Title
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Publication Date
1958-08-01
Radiation Laboratory

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KINETICS AND MECHANISMS OF ISOTOPIC EXCHANGE REACTIONS
OF THE HALOGENS
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August 1958

Printed for the U. S. Atomic Energy Commission

*University of Illinois - AT ll-l-67·Proj. 19
INTRODUCTION

The increasingly widespread availability of nuclear pile and electro-nuclear machine produced radioisotopes has placed at the disposal of the physical chemist a convenient tool for studying the dynamic relationships between chemical species at equilibrium. The broad area of isotopic exchange reaction studies has received a great deal of attention in the last twenty years and a number of review articles have dealt with this field. Of these, the most comprehensive is that of Stranks and Wilkins (51) which treated the literature through March of 1957.

The purpose of the present paper is to review the literature of isotopic exchange reactions of the halogens published since the review of Stranks and Wilkins, and covers the literature through June 1958.

NUCLEAR PROPERTIES OF SOME HALOGEN ISOTOPES

Some nuclear properties (53) of the pertinent halogen nuclides are summarized in Table 1. Even though there are suitable radio-tracers for all of the halogens (in contrast to the situation which obtains for a number of other elements of prime interest, such as nitrogen, for which the longest lived species is the 9.93 minute \(^{13}\text{N}\), or oxygen for which the longest lived species is the 118 second \(^{15}\text{O}\)), the short half life of \(^{18}\text{F}\) and \(^{82}\text{Br}\) limits somewhat the range of chemical experiments which can be carried out with these tracers. Fluorine \(^{18}\text{F}\) can be prepared in a number of ways, using both slow

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The long lived nuclide Cl\textsuperscript{36} is produced in large quantities by the reaction Cl\textsuperscript{36}(n,\gamma) using pile neutrons, and may be purchased from the U.S.A.E.C. as a solution of HCl\textsuperscript{36}. The energetic negatron of this tracer may be detected either in solid samples (e.g. AgCl, Hg\textsubscript{2}Cl\textsubscript{2}) (K3, L1), in aqueous (H8, F2) or organic solvent (H8) solutions, or in the gas phase (A1, A3, B1, H3), using G.M. counters.

The pile neutron produced Br\textsuperscript{82} has been extensively used in tracer studies and is usually employed in preference to the 4.58 hour isomer Br\textsuperscript{80m} which can be made using Ra-Be neutron sources. The tracer may be radio assayed either as a solid sample or more commonly in aqueous or organic solution (G4, N4) or in the gas phase.

Of the several moderate lifetime iodine nuclides, the tracer I\textsuperscript{131} is most commonly employed in isotopic exchange studies. Its ready availability is due to the fact that it is one of the fission products extractable from spent nuclear pile fuel elements. Radio-assay techniques for this tracer include solid sample (e.g. AgI, PdI\textsubscript{2}) counting (J1, P2, S4), aqueous (G4) and organic solution counting using G.M. tubes (G4, D1), and gamma scintillation counting using NaI(Tl) crystal (M2).

**THEORETICAL TREATMENT OF ISOTOPIC EXCHANGE REACTIONS**

A number of papers have dealt with the kinetics of exchange reactions in complex systems. Darbee, Jenkins and Harris (D1) have considered the differential equations which obtain in a system of competing equilibria:

\[
\begin{align*}
AX + CX^* & \rightleftharpoons AX^* + CX \quad (1) \\
BX + CX^* & \rightleftharpoons BX^* + CX \quad (2)
\end{align*}
\]

and several limiting solutions are presented. Plots of the ratio of rates against percent exchange for different values of rate ratios are given.

Abell, Bonner and Goishi (A2) have treated the similar case in which equilibria between three species must be considered, so that in addition to
(1) and (2), the exchange

\[ AX + BX^* \rightarrow AX^* + BX \]  

is important. These authors showed that the detailed kinetic formulation gives rise to a linear 2nd order time-dependent differential equation, which can be solved under certain conditions. The appearance of the log (1-F) vs. time plot is analogous to that of the decay of a mixture of radio-nuclides, and, as in the case of the latter, the resolution of the former depends on the ratio of the various exchange rates.

Swart and LeRoux (83) have examined the relationship between specific rate constant and dielectric constant of the solvent, for a typical ion-dipole reaction. The activation energy is formulated as a function of the direction of approach of the ion to the dipole, as well as the distance of closest approach, similar to the treatment of Kacser (K2). They conclude that if the mechanism remains unchanged by changing the reaction medium, and the degree of dissociation of the ionic species is allowed for, the dielectric constant of the solution is the predominant factor in determining the rate of ion-dipole steps in exchange reactions.

A convenient manner of classifying mechanisms of exchange reactions into three distinct groups has been suggested by the present author (H1) and is summarized in Table 2. While the classification is by no means rigid, and a good deal of overlap in reaction types can be shown to occur, nonetheless it is found that a number of identifying characteristics can be assigned to each of the three mechanisms. In the case of halogen exchanges, many of the immeasurably rapid exchanges are of type I in which the two exchanging species each contribute a halogen ion to a common ion "pool", which will, of course, give rise to the observed rapid rates. Photo sensitive reactants - especially molecular chlorine and iodine - have been shown to undergo exchanges by virtue of a type R mechanism, usually at immeasurably rapid rates.

A rigorous treatment of isotopic exchange kinetics under non equilibrium conditions has been presented by Sigler and Masters (S2) and applied to the case in which an induced exchange reaction accompanies bimolecular electron exchange. The complex rate equations can be solved for ratios of specific rate constants over discrete time intervals, and the authors were able to show that this difference method of calculating differential quantities was capable of yielding reliable kinetic data.
SURVEY OF RECENT WORK

Fluorine

The only recent fluorine exchange work reported is that of Gens (G1), who investigated the exchange behavior of alkali fluorides with a number of fluorinated hydrocarbons. It was found that all of the alkali fluorides will exchange halogen with rates increasing with increasing cation atomic number. Perfluoropropane, C$_3$F$_6$, was found to exchange more rapidly than either perfluorodiethyl ether or perfluorobutane. Typical activation energies for the former are 7, 6, 14, and 11 k cal mol$^{-1}$ for CsF, RbF, KF and NaF exchanges, respectively.

A number of qualitative considerations led Gens to conclude that at least two mechanisms were operative in the overall exchange - one giving rise to a rapid initial exchange, the other a slower, diffusion controlled exchange being observed at longer exchange times. It is suggested that the slower mechanisms originates in defect centers in the solid fluoride crystals, and that the observed rates involve ion migrations from these sites.

Chlorine

Aqueous Solution. A number of studies of exchange reactions of coordination complexes have been carried out. Grinberg and Belousov (G2) were able to show that complete chlorine exchange occurred between (NH$_4$)$_2$IrCl$_6$ and (NH$_4$)$_3$IrCl$_6$ within 1 minute in the temperature range 0 to 25°C. Basolo et al (B3) measured the exchange between trans Pten$_2$Cl$_2^{++}$ and aqueous chloride ion. The reaction is catalyzed by Pten$_2$Cl$_2$ and obeys the rate law $R = k(Pten$_2$Cl$_2^{++}$)(Pten$_2$Cl$_2$)$^n(Cl^-)$. The mechanism proposed by Pearson et al, involving a chloronium ion transfer, does not account for the results obtained by Johnson, Bailar and Herber (J2) who studied the analogous cis Pten$_2$Cl$_2^{++}$ chloride ion exchange. The absence of racemization of the optically active cis salt necessitates the invoking of a different mechanism than that suggested as applicable in the case of the trans compound.

Hawkins and Garner (H9) investigated the exchange between W$_2$Cl$_9^{++}$ and aqueous chloride ion in 8 to 13 M HCl. They observed all nine chlorine atoms to be kinetically equal, although these have been shown to be structurally different. The kinetic data did not allow a differentiation to be made between the rate law $R = k_1(W_2Cl_9^{++})$ or $R = k_2(W_2Cl_9^{++})(Cl^-)$ with $k_1 \sim 2 \times 10^{-4}$ sec$^{-1}$ or
The mechanism of the exchange is postulated to involve an intermediate (either \( WC_{14}^- \) or \( WC_{15}^- \)) which is in equilibrium with both exchanging reactants.

Non Aqueous Solution. In an attempt to prepare radio-halogen labelled organic molecules of interest in the development of insecticides, Pearce and Krause (Pl) undertook a study of the chlorine exchange between lindane (the gamma isomer of hexachlorocyclohexane) and \( AlCl_3 \). The exchange was found to be rapid above the melting point of lindane \((112.5°C)\) only in the presence of solid \( AlCl_3 \). A mechanism is suggested which involves the formation of \( AlCl_4^- \) on the surface of the solid solute, with a concomitant isomerization of the organic pentachloro radical, a suggestion which is in agreement with earlier studies by Willard and his co-workers (W1, H8) on related systems.

In a study of the behavior of pyridinium chloride toward a number of solutes, Frazer (F2) observed complete exchange with \( BCl_3 \), \( PCl_3 \), \( CH_3COCl \), \( SOCl_2 \) and \( SO_2Cl_2 \) within 3 minutes at \( 20°C \). No exchange between any of the above and chloroform was noted.

Lewis and Sowerby (L1) determined the exchange characteristics of a number of ionic solutes in halogenated solvents. The halogen exchange between \( Et_4NCl \) and \( POCl_3 \) was found to obey the rate law \( R=k_2(POCl_3)(Cl^-) \) and proceeds presumably via the formation of a \( POCl_4^- \) intermediate. Representative half lives for the exchange are 4 seconds in nitrobenzene at \( 9°C \) (one experiment only), \( 1.2 \times 10^3 \) to \( 3 \times 10^4 \) seconds in \( CHCl_3 \) at \( 0 \) to \( 25°C \), and about \( 1.8 \times 10^3 \) seconds in acetonitrile at \(-10\) to \(-20°C\). Complete exchange within the time required for separation to be effected, was observed between \( Et_4NCl \) and \( POCl_3 \) in the pure solvent, between \( Me_4NCl \) and \( AsCl_3 \), and between \( NaCl \) and \( KCl \) solutes in liquid \( SeOCl_2 \).

Extending earlier work on the exchange reactions of \( PCl_5 \), Becker and Johnson (B2) studied the halogen exchange between \( PCl_3 \) and \( PCl_5 \) in carbon tetrachloride solution. The reaction obeyed the rate law \( R=k_1(PCl_5) \) and presumably proceeds via the slow step \( PCl_5 \rightleftharpoons PCl_3 + Cl_2 \). This mechanism requires an identical rate of phosphorous exchange between the two reactants, and this was found to obtain, as shown by the following data:

<table>
<thead>
<tr>
<th>T°C</th>
<th>( k_1 \times 10^3 \text{ hr}^{-1} )</th>
<th>( k_1 \times 10^3 \text{ hr}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>( 0.94 \pm 0.09 ) P exchange</td>
<td>( 0.85 \pm 0.14 ) Cl exchange</td>
</tr>
<tr>
<td>25.00</td>
<td>( 10.1 \pm 1.5 )</td>
<td>( 11.2 \pm 2.2 )</td>
</tr>
<tr>
<td>50.00</td>
<td>( 79 \pm 13 )</td>
<td>( 86 \pm 6 )</td>
</tr>
</tbody>
</table>
An activation energy of $15.9 \pm 0.1 \text{kcal mol}^{-1}$ is calculated from these data.

Becker and Johnson (B4) have also studied the chlorine exchange between $\text{PCl}_3$ and $\text{HCl}$ and $\text{PCl}_5$ and $\text{HCl}$ in carbon tetrachloride solutions. The phosphorous trichloride exchange obeys the rate law $R = k_1 (\text{PCl}_3)$, being zero order in $\text{HCl}$, although there may be a small contribution from a bimolecular rate determining step. The $\text{PCl}_5$ exchange data fit a rate law which is first order in each of the reactants, and may arise from the equilibrium

$$\text{PCl}_5 + \text{HCl} \rightleftharpoons \text{HPCl}_6$$

in which the six chlorine atoms of the addition compound are kinetically equivalent.

Howald and Willard (H8) found that the chlorine exchange between $\text{SnCl}_4$ and 2-chlorobutane obeyed the rate law $R = k_{3/2} (\text{SnCl}_4) (\text{BuCl})^{1/2}$ in the temperature interval 140 to 160°C. To explain this rate law it is postulated that $\sim 75\%$ of the metal halide is tied up as a 1:1 complex with the organic species. The value of the specific rate constant is $k_{3/2} = 4.5 \pm 0.6 \times 10^{-6} \text{mol}^{1/2} \text{sec}^{-1}$, and the data appear to be consistent with the earlier work on the $\text{SnBr}_4$ - butyl bromide exchange of Fairbrother (F1).

Neill and Kahn (N1) have investigated the chlorine exchange between acetyl chloride and $\text{HCl}$ in the range 0°C to 29.6°C and find it to obey the rate law $R = k_2 (\text{HCl}) (\text{CH}_3\text{COCl})$ with $k_2 = 1.7 \times 10^{-1} \text{ l mol}^{-1} \text{ sec}^{-1}$ and have an activation energy of $1.55 \pm 0.11 \text{kcal mol}^{-1}$. The mechanisms proposed to account for these results postulates the formation a 1, 1 dichloroethanol-1 intermediate, which rearranges to acetylchloride, one half of the cases leading to exchange.

Norris and his students (M1) have continued their study of non-aqueous ionizing solvents, and find rapid exchanges between solute and solvent in a number of cases. The following data summarize this work:

<table>
<thead>
<tr>
<th>Solute</th>
<th>Solvent</th>
<th>Temperature</th>
<th>Half time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₄NCl</td>
<td>SOCl₂</td>
<td>25°C</td>
<td>8 min</td>
</tr>
<tr>
<td>Me₄NCl</td>
<td>SOCl₂</td>
<td>0</td>
<td>~13</td>
</tr>
<tr>
<td>Me₄NCl</td>
<td>SOCl₂ inSO₂</td>
<td>25</td>
<td>~3</td>
</tr>
<tr>
<td>SbCl₃</td>
<td>SOCl₂</td>
<td>0</td>
<td>~11</td>
</tr>
<tr>
<td>Me₄NCl</td>
<td>POCl₃</td>
<td>35</td>
<td>~13</td>
</tr>
<tr>
<td>KCl</td>
<td>SeOCl₂</td>
<td>48</td>
<td>~7</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>SeOCl₂</td>
<td>40</td>
<td>~96</td>
</tr>
</tbody>
</table>
A number of exchange reactions of BCl$_3$ have been studied by the author. A convenient method of preparing halogen labelled BCl$_3$ is by exploiting the rapid exchange of liquid trihalide with solid Me$_4$NCl (H7). This exchange presumably proceeds via the BCl$_4^-$ anion. No exchange between liquid BCl$_3$ and solid RbCl or CsCl was noted in 72 hours at 0°C. A slow exchange with LiCl was observed.

Chang and Herber (Cl) observed a rapid chlorine exchange between liquid (CH$_3$)$_3$SiCl and dissolved HCl, but found no evidence for exchange in the homogeneous gas phase.

A rapid chlorine exchange between SiCl$_4$ and Me$_4$NCl provides a convenient method of preparing radiochlorine labelled silicon tetrachloride. The same reaction has also been noted for (CH$_3$)$_3$SiCl (H5).

Gas Phase.---The chlorine exchange between SiCl$_4$ and HCl in the gas phase has been studied by the present author (H4). The reaction is found to obey the rate law $R = k_3 [\text{HCl}] [\text{SiCl}_4]^2$ with the values of $k_3$ at various temperatures reported as follows:

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$k_3$ (sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>2.66 ± 0.74 x 10^{-2}</td>
</tr>
<tr>
<td>95</td>
<td>4.05 ± 1.0 x 10^{-2}</td>
</tr>
<tr>
<td>100</td>
<td>6.11 ± 0.77 x 10^{-2}</td>
</tr>
<tr>
<td>105</td>
<td>9.04 ± 1.0 x 10^{-2}</td>
</tr>
</tbody>
</table>

From these data, $\Delta H^\pm$ is $22.4 \pm 4.5$ k cal mol$^{-1}$ and $S^\pm$ is $-17.6 \pm 3.5$ e.u. The suggested mechanism involves the formation of an HSiCl$_5$ intermediate in which the five chlorines are not kinetically (and hence presumably not structurally) equal. The rate determining step involves a bimolecular collision between HSiCl$_5$ and a second SiCl$_4$ molecule. No evidence for halogen exchange between SiCl$_4$ and NaCl, even at elevated temperatures, was observed.

The gas phase exchange reaction between SiCl$_4$ and Cl$_2$ was investigated by Cordes and Herber (H2) using gas phase counting techniques. No halogen exchange was noted in 21 hours at 30°C or in 100 hours at 100°C. Exchange was also absent in the heterogeneous system at 0°C, no transfer of Cl$^{36}$ activity being noted between liquid silicon tetrachloride and Cl$_2$. 


Bromine

Aqueous Solution. The exchange of bromine between aqueous bromide ion and Pt (IV) and Pt (VI) complexes has been investigated by Grinberg and Shagisultanova (G3). The activation energies reported are 4-10 k cal mol⁻¹ for the $K_2PtBr_4$ complex and ~17 k cal mol⁻¹ for the $K_2PtBr_6$ complex, the two exchanges occurring by different mechanisms. The kinetic data for the platinous complex suggests that the rate determining step is an aquation reaction:

$$\text{PtBr}_4^- + H_2O \rightarrow \text{PtBr}_3H_2O^- + Br^-$$

while in the case of the latter a redox equilibrium appears to be involved.

Non-aqueous Solution. Neiman, Shapovalov and Miller (N2) have studied the halogen exchange kinetics between $\text{CH}_3\text{Br}$, $\text{CH}_2\text{Br}_2$, $\text{CHBr}_3$ and $\text{CBr}_4$, and bromide ion. Their data are fitted by a second order rate law, and the following values of the specific rate constant and activation energy are reported:

<table>
<thead>
<tr>
<th>Reactant</th>
<th>$k_2$ (mol⁻¹ sec⁻¹)</th>
<th>$\Delta F^\ddagger$ (k cal mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3\text{Br}$</td>
<td>$5.42 \times 10^{-5}$</td>
<td>17.5</td>
</tr>
<tr>
<td>$\text{CH}_2\text{Br}_2$</td>
<td>$3.1 \times 10^{-5}$</td>
<td>26.6</td>
</tr>
<tr>
<td>$\text{CHBr}_3$</td>
<td>$3.2 \times 10^{-5}$</td>
<td>28.0</td>
</tr>
<tr>
<td>$\text{CBr}_4$</td>
<td>$1.6 \times 10^{-4}$</td>
<td>20.3</td>
</tr>
</tbody>
</table>

This work suggests that while with $\text{CBr}_4$, the mechanism is ionic, the other bromo compounds probably react via a molecular reaction path.

The same authors have also studied the exchange between isopropyl bromide and bromide ion in 90% alcohol (N4). An ionic mechanism is again suggested as accounting for their data. The slower exchange rates for the iso isomers, compared to the normal halides, are presumably due to greater π - σ interaction between the carbon atom and the halide ion in the former. This interaction would tend to increase $\Delta F^\ddagger$ and hence to slow the exchange rate.

The exchange reaction between mercuric bromide and Me, Et, Pr and Bu mercuric bromides in alcoholic solution has been found (N3) to be extremely rapid, being cited as evidence for the ionic nature of the HgBr bond in aliphatic mercury compounds.

Goldman and Noyes (G4) have found the kinetics of the halogen exchange between benzoyl bromide and bromine to satisfy a rate law of the form $R = k_2 (\text{BzBr}) (\text{Br}_2) + k_3 (\text{BzBr}) (\text{Br}_2)^2$. Experimental values of the kinetic parameters reported are:
The authors suggest that the 2nd order term supports an ion-pair mechanism of the type

\[
\begin{array}{c}
\text{O} \\
+ \text{X}_3^-
\end{array}
\]

while the 3rd order term presumably involves either

\[
\begin{array}{c}
\text{O} \\
+ \text{X}_5^-
\end{array}
\]

or

\[
\begin{array}{c}
\text{O}^+ \\
+ \text{X}_3^-
\end{array}
\]

The reactions appear not to involve contributions from radical mechanisms, even under illumination. The rates appear to be sensitive to dielectric constant of the solvent and to moisture, strengthening the evidence for the ionic reaction paths suggested.

**Iodine**

*Aqueous Solution.* In contrast to the results reported by earlier investigators (C2) who found a slow exchange reaction between iodine and periodate, Pavlov and Fialkov (P2) were unable to find evidence for the transfer of iodine -131 activity in 208 hours at 18°C in 2.5M H2SO4 or in 140 hours in 0.5M HNO3. They were also unable to observe halogen exchange in the systems ICl-I03- and ICl-I04- in 35-38 hours at 18°C. Exchange was however observed between ICl and I2 in 0.4M HCl, complete randomization of tracer occurring within 5 minutes. The exchange is postulated to proceed via the mechanism

\[
\text{ICl} + \text{I}_2 \rightleftharpoons \text{I}_3 \text{Cl}
\]

although no structural details of the intermediate complex are suggested.

*Non-aqueous Solution.* Kahn and Riebsomer (K1) have measured the exchange between p-fluorobenzyl iodide and KI in methanol and ethanol, and find the exchange in both cases to fit a rate law which is first order in each of the two reactants. The reported activation energies - 16.32 ± 0.45 k cal mol⁻¹ in methanol, and 16.58 ± 0.10 k cal mol⁻¹ in ethanol - suggest identical mechanisms in the two solvents. No evidence for first order dissociation of the organic iodide as a rate determining step is noted.
Two studies with iodobenzene have been reported with rather different mechanisms cited as responsible for the observed exchange. Levine and Noyes (L2) investigated the exchange with molecular iodine in hexachlorobutadiene, and find their data fit the rate law

\[ R = k_r (\phi I) (I_2) \frac{1}{2} + k_p (\phi I)^2 \]

in which the first term represents a radical-molecular path, while the second represents a polar molecular path. In hexachlorobutadiene \( k_p > k_r \), but in nitrobenzene, the radical mechanism appears to account for essentially all of the observed exchange. These authors also report the exchange between p-nitro iodobenzene and \( I_2 \) in the chlorinated solvent to be slower than the analogous iodobenzene exchange, and to be entirely due to the radical path.

Manno and Johnston (M2) in a study of very slow exchange reactions, observed the iodobenzene-KI exchange to have a half time of about 400 years in the range 16 to 46°C. It is suggested by these authors that the reaction proceeds by a combination of homogeneous (\( \Delta E^+ \sim 3.7 \text{ k cal mol}^{-1}, \Delta S^+ \sim -0.6 \text{ e.u.} \)) and heterogeneous (\( \Delta E^+ \sim 10.7 \text{ k cal mol}^{-1} \)) mechanisms. The slowness of the exchange is presumably due to the very large entropy of activation required for forming the activated complex. No mechanism for the exchange is proposed.

The exchange between ICN and \( I_2 \) and \( I^- \) has been studied by Jenkins and Harris (J1) under a wide variety of conditions. In water, water-dioxane, acetone and ethanol solutions, and over the temperature range -78 to 30.2°C, the exchange in both cases is rapid and complete. Although separation induced exchange is not ruled out, the authors suggest that the data are explained by the rapid equilibria

\[
\text{ICN} + I^- \rightleftharpoons I^-_2 \rightleftharpoons I^*_2 \rightleftharpoons I^*_2 \rightleftharpoons I^* \rightleftharpoons I^* + I^- \\
\text{ICN} + I^- \rightleftharpoons I^-_3 \rightleftharpoons I^*_3 \rightleftharpoons I^*_3 \rightleftharpoons I^* + I^-_3
\]

Darbee and Harris (D2) found that the iodine exchange between ethyl iodide and \( I_2 \) in the temperature range 45-70°C was fitted by the first order rate law \( R = k_1 (I_2) \) with \( E^1 \sim 19.5 \text{ k cal mol}^{-1} \). The ratio of exchange rates between MeI, EtI, and nPrI with \( I_2 \) were found to be dependent on the \( I_2 \) concentration, as shown by the following data:

<table>
<thead>
<tr>
<th>Relative Rates</th>
<th>MeI</th>
<th>EtI</th>
<th>nPrI</th>
</tr>
</thead>
<tbody>
<tr>
<td>( I_2 = 0.22 \text{ M liter}^{-1} )</td>
<td>8.5</td>
<td>1.0</td>
<td>0.74</td>
</tr>
<tr>
<td>( I_2 = 0.12 \text{ M liter}^{-1} )</td>
<td>6.6</td>
<td>1.0</td>
<td>0.64</td>
</tr>
</tbody>
</table>
The mechanism suggested to explain these results postulates the formation of 1:1 complex between the organic iodide (in excess) and solute I₂. Presumably in an inert solvent the rate law would correspond to second order kinetics.

The theoretical work of Swart and Le Roux (S3) cited above, was suggested on the basis of their study of the MeI - I⁻ exchange in various solvents. Their data may be summarized as follows:

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Diel const</th>
<th>ΔH⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>81.07</td>
<td>18.1 k cal mol⁻¹</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>~ 50</td>
<td>16.8</td>
</tr>
<tr>
<td>MeOH</td>
<td>31.2</td>
<td>16.0</td>
</tr>
<tr>
<td>EtOH</td>
<td>25.8</td>
<td>15.6</td>
</tr>
<tr>
<td>Acetone</td>
<td>26.6</td>
<td>13.5</td>
</tr>
</tbody>
</table>

Among these solvents, the rate is found to vary by a factor of 10⁵, and the observed effects appear to be in agreement with the ion-dipole treatment suggested.

Gas Phase. The exchange between methyl iodide and both HI and I₂ has been investigated by Schmiedt and Fink (S4) who find their data obeys a two term rate-law of the form R=k₁ (MeI) + k₂ (MeI) (I₂) for the latter. The activation energy was found to be a function of the nature of the surface of the reaction vessel, the best value of 9.0 k cal mol⁻¹ being obtained for quartz, which had been baked out overnight at 550°c. Under these conditions (e.g. negligible zero-time, reproducible kinetic data), the activation entropy was found to be -31 cal deg⁻¹ mol⁻¹. Schmiedt and Fink, interpret the second order term of their rate law as suggesting a 1:1 complex between MeI and I₂, similar to that suggested by Darbee and Harris (D2) in the case of ethyl iodide. The unimolecular reaction path is interpreted to arise from a free radical mechanism on the surface of the reaction vessel:

\[
\text{CH₃I} \rightleftharpoons \text{CH₃}^+ + \text{I}^- \quad \text{slow}
\]

\[
\text{I}^- + \text{I}_2^* \rightleftharpoons \text{I}_2^* + \text{I}^- \quad \text{rapid}
\]

or

\[
\text{CH₃}^+ + \text{I}_2^* \rightleftharpoons \text{CH₃I}_2^* + \text{I}^- \quad \text{rapid}
\]

In agreement with the earlier work on the HCl - Cl₂ exchange, the HI - I₂ exchange is found to be too rapid to be followed kinetically. The data of Magnuson and Wolfenden (M3) suggests that the exchange in CCl₄ solvent may involve an HI₃ intermediate, although no direct evidence for such a complex appears as yet at hand.
ACKNOWLEDGEMENT

The author is indebted to Professor G. T. Seaborg and the Chemistry Group of the Radiation Laboratory, University of California, for providing facilities to prepare the present review. This work was supported in part by the U. S. Atomic Energy Commission, the University of Illinois, and the University of California.

Noyes Laboratory, University of Illinois, and Radiation Laboratory, University of California

1 August 1958
### Table 1

**Properties of Some Halogen Nuclides**

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Half Life</th>
<th>Decay Mode</th>
<th>Gamma Energies in Mev</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^9$Br$^{18}$</td>
<td>112 min</td>
<td>$97% \beta^+(0.649\text{MeV})$</td>
<td>none</td>
</tr>
<tr>
<td>$^{17}$Cl$^{36}$</td>
<td>3.08x10$^5$ yrs</td>
<td>$98% \beta^-(0.714\text{MeV})$</td>
<td>none</td>
</tr>
<tr>
<td>$^{17}$Cl$^{39}$</td>
<td>55.5 min</td>
<td>$\beta^-(1.91\text{MeV})$</td>
<td>0.246, 1.27, 1.52</td>
</tr>
<tr>
<td>$^{35}$Br$^{80m}$</td>
<td>4.38 hour</td>
<td>I.T.</td>
<td>0.049, 0.037</td>
</tr>
<tr>
<td>$^{39}$Br$^{80}$</td>
<td>17.6 min (usually in equil. with $^{35}$Br$^{80m}$)</td>
<td>$92% \beta^-(1.99\text{MeV})$</td>
<td>0.62</td>
</tr>
<tr>
<td>$^{35}$Br$^{82}$</td>
<td>35.87 hour</td>
<td>$\beta^-(0.444\text{MeV})$</td>
<td>0.554, 0.618, 0.6984, 0.7769, 0.8276, 1.044, 1.317, 1.475</td>
</tr>
<tr>
<td>$^{53}$I$^{131}$</td>
<td>8.08 day</td>
<td>$\beta^-(0.608\text{MeV})$</td>
<td>0.080, 0.163, 0.264, 0.364, 0.637, 0.722</td>
</tr>
</tbody>
</table>
### Table 2
Classification of Exchange Reactions

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Atom Transfer</th>
<th>Free Radical or Hot Atom</th>
<th>Common-Ion Pool</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symbol</td>
<td>T</td>
<td>F</td>
<td>I</td>
</tr>
<tr>
<td>Scheme</td>
<td>AX</td>
<td>BX*</td>
<td>AX</td>
</tr>
<tr>
<td></td>
<td>[AXBX^*]</td>
<td></td>
<td>(A^+ + X^-)</td>
</tr>
<tr>
<td></td>
<td>AX*</td>
<td>BX</td>
<td>A + X*</td>
</tr>
<tr>
<td></td>
<td>AX*</td>
<td>BX</td>
<td>AX*</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Occurrence</th>
<th>Gas or Liquid</th>
<th>Gas or Liquid (solid for hot atom)</th>
<th>Liquid (solution)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent sens.</td>
<td>Solvent insensitive</td>
<td>Solvent insensitive (if solvent is not a free radical scavenger)</td>
<td>Solvent sensitive</td>
</tr>
<tr>
<td>Ionic Strength sens.</td>
<td>Inensitive</td>
<td>----</td>
<td>Sensitive</td>
</tr>
<tr>
<td>Rate range</td>
<td>Usually slow</td>
<td>May be rapid</td>
<td>Usually rapid to v. rapid</td>
</tr>
<tr>
<td>(E^+) range</td>
<td>May be large</td>
<td>May be large</td>
<td>Usually small</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(May involve highly energetic excited states)</td>
<td></td>
</tr>
</tbody>
</table>
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