Kinetics of Exchange of Iodine Atoms with Aromatic Iodides

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Abstract: Rates of isotopic exchange with elementary iodine have been measured for α-iodonaphthalene (αIN), β-iodonaphthalene (βIN), iodobenzene (IB), *p*-nitroiodobenzene (PINB), and *p*-iodoanisole (PIA) in the solvents hexachlorobutadiene and nitrobenzene. The kinetic behavior and the absence of inhibition by oxygen indicate that the exchange reactions involve direct substitution by an iodine atom and pass through a transition state or intermediate resembling a σ complex in which two iodines are attached symmetrically to the same carbon. Since changing solvent dielectric constant has little effect on the rate of exchange, the dipole moment of the transition state does not differ much from that of the aromatic iodide. The rates of exchange of these compounds and of the 1,2-diiodoethylenes correlate fairly well with predictions based on localization energy calculations and with the relative rates of other additions of radicals to aromatic systems. Qualitative effects of substituents on the rate of exchange of iodobenzene indicate that iodine atoms behave as electrophilic reagents, but the data do not correlate quantitatively with predictions based on substituent parameters. The rate measurements were complicated by heterogeneous effects associated with the previous history of the glass ampoules. A previous claim that iodobenzene also exchanged by a polar mechanism could not be substantiated, and the exchange by that presumed mechanism was apparently an artifact resulting from cleaning of glassware with chromic acid.

Comparatively little information exists concerning the effects of substituents on the rates of radical substitution reactions in aromatic systems, and the data available do not exhibit consistent patterns. Thus the work of Hey and coworkers[3] indicates that almost all substituents increase the rate at which benzene is arylated by phenyl radicals, while substituent effects observed by Szwarc and coworkers[4,5] indicate that $\cdot CH_3$ radicals behave as nucleophilic species and $\cdot CF_3$ radicals as electrophilic species when attacking benzene derivatives.

Data are easier to interpret when the attacking radical can cause substitution at only one position in the aromatic system. Thus Miller and Walling[6] and Milligan and coworkers[7,8] have studied the photochemical reactions of chlorine atoms with substituted bromobenzenes. Quantitative interpretation is complicated by large changes in optical absorption as reaction proceeds and by disturbing evidence[8] that chlorine and bromine chloride molecules behave differently as chlorinating species.

Iodine atoms are among the least reactive of radicals, and the isotopic substitution of aromatic iodides can be expected to go cleanly without complicating side reactions. Initial studies of iodobenzene exchange by Levine and Noyes[9] detected the expected radical reaction but indicated that a major kinetic component of the exchange was second order in iodobenzene and zero order in iodine. This kinetic contribution was ascribed to reversible formation of a diphenyliodonium iodide intermediate that almost invariably exchanged before it reverted to two iodobenzene molecules.

In the experiments described here, the previous studies have been extended to include exchange reactions of substituted iodobenzenes and of both iodonaphthalenes in two aprotic solvents with widely different dielectric constants. The results provide new information concerning radical substitution reactions in aromatic systems. However, the present studies have failed to confirm the substitution mechanism ascribed by Levine and Noyes[9] to a diphenyliodonium iodide intermediate; apparently this kinetic contribution was an artifact associated with the method of cleaning the glass ampoules.

Experimental Section

Reactants. Commercial iodobenzene (IB) was purified by two vacuum distillations at the pressure of a water aspirator. *Anal.* Calcd for C_6H_5I: C, 35.34; H, 2.44; I, 62.22. Found: C, 35.19; H, 2.57; I, 62.04.

Commercial *p*-iodonitrobenzene (PINB) was dissolved in acetone, reprecipitated by adding water, dried in a desiccator, and then crystallized twice from 95% ethanol. *Anal.* Calcd for $C_6H_4INO_2$: C, 29.05; H, 1.71; N, 5.68; I, 50.78. Found: C, 28.96; H, 1.61; N, 5.62; I, 50.97.

Commercial *p*-iodoanisole (PIA) was crystallized from 66.5% aqueous ethanol and dried in a desiccator. The purified material melted at 50.0–50.1°. *Anal.* Calcd for C_7H_7IO: C, 35.93; H, 3.02; I, 54.24. Found: C, 35.69; H, 2.86; I, 54.38.

Commercial α-iodonaphthalene (αIN) was fractionally distilled twice at 1.0–1.7 mm with a spinning-band column. The purified material retained a slight yellow color; it was not submitted for analysis.

Commercial β-iodonaphthalene (βIN) could be recrystallized by cooling from aqueous methanol or ethanol. As the saturated solution was cooled, crystals seemed to undergo a transition from flakes to amorphous form at 38°. The amorphous material turned brown during drying in the presence of light and air, but the browning could be prevented by slow drying in a covered cabinet or under nitrogen. The compound was also synthesized by diazotization of β-naphthylamine and addition to aqueous potassium iodide. Two different procedures[10,11] were tried. Comparative experiments indicated that the purified commercial material and the products of

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(1) Based on the Ph.D. Dissertation of M. Nakashima, June 1967.

(2) Based on the Ph.D. Dissertation of C. Y. Mok, June 1968.

(3) Reviewed by G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, Oxford, England, 1960.

(4) A. Rembaum and M. Szwarc, *J. Chem. Soc.*, 1127 (1957).

(5) A. P. Stefani and M. Szwarc, *J. Am. Chem. Soc.*, **84**, 2799 (1962).

(6) B. Miller and C. Walling, *ibid.*, **79**, 4187 (1957).

(7) B. Milligan, R. L. Bradow, J. E. Rose, H. E. Hubbert, and A. Roe, *ibid.*, **84**, 158 (1962).

(8) J. T. Echols, V. T.-C. Chuang, C. S. Parrish, and B. Milligan, *ibid.*, **89**, 4081 (1967).

(9) S. Levine and R. M. Noyes, *ibid.*, **80**, 2401 (1958).

(10) Procedure of H. H. Hodgson and J. Walker, *J. Chem. Soc.*, 1620 (1933), as modified by E. Berliner, M. J. Quinn, and P. J. Edgerton, *J. Am. Chem. Soc.*, **72**, 5305 (1950).

(11) A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 432.

the two syntheses all exchanged at rates that differed by no more than a very few per cent.

Commercial resublimed iodine was used either without purification or with a brief resublimation before use. The iodine-131 was obtained as carrier-free aqueous iodide solution from the Oak Ridge National Laboratory.

Solvents. Commercial hexachlorobutadiene-1,3 (HCBD) was fractionally distilled at 94° (14 mm). It contained a vile-smelling and more volatile impurity that could be collected as white crystals at the head of a reflux column and then discarded before the distillation itself was started. Gas chromatography indicated that the solvent obtained from the final distillation contained less than 1% of this impurity. When solutions of radioactive iodine were subjected to the same conditions as an exchange experiment, approximately 1% of the radioactivity could not be extracted; the solvent evidently contained about 10^{-5} mole/l. of impurity capable of binding iodine. Even though very little iodine became organically bound, some dilute solutions of iodine turned yellow when heated in this solvent. The effect was less pronounced if the solution had been degassed before heating. The color change was apparently due to ICl formation, and shaking the solution with aqueous potassium iodide regenerated iodine color between one and two times as intense as that present originally. Apparently 1 mole of I_2 could form 2 moles of ICl, each of which could regenerate I_2 by reaction with iodide ion. The effect was less important at the higher iodine concentrations used in most exchange runs, but formation of small amounts of ICl during those runs cannot be exluded.

Nitrobenzene (NB) was steam distilled in the presence of dilute sulfuric acid, washed with sodium carbonate solution, dried, and distilled under reduced pressure. It was stored in the dark over anhydrous magnesium sulfate and filtered through a fritted glass funnel before use. No impurities could be detected by gas chromatography, and tests by both radioactivity and spectrophotometry indicated that no more than 2×10^{-5} mole/l. of iodine reacted with the solvent during heating.

Procedure. The solution for a run was prepared from stock solutions containing known concentrations of organic iodide[12] and ordinary or radioactive iodine. The latter solution had been prepared by shaking the aqueous radioactive stock solution with a solution of iodine in the desired solvent and then separating the phases[13] and drying the organic solution with magnesium sulfate.

Several 10-ml ampoules containing reactant solutions were attached to a vacuum line through a common manifold, partially evacuated, chilled to Dry Ice temperature, and evacuated to below 10 μ pressure. A cycle of thawing, freezing, and reevacuating to about 1μ was repeated four or five times, and the ampoule was sealed while the contents were frozen. The ampoule was then wrapped with aluminum foil to exclude light and heated in an oil thermostat for a known period. For the shorter runs, empirical corrections were applied to account for reduced reaction during the time the ampoule was coming to the final temperature.

At the end of the heating, the ampoule was chilled and opened, and the concentration of iodine was determined spectrophotometrically on an aliquot portion. Another aliquot was diluted, and the total concentration of radioactivity was determined with a liquid-jacketed Geiger counter. A third aliquot was shaken with aqueous bisulfite solution to remove iodine, and the remaining solution of organic iodide was then washed and diluted and its radioactivity measured.

Treatment of Data. The calculation of exchange rates was somewhat more complicated than for the more common situation of no net chemical change in the system. A barely significant correction was applied for iodine reaction with solvent in the absence of aryl iodide. More serious was the decomposition of the aryl iodide with formation of increasing iodine concentration as a run proceeded. Because the aryl iodide was always present in considerable excess, the fractional change in iodine concentration was always much greater than that of aryl iodide.

Let $[I_2]_0$ and $[ArI]_0$ be the initial concentrations of iodine and aryl iodide, respectively, for a run lasting a time t. The quantities determined experimentally are: f, fraction of radioactivity organically bound at time t; f_s, fraction of radioactivity bound by solvent in the absence of aryl iodide; $\Delta[I_2] = -{}^1/_2\Delta[ArI]$, change in iodine concentration as determined spectrophotometrically.

Calculation of exchange rate from these data employed different levels of approximation depending upon the extent of decomposition. Let mean concentrations during a run be defined by

$$[I_2]_m = [I_2]_0 + {}^1/_2\Delta[I_2] \qquad (1)$$

$$[ArI]_m = [ArI]_0 - \Delta[I_2] \qquad (2)$$

and let the fraction exchange, F, be defined by

$$F = \frac{(f - f_s)(2[I_2]_0 + [ArI]_0)}{(1 - f_s)[ArI]_m} \qquad (3)$$

Then the rate of exchange, v_{ex}, can be approximated by

$$v_{ex} = -\frac{2[I_2]_m[ArI]_m}{(2[I_2]_0 + [ArI]_0)t}\ln(1 - F) \qquad (4)$$

For most runs in nitrobenzene solvent, f_s was negligible and decomposition affected iodine concentration so little that good linear plots of log $(1 - F)$ against time were obtained. For such runs, eq 4 is a satisfactory approximation to well within the limits of error.

For runs in hexachlorobutadiene, decomposition sometimes increased the concentration of iodine by a significant fraction. As will be shown in the Results section, the data could be fitted well by

$$v_{ex} = k_{ex}[ArI][I_2]^{1/2} \qquad (5)$$

Therefore, plots of $[I_2]_m{}^{1/2}\log(1 - F)$ against time should give better linearity than the conventional plots of log $(1 - F)$ suggested by eq 4. Such plots were indeed more linear and were satisfactory for evaluating rate constants for exchange of the iodonaphthalenes.

For the iodobenzenes in hexachlorobutadiene, a still more rigorous treatment was developed based on the method of Luehr, Challenger, and Masters.[14] Let the rate of decomposition, v_d, be given by

$$v_d = -d[ArI]/dt = 2d[I_2]/dt \qquad (6)$$

$$\Delta[I_2] = \frac{1}{2}\int_0^t v_d dt$$

Also let F_B be defined by substituting $[ArI]_0 - 2\Delta[I_2]$ for $[ArI]_m$ in eq 3. Then eq 4 can be replaced by the exact expression

$$\ln(1 - F_B) = -\int_0^t \frac{(2[I_2]_0 + [ArI]_0)v_{ex}\,dt}{2([I_2]_0 + \Delta[I_2])([ArI]_0 - 2\Delta[I_2])} \qquad (7)$$

in which $\Delta[I_2]$ and v_{ex} are functions of time. The decompositon data for a large number of runs could be fitted best by assuming that v_d was proportional to $[ArI]^{3/4}$. When data from a specific ampoule were substituted into eq 7 to calculate k_{ex}, values differed by no more than 0.2% whether v_d was assumed to be proportional to [ArI] or to $[ArI]^{1/2}$. Although eq 7 could not be solved in closed form for v_d proportional to $[ArI]^{3/4}$, the assumption of first-order behavior is clearly satisfactory for calculating k_{ex} in this way.

Tests for Validity of Method. Several tests were conducted to determine that the nonextractable radioactive iodine was indeed incorporated in the same organic iodide that was present initially. Carrier materials boiling near to but both lower and higher than α-iodonaphthalene were added to solutions in both solvents that had been subjected to exchange and removal of iodine by the usual procedure. The resulting mixtures were fractionally distilled, and the radioactivity concentrated appropriately in the expected fractions. Samples of purified β-iodonaphthalene were recovered by crystallization from exchanged solutions in both solvents, and the specific activities of the recovered materials were within 5% in one case and within 2% in the other of the values to be expected if all

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[12] *p*-Nitroiodobenzene is so little soluble in hexachlorobutadiene at room temperature that the material for each ampoule had to be weighed separately. Runs with some of the more concentrated solutions of the iodonaphthalenes were prepared in the same way. The contents of such ampoules were homogeneous at the reaction temperature.

[13] For studies with substituted iodobenzenes in nitrobenzene, the consistency of the results was improved if the solution of radioactive iodine was washed with 0.04 *N* aqueous sulfuric acid before it was dried. This treatment apparently eliminated effects due to residual iodide ion.

[14] C. P. Luehr, G. E. Challenger, and B. J. Masters, *J. Am. Chem. Soc.*, **78**, 1314 (1956).

Table I. Rate Constants for Exchange of Aromatic Iodides with Iodine

Compound	Solvent	Temp, °C	No. of ampoules	Ranges		10^6k_{ex}, (l./mole)$^{1/2}$ sec^{-1}
				10^3[ArI], moles/l.	10^3[I_2], moles/l.	
αIN	HCBD	143.9	15	9.6–279	1.0–50	4.01 ± 0.24
		165.7	31	3.7–219	0.6–103	25.4 ± 1.4
		177.9	15	9.1–249	1.0–13	66.1 ± 4.8
	NB	148.8	15	9.4–272	0.9–47	6.69 ± 0.7
		165.7	11	3.7–219	3.2–103	26.7 ± 1.2
		183.9	15	9.2–267	0.9–46	100.6 ± 4.9
βIN	HCBD	165.7	8	26.0–200	7.6–37	3.45 ± 0.17
		177.9	6	23.2–99	2.2–10	9.16 ± 0.32
		192.6	9	42.1–226	1.0–3.4	28.6 ± 2.2
	NB	165.7	9	11.0–204	3.2–96	5.1 ± 1.0
		177.9	18	9.9–200	1.3–16	14.3 ± 2.5
IB	HCBD	160.0	14	56–294	6.9–23	0.123 ± 0.004
		176.3	63	51–295	5.6–28	0.740 ± 0.008
		191.0	15	54–217	5.3–32	2.16 ± 0.06
	NB	147.3	15	55–304	4.5–25	0.119 ± 0.010
		160.0	18	62–294	4.1–22	0.462 ± 0.036
		176.3	18	64–319	3.8–22	1.04 ± 0.01
PIA	HCBD	147.2	10	73–148	4.8–10	0.431 ± 0.007
		160.0	14	89–177	2.1–11	1.51 ± 0.03
		170.0	15	48–208	4.4–11	3.32 ± 0.06
		180.9	13	46–96	5.3–13	7.44 ± 0.11
	NB	160.0	32	38–304	3.9–29	3.27 ± 0.32
PINB	HCBD	160.0	14	40–204	4.1–22	0.0905 ± 0.0014
	NB	160.0	13	27–217	3.7–26	0.422 ± 0.038

organically bound iodine were present as the starting iodide. A known amount of *p*-iodoanisole was added to a nitrobenzene solution used for exchange of this material, and a sample was recovered from the mixture and purified by crystallization; the specific activity was within 1% of that calculated if the nonextractable radioactivity were all present as *p*-iodoanisole. These results strongly indicate that a true isotopic exchange was being studied in these systems.

Effects of Modified Procedures. When air or pure oxygen was present, formation of ICl was increased in hexachlorobutadiene solvent, and decomposition rates increased some in both solvents; however, exchange rates in these runs agreed within experimental error with rates in degassed solutions.

Some exchange was induced by freezing solutions of *p*-iodoanisole and iodine in hexachlorobutadiene. For studies of this system, solutions of the reactants were degassed in separate ampoules such that the contents could be mixed after they had been sealed off from the vacuum line. No freezing-induced exchange was observed for any of the other systems.

If the organic iodide were undergoing hydrolysis during extraction with aqueous sulfite, it was assumed that the effect would be most pronounced for *p*-nitroiodobenzene in nitrobenzene. A solution from such an exchange was separated into aliquots that were given single and double sulfite extractions, respectively. The radioactivities in the two aliquots agreed within 0.3%.

Surface Effects. Somewhat to our surprise, the factor most seriously affecting the reliability of the results appeared to be heterogeneous acceleration associated with certain methods for cleaning the glass ampoules. Such catalysis has not been suggested by studies of any other class of organic iodides.

Levine and Noyes[9] cleaned ampoules with a conventional chromic–sulfuric acid mixture, rinsed them thoroughly with water, and dried them by heating and evacuation. Although it was realized that acidic chromate species were strongly adsorbed on the glass and removed with difficulty, it was not thought they would be of significance for reaction in a solvent of low dielectric constant like hexachlorobutadiene. Studies with these chromic acid cleaned ampoules indicated[9] that a major component of the exchange was second order in iodobenzene and zero order in iodine.

The ampoules for the present work were initially cleaned by soaking in approximately 1% aqueous solution of Alconox,[15] rinsing thoroughly, and drying by heating and evacuation. In the course of the experiments, an attempt to reproduce the iodobenzene data of Levine and Noyes[9] led to a rate barely a quarter of that previously reported. Further experiments revealed that ampoules cleaned with chromic acid gave rates in the range reported by Levine and Noyes[9] while new ampoules that had been cleaned with Alconox gave much slower rates fitting the kinetics of eq 5 with a rate constant agreeing well with that reported for the radical component of Levine and Noyes.[9] Ampoules that had previously been used for exchange runs gave somewhat larger and less reproducible rates. Heating such ampoules with a gas–oxygen flame seemed to reduce the rate to the range observed with new ampoules.

The iodonaphthalene runs reported here were made in ampoules that had been cleaned with Alconox and were frequently soaked between runs in a solution of hydrogen peroxide and sodium hydroxide. The runs reported here for unsubstituted and for substituted iodobenzenes in hexachlorobutadiene were made in ampoules that had been cleaned with 1.4% Alconox, rinsed, and dried. Even this procedure gave fast and irreproducible rates for the subsequent runs with the same compounds in nitrobenzene. Satisfactory reproducibility was obtained if the ampoules were soaked in a hot mixture of two parts concentrated sulfuric acid and one part concentrated nitric acid, rinsed, soaked in dilute acidic hydrogen peroxide, rinsed again, and dried. The same results were obtained for a few ampoules in which a solution of potassium permanganate in sulfuric acid was substituted for the sulfuric–nitric acid mixture.

Because of these complications, the rate constants reported here must be regarded with some caution. However, the rates reported could be reproduced consistently for runs once a specific cleaning procedure was adopted, rates obtained with other cleaning procedures were invariably at least as fast as those obtained with the procedure adopted, and two quite different cleaning procedures were often shown to give the same low rates. The runs reported give kinetics consistent with the most plausible *a priori* mechanism, and the frequency factors and activation energies are in agreement with what would be expected for such a mechanism. We therefore are reasonably confident that we were indeed studying a homogeneous radical reaction.

Results

The results of the measurements of exchange rates are summarized in Table I for the five aromatic iodides in the two solvents. No attempt has been made to present data for individual runs, which are available elsewhere.[1,2] For each combination of compound, solvent, and temperature, the table lists the number of ampoules studied with use of the cleaning procedure finally adopted and the ranges of mean concentrations of the reactants. Rate constants for eq 5 are reported in the last column as mean values. Estimates of

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(15) A commercial detergent marketed by Alconox, Inc., New York, N. Y.

probable error are based on deviations of individual measurements from those means.

Rate constants for the iodonaphthalenes, αIN and βIN, were calculated with the use of eq 4 either by direct computation for single ampoules or else from plots of log $(1 - F)$ against time when at least three ampoules with the same initial concentrations were available. Decomposition of these compounds was erratic but almost never amounted to more than a 20% increase in iodine concentration and a much smaller percentage change in iodonaphthalene concentration; hence eq 4 was always a satisfactory approximation.

No significant decomposition was detected for the various iodobenzenes in nitrobenzene solvent, and the runs could be treated as simple exchange processes. Rate constants were calculated from plots of v_{ex} against $[ArI][I_2]^{1/2}$.

For some runs with iodobenzenes in hexachlorobutadiene, iodine concentrations increased four- or fivefold by the time the final ampoule was measured, but the integration procedure of eq 7 gave good consistency for k_{ex} values calculated at different times for the same initial concentrations and also for different initial concentrations. For comparable conditions at 160.0°, *p*-iodoanisole (PIA) decomposed about twice as rapidly as iodobenzene (IB) and about six times as rapidly as *p*-nitroiodobenzene (PINB). The rate of decomposition was independent of iodine concentration and slightly less than first order in aryl iodide. The best empirical expression for the rate was $v_d = k_d[ArI]^{3/4}$. If $\theta = 2.303RT$ in kcal/mole, log k_d as a function of temperature was $9.8 - 32.8/\theta$ for *p*-iodoanisole and $10.1 - 34.2/\theta$ for iodobenzene.

It was originally intended to study the temperature dependence of the exchange reaction for all compounds in both solvents. As the importance of surface catalysis was realized, much of the initial work with the iodobenzenes had to be discarded. When what appeared to be satisfactory procedures were finally developed, it was decided that good relative rates for all compounds at the same temperature would be much more important than would less precise rate measurements extending over a range of temperatures. Arrhenius parameters are presented in Table II for those reactions that were studied at more than one temperature. Uncertainties are based on those assigned to the individual rate constants.

Table II. Activation Parameters for k_{ex}

Compound	Solvent	Log *A*	*E*, kcal/mole
αIN	HCBD	10.9 ± 0.5	31.1 ± 1.1
	NB	10.1 ± 0.5	29.4 ± 1.8
βIN	HCBD	10.4 ± 0.8	31.8 ± 1.7
	NB	11.3 ± 4.1	33.4 ± 8.3
IB	HCBD	11.5 ± 1.7	36.3 ± 3.5
	NB	6.5 ± 1.3	25.7 ± 2.7
PIA	HCBD	10.3 ± 0.3	32.1 ± 0.6

The log *A* values for the iodonaphthalenes in both solvents and for the iodobenzenes in hexachlorobutadiene do not differ significantly from each other or from the 10.56 observed previously[16] for the very similar exchange of iodine with *trans*-diiodoethylene in saturated hydrocarbon solvent. This consistency encourages us to believe that a homogeneous radical substitution reaction is indeed being studied. This consistency also tends to justify the decision not to measure temperature dependence for all compounds and solvents. The log *A* and *E* values for iodobenzene in nitrobenzene are definitely anomalous and suggest that surface effects may not have been completely eliminated for studies of iodobenzenes in this solvent.

Discussion

Mechanism of Exchange. The kinetics of eq 5 are consistent with exchange by a radical process involving reaction of an iodine atom with a molecule of aromatic iodide. Such a process might involve either[17] direct substitution according to the sequence of eq 8 and 9

$$\mathrm{ArI} + \mathrm{I}^* \longrightarrow \mathrm{ArI}^* + \mathrm{I} \tag{8}$$

$$\mathrm{I} + \mathrm{I_2}^* \longrightarrow \mathrm{II}^* + \mathrm{I}^* \tag{9}$$

or abstraction with formation of an aryl radical that reacts with an iodine molecule by the sequence of eq 10 and 11. Separate arguments based on energetics

$$\mathrm{ArI} + \mathrm{I}^* \longrightarrow \mathrm{Ar}\cdot + \mathrm{II}^* \tag{10}$$

$$\mathrm{Ar}\cdot + \mathrm{I_2}^* \longrightarrow \mathrm{ArI}^* + \mathrm{I}^* \tag{11}$$

and on the oxygen effect both indicate that the direct substitution mechanism (eq 8) is involved.

The argument involving energetics notes that temperature dependence of iodine atom concentration contributes 17.8 kcal/mole to the activation energy of k_{ex} and that the activation energy for eq 10 must be at least $D(\mathrm{Ar{-}I}) - D(\mathrm{I{-}I})$. Rodgers, Golden, and Benson[18] report an activation energy of 28.4 kcal/mole for eq 10 in the case of gaseous iodobenzene. Therefore, to the extent that solvent effects are negligible, the activation energy for exchange of iodobenzene by the mechanism of eq 10 and 11 should be 46 kcal/mole or about 10 kcal/mole larger than the value observed. Since the log *A* value for the exchange is normal, it appears to be impossible that the Ar–I bond is being completely broken in the rate-determining step.

The argument based on the oxygen effect notes that oxygen should compete with iodine molecules for the aryl radical reaction of eq 11. Oxygen does indeed reduce the rates of exchange of primary and secondary alkyl iodides[19] and of benzyl iodides[20,21] because of just this type of competition, but it does not significantly inhibit the exchange of the aromatic iodides studied here. Therefore, these aromatic exchange reactions do not involve free aryl radicals as intermediates.

Anbar and Rein[22] also rejected the mechanism of eq 10 and 11 for the photochemically induced exchange of *o*-iodoanisole with iodine.

Although the iodine atoms and aromatic iodides may form reversible π complexes of the type observed by Strong,[23] the iodines in the transition state must

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[16] R. M. Noyes, R. G. Dickinson, and V. Schomaker, *J. Am. Chem. Soc.*, **67**, 1319 (1945).

[17] R. M. Noyes and D. J. Sibbett, *ibid.*, **75**, 767 (1953).

[18] A. S. Rodgers, D. M. Golden, and S. W. Benson, *ibid.*, **89**, 4578 (1967).

[19] J. E. Bujake, Jr., M. W. T. Pratt, and R. M. Noyes, *ibid.*, **83**, 1547 (1961).

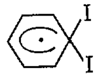
[20] M. Gazith and R. M. Noyes, *ibid.*, **77**, 6091 (1955).

[21] I. J. Gardner and R. M. Noyes, *ibid.*, **83**, 2409 (1961).

[22] M. Anbar and R. Rein, *Chem. Ind.* (London), 1524 (1963).

interact more specifically with the carbon atom to which bonding occurs.

Although the principle of microscopic reversibility does not absolutely require[24] that the reaction coordinate for exchange pass through a configuration in which the two iodines are equivalent, it appears to be most probable that the system does pass through a σ complex configuration, A, of a type proposed by Wheland.[25]



A

In this model, five π electrons are delocalized on five carbon atoms, and the two iodine atoms are placed symmetrically on opposite sides of the plane determined by the three carbon atoms closest to the reaction center. Our data give no information as to whether configuration A is a transition state or whether it is an intermediate located symmetrically between two potential energy maxima along the reaction coordinate.

The dielectric constant of hexachlorobutadiene is about 2.6 at room temperature, while that of nitrobenzene is about 35. Rate constants for exchange are invariably greater in nitrobenzene, but the ratio is never more than a factor of 4 and is less than 1.5 for the iodonaphthalenes. Whether or not the transition state for exchange does indeed resemble configuration A, its dipole moment cannot be much greater than that of the aromatic iodide from which it is formed.

Relative Rates of Substituted Iodobenzenes. Since *p*-methoxy accelerates the exchange while *p*-nitro retards it, iodine atoms behave somewhat electrophilic in this reaction. Although measurements on only three compounds are not sufficient for a detailed discussion based on the Hammett[26] substituent relationship, the data suggest that the correlation is poor. Studies by Milligan[7,8] of a chemically similar halogen atom displacement also correlate rather poorly with the Hammett[26] equation.

General Correlation of Relative Rates. The Hammett[26] equation is restricted to substituted benzene derivatives. Molecular orbital calculations based on localization energies permit an extension to a much wider range of aromatic and olefinic compounds. The results of such calculations are presented in Figure 1.

The ordinate of the plot is the logarithm of k_{rel}, the observed or interpolated rate constant for exchange at 160° relative to that for unsubstituted iodobenzene. The solvent for the aromatic iodides is hexachlorobutadiene, and that for the diiodoethylenes is decalin.[16]

The abscissa of the plot, ΔL, is the calculated π-electron localization energy in β_0 units associated with formation of the transition state. The calculation was carried out by the simple Hückel molecular orbital method as discussed by Streitwieser.[27] Inductive parameters were not used, and heteroatom parameters for iodine were assigned the values $h_{\text{I}} = 0.0$ and $k_{\text{C-I}} = 0.3$ for calculation of Coulomb and resonance integrals. Heteroatom parameters for the methoxy and nitro groups were taken directly from Streitwieser.[27] The model for the transition state was based on structure A, and the π energy was calculated as though the system had lost the attacked carbon and one π electron.

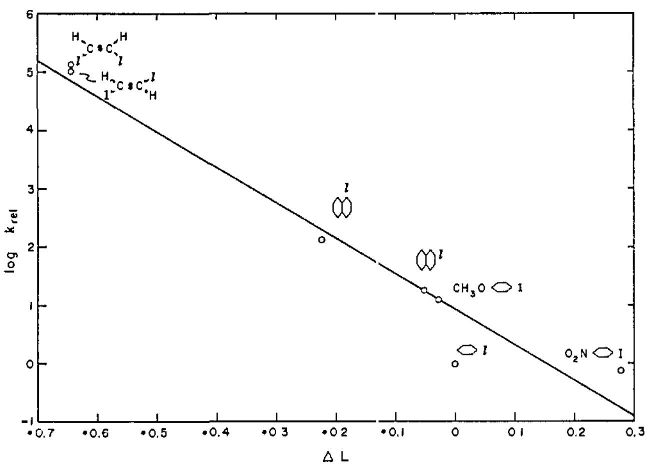


Figure 1. Variation of relative rate constant for exchange with change in calculated Hückel localization energy for exchange of olefinic and aromatic iodides in nonpolar solvents at 160°.

The slope of the least-squares line in Figure 1 is −6.187, and multiplication by $2.303RT$ gives an effective β of −12.3 kcal/mole. This change of reactivity with localization energy is very comparable to that indicated by a similar treatment for the additions of methyl[28] and trifluoromethyl[29] radicals to polycyclic aromatic hydrocarbons. However, the fit of Figure 1 for the three iodobenzenes is no better than that predicted by the simpler Hammett[26] equation.

Conclusions

Olefinic and aromatic iodides exchange with iodine atoms by a direct substitution mechanism in which the entering iodine atom saturates the valences of the carbon atom undergoing substitution and reduces by one the number of carbons involved with the π-electron system. Exchange rates varying by a factor of over 10^5 can be correlated reasonably well by molecular orbital calculations of localization energies, and the reactivity pattern is similar to that observed for other systems in which radicals add to conjugated systems. However, the relative exchange rates of substituted iodobenzenes, which vary by about a factor of 10, correlate only roughly either with localization energy calculations or with substituent parameters that have been derived for reactions that do not change the number of electrons in the aromatic π-electron system. It appears that more information will be needed before it is possible to develop a satisfactory general description of the effects of substituents on radical additions to aromatic systems.

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