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 $I \cdot\cdot CH_2 \stackrel{\cdot\cdot}{-} CH \stackrel{\cdot\cdot}{-} CH_2 \cdot\cdot I$ like that proposed independently by Hamill, Williams and Schwarz[6] 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.

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NEW YORK 27, N. Y.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

# Mechanisms of Exchange Reactions between Elementary Iodine and Organic Iodides[1]

BY RICHARD M. NOYES AND DONALD J. SIBBETT

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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 sesequence 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

$$RI + I_2^* \longrightarrow RI^* + II^*$$

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 series[2] 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 is[3]

$$\begin{array}{cr} I_2^* \, (+ h\nu) \longrightarrow 2I^* & (1) \\ RI + I^* \longrightarrow RI^* + I & (2) \\ I + I_2^* \longrightarrow II^* + I^* & (3) \\ I^{(*)} + I^{(*)} \longrightarrow I_2^{(*)} & (4) \end{array}$$

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 is[3]

$$\begin{array}{cr} I_2^* \, (+ h\nu) \longrightarrow 2I^* & (1) \\ RI + I^* \longrightarrow R + II^* & (2') \\ R + I_2^* \longrightarrow RI^* + I^* & (3') \\ I^* + I^* \longrightarrow I_2^* & (4) \\ R + I^* \longrightarrow RI^* & (5) \\ R + R \longrightarrow \text{stable products} & (6) \end{array}$$

The detailed kinetic analyses of these two mechanisms have been developed elsewhere in connection with studies of exchange with diiodoethylene[4]

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

(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).

and allyl iodide.[5] It is sufficient here to point out that the mechanisms are almost indistinguishable kinetically. In each of them the second step involves reaction of RI with I* to form a radical product which must then react with $I_2$* in order to continue the chain process. Nevertheless, there are certain criteria which sometimes permit us to differentiate between these mechanisms with considerable confidence. From our studies of various type compounds, we have obtained excellent evidence as to mechanism for certain examples and can even begin to generalize as to the structural features which favor a particular mechanism.

## Mechanisms Proposed for Specific Compounds

**Olefinic Halides.**—A considerable body of evidence establishes that the 1,2-dihaloethylenes (and presumably other olefinic halides) exchange by the direct substitution mechanism:

If organic halides react with sodium atoms, the rates increase regularly with decrease in strength of the carbon–halogen bond.[6] In the carbon radical mechanism for exchange, the halogen is removed by attack of a halogen atom in a process very similar to the removal by a sodium atom. Therefore, if the more reactive of two halides has the stronger carbon–halogen bond, it probably does not exchange by the carbon radical mechanism. Although this conclusion may not be valid for small differences in reactivity and bond strength, it is probably reliable for large differences. Diiodoethylene exchanges more rapidly than either iodobenzene or ethyl iodide,[2] yet it has a stronger carbon–iodine bond than either of these compounds. Also, dibromoethylene exchanges with bromine atoms very much more rapidly than diiodoethylene exchanges with iodine atoms.[7] This order is also the reverse of that predicted by the carbon radical mechanism.

Additional evidence is provided by comparing the rates of isomerization and exchange. Thus *cis*- and *trans*-diiodoethylene exchange fairly rapidly with iodine atoms and isomerize with the same kinetics at a much slower rate. Since the thermal isomerization is first order in diiodoethylene and half order in molecular iodine, the transition state has the empirical formula $C_2H_2I_3$. If the rapid exchange reaction goes by a carbon radical mechanism, then the $\mathrm{CHI{=}\dot{C}H}$ must retain a specific steric configuration and must almost invariably react with an iodine molecule to regenerate the original isomer of diiodoethylene. The observations can be interpreted much more plausibly by the direct substitution mechanism.

Finally, Hamill, Williams and Schwarz[9] have observed that dibromoethylene can compete efficiently with molecular bromine for the capture of atoms of bromine-80 generated by bombardment with slow neutrons. This observation cannot be explained by the carbon-radical mechanism.

**Aryl Iodides.**—Iodobenzene exchanges with iodine by an atomic mechanism[2] but no detailed kinetics have been studied. The reaction appears to be distinctly faster than the corresponding exchange of ethyl iodide, while the rates of reaction with sodium[6] suggest that the relative rates of exchange by the carbon radical mechanism would be in the opposite order. Therefore, we propose that iodobenzene exchanges by a direct substitution mechanism, but the final decision must await more detailed kinetic studies.

**Alkyl Halides.**—In a brilliant piece of work, Sullivan and Davidson[10] recently studied the kinetics of the reactions

$$\mathrm{CCl_3Br + Br_2^* \longrightarrow CCl_3Br^* + BrBr^*}$$

$$\mathrm{CCl_3Br + HBr \rightleftarrows CCl_3H + Br_2}$$

By comparing the rate of exchange with the rate of establishment of the equilibrium, they were able to demonstrate that the exchange involves the $\mathrm{CCl_3\cdot}$ radical and that the direct-substitution mechanism is not operative in this case.

Ogg and Polanyi[11] studied the iodine-catalyzed racemization of optically-active *s*-butyl iodide and concluded that it involved a direct substitution by an iodine atom with an inversion of configuration. However, their system was so complicated that the conclusion cannot be regarded as unequivocally established. The two atomic mechanisms could be differentiated in this example by a comparison of the rates of racemization and exchange. If the Ogg and Polanyi direct substitution were correct, every exchange would be accompanied by inversion; if the carbon radical mechanism were operative, no more than half of the exchanges would be accompanied by inversion. We are undertaking a comparative study of racemization and exchange but have no data to report. For the present, we can only say that Sullivan and Davidson have demonstrated that at least some saturated halides exchange by the carbon radical mechanism.

**Allyl Iodide.**—Allyl iodide exchanges with iodine at a greater rate than any other organic iodide that has been investigated.[2] The thermal exchange reaction proceeds almost entirely through a mechanism involving iodine molecules.[12] The photochemical exchange reaction proceeds chiefly by a direct substitution mechanism.[5] However, we were unable to account for the photochemical kinetics unless we assumed that the chains were terminated by a reaction coming after step (2′) of the carbon radical mechanism. According to this interpretation, the reaction $\mathrm{RI + I^* \rightarrow RI^* + I}$ at 25° is about 2000 times as rapid as the reaction $\mathrm{RI + I \rightarrow R + I_2}$. We believe that the very rapid exchange involves a transition state of the form $\mathrm{I\cdot\cdot CH_2{=}CH{=}CH_2\cdot\cdot I}$. The proof of this structure must await studies of comparative rates of isomerization and exchange of substituted allyl iodides.

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(5) D. J. Sibbett and R. M. Noyes, THIS JOURNAL, **75**, 763 (1953).

(6) E. T. Butler and M. Polanyi, *Trans. Faraday Soc.*, **39**, 19 (1943).

(7) H. Steinmetz and R. M. Noyes, THIS JOURNAL, **74**, 4141 (1952).

(8) R. M. Noyes, R. G. Dickinson and V. Schomaker, *ibid.*, **67**, 1319 (1945).

(9) W. H. Hamill, R. R. Willioms, Jr., and H. A. Schwarz, *ibid.*, **72**, 2813 (1950).

(10) J. H. Sullivan and N. Davidson, *J. Chem. Phys.*, **19**, 143 (1951).

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

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

**Benzyl Iodide.**—Benzyl iodide exchanges with iodine both thermally and photochemically.[13] The rate is less than that of allyl iodide but is greater than that of any other organic iodides that have been investigated. The carbon–iodine bond in this compound is very weak, and benzyl iodide reacts with sodium at a rate comparable with that of allyl iodide.[6] We believe that the observed rate of exchange with iodine is not inconsistent with a carbon radical mechanism, but a definite decision must await more detailed studies which are now being undertaken.[14]

## Conclusion

Even the meager kinetic data available at the present time permit us to make some rather definite generalizations as to the mechanisms of reactions in which halogen atoms replace other halogens in organic compounds.

(**A**).—If the compound contains $\pi$ electrons either in a double bond or in an aromatic ring, the transition state of lowest free energy for exchange of a neighboring halogen atom will usually involve a direct substitution in which the entering atom reacts with these electrons. Thus, olefinic and allyl halides exchange by a direct substitution in which the electrons of the double bond are involved, and aryl halides also appear to react by a direct substitution mechanism.

(**B**).—If the carbon atoms are saturated in the neighborhood of the halogen that is replaced, the reaction path of lowest free energy involves a direct attack on halogen with the formation of a free carbon radical which subsequently reacts with a halogen molecule. This mechanism appears to be operative in the case of at least some saturated halides, but it is possible that halogen atoms are sometimes able to react with inversion as nucleophilic groups do. The rate of this carbon radical reaction is accelerated by decrease in the carbon–halogen bond strength, and in allyl iodide the reaction apparently goes at a rate which is considerably less than that of direct substitution but which is nevertheless measurable at room temperature. The observed rate of exchange of benzyl iodide could be accounted for by either mechanism, and a decision must await further experimental work.[14]

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[13] S. I. Miller, unpublished observations.

[14] NOTE ADDED IN PROOF.—Studies by Mr. Moshe Gazith indicate that benzyl iodide exchanges by the carbon radical mechanism. The details will be published later.

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[CONTRIBUTION FROM THE HOUDRY LABORATORY, HOUDRY PROCESS CORPORATION]

# Homogeneous Catalytic Hydrogenation. I. Activation of Molecular Hydrogen by Solutions of Cuprous Acetate

BY SOL WELLER AND G. A. MILLS

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The catalytic activation of molecular hydrogen was studied in a homogeneous system in order to provide information more clearly interpretable than that obtained with usual more complex, solid catalyst surfaces. Detailed kinetic measurements were made at 100° for the reduction by hydrogen of two reductants, quinone or cupric ion, in quinoline catalyzed by cuprous acetate. The rate of hydrogenation can be expressed by: $-\mathrm{d}\ H_2/\mathrm{d}t = k\ p_{H_2}\ [Cu^I]_2$, independent of concentration of reductant, where $[Cu^I{}_2]$ represents a dimeric complex. The equilibrium constant for the formation of the complex was calculated to be equal to 11 $\text{mole}^{-1}$ l. The reduction reaction proceeds satisfactorily in solvents other than quinoline provided that, for those tried, the solvent is a nitrogen base, not necessarily heterocyclic, and free of complicating features such as chemical reactivity with the reductant, steric factors, or strong chelating tendency. When mixtures of hydrogen and deuterium are used, no appreciable exchange occurs during the homogeneous reduction period. However, HD was formed with solutions of reduced cupric acetate, which are relatively stable with regard to reduction to the metal. The rate of exchange is comparable to the rate of reduction of quinone or cupric ion. Hydrogen–deuterium exchange is believed to occur indirectly through the medium of a hydrogen donor which is probably aniline present as an impurity.

A mechanism of reduction of quinone or cupric ion by a stepwise alternate oxidation and reduction of cuprous ion catalyst, or the inverse, is not consistent with the data. Instead, the rate-determining step appears to be the reaction of a cuprous ion dimer with hydrogen to form a complex in which the hydrogen is *dissociated*. This complex is capable of reacting relatively rapidly with the reductant. The factors important to the effectiveness of the dimer appear to be: a structure possessing two sites capable of accommodating the two atoms of hydrogen simultaneously, an electronic structure permitting the formation of strong bonds with the hydrogen atoms, and also probably certain geometric features which make the two coördination positions available to hydrogen at the proper distance.

While in recent years the mechanism of acid catalysis has become understood in a fairly detailed manner, the exact nature of catalytic hydrogenation has remained largely unknown. The recognition of some general connection between hydrogenation catalysis and semi-conductivity of oxides and sulfides on the one one hand, and of d band character of metals on the other, have been important advances. However, a generalized concept of the nature of the active complex has not been achieved in the same sense that the carbonium ion mechanism has been successful in acid systems. It was, therefore, the purpose of this study to inquire into the manner in which molecular hydrogen is activated, following a new approach. Almost all known hydrogenation catalysts are solids and their study is made difficult by the complexity of solid surfaces. It was proposed that investigation of a catalyst molecularly dispersed in solution could lead to more interpretable results than can be obtained with solid catalysts, since in solution the molecular species are better known. Moreover, ultimately by control of the environment in which the catalyst exists, it should be possible to employ complexing agents so as to adjust the catalyst properties to a precise degree. The nature of the complexing agent is known to alter the oxidation–reduction potential. The exact nature of the