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[CONTRIBUTION FROM THE CHANDLER LABORATORY OF COLUMBIA UNIVERSITY]

Detailed Mechanisms of Exchange Reactions between Iodine and Allyl Iodide

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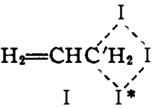
Allyl iodide-1-C^{14} has been prepared, and thermal and photochemical rates have been measured for the iodine induced isomerization to allyl iodide-3-C^{14}. The rate of thermal isomerization is about 20% of the rate at which iodine molecules exchange with allyl iodide, and the atom induced photochemical isomerization is about 50% of the rate at which iodine atoms exchange with allyl iodide. The data seem to require that both molecules and atoms of iodine can add to allyl iodide to form π-complex intermediates in which iodines become equivalent more easily than the two end carbons can become chemically identical.

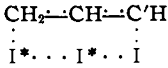
Introduction

Previous kinetic studies demonstrated that two distinct mechanisms are available for the isotopic exchange of allyl iodide with elementary iodine. In the dark at room temperature, the kinetics indicate that the facile exchange reaction involves iodine *molecules*.[3] If solutions are illuminated, the rate of exchange is greatly increased,[4] and this additional reaction certainly involves iodine *atoms*. A complex kinetic analysis of the quantum yields indicated that the atomic mechanism involves a direct substitution in which one iodine atom enters the molecule and the original one leaves either simultaneously or by dissociation of a short-lived metastable intermediate.

Two alternative structures were suggested for the transition state associated with each mechanism. For the molecular mechanism, these structures were



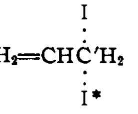
I



II

In these structures and in all subsequent ones, an asterisk (*) is used to designate an iodine atom originally present in the element, and a prime (′) is used to designate the carbon atom to which the organic iodine was attached originally. These designations correspond to the initial positions of the isotopic tracers in the experiments described below.

For the atomic mechanism, alternative structures III and IV were proposed.



III

$I^{*}..CH_2\dot{-}\!\!-\!\dot{-}CH\dot{-}\!\!-\!\dot{-}C'H_2\cdot\cdot I$

IV

Structures I and III involve mechanisms in which the entering and leaving iodine interact simultaneously with the saturated carbon atom; structures II and IV involve mechanisms in which the entering iodine interacts with the double bond. Also, exchanges through structures I and III produce allyl iodide in which the new iodine is attached to the same carbon atom that was occupied originally; while exchanges through structures II and IV produce allyl iodide in which the other end carbon is now occupied by iodine.

Sibbett and Noyes[3,4] expressed preferences for structures II and IV on the basis of the exchange kinetics of benzyl iodide. In general, allyl and benzyl compounds have comparable bond strengths and react at about the same rates. However, benzyl iodide does not appear to undergo any exchange with iodine molecules, and the rate of exchange with atoms is only about 1% of the rate for allyl iodide.[5] These differences in reactivity indicate that the double bond in allyl iodide facili-

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(1) Based on the Ph.D. Dissertation of William P. Cain. The original dissertation and microfilms thereof are available from the Library of Columbia University.

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

(4) D. J. Sibbett and R. M. Noyes, *ibid.*, **75**, 763 (1953).

(5) M. Gazith and R. M. Noyes, *ibid.*, **77**, 6091 (1955).

tates exchange in a way that is not available to benzyl iodide.

A more specific test of mechanism is to determine whether exchange is accompanied by a shift in the carbon to which the iodine is attached. One method that was considered was to distinguish the carbons by attaching a methyl group to one as was done by England and Hughes[6] in their clever demonstration of the S$_N$2′ reaction between bromide ion and the methyl allyl bromides. However, the 1-methyl and 3-methyl allyl iodides apparently have never been prepared separately, and interconversion is very rapid.[7]

The procedure finally selected was suggested by the synthesis of allyl bromide-1-C^{14} by Nystrom and Leak.[8] The corresponding allyl iodide was synthesized by a similar procedure, and the distribution of carbon-14 was determined by ozonizing the allyl iodide and isolating the number-3 carbon as formaldehyde. Then simultaneous tracer experiments with carbon and iodine were used to measure R_{isom}, the rate of the isomerization reaction

$$CH_2{=}CHC'H_2I \longrightarrow ICH_2CH{=}C'H_2 \qquad (1)$$

and R_{ex}, the rate of the exchange reaction

$$CH_2{=}CHCH_2I + I_2^* \longrightarrow CH_2{=}CHCH_2I^* + II^* \qquad (2)$$

Experimental

Synthesis of Allyl Iodide-1-C^{14}.—The basic material for this study was a sample of about 10 g. of allyl alcohol-1-C^{14} containing about 1 microcurie per millimole of alcohol. It was very kindly supplied by Professor Robert F. Nystrom of the University of Illinois. The synthetic procedure was chosen to avoid formation of an allylic carbonium ion in which the two end carbons would become equivalent and also to avoid liberation of free iodine that might equilibrate carbons by the reactions to be studied subsequently. Fuller details are available in the original dissertation.[1]

A sample of the radioactive allyl alcohol was diluted about ten-fold with inactive allyl alcohol and converted to allyl tosylate-1-C^{14} by the method of Hahn and Walter[9] as modified by Gilman and Beaber.[10] The alcohol was mixed with *p*-toluenesulfonyl chloride in ether solution, cooled with a salt–ice bath and slowly treated with powdered potassium hydroxide. The light was kept as dim as possible during these operations. The reaction mixture was poured into ice-water and extracted with ether, and the extract was dried over potassium carbonate. Ether and volatile impurities were removed by pumping under a slow stream of nitrogen. The yield of crude allyl tosylate was about 80%.

The tosylate then was added to a mixture of potassium iodide with metallic mercury and silver powder in ethylene glycol, and the whole mixture was stirred in total darkness at ice temperature under an atmosphere of nitrogen. Some iodine was formed after the initial addition of the allyl tosylate, but it was removed by the metals that were present.

The mixture from the reaction was washed with water and aqueous sulfite and mixed with silver powder, and the volatile allyl iodide was vacuum distilled in the dark at room temperature through phosphorus pentoxide into a liquid nitrogen trap. The product was weighed by the light of a ruby dark room lamp and dissolved in hexane. The solution was shaken with aqueous sulfite to remove traces of iodine and stored in the dark at −15°.

The yield was 35% based on sulfonyl chloride. *Anal.* Calcd. for C_3H_5I: C, 21.45; H, 3.00; I, 75.55. Found: C, 21.56; H, 2.98; I, 75.50. The tests described below indicate that 88.4% of the carbon-14 was in the number-1 carbon, and the remainder in the number-3 carbon.

Radioactive Characterization of Allyl Iodide.—The characterization of the allyl iodide involved isolating a sample of formaldehyde from the number-3 carbon and determining its specific activity. The hexane solution of allyl iodide was ozonized at −80° and then reduced with zinc dust and aqueous acetic acid. The mixture was filtered and freed of hexane and other volatile materials. It was then treated with 5,5-dimethyl-1,3-cyclohexanedione (dimethone), and the formaldehyde dimethone obtained was recrystallized three times from hot aqueous ethanol. *Anal.* Calcd. for $C_{17}H_{24}O_4$: C, 69.83; H, 8.27. Found: C, 70.08; H, 8.20.

The formaldehyde dimethone was slurried with water, filtered, dried, weighed and counted with a Q gas counter, and the specific activity was calculated with the self-absorption corrections determined by Horowitz, Doerschuk and King.[11]

The method assumes that the formaldehyde carbon in the formaldehyde dimethone came exclusively from the number-3 carbon of the allyl iodide. Also, if our ideas about the synthesis and the reactions of allyl iodide are correct, then the carbon-14 (initially present in the number-1 carbon of allyl alcohol) will eventually become equilibrated between the two end carbons of the allyl iodide but will not enter the number-2 position. If isotope effects are neglected, and if z is the fraction of carbon-14 present as number-3 carbon at a particular time, then

$$z = s/2s_{\text{equil}} \qquad (3)$$

where s is specific activity in counts per minute per milligram of formaldehyde carbon and s_{equil} is the specific activity of the formaldehyde from allyl iodide that has been equilibrated.

Four samples of allyl iodide-1-C^{14} in solution were kept in the dark at room temperature for about a day in the absence of iodine and then were analyzed by the above procedure. Values of s were 1114, 1019, 941 and 1032 c.p.m. Three other samples were equilibrated for one or two days with iodine at much greater concentration than was used in the kinetic experiments described below, and the values of s_{equil} obtained were 4518, 4057 and 4712 c.p.m. If z_0 is the value of z in the absence of iodine, then these data give $z_0 = 0.116$ indicating that 88.4% of the carbon-14 was still in the number-1 position.

A confirming test was kindly performed by Dr. Alfred P. Wolf of the Brookhaven National Laboratory. He burned a sample of our formaldehyde dimethone from unreacted allyl iodide and also a sample of the allyl iodide itself and measured the specific activity of the gaseous carbon dioxide from each sample. The data indicated $z_0 = 0.128$. The agreement is probably within the errors anticipated. Moreover, the difference between the two results is in the direction to be anticipated from isotope effects. The equilibrium of reaction 1 probably slightly favors carbon-14 in the number-3 carbon because the bonds to it have stronger force constants. Then the factor in equation 3 should be slightly less than 2. Since z enters logarithmically into all of the kinetic equations, no correction for isotope effect would be needed even if it could be made.

If the formaldehyde dimethone contained any carbon from the number-1 position as well as from number-3, if the equilibration reaction introduced any carbon-14 into the number-2 position or if the supposed equilibration with iodine had not gone all of the way to completion, the value of z calculated from equation 3 would be greater than the value from the gas phase counting. Since the value from equation 3 is if anything less than the other, we believe that our method of measurement is inherently sound.

We made one other test of the procedure. Three samples of inactive allyl iodide were ozonized and treated by the usual procedure. The amount of formaldehyde dimethone was weighed, and the amount of iodide ion produced was titrated by standard procedures. The amounts of formaldehyde dimethone and of inorganic iodide showed good stoichiometric equivalence in all three experiments, but the yields were less than a third of the allyl iodide taken originally. We are unable to account for these low yields unless the gas stream from the ozonizer could take allyl iodide from a solution at −80° or unless the allyl iodide polymer-

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(6) B. D. England and E. D. Hughes, *Nature*, **168**, 1002 (1951); B. D. England, *J. Chem. Soc.*, 1615 (1955).

(7) C. A. McDowell, F. P. Lossing, I. H. S. Henderson and J. B. Farmer, *Can. J. Chem.*, **34**, 345 (1956).

(8) R. F. Nystrom and J. C. Leak, THIS JOURNAL, **75**, 3039 (1953).

(9) F. L. Hahn and H. Walter, *Ber.*, **54B**, 1531 (1921).

(10) H. Gilman and N. J. Beaber, THIS JOURNAL, **47**, 518 (1925).

(11) H. H. Horowitz, A. P. Doerschuk and C. G. King, *J. Biol. Chem.*, **199**, 193 (1952).

ized in addition to the ozonization reaction. Despite the low yields, we are reassured by the consistent stoichiometric equivalence of the two products.

Other Reagents.—The hexane solvent was prepared from petroleum ether by treatment with fuming sulfuric acid as described previously.[12] It contained about 2×10^{-6} mole/l. of material capable of forming organically bound iodine under the conditions of our experiments.

Reagent grade resublimed iodine was used without further purification. Solutions were activated with carrier free iodine-131 obtained from the Oak Ridge National Laboratory on authorization of the United States Atomic Energy Commission.

For some experiments not requiring carbon-14, commercial allyl iodide was purified by the method of Sibbett and Noyes.[3]

General Kinetic Procedures.—In the thermal experiments, the concentration of allyl iodide was so much greater than that of iodine and the fractional rate of isomerization was so slow relative to that of exchange that virtually all of any iodine-131 initially present in the element would have entered the allyl iodide before there was any measurable isomerization of the carbon-14 distribution. Therefore, exchange and isomerization experiments were carried out separately. The appropriate solutions were pipetted into separate compartments in an opaque glass-stoppered flask and thermostated at 30°. The run was started by inverting and shaking the flask and returning it to the thermostat. At the end of the run, the iodine was reduced and extracted with aqueous sulfite, and customary procedures were used to measure either the fraction of iodine-131 in the aqueous layer or the specific activity of carbon-14 in the number-3 carbon of the allyl iodide.

In photochemical experiments, the times of illumination ranged from 3.9 to 10 seconds and were too short for accurate measurement. However, the quantity of interest to us is the *ratio* of rates of exchange and isomerization rather than the absolute value of either rate. Since for both reactions the logarithm of the distance from equilibrium is a linear function of the time, the ratio of the rates was calculable from the fractional distance each had gone to equilibrium even without any information as to the actual time of reaction. Solutions of iodine-131 and of allyl iodide-1-C^{14} were mixed and illuminated for short periods with the 4358 Å. line from a mercury arc. An aliquot sample of the solution was extracted with aqueous sulfite, and the radioactivity of the aqueous layer was compared with that of a control solution of iodine. The number-3 carbon of the allyl iodide then was converted to the formaldehyde dimethone, and its activity was also measured.

Calculation of Rates.—The rate of exchange (equation 2) can be calculated by standard equations. If x is the fraction of iodine-131 present in the element at time t, and if the subscripts 0 and ∞ refer to initial and equilibrium values

$$R_{ex} = \frac{2[I_2][AI]}{(2[I_2] + [AI])t} \ln \frac{x_0 - x_\infty}{x - x_\infty} \qquad (4)$$

where

$$x_\infty = \frac{2[I_2]}{2[I_2] + [AI]} \qquad (5)$$

In these expressions, AI refers to allyl iodide, and R_{ex} is the total rate of reaction 2 by all mechanisms. The specific complications of application to thermal and photochemical data are discussed in the sections on results.

The rate of isomerization (equation 1) can be calculated from the expression

$$R_{isom} = \frac{[AI]}{2t} \ln \frac{0.5 - z_0}{0.5 - z} \qquad (6)$$

where z is defined by equation 3. The factor of two enters the denominator because the equilibrium state for reaction 1 represents the change of only half the molecules from their original configuration just as in the case of optical activity where the rate at which molecules invert configuration is half the rate of racemization as customarily defined.

Thermal Results

Measurements of Exchange.—As was indicated above, measurements of thermal isomerization and exchange could not be made on the same solutions. The thermal data of Sibbett and Noyes[3] indicate that in our concentration range

$$R_{ex} = k[AI][I_2] \qquad (7)$$

where $k = 8.4 \times 10^{-3}$ liter/mole sec. at 30°. We tested these data by making four thermal exchange runs at approximately the concentrations used in the isomerization experiments. The average R_{ex} was 1.77×10^{-7} mole/liter sec. as compared to 1.78×10^{-7} predicted from the Sibbett and Noyes data. The excellent agreement was taken to justify the use of equation 7 to calculate R_{ex} throughout the narrow range of concentrations we employed.

The isomerization experiments required up to two days to cause the optimum distribution of carbon-14, while the iodine exchange experiments needed only a few hours. In order to test whether any slow side reactions were affecting the exchange characteristics, a drop of iodine-131 solution was added to a thermal isomerization run that had already been 44 hr. in the thermostat. The rate of iodine exchange after the addition was 4.58×10^{-7} mole/liter sec. as compared to 4.54×10^{-7} predicted by the Sibbett and Noyes data on freshly mixed solutions.

Comparison of Exchange and Isomerization.—Eight different solutions of allyl iodide-1-C^{14} in hexane were thermostated at 30° with iodine, and the specific activity of the number-3 carbon from each run was measured. The rate of isomerization was calculated from equation 6 with $z_0 = 0.116$ as described above. The results are presented in Table I.

TABLE I

COMPARISON OF THERMAL ISOMERIZATION AND EXCHANGE AT 30° IN HEXANE

$[I_2] \times 10^4$, mole/l.	[AI], mole/l.	$\times 10^{-4}$, sec.	$R_{isom} \times 10^8$, mole/l. sec.	$R_{ex} \times 10^8$, mole/l. sec. (calcd.)	R_{isom}/R_{ex}
5.08	0.1044	7.68	4.96	44.5	0.111
5.08	.1044	9.07	59.33	44.5	1.33
5.08	.1044	10.71	6.22	44.5	0.140
5.18	.0870	8.80	28.43	37.9	.750
5.18	.0870	9.81	15.95	37.9	.421
2.55	.0870	17.00	5.64	18.6	.303
2.55	.0870	18.33	2.20	18.6	.118
5.81	.0928	15.52	8.81	45.3	.194

The data demonstrate that iodine does indeed cause the predicted isomerization in which the two end carbons of allyl iodide are reversed, but the rate is considerably less than that of exchange of iodine.

The scatter in Table I makes quantitative inference difficult. The data suggest that R_{isom}/R_{ex} is fairly low unless there is some extraneous influence that considerably increases the rate of isomerization. The two largest values were rejected, and the other six were averaged to give $R_{isom}/R_{ex} = 0.22$. Although statistical methods indicate a probable uncertainty of ± 0.03 in this number, the assignment undoubtedly is optimistic.

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

Effect of Dielectric Constant.—During a few exchange experiments at 25°, up to half the volume of hexane ($D = 1.91$) was replaced by 1,2-dichloroethane ($D = 10.1$). The rate of exchange was increased by a factor of 1.6 for 25 volume % dichloroethane and by a factor of 2.6 for 50 volume % dichloroethane.

Two identical isomerization experiments were run at 30° in 50 volume fraction dichloroethane. The values of $R_{\text{isom}}/R_{\text{ex}}$ were 0.111 and 0.578. Although the discrepancy is disturbingly large, there is no evidence that the increase in dielectric constant has greatly changed the ratio of the rates of the two reactions.

Photochemical Results

Treatment of Exchange Data.—The photochemical experiments introduced several complications not involved in the thermal measurements. During each run, the allyl iodide and iodine-131 were present in the same solution for about 15 minutes but were illuminated for no more than ten seconds of this time. The total exchange includes contributions from both thermal and photochemical mechanisms. The rate of photochemical exchange can be computed from equation 4 if t is time of illumination and if x_0 is replaced by x_{d} where x_{d} is the fraction of activity remaining in the element if a solution receives identical treatment except that it is not illuminated. Values of x_{d} were measured for a few solutions, and equations 7 and 4 were combined to estimate the values of x_{d} that would be applicable to the specific photochemical experiments. Since x_{d} was always greater than 0.8 while x in any experiment was always less than 0.3, the uncertainties in this thermal correction did not cause significant error.

Since the experimental conditions required that exchange proceed for at least two half-lives in order that the extent of isomerization be easily measurable, potential uncertainties in x_∞ are much more important than those in x_{d}. Three exchange runs of the concentrations used in photochemical experiments were left in the dark for 20 hr. until equilibrium should have been virtually complete. The measured values of x were consistently about 0.029 greater than the value of 0.084 calculated for x_∞ by equation 5. The discrepancy could be explained if 3.3% of the allyl iodide were hydrolyzed during the sulfite extraction. In a separate test, a solution of radioactive allyl iodide was extracted with sulfite, and 1.9% of the iodine-131 was found in the water layer. The values of x for the photochemical runs were therefore corrected for 3.3% hydrolysis of the allyl iodide. This correction is only important when the exchange has gone so nearly to completion that a large fraction of the iodine-131 is organically bound.

An unexplained complication was that illuminations for different times did not obey equation 4. The rate of exchange seemed to drop to almost nothing before the calculated equilibrium was reached, and the situation was not improved if the flask was shaken during illumination to reduce effects arising because most of the light was absorbed in the front of the cell. As discussed in the preceding paragraph, the expected position of equilibrium could be approached fairly satisfactorily in the dark. The discrepancy did not involve a side reaction affecting the iodine concentration, for illumination for 12 minutes only increased $[I_2]$ by 3%; the illuminations in our actual runs were never more than ten seconds. The data suggest that some of the organically bound iodine is becoming inaccessible for exchange. Such a reaction might be the isomerization of allyl iodide to $CH_3CI{=}CH_2$ or to $CH_3CH{=}CHI$, but we would hardly expect these hydrogen migrations to compete with a reaction having a half-life of a few seconds. In the following treatment, we have assumed that the ratio $R_{\text{isom}}/R_{\text{ex}}$ is not affected by any side reactions that may be going on.

Finally, the interpretation of the exchange results is complicated because not all exchanges between iodine atoms and allyl iodide molecules result in organic binding of iodine originally present in the element. The steps (S1) to (S9) comprise the previously proposed mechanism[4]

$$I_2 + h\nu \longrightarrow 2I \qquad \text{(S1)}$$

$$AI + h\nu \longrightarrow A + I \qquad \text{(S1')}$$

$$I^* + AI \longrightarrow AI^* + I \qquad \text{(S2)}$$

$$I + I_2^* \longrightarrow II^* + I^* \qquad \text{(S3)}$$

$$I + AI \longrightarrow A + I_2 \qquad \text{(S4)}$$

$$A + I_2 \longrightarrow AI + I \qquad \text{(S5)}$$

$$A + O_2 \longrightarrow AO_2 \qquad \text{(S6)}$$

$$I + I \longrightarrow I_2 \qquad \text{(S7)}$$

$$I + AO_2 \longrightarrow \text{stable products} \qquad \text{(S8)}$$

$$AO_2 + AO_2 \longrightarrow \text{stable products} \qquad \text{(S9)}$$

Radioactive iodine can be incorporated into allyl iodide either by step S2 or S5. However, the previous kinetic analysis indicated that k_2 was about 2000 times k_4. In addition, the oxygen of the air competes with iodine for the allyl radicals produced in S4. We can safely neglect steps S4 and S5 and assume that all of the exchange involves the sequence S2-S3.

The quantity measured experimentally is R_{ex}, the rate at which iodine originally present in the element becomes incorporated in allyl iodide, but the quantity we want to compare with R_{isom} is R_2, the rate at which step S2 takes place regardless of the origin of the iodine atom involved. The two quantities differ to the extent that iodine atoms produced from allyl iodide by step S2 react again by S2 before they have a chance to exchange with iodine by step S3. Because of this competition between S2 and S3, we can write[13]

$$R_{\text{ex}} = R_2 \frac{1}{1 + F} \qquad (8)$$

where

$$F = \frac{k_2[\text{AI}]}{k_3[\text{I}_2]} \qquad (9)$$

Sibbett and Noyes[4] proposed that at 25° $k_2/k_3 = 0.0685$. Then $1 + F$ was in the range 2.3 to 2.5 for the experiments in this study, and R_2 was assumed to be greater than R_{ex} by this factor.

Treatment of Isomerization Data.—The photochemical experiments also introduced complications into the treatment of the isomerization

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(13) The reasoning is discussed by R. M. Noyes and J. Zimmerman, *J. Phys. Chem.*, **18**, 656 (1950).

reaction. Thus the z_0 in equation 6 should be replaced by z_d, the value of z for allyl iodide that had had the same treatment except for illumination in the presence of iodine. In three different experiments, solutions of allyl iodide-1-C^{14} were illuminated with no iodine present, then mixed with iodine in the dark and allowed to stand for about 15 minutes and finally analyzed for carbon-14 distribution. The three experiments gave values of z_d of 0.137, 0.104 and 0.130. These results are not significantly greater than the value of 0.116 obtained from four measurements of z_0. All measurements were averaged, and the photochemical isomerization experiments used $z_d = 0.119$.

Results.—Since exchange and isomerization were measured for the same illuminated solutions, the time of illumination did not need to be known accurately in order to calculate R_{isom}/R_{ex} from the ratio of equations 6 and 4. The ratio R_{isom}/R_2 then could be calculated from equations 8 and 9. Of course all of these rates refer only to photochemical contributions after thermal rates have been neglected by substituting x_d and z_d for x_0 and z_0.

Table II contains the results of four experiments run for illuminations of only a few seconds. Both isomerization and exchange take place much more rapidly than in the dark, and R_{isom}/R_{ex} is greater than unity. However, R_{isom}/R_2 is only 0.53 ± 0.10 if the mechanistic interpretations of Sibbett and Noyes[4] are correct.

TABLE II

COMPARISON OF PHOTOCHEMICAL ISOMERIZATION AND EXCHANGE AT 25° IN HEXANE

[AI]	0.0348	0.0348	0.0366	0.0366
$[I_2]$	.00181	.00175	.00167	.00167
$\frac{x - x_\infty}{x_d - x_\infty}$	.034	.081	.276	.180
$R_{ex}t$	.01109	.00799	.00394	.00525
R_{isom}/R_{ex}	1.51	1.45	1.06	1.09
R_{isom}/R_2	0.650	0.614	0.425	0.434

Discussion

Molecular (Thermal) Mechanism.—The data in Table I indicate that in the dark iodine promotes an isomerization reaction in which the end carbons of allyl iodide become interchanged, but the rate is much slower than the rate of exchange of iodine-131 with iodine molecules. Also, the rate of isomerization seems to be much more erratic than the rate of molecular exchange.

The data do not establish whether this slow isomerization is due to iodine atoms or molecules. At 30°, the equilibrium constant for the reaction $I_2 \rightarrow 2I$ is about 10^{-22} mole/liter, and the equilibrium concentration of atoms would be about 2×10^{-13} *M*. Sibbett and Noyes[4] estimate that k_2 (for reaction S2) is about 5×10^6 liter/mole sec. If, as is indicated by the photochemical data, atoms cause isomerization at a rate comparable to that of reaction S2, then the isomerization in Table I could be explained as an atomic reaction *provided* the equilibrium concentration of iodine atoms were maintained. However, the normal photostationary concentration of iodine atoms most certainly is *not* maintained in an illuminated solution containing iodine, allyl iodide and oxygen.[4] The equilibrium concentration of atoms might still be approximated in the dark if the reaction

$$AO_2 \longrightarrow A + O_2 \qquad (S10)$$

competed effectively with reaction S9 at the low radical concentrations prevailing in unilluminated solutions. However, the thermal exchange kinetics of Sibbett and Noyes[3] are not consistent with an iodine atom concentration approximating the thermal equilibrium value. We therefore believe that much of the isomerization reported in Table I is caused by iodine molecules.

The study was undertaken to obtain information about the transition state for the molecular exchange reaction. The low value of R_{isom}/R_{ex} definitely rules out transition state II as the most important exchange mechanism. The data reported here are not inconsistent with transition state I.

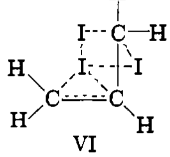
Another possible exchange mechanism would involve a transition state that approximated the ion pair intermediate V. Such a transition state

$$C_3H_5^+I_3^- \quad V$$

would have to retain enough structure that the end carbons were usually not interchanged. For such a model, the rate of exchange should increase markedly with dielectric constant of the medium, and increasing dielectric constant should also make interchange of end carbons more easy and so increase R_{isom}/R_{ex}.

The data reported above do indicate an effect of dielectric constant in the direction of a greater dipole moment for the transition state than for allyl iodide, but the effect is very much less than that observed for another exchange reaction in which the transition state is thought to approximate an ion pair.[14] The meager data do not show much about the effect of dielectric constant on R_{isom}/R_{ex}, but one of the two runs with dichloroethane gave a value as low as any obtained in hexane. We are inclined to rule out a major contribution of transition state V to the molecular exchange reaction.

The absence of any molecular exchange between iodine and benzyl iodide[5] still remains a strong argument against transition states I and V, and we have attempted to devise a reaction path not accessible to benzyl iodide but attaching entering and leaving iodine atoms to the same carbon of allyl iodide. A plausible transition state is represented very roughly as VI.



VI

In this diagram, the plane determined by the three carbon atoms lies below the plane determined by the three iodine atoms. Exchange is proposed to result from rearrangement of a loose complex between allyl iodide and molecular iodine that

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(14) A. Goldman and R. M. Noyes, THIS JOURNAL, **79**, 5370 (1957).

certainly exists. If one of the iodines of the original molecule interacts more strongly with the electrons of the double bond between carbons 2 and 3, it is easy to devise a situation in which the other iodine of the original molecule and the original iodine of the allyl iodide interact equally with carbon-1 and also interact equally with the iodine that is complexed to the double bond. The breaking up of such a structure would result in iodine exchange half the time but would not change the point of attachment of the organically bound iodine. Only a small additional rearrangement would be necessary to produce a structure in which the two end carbons were subject to equivalent bonding, and this would result in the observed isomerization reaction.

A structure like VI would also have a dipole moment intermediate between those of allyl iodide and of an ion-pair, and the compressed nature might help to account for an entropy of activation for thermal exchange[3] that is surprisingly low for a reaction between neutral species in a non-polar solvent. Although the representation is somewhat unconventional, we find this structure the most satisfactory explanation of our observations.

Atomic (Photochemical) Mechanism.—The photochemical data in Table II indicate that iodine atoms cause a rapid equilibration of the 1 and 3 carbon atoms in allyl iodide just as had been anticipated. In all four runs, the rate of this isomerization reaction is greater than the rate at which iodine-131 is becoming incorporated into allyl iodide.[15]

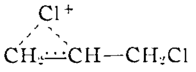
Our further conclusions rest upon two points from the involved interpretation of the photochemical exchange kinetics by Sibbett and Noyes.[4] These points are: (1) most of the iodine-131 becomes incorporated in allyl iodide by the sequence S2-S3 rather than by the sequence S4-S5. (2) If isotopic distribution of iodine is neglected, the rate of reaction S2 in our solutions was at least as great as the rate of reaction S3.

Point (1) was required by Sibbett and Noyes[4] to explain the depression by allyl iodide of the quantum yield for exchange. It is supported by the scavenger experiments of Lampe and Noyes[16] which substantiate other aspects of the Sibbett and Noyes mechanism and also suggest that k_4 is indeed of the order of 3×10^3 l./mole sec. as estimated in the previous work; this value is too small to be responsible for the rapid exchange. Finally, the observation of Hamill, Williams and Schwarz[17] that allyl bromide competes with hydrogen bromide for thermalized recoil bromine atoms requires that reaction S2 be important in the analogous bromine case.

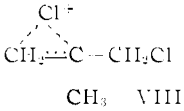
Point (2) must be valid to justify the conclusion discussed below that R_{isom}/R_2 is certainly less than unity. The value of F (equation 9) depends upon the ratio k_2/k_3. This ratio is estimated from the tendency of allyl iodide to depress the quantum yield for exchange. In the present experiments, the iodine concentration is four times the highest value used by Sibbett and Noyes,[4] but we see no reason to doubt the extrapolation that reaction S3 in our solutions was only about 60% as fast as reaction S2. The uncertainty discussed in footnote 15 acts in the direction to reduce the dependence of our argument on point 2.

The basic conclusion from these experiments is that R_{isom}/R_2 is of the order of 0.5 and is certainly less than unity. If all of the atomic exchange went by transition state III, the ratio R_{isom}/R_2 would be zero; transition state IV predicts a ratio of unity. Our results are certainly consistent with approximately equal contributions of both mechanisms to the exchange. However, transition states III and IV result from entirely different types of interaction between an iodine atom and an allyl iodide molecule, and it would give more aesthetic satisfaction if all of the data could be accommodated in terms of a single type of interaction. Such an accommodation requires a transition state for exchange that involves partial but not complete discrimination between the two end carbons of the allyl iodide.

A plausible transition state is suggested by the clever studies of de la Mare and co-workers.[18,19] By working with isotopic chlorine, they studied the positive ions VII and VIII. These ions were formed irreversibly from the action of Cl^+ (or $ClOH_2^+$) on the appropriate allylic chlorides. In 88% of the cases, ion VII reacted further before the binding of the two chlorines became equivalent; ion VIII reacted only 62% of the time before equilibration of the chlorines.

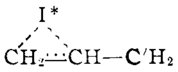


VII

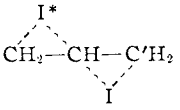


VIII

In our system, iodine atoms undoubtedly add reversibly to the double bond in allyl iodide. If the resulting radical intermediate were a π-complex like IX, both the iodine and the carbon atoms would retain their identities during formation and decomposition, and neither exchange nor isomerization would take place. The intermediate IX would undergo isomerization and exchange at equal rates if it rearranged to a symmetrical species either like IV (regarded as a radical intermediate rather than as a transition state) or like X.



IX



X

Although such symmetrical configurations may well be involved in the rapid isomerization that we

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[15] The data in Table II suggest that $R_{\text{isom}}/R_{\text{ex}}$ increases monotonously as the reactions approach equilibration. Such an effect could be associated with the failure of the photochemical exchange to approach the equilibrium calculated from stoichiometry, and it is not certain that $R_{\text{isom}}/R_{\text{ex}}$ is actually greater than unity at short times. The uncertainty does not affect the conclusions of the argument presented here.

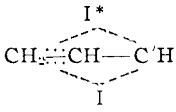
[16] F. W. Lampe and R. M. Noyes, THIS JOURNAL, **76**, 2140 (1954).

[17] W. H. Hamill, R. R. Williams, Jr., and H. A. Schwarz, *ibid.*, **72**, 2813 (1950).

[18] P. B. D. de la Mare and J. G. Pritchard, *J. Chem. Soc.*, 3910, 3990 (1954).

[19] P. Ballinger and P. B. D. de la Mare, *ibid.*, 1481 (1957).

do observe, there must be an additional transition state of slightly lower free energy that leads to exchange without isomerization. Such a transition state could be represented as XI. Of course our


XI

data provide no information as to whether the two iodines in XI are on the same or on opposite sides of the plane determined by the three carbon atoms, but XI could revert to IX and then dissociate to cause iodine exchange without carbon isomerization. If dissociation of IX took place about as easily as rearrangement to a symmetrical species like IV or X, all of our observations of both atomic and molecular mechanisms could be accommodated to the reversible formation of π-complexes in which iodine exchange is easier than the formation of species containing more conventional valence bonds. These mechanisms somewhat resemble other reactions like the hydration of olefins[20] in which significant free energy barriers apparently oppose the rearrangements between π-complexes and conventionally bound species.

Acknowledgments.—Professor Robert F. Nystrom of the University of Illinois provided the allyl alcohol-1-C^{14} without which this study would have been impossible.

Professor Robert R. Becker of Columbia University provided valuable advice and facilities in connection with counting carbon-14, and Dr. Alfred P. Wolf of the Brookhaven National Laboratory carried out some measurements that helped in the characterization of our material.

During some of the period of this investigation, William Cain held a special teaching assistantship provided by the du Pont Chemical Corporation. The research also was supported in part by the U. S. Atomic Energy Commission under Contract AT(30-1)-1314.

[20] P. Riesz, R. W. Taft, Jr., and R. H. Boyd, THIS JOURNAL, **79**, 3724 (1957).

EUGENE, OREGON

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The Kinetics of the Photolysis of 2,2'-Azo-bis-isobutyronitrile

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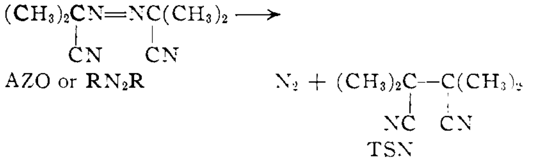
The kinetics of the photolysis of 2,2'-azo-bis-isobutyronitrile, AZO, in deaerated benzene solution at 25.00 ± 0.02° have been investigated employing 366 mμ radiation, isolated from the output of a medium pressure, mercury–quartz lamp with Corning filters C.S. No. 7-37 and 0-52. The initial concentration of AZO was varied between 0.0144 and 0.0699 *M* and the reaction pursued to as far as *ca.* 80% destruction of AZO in some cases. The reaction course was followed spectrophotometrically over the 290–400 mμ range. All changes in optical density observed agree with the supposition that the only reaction product that absorbs radiation at 290–400 mμ is dimethyl-N-(2-cyano-2-propyl)-ketenimine, DKI. Throughout every run $-R[\text{AZO}] = \phi I_{\text{abs}}$, where ϕ is 0.47 ± 0.02 mole einstein^{-1}, and the fractional molar conversion, *f*, of AZO into DKI did not vary detectably, *viz.*, $+R[\text{DKI}] = f\phi I_{\text{abs}}$. The value of *f* has been estimated to be 0.59 ± 0.02 and 0.58 ± 0.02 by two different methods. For the purpose of settling some of the aforementioned points, a specimen of DKI, 99.3 ± 0.6 mole % pure, was prepared by the thermal decomposition of AZO. Its absorption spectrum in benzene solution over the 290–404 mμ range is reported. As previously suggested by Talât-Erben and Bywater, its extinction coefficient about 360–380 mμ is small. Finally, the results obtained are discussed.

Introduction

The simple photolysis of 2,2'-azo-bis-isobutyronitrile, AZO, has had little attention. Its likely similarity to the much investigated, thermally induced decomposition and its possible suitability as an actinometric reaction prompted the present work. There appears to have been only one attempt so far to investigate the kinetics of this process.[2] This was in benzene solution at 25° using impure 366 mμ mercury radiation. The reported results refer to only one initial concentration of AZO. The reaction course was followed spectrophotometrically at one wave length, 345 mμ. Evidence was given that thermally decomposing AZO in benzene solution can form material that absorbs appreciably at 345 mμ. In view of the liklihood that photochemically decomposing AZO might display a similar effect, no greater accuracy was claimed for the results obtained.

The thermal decomposition of AZO in solution has been studied extensively over the 30–105° range. It follows simple first-order kinetics at about the same rate in a variety of solvents, with no evidence of induced chain processes. The evolution of nitrogen is quantitative and in unreactive media, such as carbon tetrachloride or toluene, the final organic products are tetramethylsuccinonitrile, TSN, and small amounts of material thought to arise from disproportionation of 2-cyano-2-propyl radicals, R·, for example, isobutyronitrile. Leaving aside these disproportionation products, the reaction stoichiometry is



$$\underset{\text{AZO or RN}_2\text{R}}{(CH_3)_2\underset{\displaystyle CN}{\underset{|}{C}}N{=}N\underset{\displaystyle CN}{\underset{|}{C}}(CH_3)_2} \longrightarrow N_2 + \underset{\text{TSN}}{(CH_3)_2\underset{\displaystyle NC}{\underset{|}{C}}{-}\underset{\displaystyle CN}{\underset{|}{C}}(CH_3)_2} \qquad (1)$$

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[1] This paper is based partly upon a thesis submitted by A. M. Rosenberg in partial fulfillment of the requirements for the degree of Master of Science at Purdue University, January, 1958.

[2] R. Back and C. Sivertz, *Can. J. Chem.*, **32**, 1061 (1954). There has also been a study of the scavenging action of molecular iodine in this system, J.-C. Roy, J. R. Nash, R. R. Williams and W. H. Hamill, THIS JOURNAL, **78**, 519 (1956).