Measurements and Results

The heat capacity calorimeter and method of operation have been described.[4] Results are reported in defined calories (1 cal. = 4.1840 abs. joules) per deg. mole. All weighings were corrected to vacuum and molecular weights accord with the 1954–55 Report on Atomic Weights.[5] The masses of the compounds used in the measurements were 184.16 g. of sesquioxide, 407.98 g. of red monoxide and 487.04 g. of yellow monoxide.

The measured heat capacity values are listed in Table I. The heat capacity of the yellow monoxide exceeds that of the red by 5.7% at 50°K., decreasing to 2.6% at 100°K. and to zero at 298°K. Using the data of Millar[3] for the dioxide, it is observed that the heat capacity of the sesquioxide is less than the sum for the dioxide and either of the monoxides at temperatures above about 150°K.; at lower temperatures the reverse holds.

Entropies at 298.15°K.—The entropy increments between 51.00 and 298.15°K. were obtained by Simpson-rule integrations of C_p against log T plots. The extrapolated portions of the entropies (0–51.00°K.) were obtained from these empirical combinations of Debye and Einstein functions, which fit the measured heat capacities within the limits indicated:

Pb_2O_3: $D(79.4/T) + 2E(220/T) + 2E(653/T)$ (51–298° K.; 2.0%)
PbO(red): $D(156/T) + E(481/T)$ (51–250°K.; 1.3%)
PbO(yellow): $D(145/T) + E(473/T)$(51–250°K.; 1.0%)

The results of the entropy calculations are in Table II.

TABLE II

ENTROPIES (CAL./DEG. MOLE)

Substance	S^0_{51} (extrap.)	$S^0_{298.51} - S^0_{51}$ (meas.)	$S^0_{298.15}$
Pb_2O_3	6.51	29.80	36.3 ± 0.7
PbO(red)	2.48	13.11	15.6 ± .2
PbO(yellow)	2.78	13.33	16.1 ± .2

The entropy of yellow lead monoxide is 0.5 cal./deg. mole less than the result estimated by Kelley[6] from the data of Nernst and Schwers.[2] According to Table II, the entropy of transformation of red to yellow monoxide is $\Delta S^0_{298.16} = 0.5$. This value may be projected to the equilibrium point (762°K.)[7] by means of the high temperature data listed by Kelley.[8] The result is $\Delta S^0_{762} = 0.2$, corresponding to a heat of transformation of 150 cal./mole. The latter is equivalent to $\Delta H_{298} = 270$ cal./mole, which agrees substantially with the difference in heats of formation (330 cal.) given in NBS Circ. 500.[9]

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(5) E. Wicbers, THIS JOURNAL, **78**, 3235 (1956).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

Mechanisms of Exchange Reactions between Elementary Iodine and Aromatic Iodides

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The thermal exchange of elementary iodine with iodobenzene and with *p*-nitroiodobenzene has been studied in the solvents hexachlorobutadiene-1,3 and nitrobenzene. Two independent processes contribute to the rate. One process is the expected direct radical exchange between an iodine atom and a molecule of aromatic iodide. The rate constants for this process are not significantly affected by change of solvent, but substitution with a *p*-nitro group slows the rate somewhat. This effect of substitution is opposite to the direction usually predicted and observed for radical reactions. The other exchange process is second order in aromatic iodide and is usually *zero* order in iodine. Change of solvent from hexachlorobutadiene to nitrobenzene inhibits this process for iodobenzene but accelerates it for *p*-nitroiodobenzene. When both aromatic iodides are present in a solution, the rate constant for the exchange process involving one molecule of each is greater than the rate constant for either process involving two identical molecules. We propose that this exchange process involves reversible formation of a diphenyliodonium iodide ion pair and rapid exchange of molecular iodine with the iodide portion of it. The proposed mechanism explains some peculiar observations reported previously on the exchange of iodobenzenes with sodium iodide. These aromatic iodides also decompose with formation of molecular iodine. The rates are erratic but seem to follow first-order kinetics when only one aromatic iodide is present. If both iodobenzene and *p*-nitroiodobenzene are present, an additional decomposition is ascribed to rearrangement of the diphenyliodonium iodide ion pair to form iodine and a monosubstituted diphenyl.

Introduction

The results reported in this paper are part of a program of study of the mechanisms of exchange reactions in solution between isotopically labelled elementary iodine and various organic iodine compounds. The primary objective of the studies is to obtain quantitative information about the reactions of iodine atoms in the expectation that this information will be of value in the interpretation of other more complicated reactions involving free radicals. However, the present investigation and some others have demonstrated the existence of unexpected non-radical reactions taking place in certain systems.

Experimental

Materials.—Iodobenzene was prepared by the diazotization of freshly distilled aniline.[2] The resulting product was washed with hydrochloric acid and sodium carbonate

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(1) The data on which this paper is based are contained in the Ph.D. Dissertation of Samuel Levine. The original dissertation and microfilms thereof are available from the Library of Columbia University.

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(2) "Organic Syntheses," Vol. II, edited by A. H. Blatt, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 351.

solutions, dried over calcium chloride, and distilled at 63° and 8 mm. The final product was stored in the dark under refrigeration.

Commercial *p*-nitroiodobenzene was dissolved in acetone and reprecipitated with water and then was recrystallized twice from ethanol. The final product melted at 171–172° (corrected).

The solvent for most of the kinetic experiments was hexachlorobutadiene-1,3 obtained from the Hooker Electrochemical Company. The material was redistilled under reduced pressure, and the middle fraction was used for the experiments. Blank runs indicated that under the conditions for the kinetic studies no more than 3% of iodine present reacted irreversibly with the solvent.

Some additional experiments were conducted in commercial C.P. nitrobenzene. Both distilled and untreated samples of this material darkened when heated with iodine, and as much as 14% of the initial iodine sometimes was consumed during prolonged heating at the highest temperature.

Reagent grade resublimed iodine was used without further treatment. Stock solutions were activated by shaking with aqueous solutions of iodine-131 obtained on allocation from the United States Atomic Energy Commission. These solutions were dried with magnesium sulfate and filtered through fritted glass before they were used for the exchange experiments.

Procedure.—Solutions of labelled iodine and of inactive aromatic iodide were pipetted into ampules to be used for the runs. Since *p*-nitroiodobenzene was only soluble to about 0.03 *M* in hexachlorobutadiene at room temperature, the more concentrated solutions were prepared and pipetted at 108°, but the concentrations reported are those that would have prevailed at room temperature if the thermal expansion of the solution were the same as that of solvent.

The mixed solutions were degassed by repeated freezing and pumping at Dry Ice temperature, and the ampules were sealed off. They were then heated in an insulated thermostat containing fused alkali nitrates. The temperatures for the experiments ranged from 167 to 210° and were checked to 0.1° with a thermometer calibrated by the National Bureau of Standards.

At the end of a run, each ampule was rapidly cooled and opened. The contents were diluted with chloroform if necessary to prevent *p*-nitroiodobenzene from precipitating, and the iodine in an aliquot portion of solution was reduced with aqueous sulfite. The layers containing organic and inorganic iodide were separated and counted with a thin-walled Geiger counter, empirical counting corrections being applied for the different solvents. Another aliquot portion of the solution was used for spectrophotometric measurement of the concentration of elementary iodine present at the end of the run.

The separation procedure did not induce significant exchange. In order to test the validity of the assumption that iodine became organically bound as the result of an exchange reaction, the organic layer from a run with iodobenzene was fractionated with additional iodobenzene as carrier. All but a few per cent. of the radioactivity distilled with the iodobenzene.

Treatment of Data.—The numerical treatment of the data was complicated because the exchange reaction was accompanied by a decomposition of the organic iodide with the production of additional elementary iodine. This change in concentrations of the iodine containing species was sometimes sufficient to vitiate the conventional procedure for calculating the rate of an exchange reaction from the isotopic distribution at two known times. Luehr, Challenger and Masters[3] have discussed the general problem posed by exchange reactions involving species whose concentrations are changing with time. However, their equations are not generally integrable for situations like the present in which exchange involves two parallel paths exhibiting different kinetics. We therefore have developed the following procedure, which provides a satisfactory approximation for almost all cases encountered in this study:

a = initial concn. of molecular iodine, mole/l.
b = initial concn. of organic iodide, MI, mole/l.
c = concn. of iodine (calcd. as I_2) that becomes organically bound by reaction with solvent. As indicated above, c is never more than $0.03a$, and most of this reaction with solvent takes place almost immediately. We may therefore assume that the isotopic distribution in this material is very nearly the same as in the original iodine. Corrections involving this term are usually without experimental significance
$D = 2\dfrac{d[I_2]}{dt} = -\dfrac{d[MI]}{dt}$ = rate at which MI decomposes with formation of additional iodine

If D is constant during the time of interest, the concentrations of species at time t are

$$[I_2] = a - c + \frac{1}{2}Dt$$

$$[MI] = b - Dt$$

At any time, all radioactive iodine is present as the element, as MI, or as the product of reaction with solvent.

x = fraction of radioactivity present in MI
y = fraction of radioactivity present in I_2
w = fraction of radioactivity tied up by solvent

Of necessity, $x + y + w = 1$. Let

$z = x + w$ = organically bound radioactivity measured experimentally

Finally, let R be the rate of the exchange reaction

$$MI + I_2^* \longrightarrow MI^* + II^* \qquad (1)$$

where the asterisks are used to follow changes in chemical bonding of atoms whether or not they are radioactive. The object of the measurements is to calculate R from measurements of z, provided c is known from separate studies with solvent alone and D is calculated from spectrophotometric measurements on the same solution. During a specific run, z will tend to increase because of exchange (reaction 1) but will also be decreased by the decomposition of MI that has already exchanged. The differential equation describing this situation is

$$\frac{dz}{dt} = R\left[\frac{1 - z}{2a - 2c + Dt} - \frac{z - w}{b - Dt}\right] - \frac{D(z - w)}{b - Dt} \qquad (2)$$

If it is assumed that R and D are independent of time, the solution of equation 2 is

$$R = D\,\frac{\log\left[1 - \dfrac{(2a + b - 2c)(z - w)}{(b - Dt)(1 - w)}\right]}{\log\dfrac{1 - Dt/b}{1 + Dt/(2a - 2c)}} \qquad (3)$$

As D approaches zero, a series expansion of this equation approaches the conventional expression for exchange in a system that is stable chemically. The derivation assumes that R and D do not change enough to affect the mathematical solution even though the concentrations of the reactants are chahging. Since MI is almost always present in excess over I_2, the decomposition reaction causes a much greater percentage change in the concentration of elementary iodine than of the organic iodide. As is shown below, the rates of both the exchange and decomposition reactions depend rather little on iodine concentration, and the approximations involved in equation 3 introduce much less error than the scatter of individual runs.

The experiments in nitrobenzene could not be treated in the same way because the darkening of the solvent prevented spectrophotometric determination of the extent of decomposition. The rates of exchange in these solutions were calculated with conventional equations neglecting decomposition effects.

Results

Exchange of Iodobenzene.—The exchange experiments with iodobenzene in hexachlorobutadiene could be described very satisfactorily by the expression

$$R = k_r[C_6H_5I][I_2]^{1/2} + k_p[C_6H_5I]^2 \qquad (4)$$

where C_6H_5I denotes iodobenzene, and where the subscripts r and p stand for radical and polar, respectively. Throughout most of the range of concentrations employed, the polar term contributed

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[3] C. P. Luehr, G. E. Challenger and B. J. Masters, THIS JOURNAL, **78**, 1314 (1956).

the greater portion of the observed exchange. At each temperature, the rate constants were evaluated by unweighted least squares from a plot of $R/[C_6H_5I]^2$ against $[I_2]^{1/2}/[C_6H_5I]$. The runs at each set of concentrations are summarized in Table I, and the rates calculated from the rate constants are compared with those observed.

TABLE I

EXCHANGE AND DECOMPOSITION OF IODOBENZENE IN HEXACHLOROBUTADIENE

$10^3[I_2]$, mole/l.	$10^3[C_6H_5I]$, mole/l.	10^9R, mole/l. sec. Obsd.	10^9R, mole/l. sec. Calcd.	10^9D, mole/l. sec. Obsd.	10^9D, mole/l. sec. Calcd.
		167.2°			
8.25	224	36.1	35.6	4.83	5.20
11.16	149	17.8	17.9	4.22	3.46
8.18	112	10.3	10.5	5.00	2.60
4.65	112	9.22	9.71	3.17	2.60
1.278	112	9.50	8.51	0.88	2.60
0.655	112	7.44	8.13	.91	2.60
0.327	112	7.61	7.86	.76	2.60
8.36	56	3.47	3.50	1.83	1.30
4.42	56	3.08	3.03	1.56	1.30
0.673	56	2.42	2.29	0.46	1.30
8.72	28	1.31	1.32	1.57	0.65
0.976	28	0.78	0.74	0.72	.65
.652	28	.66	.67	.59	.65
.644	14	.17	.23	.09	.32
		177.0°			
1.125	224	86.1	73.2	..	..
0.748	224	77.2	71.8	..	..
8.43	112	25.0	26.6	13.9	6.47
4.22	112	24.2	23.6	5.22	6.47
2.12	112	27.8	21.5	5.14	6.47
0.63	112	19.7	19.2	..	..
4.20	56	9.78	7.71	3.81	3.24
2.16	56	6.36	6.69	2.78	3.24
1.16	56	5.53	6.00	0.67	3.24
		191.0°			
8.55	280	327	310	24.3	54.0
51.5	222	297	280	78.3	42.8
51.6	109	110	98.6	14.3	21.0
10.28	111.5	78.6	66.0	14.9	21.5
0.900	112	40.3	47.6	21.2	21.6
10.71	53.9	22.3	22.4	14.8	10.4
0.890	55.1	10.9	13.5	21.6	10.6
10.76	20.5	6.22	6.36	4.50	3.96
1.76	22.1	3.33	3.74	1.67	4.26
0.92	11.0	1.17	1.17	0.86	2.12
		210.6°			
51.92	218	2834	2062	204	368
9.01	221	1190	1765	278	373
51.64	107	475	641	133	181
9.74	108	1163	489	149	183
0.846	111.6	833	427	103	189
0.828	55.7	528	115	162	94.1
52.32	38.0	163	147	63.1	64.2
9.52	40.7	52.2	100	56.4	68.8
3.27	8.7	9.17	8.86	19.9	14.7
1.50	9.7	5.78	7.36	17.3	16.4

In nitrobenzene, iodobenzene exchanged much more slowly than it did in hexachlorobutadiene, and the kinetics corresponded to the first of the two terms of equation 4. Rate constants were fitted to equation 4 by plots of $R/[C_6H_5I][I_2]^{1/2}$ against $[C_6H_5I]/[I_2]^{1/2}$, and observed and calculated rates are compared in Table II. Values of k_r were identical within the probable errors with the values at the same temperatures in hexachlorobutadiene. At one temperature k_p in nitrobenzene was about 5% of the value in hexachlorobutadiene, and at the other temperature the least squares analysis actually indicated a small but not significant negative value for k_p. The effect of changing solvent is obviously the almost complete suppression of the mechanism that makes the dominant contribution in hexachlorobutadiene.

TABLE II

EXCHANGE OF IODOBENZENE IN NITROBENZENE

$10^3[I_2]$, mole/l.	$10^3[C_6H_5I]$, mole/l.	10^9R, mole/l. sec. Obsd.	10^9R, mole/l. sec. Calcd.
		167.2°	
7.44	224	8.28	6.88
0.744	224	2.67	3.06
7.44	112	4.11	3.12
0.744	112	1.56	1.21
7.44	56	1.18	1.48
0.744	56	0.428	0.520
0.744	28	0.161	0.241
		191.0°	
7.44	224	47.5	48.5
50	112	59.4	63.2
7.44	112	23.2	24.3
0.744	112	8.20	7.63
50	56	35.3	31.6
7.44	56	13.1	12.2
0.744	56	3.47	3.84
0.744	28	1.85	1.97

Exchange of *p*-Nitroiodobenzene.—The exchange of *p*-nitroiodobenzene in hexachlorobutadiene was considerably slower than the exchange of iodobenzene under the same conditions. The dominant contribution was made by the term $k_r[PI][I_2]^{1/2}$ where PI is *p*-nitroiodobenzene. Values of k_r at any temperature were somewhat less than those for iodobenzene, but the difference was never as much as a factor of two. The exchange not accounted for by the radical mechanism was second order in PI but also depended on the iodine concentration unlike the observations with iodobenzene. The exchange rates could be fitted with almost equal precision by assuming that the additional term was $k[PI]^2[I_2]$ or $k[PI]^2[I_2]^{1/2}$. Although the data hardly justified a description in terms of three parameters, it was felt for theoretical reasons that the best description should be $k[PI]^2[I_2]/(1 + k'\cdot[I_2])$, and this form frequently gave a markedly better fit than any other that was tried. The final equation that was adopted was

$$R = k_r[PI][I_2]^{1/2} + \frac{k_p[PI]^2}{1 + k_x/[I_2]} \qquad (5)$$

The value of k_r was calculated from the intercept of a plot of $R/[PI][I_2]^{1/2}$ against [PI], and the values of k_p and k_x were obtained by assuming this value of k_r and working only with the data at high concentrations of PI. The fit of calculated and observed rates is illustrated in Table III.

TABLE III

EXCHANGE AND DECOMPOSITION OF *p*-NITROIODOBENZENE IN HEXACHLOROBUTADIENE

$10^3[I_2]$, mole/l.	10^3[PI], mole/l.	10^9R, mole/l. sec. Obsd.	Calcd.	10^9D, mole/l. sec. Obsd.	Calcd.
		167.2°			
8.40	200.0	8.39	9.23	11.8	5.38
3.3	197.4	6.83	5.97	1.37	5.31
1.06	199.3	1.02	3.09	3.90	5.36
8.31	106.6	3.81	3.53	3.16	2.87
1.173	106.5	1.20	1.29	4.16	2.86
2.40	46.9	0.564	0.639	0.478	1.26
0.883	47.0	.339	.369	1.16	1.26
2.44	24.1	.246	.288	0.736	0.648
0.846	24.4	.201	.166	0.342	0.656
		177.0°			
7.84	210	14.7	22.9	11.7	22.5
7.78	112	8.70	8.80	3.86	12.0
1.82	99	4.50	4.23	23.9	10.6
7.62	52.4	3.14	3.10	11.6	5.61
2.41	47.1	1.62	1.68	15.7	5.04
1.094	24.4	0.386	0.503	0.557	2.61
2.11	24.4	.494	.690	.283	2.61
4.19	24.3	.722	.943	.203	2.60
0.862	24.3	.372	.443	.861	2.60
		191.0°			
20.5	199.4	163	147	18.4	29.5
8.45	199.2	91.1	83.2	54.4	29.5
1.78	238.2	37.2	35.8	...	...
48.5	106.6	80.0	84.9	...	...
8.38	100.3	26.9	29.0	25.0	14.8
2.91	103.2	14.3	15.2	33.1	15.3
1.2	105.1	8.95	8.80	...	...
50.8	46.0	27.3	26.5	4.06	6.81
21.2	45.8	15.0	17.0	4.67	6.78
10.29	46.6	13.6	11.6	3.19	6.90
7.79	46.9	8.89	9.91	4.75	6.94
2.59	46.7	5.03	5.17	7.36	6.91
1.12	46.6	3.42	3.19	7.95	6.90
2.37	24.3	2.13	2.33	2.25	3.60
0.90	24.2	1.28	1.37	3.19	3.58
0.918	9.75	0.54	0.53	0.71	1.44
2.89	9.10	1.34	0.90	7.58	1.35
		210.6°			
48.2	250.7	1022	1038	50.0	197
48.96	232.3	1048	921	170	182
22.51	237.5	782	762	360	186
8.62	218.5	409	458	242	172
48.7	175.8	605	594	66.9	138
48.5	159.7	472	508	23.6	125
49.06	112.3	261	307	9.00	88.2
9.09	106.6	171	149	47.2	83.7
21.70	95.9	178	183	88.3	75.3
10.47	91.24	324	126	85.8	71.6
8.71	45.2	44.2	43.5	54.2	35.5
2.82	45.8	35.0	24.5	16.7	36.0
9.18	21.6	17.7	17.9	24.1	17.0
3.59	21.5	9.42	11.04	16.5	16.9
1.81	24.4	5.44	8.85	18.3	19.2
8.70	7.47	5.67	5.33	16.1	5.86
3.53	6.92	2.70	3.12	9.83	5.43
1.56	8.30	2.23	2.49	9.50	6.52

In nitrobenzene, the exchange of *p*-nitroiodobenzene was much faster than it was in hexachlorobutadiene, and it was also much faster than the exchange of iodobenzene in nitrobenzene. The rates could be fitted very well to equation 4. Although the term in k_r made almost negligible contributions to the exchange rates at the lower temperature, the value of k_r at each temperature was clearly in the same range as other values of k_r for different solvents or aromatic iodides. The fit of calculated and observed rates is illustrated in Table IV.

TABLE IV

EXCHANGE OF *p*-NITROIODOBENZENE IN NITROBENZENE

$10^3[I_2]$, mole/l.	10^3[PI], mole/l.	10^9R, mole/l. sec. Obsd.	Calcd.
	167.2°		
7.28	193	126	125
7.44	100	26.4	32.3
0.744	100	38.6	34.0
7.44	50	8.50	7.44
0.744	50	8.39	8.30
0.744	25	1.78	1.98
	191.0°		
7.5	199	358	386
50	100	118	129
7.44	100	110	105
50	50	41.9	41.9
8	50	33.6	30.3

Decomposition Reactions.—The decomposition of the aromatic iodides was followed in hexachlorobutadiene by spectrophotometric measurement of the iodine produced. As has been mentioned, darkening of the solvent prevented this type of measurement in nitrobenzene.

The decomposition rates scattered much more than those for exchange. The reaction seemed to be first order in organic iodide, although sometimes there was a suggestion of an additional second-order contribution. No kinetic dependence on iodine concentration could be made to fit the data at all temperatures. With iodobenzene, the rate was accelerated by iodine at the lowest temperature and the data could be fitted fairly well to the expression $D = k[C_6H_5I] + k'[C_6H_5I][I_2]^{1/2}$, but at the highest temperature the rates were somewhat inhibited by iodine. Data with *p*-nitroiodobenzene showed more scatter and no uniform trend with changing iodine concentration.

The only kinetic expression justified by the data seemed to be

$$D = k_d[\text{MI}] \qquad (6)$$

In Tables I and III, the observed rates are presented along with those calculated from this equation.

Runs with Mixtures.—The exchange experiments indicated that much of the reaction involved a transition state containing two molecules of organic iodide. It seemed instructive to examine the behavior of solutions containing both iodobenzene and *p*-nitroiodobenzene. A few such experiments were run in both solvents, and the total amount of organically bound radioactivity was measured without any attempt to determine the distribution between the two compounds. This mathematical treatment of the data assumes exchangeable

TABLE V

MIXED RUNS IN HEXACHLOROBUTADIENE

$10^3[I_2]$, mole/l.	$10^3[C_6H_5I]$, mole/l.	$10^3[PI]$, mole/l.	10^9R, mole/l. sec.	10^9R_{excess}, mole/l. sec.	10^7k_{me}, l./mole sec.	10^9D, mole/l. sec.	10^9D_{excess}, mole/l. sec.	10^7k_{md}, l./mole sec.
				177.0°				
6.77	37.7	33.4	10.9	4.3	34.2	28.2	22.4	178
6.20	37.7	33.4	15.6	9.2	73.1	19.0	13.2	105
1.73	55.7	51.2	19.7	11.7	41.0	46.7	38.0	133
2.10	55.3	99.4	46.7	35.7	64.9	91.1	77.3	141
				191.0°				
10.04	55	100	172	117	213	307	282	513
11.94	55	49	112	75	278	78.1	60.2	223
51.8	55	103	376	254	448	73.1	47.3	83

iodine to enter both compounds at random, and failure of this assumption would vitiate the rate calculations if iodine were present in excess or if the reaction were to proceed for several half-lives. For our conditions, the true rates would not differ greatly from those calculated even if only one of the organic iodides were exchanging.

The observed rate of exchange was invariably in considerable excess over that calculated from equations 4 and 5 for the separate compounds. If the difference between observed and calculated exchange is called R_{excess}, the rather limited data are not inconsistent with the equation

$$R_{excess} = k_{me}[C_6H_5I][PI] \qquad (7)$$

where the subscript stands for mixed exchange. The results of these experiments are presented in Tables V and VI. Values of k_{me} calculated from individual runs showed standard deviations from the mean as high as 35%. However, R_{excess} was obtained as the difference between observed and calculated exchange rates, and the scatter in k_{me} is about the magnitude to be anticipated if R for the solution of mixed iodides could be measured with about the same percentage precision as could the value for a single organic iodide.

In hexachlorobutadiene, the rate of decomposition was also invariably much more than that calculated from equation 6 for the separate compounds, and the excess was fitted to the equation

$$D_{excess} = k_{md}[C_6H_5I][PI] \qquad (8)$$

where the subscript stands for mixed decomposition. The results are included in Table V. The scatter of the individual values reflects the generally less satisfactory nature of decomposition kinetics compared to those for exchange.

Runs in Air.—All of the data presented in Tables I to VI were obtained with solutions in ampules that had been sealed off under vacuum. A few experiments with either iodobenzene or *p*-nitroiodobenzene in hexachlorobutadiene were run at 210.6° without removing air. The results are presented in Table VII and compared with the rates anticipated for degassed solutions. The data indicate some decrease in the rate of exchange, particularly in the case of iodobenzene, but there is no evidence that the decrease is due to influence on the radical reaction. The decomposition reaction may be slightly accelerated by air, but the effect is not of certain significance. Oxygen does not seem to exert a major influence on the kinetics of these reactions.

Effect of Temperature.—The calculated values for all of the above empirical rate constants are presented in Table VIII. The uncertainty indicated for each rate constant is a probable error based on the precision with which individual runs fitted the assumed kinetics.

TABLE VI

MIXED RUNS IN NITROBENZENE

$10^3[I_2]$, mole/l.	10^3 $[C_6H_5I]$, mole/l.	$10^3[PI]$, mole/l.	10^9R, mole/l. sec.	10^9R_{excess}, mole/l. sec.	10^7k_{me}, l./mole sec.
		167.2°			
7.35	55.2	103.7	57.8	21.5	37.6
7.40	111	50.8	44.4	33.6	59.6
0.735	55.2	98.9	64.7	30.9	56.6
0.740	111	50.3	29.7	20.1	36.0
		191.0°			
5	71	33	58.1	31.6	135
35	34	70	116.9	34.0	143
4.96	34	67	96.4	41.8	184
4.96	71	67	127.8	66.6	140
7.34	224	103.8	666.7	506.2	218
35.2	71	33	86.7	32.5	139
48.6	224	98	717.0	468.6	214
35.2	71	67	204.2	108.3	228
0.496	34	67	97.2	52.3	230
0.496	142	67	276.1	225.3	237

TABLE VII

RUNS IN AIR AT 210.6°

$10^3[I_2]$, mole/l.	$10^3[MI]$, mole/l.	10^9R, mole/l. sec.		10^9D, mole/l. sec.	
		Obsd.	Calcd. for vacuum	Obsd.	Calcd. for vacuum
		Iodobenzene, C_6H_5I			
49.8	222	1170	2120	254	375
21.2	222	610	1910	214	375
21.3	93	538	429	271	157
		p-Nitroiodobenzene, PI			
49.3	93.3	189	237	72.0	73.2
22.0	44.7	51.7	65.1	93.6	35.1
50.7	199.4	650	731	169	157
24.5	197.1	373	576	253	155

The data for each rate constant were fitted to the standard Arrhenius equation

$$k = Ae^{-E/RT} \qquad (9)$$

and values of log A and E were calculated by weighted least squares. The accuracies of these parameters were estimated from the probable errors assigned the individual rate constants. The results of these calculations are presented in the last

TABLE VIII

RATE CONSTANTS AS FUNCTIONS OF TEMPERATURE

Temperature, °C.

Rate constant and units	Aromatic iodide, MI	Solvent	Temperature, °C.				log A	E, kcal./mole
			167.2	177.0	191.0	210.6		
10^7k_r, $l.^{1/2}/mole^{1/2}$ sec.	C_6H_5I	C_4Cl_6	3.30 ± 0.27	9.9 ± 3.7	23.6 ± 1.3	120 ± 60	10.2 ± 0.8	33.7 ± 1.1
	C_6H_5I	$C_6H_5NO_2$	2.9 ± 0.6	.....	25.3 ± 1.2	.....	(11.7 ± 1.9)	(36.7 ± 3.9)
	PI	C_4Cl_6	2.03 ± 0.16	5.0 ± 0.4	17.6 ± 1.6	71 ± 6	10.6 ± 0.5	34.8 ± 1.1
	PI	$C_6H_5NO_2$	−2.9 ± 2.6	.....	17.4 ± 2.4	.....	......	....
10^7k_p, l./mole sec.	C_6H_5I	C_4Cl_6	5.75 ± 0.34	13.1 ± 2.1	31.7 ± 3.2	310 ± 210	8.7 ± 0.9	30.0 ± 1.9
	C_6H_5I	$C_6H_5NO_2$	0.26 ± 0.16	.....	−0.1 ± 0.6	.....	....	....
	PI	C_4Cl_6	2.0 ± 0.5	3.59 ± 0.19	66 ± 7	117 ± 10	(15.5 ± 1.5)	(44.1 ± 3.0)
	PI	$C_6H_5NO_2$	34.8 ± 2.5	.....	90 ± 6	.....	(2.6 ± 0.8)	(16.2 ± 1.7)
10^8k_x, mole/l.	PI	C_4Cl_6	3.6 ± 2.4	1.19 ± 0.37	35 ± 6	6.8 ± 3.8	(4.7 ± 5.9)	(14.6 ± 12.4)
10^8k_d, sec.$^{-1}$	C_6H_5I	C_4Cl_6	2.3 ± 0.4	5.8 ± 1.3	19.3 ± 3.2	169 ± 19	13.2 ± 0.9	42.1 ± 1.9
	PI	C_4Cl_6	2.7 ± 0.4	10.7 ± 2.8	14.8 ± 1.5	78 ± 9	8.4 ± 0.8	32.2 ± 1.7
10^7k_{me}, l./mole sec.	Both	C_4Cl_6	.....	53 ± 6	310 ± 50	.....	(20.2 ± 2.9)	(53.0 ± 6.0)
	Both	$C_6H_5NO_2$	47 ± 4	.....	186 ± 9	.....	(6.3 ± 0.9)	(23.3 ± 1.8)
10^7k_{md}, l./mole sec.	Both	C_4Cl_6	.....	139 ± 10	270 ± 85	.....	(4.8 ± 5.4)	(20.0 ± 11.0)
10^7k_7, l./mole sec.	Both	C_4Cl_6	.....	192 ± 12	580 ± 100	.....	(11.2 ± 2.7)	(32.8 ± 5.6)

two columns of Table VIII. Values in parentheses were calculated from only two temperatures or also involve rate constants that could not all be fitted to equation 9 within twice the estimated probable errors; these values should not be taken as seriously as those not in parentheses.

Discussion

The data lead inescapably to the unexpected conclusion that two parallel processes involving very different mechanisms are contributing to the exchange reaction. One of these processes exhibits conventional kinetics for a radical reaction initiated by iodine atoms; the other process apparently involves two molecules of aromatic iodide in a polar transition state.

The Radical Mechanism.—An encouraging piece of support for the complex kinetic analysis we have employed is the fact that the exchange rates are invariably consistent with the hypothesis that a contributing term is first order in organic iodide and half order in iodine and that at any temperature the numerical value of the indicated rate constant is nearly the same independent of solvent and independent of whether or not the iodobenzene has been substituted with a nitro group. We propose that the mechanism involved in this exchange is

$$I_2^* \rightleftarrows 2I^* \qquad (S1)$$

$$MI + I^* \longrightarrow MI^* + I \qquad (S2)$$

Then if K_1 is the equilibrium constant for reaction (S1)

$$k_r = k_2K_1^{1/2} \qquad (10)$$

The kinetic form would be satisfied equally well by the steps

$$MI + I^* \longrightarrow M + II^* \qquad (S2a)$$

$$M + I_2^* \longrightarrow MI^* + I^* \qquad (S2b)$$

However, two types of argument militate against a mechanism involving free organic radicals. First, the rate of exchange is not significantly affected whether the reaction takes place in an aerated or evacuated solution, and any free phenyl radicals would certainly react with oxygen in competition with step (S2b).

The second argument against steps (S2a) and (S2b) is based on energetics. If this mechanism held, the energy of activation for k_r in kcal./mole would be $17.5 + E_{2a}$ where 17.5 is half the energy of dissociation of molecular iodine and E_{2a} is the activation energy of step (S2a). E_{2a} must be at least as great as the difference between the C–I and I–I dissociation energies. Estimates of the C–I dissociation energy in iodobenzene are 54 kcal./mole and greater than 57 kcal./mole.[4] If the lower value is taken as a minimum, the energy of activation for k_r must be at least 36.5 kcal./mole for iodobenzene. The value of 33.7 kcal./mole reported in Table VIII is less than this by more than twice the estimated probable error. Finally, the values for A in hexachlorobutadiene are $10^{10.25}$ and $10^{10.57}$ l./mole sec., for iodobenzene and for *p*-nitroiodobenzene, respectively. These agree with the value of $10^{10.56}$ for *trans*-diiodoethylene[5] which exchanges by adding an iodine atom to a multiple bond similar to the proposed mechanism for step (S2), and they are less than the value of $10^{12.42}$ for benzyl iodide[6] which exchanges by abstraction of an iodine atom similar to the mechanism for step (S2a). All of these numerical arguments are based on differences that are not many times the estimated errors, but the differences always lie in the direction of support for step (S2) against (S2a).

The detailed mechanism of radical exchange presumably involves atom addition to the ring to form a σ-complex similar to that in other aromatic radical substitution reactions. When hydrogen is the species substituted, it has been claimed that, "All theories have indicated that, for true free-radical attack, provided complicating effects are absent, the nucleus of C_6H_5X is always activated relative to benzene."[7] The same theoretical considerations seem to predict that substitution of iodobenzene would increase the rate of radical exchange with an iodine atom. However, the data in Table VIII invariably agree that for a given set of conditions k_r for *p*-nitroiodobenzene is less than for iodobenzene. The effects are never more than about a factor of two, but they are opposite to the direction

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(4) M. Szwarc, *Chem. Revs.*, **47**, 75 (1950).

(5) R. M. Noyes, R. G. Dickinson and V. Schomaker, THIS JOURNAL, **67**, 1319 (1945).

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

(7) D. R. Augood and G. H. Williams, *Chem. Revs.*, **57**, 123 (1957). The quotation is on p. 183.

anticipated and suggest that more information on the effects of substituents would be of interest.

The Polar Exchange Mechanism.—The polar transition state always involves two molecules of aromatic iodide and shows surprising sensitivity to effects of substitution and changing solvent. Any satisfactory mechanism must be consistent with the following facts.

(a) The rate of polar exchange seems independent of iodine concentration for iodobenzene in hexachlorobutadiene, for *p*-nitroiodobenzene in nitrobenzene, and for the exchange of mixed iodides in both solvents. The exchange of *p*-nitroiodobenzene in hexachlorobutadiene accelerates with increasing iodine concentration.

(b) Going from hexachlorobutadiene to nitrobenzene almost completely suppresses the polar exchange of iodobenzene. The same change of solvent greatly accelerates the polar exchange of *p*-nitroiodobenzene and eliminates the dependence of the rate on iodine concentration.

(c) Iodobenzene exchanges much more rapidly in hexachlorobutadiene than *p*-nitroiodobenzene does. In nitrobenzene, *p*-nitroiodobenzene is far the more reactive.

(d) For a given solvent and temperature, k_{me} for exchange involving one molecule each of iodobenzene and of *p*-nitroiodobenzene is invariably greater than either k_{p} for exchange involving two molecules of the same aromatic iodide.

We believe that all of these observations can be rationalized (after the experimental data are known!) in terms of this proposed mechanism. Steps (S3) to (S6) apply if the two molecules of aromatic iodide are identical (either C_6H_5I or PI), and steps (S7) to (S10) apply if they are different.

$$2MI \longrightarrow M_2I^+I^- \tag{S3}$$

$$M_2I^+I^- + I_2^* \longrightarrow M_2I^+I^{*-} + II^* \tag{S4}$$

$$M_2I^+I^- \longrightarrow 2MI \tag{S5}$$

$$M_2I^+I^- \longrightarrow M_2 + I_2 \tag{S6}$$

$$C_6H_5I + PI \longrightarrow (C_6H_5IP)^+I^- \tag{S7}$$

$$(C_6H_5IP)^+I^- + I_2^* \longrightarrow (C_6H_5IP)^+I^{*-} + II^* \tag{S8}$$

$$(C_6H_5IP)^+I^{*-} \longrightarrow C_6H_5I + PI^* \tag{S9}$$

$$(C_6H_5IP)^+I^- \longrightarrow C_6H_5P + I_2 \tag{S10}$$

In these expressions, asterisks are used to follow iodine atoms through a particular step, and $M_2I^+I^-$ represents a diphenyliodonium iodide ion pair intermediate present in small concentration.[8]

For a solution containing only one type of aromatic iodide, this mechanism predicts that

$$R = k_3[\mathrm{MI}]^2 \frac{k_4[\mathrm{I}_2]}{k_4[\mathrm{I}_2] + k_5 + k_6} \frac{k_5}{k_5 + k_6} \tag{11}$$

This equation has been deliberately written to show three distinct parts. The first part is the rate of formation of $M_2I^+I^-$, the second part is the probability that the ion pair so formed will exchange by reaction (S4) before it is decomposed, and the third part is the probability that the decomposition of the ion pair will go to 2MI rather than to $M_2 + I_2$. The empirical rate constants can be related to the rate constants for the individual steps by

$$k_{\mathrm{p}} = \frac{k_3 k_5}{k_5 + k_6} \tag{12}$$

$$k_{\mathrm{x}} = \frac{k_5 + k_6}{k_4} \tag{13}$$

Step (S6) has been included for the sake of similarity with step (S10). However, there was no certain second-order contribution to the decomposition reaction. Therefore, $k_6 << k_5$, and the expressions reduce to

$$k_{\mathrm{p}} = k_3 \tag{14}$$

$$k_{\mathrm{x}} = k_5/k_4 \tag{15}$$

The rate of polar exchange will be independent of iodine concentration if $k_5 << k_4[\mathrm{I}_2]$, and the concentration range in our experiments was such that we could not have detected a significant iodine effect if k_{x} were much less than about 10^{-4} mole/l. Step (S4) could be very rapid for all species and might even be diffusion controlled, but k_4 could not be greater than about 10^{10} l./mole sec. Hence, the observed kinetics could apply only if k_5 is certainly less than 10^6 sec.$^{-1}$. Beringer and co-workers[9] studied reaction (S5) for the unsubstituted iodide in diphenylformamide solvent at temperatures below 100°. An extrapolation of their data to 210° would give k_5 = 5 sec.$^{-1}$. These authors found that the rate increased as the solvent became less polar, and the rate in hexachlorobutadiene is probably greater than in diphenylformamide; however a solvent effect of less than 10^5 would still be consistent with our data. The same group[10] also found that substitution of a nitro group in one of the benzene rings increased the value of k_5. Their data thus predict that di-*p*-nitrodiphenyliodonium iodide in hexachlorobutadiene would have the largest k_5 of any of the cases studied in this paper, and this is the only case for which we find a significant value of k_{x}. For all other cases, the iodine seems sure to exchange with the ion pair before it decomposes. Therefore, the observations in (a) can be explained.

The effects of changing solvent on rate may be due to influences on either the ground state or the transition state, and we believe that both must be invoked to explain the complex behavior described in (b) and (c). Step (S3) involves displacement of iodide ion by nucleophilic attack of a molecule of MI. The transition state will be strongly dipolar, and because of dielectric effects it will be stabilized in nitrobenzene relative to hexachlorobutadiene. However, if a molecule of iodobenzene can act as a nucleophilic reagent relative to another molecule of iodobenzene, it will be even more nucleophilic relative to nitrobenzene and may tend to complex formation. Apparently, the shift from hexachlorobutadiene to nitrobenzene results in a complexing that reduces the activity of iodobenzene much more than it reduces the activity of the transition state and consequently almost suppresses step (S3). Since *p*-nitroiodobenzene is a poorer nucleophilic reagent than is iodobenzene, its activity will not be reduced so much by specific interaction with nitro-

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[8] Very similar kinetics would be obtained if the mechanism involved ionization and subsequent exchange of I^- with molecular iodine. We find it unpleasant enough to have to postulate discrete ion pairs in a chlorinated hydrocarbon solvent, and we shall avoid consideration of free ions unless the experimental evidence seems inescapable.

[9] F. M. Beringer, E. J. Geering, I. Kuntz and M. Mausner, *J. Phys. Chem.*, **60**, 141 (1956).

[10] F. M. Beringer, A. Brierley, M. Drexler, E. M. Gindler and C. C. Lumpkin, THIS JOURNAL, **75**, 2708 (1953).

benzene. On the other hand, its transition state will still be stabilized by the increasing dielectric constant, and the net effect will be an increase in the rate of step (S3). The balance in solvent effects as drawn in Fig. 1 has been chosen to account quantitatively for the observed effects on the free energy of activation at 167.2°. It would be of interest to learn the activity coefficients of these iodides in these solvents.

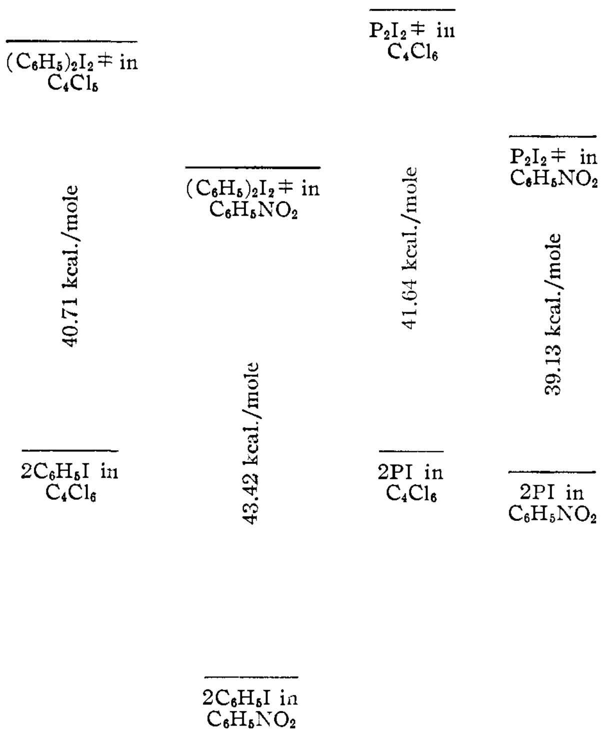

Fig. 1.—Solvent effects on ground and transition states for k_p at 167.2°. Numbers are $\Delta F^{\circ\ddagger}$ in kcal./mole for transition state formulation with standard states in moles/liter. Solvent effects on transition states are identical, while solvent effect on ground state is 10 times as great for C_6H_5I as for PI. To magnify effects, 30 kcal./mole has been omitted from the plotted distances between ground and transition states.

The data with mixed solutions (observations in (d)) provide interesting support for the proposed mechanism. By reasoning analogous to that for the symmetrical case, steps (S7) to (S10) predict that

$$R_{\text{excess}} = k_7[\text{C}_6\text{H}_5\text{I}][\text{PI}]\,\frac{k_8[\text{I}_2]}{k_8[\text{I}_2] + k_9 + k_{10}}\,\frac{k_9}{k_9 + k_{10}} \qquad (16)$$

Since there is no measurable dependence of the rate on iodine concentration, $k_8[\text{I}_2] >> (k_9 + k_{10})$ as discussed above, and

$$k_{\text{me}} = \frac{k_7 k_9}{k_9 + k_{10}} \qquad (17)$$

By similar reasoning

$$k_{\text{md}} = \frac{k_7 k_{10}}{k_9 + k_{10}} \qquad (18)$$

and

$$k_7 = k_{\text{me}} + k_{\text{md}} \qquad (19)$$

If the two aromatic groups entered symmetrically into the transition state for polar exchange, k_7 would presumably be intermediate between the values of k_3 for the substituted and unsubstituted iodides. However, an examination of Table VIII reveals that even k_{me} is invariably larger than either of the values of k_p for the same solvent and temperature, and the difference usually exceeds the factor of two involved when bimolecular rate constants for identical and non-identical molecules are compared. Apparently the presence of one nitro group always facilitates the formation of the intermediate leading to exchange, while at least in hexachlorobutadiene the presence of two nitro groups on different rings decidedly hinders the formation relative to no substitution at all. We believe these observations require that the two benzene rings are not equivalent in the transition state for step (S3).

If the polar exchange mechanism does indeed involve a nucleophilic attack of one molecule of aromatic iodide on another, the unsubstituted iodobenzene should be the nucleophilic reagent in the mixed exchange, and the iodide ion in the ion pair should come from the *p*-nitroiodobenzene and return to it during step (S9). Thus Beringer, *et al.*,[10] found that 3-nitrodiphenyliodonium bromide, $(p\text{-O}_2\text{NC}_6\text{H}_4\text{IC}_6\text{H}_5)^+\text{Br}^-$ decomposed to iodobenzene and *p*-nitrobromobenzene. Also, Juliusburger, Topley and Weiss[11] showed that only the iodide portion of a diphenyliodonium iodide could exchange with iodide ion and hence presumably with the element. Therefore, our mechanism predicts definitely that all of the excess organic radioactivity in mixed exchange should be found in the *p*-nitroiodobenzene. This prediction has not yet been tested experimentally.

Alternative Mechanistic Suggestions.—The experimental observations merely require that two molecules of aromatic iodide react to form a species that is sure to exchange with iodine even though no iodine molecule is present at the time of the reaction. Instead of the proposed ion pair, the product of the reaction might be an iodine atom and a diphenyliodine radical, $\text{M}_2\text{I}\cdot$. The existence of such radicals is suggested by the work of Beringer on the polarography of diphenyliodonium salts.[12] If the exchange does involve such a radical, it must be unreactive with oxygen. Also, the principle of microscopic reversibility requires that the radical be destroyed only by a step that is the reverse of its formation, so it must react only with iodine atoms and not with iodine molecules to regenerate aromatic iodide. Because of these considerations, and because large solvent effects are unusual for radical reactions, we favor the ion pair mechanism discussed above.

Our data do not rule out a diphenyliodonium triiodide intermediate like $\text{M}_2\text{I}^+\text{I}_3^-$, and its formation offers a logical path for the exchange steps (S4) and (S8). However, application of microscopic reversibility to our kinetics requires that decomposition to aromatic iodide involves steps (S5) and (S9) rather than decomposition of a triiodide ion pair like this.

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(11) F. Juliusburger, B. Topley and J. Weiss, *J. Chem. Soc.*, 1295 (1935).

(12) H. E. Bachofner, F. M. Beringer and L. Meites, American Chemical Society meeting in Atlantic City, September, 1956 (Abstracts of Papers, p. 85-O).

Decomposition Mechanisms.—Although the proposed exchange kinetics are rather complex, they provide a satisfactory description of rates that vary by a factor of as much as 500 for the same temperature and solvent. The decomposition rates show smaller ranges but more scatter from the proposed kinetics, and the mechanistic conclusions cannot be discussed with as much confidence. The first-order rate constants we have calculated correspond most logically to a unimolecular non-chain decomposition. The carbon–iodine bond is the most plausible one to break in the initiation of such a reaction, but the apparent activation energies reported in Table VIII are less than the reported bond strengths.[4] The mechanism is obviously complicated either by chain steps or by a parallel reaction having a lower activation energy, and the data do not justify detailed discussion.

The decomposition step (S10) is proposed to form a diphenyl derivative and molecular iodine. The kinetic evidence for this step is based on rather few runs, and it seems important only for an unsymmetrically substituted diphenyliodonium ion. It is easy to imagine a process in which the two carbons attached to the positive iodine form a bond to each other instead, and the formation of such a bond will be easiest if the two carbons have different electron densities. The proposed mechanism suggests that a mixture of *p*-nitroiodobenzene and *p*-methoxyidobenzene should decompose rapidly to produce iodine at these temperatures.

Comparison with Iodide Ion Exchange.—The rate-determining step of the proposed mechanism is the formation of an ion pair containing an iodide ion that can exchange rapidly with the element. Any inorganic iodide should also exchange easily with the same ion pair, and the exchange kinetics should contain a term identical with that for the polar mechanism of exchange with the element. Some apparently anomalous results on the exchange of aromatic iodides with sodium iodide can be rationalized by our mechanism, but solvent effects prevent a quantitative comparison.

Kristjanson and Winkler[13] studied the exchange of iodobenzene and of the three nitroiodobenzenes with sodium iodide in acetonitrile as solvent. The temperature range from 238° to as low as 100° was unusually wide for a kinetic study, and the data did not fit the Arrhenius equation very well. Such a failure suggests but does not prove the existence of parallel paths with different activation energies. Kristjanson and Winkler assumed a bimolecular reaction between organic iodide and iodide ion but noticed that the apparent rate constants increased with $[\mathrm{MI}]/[\mathrm{I}^-]$. If exchange involves a nucleophilic substitution by iodide ion and also exchange with an ion pair formed reversibly as discussed above, one would observe

$$R = k_\alpha[\mathrm{MI}][\mathrm{I}^-] - k_\beta[\mathrm{MI}]^2 \qquad (20)$$

The concentration ranges of Kristjanson and Winkler were not extensive enough to justify a detailed treatment, and the interpretation is clouded by uncertainty about the degree of ionization of sodium iodide. However, the data certainly are not inconsistent with equation 20, and rough values of the rate constants have been calculated. Values of k_β for *p*-nitroiodobenzene in acetonitrile are in the same range as our values of k_p for the same compound in both hexachlorobutadiene and nitrobenzene. The values of k_β for iodobenzene in acetonitrile are less than a per cent. of our values of k_p in hexachlorobutadiene and are less than the limits of error for our zero values of k_p in nitrobenzene. The studies support the postulate of a common mechanism with comparable rate constants contributing to the exchange with sodium iodide in acetonitrile and the exchange with molecular iodine in nitrobenzene.

There is also a cursory study[14] of the exchange between iodobenzene and sodium iodide in *sec*-octyl alcohol at 240°. The rate was independent of sodium iodide concentration. The authors claimed the rate was first order in iodobenzene but apparently never varied the concentration of this species. If the rate is indeed first order in iodobenzene, the rate in *sec*-octyl alcohol is less than a tenth that in acetonitrile; but if the second term of equation 20 is responsible for most of the exchange, the rates in the two solvents are very comparable.

These data also permit a common mechanism that can contribute to exchange with both iodide ions and elementary iodine, but more extensive studies would be necessary to establish it.

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[13] A. M. Kristjanson and C. A. Winkler, *Can. J. Chem.*, **29**, 154 (1951).

[14] S. May, M. Sarraf, A. Vobauré and P. Daudel, *Compt. rend.*, **233**, 744 (1951).