lengths than that obtained from the corresponding benzenoid compound, *p*-distyrylbenzene.[9] The isomeric condensation product with 2-picoline shows a single maximum at 354 mμ and a slight change of slope in the expected region of secondary absorption, *ca.* 280 mμ. It should further be noted that the intensity of the absorption of the di-condensation products is approximately double that of the mono-aldehyde pyridine condensates.

Acknowledgment.—The authors wish to express their appreciation to Miss Esther Polson and Mr. W. A. Davis for the determination of the absorption spectra reported in this paper.

Experimental

General Method.—The pyridine condensation products were prepared in the usual manner[10] by refluxing for approximately fifteen hours with acetic anhydride using 1 to 3 times the molar proportion of aldehyde. The dark colored reaction mixtures were dissolved in chloroform extracted with dilute hydrochloric acid, and the acid layer neutralized under cooling with concentrated ammonium, hydroxide. The free bases were separated either by decanting the aqueous layer or by extracting it with ether. The 2,6- and 2,4,6-styrylpyridines separated as their hydrochloride salts. The free bases were isolated by treating the salts with alcoholic sodium hydroxide in alcohol–benzene suspension. They were recrystallized from the solvents indicated in Table I.

The picoline–phthalaldehyde condensation products formed in small yields (*ca.* 5%) except in the case of 2-picoline-terephthalaldehyde, which gave 73% yield.

Eastman Kodak Co. stilbene was used without further purification.

***m*-Distyrylbenzene** was prepared by adding an ethereal solution of 1.5 g. of isophthalaldehyde to benzylmagnesium bromide in proportion of 1:2 moles. The dark red addition complex which formed at once was hydrolyzed with cold 20% sulfuric acid. The resulting carbinol was dehydrated by refluxing with excess acetyl chloride and slowly heating the product to 275° to remove the elements of acetic acid from the molecule. *m*-Distyrylbenzene crystallized from hexane as white plates, melting point 169.5–170°, yield 0.30 g.

1,4-Diphenylbutadiene-1,3 was prepared by the method of Corson (ref. *k*, Table I).

The absorption spectra measurements were made on a Beckman quartz spectrophotometer model DU using a 1-cm. quartz cell and a hydrogen tube as an ultraviolet source. Absolute ethyl alcohol was used as a solvent throughout. All the samples were 1×10^{-5} M except 2-(δ-phenylbutadiene-α,γ)-pyridine and 4-(δ-phenylbutadiene-α,γ)-pyridine (both 1.485×10^{-5} M); 6-methyl, 2-(δ-phenylbutadiene-α,γ-pyridine) (1.185×10^{-5} M); and *p*-(β,β′-di-2-pyridyl)-divinylbenzene (3×10^{-5} M).

Summary

Examination of the spectra of several substituted pyridines has shown them to be different from their hydrocarbon analogs. These differences have been correlated with the electronic nature of the compounds.

Cambridge 39, Mass. Received April 23, 1945

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[9] Hertel and Siegel, *Z. physik. Chem.*, **B52**, 174 (1942), give log E = 4.76 at 340 mμ for *p*-distyrylbenzene.

[10] Shaw and Wagstaff, *J. Chem. Soc.*, 26 (1933).

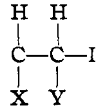
[Contribution from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, No. 991]

The Kinetics of the *cis–trans* Isomerization of Diiodoethylene and of its Exchange with Iodine

By Richard M. Noyes, Roscoe G. Dickinson,[1] and Verner Schomaker

The iodine catalysis of *cis–trans* isomerization has been investigated by several workers, the thermal[1a] and photochemical[2] isomerization of the cinnamic acids and the thermal isomerization of the dichloroethylenes[3] being among the reactions studied in solution. The rates of isomerization observed were proportional to the square root of the concentration of iodine in thermal experiments, and to the square root of the intensity of illumination in photochemical experiments in which the concentration of iodine did not vary, indicating, as the authors pointed out, that the isomerizations are induced by iodine atoms.

For isomerization reactions of this type Berthoud and Urech[2] suggested a mechanism involving addition of the catalytic halogen atom to one of the carbon atoms of the double bond to produce an intermediate, represented by the authors as



$$\begin{array}{ccc} H & H & \\ | & | & \\ C & -C- & I \\ | & | & \\ X & Y & \end{array} \qquad (1)$$

in which the carbon–carbon double bond has been converted into a single bond about which internal rotation can occur. Isomerization then results if at the time of dissociation of the halogen atom from the complex the groups attached to the two carbon atoms have undergone a relative rotation of 180°. If both X and Y are iodine atoms, then the formation of a complex like (1) may result in exchange with the added iodine atom either concurrently with the isomerization or separately. The relative probabilities of the three possible processes—exchange, isomerization, and isomerization with exchange—should depend upon the actual properties of the reaction intermediate

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[1] This manuscript in essentially its present form was completed before the death of Dr. Dickinson on July 13, 1945. The junior authors have assumed responsibility for some minor changes made during his last illness.

[1a] Roscoe G. Dickinson and H. Lotzkar, This Journal, **59**, 472–475 (1937).

[2] A. Berthoud and C. Urech, *J. chim. phys.*, **27**, 291–306 (1930).

[3] Reuben E. Wood and Roscoe G. Dickinson, This Journal, **61**, 3259–3262 (1939).

(1) and the energy given it, and are not predictable on the basis of the general statement of the mechanism of the isomerization reaction given by Berthoud and Urech.

Another possible mechanism for the isomerization of a dihaloethylene by the corresponding halogen has been proposed by Olson.[4] Briefly, Olson's theory assumes that the catalytic group, following a path in the plane of the molecule, approaches a carbon atom from the side directly opposite one of the halogen atoms of the molecule, and that an inversion similar to a Walden inversion takes place. The halogen originally bound to the carbon leaves the molecule, and the isomeric configuration of the haloethylene is changed because of the inversion which accompanies the substitution. If this mechanism were correct for the atom-catalyzed isomerization, every molecule which isomerized would also exchange.

Workers at University College, London,[5] compared the rates of racemization of certain optically active halogen compounds by the corresponding halide ion with the accompanying rates of halogen exchange and demonstrated that each exchange was accompanied by an inversion of the carbon atom. It was felt that a similar comparison of a halogen atom-catalyzed *cis–trans* isomerization with the accompanying halogen exchange reaction would provide new information about the mechanisms of these reactions and might make it possible to evaluate the two proposed mechanisms mentioned in the preceding paragraphs. Since several iodine catalyzed *cis–trans* isomerization reactions had already been studied in this Laboratory,[1a,3,6,7] the diiodoethylenes were chosen for the investigation.

Experimental Method

Apparatus.—Isomerization reactions were followed by measuring the dielectric constants of the solutions. The apparatus employed was that used in the study of the iodine-catalyzed isomerization of the dichloroethylenes.[3]

The activities of radioactive samples were measured with a lead-shielded quartz-fiber Lauritsen electroscope.

Photochemical experiments were conducted in a Pyrex cell with flat sides; the illuminated volume was about 15 ml. The temperature was controlled to about one degree, and illumination was provided by two 500-watt incandescent bulbs on opposite sides of the tube operated at 113 volts. The light was filtered through a dilute solution of copper chloride to remove the infra-red, but it was not monochromatized. Aside from manual control of voltage, no attempt was made to ensure constancy of the intensity of illumination, but no systematic variation in the rate constant of a photochemical reaction was observed during a series of experiments. In some experiments the intensity of illumination was diminished by screens of 29% transmission placed in the optical path. Since the local intensity of absorption varied greatly throughout the reaction cell, it was deemed advisable to stir the solution (magnetically). It was found, however, that stirring had no detectable effect on the rate of the more rapid, exchange reaction, apparently because of convection; consequently it was not used in the study of the much slower isomerizations.

Thermal experiments were made in Pyrex ampules which were thermostated in an electrically heated furnace or in a vapor bath.

Materials.—The *trans*-diiodoethylene was prepared by passing acetylene into a solution of iodine in alcohol as directed by Kaufmann.[8] The commercial tank acetylene was purified by water and sulfuric acid according to the method of Reichert and Nieuwland.[9] The crystals were filtered and repeatedly recrystallized from 95% ethyl alcohol. After its final crystallization, the product melted at 72.5–73°. Experiments showed that iodine neither added to this *trans*-diiodoethylene nor was liberated from it under the conditions of the investigation.

Several samples of *cis*-diiodoethylene were prepared by adding acetylene to iodine at 150–160°,[10] but a large number of the preparations were unsuccessful. It was found that a more satisfactory method of preparation was to isomerize *trans*-diiodoethylene by heating it at about 160° for two days in the presence of a little iodine. The *trans* isomer separated out of the resulting mixture upon cooling and was removed by repeated filtrations at successively lower temperatures. The iodine was removed by washing with a solution of sulfite and then with water, and the sample was vacuum distilled and washed with sulfite again. Finally, the distillate was fractionally crystallized to a practically invariant dielectric constant of 4.36 at 25° and 1.7 megacycles. The final product froze at −12°; the melting point reported by Chavanne and Vos[11] was −13.5°. The purified material kept well in the dark, although occasionally a trace of iodine was formed.

Iodine was purified by sublimation from potassium iodide–iodine mixture and was resublimed.

The hexane used in the photochemical experiments was 60–70° petroleum ether. It was stirred with successive portions of concentrated sulfuric acid and was then treated for four several-hour periods with fuming 30% sulfuric acid and washed with sodium carbonate solution. After it had been treated with acid permanganate, it was washed with water, distilled, and stored over sodium. Trial runs in which solutions of iodine were examined with a photometer before and after illumination indicated that iodine did not add to the solvent in appreciable amounts under the conditions employed in the experiments.

Commercial decalin was stirred with concentrated sulfuric acid until the rate of darkening of fresh acid was quite slow and was then isomerized to the *trans* form by stirring with aluminum chloride for one day at room temperature.[12] After several treatments with 10% fuming sulfuric acid it was vacuum distilled and stored over sodium. When solutions of iodine in this decalin were heated under conditions identical with those employed in the studies of the thermal isomerization reaction, the dielectric constants of the solutions were practically unaffected, and subsequent titrations showed that little if any iodine had added to the solvent.

The radioactive iodine used in the exchange experiments was prepared at the Radiation Laboratory of the University of California through the courtesy of Dr. Martin Kamen and Dr. Fred J. Leitz, Jr. Two samples were prepared from tellurium which had been bombarded with deuterons by dissolving the tellurium in nitric acid and dis-

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[4] A. R. Olson, *J. Chem. Phys.*, **1**, 423 (1933).

[5] E. D. Hughes, F. Juliusburger, S. Masterman, B. Topley, and J. Weiss, *J. Chem. Soc.*, 1525–1529 (1935); E. D. Hughes, F. Juliusburger, A. D. Scott, B. Topley, and J. Weiss, *ibid.*, 1173–1175 (1936); W. A. Cowdrey, E. D. Hughes, T. P. Nevell, and C. L. Wilson, *ibid.*, 209–211 (1938).

[6] Reuben E. Wood and D. P. Stevenson, This Journal, **63**, 1650–1653 (1941).

[7] Richard M. Noyes and Roscoe G. Dickinson, *ibid.*, **65**, 1427–1429 (1943).

[8] H. P. Kaufmann, *Ber.*, **55B**, 249–267 (1922).

[9] J. S. Reichert and J. A. Nieuwland, "Organic Syntheses," Collective Volume I, John Wiley and Sons, New York, 1932, pp. 224–226.

[10] G. Latiers, *Bull. soc. chim. Belg.*, **31**, 73–84 (1922).

[11] G. Chavanne and J. Vos, *Compt. rend.*, **158**, 1582–1585 (1914).

[12] N. Zelinsky and M. Turowa-Pollak, *Ber.*, **65B**, 1299–1301 (1932).

tilling the iodine without carrier into a solution of sodium hydroxide. The iodine obtained consisted of a mixture of isomers with an apparent half life of about ten days during the period in which investigations were carried out. A few experiments were also made using radioactive iodine prepared from fission of uranium by slow neutrons. However, the amount of several-day iodine produced was so small that only a few experiments could be performed with it; therefore the preparation was not repeated.

Procedure for Exchange Experiments.—Stock solutions of radioactive iodine in hydrocarbon solvent were prepared by utilizing the rapid exchange of iodide ion with elementary iodine.[13] An acidified portion of the aqueous solution of radioactive iodide described in the preceding paragraph was shaken with a portion of hydrocarbon solvent to which a known amount of iodine had been added, the phases were separated, and the hydrocarbon solution was dried over anhydrous magnesium perchlorate. The amounts of the reagents were so chosen that the final solution contained either 1 or 2 mg. of iodine per ml.

To prepare for an exchange experiment, samples of stock solutions of the active iodine and of diiodoethylene were pipetted into the photochemical reaction cell or into one of the ampules used in thermal experiments. The mouth of the cell or ampule was connected to a calcium chloride tube to prevent condensation of water from the atmosphere. The solution was then cooled until the vapor pressure of solvent was so low that the neck of the container could be sealed without danger of pyrolysis. Since oxygen was found to cause side reactions during studies of the thermal isomerization, the ampules containing the chilled samples for thermal exchange were swept out with a stream of tank nitrogen which had been passed over hot copper and through a calcium chloride tube and were then sealed. Blank experiments indicated that no significant amount of photochemical exchange occurred while the above operations were being performed provided that the lights in the room were dimmed.

The prepared sample was illuminated or heated for the desired time. The elementary iodine was then separated from the diiodoethylene by extraction from the hydrocarbon solution with a little sodium sulfite in 0.6 *N* nitric acid. The light in the room was kept dim up to this point. The hydrocarbon layer was washed with water and the iodide was precipitated from the combined water extracts with silver nitrate.

The hydrocarbon layer containing the diiodoethylene was mixed with 20 ml. of a 10% solution of potassium hydroxide in alcohol and was refluxed for an hour and a half if the solvent was hexane and for half an hour if it was the higher boiling decalin. The mixtures from the experiments conducted in hexane were then evaporated to dryness, and the residues of potassium iodide and hydroxide were dissolved in water, acidified, and precipitated with silver nitrate. Mixtures from experiments in decalin were boiled to remove alcohol and extracted with water; the aqueous extracts were acidified and precipitated with silver nitrate. Test experiments in which the resulting precipitates were weighed showed that the above procedure removed the iodine quantitatively from the diiodoethylene.

The precipitates of radioactive silver iodide from both the iodine and diiodoethylene were filtered with suction, washed with water and with acetone, and sucked dry. The activity of a sample was measured by averaging the times necessary for the discharge of the electroscope over a certain interval of the scale while the sample was in each of four equivalent orientations which differed by rotations of 90°. Successive measurements of the activity of a given sample of precipitated radioactivity performed by the above procedure agreed to within 1%; and equal amounts of radioactive iodine were reduced, precipitated, and measured with a reproducibility of 2%.

The solutions employed in most experiments contained 50 mg. of iodine in the diiodoethylene and 10 mg. of iodine in the molecular state. Because the silver iodide precipitate absorbed some of the radiation itself, the amount of radioactivity observed in a sample of iodide was dependent upon the amount of carrier with which it was precipitated; therefore, the activities measured in samples containing different amounts of iodine were corrected by empirical factors.

Procedure for Isomerization Experiments.—The isomerization reaction was studied in five and ten mole per cent. solutions of diiodoethylene in hexane or decalin. Fifteen ml. of the solution to be studied was pipetted into the reaction cell or ampule which was sealed off and was then illuminated or heated exactly as was done in the exchange experiments. At the end of an experiment the dielectric constant of the solution was measured, and the isomeric composition of the solute was calculated from calibration data. After the dielectric constant had been measured, the amount of iodine present was determined by the titration of an aliquot portion of the solution with standardized thiosulfate. A small amount of iodine was found to have been liberated at the temperatures of the thermal runs, but it was never more than a few mg., and it probably did not greatly affect the apparent isomeric composition of the solution as indicated by the dielectric constant.

The first studies of the thermal isomerization reaction in decalin were vitiated by a side reaction. If the ampule was swept out with nitrogen free from oxygen before it was sealed, the isomerization reaction appeared to be the only one which occurred when the sample was heated.

Exchange Results

Photochemical Experiments.—When a solution of iodine is illuminated by light of a suitable wave length, some of the molecules absorb radiation and are dissociated into free atoms. The atoms tend to recombine with each other, and a steady state is soon established such that the concentration of free atoms at any point in the solution is proportional to the square root of the local rate of absorption of radiation. If it is assumed that the exchange reaction under consideration proceeds bimolecularly between diiodoethylene molecules and iodine atoms formed by the photochemical dissociation of iodine molecules, the local rate of exchange will be proportional to the concentration of the diiodoethylene and to the square root of the local rate of absorption of radiation. In order to treat the reaction mathematically it is also necessary to assume that at any instant the fraction of the free iodine atoms which are radioactive is essentially equal to the fraction of the iodine atoms present in iodine molecules which are radioactive. This assumption will be valid if the rate at which iodine atoms combine with each other or exchange with iodine molecules is large compared with the rate at which they exchange with diiodoethylene molecules. If the second assumption is not strictly valid, the true rate of exchange of the iodine atoms with the diiodoethylene will be somewhat greater than the apparent rate calculated from the results of the experiments.

If the above assumptions are made, the local rate of change in distribution of the radioactivity between the iodine and diiodoethylene at any point in the solution is given by

$$\frac{\mathrm{d}(2ax)}{\mathrm{d}t} = -kbI_a^{1/2}\left[x - \frac{a}{b}(1 - x)\right] \qquad (2)$$

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(13) D. E. Hull, C. H. Shiflett and S. C. Lind, THIS JOURNAL, 58, 535 (1936).

in which a and b are the concentrations of iodine and diiodoethylene, respectively, and x is the fraction of the radioactive iodine (initially all present in the free iodine) which is present in the free iodine at time t. The rate constant for the exchange reaction is given by k, and I_a is the local rate of absorption of radiation. The expression $2ax$ represents the concentration of that iodine which was initially present in the elementary iodine which is in the iodine at time t. The factor of 2 is retained even though units are arbitrary so that it will be possible to make a direct comparison of the rate of exchange with the rate of isomerization observed in the same optical system.

If stirring, diffusion, or convection keep the products and reactants so uniformly distributed that the value of x is the same in all parts of the solution at any given time, it is possible to write an expression for the average rate of reaction in the solution as a whole which will be the same as (2) except that I_a will have been replaced by a quantity i_a defined by the relationship

$$i_a^{1/2} = \frac{\int I_a^{1/2} \mathrm{d}V}{V} \qquad (3)$$

in which $\mathrm{d}V$ is an element of volume of the solution and the integral is taken over the entire solution. Thus $i_a^{1/2}$ is the average square root of the rate of absorption of chemically effective radiation through the solution. Integration of this new rate expression and solution for the rate constant yield

$$k = -\frac{2a}{(a+b)ti_a^{1/2}} \ln \left[\frac{a+b}{b} x - \frac{a}{b}\right] \qquad (4)$$

In the calculation of k from the experimental data, i_a was taken to be unity when no screens were used to cut down the intensity of illumination, and t was expressed in seconds.

Continuous radiation was used to illuminate the solutions employed in the study of the photochemical exchange of iodine and diiodoethylene in hexane. Since the absorption coefficients of iodine at different wave lengths are very different, there is no simple relationship between the concentration of iodine in a solution and the total amount of chemically effective radiation absorbed by it in a cell of moderate thickness and it would not be possible to correlate the rates of reaction observed in solutions in which the concentrations of iodine were different. Consequently, the same concentration of iodine was used in all photochemical experiments.

Some typical runs from the first series of photochemical exchange experiments are summarized in Table I. All experiments were made with *trans*-diiodoethylene, and the solution used in each run contained 10 mg. of iodine in 15 ml. The activity of each sample is expressed in terms of the rate of discharge of the electroscope over a fixed interval in divisions per second. To determine the total activity which is given in column 3, the same amount of the stock solution of radioactive iodine as was used in a run was precipitated, and its activity was measured. In every experiment all the activities were measured within a few hours of each other and corrected to the same time by means of the assumption that the activity of a sample decreased by one per cent. every three and a half hours. Precipitates containing 50 mg. or less of iodide as carrier were corrected empirically to the activity they would have had in 10 mg. of carrier, the maximum correction being 10% of the activity observed; no attempt was made to evaluate the activity if the precipitate contained more than 50 mg. of iodide. Only those experiments are presented in which activity was conserved to 3% or better.

TABLE I

PHOTOCHEMICAL EXCHANGE OF IODINE AND *trans*-DIIODOETHYLENE IN HEXANE AT 25°

1 Concn. $C_2H_2I_2$ (mg. of 1/15 ml.)	2 Time, sec.	3 Total activity	4 Activity in I_2	5 Activity in $C_2H_2I_2$	6 $k \times 10^4$ (3 + 4)	7 $k \times 10^4$ (3 + 5)	8 $k \times 10^4$ (4 + 5)
50	500	0.158	0.132	0.026	1.46	1.46	1.46
50	1000	.158	.110	.046	1.51	1.43	1.45
50	1500	.158	.096	.060	1.42	1.35	1.38
50	2500	.295	.133	.166	1.44	1.50	1.46
50	3000	.271	.109	.164	1.40	1.44	1.42
50	4000	.271	.090	.187	1.35	1.47	1.38
5	6000	.192	.159	.033	1.61	1.61	1.61
5	8000	.180	.143	.036	1.60	1.53	1.54
10	3000	.192	.161	.037	1.29	1.61	1.56
10	4000	.192	.147	.046	1.58	1.62	1.62
25	2000	.205	.143	.059	1.57	1.47	1.50
25	3000	.192	.122	.069	1.36	1.33	1.34
100	1000	.251	.128		1.41		
100	1500	.251	.096		1.38		
250	500	.243	099		1.47		
250	300	.243	.141		1.47		
50	3000[a]	.252	.144	.112	1.48	1.57	1.53
50	2000[a,c]	.148	.105	.049	1.33	1.56	1.49
50	4000[a,c]	.143	.072	.077	1.40	1.60	1.49
50	6000[b]	.233	.128	.097	1.54	1.37	1.44
50	5000[b]	.233	.164	.067	1.05	1.01	1.02
50	7000[b]	.219	.122	.091	1.29	1.17	1.22
50	2000[c]	.219	.109	.106	1.54	1.45	1.49
50	1500[c]	.201	.116	.081	1.57	1.47	1.51
50	1500[d]	.221	.133	.089	1.44	1.46	1.46
50	2000[d]	.221	.110	.107	1.54	1.45	1.49
50	1800[e]	.179	.095	.080	1.53	1.42	1.47
50	1800[f]	.179	.099	.077	1.42	1.34	1.38
50	1500[f]	.221	.126	.092	1.61	1.54	1.56
50	2000[f]	.205	.103	.102	1.51	1.51	1.51
250	41400[g]	.233	.227	.003	0.0005	0.0002	0.0003

[a] Intensity of illumination decreased by screens of 29% transmission. [b] Intensity of illumination decreased by crossed screens of 29% transmission each. [c] Solution was stirred during illumination. [d] Air was swept out with nitrogen before cell was sealed. [e] Air was swept out with oxygen before cell was sealed. [f] Enough water was added to form a second phase. [g] Blank experiment. The solution was kept in the dark for the indicated time, and i_a was set equal to unity in the calculation of k.

In most experiments presented in Table I it is possible to evaluate x in expression (4) from any two of the three activities in columns 3, 4, and 5, and the rate constant in the arbitrary units has been calculated from each possible combination of activities. It is seen that the rate constant is independent of the diiodoethylene concentration over a fifty-fold variation from 5 to 250 mg./15 ml., and that the assumption that the rate is proportional to the square root of the intensity of illumination leads to fairly consistent values for the rate constant. The rate of reaction is also seen to be unaffected by saturating the solution with water, by stirring during illumination, or by sweeping out the air with either oxygen or nitrogen. The last experiment shows that the dark reaction is entirely negligible. A few attempts to estimate the temperature coefficient of the reaction were in agreement with the determinations over a larger temperature interval which are presented in Table II.

TABLE II

PHOTOCHEMICAL EXCHANGE OF IODINE AND DIIODOETHYLENE IN HEXANE

1	2	3	4	5	6	7	8	9
Concn. $C_2H_2I_2$ (mg. of 1/15 ml.)	Time, sec.	Temp., °C.	Total activity	Activity		$k \times 10^4$		
				in I_2	in $C_2H_2I_2$	(4 + 5)	(4 + 6)	(5 + 6)
				trans Isomer				
50	3000	15	0.233	0.132	0.087	0.81	0.66	0.72
50	2000	25	.271	.159	.099	1.14	0.96	1.02
50	1500	25	.251	.169	.072	1.11	0.94	0.99
50	2000	25	.361	.219	.139	1.06	1.03	1.05
50	1500	35	.332	.174	.149	1.87	1.72	1.79
50	2000	35	.332	.142	.174	1.93	1.65	1.80
50	1000	50	.221	.097	.117	3.73	3.36	3.55
978	100	25	.250	.151		1.03		
1958	50	25	.235	.151		0.90		
				cis Isomer				
50	3000	15	0.233	0.121	0.108	0.95	0.90	0.93
50	2500	15	.233	.136	.096	0.92	0.91	0.91
50	1500	25	.227	.132	.082	1.55	1.26	1.37
50	2000	25	.309	.154	.149	1.54	1.44	1.49
100	1000	25	.309	.159		1.38		
20	4000	25	.309	.180	.113	1.64	1.32	1.44
50	4000	25[a]	.309	.156	.141	1.39	1.23	1.30
50	6000	25[b]	.271	.160	.107	1.35	1.27	1.30
50	1500	35	.233	.109	.122	2.26	2.20	2.22
50	2000	35	.332	.126	.191	2.28	1.95	2.14
50	1000	50	.221	.084	.135	4.55	4.40	4.49
50	700	50	.221	.111	.107	4.32	4.13	4.23

[a] Intensity of illumination decreased by screens of 29% transmission. [b] Intensity of illumination decreased by crossed screens of 29% transmission each.

The few experiments with radioactive iodine prepared by fission of uranium are not reported in detail, for the radioactivities of the samples were so small that it was not possible to measure them with much accuracy. Two samples of this iodine in solution with ethyl iodide were illuminated for twelve hours at 50°, but it was impossible to detect any indication of exchange. Hull, Shiflett, and Lind[13] were unable to detect any evidence of thermal exchange between iodine and ethyl iodide when they were heated to 90° for fifteen minutes.

The second major series of photochemical exchange experiments is summarized in Table II. Since the optical system was modified slightly between the times when the two investigations were carried out, it is impossible to compare the absolute rates reported in Tables I and II. All samples were precipitated and activities measured in 50 mg. of iodide as carrier, and all solutions were stirred during illumination; but otherwise the procedure was the same as in the first series of experiments. The *cis* isomer exchanges with the same kinetics as the *trans*, but the rate at which it reacts is slightly greater at all temperatures studied. The last two experiments with the *trans* isomer show that the first order dependence of the rate of exchange upon diiodoethylene concentration holds quite well up to concentrations greater than those employed in the study of the isomerization reaction. The apparent slight falling off of the rate constant with decreasing intensity of illumination may be real; however, the rate of exchange is approximately proportional to the square root of the intensity of absorbed radiation and is certainly very far from being proportional to the first power.

The rate constants observed in experiments in which solutions containing 50 mg. of iodine in the diiodoethylene were illuminated without screens are plotted against reciprocal temperature in Fig. 1. If the data are fitted to the equation

$$k = AT^{1/2}e^{-E/RT} \qquad (5)$$

the value of E obtained is 8500 cal./mole for the *trans* exchange and 7900 cal./mole for the *cis*. A, in terms of the arbitrary unit of intensity used to calculate the rate constants, is 12 for the *trans* exchange and 5.2 for the *cis*, when time is expressed in seconds.

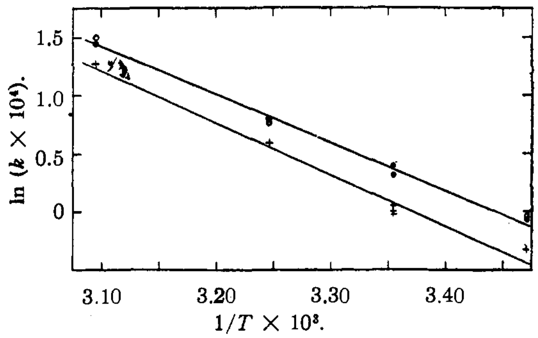

Fig. 1.—Temperature dependence of rate of photochemical exchange of diiodoethylene with iodine: +, *trans*, O, *cis*.

Thermal Experiments.—The derivation of the rate constant for the thermal exchange reaction is similar to that for the photochemical reaction presented in the preceding section. Since the instantaneous concentration of iodine atoms is probably constant throughout the solution, no assumption about mixing need be made, but it is still necessary to assume that the ratios of radioactive to non-radioactive iodine atoms in the atomic and molecular species of the free iodine are the same. If this reaction is also assumed to take place bimolecularly between an iodine atom and a diiodoethylene molecule, the value of the

Table III

Thermal Exchange of Iodine and Diiodoethylene in Decalin

1	2	3	4	5	6	7	8	9	10
					Activity		$k \times 10^3$ (ml./mole)$^{1/2}$ sec.$^{-1}$		
Concn. I_2 (mg./15 ml.)	Concn. $C_2H_2I_2$ (mg. of I/15 ml.)	Time, hr.	Temp., °C.	Total activity	in I_2	in $C_2H_2I_2$	(5 + 6)	(5 + 7)	(6 + 7)
trans Isomer									
10	50	20	99.8	0.372	0.166	0.204	3.1	3.1	3.1
10	100	10	99.8	.375	.149		3.4		
10	20	40	99.8	.355	.173	.144	4.2	2.7	3.2
50	50	10	99.8	.318	.261	.048	3.4	2.7	2.9
50	50	20	99.8	.211	.153	.053	3.0	2.7	2.8
50	50	40	99.8	.369	.223	.136	3.0	2.5	2.7
10	50	20	99.8[a]	.275	.130	.144	2.9	2.8	2.8
10	50	50	76.0	.278	.220	.051	0.33	0.29	0.29
10	50	106	76.2	.213	.140	.072	0.29	0.28	0.28
10	50	69	76.3[b]	.267	.203	.061	0.28	0.27	0.27
10	50	20	99.9[b]	.250	.125	.128	2.6	2.7	2.7
cis Isomer									
10	50	20	99.8	0.372	0.143	0.233	3.8	4.0	3.9
10	100	10	99.8	.375	.135		3.8		
10	20	40	99.8	.355	.156	.158	5.2	3.1	4.0
50	50	10	99.8	.318		.063		3.8	
10	50	20	99.8[a]	.275	.104	.159	3.9	3.4	3.7
10	50	50	76.0	.278	.207	.063	0.42	0.36	0.38
10	50	106	76.2	.213	.125	.088	0.37	0.37	0.37
10	50	69	76.3[b]	.267	.200	.075	0.30	0.34	0.33
10	50	20	99.9[b]	.250	.110	.137	3.2	3.1	3.1

[a] Water was added before starting the run. [b] Hexane was used for solvent instead of decalin.

rate constant in terms of experimentally observable quantities is

$$k = -\frac{2a^{1/2}}{(a+b)t} \ln \left[\frac{a+b}{b} x - \frac{a}{b}\right] \qquad (6)$$

in which the symbols have the same significance as in (2). In the data presented, the concentrations of the reactants are expressed in mg. of iodine in 15 ml. of solution at 25°, and the time is expressed in hours; however, the rate constants are calculated in the more customary units (ml./mole)$^{1/2}$ sec.$^{-1}$.

The results of the thermal exchange experiments are presented in Table III. Decalin was used for solvent in most experiments so that the results could be compared with those of the thermal isomerization experiments, but a few determinations were made in hexane solution so that the activation energies of the thermal and photochemical exchange reactions could be compared in the same solvent.

It is apparent that the reaction in decalin proceeds according to the assumed kinetics and that the rate is practically unaffected by the presence of water. The reaction is perhaps a little slower in hexane than it is in decalin, but it is impossible to say that there is any difference between the activation energies in the two solvents. One experiment in which the solution had never been dried with magnesium perchlorate indicated the same rate of reaction.

The energy of activation, E, calculated by means of equation (5) is 25,800 cal./mole for the *trans* exchange and 25,200 cal./mole for the *cis* The value of the A term in (ml./mole)$^{1/2}$ sec.$^{-1}$ is 2.0×10^{11} for the *trans* exchange and 1.3×10^{11} for the *cis*.

Isomerization Results

Photochemical Experiments.—The derivation of the rate constant for the photochemical isomerization reaction is very similar to the treatment of exchange in the same system. The local rate of reaction is assumed to be proportional to the square root of the local rate of absorption of radiation, and the same equation form is applied to the average rate for the solution as a whole on the assumption that the products of reaction in regions where the local rate is high are dispersed throughout the solution sufficiently rapidly with respect to the rate of reaction so that the ratio of the local concentrations of the two isomers is essentially the same everywhere in the solution at any particular time. If it is also assumed that the rate of each isomerization reaction is proportional to the concentration of the isomer reacting, the forward rate constant for the reaction $C_2H_2I_2$ (*trans*) $\rightleftarrows$ $C_2H_2I_2$ (*cis*) is

$$k_1 = -\frac{K}{(K+1)ti_a^{1/2}} \ln \left[(K+1)\alpha - K\right] \qquad (7)$$

if the diiodoethylene were initially in the *cis* form, and is

$$k_1 = -\frac{K}{(K+1)ti_a^{1/2}} \ln \left[\frac{K-(K+1)\alpha}{K}\right] \qquad (8)$$

if the diiodoethylene were initially in the *trans* form. In the expressions $i_a^{1/2}$ is the average square root of the rate of absorption of radiation as defined in (3), K is the equilibrium constant for the reaction, and α is the fraction of the diiodoethylene present in the *cis* form at time t. The rate constant for the reverse reaction, k_2, can be calculated from the relationship

$$k_1/k_2 = K \tag{9}$$

Since none of the photochemical isomerization experiments was continued until the solution was near to equilibrium, and since it was not considered to be justifiable to extrapolate the equilibrium constant for the thermal isomerization to the lower temperatures which were employed for the photochemical studies, the equilibrium constants used in the above expressions were calculated from the relative rates of the two isomerization reactions. At each temperature which was studied, solutions containing each isomer were illuminated for the same length of time, and the equilibrium constant was calculated from the relationship

$$K = \alpha_1/(1 - \alpha_2) \tag{10}$$

in which α_1 is the fraction of *cis*-diiodoethylene in the solution which initially contained only the *trans* isomer, and α_2 is the fraction of *cis* in the solution which initially contained only the *cis* isomer. The rate constants were then calculated by means of equations (7) or (8), and (9); by this treatment it was only possible to calculate one set of values for k_1, k_2 and K from a pair of rate experiments at a specific temperature.

A few samples of five mole per cent. solutions of diiodoethylene in hexane containing the same iodine concentration as the exchange experiments presented in Table II were illuminated under the same experimental conditions. The isomerization reaction was found to be much slower than the exchange, and illuminations for twenty-four hours at 50° produced only about 10% change in isomeric composition. The approximate rate constants for the reactions when time was expressed in seconds and intensity in arbitrary units were 1.1×10^{-6} for the isomerization of *trans*- to *cis*-diiodoethylene (k_1) and 1.4×10^{-6} for the isomerization of *cis* to *trans* (k_2). The rate constants for the corresponding exchange reactions at the same temperature are 3.6×10^{-4} for the *trans* isomer and 4.4×10^{-4} for the *cis*. Therefore, approximately 300 molecules exchange at 50° for every one which isomerizes.

In order to measure the energy of activation for the reaction, several solutions were illuminated at higher temperatures. In these experiments decalin was used for solvent instead of hexane, and the reaction cell was swept out with nitrogen free from oxygen before it was sealed. The rate of isomerization appeared to be proportional to the square root of the intensity of illumination just as was postulated in the derivation of the rate equation and as the rate of exchange was found to be in the experiments described above. Photometric examinations of the solutions before and after reaction indicated that considerable amounts of iodine were liberated during exposure. Since it is impossible to correct for the effect of this additional iodine without a detailed knowledge of the absorption coefficients of the solution for the radiation with which it was illuminated, the rate constants which are shown in Table IV must be viewed with some suspicion.

TABLE IV

PHOTOCHEMICAL ISOMERIZATION OF DIIODOETHYLENE IN DECALIN

(Same experimental conditions as in Table II)

Initial isomer	Temp., °C.	Time, hr.	% *cis*	$k_1 \times 10^6$	$k_2 \times 10^6$
cis	77	20	68.3	3.1	6.0
trans	77	20	16.2		
cis	100	35	49.5	11	14
trans	100	35	41.0		
trans	100	5	13.4		
cis	114	5	65.0	20	29
trans	114	5	23.7		

If the rate constants are plotted against reciprocal temperature and the equations of the best curves through the points are fitted to equation (5), the values of E are 13,300 cal./mole for k_1 and 11,000 cal./mole for k_2. The values of A in the arbitrary units are 36 for k_1 and 2.2 for k_2.

Thermal Experiments.—The results of experiments to determine the equilibrium of ten mole per cent. solutions of diiodoethylene in decalin at different temperatures are shown in Table V. Since the investigation was somewhat hurried, the data are not as extensive as might be desired but indicate the approximate values of the equilibrium constants at the temperatures studied. For the reaction in decalin solution $C_2H_2I_2$ (*trans*) $\rightleftarrows$ $C_2H_2I_2$ (*cis*) at 144°, $\Delta F^0 = 240 \pm 70$ cal./mole, $\Delta H^0 = 1800 \pm 1000$ cal./mole, and $\Delta S^0 = 3.7 \pm 2.5$ cal./mole deg.

TABLE V

THERMAL EQUILIBRIUM OF DIIODOETHYLENE IN DECALIN

Initial isomer	Temp., °C.	Time, hr.	I_2 concn. (mg./15 ml.) Initial	I_2 concn. (mg./15 ml.) Final	% *cis*	Equilibrium % *cis*	K $\frac{\% \textit{cis}}{\% \textit{trans}}$
cis	129.8	211.5	75.0	90.2	42.5	40.5	0.681
trans	129.8	211.5	74.4	92.2	39.1		
cis	144.1	111.4	73.1	101	42.8	42.7	0.745
trans	144.1	111.4	74.3	99.4	42.6		
cis	159.2	45.0	74.4	92.0	44.6	44.2	0.792
trans	159.2	45.0	75.5	104	43.9		

The forward rate constant for the iodine atom catalyzed thermal reaction $C_2H_2I_2$ (*trans*) $\rightleftarrows$ $C_6H_2I_2$ (*cis*) is given by the expression

$$k_1 = -\frac{K}{(K+1)t[I_2]^{1/2}} \ln\left[(K+1)\alpha - K\right] \tag{11}$$

if the diiodoethylene was initially in the *cis* form; while the logarithmic term is altered as in (8) if

TABLE VI

THERMAL ISOMERIZATION OF DIIODOETHYLENE IN DECALIN

Initial isomer and concn. in mole per cent.	Temp., °C.	Time, hr.	Initial concn. I_2 (mg./15 ml.)	Final concn. I_2 (mg./15 ml.)	% *cis*	K (assumed)	$k_1 \times 10^3$ ((ml./mole)$^{1/2}$ sec.$^{-1}$)	$k_2 \times 10^3$ ((ml./mole)$^{1/2}$ sec.$^{-1}$)
cis (5)	144.0	37.5	0.0	2.2	96.5	0.745	0.4	0.5
trans (5)	144.0	20.0	0.0	1.9	4.2	.745	1.2	1.7
trans (5)	144.1	20.0	74.3	82.4	26.9	.745	1.30	1.74
cis (5)	144.0	20.0	74.3	81.7	64.0	.745	1.29	1.73
trans (5)	144.1	67.2	74.3	92.2	41.4	.745	1.3	1.7
cis (5)	144.1	67.2	74.3	90.2	45.3	.745	1.2	1.6
trans (5)	144.1	20.0	74.3	81.4	26.2	.745	1.24	1.67
trans (5)	144.1	20.0	18.6	21.6	16.6	.745	1.26	1.69
cis (5)	144.1	20.0	18.6	17.6	77.8	.745	1.33	1.78
trans (10)	144.0	20.0	74.3	83.4	24.8	.745	1.13	1.52
cis (10)	144.0	20.0	73.1	82.4	63.7	.745	1.32	1.77
trans (10)	144.1	30.0	74.3	86.3	31.3	.745	1.13	1.52
cis (10)	144.1	31.2	73.1	85.3	53.4	.745	1.40	1.87
cis (10)	157.5	15.0	19.0	22.6	60.0	.786	4.4	5.5
trans (10)	157.5	15.0	18.4	22.6	27.3	.786	3.4	4.3
trans (10)	142.8	20.0	73.5	79.5	22.6	.739	1.00	1.35
trans (10)	142.8	20.0	73.9	82.4	24.2	.739	1.09	1.48
cis (10)	132.1	50.0	75.5	78.9	75.5	.695	0.27	0.39
trans (10)	132.1	50.0	73.5	79.8	22.4	.695	0.40	0.58

the *trans* isomer was present initially. In this expression $[I_2]$ is the concentration of iodine, and the other terms have been defined previously. The rate constant for the reverse reaction can be calculated with the use of equation (9). These expressions assume that the iodine concentration was constant throughout the course of a single experiment, whereas in reality it increased somewhat due to decomposition of the diiodoethylene. However, since the percentage change in iodine concentration was not large, a satisfactory rate constant can be obtained by substitution of the average concentration into (11).

The results of studies of the kinetics of the reaction are summarized in Table VI. The concentration of the iodine is expressed in mg./15 ml. and the time in hours, but the rate constants are calculated in (ml./mole)$^{1/2}$ sec.$^{-1}$ as in Table III. The rate is proportional to the first power of the diiodoethylene and the half power of the iodine concentrations. The only isomerization observed in the runs in which iodine was not present initially can easily be accounted for on the basis of catalysis by the few mg. of iodine liberated by decomposition of the diiodoethylene. The variations of the rate constants with temperature are plotted in Fig. 2.

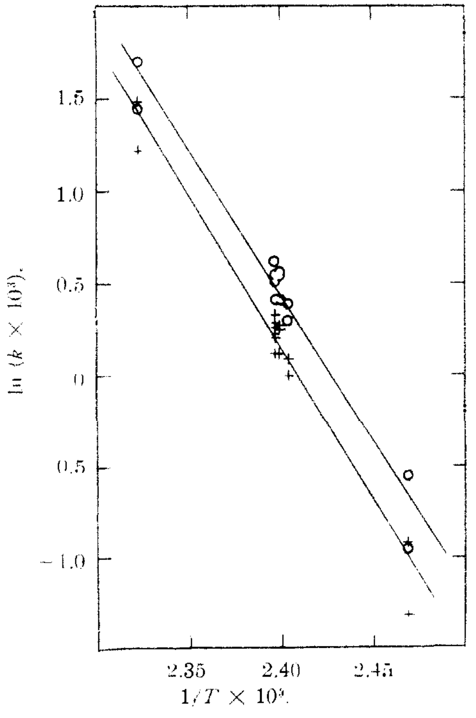

Fig. 2.—Temperature dependence of rate of iodine-catalyzed thermal isomerization of diiodoethylene: +, *trans* (k_1). O, *cis* (k_2).

The energy of activation, E, calculated by means of equation (5) is 32,900 cal./mole for the *trans* isomerization (k_1) and 31,300 cal./mole for the *cis* (k_2). The value of the A term in (ml./mole)$^{1/2}$ sec.$^{-1}$ is 1.1 × 10^{13} for k_1 and 2.0 × 10^{12} for k_2. The data are not at all precise, and the errors in the energies of activation may be as much as 5000 cal./mole; however, there was no time in which to make any more accurate determinations.

Discussion of Results

The results of the calculations of the rate constants for the reactions described in the preceding sections are summarized in Table VII. The values of A and k for photochemical reactions are expressed in the same arbitrary units described previously; the values for thermal reactions are expressed in (ml./mole)$^{1/2}$sec.$^{-1}$. The values of E are always expressed in cal./mole.

TABLE VII

RATE DATA FOR REACTIONS BETWEEN IODINE AND DIIODOETHYLENE

Type of reaction		Solvent	A	E	Rate const. at temp. indicated	
		trans Reactions				
Photochemical	Exchange	Hexane	12	8500	3.6×10^{-4}	(50)
	Isomerization	Decalin	36	13300	6.0×10^{-7a}	(50)
	Isomerization	Hexane			1.1×10^{-6}	(50)
Thermal	Exchange	Decalin	2.0×10^{11}	25800	0.13^{a}	(144)
	Isomerization	Decalin	1.1×10^{13}	32900	1.3×10^{-3}	(144)
		cis Reactions				
Photochemical	Exchange	Hexane	5.2	7900	4.4×10^{-4}	(50)
	Isomerization	Decalin	2.2	11000	1.5×10^{-6a}	(50)
	Isomerization	Hexane			1.4×10^{-6}	(50)
Thermal	Exchange	Decalin	1.3×10^{11}	25200	0.15^{a}	(144)
	Isomerization	Decalin	2.0×10^{12}	31300	1.7×10^{-3}	(144)

[a] Extrapolated value.

The rates of the thermal and photochemical isomerization reactions are known with moderate precision at only one temperature, and the values of A and E calculated from the temperature dependence of the rates are less reliable than the values for the corresponding exchange reactions. In Table VIII the energies of activation, E, of the isomerization reactions have also been calculated from the rate constants, k, at the temperatures at which they are known most reliably by assuming the values of A from the corresponding exchange reactions. For reasons discussed below these energies of activation are probably somewhat more reliable than those presented in Table VII.

TABLE VIII

ENERGIES OF ACTIVATION OF ISOMERIZATION REACTIONS RECALCULATED WITH THE USE OF A FACTORS FROM CORRESPONDING EXCHANGE REACTIONS

Type of reaction	Solvent	A (assumed)	E (calcd.)	Rate const. at temp. indicated (obs.)	
		trans Reactions			
Photochemical	Hexane	12	12200	1.1×10^{-6}	(50)
Thermal	Decalin	2.0×10^{11}	29600	1.3×10^{-3}	(144)
		cis Reactions			
Photochemical	Hexane	5.2	11600	1.4×10^{-6}	(50)
Thermal	Decalin	1.3×10^{11}	29000	1.7×10^{-3}	(144)

The differences between the energies of activation for the thermal and photochemical reactions provide an indication of the self-consistency and accuracy of the data. In connection with a study of the iodine-catalyzed isomerization of cinnamic acid, Dickinson and Lotzkar[1] showed that in any solvent the difference between the thermal and photochemical activation energies ($E_t - E_p$) for any iodine atom catalysis of this type should be equal to half the change in heat content upon dissociation of molecular iodine in that solvent. The treatment assumed that the photochemical absorption coefficients of iodine were independent of temperature over the interval studied and that the recombination of iodine atoms to form molecules proceeded without activation energy. It also assumed that any electronic excitation or extraordinary translational energy of an iodine atom at the time of photochemical dissociation was almost immediately lost by interaction with solvent molecules, and that therefore the chemical behavior of an atom formed by photochemical dissociation was indistinguishable from that of an atom formed by thermal dissociation.

One half the heat content of dissociation of molecular iodine in the gas phase at 18° is 18,135 cal./mole.[14] Dickinson and Lotzkar calculated that $E_t - E_p$ for the iodine-catalyzed isomerization of cinnamic acid in benzene solution was 19,400 cal./mole, in fair agreement with this value. When Wood and Dickinson studied the iodine-atom catalyzed isomerization of the dichloroethylenes in decalin solution, they observed an energy of activation of 30,200 cal./mole for the thermal isomerization of the *cis* isomer,[3] and of 13,400 cal./mole for the photochemical isomerization.[15] The difference is 16,800 cal./mole. The values of $E_t - E_p$ for the reactions studied in the present investigation are presented in Table IX. It is apparent that the differences between the energies of activation for the isomerization reactions presented in Table VIII are in

TABLE IX

DIFFERENCES IN ENERGIES OF ACTIVATION FOR THERMAL AND PHOTOCHEMICAL REACTIONS OF IODINE AND DIIODOETHYLENE

Isomer reacting	Type of reaction	$E_t - E_p$ Data from Table VII	$E_t - E_p$ Data from Table VIII
trans	Exchange	17,300	
	Isomerization	19,600	17,400
cis	Exchange	17,300	
	Isomerization	20,300	17,400

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(14) F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936, p. 13.

(15) Reuben E. Wood, private communication.

much better agreement with the corresponding differences for the exchange reactions than are the values calculated from the data for isomerization reactions in Table VII, but even these are in satisfactory agreement in view of the estimated experimental error for E of several kilocalories. The differences calculated from the data in Table VIII are also in better agreement with the 16,800 cal./mole difference observed by Wood and Dickinson for another iodine-catalyzed reaction in a saturated hydrocarbon solvent.[16]

As was indicated in the introduction, this investigation was undertaken in the expectation that a comparison of the rate constants of the exchange and isomerization would yield information concerning the mechanism of the reactions. At 50° the photochemical exchange reactions in hexane are about 300 times as fast as the corresponding isomerizations; and if the rates of thermal exchange in decalin are extrapolated to 144° by the use of the activation energies observed below 100°, the reactions are found to be about 100 times as fast as the corresponding isomerizations. Obviously most of the molecules which exchange do so without any change in configuration. The problem of accounting for the rapid exchange reaction by some mechanism which would not lead to an accompanying isomerization is an interesting one, and it is instructive to consider the conditions which any satisfactory explanation must account for:

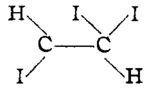
(1) *Both the exchange and the isomerization reactions involve iodine atoms.* The kinetics data are completely in accord with this conclusion, and the differences between the energies of activation of the thermal and photochemical reactions which have been discussed above provide additional support.

(2) *The exchange of diiodoethylene with iodine goes faster than the isomerization under the same conditions because the energy of activation for the first reaction is less* and not because there is a greater number of molecular collisions in which the configurational relationships are more favorable to exchange than to isomerization. Although the rate of isomerization is always much less than that of exchange under the same conditions, the values of the A terms calculated for the isomerization reactions in Table VII are, if anything, larger than those for the corresponding exchange reactions. If the A terms are assumed to be identical for isomerization and exchange as was done in Table VIII, the differences between the energies of activation for the isomerization and exchange reactions are 3700 cal./mole for the photochemical reactions of both isomers and 3800 cal./mole for the thermal reactions. The differences are probably in fair approximation to the differences in the energies of the critical complexes associated with isomerization and exchange.

(3) *The presence of a carbon–carbon double bond is essential to the exchange reaction.* Ethyl iodide fails completely to exchange with iodine under conditions which lead to rapid exchange of the diiodoethylenes, and the difference in behavior of the two compounds can hardly be ascribed to the presence of iodine atoms on the adjacent carbon atoms of the diiodoethylene. This extreme difference in reactivity cannot be the result of a difference of the energies of the bonds which are broken during exchange in the two compounds, for the carbon–halogen bond distance in the dihaloethylenes is smaller than the value to be expected from the normal covalent radii.[17] Moreover, in many types of reactions a halogen atom adjacent to a carbon–carbon double bond is *less* readily removed from the molecule than is a halogen atom bound to a saturated aliphatic radical. (Possibly, however, this relative non-reactivity of halogen on doubly-bound carbon may only be observed in ionic and not atomic reactions.) We believe that a plausible mechanism for the exchange reaction should involve an interaction of the iodine atom with the electrons of the double bond.

(4) *The same structure cannot exist as an intermediate in the exchange reactions of both isomers.* This conclusion is a result of the principle of microscopic reversibility and the fact that both isomers exchange much more frequently than they isomerize.

While these conditions are incompatible with Olson's proposed mechanism,[4] what has seemed to us the most satisfactory explanation of the data is offered by an application of the concept of restricted rotation to the theory of Berthoud and Urech.[2] According to this theory the iodine atom adds to one of the carbon atoms to form a complex which we believe can be reasonably described as consisting of two groups joined by a single bond—an approximately planar CHI group, with an additional electron in the fourth bond-forming orbital of the carbon atom, and the pyramidal CHI_2 group



(12)

It appears to us that such a complex could be formed most easily if the entering iodine atom approached from out of the plane of the original molecule and interacted with the p_z orbitals[18] of the double bond. As the entering atom formed

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[16] Another argument in favor of the data in Table VIII may be based on the fact that the rate at 150° of the iodine-catalyzed thermal isomerization of *trans*-diiodoethylene in decalin is almost the same as that of the isomerization of *trans*-dichloroethylene under the same conditions,[3] and the equality in the rates of these very similar reactions is most plausible if the values of A and E are nearly the same for both reactions. The values observed by Wood and Dickinson were 7.5×10^{10} $(\text{ml./mole})^{1/2}$ sec.^{-1} and 29,200 cal./mole for A and E, respectively. These values are in much better agreement with those in Table VIII than they are with those in Table VII.

[17] Linus Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, pp. 214–217.

[18] Linus Pauling, *ibid.*, p. 89.

a bond with one of the carbon atoms,[19] the other iodine atom attached to the same carbon would be forced out of the original plane of the molecule on the opposite side. When the situation was attained in which these two iodine atoms were equidistant from the plane determined by the two carbon atoms and the third iodine atom, they would be equivalent to each other; and the decomposition of the complex into an iodine atom and a diiodoethylene molecule would be as apt to result in exchange as in the loss of the iodine atom whose addition produced the complex. No matter which iodine atom was lost, the reaction would not result in an isomerization of the original diiodoethylene molecule, and the formation of any configuration which would result in isomerization upon loss of an iodine atom would require more rotation about the carbon–carbon bond than would be involved in the formation of the configuration just described. Further distortion of the groups and relative rotation from the configuration which allows exchange without isomerization would be necessary in order that isomerization should occur. It is not possible to predict the critical angle of relative rotation for isomerization, nor is it clear whether at this critical angle the complex is even approximately symmetrical[20] with respect to the iodine atoms, but it seems certain, at least, that its energy should be greater than that of the critical complex for the exchange reaction. It would be expected that the internal rotation would be hindered by the direct interaction of the large iodine atoms and also, probably, by interactions of the unshared electron of the trivalent carbon atom with the iodine atoms attached to the other carbon atom, and with that atom itself, giving the carbon–carbon bond some residual double bond character. The observed 3800 cal./mole difference in the energies of activation of exchange and of isomerization would appear to be a reasonable value for the effective barrier opposing internal rotation as referred to the energy of the most stable configuration in which the two iodine atoms on the same carbon are equivalent.

Acknowledgment.—We wish to express our gratitude to Dr. Martin Kamen and Dr. Fred J. Leitz, Jr., of the Radiation Laboratory of the University of California who provided the radioactive iodine without which the exchange experiments would have been impossible. We are also indebted to Mr. Harold S. Johnston for assistance in some of the experimental work and to Dr. Saul Winstein for helpful suggestions as to the possible mechanism of the exchange reaction.

Summary

cis- and *trans*-diiodoethylene exchange iodine with the element both photochemically and thermally in saturated hydrocarbon solvents. The kinetics indicate that the reaction occurs between a molecule of diiodoethylene and an iodine atom with an activation energy of about 8000 cal./mole for each isomer.

The *cis*- and *trans*-diiodoethylenes are slowly isomerized by elementary iodine both thermally and photochemically. The rate of the isomerization reaction is less than one per cent. of that of the exchange reaction under the same conditions but shows the same dependence upon the concentrations of the reactants and upon the intensity of illumination. The activation energy required for isomerization catalyzed by iodine atoms is approximately 4000 cal./mole more than that necessary for exchange.

The fact that ethyl iodide does not exchange photochemically with free iodine at 50° suggests that iodine atoms do not easily replace those in saturated organic iodine compounds, even though the same atoms exchange rapidly with those attached to ethylenic carbon atoms.

A molecular mechanism to account for these observations has been proposed.

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[19] A symmetrical three-membered-ring complex similar to those proposed by I. Roberts and G. E. Kimball (THIS JOURNAL, **59**, 947 (1937)) to account for the *trans* addition of halogen to double bonds and by S. Winstein and H. J. Lucas (*ibid.*, **61**, 1576, 2845 (1939)) to account for retention of configuration during replacement reactions might be formed as an intermediate in this reaction; however, the existence of such an intermediate would not be essential to either the exchange or the isomerization reaction.

[20] In spite of this it can be said with some confidence that just one half of the isomerization reactions will occur with exchange because, with the greater energy of activation for isomerization as compared to exchange, a reaction process corresponding to exchange followed by isomerization will be no less probable than one leading directly to isomerization.