

**SUBSTITUTION BY FREE ATOMS AND WALDEN
INVERSION. THE DECOMPOSITION AND
RACEMISATION OF OPTICALLY ACTIVE SEC-
BUTYL IODIDE IN THE GASEOUS STATE.**

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In a previous communication ² examples have been given of the racemisation of simple optically active alkyl halides by the corresponding halide ions in acetone solution. Similar reactions are known for halogenated succinic acids in aqueous solution.³ These are examples of the

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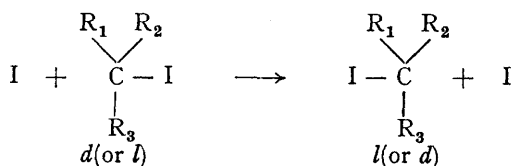
² E. Bergmann, M. Polanyi and A. Szabo, *Z. physik. Chem.*, **20B**, 161, 1933; A. Szabo, *Dissertation*, Berlin, 1933.

general rule which has been first noticed by B. Holmberg,³ and has been given a theoretical foundation by N. Meer and M. Polanyi;⁴ that replacement in an organic compound of a negative substituent by a negative ion leads to optical inversion. It has been pointed out by the latter authors,⁵ that in such reactions the negative ion approaches the positive end of the carbon-halogen (or other negative substituent) dipole, and hence that optical inversion necessarily results.

It is of interest to consider substitution by a free atom rather than by a negative ion. In this case no appreciable electrostatic forces influence the approach of the uncharged atom. However, in the reaction of a free monovalent atom with a diatomic molecule (consisting of two monovalent atoms) it has been shown⁶ that the activation energy resulting from interchange forces is a minimum when the three atomic nuclei lie on a straight line. While the situation is considerably more complicated in the case of a monovalent atom attacking a hydrocarbon radical bound to another monovalent atom, it nevertheless appears that essentially the same general principles must apply to the latter case as to the former, and that the activation energy is a minimum when the approach of the atom is along the axis of the linkage attached. Hence optical inversion is to be expected in substitution by a free atom as well as in that by a negative ion.

Heretofore there has been no experimental evidence in support of this conclusion, and the object of the present investigation was to supply such evidence. The possible scope of such an investigation is limited by the tendency of most free atoms to effect rather deep-seated changes in organic molecules, which would mask the reaction sought. Thus gaseous hydrogen atoms cause rupture of carbon-hydrogen, and probably also carbon-carbon bonds. Chlorine and bromine atoms induce halogenation through reaction chains involving free hydrocarbon radicals. Iodine atoms would appear to be the only ones sufficiently inert to cause substitution without serious side reactions.

From the above conclusion it is to be expected that free iodine atoms would effect in optically active alkyl iodides a substitution accompanied by optical inversion—a reaction which by its reversibility must lead to the racemisation of the iodide,



Experiments were therefore undertaken with the object of establishing the occurrence of a reaction of this sort, preferably in the gas phase, and of studying its kinetics.

Preliminary Observations.

The iodide chosen for these experiments was methyl ethyl iodo-methane *i.e.*, *sec*-butyl iodide, as being the simplest and presumably most stable

³ B. Holmberg, *J. prakt. Chem.* (2), **88**, 576, 1913; A. R. Olson and F. A. Long, *J. Am. Chem. Soc.*, **56**, 1294, 1934.

⁴ *Z. physik. Chem.*, **19B**, 164, 1932.

⁵ See also M. Polanyi, *Proc. Roy. Soc.*

⁶ F. London, *Sommerfeld Festband*, 1928, p. 104. H. Eyring and M. Polanyi, *Z. physik. Chem.*, **12B**, 279, 1931.

optically active alkyl iodide. Tests of the stability of this substance in the gas phase were made by heating in an air bath sealed bulbs (of German soda glass) containing the pure vapour at pressures around a few hundred mm. Hg, and judging the extent of decomposition by the quantity of iodine produced. At temperatures up to about 200° C. the iodide was practically unaffected, only a faint coloration appearing after several hours. Above 200° C. the decomposition was noticeable, although not rapid below about 270° C. This decomposition appeared to produce only iodine and low boiling, inflammable hydrocarbons, giving a strong test for unsaturation. No hydrogen iodide was detected. These facts, coupled with the nearly 50 per cent. increase of pressure on total decomposition (*vide infra*), suggest that the decomposition yields chiefly butane and butylene.



This is entirely analogous to the decomposition of the closely related *iso*-propyl iodide, observed by Glass and Hinshelwood.⁷

Heating of the iodide vapour in bulbs containing iodine caused no appreciable decomposition at temperatures below 200° C.

The above experiments were made with the racemic iodide. The rotation of the optically active substance was found to be practically unaffected by heating the pure vapour below 200° C. However, if the vapour was heated with small amounts of iodine (10-50 mm. Hg pressure), the iodide after recovery and purification was found to have undergone a considerable loss of optical activity, being completely inactive after extended heating. This racemising action was found to be moderately rapid at temperatures as low as 150° C.

It at first appeared that this was the reaction sought. However, a brief study of its kinetics at 150-180° indicated the reaction velocity to have an abnormally small temperature coefficient, while a comparison of reaction rates in bulbs of different surface-volume ratios (produced by packing with bits of broken tubing) indicated that the reaction is almost completely heterogeneous at these temperatures.

This racemisation of active *sec*-butyl iodide by iodine at a glass surface is not without interest (see the discussion), but is hardly as satisfactory a proof of the original thesis as would be the homogeneous gas reaction, and hence attempts were continued to find the latter. Since the heterogeneous reaction has a very small temperature coefficient (corresponding to an activation energy of some 8000 gram calories per mol.) while a much larger one is to be expected for the homogeneous reaction, it appeared that the latter would predominate at higher temperatures. However, the racemisation in the presence of added iodine was found to be still partially heterogeneous at 200-210° C., while at higher temperatures it was too rapid to allow of accurate measurement of the rate.

To circumvent this difficulty, recourse was had to a study of the racemisation of active *sec*-butyl iodide caused by the iodine resulting from its own partial decomposition at still higher temperatures. At 240-280° the racemisation of the *undecomposed* iodide was found to be very extensive, even when the decomposition had proceeded to the extent of only a few per cent. of the original material. The homogeneity of the reaction under these conditions was tested by heating simultaneously in an air bath bulbs containing equal concentrations of the vapour of pure active *sec*-butyl iodide. The surface-volume ratio of the bulbs differed ten-fold as a result of packing one of them with bits of broken tubing. After heating for a suitable period, the bulbs were removed and cooled simultaneously. The undecomposed fraction of iodide from each was then recovered, and after purification as described below, its optical rotation was determined.

In several sets of experiments made at approximately 240° C. and at pressures of *sec*-butyl iodide vapour of about 200 mm. Hg the rotations

⁷ J. V. S. Glass and C. N. Hinshelwood, *J. Chem. Soc.*, 1929, 1804.

of the iodide from the packed and empty bulbs were found to be identical within the experimental error. This is a satisfactory proof of the homogeneity of the racemisation under these conditions. Since the subsequent kinetic measurements were made in a reaction vessel of a glass identical with that used in these experiments, in the temperature range 238-276° C. and at pressures of *sec*-butyl iodide vapour of 100-200 mm. Hg, it seems reasonable to infer that they deal with an essentially homogeneous reaction.

The homogeneity of the racemisation process is itself a strong argument for the homogeneity of the decomposition which produces the necessary iodine. This was further verified by direct measurement of the iodine produced, the ratio of iodine to *sec*-butyl iodide proving to be the same for the packed and unpacked reaction vessels.

To remove any possible doubt that the loss in optical activity by active *sec*-butyl iodide under the above treatment is really the result of a racemisation and not of some chemical change, a few grams of the pure racemic liquid was sealed up in a large evacuated glass bulb, which was then heated for some hours at around 240°—a procedure sufficient to cause complete loss of optical activity by the active iodide. The liquid was then collected and purified of iodine. The boiling-point and index of refraction of the purified liquid proved to be identical with those for pure *sec*-butyl iodide, indicating that no chemical change or molecular rearrangement had taken place.

The occurrence of the decomposition of *sec*-butyl iodide and of the racemisation of active *sec*-butyl iodide as homogeneous gas phase reactions under the above conditions having been established, the quantitative study of the kinetics of these two processes was undertaken, as described below.

Experimental Details of Reaction Rate Measurements.

Preparation of Materials.—The racemic *sec*-butyl alcohol used was a British Drug Houses product, and was carefully fractionated before use, the middle fraction boiling at 99.5-100° C. It was separated into its optical antipodes by the method of Pickard and Kenyon.⁸ Since optical purity was unessential, the brucine salt was divided into only three crystal fractions.

Racemic *sec*-butyl iodide was prepared according to the method of Norris,⁹ by distilling racemic *sec*-butyl alcohol with three molar equivalents of concentrated hydriodic acid. It was washed with dilute alkali and water, and then dried and distilled, yielding a colourless liquid B.P. 117.5° C.

d-*Sec*-butyl iodide was prepared in accordance with the directions of Szabo¹⁰ by saturating *l*-*sec*-butyl alcohol with dry hydrogen iodide at 0° C., and then heating it in a sealed tube for one-half hour at 50° C. It was purified in the same manner as the racemic substance. The product used in this investigation boiled at 117.5° C., and had a value of $[\alpha]_D^{300}$ in acetone solutions of + 6.32°.

Both the racemic and active iodides were stored in the dark when not in use, and remained colourless over the period required for the investigation.

Apparatus and Procedure.—Since for practical reasons it was not feasible to determine the rotation of the active *sec*-butyl iodide in the gaseous state, the rate of racemisation was found from successive experiments made with separate samples. Measured quantities of the substance were heated in the vapour state for ascertained time intervals, and after condensation and purification the specific rotations were determined in acetone solution. In these experiments the iodine formed by decomposition was also collected and quantitatively estimated by chemical analysis.

⁸ R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **99**, 45, 1911.

⁹ J. F. Norris, *Am. Chem. Journ.*, **38**, 627, 1907.

¹⁰ A. Szabo, *Dissertation*, Berlin, 1933.

The decomposition velocity of the racemic *sec*-butyl iodide was measured by following the pressure change attending the reaction at constant volume.

The essential details of the apparatus employed are shown in Fig. 1. The construction was of German soda glass throughout. The reaction vessel was a cylindrical bulb of some 400 cm.³ capacity, surrounded by a mantle in which the vapour of a liquid boiling under atmospheric pressure was refluxed. A constant temperature was thus assured. The liquids chiefly used were acenaphthene (B.P. 277° C.), diphenyl (255°) and *p*-nitrotoluene (238°). The data in the Landolt-Börnstein Tabellen were used to correct the boiling-points for differences of barometric pressure.

Gas pressure in the reaction cell was measured with a mercury manometer, using an intervening glass "click gauge" ¹¹ as a null instrument. The glass tubing joining the cell to the click gauge and to the tap connecting with the remaining system was of very small diameter to reduce the outside volume. This tubing, as well as tap C and the large tubing surrounding the clicker, were all wound with heating wire and lagged with asbestos, and hence could be maintained at some 150° C. to prevent condensation of iodine and *sec*-butyl iodide. The small bare side arm B,

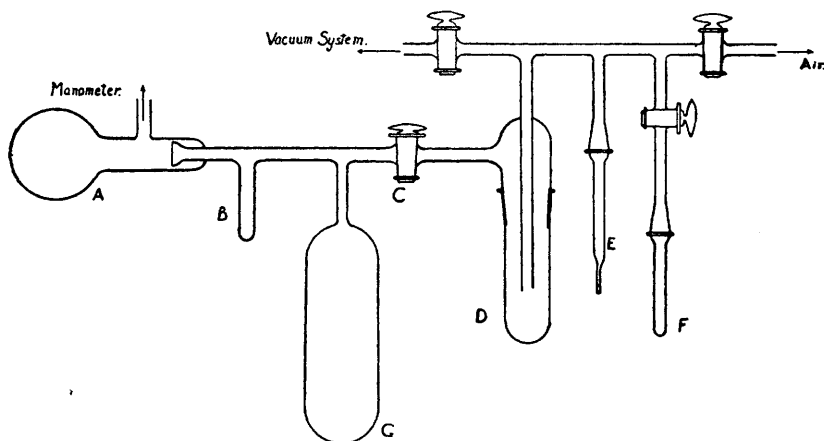


FIG. 1.

when not in use, was covered with a tiny auxiliary heater to prevent condensation. The tap C was lubricated with a hard vacuum wax, found to have approximately the correct consistency at the above temperature. This wax appeared also to be quite resistant to attack by iodine vapour.

The system could be evacuated through a liquid air trap with a three-stage mercury diffusion pump to some 10^{-6} mm. Hg.

The procedure of a typical experiment dealing with the racemisation follows. The appropriate quantity (generally 0.2-0.5 g.) of active *sec*-butyl iodide was introduced into F, and after evacuation of the system (the iodide being first cooled with solid carbon dioxide and acetone) was condensed in the small side arm B by cooling with solid carbon dioxide. Tap C was then closed, and the iodide was rapidly vaporised by flaming B, the stop-watch being started simultaneously. The pressure was then measured. After a suitable time interval the reaction was stopped by condensing the iodide in P. Both the vaporisation and condensation occupied less than five seconds—a correction that was usually negligible. Tap C was then opened, and the condensed iodide and iodine were allowed to distill at very low pressure into the trap D, cooled by solid carbon dioxide. Removal of the volatile

¹¹ J. A. Leermakers and H. Ramsperger, *J. Am. Chem. Soc.*, **54**, 1837, 1932.

hydrocarbons and transfer of the last trace of I_2 from the reaction vessel to D were effected by finally evacuating directly with the pump. Tap C was then closed, and after admitting air the bottom part of D was removed. A few drops of mercury were added to the condensed iodide and shaken, thereby absorbing the iodine and leaving the iodide colourless. The bottom half of D was then replaced, and after cooling of the iodide with solid carbon dioxide the system was again exhausted to a very low pressure. The purified *sec*-butyl iodide was then condensed in E, leaving mercury and mercury iodides in D. Air was again admitted, and E was removed. The sharp tip, previously file-scratched, was inserted into the neck of a 3 cm.³ volumetric flask and snapped off, allowing the *sec*-butyl iodide to run into the flask. By this procedure the loss of liquid was minimised. The flask plus iodide was then weighed, and after addition of acetone to the mark, the rotation of the resulting solution in a 20 cm. micropolarimeter tube was measured. The small bit of glass (from the tip of E) was extracted and weighed, and the corresponding correction applied to the weight of the iodide. The mercury and mercury iodides remaining in D were boiled with zinc dust and a small quantity of water for a few minutes, causing quantitative reduction to soluble zinc iodide and mercury. After filtration and washing of the residues the filtrate was analysed for iodide ion by titration with 0.02 N $AgNO_3$ solution, using K_2CrO_4 as an indicator.

The optical rotations were measured with a Hilger instrument, using a Pirani sodium lamp as a source of the D lines. Duplicate readings generally agreed to better than 0.01°, the difference never exceeding 0.02°. The actual rotations measured were generally 0.10°–1.00°. The probable error was thus usually only a few per cent.

The few experiments made on the racemisation in the presence of added iodine did not differ greatly in technique from the above. After the measurement of the pressure of *sec*-butyl iodide vapour the substance was condensed again in B with solid carbon dioxide. Tap C was then opened and iodine was allowed to sublime into B from D—a very slow process. C was then closed, and after vaporisation of the contents of B the total pressure was measured. The partial pressure of iodine vapour was thus determined by difference. The succeeding operations were identical with the above—only the analysis for I_2 being omitted.

The start of an experiment on the decomposition of racemic *sec*-butyl iodide was identical with that for the racemisation. However, the experiments were extended over much greater periods, and readings of the pressure were made at frequent intervals. Initial pressures were obtained by extrapolation. In several experiments the decomposition was allowed to proceed to completion in order to find the ratio of final to initial pressure. Experiments on the rate of decomposition in the presence of added iodine were carried out in the fashion described in the preceding paragraph, *i.e.*, the pressure of added I_2 vapour was determined by difference.

The accuracy of the experiments dealing with decomposition of the iodide is inferior to that of those on the racemisation. This is due in large part to the somewhat erratic behaviour of the heated soft glass click gauge (such gauges are most satisfactory when made of Pyrex glass and operated at room temperature), introducing considerable errors into the measurement of small pressure differences. Nevertheless, the accuracy was adequate to show clearly the general character of the decomposition.

Experimental Results.

The Heterogeneous Racemisation of Active *sec*-Butyl Iodide by Iodine.

Results of the few experiments made were best represented by the rate expression

$$-\frac{d\alpha}{dt} = k_1(I_2)^{\frac{1}{2}}\alpha, \quad \dots \quad (1)$$

or rather by the integrated form

$$\ln \frac{\alpha_0}{\alpha_t} = k_1(I_2)^{\frac{1}{2}}t, \quad (2)$$

where α_0 represents the initial specific rotation and α_t that after time t . Constants calculated on the basis of this equation are shown in Table I. The temperatures used were the boiling-points of bromobenzene and aniline.

TABLE I.—RATE OF HETEROGENEOUS RACEMISATION.

T. °C.	P _{BuI} mm. Hg.	P _{I₂} mm. Hg.	t. secs.	$[\alpha_0]_D^{20^\circ}$ o.	$[\alpha_t]_D^{20^\circ}$ o.	$\frac{k_1 \times 10^4}{\left(\frac{\text{mol.}}{\text{cc.}}\right)^{\frac{1}{2}}}$ sec. ⁻¹ .
184	82.3 101.0	23.8 11.5	1,500 3,200	+ 7.55	+ 6.40 + 6.00	1.210 1.135
156	83.1 91.5	29.0 10.4	9,600 19,200		+ 3.80 + 3.58	0.688 0.624

The agreement is seen to be satisfactory. The energy of activation, calculated from the average values at the two temperatures, is found to be some 8000 gram calories per mole. These figures are not of great accuracy, but suffice to show the salient characteristics of the heterogeneous reaction.

The Homogeneous Racemisation of Active *sec*-Butyl Iodide.

The loss of optical activity on heating the pure substance in the vapour state was found to obey the expression

$$\ln \frac{\alpha_0}{\alpha_t} = k_2(C_4H_9I)^{\frac{1}{2}}t \quad (3)$$

The rate of formation of iodine in these experiments (determined by chemical analysis) was given essentially by the rate expression

$$\frac{d(I_2)}{dt} = k_3(C_4H_9I) \quad (4)$$

used in the integrated form

$$(I_2)_t = k_3(C_4H_9I)t \quad (5)$$

These facts indicate that the true rate expression for the racemisation of the active *sec*-butyl iodide by iodine is

$$-\frac{d\alpha}{dt} = k_4(I_2)^{\frac{1}{2}}\alpha \quad (6)$$

which in integrated form is

$$\ln \frac{\alpha_0}{\alpha_t} = k_4(I_2)^{\frac{1}{2}}t \quad (7)$$

That this is the correct expression follows from the fact that the experimentally observed equation (3) can be derived from (5) and (6).

From (5), at time t ,

$$(I_2)^{\frac{1}{2}} = k_3^{\frac{1}{2}}(C_4H_9I)^{\frac{1}{2}}t^{\frac{1}{2}}$$

Substituting in (6)

$$-\frac{d\alpha}{dt} = k_4 k_3^{\frac{1}{2}}(C_4H_9I)^{\frac{1}{2}}t^{\frac{1}{2}}\alpha$$

Integrating and evaluating the integration constant

$$\ln \frac{\alpha_0}{\alpha_t} = \frac{2}{3} k_4 k_3^{\frac{1}{2}}(C_4H_9I)^{\frac{1}{2}}t^{\frac{3}{2}} \quad (9)$$

This is seen to be identical with equation (3). Hence the desired rate constant is derived from the observed ones by the expression

$$k_4 = \frac{3}{2} \frac{k_2}{k_3} \quad (10)$$

In Table II. are given the data for the experiments on the racemisation, together with the observed values of k_2 and k_3 , and the values of k_4 , calculated from equation (10). In each of these experiments the fraction of the *sec*-butyl iodide decomposed was so small that (C_4H_9I) could be considered constant without introducing an appreciable error. In three of the experiments at the lowest temperature (238° C.) mishaps prevented the determination of the amount of iodine formed, and hence the corresponding

TABLE II.

$T, ^\circ C.$	$P_{BuI},$ mm. Hg.	$t,$ secs.	$[\alpha]_D^{20},$ o.	$[\alpha]_D^{20},$ o.	Vol. Cell. cc.	Vol. 0.02N. AgNO ₃ , cc.	$k_2 \times 10^2,$ $\left(\frac{\text{mol.}}{\text{cc.}}\right)^{-1},$ sec. ⁻¹	$k_3 \times 10^4,$ sec. ⁻¹	$k_4,$ $\left(\frac{\text{mol.}}{\text{cc.}}\right)^{-1},$ sec. ⁻¹
276.0	113.6 113.3 109.3 117.5 113.3 189.5 188.9	360 360 540 90 180 180 360	+ 6.32	+ 2.68 2.31 1.19 5.60 4.55 4.02 1.90	400.0	5.480 6.840 9.500 1.848 2.900 4.810 9.800	69.0 81.0 9.500 74.6 76.3 74.9 79.6 75.2 Av. 75.9	115.0 148.7 138.5 150.4 122.2 121.1 123.8 132.0	9.65 9.95 9.50 9.34 10.17 10.84 10.14 9.94
255.5	169.5 189.1 167.5 228.2 96.8 103.5 103.5 105.1	720 1080 360 720 720 1080 360 1800	+ 6.32	+ 3.87 2.28 5.22 3.60 4.31 3.03 5.46 1.42	400.0	4.200 7.585 2.080 6.310 2.520 4.418 1.420 7.450	11.20 11.99 12.37 11.10 11.61 11.72 12.06 10.97 Av. 11.63	28.4 30.7 28.6 31.8 28.9 27.7 31.4 32.4 30.6	3.15 3.24 3.46 2.95 3.24 3.34 3.22 2.89 3.18
238.0	100.8 101.9 112.7 111.5 182.0 171.2 206.8	7800 1200 3600 2400 1200 2400 3600	+ 6.32	+ 0.42 5.34 2.64 3.84 5.14 3.58 2.11	380.0	* 1.250 3.970 * 2.250 * 7.410	2.22 2.28 2.15 2.27 2.09 2.09 1.99 Av. 2.16	* 8.60 8.25 * 8.70 * 8.35 8.48	* * * * * 1.112

values of k_3 are missing from the table (the omissions are marked by asterisks). Therefore the average value of k_4 at this temperature is calculated from the average values of k_2 and k_3 . This procedure is justified by the fact that at the other two temperatures there is a close agreement between the values of k_4 obtained by averaging the individual quantities and those calculated from the averages of k_2 and k_3 .

It is seen that the random fluctuations around the mean values of the constants are some ± 5 per cent. Differences of this magnitude are within the experimental error. The range of conditions is fairly wide, and hence the essential validity of the rate expressions (3), (4) and (6) is confirmed.

The activation energies Q_2 , Q_3 and Q_4 , corresponding respectively to the rate constants k_2 , k_3 and k_4 , are calculated by the usual Arrhenius equation for the different temperature intervals employed. The average

values Table (II.) of the constants at the respective temperatures are used for these calculations. The results are given in Table III.

The values corresponding to the different intervals are in satisfactory

TABLE III.—ACTIVATION ENERGIES.

Temperature. Interval °C.	Q_2 , Cals./mol.	Q_3 , Cals./mol.	Q_4 , Cals./mol.
276.0-238.0°	52,280	40,320	32,180
276.0-255.5°	52,720	41,090	32,040
255.5-238.0°	51,780	39,480	32,320

agreement, indicating that the Arrhenius equation is accurately obeyed. The activation energies which we shall select as the most probable are those for the entire temperature range, *i.e.*, those given in the first row of Table III. These are probably correct to within 1000 cal./mol. It should

be noted that from equation (10) a relation must obtain between Q_2 , Q_3 and Q_4 .

$$Q_2 = \frac{1}{2}Q_3 + Q_4.$$

This is verified by the values given, any slight differences arising from the methods of averaging the constants.

The Homogeneous Decomposition of Racemic *sec*-Butyl Iodide.

This reaction was studied in the same temperature range as the above racemisation. In this range the ratio of final to initial pressure was found to be 1.47, practically independent of temperature and initial pressure of the iodide. Hence at a total pressure, P , the partial pressure of undecomposed iodide was given by the expression

$$P_{\text{BuI}} = \frac{1.47 P_0 - P}{0.47},$$

where P_0 represents the initial pressure of the pure iodide. The decomposition was found to be autocatalytic, and experiments with added iodine showed that it was this substance which produced acceleration of the reaction.

The experimental results on the rate were represented best by the kinetic expression

$$-\frac{d(\text{C}_4\text{H}_9\text{I})}{dt} = k_5(\text{C}_4\text{H}_9\text{I}) + k_6(\text{I}_2)^{\frac{1}{2}}(\text{C}_4\text{H}_9\text{I}). \quad (11)$$

A similar expression was found by Arnold and Kistiakowsky,¹² to obtain for the decomposition of ethylene iodide. Equation (11) was tested by plotting the quantity

$$\frac{\Delta(\text{C}_4\text{H}_9\text{I})}{\Delta t} \cdot \frac{1}{(\text{C}_4\text{H}_9\text{I})_{\text{av}}}.$$

(for successive short time intervals) against $(\text{I}_2)^{\frac{1}{2}}$. The result should be a straight line whose intercept is k_5 and whose slope is k_6 . Fig. 2 represents such an analysis of the experimental results. The three different lines in Fig. 2 refer to sets of experiments at 276°, 254° and 238° C. respectively. The range of initial pressures of *sec*-butyl iodide was 100-250 mm. Hg. In computing iodine concentrations it was assumed that 2 molecules of the iodide decomposing yield 1 molecule of iodine. On the whole the agreement of the results with equation (11) is fairly satisfactory. The scattering of the experimental points is attributed to errors in pressure measurement resulting from the erratic behaviour of the click gauge.

In Table IV. are listed the values of the constants k_5 and k_6 obtained

¹² L. B. Arnold, Jr., and G. B. Kistiakowsky, *J. Chem. Physics*, **1**, 166, 1933.

TABLE IV.—RATE CONSTANTS.

T. °C.	$k_s \times 10^5$ sec. ⁻¹	$k_d \times 10^2$ $\left(\frac{\text{mol.}}{\text{cc.}}\right)^{-\frac{1}{2}} \text{sec.}^{-1}$
276.0	19.00	26.4
254.0	4.00	6.67
238.0	1.30	2.40

TABLE V.—ACTIVATION ENERGIES.

Temperature. Interval °C.	Q_s , Cals./Mol.	Q_d , Cals./Mol.
276.0-238.0	39,420	35,220
276.0-254.0	40,800	36,040
254.0-238.0	37,600	34,190

from Fig. 2, and in Table V. the corresponding activation energies Q_s and Q_d for the different temperature intervals.

From Table V. it is seen that the Arrhenius equation is obeyed. For the most probable values of Q_s and Q_d we shall choose those referring to the extremes of temperature, *i.e.*, those in the first row of Table V.

It is of interest to compare the above results with those on the racemisation. The rate constant k_1 (Table II.) relates to a racemisation of the iodide by iodine, k_s to a decomposition. For both reactions the rate is proportional to $(I_2)^{\frac{1}{2}}$. In this temperature range k_s is seen to be some forty times larger than k_d . This large difference allows the racemisation to be studied essentially separate from the decomposition. Q_s is also seen to be some 3000 calories larger than Q_d . There is thus no doubt that the racemisation and decomposition processes are entirely separate.

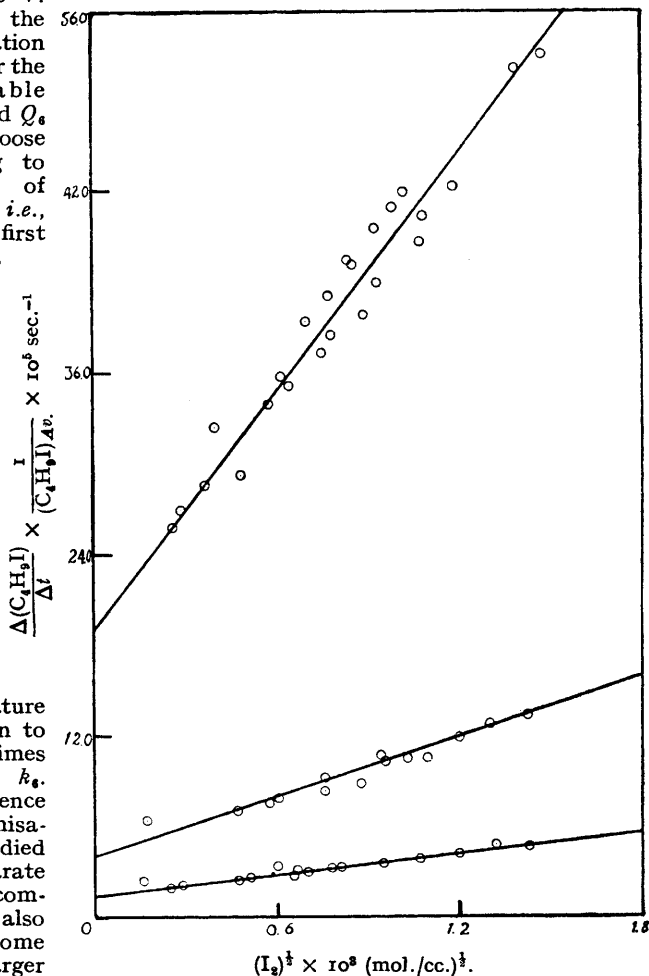
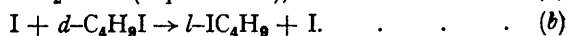


FIG. 2.—Decomposition of *sec*-butyl iodide. The three lines refer to experiments at 276°, 254° and 238° C.

k_s measures the rate of decomposition of *sec*-butyl iodide by a monomolecular reaction at a vanishing concentration of iodine. The rate of production of iodine should then be $\frac{1}{2}k_s$. Now k_s (Table II.) gives the rate of formation of I_2 (as determined by chemical analysis) in the early stages of decomposition. The values of k_s are seen to be in essential agreement with those of $\frac{1}{2}k_s$ at corresponding temperatures, but are some 30 per cent. larger than the latter. This difference is of the direction and magnitude to be expected, since in the experiments used to determine k_s the average iodine concentration was of an appreciable finite value, and hence an increase in rate due to the sensitised decomposition (k_s) resulted. Likewise, Q_s (Table III.) is slightly higher than Q_b , but essentially of the same size. This agreement between entirely independent methods of measuring the decomposition velocity gives considerable confidence in their correctness.

Discussion.

The rate expression for the racemisation of active *sec*-butyl iodide by iodine (equation (6)) is explained by the following mechanism:



Reaction (b) is seen to be an example of the optical inversion predicted in the first section.

It will be observed that each *sec*-butyl iodide molecule undergoing reaction (b) leads to the formation of a *pair* of racemic molecules, and hence that the rate of racemisation is just twice the rate of (b). If the rate of (b) is denoted by k_b , and the dissociation constant of iodine as K_{I_2} , then the relation to the observed rate constant k_4 (equation (6) and Table II.) is

$$k_b = \frac{k_4}{2K_{I_2}^{1/2}}$$

Likewise, if the energy of activation of (b) is Q_b and the heat of dissociation of iodine H_{I_2} , then

$$Q_b = Q_4 - \frac{1}{2}H_{I_2}.$$

The dissociation constants and heat of dissociation of iodine may be

TABLE VI.

RATE OF OPTICAL INVERSION BY IODINE ATOMS.

T. °C.	K_{I_2} , mol./cc.	k_4 , (mol./cc.) ⁻¹ sec. ⁻¹ .	$k_b \times 10^{-7}$ (mol./cc.) ⁻¹ sec. ⁻¹ .
276.0	15.60	9.94	3.98
255.5	4.36	3.18	2.40
238.0	1.368	1.112	1.50

calculated from the equation of Bodenstein and Starck.¹³ In the temperature range covered in these experiments the mean value of H_{I_2} is 36,800 cal./mol. The most probable value for Q_4 (Table III.) is 32,180 cal./mol. Therefore the value of Q_b is 13,780 cal./mol. In Table VI. are given the values of k_4 , K_{I_2} and the calculated values of k_b at the various temperatures.

The energy of activation, or rather critical increment, calculated from the values of k_b in Table VI., is some 14,300 cal./mol. This is, of course, equal to $Q_b + \frac{1}{2}RT$, a relation seen to be numerically satisfied by the

¹³ M. Bodenstein and H. Starck, *Z. Electrochem.*, **16**, 961, 1910.

above value of 13,780 cal./mol. for Q_b . In this temperature range the value of k_b may be expressed as $5.00 \times 10^{11} T^{\frac{1}{2}} e^{-\frac{13,780}{RT}} \left(\frac{\text{mol.}}{\text{cc.}}\right)^{-1} \text{sec.}^{-1}$.

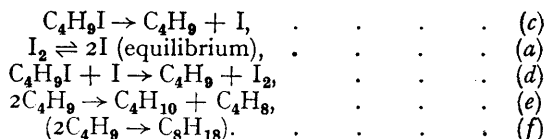
Therefore, the rate of collisions between iodine atoms and *sec*-butyl iodide molecules effective in causing reaction (b) is given by

$$5.00 \times 10^{11} T^{\frac{1}{2}} \left(\frac{\text{mol.}}{\text{cc.}}\right)^{-1} \text{sec.}^{-1}.$$

This corresponds to an effective collision diameter of 1.56×10^{-8} cm. If the "true collision diameter" is assumed to be some 5×10^{-8} cm., this corresponds to a steric factor of approximately 0.1. Hence, the agreement of the rate with kinetic theory is entirely satisfactory, and in fact rather fortuitous, since there is some uncertainty in the activation energy.

But little can be said concerning the racemisation of *sec*-butyl iodide by iodine at a glass surface. The fair agreement of the experiments with equation (1) suggests that this is also an atomic exchange reaction, the iodine atoms and iodide molecules being absorbed on the glass surface. The smallness of the heat of activation (8000 cal./mol.) suggests that the heat of dissociation of iodine molecules on the surface is extremely small, and also that the optical inversion is easier than in the gas phase. This could well be due to a weakening of the carbon-iodine linkage by adsorption on the glass surface.

The rate expression for the decomposition of *sec*-butyl iodide (equation (11)) is explained by the mechanism



The rate controlling steps are the concurrent reactions (c) and (d). The rate of (c) is given by the constant k_5 (equation (11)). The overall rate of (a) followed by (d) is given by k_4 . The secondary reactions (e) and (f) account for the products of decomposition. Reaction (e) is certainly the predominating step, but the fact that the final pressure increase is not quite 50 per cent. suggests the possibility of (f).

Reaction (c) is analogous to that found for the dissociation of primary aliphatic iodides,¹⁴ methyl iodide for example. However, an important difference is to be noticed. In the dissociation of methyl iodide the reverse reaction (recombination of methyl radicals with iodine atoms) plays an important rôle, while it is apparently negligible here. Further, with methyl radicals the reaction analogous to the reverse of (d) is important, and again appears to play no significant rôle here. That the reverse of (c) and (d) are not important follows from the fact that iodine does not retard these processes. Also, were the reverse of (d) important, such a mechanism would cause a racemisation of the active iodide, since the free hydrocarbon radicals would most probably be racemised very rapidly. The above experiments on the racemisation show no evidence that such a reaction occurs. This difference in behaviour between methyl iodide and *sec*-butyl iodide may be explained by assuming that in the case of methyl radicals the reactions analogous to (e) and (f) are very much slower than with *sec*-butyl radicals.

¹⁴ R. A. Ogg, Jr., *J. Am. Chem. Soc.*, **56**, 526, 1934.

The activation energy of (c) is given by Q_5 , whose probable value is some 39,420 cal./mol. (Table V.). Since the corresponding activation energy for the dissociation of primary aliphatic iodides is 43,000 cal./mol.,¹⁴ it appears that the secondary carbon-iodine linkage is correspondingly weaker than is the primary linkage. In this temperature range the value of k_5 may be expressed as $8.9 \times 10^{11} e^{-\frac{39,420}{RT}}$ sec.⁻¹.

The temperature independent factor is of similar magnitude to those for the unimolecular decomposition of primary iodides.¹⁴

The constant k_d for the rate of reaction (d) is related to k_5 by the expression

$$k_d = \frac{k_5}{K_{I_2}}$$

while $Q_d = Q_5 - \frac{1}{2}H_{I_2}$, exactly as for reaction (b). Hence

$$Q_d = 35,220 - 18,400 = 16,820 \text{ cal./mol.}$$

In Table VII. are given the calculated values of k_d at the various temperatures. The calculations are exactly as for k_5 (Table VI.).

In the given temperature range the value of k_d may be expressed as $4.25 \times 10^{11} e^{-\frac{16,820}{RT}}$ (mol./cc.)⁻¹ sec.⁻¹. This corresponds to an

TABLE VII.

RATE OF DECOMPOSITION BY IODINE ATOMS.

T. °C.	$K_{I_2} \times 10^{15}$ Mol./cc.	$k_5 \times 10^2$ (mol./cc.) ⁻¹ sec. ⁻¹ .	$k_d \times 10^{-5}$ (mol./cc.) ⁻¹ sec. ⁻¹ .
276.0	15.60	26.4	21.2
254.0	4.01	6.67	10.52
238.0	1.368	2.40	6.49

effective collision diameter of 1.38×10^{-8} cm., practically identical with that found for reaction (b). Thus the reactions (b) and (d) apparently have essentially the same "steric factor," and the difference in their rates is due only to the difference of activation energies.

The reactions (b) and (d) represent two entirely different processes, involving the same reacting system—an iodine atom and a *sec*-butyl iodide molecule. The independence of the two processes is due to the difference of configuration which they require, as well as to a difference of activation energy. The discovery of such a case lends considerable weight to the conception that spatial relationships play a very important rôle in chemical reactions.

The heat effect in reaction (d) should be the difference in dissociation energies of molecular iodine and of the carbon-iodine linkage in *sec*-butyl iodide. The activation energy Q_5 for the unimolecular dissociation of the latter is some 39,400 cal./mol. If we assume this to represent the actual heat of dissociation, then reaction (d) is endothermic by some 2600 cal./mol. Therefore, if the activation energy of (d) is 16,800 cal./mol. the activation energy of the reverse process (*i.e.* the reaction of the free *sec*-butyl radical with iodine) must be $16,800 - 2600 = 14,200$ cal./mol. This is thus an example of an exothermic "elementary reaction" possessing a considerable activation energy. Incidentally, the magnitude of this activation energy explains the failure of the reverse of (d) to play an appreciable rôle in the kinetics of the decomposition—the *sec*-butyl radicals are consumed by the presumably much faster reaction (c).

In conclusion, it may be repeated that the discovery of a Walden inversion caused by iodine atoms acting on *sec*-butyl iodide molecules is evidence in favour of the original hypothesis that substitution by free atoms in organic molecules is attended by optical inversion.

Summary.

The homogeneous gas phase decomposition of *sec*-butyl iodide has been studied in the temperature range 238-276° C. The reaction was found to be of complex order, the two concurrent rate controlling steps being interpreted respectively as a uni-molecular dissociation into a free radical and iodine atom, and a bimolecular reaction of a *sec*-butyl iodide molecule with an iodine atom, yielding an iodine molecule and free *sec*-butyl radical. The rate constants for the two processes are given respectively by

$$8.9 \times 10''e - \frac{39,420}{RT} \text{ sec.}^{-1}, \text{ and } 4.25 \times 10''T^{\frac{1}{2}}e - \frac{16,820}{RT} (\text{mol./cc.})^{-1} \text{ sec.}^{-1}.$$

The racemisation (of the undecomposed fraction) attending the decomposition of optically active *sec*-butyl iodide under the above conditions was also studied. The rate controlling process was found to be a Walden inversion caused by the substitution taking place on collisions between iodine atoms and *sec*-butyl iodide molecules. The rate constant for this process

$$\text{was found to be } 5.00 \times 10''T^{\frac{1}{2}}e - \frac{13,780}{RT} (\text{mol./cc.})^{-1} \text{ sec.}^{-1}.$$

A racemisation of active *sec*-butyl iodide by iodine at a soft glass surface was found at lower temperatures. The effect appeared to be caused by iodine atoms on the surface.

The results on the racemisation constitute evidence for the hypothesis that substitution by free atoms in organic molecules causes optical inversion.

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