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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

Kinetics of the Thermal Exchange between Iodine and Allyl Iodide

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Allyl iodide and molecular iodine exchange thermally in hexane solution at room temperature. Apparently most of the exchange takes place by a bimolecular mechanism with an energy of activation of 13.1 kcal./mole and an entropy of activation of −27 cal./mole deg. No other organic halide has been observed to exchange with the free halogen by a non-atomic mechanism. We propose that the exchange involves the interaction of the molecular iodine with the double bond to form an activated complex having a configuration very similar to the unknown glycerol triiodide.

Introduction

Preliminary studies[2] indicated that iodine in non-polar solvents exchanges with allyl iodide more rapidly than with any other organic iodide yet investigated. The reaction is greatly accelerated by visible light, and the present study was undertaken to obtain quantitative kinetic information. It was anticipated that exchange would proceed entirely through a mechanism involving iodine atoms, but the thermal studies indicate a non-radical mechanism involving molecular iodine.

Experimental

Materials.—The hexane solvent was freed of unsaturated material with fuming sulfuric acid as described previously.[3] It did not react with iodine even under strong illumination.

Commercial allyl iodide was purified in a dark room. The purification consisted of washing with aqueous sodium sulfite to remove free iodine, drying with magnesium sulfate, and distilling at 21 mm. The resulting very pale yellow liquid was weighed rapidly in a dimly-lighted room and dissolved immediately in hexane. Such a solution could be stored in a light-tight container at −5° for up to three months before traces of iodine coloration appeared. The remaining solution was discarded as soon as any coloration was observed. Different batches of allyl iodide prepared by this procedure gave identical kinetic results within the precision of the measurements.

Commercial resublimed reagent-grade iodine was used without further purification. Solutions in hexane were rendered radioactive by equilibration with aqueous carrier-free solutions of iodine-131 obtained on allocation from the United States Atomic Energy Commission.

Procedure.—The reactions were carried out in 250-ml. glass-stoppered flasks fitted with a center well of approximately 6-ml. capacity. In some cases the flask had a side-arm attachment to permit bubbling gas through the contents. All flasks were covered with an opaque coating of black glyptal.

At the start of a run, the radioactive iodine was pipetted into the center compartment and the allyl iodide into the outside. The only light available during the pipetting of the allyl iodide was provided by a ruby dark-room light. The flask was brought to temperature in a water (or ice and water) thermostat, shaken, and placed in a closed can in the thermostat.

At the completion of the run, the reaction was stopped by the addition of dilute aqueous sulfite. The liquid layers were separated, and the activity of the aqueous layer was measured and compared with that of a control solution containing the same amount of unreacted iodine-131.

Tests for Undesirable Effects.—When identical solutions reacted for different times, the results could be fitted to the standard rate expression for an isotopic exchange reaction, and the equilibrium distribution of radioactivity closely approached the calculated value. Therefore, the allyl iodide did not contain significant amounts of impurities exchanging at different rates.

The solution resulting from one exchange experiment was examined for evidence of other iodides. After the iodine had been extracted, toluene and xylene were added in order to provide a carrier for the allyl iodide and to ensure a residue after the distillation. The solution was then distilled at atmospheric pressure, and the radioactivity in the different fractions was measured. A plot of activity against boiling point gave a single sharp peak at the boiling point of allyl iodide.

Spectrophotometric studies demonstrated that the concentration of free iodine in these solutions did not change during the course of a run. All of the above tests indicate that we were studying a simple exchange reaction without complicating side effects.

In some experiments, the air in the reaction flask was swept out with "prepurified" nitrogen or oxygen. The rate under nitrogen was faster than that under air, but the increase was never more than 12%. At 15°, oxygen appeared to increase the rate slightly.

Some unsuccessful attempts were made to measure the

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

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

rate in degassed solutions by means of a technique described previously.[4] However, the reaction was sensitive to uncontrolled factors connected with the preparation of sealed ampules containing reactants. Rates estimated by this technique scattered by a factor of five or more but usually bracketed the rates obtained in air. We conclude that oxygen has little if any effect on the rate of the thermal exchange reaction.

Some solutions were dried with drierite, and others were treated with a few drops of water. The rates were indistinguishable from those observed in untreated solutions.

Results

The results of the 196 individual thermal exchange runs are summarized in Table I. Each line in this table is based on a series of from 4 to 10 runs at the same iodine concentration. In each of these series, the concentration of allyl iodide was varied over a range of 20- to 50-fold. The rate of exchange, R, for every run was calculated with the standard expression

$$R = -\frac{2ab}{(2a + b)t}\ln\left[1 - \frac{2a}{b}(1 - x)\right] \qquad (1)$$

where a is the concentration of molecular iodine, b is the concentration of allyl iodide (AI) and x is the fraction of the radioactivity (initially all present in the iodine) which was present in the iodine at time t.

In Fig. 1 we present a typical plot for a series of runs at constant iodine concentration. In every series of runs, R varied linearly with the concentration of allyl iodide, but the best straight line through the points usually gave a small positive intercept at zero concentration of allyl iodide.

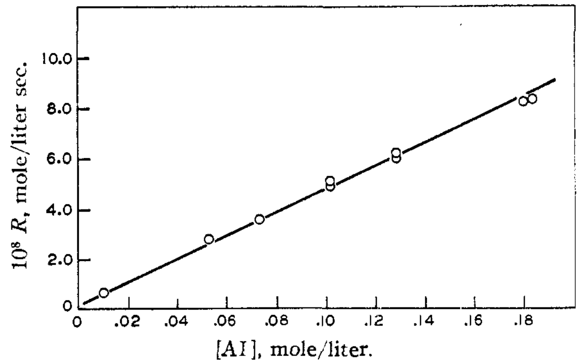

Fig. 1.—Rate of thermal exchange at 0.0°: iodine concentration, 5.975×10^{-4} M.

The data could be interpreted most satisfactorily by assuming that most of the exchange proceeded through a second-order mechanism which was first order in each of the reacting species. The rate of the small additional exchange reaction appeared to be proportional to the concentration of iodine and roughly independent of the concentration of allyl iodide. In order to separate out the contribution due to the second-order reaction, the pseudo first-order constant was evaluated for each series of runs at constant iodine concentration. This constant was regarded as the limiting slope of a plot like that in Fig. 1; it was evaluated by plotting $R/[\mathrm{AI}]$ against $1/[\mathrm{AI}]$ and extrapolating the plot to $1/[\mathrm{AI}] = 0$. The second-order rate constant, k, was calculated by dividing the limiting slope by the concentration of iodine. The data presented in Table I show that this treatment gives rate constants which are satisfactory over a range of up to 100-fold in iodine concentration.

TABLE I

THERMAL EXCHANGE BETWEEN IODINE AND ALLYL IODIDE

Temp., °C.	$[I_2]$, mole/liter	Limiting slope $R/[\mathrm{AI}]$, sec.$^{-1}$	$10^4 k$, liter/mole sec.
0.0	5.731×10^{-5}	4.83×10^{-8}	8.43
	3.252×10^{-4}	2.44×10^{-7}	7.50
	5.975×10^{-4}	4.38×10^{-7}	7.34
	3.262×10^{-3}	2.42×10^{-6}	7.42
	5.925×10^{-3}	4.54×10^{-6}	7.66
		Average	7.67 ± 0.26
15.0	4.120×10^{-5}	1.09×10^{-7}	26.5
	1.197×10^{-4}	2.53×10^{-7}	21.1
	4.234×10^{-4}	1.00×10^{-6}	23.6
		Average	23.7 ± 1.5
25.0	4.071×10^{-5}	2.30×10^{-7}	56.5
	6.094×10^{-5}	3.59×10^{-7}	58.9
	6.382×10^{-5}	3.45×10^{-7}	54.1
	1.085×10^{-4}	7.40×10^{-7}	68.2
	1.19×10^{-4}	6.50×10^{-7}	54.6
	2.026×10^{-4}	1.06×10^{-6}	52.3
	4.184×10^{-4}	2.38×10^{-6}	56.9
	2.038×10^{-3}	1.15×10^{-5}	56.4
	3.060×10^{-3}	2.13×10^{-5}	69.6
	5.621×10^{-3}	4.29×10^{-5}	76.3
		Average	60 ± 5
35.0	4.016×10^{-5}	4.50×10^{-7}	112.1
	6.297×10^{-5}	7.47×10^{-7}	118.6
	1.070×10^{-4}	1.20×10^{-6}	112.1
	2.520×10^{-4}	2.90×10^{-6}	115.1
	4.127×10^{-4}	4.84×10^{-6}	117.3
		Average	115.0 ± 1.8
40.0	5.965×10^{-5}	1.07×10^{-6}	179
	1.095×10^{-4}	1.80×10^{-6}	164
	2.995×10^{-3}	5.35×10^{-5}	179
	5.502×10^{-3}	9.7×10^{-5}	176
		Average	174 ± 4

The temperature dependence of the rate constant was treated by conventional methods. Calculations by a weighted method of least squares indicated that $k = 10^{(7.39 \pm 0.14)}e^{-(13,140 \pm 200)/RT}$ liter/mole sec. The entropy of activation[5] at 25° is -26.7 ± 0.6 cal./mole deg. when the standard state is in mole/liter.

Discussion

The data demonstrate beyond question that most of the thermal exchange proceeds by a bimolecular mechanism involving iodine molecules. As far as we are aware, atomic mechanisms have been postulated to account for all other data on exchange reactions between organic halides and free halogens. The unusually negative entropy of activation suggests that the bulky iodine atoms impose rather severe steric restrictions on the transi-

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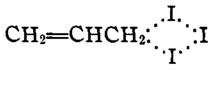
(4) H. Steinmetz and R. M. Noyes, THIS JOURNAL, **74**, 4141 (1952).

(5) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 199.

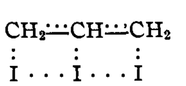
tion state and limit the types of motion available to it.

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



$$CH_2{=}CHCH_2\!:\!\overset{.I.}{\underset{\cdot I\cdot}{\quad}}\!:\!I$$

I



$$\begin{array}{ccccc} CH_2 & \cdots & CH & \cdots & CH_2 \\ \vdots & & \vdots & & \vdots \\ I & \cdots & I & \cdots & I \end{array}$$

II

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.

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Kinetics of the Photochemical Exchange between Iodine and Allyl Iodide

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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 paper[2] 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.[3] 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. 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

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

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