

The Approximate Rate of Exchange between Iodine Atoms and Molecules

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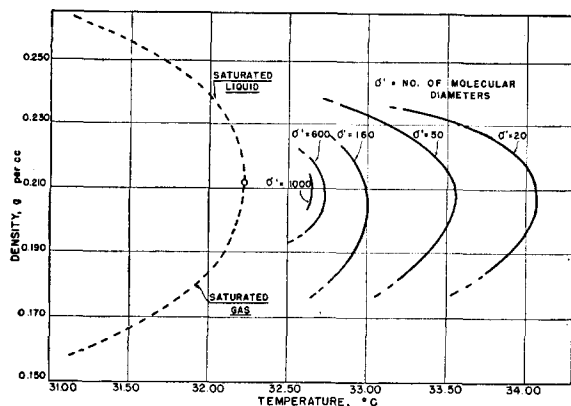


FIG. 5. Distance of molecular interaction or cluster diameter (expressed in molecular diameters) calculated from Ornstein and Zernike's equation. (Based on the scattering of the green and blue lines.)

The dependence of scattering on wave-length is shown in Fig. 4. In this case, runs were made far enough down into the mixed liquid-vapor phase to indicate that the λ^{-4} -law applies less than a degree below the critical point.

Cluster diameters calculated from Eq. (5) of the previous article are shown in terms of molecular diameters in Fig. 5.

From the results of those introductory works it can be seen that no theory so far developed completely describes the phenomena in the critical region. For a complete test, it will be necessary to obtain more accurate densities (in this work they were limited by the accuracy of one p.s.i. in the pressure reading) and to measure transmitted as well as scattered light. Both these refinements are being undertaken in this laboratory.

The Approximate Rate of Exchange between Iodine Atoms and Molecules

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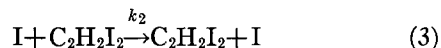
The rate constant for the exchange reaction of iodine atoms with iodine molecules in hexane at 25° has been estimated by an indirect method. The rate constant is approximately 1.3×10^{-13} (atom/ml) $^{-1}$ sec. $^{-1}$ or 8×10^{10} (mole/ml) $^{-1}$ sec. $^{-1}$. The energy of activation for the exchange is probably between 2 and 3 kilocalories.

INTRODUCTION

THE exchange reactions between halide ions and halogen molecules are known to proceed rapidly. Dodson and Fowler¹ showed that bromide and iodide ions exchange completely with the corresponding halogens in less than 1 minute, and Halford² from a comparison of competing reactions showed that the rate constant for the formation of trichloride ion from chlorine and aqueous chloride ion lies between 6.7×10^6 and 1.7×10^{13} (mole/ml) $^{-1}$ sec. $^{-1}$. There do not appear to be any corresponding data on the isotopic exchange between halogen atoms and molecules. In fact, to our knowledge the ortho-para conversion of hydrogen³ is the only study of the rate of exchange of a neutral atom with a diatomic molecule of the same element.

In connection with a study⁴ of the exchange of iodine

atoms with *trans*-diiodoethylene in hexane solution at 25°, it became apparent that the data provided an approximate rate constant for the exchange reaction between iodine atoms and molecules. If a solution of iodine and *trans*-diiodoethylene is illuminated with visible light, the following processes take place:



where reactions (3) and (4) represent exchanges which can be followed with the use of isotopic tracers, and the k 's are rate constants (in (atom/ml) $^{-1}$ sec. $^{-1}$) for the indicated reactions. Let us adopt the following conventions:

q_a = number of quanta absorbed per ml per second,

ϕ = primary quantum yield of process (1) so defined that $\phi = 1$ corresponds to the formation of two iodine atoms for each quantum absorbed,

I = concentration of iodine atoms per ml,

* Based on a Dissertation submitted by Joseph Zimmerman to the Faculty of Pure Science of Columbia University in partial fulfillment of the requirements for the Ph.D. degree in Chemistry.

¹ R. W. Dodson and R. D. Fowler, J. Am. Chem. Soc. **61**, 1215 (1939).

² R. S. Halford, J. Am. Chem. Soc. **62**, 3233 (1940).

³ K. H. Geib and P. Harteck, Zeits. f. physik. Chemie (Bodenstein Festband), 849 (1931); A. Farkas and L. Farkas, Proc. Roy. Soc. **152A**, 124 (1935).

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

a = concentration of iodine molecules in any convenient units,

b = concentration of *trans*-diiodoethylene in the same units as a , and

x = fraction of iodine-131, initially all present as I_2 , which is present in I_2 at time t .

If it is assumed^{4,5} that the distribution of iodine-131 in the atoms and molecules is the same, the rate of exchange with the diiodoethylene is given by

$$-d(2ax)/dt = k_2 I[(a+b)x - a]. \quad (5)$$

However, process (3) will, on the average, result in a change in the distribution of radioactivity only if the entering iodine atom last reacted by process (1) or (4); if the iodine atom last reacted by process (3), an additional exchange with diiodoethylene will not be detected. At any instant the fraction of iodine atoms which last reacted by process (1) or (4) rather than by process (3) is

$$\frac{2\phi q_a + k_4 a I}{2\phi q_a + k_4 a I + k_2 b I}. \quad (6)$$

Then the corrected expression for the rate of transfer of radioactivity to the diiodoethylene is

$$-\frac{d(2ax)}{dt} = k_2 I[(a+b)x - a] \frac{2\phi q_a + k_4 a I}{2\phi q_a + k_4 a I + k_2 b I}. \quad (7)$$

This equation reduces to Eq. (5) if $(2\phi q_a + k_4 a I) \gg k_2 b I$, which will be the case except in weak light and a very high value of b/a . In our experiments $b \gg a$, and the runs were stopped when $b x \gg a$. Then integration of Eq. (7) leads to

$$-\ln x = \frac{k_2 b I (2\phi q_a + k_4 a I)}{2a(2\phi q_a + k_4 a I + k_2 b I)} \quad (8)$$

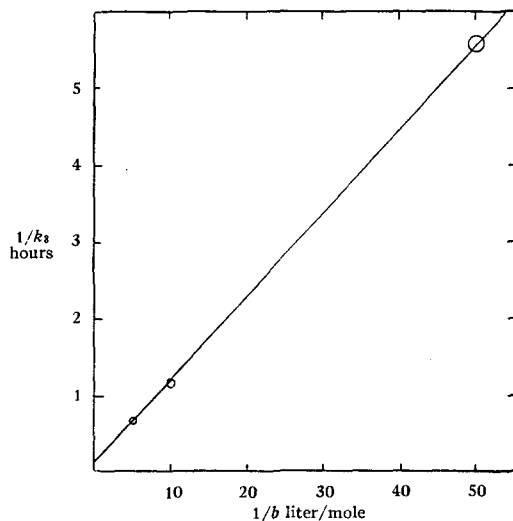


FIG. 1. Relation between rate of exchange and concentration of diiodoethylene.

⁵ Noyes, Dickinson, and Schomaker, J. Am. Chem. Soc. 67, 1319 (1945).

TABLE I. Effect of diiodoethylene concentration on rate of exchange.*

b = Conc. $C_2H_2I_2$ (moles/liter)	k_2 hours ⁻¹	Average k_2	k_2/b (moles/ liter) ⁻¹ hr. ⁻¹
2.00×10^{-2}	0.179	0.179	8.95
	0.179		
1.00×10^{-1}	0.856	0.861	8.61
	0.866		
2.00×10^{-1}	1.504	1.494	7.47
	1.484		

* Conditions: a = Conc. $I_2 = 3.46 \times 10^{-5}$ moles/liter. $q_a = 2.7 \times 10^{11}$ quanta/ml sec. Temp. = 25.0°. $\lambda = 436$ mμ.

TABLE II. Rate constants for reactions of iodine atoms in hexane.

Rate constant $k = CT^{1/2} e^{-E/RT}$	Value at 25° (atom/ml) ⁻¹ sec. ⁻¹	$CT^{1/2}$ at 25° (atom/ml) ⁻¹ sec. ⁻¹	E cal./mole
k_1	1.8×10^{-11}		
k_2	4.3×10^{-18}	7.5×10^{-12}	8500 ⁶
k_4	1.3×10^{-13}		

and $-\log x = k_3 t$ where

$$1/k_3 = \frac{4.605a}{k_2 I b} + \frac{4.605a}{2\phi q_a + k_4 a I} = A/b + B. \quad (9)$$

For a series of runs in which a and ϕq_a are constant, if $1/k_3$ is plotted against $1/b$, a straight line should be obtained from whose slope and intercept it is possible to calculate k_2 and k_4 .

EXPERIMENTAL RESULTS

The procedure for carrying out the exchange experiments has been described elsewhere.⁴ In Table I are presented the results of a series of experiments performed in a degassed system with the same solution of radioactive iodine and different concentrations of diiodoethylene. The data demonstrate that the apparent first-order rate constant falls off as b is increased, and the plot in Fig. 1 shows that Eq. (9) is obeyed to the precision of the experiments.

DISCUSSION

The best values of A and B from Eq. (9) are $A = 0.109$ (mole-liter) hour and $B = 0.106$ hour. Then $A/B = 1.02$ mole/liter. If we use the modified value of Rabinowitch and Wood^{4,6} that $I/q_a^{1/2} = 1.8 \times 10^5$, then $k_2 = 4.34 \times 10^{-18}$ (atom/ml)⁻¹ sec.⁻¹ = 2.61×10^6 (mole/ml)⁻¹ sec.⁻¹. Also, $A/B = (2\phi q_a + k_4 a I)/k_2 I = (1/\tau_s + k_4 a)/k_2$, where τ_s is the mean lifetime of an atom chain and is of the order of 0.31 sec.⁴ Then $k_4 = 1.3 \times 10^{-13}$ (atom/ml)⁻¹ sec.⁻¹ = 8×10^{10} (mole/ml)⁻¹ sec.⁻¹. The precision of duplicate runs in Table I indicates that A is prob-

⁶ E. Rabinowitch and W. C. Wood, Trans. Faraday Soc. 32, 547 (1936).

ably known to at least ± 2 percent; the uncertainty in the absolute value of k_2 is considerably greater because the calculation involves the photo-stationary concentration of iodine atoms. The data do not permit an accurate evaluation of k_4 , but it does not appear that this quantity can be less than 0.6×10^{-13} nor more than 2×10^{-13} .

Since the experiments were only carried out at one temperature, we do not know the energy of activation for process (4). However, certain limits can be set with some confidence by comparison with the rates of other iodine atom reactions in the same solvent. The pertinent data on these reactions are presented in Table II.

A decision as to activation energy depends upon whether the exchange of iodine atoms with molecules is activation controlled or diffusion controlled.

If process (4) is activation controlled, it can presumably be fitted by an equation of the form $k = CT^{\frac{1}{2}}e^{-E/RT}$ where E is the energy of activation for the exchange. The configurational requirements for the exchange of an atom with an iodine molecule can hardly be more severe than those for exchange with a diiodoethylene molecule. Then 7.5×10^{-12} is a lower limit to $CT^{\frac{1}{2}}$ at 25° , and 2.4 kcal. is a lower limit for the activation energy. On the other hand, $CT^{\frac{1}{2}}$ can hardly be greater than 9.2×10^{-11} , the calculated⁴ rate constant for the collision of iodine atoms in the gas phase. Hence the maximum activation energy is 3.9 kcal.

The activation energies in the preceding paragraph are of the order of magnitude to be expected for dif-

fusion processes. It therefore seems profitable to compare the rate of process (4) with the rate of recombination of iodine atoms, which is presumably a diffusion-controlled reaction which proceeds without activation energy. If the difference between k_1 and k_4 is entirely an energy effect, the energy of activation for the exchange of atoms and molecules is 2.9 kcal. Actually, the energy of activation can be expected to be somewhat less because of steric requirements for the $I + I_2$ reaction which are lacking in the recombination of atoms.

If the energies of activation for the diffusion and exchange reactions are almost equal, the interpretation of the data is more complicated, but the range of permissible activation energies should not be much affected. It therefore appears that the energy of activation of the process almost certainly lies between 2 and 3 kilocalories, but it cannot be determined with precision. This result is in agreement with the 2.0 kcal. calculated with the assumption⁷ that the activation energy is 5.5 percent of the energy of the bond that is broken.

ACKNOWLEDGMENT

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One of us (JZ) is indebted to the Allied Chemical and Dye Corporation for a fellowship.

⁷ J. O. Hirschfelder, J. Chem. Phys. **9**, 645 (1941).

The Primary Quantum Yield of Dissociation of Iodine in Hexane Solution

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The primary quantum yield for the photo-dissociation of iodine in degassed hexane at 25° has been calculated from measurements of the mean lifetime of the chains involved in the exchange of iodine atoms with *trans*-diiodoethylene. The primary quantum yield to an accuracy of ± 15 percent is 0.59 at 436 $m\mu$ and 0.37 at 578 $m\mu$. The deviation of this quantity from unity is affected both by the "primary recombination" of atoms which fail to escape from the original "cage" of solvent molecules, and by the "secondary recombination" of the original atoms by diffusion during a time which is very short compared to that in which either is apt to encounter an atom from another molecule.

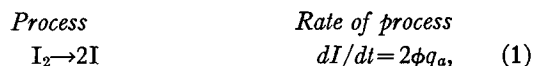
The specific rate constant for the recombination of iodine atoms in hexane solutions has been determined and has been shown to be about one fifth of the rate constant for collision in the gas phase.

The presence of air decreases the rate constant for the photochemical exchange of iodine with diiodoethylene by a factor of four and increases the apparent mean lifetime of iodine atoms by a factor of one hundred.

INTRODUCTION

WHEN a solution of iodine in a non-polar solvent such as hexane is illuminated with visible light of suitable wave-length, dissociation of the iodine to

atoms occurs according to the following equations:



where q_a is the number of quanta absorbed per ml per second, ϕ is the primary quantum yield of dissociation so defined that $\phi = 1$ corresponds to two iodine atoms

* Based on a Dissertation submitted by Joseph Zimmerman 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 obtain a microfilm thereof may address the Library, Columbia University, New York, New York.