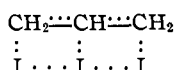


tion state and limit the types of motion available to it.

Of course the data do not completely demonstrate the mechanism of the exchange, but we can only think of two plausible configurations for the transition state. One of these configurations involves replacement on the same carbon atom by formation of the transition state designated as I. The other configuration involves interaction of the iodine with the double bond to form the transition state designated as II. These two mechanisms could be differentiated by comparing rates of isomerization and exchange in substituted allyl iodides. In the absence of experimental information, we are very much in favor of configuration II. The exchange



I



II

may even involve glycerol triiodide as a metastable intermediate; this compound does not appear to have been prepared.

We cannot say much about the apparent additional exchange which is not accounted for by the above kinetics. This exchange is usually 10% or less of the total at 0.05 *M* allyl iodide and is proportionately less important at higher concentrations. The percentage effect appears to be independent of temperature and of iodine concentration. Although this extra exchange may arise from a side reaction having about the same activation energy, we are more inclined to regard it as a mathematical artifact or an exchange induced during the separation procedure.

We are indebted to the United States Atomic Energy Commission for the allocation of the iodine-131 used in these experiments.

NEW YORK 27, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

Kinetics of the Photochemical Exchange between Iodine and Allyl Iodide

BY DONALD J. SIBBETT¹ AND RICHARD M. NOYES

RECEIVED JULY 21, 1952

Allyl iodide in hexane solution exchanges rapidly with photochemically-produced iodine atoms. The kinetics in the presence of air indicate that the exchange reaction is accompanied by a much slower oxidation which causes most of the chains to be terminated by a process that is first order in chain-carrying intermediates. The data have been fitted by a rate expression more complex than is usually required for reactions of this sort. According to our interpretation, an iodine atom at 25° exchanges with allyl iodide about 2000 times more rapidly than with *trans*-diiodoethylene and about 16 times less rapidly than with molecular iodine. We believe that the entering iodine atom attacks the opposite end of the molecule from that occupied by the leaving iodine atom.

Introduction

Data presented in the previous paper² have demonstrated that the thermal exchange reaction between allyl iodide and elementary iodine involves iodine molecules. However, the rate of exchange is greatly accelerated by visible light; therefore the reaction can also proceed by a mechanism involving iodine atoms. We have studied the kinetics of this atomic reaction and have found some unusual features which have not been observed in any previous study.

Experimental

The materials used have been described previously.² Thermostated solutions of radioactive iodine and of allyl iodide in hexane were mixed in a cylindrical reaction cell and were illuminated with the 4358 Å. line from an AH4 mercury arc. The iodine and allyl iodide were separated and the activities were counted by the procedure described previously.

The 4358 mercury line was isolated with glass filters. In some experiments two sets of filters were used in order to reduce the intensity of illumination by a factor of 2.38 (as measured with a Beckman spectrophotometer). The absolute intensity of the lamp was measured with a thermopile calibrated with a lamp from the Bureau of Standards.

(1) Based on a dissertation submitted by Donald J. Sibbett to the Faculty of Pure Science of Columbia University in partial fulfillment of the requirements for the Ph.D. degree in Chemistry. Persons desiring to consult the more complete report or to obtain a microfilm thereof may address the Library, Columbia University, New York 27, N. Y.

(2) D. J. Sibbett and R. M. Noyes, *THIS JOURNAL*, **75**, 761 (1953).

A phototube circuit was used to monitor the intensity because it had greater precision than the thermopile and because it could be used behind a cell thermostated at other than room temperature. The extinction coefficients of the solutions were measured with a spectrophotometer. Two lengths of cell were used with different iodine concentrations so that no more than 10% of the incident radiation was absorbed in any experiment; therefore the absorption could be assumed to be uniform throughout the cell. This apparatus has been described elsewhere in more detail.³

The experiments demonstrated that the thermal and photochemical reactions went by entirely different mechanisms. Therefore, the rates of the two processes were assumed to be independent of each other. The observed exchange was corrected for the thermal reaction computed from the time the solutions were mixed until they were separated, and the remaining exchange was ascribed to the photochemical process during illumination. The thermal correction was usually fairly small but became as great as half the total exchange in experiments at 35° and high allyl iodide concentrations.

Several experiments were performed to demonstrate that the calculated quantum yield was independent of the duration of illumination and that the organically-bound iodine was present as allyl iodide. One solution containing inactive iodine was illuminated and examined periodically with a spectrophotometer for change in concentration of iodine. No change was observed during periods as long as those used in the exchange experiments. A subsequent slow production of iodine took place with a quantum efficiency only about 1% of that calculated for the exchange reaction.

Results

Exchange experiments were performed at 15, 25

(3) J. Zimmerman and R. M. Noyes, *J. Chem. Phys.*, **18**, 658 (1950).

and 35°. At each temperature the data consist of several series in which the iodine concentration remained constant while the allyl iodide concentration was varied over a range of at least 40-fold. Requirements of satisfactory light absorption meant that concentrations of iodine in different series could only be varied over a 10-fold range. The data for most series were obtained at each of two light intensities differing by a factor of 2.38.

In Fig. 1 we have plotted the quantum yields obtained in all experiments at 15° with the same lamp intensity. Similar results were obtained at other temperatures. The points indicate a very unusual behavior and the peculiarity is emphasized by a realization that all of the curves shown in Fig. 1 must pass through the origin!

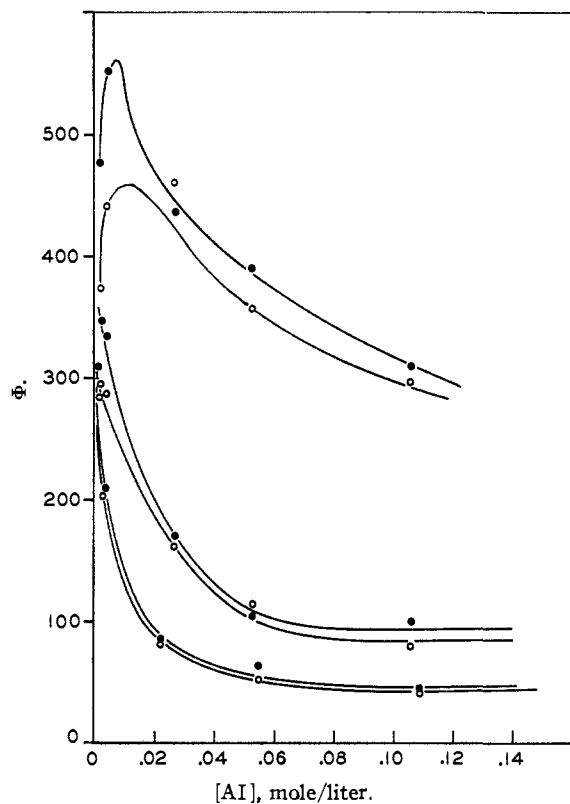


Fig. 1.—Quantum yield at 15° as a function of allyl iodide concentration. Closed circles are at light intensities 2.38-fold less than accompanying open circles. Iodine concentrations: $4.234 \times 10^{-4} M$ for top curves, $1.197 \times 10^{-4} M$ for middle curves, $4.120 \times 10^{-5} M$ for bottom curves.

In Table I we present data which show the effects of oxygen and nitrogen on the quantum yields

TABLE I

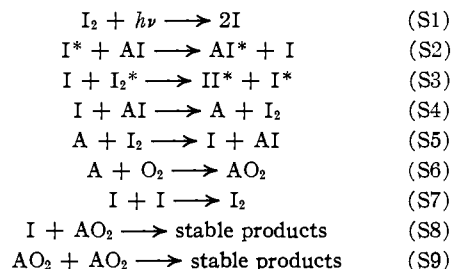
EFFECTS OF OXYGEN AND NITROGEN IN PHOTOCHEMICAL EXCHANGE BETWEEN IODINE AND ALLYL IODIDE

Temp., °C.	[I ₂], mole/liter	[AI], mole/liter	$\frac{\Phi_{O_2}}{\Phi_{air}}$	$\frac{\Phi_{N_2}}{\Phi_{air}}$
15.0	1.147×10^{-4}	0.002652	0.86	1.0
		.1064	.79	2.3
25.0	4.184×10^{-4}	.002621	.51	4.6
		.1051	.48	6.3
25.0	4.071×10^{-5}	.002690	.97	4.6
		.1080	1.0	24

in representative experiments. The data indicate the desirability of studying the reaction in an oxygen-free system; however, the thermal exchange was so rapid that we were unable to develop a satisfactory procedure for working with degassed solutions.

Discussion

For reasons that are discussed in detail below, we are convinced that the mechanism of the exchange reaction includes the following steps. In these equations, the asterisks are used merely to indicate the ways in which iodine atoms change their bonding during an individual step.



In order that the above mechanism be consistent with the experimental observations, it is necessary to postulate that step (S2) is much more probable than (S4), that in the presence of air (S6) is at least as probable as (S5), and that the rate constants for (S7), (S8) and (S9) are comparable.

The mechanism indicates that the exchange reaction is associated with a slow oxidation reaction which changes the species in the solution. However, in none of our experiments could the chemical change have consumed more than 0.1% of the allyl iodide or increased the iodine by more than 1%; therefore we are justified in using the standard kinetic expressions developed for simple exchange reactions.

In the following sections, we present our reasons for selecting the specific steps proposed for this chain reaction.

Chain Initiation.—Molecular iodine was certainly responsible for most of the absorption of light in these solutions. Although allyl iodide or some impurity in it may have contributed to the absorption in the more concentrated solutions, we do not see how most of the chains could have been initiated by any process other than (S1).

Chain Termination.—The quantum yields shown in Fig. 1 are almost independent of intensity of illumination when the allyl iodide concentration is high. At low allyl iodide concentrations, the quantum yield becomes more dependent upon intensity of illumination and the effect is greatest at high iodine concentrations where the rate of initiation of chains is greatest. However, the fractional increase in quantum yield is never as great as the fractional decrease in the square root of the light intensity. These observations indicate that two types of chain-terminating processes are in competition. One process is first order in the chain-carrying intermediates and involves allyl iodide or some species derived from it; the other process is second order in chain-carrying intermediates and is important only at low concentrations of allyl iodide.

The first-order termination must produce some species having an odd number of electrons which is so stable that it will not react in this system with the formation of iodine atoms. The only species we can suggest which might satisfy this criterion is an allyl peroxy radical formed by reaction (S4) rapidly followed by (S6). However, we doubt that any radical species of this sort would be so stable that it would not react with other radicals; therefore we have included reaction (S8) in addition to the second-order chain-terminating step (S7).

If the light intensity is the only factor that is varied, the quantum yield should vary proportionately to the average lifetime of an iodine-atom chain. If reaction (S4) is almost always followed by reaction (S6), then at finite light intensities the rate of irreversible destruction of iodine atoms is

$$k_4[\text{AI}][\text{I}] + 2k_7[\text{I}]^2 + k_8[\text{AO}_2][\text{I}] \quad (1)$$

and the average lifetime of an atom-propagated chain is

$$\frac{1}{k_4[\text{AI}] + 2k_7[\text{I}] + k_8[\text{AO}_2]} \quad (2)$$

As the light intensity is reduced, the concentrations of radical species become less and the quantum yield will approach a limiting value. If we let Φ_0 be the limiting quantum yield in dim light when all chains are terminated by the first-order process, then

$$\frac{\Phi_0}{\Phi} = \frac{k_4[\text{AI}] + 2k_7[\text{I}] + k_8[\text{AO}_2]}{k_4[\text{AI}]} \quad (3)$$

We cannot carry the treatment further without making some assumptions about relative rate constants for radical-radical reactions. Presumably these reactions require very little activation energy and occur almost invariably when the radicals diffuse together. Since small molecules have very similar diffusion coefficients in a given solvent, we have made the assumption that all radical species show equal tendency to react with all other radical species in our system. If we let $[\text{C}]$ be the total concentration of radical species, then $[\text{C}] = [\text{I}] + [\text{A}] + [\text{AO}_2]$. The rate of production of new radicals is $2\phi q_a$ where ϕ is the quantum yield for the production of atoms that escape from their original partners and q_a is the rate of absorption of radiation in quanta/ml. sec. The rate of destruction of radicals is $2k_t[\text{C}]^2$ where k_t is the rate constant for reaction between like radicals. From the usual steady-state approximation, we obtain

$$[\text{C}] = (\phi q_a / k_t)^{1/2} \quad (4)$$

We can also write⁴

$$k_t = k_7 = \frac{1}{2} k_8 = k_9 \quad (5)$$

If we substitute equations (4) and (5) into (3), we obtain⁵

(4) The factor of $1/2$ arises because the conventional rate constant for self-termination between like radicals is half as great as the conventional rate constant for cross-termination between unlike radicals having the same reactivity. If a and b denote concentrations of different radicals, $k(a+b)^2 = ka^2 + 2kab + kb^2$. This factor of 2 is related to the factor introduced in any introductory text on physical chemistry during the derivation of equations for numbers of collisions between like and unlike molecules.

(5) The formal treatment assumes that A is present in small con-

$$\frac{\Phi_0}{\Phi} = 1 + \frac{2k_t[\text{C}]}{k_4[\text{AI}]} = 1 + \frac{2\sqrt{\phi k_t q_a}}{k_4[\text{AI}]} = 1 + K_b \frac{\sqrt{q_a}}{[\text{AI}]} \quad (6)$$

The validity of this treatment is indicated by the fact that at each temperature all of the effects of varying light intensity at constant composition can be explained satisfactorily with a single value of K_b .

The data in most series suggest that the "best" value of K_b varies slightly with allyl iodide concentration. The effect is probably within experimental error but is in the direction to be expected if $k_8^2 > 4k_7k_9$; this inequality would be observed if reaction (S9) does not go at every encounter in solution. Values of K_b also appear to decrease slightly with decreasing iodine concentration; this result would be expected if (S5) could compete somewhat with (S6) at the highest iodine concentrations.

We have also examined the effect of light intensity with the assumption that the product from the first-order termination reaction cannot react with an iodine atom. This treatment eliminates reaction (S8) from the proposed mechanism. The agreement with the observed effects of light intensity is not as satisfactory as in the treatment presented above.

Chain Propagation.—We are convinced that most of the exchange takes place through the sequence (S2-S3). An alternative sequence is suggested by (S4-S5), but this sequence would not lead to a decrease in Φ_0 with increasing allyl iodide at constant iodine concentration. Hamill, Williams and Schwarz⁶ have shown that allyl bromide competes very efficiently with hydrogen bromide for the capture of recoil bromine atoms produced by bombardment with slow neutrons. Such an observation could be explained by reaction (S2) but not by (S4).

Additional Steps.—The above sections indicate reasons for proposing all of the reaction steps from (S1) to (S9). Attempts to fit the data quantitatively indicate that at least one additional step is necessary, and we can suggest two alternative interpretations. If (S5) is unimportant compared to (S6), we can write⁷

$$\Phi_0 = \frac{2\phi k_2}{k_4} \left\{ \frac{k_3[\text{I}_2]}{k_2[\text{AI}] + k_3[\text{I}_2]} \right\} \quad (7)$$

where the term in brackets is the probability that the iodine atom reacting by (S2) was formed from an iodine molecule rather than from an allyl iodide molecule. Then a plot of $1/\Phi_0$ against $[\text{AI}]/[\text{I}_2]$ would give a straight line for all data at a given temperature. If only absorption by iodine is used in calculating the quantum yields, plots at constant iodine concentrations seem to have a common intercept but are concave down. At each temperature, it is possible to choose an empirical value of K_d such that all of the data are fitted by an equation of the form

centration compared to I or AO_2 . The result presented in equation (6) is not violated by failure of this assumption, but it would be necessary to add reactions of $\text{A} + \text{I}$, $\text{A} + \text{A}$ and $\text{A} + \text{AO}_2$ to the mechanism as presented above.

(6) W. H. Hamill, R. R. Williams, Jr., and H. A. Schwarz, *THIS JOURNAL*, **72**, 2813 (1950).

(7) The reasons for this sort of equation are discussed in (a) R. M. Noyes and J. Zimmerman, *J. Chem. Phys.*, **18**, 656 (1950), and in (b) H. Steinmetz and R. M. Noyes, *THIS JOURNAL*, **74**, 4141 (1952).

$$\frac{1 + K_d[AI]}{\Phi_0} = K_a + K_c[AI]/[I_2] \quad (8)$$

In Fig. 2, we show the applicability of this equation to the data from Fig. 1; the values of the constants are presented in Table II.

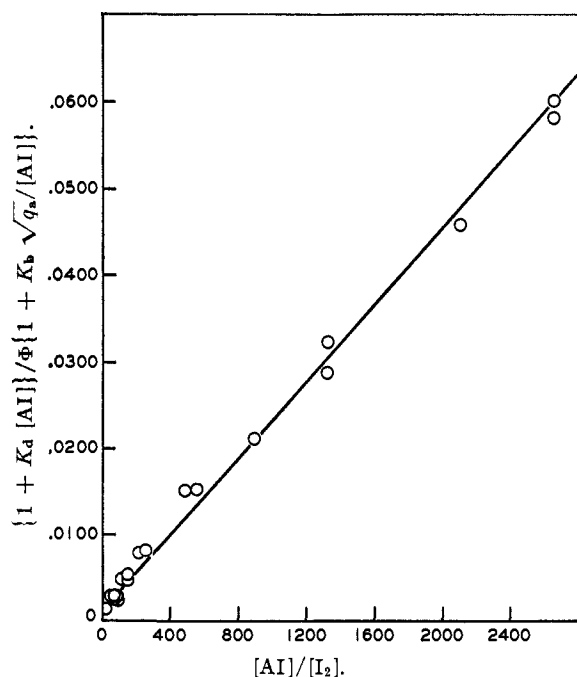
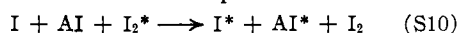


Fig. 2.—Data from Fig. 1 plotted to show validity of equation (8).

TABLE II
EMPIRICAL CONSTANTS FOR PHOTOCHEMICAL EXCHANGE REACTION

Temperature, °C.	15.0	25.0	35.0
$K_a \times 10^4$	9.0 ± 1.2	4.7 ± 1.0	2.6 ± 0.8
K_b , molecule ^{1/2} sec. ^{1/2} ml. ^{-1/2} × 10 ⁻¹²	1.67 ± 0.41	2.53 ± 0.51	3.17 ± 0.45
$K_c \times 10^5$	2.22 ± 0.20	3.22 ± 0.22	4.65 ± 0.35
K_d , ml./molecule × 10 ²⁰	2.34 ± 0.42	2.62 ± 0.42	2.89 ± 0.65

These observations demonstrate that with increasing allyl iodide concentration the apparent quantum yield falls off less rapidly than would be predicted by equation (7). One possible explanation is to add the reaction step

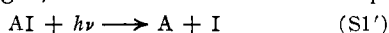


This reaction is plausible if we assume that step (S2) involves the radical intermediate $ICH_2 \cdot CHCH_2I$ which can react with molecular iodine to produce a free atom and the $C_3H_5I_3$ intermediate involved in the thermal exchange.² If (S10) is included, equation (7) is modified to read

$$\Phi_0 = \frac{2\phi k_2 \left\{ \frac{k_3[I_2] + k_{10}[AI][I_2]}{k_2[AI] + k_3[I_2] + k_{10}[AI][I_2]} \right\}}{k_4} = \frac{2\phi k_2 \left\{ \frac{1 + k_{10}[AI]/k_3}{1 + (k_2/k_3 + k_{10}[I_2]/k_3)[AI]/[I_2]} \right\}}{k_4} \quad (9)$$

If $k_{10}[I_2] \ll k_3$, this reduces to equation (8).

An alternative interpretation is to assume that allyl iodide or some impurity associated with it is also absorbing light, and to add the initiation step



Although a few tests failed to indicate significant

absorption by our solutions, subsequent observations⁸ demonstrate that solutions of at least some samples of allyl iodide absorb slightly at this wave length and produce free iodine. If we retroactively apply the new extinction coefficients to the data in this paper, we obtain straight-line plots of $1/\Phi_0$ against $[AI]/[I_2]$ at constant iodine concentration. The plots at different iodine concentrations do not coincide, but the deviations can be fitted quantitatively by assuming that (S5) and (S6) go at about equal rates at the highest iodine concentrations studied. Of course, (S5) becomes unimportant at lower iodine concentrations. This explanation is supported by the data in Table I, which suggest that iodine and oxygen are in competition for some intermediate. At low iodine concentrations, the oxygen in air-saturated solutions is at sufficient concentration that a fivefold increase does not improve its efficiency; but at high iodine concentrations, substitution of oxygen for air doubles the efficiency for termination of chains.

The same values for the empirical constants K_b and K_c are given by either interpretation; therefore, the arguments presented below apply regardless of how the detailed fit of the data is obtained.

An investigation of this sort is normally considered successful when the data have been fitted to a straight-line relationship which can be accounted for in terms of a specific mechanism. However, it is legitimate to question the uniqueness of any treatment involving four arbitrary constants.

Individual Rate Constants.—The values of the empirical constants in equations (6) and (8) can be used to furnish additional support for the main features of our mechanism. The applicable constants are related to the rate constants for the individual steps by

$$K_a = k_4/2\phi k_2 \quad (10)$$

$$K_b = 2(\phi k_t)^{1/2}/k_4 \quad (11)$$

$$K_c = k_4/2\phi k_3 \quad (12)$$

At 25°

$$K_b K_c = k_t^{1/2}/\phi^{1/2} k_3 = 8.1 \times 10^7 \text{ molecule}^{1/2} \text{ sec.}^{1/2} \text{ ml.}^{-1/2} \quad (13)$$

We have evaluated the individual rate constants in equation (13) by studies of another reaction in the same solvent^{3,7a} and have found $\phi = 0.59$, $k_t = 1.8 \times 10^{-11}$ ml./molecule sec., and $k_3 = 1.3 \times 10^{-13}$ ml./molecule sec. The net results indicate that

$$k_t^{1/2}/\phi^{1/2} k_3 = 4.2 \times 10^7 \text{ molecule}^{1/2} \text{ sec.}^{1/2} \text{ ml.}^{-1/2} \quad (14)$$

The agreement is as good as could be anticipated from the probable errors assigned to K_b and k_3 . Since the quantities in equation (14) were evaluated by completely independent methods on another reaction, the agreement furnishes support for our complex interpretation of this reaction.

Since K_a , K_c and k_3 are known at 25°, we can evaluate k_2 as 9×10^{-15} ml./molecule sec. = 5×10^9 ml./mole sec. This result indicates that allyl iodide exchanges with iodine atoms about 2000 times as rapidly as does *trans*-diiodoethylene.^{7a}

We have applied other tests for the consistency of the proposed mechanism. The only difficulties

(8) F. W. Lampe and R. M. Noyes, unpublished observations.

we have encountered arose because the temperature dependence of K_a indicates an excessive energy of activation for (S2). In plots like Fig. 2, the slopes are known with reasonable reliability, but the intercepts are poorly defined. Therefore, we are confident of the values of K_c but distrust the values of K_a .

Detailed Mechanism.—Our data do not demonstrate which end of the molecule is occupied by the entering iodine atom. Since halogen atoms add easily to double bonds and since saturated halides do not exchange easily with halogen atoms, we are

inclined to favor a transition state of the form $I \cdots CH_2 \cdots CH \cdots CH_2 \cdots I$ like that proposed independently by Hamill, Williams and Schwarz⁶ for the exchange of bromine atoms with allyl bromide. A final decision must await comparative kinetic studies of isomerization and exchange reactions of substituted allyl halides.

Acknowledgment.—We are indebted to the United States Atomic Energy Commission for the allocation of the iodine-131 used in these experiments.

NEW YORK 27, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

Mechanisms of Exchange Reactions between Elementary Iodine and Organic Iodides¹

BY RICHARD M. NOYES AND DONALD J. SIBBETT

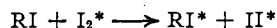
RECEIVED OCTOBER 6, 1951

Organic compounds which contain iodine undergo exchange with the free element, and the reaction usually proceeds by the action of free iodine atoms. The mechanism may involve either a direct substitution of one iodine atom for another or else removal of iodine to form an organic radical which subsequently reacts with a molecule of iodine. The information already at hand indicates that the direct substitution mechanism is the chief path for exchange of those compounds like olefinic, allylic and aryl iodides in which the electrons of a double bond or aromatic ring are available for reaction with the iodine atom. Other data suggest that the carbon radical mechanism is the path for exchange reactions of alkyl halides and also represents a slower alternative path for the exchange of allyl iodide. The evidence available for benzyl iodide is insufficient to establish the mechanism of its exchange with iodine.

The halogen in organic halides can be removed or replaced by a variety of different reactions. One type of reaction which has been studied extensively is nucleophilic substitution by iodide ion or by some other substance containing an unshared pair of electrons. Removal of the halogen by the action of a sodium atom in the gas phase is another type of reaction which has been examined carefully. As the nature of the compound is changed, the rates for both of these types of reactions vary in the sequence allyl, benzyl > alkyl > aryl > olefinic. This sequence is the inverse of the sequence for carbon-halogen bond strengths.

Another type of reaction is replacement of the halogen by a halogen atom containing an unpaired electron. We have examined several reactions of this type between organic iodides and elementary iodine containing the radioactive isotope of mass 131, and the data have permitted us to elucidate the mechanisms of some of these radical substitution reactions.

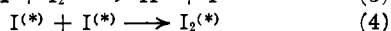
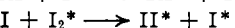
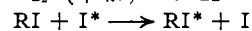
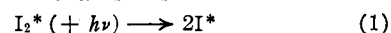
The over-all equation for these reactions is



where RI is any organic iodide and the asterisk denotes an atom initially incorporated in the molecular iodine. All of these exchange reactions are greatly accelerated by visible light and must proceed at least in part through mechanisms involving free iodine atoms. Although only a few type compounds have been studied, and quantitative kinetic data are not even available for all of these cases, the rates of reaction now known fall cleanly in the

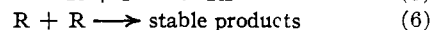
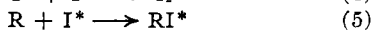
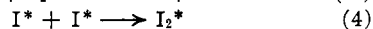
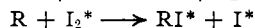
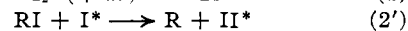
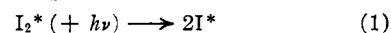
series² allyl > benzyl > olefinic > phenyl > alkyl.

Two alternative mechanisms can be proposed for these reactions. One involves a direct substitution by an iodine atom, and the other involves the formation of a carbon radical which then reacts with an iodine molecule. The sequence of steps in the direct-substitution mechanism is³



In this sequence we have chosen to denote step 2 as a single process. In some reactions there may be an intermediate RII^* which persists for a short time, but the kinetics will be unaffected unless the intermediate undergoes additional reactions with some of the species present in the system.

The sequence of steps in the alternative carbon radical mechanism is³



The detailed kinetic analyses of these two mechanisms have been developed elsewhere in connection with studies of exchange with diiodoethylene⁴

(2) R. M. Noyes, *THIS JOURNAL*, **70**, 2614 (1948).

(3) Chain initiation may be thermal or photochemical. The parentheses in step 1 indicate the photochemical mechanism of initiation. The parentheses in the superscripts in step 4 indicate that iodine atoms may enter the chain-termination step whether or not they were initially present in I_2 .

(4) J. Zimmerman and R. M. Noyes, *J. Chem. Phys.*, **18**, 656, 658 (1950).

(1) This paper was presented before the XIIth International Congress of Pure and Applied Chemistry, New York, N. Y., September 10, 1951.