Mechanisms of Exchange Reactions of Primary and Secondary Alkyl Iodides with Elementary Iodine

BY JOHN E. BUJAKE, JR.,[1] M. W. T. PRATT AND RICHARD M. NOYES[2]

RECEIVED MAY 17, 1960

Several primary and secondary alkyl iodides exchange thermally with iodine-131 in hexachlorobutadiene between 130 and 200°. If the solutions are saturated with oxygen at one atmosphere, rates of exchange fit the kinetic expression $k_b[RI][I_2]^{1/2}$. Degassed solutions always exchange faster than oxygen saturated ones, but methyl, ethyl and n-propyl iodides show the same kinetics as with oxygen. Exchange rates of degassed isopropyl and neopentyl iodides also show contributions from a $k_a[RI]$ term. Exchange in degassed ethylene dichloride is 3 to 4 times as fast as in degassed hexachlorobutadiene. Activation energies for k_b are usually about 27 to 31 kcal./mole. Effects of substitution on α carbon are illustrated by the rate sequence methyl < ethyl < i-propyl = sec-butyl. Effects of substitution on β carbon are illustrated by the rate sequence ethyl < n-propyl >> neopentyl. The observations can be best explained if iodine atoms can abstract iodine with formation of free alkyl radicals and can also cause direct substitution with inversion of a saturated carbon atom similar to the accepted mechanism of direct nucleophilic substitution. Both processes seem to go at comparable rates in most of our systems. This interpretation is difficult to accept unless currently accepted bond dissociation energies for methyl and ethyl iodides be several kcal./mole too high. Since the rates of exchange of methyl, ethyl and i-propyl iodides vary in the opposite direction from the sequence for bimolecular nucleophilic substitution, the explanation proposed suggests that for nucleophilic substitution the effect of added methyl groups on an α carbon is a steric hindrance to solvation by solvent dipoles rather than a steric hindrance to the group attacking the carbon atom itself.

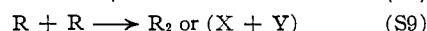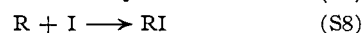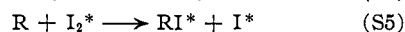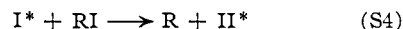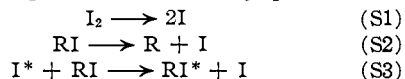## Introduction

The understanding of nucleophilic substitution mechanisms has been greatly facilitated by investigations of saturated compounds.[3] By systematically observing the kinetic effects of various group replacements at and near the reacting center, mechanistic detail has been considerably clarified.

No comparable data are available for radical reactions. Although much is known about the relative rates at which different radicals extract primary, secondary and tertiary hydrogens atoms,[4] there seems to be little systematic information concerning the abstraction of other groups by any radicals except sodium atoms. Some non-ionic substitution reactions of saturated halides with halogens have been studied by various workers, but the results are not clear and do not always demonstrate that radical mechanisms are involved. These observations are discussed at appropriate places below.

The present paper reports a study of the exchange of isotopically labelled elementary iodine with a number of alkyl iodides representing modifications at or near the reaction site. Only primary and secondary iodides are discussed here; t-butyl iodide was found to exchange by an entirely different mechanism with no detectable contribution from radical processes, and these experiments are presented separately.[5]

If only radical species are contributing to exchange in a solution containing iodine and alkyl iodide, RI, the possible elementary processes are

$$I_2 \longrightarrow 2I \qquad (S1)$$
$$RI \longrightarrow R + I \qquad (S2)$$
$$I^* + RI \longrightarrow RI^* + I \qquad (S3)$$

$$I^* + RI \longrightarrow R + II^* \qquad (S4)$$
$$R + I_2^* \longrightarrow RI^* + I^* \qquad (S5)$$
$$I + I_2^* \longrightarrow II^* + I^* \qquad (S6)$$
$$2I \longrightarrow I_2 \qquad (S7)$$
$$R + I \longrightarrow RI \qquad (S8)$$
$$R + R \longrightarrow R_2 \text{ or } (X + Y) \qquad (S9)$$

In these equations, an asterisk is used to follow specific iodine atoms if they do not all remain equivalent during the particular reaction. In reaction S9, X and Y are the products of disproportionation of two R radicals, and R_2 is the product of combination by the same radicals.

Reactions S3 and S4 have identical kinetics but represent different mechanisms and are referred to as direct substitution and abstraction, respectively. Since the direct substitution presumably goes with inversion of configuration, measurements with optically active compounds can sometimes distinguish the two mechanisms. Such studies[6,7] have indicated that sec-butyl iodide reacts by both mechanisms at comparable rates. Studies with optical activity are not general and cannot be applied to primary or to symmetrical secondary iodides. We have therefore tried to distinguish the contributions of the two mechanisms by using the fact that elementary oxygen is a very efficient scavenger for free alkyl radicals. The reactions were carried out in an inert solvent to avoid the heterogeneous effects that have interfered with gas-phase studies of some reactions of this sort.

Experimental

Materials.—Methyl, ethyl, n-propyl and iso-propyl iodides were obtained commercially. All except ethyl iodide were shaken with copper powder, magnesium sulfate and silica gel and were carefully fractionated at atmospheric pressure. After distillation at atmospheric pressure, ethyl iodide was twice vacuum distilled and used as quickly as possible. Gas chromatography failed to reveal any evidence of impurities in any of the compounds.

Neopentyl iodide (1-iodo-2,2-dimethylpropane) was prepared from neopentyl alcohol, triphenyl phosphite and

(1) Based in part on the Ph.D. Dissertation of John E. Bujake, Jr. The original dissertation and microfilms thereof are available from the Library of Columbia University.

(2) To whom inquiries should be sent: Department of Chemistry, University of Oregon, Eugene, Oregon.

(3) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter VII.

(4) E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd Ed., Reinhold Publishing Corporation, New York, N. Y., 1954.

(5) J. E. Bujake, Jr., and R. M. Noyes, THIS JOURNAL, 83, 1555 (1961).

(6) R. A. Ogg, Jr., and M. Polanyi, Trans. Faraday Soc., 31, 482 (1935).

(7) R. A. Herrmann and R. M. Noyes, THIS JOURNAL, 78, 5764 (1956).

methyl iodide as proposed by Kornblum and Iffland.[8] The material used boiled 68.5–69.0° at 98 mm. Elementary analysis was satisfactory, and neither infrared spectroscopy nor gas chromatography indicated any impurities.

Resublimed reagent-grade iodine was used without further purification. Stock solutions were activated by shaking with aqueous solutions of carrier-free iodine-131 from the U.S. Atomic Energy Commission. They were then dried with magnesium sulfate and filtered prior to use.

Two solvents were used for these studies. Commercial hexachlorobutadiene-1,3 was vacuum distilled at less than 15 mm. and was shown to be almost inert to reaction with iodine under the conditions of our experiments. Ethylene dichloride was shaken with concentrated sulfuric acid, washed with sodium carbonate solution and water, dried over calcium chloride and distilled at atmospheric pressure.

Apparatus.—The reactions were studied in Pyrex ampules immersed in conventional thermostats containing wax at temperatures below 150° and fused alkali nitrates at higher temperatures. Temperatures were controlled to 0.1° with mercury-in-glass regulators, and absolute values were determined with a National Bureau of Standards thermometer.

Radioactivity was measured with commercial liquid-jacketed Geiger tubes and a conventional scaler. A Beckman DU spectrophotometer was used to measure iodine concentrations.

Experimental Procedure.—Reaction mixtures were prepared from solutions of the organic iodide and of isotopically labelled iodine. For a "degassed" run, the ampule containing the mixture was submitted five times to a cycle that involved freezing to Dry Ice temperature, evacuating with a mercury diffusion pump and warming to room temperature. After the fifth evacuation, the ampule was sealed while the sample was still frozen. For an "oxygen" run, the ampule was frozen, flushed for ten minutes with tank oxygen and sealed. The sealed ampule was shaken at room temperature to ensure rapid solution of oxygen. A few trials showed that this procedure gave results comparable to those when the ampule was degassed, oxygen was admitted to one atmosphere pressure and the ampule was sealed.

Sealed ampules were wrapped in aluminum foil to prevent photochemical reaction at higher temperatures. They were then thermostated for measured times and cooled rapidly after removal from the thermostat. Extent of decomposition was determined by spectrophotometric measurement of iodine concentrations before and after heating. Extent of isotopic exchange was determined by extracting the iodine with aqueous sulfite and comparing the radioactivity of the extract with that of the original iodine. Subsequent extraction of the organic phase demonstrated that this procedure caused negligible hydrolysis or extraction of the organic iodide.

Calculations.—The quantity R_{ex} is defined as the rate of the exchange reaction

$$RI + I_2{}^* \longrightarrow RI^* + II^* \qquad (1)$$
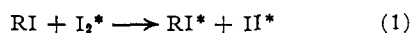
It was calculated by the equation

$$R_{ex} = \frac{2[I_2][RI]}{(2[I_2] + [RI])t} \ln \frac{x_\infty - x_0}{x_\infty - x} \qquad (2)$$

where x is the fraction of radioactive iodine organically bound at time t. Of course x_0 is the value of x at time zero, and x_∞ is the computed equilibrium value. Individual values of R_{ex} reported in the supplementary tables were usually averages of rates calculated from three different reaction times. In making the calculations, average concentrations of iodine and alkyl iodide were used. Since the increase in iodine concentration was almost never more than about 10% and was usually much less and since the decrease in alkyl iodide was a much smaller percentage change, this approximation is satisfactory.

The quantity R_d is the average rate of decomposition of alkyl iodide during a run; it was computed by the equation

$$R_d = 2\Delta[I_2]/t \qquad (3)$$

where $\Delta[I_2]$ is the change in iodine concentration during time t.

A third rate of interest is

$$R_I = k_1[I_2] \qquad (4)$$

where R_1 is the rate at which iodine molecules are dissociating to atoms by reaction S1. In the subsequent treatment, we have assumed that

$$k_1 = 10^{13.00} e^{-35,500/RT} \text{ sec.}^{-1} \qquad (5)$$

where R is in cal./mole deg. Previous measurements[9] have indicated that this calculation is accurate to within a factor of two at 36°. The extrapolation to higher temperatures uses the 35.5 kcal./mole heat of dissociation of iodine in gas phase. This number will be too small by the amount of any activation energy for the recombination of atoms in solution, and it will be too large by any extent to which iodine atoms are solvated more strongly than molecules. Unless the net discrepancy is as large as 4 kcal./mole, equation 5 will be accurate to better than a factor of ten even at 200°.

Effects of Potential Variables

Effects of Oxygen Pressure.—Solutions in hexachlorobutadiene saturated with oxygen at one atmosphere almost invariably exchanged more slowly than equivalent solutions that had been degassed. In the subsequent discussion, it is assumed that oxygen reduces the rate to a limiting value and that this value is already attained at pressures below one atmosphere. Although this assumption was not tested directly for all possible conditions, it was tested for ethyl iodide and for isopropyl iodide at 160°. With ethyl iodide, at ³/₄ and at 1 atmosphere of oxygen the rates were not significantly different but were less than the rate at ¹/₂ atmosphere. With isopropyl iodide, the rate of exchange had fallen to its limiting value when the oxygen pressure was 222 mm. In the discussion, we present additional arguments to indicate that the reported oxygen runs usually had been reduced to limiting rates.

Effects of Surface.—As is pointed out below, many gas phase studies of similar reactions have been complicated by heterogeneous effects. When the surface to volume ratio was increased by a factor of about ten with Pyrex helices, the rate of isopropyl iodide exchange in degassed hexachlorobutadiene solution was not significantly affected.

When powdered glass was added to similar runs with ethyl iodide, the degassed rate of exchange increased by less than a factor of two, and the oxygen rate increased by a factor of about five. The observations show that the rates can be affected by extreme increases in surface, but they do not indicate much heterogeneous contribution in the unpacked ampules used for the regular runs. Diffusion coefficients in solution are so small that a great many minutes are required for molecules to traverse distances of the order of a millimeter.

Effects of Light.—It is hardly surprising that these reactions are photochemically sensitive. With a 100-watt lamp at a distance of six inches, a solution of isopropyl iodide in hexachlorobutadiene at 100° exchanged about as rapidly as a solution at 160° in the dark. As has been indicated above, precautions were taken to prevent photochemical influence on the hot solutions.

Tests for Side Reactions.—Gas chromatograms of reaction mixtures failed to indicate any species except the solvent and the original iodide. Distillation of similar mixtures indicated that the organically bound radioactivity was concentrated in the original iodide.

Since hydrogen iodide was suspected as a product during the exchange of isopropyl iodide, an exchange experiment was conducted with about 0.02 mole/liter of iodine in ethylene dichloride, and the resulting solution was extracted with about four times its volume of water. The pH of the extract was about 5, and only about 2% of the inorganic iodine was extractable with water that did not contain a reducing agent. Any hydrogen iodide must be present in negligible concentration compared to molecular iodine.

Numerical Results

Individual Rate Experiments.—Values of R_{ex}, R_d and R_I were measured at different temperatures and concentrations for five different organic iodides. The individual data are collected in Tables I–V which are not published here but which are available from the American Documentation Institute.[10]

(8) N. Kornblum and D. C. Iffland, THIS JOURNAL, **77**, 6653 (1955).

(9) M. Gazith and R. M. Noyes, *ibid.*, **77**, 6091 (1955).

(10) Document No. 6422, available from American Documentation Institute, Library of Congress, Washington. 25, D. C. Cite Document number and remit $1.25 for photoprints or $1.25 for 35 mm. microfilm.

Fig. 1.—Exchange of methyl iodide with iodine in hexa-chlorobutadiene at 159.9°: ●, degassed; O, oxygen.
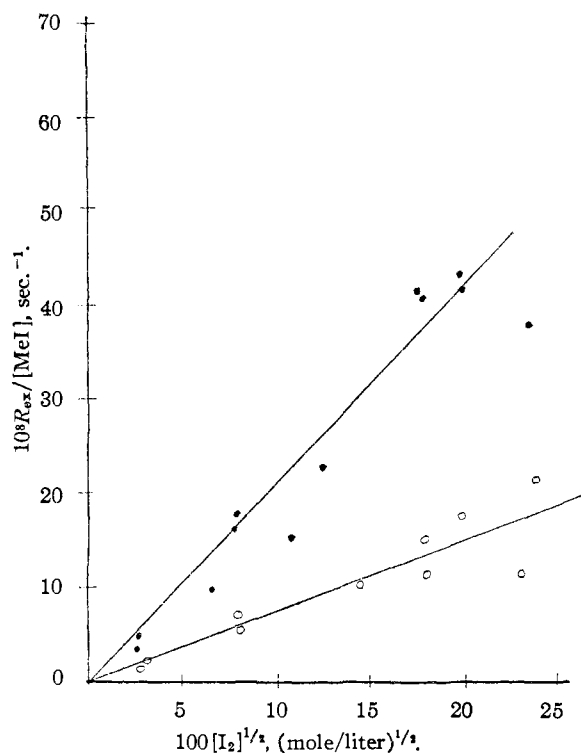

Fig. 2.—Exchange of n-propyl iodide with iodine in hexa-chlorobutadiene at 159.9°: ●, degassed; O, oxygen.

The measurements on most compounds were reasonably straightforward, but ethyl iodide was erratic. When it was twice vacuum distilled and then used immediately, the rate of degassed exchange with iodine was less than 10% of the rate at the same concentrations with material that had been distilled at atmospheric pressure and dried over magnesium sulfate. When a solution of the vacuum distilled ethyl iodide stood in contact with air for a week, the rate of exchange increased by a factor of three. When one drop of ethanol was added to 5 ml. of a solution of freshly vacuum distilled ethyl iodide, the rate of exchange increased by over a factor of two. The results suggest that at least some of the erratic behavior resulted from strong catalysis of the exchange by traces of ethanol formed from atmospheric moisture. Traces of acetaldehyde also might have contributed to the difficulty. All the runs reported were made with ethyl iodide that had been freshly vacuum distilled.

Rate Constants for Exchange Reactions.—There seemed to be no reason to reject the hypothesis that all of these exchange reactions were first order in organic iodide. Plots of $R_{ex}/[RI]$ against $[I_2]^{1/2}$ almost invariably gave the best linearity of any relations that were tested. Figures 1-4 illustrate such plots at 159.9° for measurements with four iodides in hexachlorobutadiene. Although all figures cover the same range of iodine concentrations, they need quite different scales to represent $R_{ex}/[RI]$.

For all of the runs with methyl and n-propyl iodides and for oxygen runs in hexachlorobutadiene with isopropyl and neopentyl iodides plots of the type shown in the figures gave least-squares lines passing through the origin to within the accuracy anticipated from the deviations of individual points from the lines. Hence all of these data were consistent with a kinetic equation of the form

$$R_{ex} = k_b[RI][I_2]^{1/2} \qquad (6)$$

This equation also fitted the degassed exchange of iso-propyl iodide in hexachlorobutadiene at 130.6°. The studies with ethyl iodide were not extensive enough to establish kinetics, and the data were also assumed to be consistent with equation 6.

For degassed hexachlorobutadiene runs with neopentyl iodide at all temperatures and with iso-propyl iodide at the two upper temperatures, the plots of $R_{ex}/[RI]$ against $[I_2]^{1/2}$ gave significant positive intercepts. The data were best
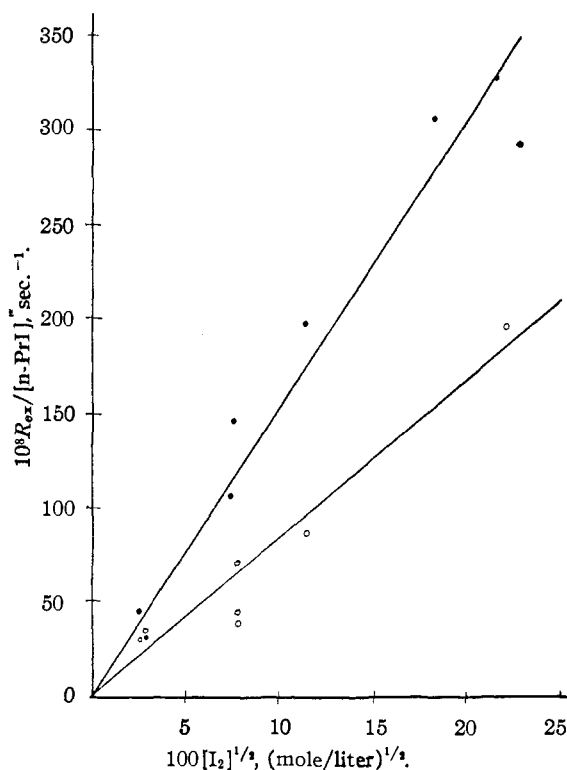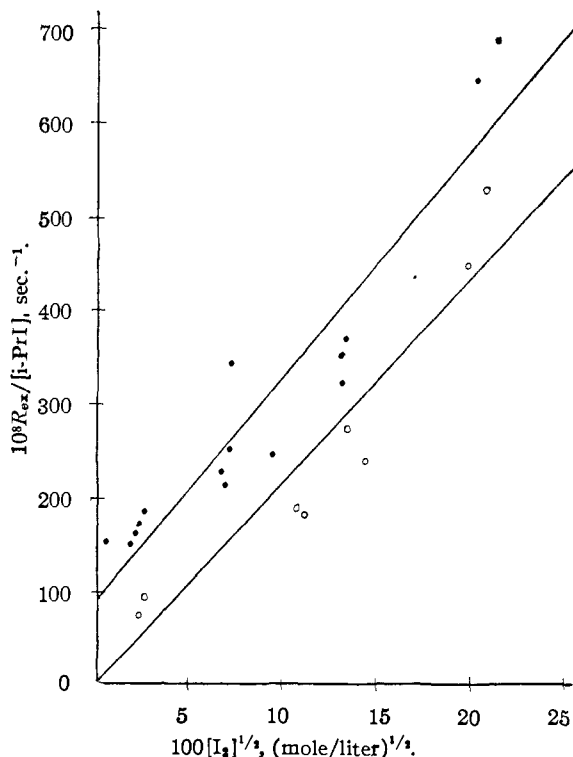

Fig. 3.—Exchange of isopropyl iodide with iodine in hexachlorobutadiene at 159.9°: ●, degassed; O, oxygen.

described by the kinetic equation

$$R_{ex} = k_a[RI] + k_b'[RI][I_2]^{1/2} \qquad (7)$$

The exchange of isopropyl iodide in ethylene dichloride was anomalous. For the degassed solutions, plots of $R_{ex}/$
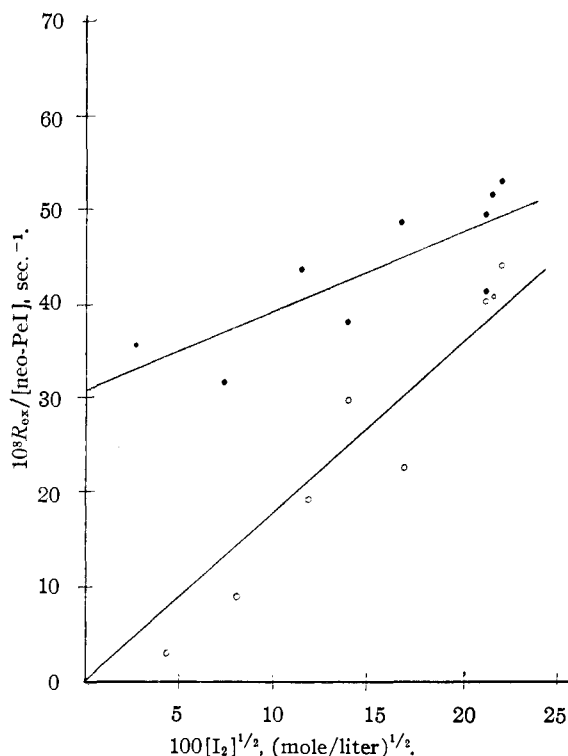
Fig. 4.—Exchange of neopentyl iodide with iodine in hexachlorobutadiene at 159.9°: ●, degassed; O, oxygen.

[RI] against $[I_2]^{1/2}$ gave significantly negative intercepts for the best straight lines. A satisfactory fit would require a term like $k[RI][I_2]$ that was greater than half order in molecular iodine. However, the data in degassed solutions also indicated considerable contribution from a term that was half-order. For the purposes of presenting the data, equation 6 was used. The oxygen runs in this solvent were even more peculiar. The rate of exchange at 130.6° was actually *faster* than in the degassed solutions and seemed to be somewhat more than first order in molecular iodine. No attempt has been made to establish definite kinetics for these oxygen runs. The behavior of isopropyl iodide in this polar solvent is obviously complex, particularly at the lowest temperature studied. The work with *t*-butyl iodide[5] suggests that non-radical processes may be important under these conditions.

Table VI presents the best values of the rate constants from either equation 6 or 7 calculated by least-squares fit of plots of $R_{ex}/[RI]$ against $[I_2]^{1/2}$. The indicated uncertainties are probable errors estimated from the scatter of individual measurements about the best line. The table includes previously reported[7] studies of *sec*-butyl iodide also.

TABLE VI

RATE CONSTANTS FOR EXCHANGE REACTIONS

Solvent	Conditions	Temp., °C.	10^6 (k_b or k'_b), (l./mole)$^{1/2}$ sec.$^{-1}$	$10^8 k_a$, sec.$^{-1}$
Methyl iodide (MeI)				
Hexachlorobutadiene	Degassed	159.9	2.05 ± 0.15	
		178.6	6.8 ± 0.4	
		200.8	38.2 ± 1.8	
	Oxygen	159.9	0.74 ± 0.08	
		178.6	3.4 ± 0.4	
		200.8	16.9 ± 1.9	
Ethylene dichloride	Degassed	130.6	0.78 ± 0.08	
		159.9	7.7 ± 0.6	
	Oxygen	159.9	1.25	
Ethyl iodide (EtI)				
Hexachlorobutadiene	Degassed	160.0	5.1 ± 2.8	
		180.0	28 ± 9	
	Oxygen	160.0	1.3 ± 1.1	
		180.0	7.6 ± 1.0	

n-Propyl iodide (*n*-PrI)

Hexachlorobutadiene	Degassed	130.6	1.74 ± 0.06	
		159.9	15.0 ± 0.9	
		178.6	83 ± 12	
	Oxygen	130.6	0.84 ± 0.04	
		159.9	8.2 ± 0.7	
		178.6	32 ± 5	

Isopropyl iodide (*i*-PrI)

Hexachlorobutadiene	Degassed	130.6	2.9 ± 0.4	
		159.9	24.2 ± 1.6	91 ± 17
		178.6	125 ± 13	620 ± 160
	Oxygen	130.6	1.7 ± 0.3	
		159.9	21.6 ± 2.0	
		178.6	97 ± 15	
Ethylene dichloride	Degassed	130.6	10.6 ± 0.6	
		159.9	87 ± 6	

sec-Butyl iodide (*sec*-BuI)

Hexachlorobutadiene	Degassed	130.0	3.34 ± 0.20	
		149.4	13.3 ± 0.8	
		160.3	24.3 ± 1.0	
		170.4	92 ± 8	

Neopentyl iodide (*neo*-PeI)

Hexachlorobutadiene	Degassed	159.9	0.87 ± 0.16	30 ± 3
		178.6	5.5 ± 1.0	155 ± 14
		200.8	97 ± 6	430 ± 90
	Oxygen	159.9	1.80 ± 0.16	
		178.6	6.6 ± 0.3	
		200.8	44 ± 4	

The values of k_b (or k_b') were fitted to the conventional Arrhenius equation

$$k_b = A_b e^{-E_b/RT} \qquad (8)$$

The values of the parameters are presented in Table VII. The indicated uncertainties are calculated from the error estimates of Table VI rather than from the fit to equation 8.

The oxygen runs with methyl iodide and with both propyl iodides fitted equation 8 considerably better than would be

TABLE VII

PARAMETERS FOR TEMPERATURE DEPENDENCE OF EXCHANGE KINETICS

Iodide	Solvent	Conditions	log A_b	E_b, kcal./mole
MeI	Hexachlorobutadiene	Degassed	9.3 ± 0.4	29.8 ± 0.8
		Oxygen	9.7 ± .7	31.3 ± 1.5
	Ethylene dichloride	Degassed	8.6 ± .8	27.2 ± 1.5
EtI	Hexachlorobutadiene	Degassed	11.5 ± 4.9	33.2 ± 10.1
		Oxygen	11.5 ± 5.9	34.4 ± 12.2
n-PrI	Hexachlorobutadiene	Degassed	8.8 ± 0.4	26.8 ± 0.7
		Oxygen	8.7 ± .5	27.3 ± 0.9
i-PrI	Hexachlorobutadiene	Degassed	9.8 ± .6	28.6 ± 1.3
		Oxygen	10.8 ± .8	30.5 ± 1.6
	Ethylene dichloride	Degassed	8.5 ± .5	25.0 ± 1.0
sec-BuI	Hexachlorobutadiene	Degassed	8.2 ± 1.0	25.4 ± 1.8
			(10.5 ± 2.0)^a	(30.1 ± 3.5)^a
neo-PeI	Hexachlorobutadiene	Degassed	(18.3 ± 0.8)	(48.4 ± 1.6)
		Oxygen	10.5 ± 0.6	32.3 ± 1.2

^{a} Calculated from upper three temperatures only.

anticipated from the estimated uncertainties in the individual rate constants. All of the degassed studies in hexachlorobutadiene and also the oxygen runs with neopentyl iodide fitted the equation somewhat less well than expected from the error estimates for individual rate constants, and the deviation was always in the direction to make plots of log k_b against $1/T$ concave up. The same behavior in more extreme form was observed previously with *sec*-butyl iodide.[7]

Kinetic Predictions

Degassed Kinetics.—If possibilities are confined to the nine elementary processes presented in the Introduction, the rate of over-all reaction 1 is given by eq. (9).

$$R_{ex} = k_5[R][I_2] + \{k_3[RI][I] + k_8[R][I]\} \times$$
$$\frac{2k_1[I_2] + k_5[R][I_2] + k_6[I_2][I]}{2k_1[I_2] + k_2[RI] + k_3[RI][I] + k_5[R][I_2] + k_6[I_2][I]} \quad (9)$$

The fraction multiplying the term in braces is the probability that a particular iodine atom was formed from molecular iodine rather than from organic iodide. It is introduced because the distribution of radioactivity in the iodine atoms is not necessarily the same as in the molecules.[11] Fortunately the term $k_6[I_2][I]$ is undoubtedly very much larger than any of the other terms, and the fraction can be set equal to unity.

Because most of the radicals in a given solution are undoubtedly iodine atoms, the rate of step S9 is probably negligible compared to the other terminating steps. To this approximation, microscopic reversibility permits us to write the equalities

$$k_1[I_2] = k_7[I]^2 \quad (10)$$
$$k_2[RI] = k_8[R][I] \quad (11)$$
$$k_4[RI][I] = k_5[R][I_2] \quad (12)$$

When these equalities are introduced, equation 9 can be rearranged to give

$$R_{ex} = k_2[RI] + (k_3 + k_4)(k_1/k_7)^{1/2}[RI][I_2]^{1/2} \quad (13)$$

This equation is of the same form as empirical equation 7, and it corresponds to equation 6 if k_2 is sufficiently small.

This kinetic analysis permits certain tests of the experimental data based on energetics. The activation energy for the empirical k_a should be equal to that for the elementary process S2 and should be quite close to the C–I bond dissociation energy of the organic iodide. If E_d is this bond dissociation energy, we can make a rough estimate that
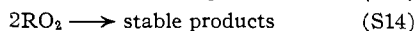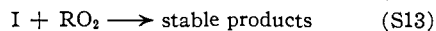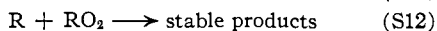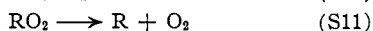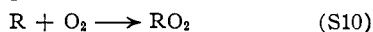
$$k_a = 10^{13}e^{-E_d/RT} \text{ sec.}^{-1} \quad (14)$$

in order to test whether k_a would have been expected to make a significant contribution to the exchange at a particular temperature.

Since the empirical k_b' is a composite containing contributions from two paths having identical kinetics, it does not necessarily have a simple temperature dependence. However, if steps S3 and S4 both contribute significantly, they probably have very comparable activation energies. The activation energy for step S4 should be very close to $E_d - 35,500$ where 35,500 cal./mole is the dissociation energy of molecular iodine. Since k_1/k_7 is the equilibrium constant for iodine dissociation, we can write to a fair approximation

$$E_b = E_d - 17,800 \text{ cal./mole} \quad (15)$$

Oxygen Kinetics.—Addition of oxygen greatly complicates the kinetics. These elementary processes are obvious possibilities

$$R + O_2 \longrightarrow RO_2 \quad (S10)$$
$$RO_2 \longrightarrow R + O_2 \quad (S11)$$
$$R + RO_2 \longrightarrow \text{stable products} \quad (S12)$$
$$I + RO_2 \longrightarrow \text{stable products} \quad (S13)$$
$$2RO_2 \longrightarrow \text{stable products} \quad (S14)$$

Any attempt at an exact kinetic treatment will bog down in a morass of algebra. However, it is clear that addition of oxygen will tend to reduce

(11) R. M. Noyes and J. Zimmerman, *J. Chem. Phys.*, **18**, 656 (1950).

the concentration of free R radicals. Since our data indicate that R_{ex} can be reduced to a finite value that is not significantly influenced by further addition of oxygen, this limiting value must represent a situation where terms in [R] in equation 9 have been suppressed. For this limiting rate in the presence of oxygen

$$R_{ex} = k_3[RI][I] \quad (16)$$

We can also equate the rates of formation and destruction of iodine atoms to obtain

$$2k_1[I_2] + k_2[RI] + k_5[R][I_2] =$$
$$2k_7[I]^2 + k_8[R][I] + k_4[RI][I] + k_{13}[RO_2][I] \quad (17)$$

If we again assume that at sufficiently high oxygen concentrations we can disregard the terms in [R] and if we also neglect the term in k_{13} (for which there is no direct evidence), we can solve for the iodine atom concentration and obtain

$$[I] = \frac{k_4[RI]}{4k_7}\left\{-1 + \sqrt{1 + \frac{8k_7(2k_1[I_2] + k_2[RI])}{k_4^2[RI]^2}}\right\} \quad (18)$$

Since R–I bonds are 10 kcal./mole or more stronger than the bond in molecular iodine, we can almost certainly say that for all of our solutions $k_1[I_2] \gg k_2[RI]$.

Under limiting conditions, equation 18 reduces to two simpler kinetic expressions. If the concentration of RI is sufficiently small, most of the iodine atoms in the solution will combine with other atoms without abstracting iodine from RI molecules. The kinetics of exchange will then be

$$R_{ex} = k_3(k_1/k_7)^{1/2}[RI][I_2]^{1/2} \quad (19)$$

At the other limit when the concentration of RI is sufficiently large, practically every iodine atom that is produced will result in formation of RO_2 by the sequence (S4)+(S10). The kinetics of exchange then will be

$$R_{ex} = \frac{k_3}{k_4}\{2k_1[I_2] + k_2[RI]\} \quad (20)$$

where the term in [RI] will be negligible.

The oxygen experiments fit equation 19 much better than equation 20. The rates do seem to be somewhat less than first order in RI but are certainly much more than zero order, and the order in iodine is much closer to one-half than it is to one. For methyl and neopentyl iodides the values of R_{ex} are smaller than the values of R_1 calculated by equation 5; such an inequality is necessary for equation 19 to be valid. The data for the propyl iodides do not always satisfy this requirement. It may be that the activation energy for step S1 is distinctly greater than the gas phase bond dissociation energy and that equation 5 gives too low a value of R_1 at these elevated temperatures.

If equation 19 is applicable, the analysis predicts that

$$\frac{k_b \text{ (degassed)}}{k_b \text{ (oxygen)}} = 1 + k_4/k_3 \quad (21)$$

Discussion of Individual Compounds

Methyl Iodide (MeI).—Methyl iodide reacted very slowly but gave the cleanest kinetics of any of the compounds that were studied. The same reaction has been studied in gas phase by several workers with rather divergent results.

Clark, Pritchard and Trotman-Dickenson[12] were not able to eliminate heterogeneous effects in a static gas system but thought they had measured the homogeneous contribution at 375° in a flow system. They calculated a rate constant equivalent to our k_b of about 3 (liter/mole)$^{1/2}$sec.$^{-1}$. Our data in both degassed and oxygen solutions extrapolate to about one tenth of this rate at that temperature. The agreement is reasonably good for an extrapolation of 175°.

Our results do not agree at all with the data of Schmied and Fink[13] who studied the same exchange in gas phase between 60 and 140°. They claimed the reaction was first order in molecular iodine with an activation energy of only 9 kcal./mole. At the highest temperature they studied, their relation predicts rates about four powers of ten faster than are predicted by a 30° downward extrapolation of our data, and the discrepancy would be worse at lower temperatures! They apparently failed to eliminate heterogeneous catalytic effects.

Laurence and Stranks[14] studied neutron activation of methyl iodide in gas phase near room temperature and found evidence that thermalized recoil iodine atoms could substitute in methyl iodide with an activation energy of about 14 kcal./mole. Their estimated rate constant at 20° is about 10^3 greater than that predicted by the extrapolation of our data over a 140° range. The discrepancy may suggest that they also were having troubles with heterogeneity, but the extrapolation of our data is a long one.

We have not yet had access to the study of this reaction by Miller, Neiman and Solodovnikov,[15] but an abstract suggests that the gas phase exchange they studied was heterogeneous and non-radical.

The above comparisons illustrate the dangers of heterogeneous effects in gas phase studies and the corresponding advantages of working with inert solvents when radical reactions are being studied.

If methyl radicals are produced in the degassed exchange, the 30 kcal./mole activation energy indicates that the bond strength in methyl iodide is not more than about 48 kcal./mole; the presently accepted value[16] is about 54 kcal./mole. This discrepancy seems rather hard to resolve if free methyl radicals are indeed produced in a significant path for exchange. The still lower activation energy in ethylene dichloride than in hexachlorobutadiene suggests that there may be solvation effects that lower the dissociation energy of the C–I bond, but it seems doubtful that these effects could be as large as 6 kcal./mole.

Even if the dissociation energy in methyl iodide were only 48 kcal./mole, equation 14 predicts that the empirical term in k_a should not have been detectable in our experiments.

(12) D. Clark, H. O. Pritchard and A. F. Trotman-Dickenson, J. Chem. Soc., 2633(1954).

(13) H. Schmied and R. W. Fink, J. Chem. Phys., 27, 1034 (1957).

(14) G. S. Laurence and D. R. Stranks, private communication.

(15) V. B. Miller, M. B. Neiman and S. P. Solodovnikov, Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk, 247 (1959).

(16) A. F. Trotman-Dickenson, "Gas Kinetics. An Introduction to the Kinetics of Homogeneous Gas Reactions," Butterworths Scientific Publications, London, England, 1955, p. 15.

Applications of equation 21 give values of k_4/k_3 varying from 1.0 to 1.8 suggesting that reactions S3 and S4 go at very comparable rates.

Ethyl Iodide (EtI).—A colleague once asked, "Why do you study the exchange of all these complicated iodides; why don't you look at something simple like ethyl iodide?" It is now almost a quarter of a century since the first attempt[17] to get qualitative information about this reaction. Schuler[18] abandoned an attempt to study the kinetics because the results were so irreproducible. Darbee and Harris[19] published some rate measurements but also complained about irreproducibility. The present study does not even begin to establish the kinetics of this reaction. However, we have obtained a possible explanation for the poor reproducibility.

If the exchange mechanism is the same as seems to apply to both methyl and n-propyl iodides, then the rate constants we calculate are intermediate between those for these compounds. Moreover, our data agree with the semi-quantitative results of Neiman, Miller and Shapovalov[20] that ethyl iodide exchanges about twice as rapidly as methyl iodide. These observations give us some confidence that the results reported here are not grossly in error.

If ethyl iodide were not one of the most logical compounds with which to start a study of the exchange of iodine with organic iodides, a comprehensive kinetic study of many alkyl iodide exchanges undoubtedly would have appeared before this paper. Bitter experience teaches kineticists that the most obvious and apparently straightforward experiments are not always the easiest.

n-Propyl Iodide (n-PrI).—We are not aware of any previous studies of exchange of this compound except the semi-quantitative observation of Neiman, Miller and Shapovalov[20] that it is about 2.8 times as fast as methyl iodide. We observe about the same ratio in degassed solutions and a larger ratio in the presence of oxygen.

Since the activation energies are about 27 kcal./mole, energetic arguments like those with methyl iodide indicate the bond dissociation energy of the alkyl iodide is not more than about 45 kcal./mole. The value claimed[16] for gas phase is about 54 kcal./mole. Even the smaller value is sufficiently great that the term in k_a should not influence our kinetics significantly, and it is not observed.

Application of equation 21 gives values of k_4/k_3 varying from 0.8 to 1.6 indicating no significant difference from the behavior of methyl iodide.

Isopropyl Iodide (i-PrI).—Unlike the compounds discussed above, isopropyl iodide exhibits a significant k_a term at the two highest temperatures for degassed exchange in hexachlorobutadiene. The data are consistent with the formula $k_a = 10^{14.1 \pm 3.0}e^{-(39.9 \pm 6.1)/1000RT}$ sec.$^{-1}$. This formula predicts that k_a should not have been detectable at the lowest temperature, and we did not find any evidence for it there.

(17) D. E. Hull, C. H. Schiflett and S. C. Lind, THIS JOURNAL, 58, 535 (1936).

(18) R. H. Schuler, private communication, November 25, 1951.

(19) L. R. Darbee and G. M. Harris, J. Phys. Chem., 61, 111 (1957).

(20) M. B. Neiman, V. B. Miller and Yu. M. Shapovalov, Zhur. fiz. Khim., 30, 492 (1956).

The significance of this term is somewhat ambiguous. Although the observed activation energy for k_a is not inconsistent with the 45 kcal./mole once claimed for the bond dissociation energy of this compound, the currently accepted value of 51 kcal./mole is much too high for such an interpretation. Moreover, Holmes and Maccoll[21] claim that reaction S2 does not take place even at temperatures above 200° and that instead there is a unimolecular dissociation according to the equation

$$i\text{-}C_3H_7I \longrightarrow C_3H_6 + HI \qquad (P1)$$
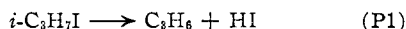
The rate constant for this reaction is given by $k = 10^{14.46} e^{-48.2/1000RT}$ sec.$^{-1}$, but this equation predicts values too small to have been of significance for our system. Holmes and Maccoll postulate the additional reaction

$$i\text{-}C_3H_7\cdot + HI \longrightarrow C_3H_8 + I \qquad (P2)$$
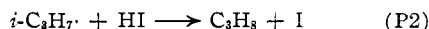
with the isopropyl radicals being generated by reaction S4. This sequence would not lead to exchange even if it did take place.

McMillan and Noyes[22] proposed the reaction

$$i\text{-}C_3H_7I + I \longrightarrow C_3H_6 + HI + I \qquad (P3)$$
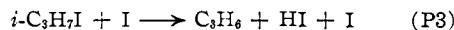
They studied the gas-phase photochemistry of isopropyl iodide and found that propylene was formed in considerable excess over propane. However, neither they nor we were able to detect any hydrogen iodide, and we estimate that reaction P3 is endothermic by almost 30 $_r$ kcal./mole. If this reaction were followed by P2, the net reaction would be decomposition without exchange. Hence our failure to detect HI provides little evidence about its possible presence as an intermediate in reactions not leading to exchange.

Neiman, Miller and Shapovalov[20] claimed that isopropyl iodide exchanged about 80 times as fast as methyl iodide. Our values of k_b for the two compounds are in a somewhat smaller ratio, but we find additional contribution from the k_a term that is missing with methyl iodide. The two studies are not inconsistent.

Application of equation 21 gives values of k_4/k_3 that are all less than 0.7. This ratio is slightly less than that observed with the primary iodides.

Runs with isopropyl iodide in ethylene dichloride were the only ones for which the apparent order with respect to iodine was significantly greater than one half. This is also the system in which one would most expect contribution from a non-radical mechanism such as is observed with t-butyl iodide.[5] Even in this isopropyl iodide system, the radical mechanism seems to be the more important at least in degassed solutions.

sec-Butyl Iodide (sec-BuI).—At the temperatures where direct comparison is possible, values of k_b' are almost identical for isopropyl iodide and sec-butyl iodide.[7] Close similarity would be anticipated, and it is gratifying to find such consistency for two different experimental studies conducted several years apart.

The present work with isopropyl iodide did not find any evidence for the anomalously fast ex-change rates observed with sec-butyl iodide[7] at the lowest iodine concentrations.

Neopentyl Iodide (neo-PeI).—We are not aware of any previous studies of the exchange of neopentyl iodide. Our own kinetics are not entirely satisfactory. The degassed kinetics show pronounced intercepts for the plots of $R_{ex}/[RI]$ against $[I_2]^{1/2}$, and the temperature dependence of these intercepts is best described by $k_a = 10^{6.9} e^{-26,400/RT}$ sec.$^{-1}$. This behavior cannot possibly be consistent with the postulated identification of k_a with k_2.

For all other compounds reported here, R_{ex}-(degassed) $- R_{ex}$(oxygen) was larger at high iodine concentrations as would be expected if the oxygen were inhibiting a reaction promoted by iodine. For neopentyl iodide at the lower two temperatures, this same quantity decreases as the iodine concentration increases. This behavior implies that the oxygen is not being completely effective as an inhibitor.

The temperature dependence of k_b' for the degassed runs is also inconsistent with any reasonable mechanistic interpretation. Therefore the values in Table VII have been put in parentheses.

Although unresolved kinetic factors are obviously affecting the exchange, the rate for neopentyl iodide in hexachlorobutadiene is unequivocally less than would be anticipated from any extrapolation of the rates observed for the other primary iodides. Since any plausible side reactions would tend to increase the rate at which iodine became organically bound, the unsatisfactory kinetics do not vitiate arguments based on the low exchange reactivity of neopentyl iodide.

A few experiments investigated the exchange of neopentyl iodide with iodine in more polar solvents. Measurements in benzonitrile at 159.9° were anomalous, the rate of exchange increasing with time. Except for one inexplicably fast run at low iodine concentration, the initial rates seemed to be more than first order in iodine.

Some runs in nitrobenzene were only slightly more satisfactory. The degassed solutions darkened and become viscous, and the exchange rates decreased with time. At low iodine concentrations, the rate of exchange was the same or a little less than that in degassed hexachlorobutadiene; and at high iodine concentrations, the rate was much greater than in hexachlorobutadiene. Initial exchange rates fitted rather cleanly the kinetic expression

$$R_{ex} = k_n[neo\text{-}PeI][I_2] \qquad (22)$$

Values of k_n were 1.0×10^{-4} liter/mole sec. at 159.9° and 7.2×10^{-4} at 200.8°; these values can be fitted by $k_n = 10^{6.0} e^{-19.7/1000RT}$ liter/mole sec. Nitrobenzene is much more polar than any of the other solvents used in this study, and the exchange apparently involves a non-radical mechanism analogous to that observed for t-butyl iodide under milder conditions.

General Discussion

Evidence on Existence of Direct Substitution Mechanism.—One of the main objectives of this study was to determine whether the exchange

(21) J. L. Holmes and A. Maccoll, *Proc. Chem. Soc.*, 175 (1957).
(22) G. R. McMillan and W. A. Noyes, Jr., THIS JOURNAL, **80**, 2108 (1958).

induced by atomic iodine went entirely through an abstraction mechanism with formation of a free radical (step S4), or whether there was significant contribution from a direct substitution mechanism that presumably involved inversion at a saturated carbon atom (step S3). The following observations bear on this question:

(a) Oxygen reduces the rate of the exchange reaction, but the rate falls to a limit that is significant compared to the degassed rate and that is not affected by further increases in oxygen concentration. This observation is hard to explain if exchange requires formation of a free alkyl radical that can react either with oxygen or iodine molecules. It can be explained easily if some exchange goes by a direct substitution step. It can also be explained if the exchange goes by abstraction to form a free radical, but the free radical can sometimes react with the *same* iodine molecule that was produced in the act of radical formation; this sort of reaction would take place so rapidly that dissolved oxygen could not compete with it to influence the fate of the freshly produced radical.

(b) Herrmann and Noyes[7] found that optically active *sec*-butyl iodide in hexachlorobutadiene solvent was racemized by iodine with a rate constant greater than that for exchange. These observations require either that there is direct substitution with inversion of carbon or that the *sec*-butyl radicals frequently react with the same iodine molecule formed with them.

(c) Ogg and Polanyi[6] studied the racemization of *sec*-butyl iodide in the gas phase. Isotopic iodine was not available for simultaneous exchange studies, and they had heterogeneous complications. However, if they were correct in their interpretation of the processes going on in the system, their data require a direct substitution reaction with inversion of carbon.

(d) Laurence and Stranks[14] find that thermalized iodine atoms recoiling from neutron activation can exchange with gaseous methyl iodide. If they can demonstrate unequivocally that the reaction is homogeneous, these observations would provide irrefutable evidence for a direct substitution reaction without intermediate formation of methyl radicals.

(e) The rate of degassed exchange of methyl iodide at 159.9° increases by a factor of 3.7 when the solvent changes from hexachlorobutadiene to ethylene dichloride, but the exchange in oxygen saturated solutions only increases by a factor of 1.7 for the same change of solvent. According to our interpretation, the degassed exchange can involve both abstraction and direct substitution while the oxygen exchange involves only direct substitution. The abstraction mechanism undoubtedly involves a more polar transition state and should be accelerated more by increasing dielectric constant of the solvent.

(f) Presently accepted values[16] for the C–I bond dissociation energies are in excess of 50 kcal./ mole, while the activation energies we observe are hard to reconcile with iodine atom abstraction unless these dissociation energies are about 45 kcal./mole.

(g) The rate of exchange of primary iodides increases in the sequence methyl < ethyl < *n*-propyl, but neopentyl iodide is much slower again. No studies were made on isobutyl iodide. This sequence is hard to explain if iodine atoms are causing abstraction, but it is what would be anticipated if the atom attacks the back side of the primary carbon as would be the case for direct substitution.

(h) Equation 13 predicts that in degassed runs the k_b term contains contributions from two parallel paths with identical kinetics. If such a situation pertains, the apparent activation energy will be intermediate between the values for the two reactions, and it will increase with temperature. Equation 19 predicts that only one path contributes to the oxygen exchange runs. Although the effects are at a low level of probable significance, it is interesting to note that all degassed studies indicate an activation energy that increases with temperature, while all oxygen studies except with neopentyl iodide fit the Arrhenius equation extremely well.

(i) Effects of structure are much smaller than for bimolecular nucleophilic substitution of similar compounds,[3] but rates of exchange increase in the series methyl < ethyl < isopropyl. Rates of bimolecular nucleophilic substitution decrease in the same series. This sequence is what would be anticipated for an abstraction mechanism; it is not what would be anticipated for direct substitution because the methyl groups in isopropyl iodide would presumably offer some resistance to the direct substitution reaction.

The dilemma can be resolved if structural effects in nucleophilic substitution are primarily concerned with solvation. All nucleophilic substitution reactions take place in polar solvents and involve considerable localized charge. The sequence methyl, ethyl, isopropyl represents a steady increase in the number of insulating methyl groups that hinder the approach of dipolar solvent molecules. If this steric hindrance to solvation is more important than steric hindrance to attack by the entering group, it is possible to explain the existence of one reactivity sequence for nucleophilic substitution and of the reverse sequence for a radical substitution where solvation is unimportant.

(j) The ratio of degassed and oxygen rates is supposed to be a measure of the relative contributions of abstraction and direct substitution mechanisms. The ratio is surprisingly constant for all of the compounds studied, and the small variation is in a direction to indicate that direct substitution is relatively more important with isopropyl iodide than with methyl iodide. We would expect the trend to be in the opposite direction.

Conclusions from this Evidence.—We cannot reach any detailed mechanistic conclusions unambiguously consistent with all of the above observations. The kinetics demonstrate unequivocally that at least most of the exchange goes by a free radical mechanism. Observations a to f certainly make a strong case for a direct substitution mechanism, and we feel that it must be accepted as one of the processes taking place.

Some of the same arguments make it hard to understand how the abstraction mechanism can be important for all compounds at all temperatures. Unless reported carbon–iodine bond dissociation energies are badly in error, some other explanation must be found for the oxygen inhibition. The results could be accommodated by the reversible formation of an IO_2 intermediate that was about half as reactive as a free atom, but a considerable body of evidence at lower temperatures[23] argues against the existence of such an intermediate.

A reasonably satisfactory explanation of all of our observations is possible if carbon–iodine bond dissociation energies are not much more than about 45 kcal./mole instead of the higher values claimed and if the effects of α-methyl replacement on the rate of nucleophilic substitution is primarily a steric inhibition of solvation rather than a steric hindrance for attack on the carbon undergoing the substitution. However, these revisions of current ideas are too drastic to accept without more evidence than we have accumulated here.

Chain Initiating Reactions.—Calculated values of R_1 are based on extrapolations of over a hundred degrees of measurements made at lower temperatures. They serve only to indicate orders of magnitude, but the calculations certainly indicate that chain lengths often are quite short. In fact,

(23) (a) J. Zimmerman and R. M. Noyes, *J. Chem. Phys.*, **18**, 658 (1950); (b) D. J. Sibbett and R. M. Noyes, This Journal, **75**, 763 (1953); (c) F. W. Lampe and R. M. Noyes, *ibid.*, **76**, 2140 (1954).

it is hard to explain some of the oxygen kinetics unless iodine atom production is somewhat faster than our computed values of R_1. If iodine atoms are produced by uncatalyzed dissociation of I_2 molecules, the activation energy must be at least 3 kcal./mole greater than the gas phase bond dissociation energy. Such a difference is quite plausible.

Decomposition Reactions.—The rates of decomposition are too scattered for us to draw any reliable mechanistic conclusions. The irreproducibility of these measurements suggests that trace impurities are at least partly involved in the processes causing iodine production. However, it may be significant that decomposition rates are lower for methyl and neopentyl iodides than for the others. These compounds do not have hydrogens on carbons beta to iodine, and they are the only compounds studied that cannot undergo processes like P1 and P2 mentioned in the discussion of isopropyl iodide.

Mechanisms of Exchange Reactions of t-Butyl Iodide with Elementary Iodine

By John E. Bujake, Jr.,[1] and Richard M. Noyes[2]

Received May 17, 1960

t-Butyl iodide exchanges with elementary iodine near room temperature by two parallel non-radical mechanisms that are not influenced by light. The *bimolecular* mechanism is first order each in t-butyl iodide and in molecular iodine and at 25° is significant only in the solvents chlorobenzene and ethylene dichloride that have dielectric constants greater than 5. The rate depends on dielectric constant more strongly than has been found for other reactions known to form ion pairs, and it is proposed that the exchange involves an ion pair intermediate $C_4H_9^+I_3^-$. The *termolecular* mechanism is first order in t-butyl iodide and second order in molecular iodine and shows a dependence on dielectric constant comparable to that for reactions forming ion pairs. It is proposed that the exchange involves either nucleophilic attack by an iodine molecule on a $C_4H_9I_3$ neutral complex or by an I_3^- component of an ion pair on the $C_4H_9I_2^+$ component. Cooling solutions to Dry Ice temperatures causes complete exchange apparently induced on the surface of iodine precipitated by the cooling. At 25°, the exchange of t-butyl iodide with 0.02 M iodine in hexachlorobutadiene is 7×10^6 times as fast as the exchange of isopropyl iodide under the same conditions as predicted by extrapolation from 130°. This extreme difference in reactivity suggests that for reactions proceeding through ionic or ion-pair intermediates the effects of structure on reactivity will be most pronounced in less polar solvents because in these solvents the separation of charge is promoted less by solvation and more by the nature of the species in which charge separation is occurring.

Introduction

The work described here is part of a systematic study of the exchange of elementary iodine with various alkyl iodides that was undertaken to learn more about the effects of changing structure on the parameters affecting rates of radical reactions. All of the primary and secondary iodides that were studied[3] did indeed appear to exchange by radical

(1) Based in part on the Ph.D. Dissertation of John E. Bujake, Jr. The original dissertation and microfilms thereof are available from the Library of Columbia University.

(2) To whom inquiries should be sent: Department of Chemistry, University of Oregon, Eugene, Oregon.

processes initiated by free iodine atoms. However, t-butyl iodide exchanged much more rapidly than these other iodides. The reaction obviously received negligible contribution from free radical processes and involved a highly polar transition state. It has seemed appropriate to report these observations separately from the others.

Experimental

Materials.—Commercial t-butyl iodide was vacuum distilled. The distilled material remained colorless for several

(3) J. E. Bujake, Jr., M. W. T. Pratt and R. M. Noyes, This Journal, **83**, 1547 (1961).