in the main exchange experiments. In the conditions employed, the side reaction was found to be responsible for some 10—15% of the total observed exchange.

Like other Finkelstein substitutions, the iodine exchange reaction shows a negative salt effect, which is the subject of a separate investigation later to be published by Dr. R. W. Broadbank. His results have been used in order to make the small corrections necessary for the purpose of reducing the present rate constants to a comparable basis at the common salt concentration 0·1M.

The kinetic results are in Table 1, except that here the rate constants for the exchange reaction of *tert.*-butyl iodide remain uncorrected for the side reaction. The data permitting this correction, and the corrected rate constants for the exchange of *tert.*-butyl iodide, are given in Table 2. In Table 1, C, $C - X_1$, $C - X_2$, are counting rates applying to the main series of exchange runs. They represent respectively the specific activity of the sodium iodide initially, on separation at a time t_1, soon after the reaction solution had

TABLE 1. *Second-order rate constants (k_2 in sec.$^{-1}$ mole^{-1} l.) of iodine exchange between alkyl iodides and sodium radio-iodide in acetone.*

Ethyl iodide

Temp. (c)	a = [AlkI]	b = [LiBr]	$t_2 - t_1$ (min.)	Counting rates C	$C - X_1$	$C - X_2$	10^5k_2 (b)	10^5k_2 (0·1)	Mean
− 5·7°	0·3408	0·1004	18·2	367·0	321·0	159·9	225 ± 6	225	—
,,	0·3453	,,	25·2	,,	,,	136·1	211 ± 5	211	—
,,	0·3396	,,	20·2	,,	,,	154·2	218 ± 7	218	218
−17·3	0·3495	0·1022	34·0	439·0	398·2	290·1	48·8 ± 2·3	48·9	—
,,	0·3514	,,	56·0	,,	,,	239·5	49·6 ± 1·5	49·7	—
,,	0·3551	,,	76·0	,,	,,	207·8	48·3 ± 1·3	48·3	49·0
−27·3	0·3650	0·1035	107·0	439·0	424·7	324·3	12·2 ± 0·8	12·2	—
,,	0·3632	,,	121·0	,,	,,	313·2	12·3 ± 0·7	12·4	12·3

iso*Propyl iodide*

10^5k_2 (b)	10^5k_2 (0·1)
0·1199, *b* 0·0839; 25·0°	
62·8 ± 1·4	61·8
56·9 ± 1·3	56·0
57·4 ± 1·3	56·5
61·3 ± 1·4	60·3
59·9 ± 1·4	58·9
Mean	58·7
a 0·1243, *b* 0·0869; −0·1°	
2·83 ± 0·08	2·79
3·26 ± 0·09	3·21
2·92 ± 0·08	2·88
2·94 ± 0·08	2·91
2·90 ± 0·08	2·86
Mean	2·93

tert.-Butyl iodide *

10^5k_2 (b)	10^5k_2 (0·1)
a 0·1118, *b* 0·0944; 44·6°	
165 ± 7	164
181 ± 8	180
193 ± 8	192
198 ± 9	197
167 ± 7	166
Mean	180
a 0·1151, *b* 0·0972; 25·0°	
21·6 ± 0·6	21·6
22·9 ± 0·6	22·8
21·8 ± 0·6	21·7
21·7 ± 0·6	21·7
20·5 ± 0·6	20·5
Mean	21·7
a 0·2085, *b* 0·0838; 25·0°	
20·8 ± 0·7	20·3
20·1 ± 0·7	19·6
21·4 ± 0·7	19·9
19·6 ± 0·7	19·1
21·5 ± 0·7	21·0
Mean	20·2
a 0·5142, *b* 0·0572; 25·0°	
22·0 ± 1·0	21·3
22·8 ± 1·0	22·1
21·4 ± 0·9	20·7
Mean	21·4
a 0·5142, *b* 0·1434; 25·0°	
17·3 ± 0·5	17·9
16·5 ± 0·5	17·1
Mean	17·5
a 0·2160, *b* 0·0868; −0·1°	
0·684 ± 0·026	0·677
0·747 ± 0·028	0·740
0·744 ± 0·028	0·737
0·704 ± 0·027	0·697
0·690 ± 0·026	0·683
Mean	0·707

neo*Pentyl iodide*

10^5k_2 (b)	10^5k_2 (0·1)
a 0·1705, *b* 0·0781; 64·7°	
9·48 ± 0·20	9·20
9·10 ± 0·16	8·84
9·31 ± 0·15	9·04
9·46 ± 0·14	9·18
Mean	9·06
a 0·1760, *b* 0·0806; 44·6°	
1·19 ± 0·03	1·17
1·16 ± 0·03	1·13
1·11 ± 0·03	1·08
1·16 ± 0·02	1·13
Mean	1·13
a 0·1786, *b* 0·0818; 35·0°	
0·484 ± 0·011	0·474
0·446 ± 0·010	0·437
0·442 ± 0·010	0·433
Mean	0·448

* Rates uncorr.; see Table 2.

TABLE 2. *Rate corrections calculated as coefficients (k_2' in sec.$^{-1}$ mole^{-1} l.) of the side reaction of* tert.*-butyl iodide in acetone, and corrected rate constants (k_2 in sec.$^{-1}$ mole^{-1} l.) of iodine exchange between* tert.*-butyl iodide and sodium radio-iodide in acetone.*

Temp. (c)	a = [ButI]	t' (min.)	Counting rates C	$C - X'$	$10^5k_2'$	10^5k_2 (0·1) Uncorr.	Corr.
44·6°	0·112	34	618·2	588·6	22	180	158
25·0	0·115	240	682·2	647·9	3·2	21·7	18·5
,,	0·208	234	711·0	666·4	2·1	20·2	18·1
,,	0·514	195	533·4	492·3	2·0	21·4	19·4
,,	0·514	195	553·4	529·0	0·7	17·5	16·8
−0·1	0·216	7470	488·0	453·5	0·077	0·707	0·630

attained the temperature of the thermostat, and on separation at some later time t_2. In Table 2, C and $C - X'$ are counting rates applying to the blank runs, which were made with *tert.*-butyl iodide for the purpose of measuring the side-reaction. They represent respectively the specific activity of the sodium iodide when untreated, and when recovered after having been mixed with a solution of *tert.*-butyl iodide which had previously been kept for a period t' at the experimental temperature. The ± errors attached to the rate-constants entered in Table 1 are errors deriving from the probable errors of radioactive counting, which are calculable from the size of the counts.

Because of the side-reaction, the measurements on *tert.*-butyl iodide are less satisfactory than those on the other alkyl iodides. Although the side-reaction is probably unimolecular, the main reaction of exchange, as is shown by the experiments conducted at 25° with

different concentrations of sodium iodide, must have substantially a second-order kinetic form.

Table 3 assembles the parameters of the Arrhenius equation for these exchange reactions, and the absolute and relative rates at 25°, as given by the Arrhenius equation with the parameters listed. The data will be discussed in Part XLIX.

TABLE 3. *Rate constants (k_2 in sec.$^{-1}$ mole^{-1} l.), relative rates at a common temperature and parameters (B_2 in sec.$^{-1}$ mole^{-1} l., and E_A in kcal. mole^{-1}) of the equation $k_2 = B_2 \exp(-E_A/\boldsymbol{R}T)$ for the reactions of sodium radio-iodide with alkyl iodides in acetone.*

Alkyl iodide	Et	Pr^i	Bu^t	*neo*Pe
$10^5 k_2$ (25°)	6000	53	18	0·11
Rel. k_2 (25°)	1	0·0088	0·0030	0·000018
$\log_{10} B_2$	11·5	11·0	12·0	10·2
E_A	17·4	19·4	21·5	22·0

EXPERIMENTAL

The acetone and the alkyl iodides were purified or prepared as described in Part XLIV. The *neo*pentyl iodide had b. p. 67°/90 mm., n_D^{20} 1·4885, n_D^{25} 1·4860. The *tert.*-butyl iodide, after purification by fractionation under nitrogen, had b. p. 25°/60 mm., 48·5°/120 mm., was kept with mercury in small sealed tubes, and was redistilled at 10 mm. immediately before use.

The National Institute for Medical Research very kindly made available solutions containing carrier-free iodine (half-life 8 days) as iodide ions, together with a little stabilising material, usually sodium hydrogen sulphite. It was not thought necessary to remove the latter, since the amount present, after dilution of the sample with inactive iodide, was only of the order of 0·001% of the weight of sodium iodide. The solution of radioactive material was added to about 10 g. of sodium iodide dissolved in acetone, and the solution was filtered and evaporated. The residual radioactive sodium iodide was dried in a vacuum and dissolved in dry acetone.

The sealed-tube method was used for the kinetics. For the reactions of *iso*propyl, *tert.*-butyl, and *neo*pentyl iodide, solutions of the alkyl iodide and of sodium radio-iodide were delivered by automatic pipettes protected from atmospheric moisture by tubes of calcium chloride, into dried ampoules. Each ampoule was immediately sealed, and cooled to and kept at −80° until required. The additional precautions taken with *tert.*-butyl iodide have already been noted.

For these alkyl iodides, reaction was stopped by strongly cooling the ampoules withdrawn from the thermostat. The separation of the organic from the inorganic iodide was effected by evaporation below 0° with the aid of a high-capacity pump. Similar methods were used in blank determinations of the side reaction undergone by *tert.*-butyl iodide.

The exchange reaction of ethyl iodide was too rapid to admit the above technique. In this case the reaction mixtures were made by breaking a bulb containing a weighed amount of ethyl iodide within an ampoule containing the sodium radio-iodide in the acetone at −80°. After a period in the thermostat, reaction was stopped by cooling the withdrawn ampoule to −80°. The ethyl iodide was then separated from the sodium iodide by partition between water and ether. The aqueous solution of sodium iodide was evaporated to dryness, and the residue was, as usual, dissolved in water, and made up to a suitable volume for counting.

The general procedure of counting and calculation is as given in Parts XLII and XLV. In the present case, the amount of radioactive decay during a single run was appreciable, but small, and it was thus an easy matter to correct the counts to a standard time by means of the known decay constant of the single radioactive species. Second-order kinetic constants were corrected for thermal expansion of the solvent, and were adjusted to correspond to the salt concentration 0·1M as already described.

Correction for the side reaction of *tert.*-butyl iodide was effected by calculating as a second-order rate-constant the measured exchange due to the side-reaction in a time approximately equal to that of the exchange run to which the correction was to be applied, and then subtracting the constant from the second-order rate constant deduced from the exchange run, or rather, in practice, from the mean of such constants obtained from a group of similar exchange runs.

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