those for $K_4Fe(CN)_6$[1] at corresponding molalities, but the shape of the curves $-\log \gamma_{\pm}$ *vs.* $m^{1/2}$ are similar. The activity coefficients for $Pt(en)_3Cl_4$ are lower than those for the two 1–4 salts.

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EAST LANSING, MICH.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

Reactions of 2-Iodobutane with Iodine. Evidence for a Radical Reaction with Inversion of Carbon

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Optically active 2-iodobutane undergoes iodine-catalyzed racemization and also exchanges with isotopically labeled elementary iodine. The two simultaneous thermal reactions have been studied between 130 and 170° in hexachlorobutadiene-1,3. If iodine atoms caused exchange only by direct substitution involving inversion of carbon, the ratio of rates of racemization to exchange would be 2.0; if they reacted only by abstracting iodine to form racemic butyl radicals, the ratio would be 1.0. The observed ratio is 1.54 ± 0.06 independent of temperature and of concentration of either species. The results provide strong evidence for an inversion of a carbon atom caused by a radical reagent, but we cannot completely exclude the less plausible interpretation that a large fraction of racemic *sec*-butyl radicals react with the identical iodine molecules formed at their own geneses. Experiments are suggested which might more firmly establish the presence or absence of a radical inversion reaction in this system.

Introduction

Nucleophilic reagents containing a free pair of electrons usually react with organic compounds either by substitution with inversion of a carbon atom or by abstraction of a species (most frequently but by no means invariably a proton) attached to carbon, nitrogen or oxygen. Radical reagents usually react either by addition to a multiple bond or by abstraction of a species. The possibility has been recognized that radicals might cause substitution with inversion of a carbon atom, but until very recently no examples had been clearly demonstrated.

Theoretical calculations[2] could not make a clear prediction whether an iodine atom would react with an alkyl iodide by abstraction of iodine or by substitution with inversion of carbon.

Most attempts to obtain experimental evidence for inversion by halogen radicals have yielded results that were negative or inconclusive. Thus Brown, Kharasch and Chao[3] showed that the chlorination of optically active 1-chloro-2-methylbutane yielded inactive 1,2-dichloro-2-methylbutane. This result demonstrates only that if the reaction involved displacement of hydrogen by a chlorine atom, then the product was racemized as fast as it was formed. Yuster and Reyerson[4] failed to find evidence for hydrogen atoms during the chlorination of propane, and Franklin and Shepherd[5] similarly failed to detect iodine atoms from the reaction of methyl radicals with isopropyl iodide, but it is not certain that the analytical methods in the first study were sufficiently sensitive.

The elegant work of Davidson and Sullivan gave more clearly negative results. These authors studied the exchange of labeled bromine with bromotrichloromethane and also measured the rate of the bromine atom initiated reaction

$$Cl_3CBr + HBr \longrightarrow Cl_3CH + Br_2$$

The rate of exchange could be equated quantitatively to the rate of the process

$$Cl_3CBr + Br \longrightarrow Cl_3C\cdot + Br_2$$

and the direct displacement of one bromine atom by another was clearly too slow to detect under these conditions.

The kinetic study of Ogg and Polanyi[7] provides the most positive evidence for a halogen radical inversion reaction. These authors studied the gas phase racemization of 2-iodobutane caused by the iodine produced in its own decomposition at 240–280°. The kinetics clearly indicated that racemization involved reaction of an iodine atom with 2-iodobutane. It was argued that this reaction was an inversion reaction and could not involve abstraction of iodine to form a racemic *sec*-butyl radical because a significant reaction of these radicals with iodine would cause iodine inhibition of the decomposition of 2-iodobutane. This decomposition would presumably involve the same radicals, and no inhibition by iodine was observed. The results are certainly suggestive, but they hardly seem conclusive because the data were complicated by heterogeneous effects and because the authors failed to consider that racemization might also occur through abstraction of iodine from 2-iodobutane by a *sec*-butyl radical.

While our work was in process, Steacie and coworkers failed to find evidence for the reaction[8]

$$H + CH_3C_6H_5 \longrightarrow CH_4 + C_6H_5$$

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[1] Based on the Ph.D. Dissertation of Raymond A. Herrmann. The original dissertation and microfilms thereof are available from the Library of Columbia University.

[2] E. Gorin, W. Kauzmann, J. Walter and H. Eyring, *J. Chem. Phys.*, **7**, 633 (1939).

[3] H. C. Brown, M. S. Kharasch and T. N. Chao, THIS JOURNAL, **62**, 3435 (1940).

[4] S. Yuster and L. H. Reyerson, *J. Phys. Chem.*, **39**, 859 (1935).

[5] J. L. Franklin and G. R. L. Shepherd, THIS JOURNAL, **76**, 609 1954).

[6] N. Davidson and J. H. Sullivan, *J. Chem. Phys.*, **17**, 176 (1949); J. H. Sullivan and N. Davidson, *ibid.*, **19**, 143 (1951).

[7] R. A. Ogg, Jr., and M. Polanyi, *Trans. Faraday Soc.*, **31**, 482 (1935).

[8] A. T. Blades and E. W. R. Steacie, *Can. J. Chem.*, **32**, 1142 (1954).

but did obtain data supporting the elementary process[9]

$$CH_3 + CH_3HgCH_3 \longrightarrow C_2H_6 + Hg + CH_3$$

This reaction most plausibly involves attack of a radical on carbon.

The present study was undertaken to reëxamine the reaction of Ogg and Polanyi but to work in solution where heterogeneous effects could be avoided and to use isotopic tracers that were unavailable at the time of the original study. The principles involved are the same as those in the classic study with iodide ions by Hughes and co-workers.[10] If the exchange proceeds by an abstraction of iodine similar to other known radical reactions, the steps are

$$d\text{-BuI} + I^* \longrightarrow dl\text{-Bu} + II^* \qquad (A1)$$

$$dl\text{-Bu} + I_2^* \longrightarrow dl\text{-BuI}^* + I^* \qquad (A2)$$

In these expressions, BuI denotes 2-iodobutane, *dl* denotes a species that may exist in dextro or levo form with equal probability, and I* denotes an iodine atom originally present in the element. According to this mechanism, one molecule of racemic 2-iodobutane is produced for each iodine atom that is exchanged, and the ratio of the rates of racemization and exchange should be unity.

If the exchange proceeds by the radical substitution reaction proposed by Ogg and Polanyi, the important step is

$$d\text{-BuI} + I^* \longrightarrow l\text{-BuI}^* + I \qquad (S1)$$

According to this mechanism, exchange of one iodine atom in a solution of *d*-BuI produces the same net optical effect as racemization of two molecules of the organic iodide, and the ratio of the rates of racemization and exchange should be two.

In addition to measuring the ratio between the two rates, the study also furnishes information on the kinetics of the individual reactions and on the thermal decomposition of 2-iodobutane. Since the absolute rates of these reactions seemed to be affected by extraneous influences that could not be completely controlled from run to run, the ratios of racemization to exchange were always calculated from measurements on the *same* thermostated sample.

Experimental

Materials.—The solvent used in all experiments was hexachlorobutadiene-1,3 purchased from the Hooker Electrochemical Company and used without further purification. Blank tests under the conditions of the experiments showed that this material was inert except for reaction with an amount of iodine that was no more than 2% of the most dilute concentrations used.

Optically active 2-iodobutane was prepared from alcohol resolved by crystallization of the brucine salt of the monoester of phthalic acid. The monoester was prepared by the method of Pickard and Kenyon,[11] and the brucine salt was prepared and resolved both by a method furnished by Professor Robert L. Burwell, Jr. of Northwestern University[12] and also by the method of Kantor and Hauser.[13] The partially resolved salt was hydrolyzed and saponified to yield *l*-2-butanol that was 50% resolved. The 2-iodobutane was prepared from the alcohol by HI,[11] washed both with hydrochloric acid and with sodium carbonate, dried over magnesium sulfate, and vacuum distilled under nitrogen.

A few preliminary experiments were made with racemic 2-iodobutane obtained from the Eastman Kodak Company and purified in the same way. The rate of exchange of this material agreed to within about 10% with the rate obtained with the resolved iodide.

Resublimed reagent grade iodine was used without further purification. Solutions were activated with aqueous carrier-free solutions of iodine-131 obtained on allocation from the United States Atomic Energy Commission. The solutions were dried over magnesium sulfate and filtered through fritted glass before use.

Preparation and Heating of Ampules.—Stock solutions of isotopically labeled iodine and of optically active 2-iodobutane were mixed in Pyrex ampules to prepare 15 ml. for each run. The mixture was degassed by a procedure that involved fivefold freezing to Dry Ice temperature and pumping with a mercury diffusion pump, and the evacuated ampule was sealed.

A wax thermostat was used for heating at 130°, and at higher temperatures the bath contained a mixture of fused alkali nitrates. Temperatures were controlled to 0.1° or better by mercury-in-glass regulators and were measured with a Bureau of Standards partial immersion thermometer. Ampules were heated for known times and cooled rapidly. Precautions were taken to prevent exposure of hot ampules to illumination.

Methods of Measurement.—The contents of each ampule could be analyzed for amounts of decomposition, racemization and exchange.

The amount of decomposition was calculated from measurements of optical density at 519 mμ with a Beckman spectrophotometer. At the higher iodine concentrations, a 1-ml. sample of the solution was pipeted and diluted with solvent before it was placed in the spectrophotometer.

After optical density had been measured with the spectrophotometer, the iodine was removed by adding about 1 g. of electrolytic copper dust, letting the mixture stand for about half an hour with occasional shaking, and filtering. This procedure was more convenient than extraction of the iodine with aqueous sulfite, and tests showed that the same rates of racemization and exchange were obtained with either method of extraction.

Optical rotation of the solution was then measured after it had been thermostated at 25° in a 400 mm. semimicro polarimeter tube. This step was omitted for solutions containing the lowest concentration of iodine because the rate of racemization was so slow that changes in rotation could not be measured with significance.

The final measurement for exchange involved diluting a 10-ml. sample of the solution to 50 ml. and counting with a liquid jacketed Geiger counter. An aliquot of the original iodine solution was diluted and counted in the same way, and the data were used to calculate the fraction of iodine-131 that was unreactive with copper.

Calculation of Results.—The interpretation of the results involves a subtle distinction of a factor of two, and there are many places where incorrect calculations could introduce such a factor spuriously. Therefore, we shall present our equations in somewhat more detail than is often necessary.

Because of the decomposition reaction, the concentrations of iodine and of 2-iodobutane were not constant. During the time intervals of interest, concentrations of iodine increased a maximum of 20.3% and an average of 7.4%. For the 15 runs of importance in determining the ratio of racemization to exchange, the maximum increase was 12.2% and the average was 4.7%. Because the iodine was usually in smaller concentration and changed by small percentages when it was more concentrated, the concentration of 2-iodobutane never decreased by more than 12.2%, and in 85% of the runs the change was less than 3%. Because the percentage changes were so small, it was permissible to use average concentrations in all rate expressions. These concentrations were calculated from the equations

$$[I_2]_{av} = \frac{D_1 + D_2}{2D_0}[I_2]_0 \qquad (1)$$

$$[BuI]_{av} = [BuI]_0 - 2([I_2]_{av} - [I_2]_0) \qquad (2)$$

where D is optical density and the subscripts 0, 1 and 2 refer to the initial value and the values at the two times used to determine rate of reaction.

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[9] H. G. Oswin, R. Rebbert and E. W. R. Steacie, *Can. J. Chem.*, **33**, 472 (1955).

[10] E. D. Hughes, F. Juliusburger, S. Masterman, B. Topley and J. Weiss, *J. Chem. Soc.*, 1525 (1935).

[11] R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **99**, 45 (1911).

[12] Private report by J. Dyer, Northwestern University.

[13] S. W. Kantor and C. R. Hauser, This Journal, **75**, 1744 (1953).

If x_i is the fraction of radioactivity (initially all present in the iodine) that is organically bound at time *i*, then

$$x_\infty = [\mathrm{BuI}]_{\mathrm{av}}/([\mathrm{BuI}]_{\mathrm{av}} + 2[\mathrm{I_2}]_{\mathrm{av}})$$

If $F_i = 1 - x_i/x_\infty$, then the rate of exchange, R_{ex}, is given by the equation

$$R_{\mathrm{ex}} = \frac{2[\mathrm{I_2}]_{\mathrm{av}}x_\infty}{t_2 - t_1} \ln (F_1/F_2) \qquad (3)$$

Since the rate of loss of optical activity is proportional to the angle of rotation in any racemization, we can write

$$k_{\mathrm{rac}} = \frac{\ln (\alpha_1/\alpha_2)}{t_2 - t_1} \qquad (4)$$

where α is the angle of rotation.

Since the products of decomposition of the 2-iodobutane are presumably racemized, the decrease in angle of rotation is due both to formation of inverted 2-iodobutane and to decomposition. The ratio of interest is the rate of formation of racemic molecules of 2-iodobutane divided by the rate of incorporation of iodine from the element into 2-iodobutane. The ratio, *U*, is given by

$$U = \frac{k_{\mathrm{rac}}[\mathrm{BuI}]_{\mathrm{av}} - 2R_{\mathrm{dec}}}{R_{\mathrm{ex}}} \qquad (5)$$

where

$$R_{\mathrm{dec}} = \mathrm{d}[\mathrm{I_2}]/\mathrm{d}t = \frac{[\mathrm{I_2}]_2 - [\mathrm{I_2}]_1}{t_2 - t_1} \qquad (6)$$

This correction for decomposition was 30% in one run, but it only averaged 7.7% and its application did not significantly affect the conclusions of this investigation. As was indicated above, *U* would be 2.00 if all exchange went with inversion of configuration and would be 1.00 if all exchange went with formation of a racemic radical.

Results and Discussion

Ratio of Racemization to Exchange.—Rates of racemization and exchange were measured simultaneously for 22 runs at four temperatures, but not all runs were equally reliable. At low iodine concentrations, scarcely any detectable racemization of the 2-iodobutane took place during a time in which the major fraction of the radioactivity became organically bound. Therefore, the ratio, *U*, was calculated from the 15 runs in which the concentration of iodine was 10^{-2} mole/liter or greater.

The results of these runs are presented in Table I. For each run, the probable error in ln *U* was calculated from the estimate that *F* could be measured with a probable error of 0.01 and that α could be measured with a probable error of 0.01°. For the seven rejected runs at low iodine concentrations, assumption of these probable errors indicates that *U* is uncertain in each case by at least a factor of 2, so these runs are worthless for discriminating between the two mechanisms. If the runs in Table I are weighted inversely as the estimated probable errors in ln *U*, the weighted average gives $\ln U = 0.433 \pm 0.024$ and $U = 1.54 \pm 0.04$. Individual values of ln *U* deviate from 0.433 by an average of 2.17 times and a maximum of 3.88 times the estimated individual probable errors.

The data at 149.4 and 160.3° lend themselves to a factorial analysis[14] for the influence of different variables. Values of *U* are not significantly dependent on concentration of iodine or of 2-iodobutane. This analysis suggests that *U* tends to increase with temperature, but a weighted least squares analysis of the data at all four temperatures indicates that any trend is barely greater than the uncertainty based on the estimated probable errors of the measurements.

The data seem to be consistent with the interpretation that *U* does not change with temperature or concentration of either reactant and that radioactivities and angles of rotation can be measured with no worse than about twice the assumed uncertainties. An application of Student's *t* test[14] to the weighted data indicates 50% confidence that *U* lies between 1.49 and 1.60 and 99% confidence that it lies between 1.32 and 1.80.

TABLE I

RATIO OF RATES OF RACEMIZATION AND EXCHANGE

Temp., °C.	$[\mathrm{I_2}]_{\mathrm{av}}$, mole/l.	$[\mathrm{BuI}]_{\mathrm{av}}$, mole/l.	10^6R_{ex}, *M*/l. min.	10^5k_{rac}, min.$^{-1}$	Ratio, *U*	Probable error, $\delta \ln U$
130.0	0.0300	0.300	9.75	4.64	1.38	0.055
	.0311	.0978	3.72	6.03	1.51	.058
149.4	.0122	.296	23.1	11.7	1.38	.114
	.0107	.0986	4.36	11.4	2.45	.182
	.0107	.0286	1.62	14.1	2.46	.194
	.0321	.296	55.5	25.4	1.20	.069
	.0328	.0944	16.1	22.0	1.21	.090
	.0328	.0244	6.25	23.5	0.81	.233
160.3	.0108	.298	38.4	17.4	0.95	.250
	.0104	.0992	12.6	28.2	2.14	.147
	.0102	.0296	4.45	25.2	1.54	.165
	.0306	.299	81.7	53.0	1.84	.063
	.0300	.100	29.0	56.7	1.94	.059
	.0310	.028	7.05	52.0	1.93	.094
170.4	.0326	.295	293	148	1.34	.052

There seems to be no question that the ratio is greater than the value of unity to be expected if racemization and exchange take place only by abstraction of an iodine atom. According to the argument of the introduction, a value greater than unity indicates contribution by a mechanism in which substitution is accompanied by inversion of carbon. We have tried to imagine all other processes that could cause an increased rate of racemization relative to exchange and have only found three, none of which seem consistent with available information.

One process leading to racemization without exchange could be a spontaneous racemization of a 2-iodobutane molecule without any involvement with iodine atoms or molecules coming from the element. Such a process might be dissociation to a racemic butyl radical and iodine atom and subsequent recombination of the same species without escape from the solvent cage. If such a process were contributing significantly to the racemization, its importance relative to exchange would decrease with increasing iodine concentration, and its energy of activation would probably be over 10 kcal./mole greater than the value observed for the iodine atom catalyzed processes. There is no evidence for the variation of *U* predicted by this process.

Racemization would also be increased relative to exchange if racemic butyl radicals abstracted iodine atoms from optically active molecules of 2-iodobutane. Such a process might be written

$$d\text{-BuI} + dl\text{-Bu}' \longrightarrow dl\text{-Bu} + dl\text{-Bu}'\mathrm{I} \qquad (\mathrm{T})$$

where the primes are used merely to designate individual species and not to suggest isotopic labeling.

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[14] E. B. Wilson, Jr., "An Introduction to Scientific Research," McGraw-Hill Book Co., New York, 1952, pp. 48 and 239.

This process is eminently plausible, but U would show a strong dependence on 2-iodobutane concentration if such a reaction were reponsible for values in excess of unity.

A third way to describe an enhanced value of U without invoking step (S1) is to propose that step (A2) frequently involves the *identical species* formed in (A1). If the initial process is abstraction of iodine, and if the resulting butyl radical and iodine molecule live long enough to "forget" any initial relative configurations, then there is 50% probability that the racemic radical would regain the iodine atom with which it was associated originally and would not appear to have exchanged. If a butyl radical always reacted with the identical molecule of iodine formed at its own genesis, the value of U would be 2.0 just as it would be if exchange only involved step (S1).

If U is to be increased significantly by such a reaction of original species, step (A2) must have almost no energy of activation and its rate constant must be of the order of 10^{10} liter/mole sec. There is not much information on rates of reaction of molecular iodine with radical species, but the rate constants seem too small for the effect observed here. Thus, the exchange of an iodine atom with an iodine molecule[15] has a rate constant of the order of 10^8 liter/mole sec. at room temperature in hexane. At 36° in hexachlorobutadiene,[16] the rate constant is no more than about 3×10^6 liter/mole sec. for the reaction of a benzyl radical with iodine by a step like (A2). However, benzyl radicals are notoriously sluggish in their reactions, and the energy of activation for reaction with an iodine molecule is about 6 kcal./mole. The energetics discussed below indicate that the energy of activation may be only 2 kcal./mole or even less for the reaction of a *sec*-butyl radical with iodine. Therefore, we cannot completely rule out the reaction of original partners as an explanation of our results. A critical test would be repetition of the experiments in gas phase, provided it were possible to eliminate the heterogeneous effects that plagued Ogg and Polanyi.[7] If U were also greater than unity under these conditions, we do not see any possible explanation except a radical inversion reaction.

Kinetics and Mechanism of Exchange.—The rates of racemization could only be studied in fairly concentrated solutions because otherwise the angles of rotation were too small or changed too slowly. These restrictions did not apply to the exchange reaction, and rates were measured for concentrations of iodine between 4×10^{-4} and 3×10^{-2} M and of 2-iodobutane between 0.01 and 0.3 M. The above discussion has assumed that the exchange reaction involves iodine atoms regardless of whether they react by abstraction or inversion. If this assumption is correct, the rate should conform to a kinetic equation of the form

$$R_{ex} = k_{ex}[\mathrm{BuI}]_{av}[\mathrm{I_2}]_{av}^{1/2} \qquad (7)$$

These simple kinetics apply if iodine atoms are the chief radical species present. This condition is certainly fulfilled for the exchange involving inversion (step S1). To the extent that the exchange involves abstraction (steps A1 and A2), the relative amounts of radical species depend on the equilibrium constant for

$$\mathrm{BuI} + \mathrm{I} \rightleftarrows \mathrm{Bu} + \mathrm{I_2} \qquad (A)$$

The I–I bond strength is about 35.5 kcal./mole, and the C–I bond strength in a secondary iodide[17] is probably about 46 kcal./mole. Since ΔS^0 is probably small in absolute magnitude, butyl radicals were much less common than iodine atoms in all of our solutions even if the reported C–I bond strength is high by 3 kcal./mole. To the extent that exchange proceeds by abstraction, the apparent energy of activation for k_{ex} is $^1/_2 \times 35.5 + (46 - 35.5) + E_2 = 28 + E_2$ kcal./mole, where E_2 is the activation energy for the reaction of a butyl radical with an iodine molecule (step A2).

The 35 exchange runs at four temperatures are clearly first order in 2-iodobutane, and Fig. 1 shows a log-log plot of $R_{ex}/[\mathrm{BuI}]_{av}$ against $[\mathrm{I_2}]_{av}$. The rates at low iodine concentrations are anomalously high, but at concentrations above 0.01 M (the range accessible to simultaneous racemization study), the data can be fitted fairly satisfactorily to eq. 7. The scatter of these individual runs from the mean k_{ex} at a particular temperature is sometimes as much as 6.5 times the probable error if F can be measured to 0.01; hence it appears that absolute rates of exchange were influenced by factors that did not have as much effect on the ratio of racemization to exchange.

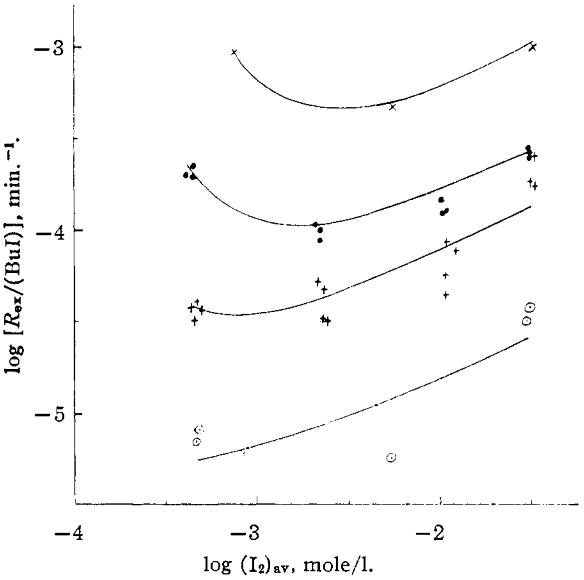

Fig. 1.—Dependence of exchange rate on temperature and iodine concentration: ⊙, 130.0°; +, 149.4°; ●, 160.3°; ×, 170.4°.

The temperature dependence of k_{ex} cannot be fitted satisfactorily to the Arrhenius equation. The plot of log k_{ex} against $1/T$ is definitely curved, and the activation energy calculated by least squares varies from 22.8 kcal./mole for the lower three temperatures to 30.1 kcal./mole for the upper three. Also, the pre-exponential factors are lower than have been observed for similar reactions. If a

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[15] R. M. Noyes and J. Zimmerman, *J. Chem. Phys.*, **18**, 656 (1950).

[16] M. Gazith and R. M. Noyes, This Journal, **77**, 6091 (1955).

[17] M. Szwarc, *Chem. Revs.*, **47**, 75 (1950).

pre-exponential factor is assumed and substituted into an Arrhenius expression for k_{ex}, values at all four temperatures give the same calculated activation energy within ± 0.4 kcal./mole. For a pre-exponential factor of $10^{10.66}$ liter/mole sec. (the value for the exchange of *trans*-diiodoethylene[18]), the calculated activation energy is 29.8 kcal./mole; for a factor of $10^{12.42}$ (the value for benzyl iodide[16]), the calculated activation energy is 33.4 kcal./mole. This behavior with temperature suggests that exchange is accelerated by an extraneous influence that is most important at lower temperatures, and that in the absence of this effect the apparent activation energy for k_{ex} would be in the range 29–34 kcal./mole. If the assumed C–I bond strength of 46 kcal./mole is correct, this activation energy would put E_2 in the range 1–6 kcal./mole and would rule out significant reaction of butyl radicals with iodine molecules formed at their geneses. However, neither bond strength nor exchange activation energy is known with sufficient accuracy for this argument from energetics to be compelling.

The rates at low iodine concentration are greater than predicted by eq. 7, and in some cases the *absolute* rate actually increases as the iodine concentration is lowered. The data can be fitted purely empirically by an equation of the form

$$R_{ex} = \frac{k_{ex}[\mathrm{BuI}]_{av}[\mathrm{I}_2]_{av}^{1/2}}{1 - k'/[\mathrm{I}_2]_{av}^{1/2}} \tag{8}$$

where k' has an apparent activation energy of 7.6 kcal./mole. These kinetics are consistent with a mechanism in which chains can branch by a process that is one order less in iodine atoms than the termination process, but we cannot conceive any plausible branching reaction and are inclined to regard the effect as an artifact.

Because the exchange rates were so peculiar, especially at low iodine concentrations, a special search was made for evidence of side reactions. Samples of *d*-, *l*- and *racemic*-2-iodobutane exchanged at the same rates within about 10% despite considerable differences in preparation prior to purification; and some experiments for longer times showed that the exchange followed the exchange law for at least three half-lives. A run containing the lowest concentration of iodine used in the kinetic runs was heated for about two half-lives and was distilled after addition of toluene, 2-iodobutane and chlorobenzene as carriers. Virtually all of the organically bound iodine distilled with the 2-iodobutane, although some of it tended to come over at a lower temperature. Aqueous extracts of reacted solutions were neutral, indicating that HI is not produced in the decomposition reaction. There is thus no evidence that the iodine is being organically bound in any form other than 2-iodobutane or that the rate is being influenced by any impurities that are removed during the course of reaction. Because of the failure of these tests for the influence of impurities, it is all the more difficult to account for the apparent accelerations at low temperatures and low concentrations of iodine.[19]

Kinetics and Mechanism of Decomposition.—The rate constant for dissociation of molecular iodine in this solvent[16] at 36° is 1.4×10^{-12} sec.$^{-1}$. Measurements below 100° in this solvent[16] and in hexane[20] have indicated that concentrations of iodine atoms are very close to those calculated from the gas-phase spectroscopic equilibrium constant. Combination of these data suggests that the rate constant of the dissociation process

$$\mathrm{I}_2 \rightleftarrows 2\mathrm{I} \tag{1}$$

can be estimated very satisfactorily as $10^{13} \cdot e^{-35{,}500/RT}$ sec.$^{-1}$. In our runs, the rate of formation of new molecular iodine by decomposition of 2-iodobutane was never more than twice the rate of formation of iodine atoms calculated in this rather crude way. In most exchange runs, and in all runs of significance in estimating the ratio U, the rate of decomposition was considerably less than the rate of dissociation of molecular iodine. There is no evidence that the decomposition reaction is a chain process, and it probably is associated in some way with one of the termination steps.

Rates of decomposition were more erratic than for exchange and were very sensitive to impurities. It was only after several methods of purification had been tried that decomposition rates were reduced to the point that exchange and racemization could be studied without too great an accompanying formation of iodine. In the runs with material purified by the method finally adopted, R_{dec} was usually 5–20% of R_{ex} and tended to be a somewhat smaller percentage at lower concentrations of iodine where the anomalous acceleration of exchange set in. The decomposition reaction was first order (or slightly more) in 2-iodobutane and was rather little affected as the iodine concentration was changed over a 100-fold range. At lower temperatures, the rate of decomposition did increase somewhat with iodine concentration, and at higher temperatures it decreased during the same changes.

These kinetic data do not indicate much contribution from the reaction

$$\mathrm{C_4H_9 + C_4H_9I \longrightarrow C_4H_{10} + C_4H_8 + I}$$

which had been proposed earlier by Ogg and Polanyi.[7] However, they are consistent with a mechanism in which butyl radicals face competition between reaction with iodine (step A2) and reaction with an impurity that is most plausibly residual oxygen. If the peroxy radicals subsequently react with each other, the net effect of the oxygen reaction will be an increase in iodine concentration. Since iodine seems to compete with the impurity more effectively at higher temperatures, it would appear that step (A2) does indeed have a small activation energy. If this interpretation is justified, we are forced to conclude that the values of U greater than unity require that iodine atoms are also reacting in our system by the inversion step (S1).

The sensitivity of this reaction to oxygen suggests an additional test of the conclusions from this study. Although oxygen reacts rapidly with organic rad-

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(18) R. M. Noyes, R. G. Dickinson and V. Schomaker, THIS JOURNAL, **67**, 1319 (1945).

(19) Some unpublished observations by Dr. A. G. Maddock of Cambridge University suggest that heterogeneous influences may be important at low concentrations of iodine.

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

icals, all of our previous measurements[16,20-22] are quantitatively consistent with the assumption that the presence of oxygen has no influence on the reactivity of iodine atoms. In the present system, exchange proceeding by the iodine abstraction mechanism is subject to oxygen inhibition of step (A2), while exchange proceeding by the direct substitution mechanism (S1) should be unaffected. The major conclusions of this study would be supported by the presence of a residual exchange reaction whose rate remained constant over a considerable range of partial pressures of oxygen. However, since the concentration of oxygen could not be increased sufficiently for it to compete with the suggested reaction of butyl radicals with iodine molecules formed at their own geneses,[23] the oxygen effect would not of itself distinguish between the alternative explanations of the high ratio of racemization to exchange.

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The Decomposition of Thiourea in Water Solutions

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Rate measurements were made at various thiourea concentrations ranging from 5 to 960 millimolar. The reaction was shown to be first order with respect to thiourea. Runs were also made in media containing various acids and salts. The reaction rate was found to be independent of acid concentration over a wide range and did not depend on ionic strength. Data collected at 10° temperature intervals from 90 to 130° were analyzed and a frequency factor and activation energy are reported. A discussion of these and other findings is presented.

Introduction

In a stimulating account of his pioneering researches, Reynolds[3] first reported the synthesis of thiourea and its isomerization to ammonium thiocyanate. Kinetic studies of the reaction in the absence of solvent have been made by Waddell,[4] Atkins and Werner,[5,6] Kappanna,[7] and Kodama, *et al.*[8] Ure and Edwards[9] have investigated the reaction with ethylene glycol as a solvent. The only moderately extensive data on the decomposition of thiourea in aqueous media that could be found in the literature were reported by Dutoit and Gagnaux[10] although scattered information from various sources is also available. Studies on the phase relationships[11-13] and the equilibrium[5-7,12,13] between thiourea and ammonium thiocyanate have been made in the absence of solvent. This equilibrium has also been investigated in water,[5,10] simple alcohols[5,13] and ethylene glycol.[14] A recent study of the effect of pressure[15] on the kinetics of this reaction and the position of equilibrium in the absence of solvent should also be mentioned.

Data on the decomposition of urea in aqueous media have been presented in a previous communication[16] from this Laboratory. The reaction was shown to be first order with respect to urea over a wide concentration range. No significant salt effects were observed and the decomposition reaction was not catalyzed by any of the common inorganic acids tested. The products of the reaction in the absence of acid were ammonium ions and cyanate ions.

Since no complete data on the kinetic behavior of thiourea in aqueous solutions could be found in the literature, the present investigation was undertaken with two objectives in mind: to collect such data, and to compare the findings with those previously obtained with urea. It was hoped that such a comparison might provide clearer insight into the mechanisms of both reactions.

Experimental

Apparatus and Technique.—Aqueous solutions of thiourea were sealed in glass ampoules and placed in an oil-bath maintained at the reaction temperature. After 15 min. blanks were withdrawn and quenched in water. The remaining ampoules were left in the bath for reaction periods varying from 3 to 48 hr. In the equilibrium studies

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