This equation predicts that alkylation *G*-values should vary directly with propylene concentration and inversely with the square root of dose rate. The experimental data fit this prediction well. Equation 5 also predicts that the alkylation *G*-values should vary directly with total pressure. The experimental pressure effect is much larger than this, but the discrepancy could result from the neglect of cracking side reactions in the mechanism. The *G*-value should have a positive temperature coefficient and should, in fact, increase with temperature with the same activation energy as that of the addition step 2. The reason for this is that the initiation step is temperature independent, being radiation-induced, and the termination step has zero or only slight activation energy.

As pointed out, the addition reaction accounts for less than half of the total reaction. Of the many side reactions observed, many can be reconciled with free radical theory by considering that the net reaction is made up of chain decomposition reactions of paraffins, chain alkylation between paraffins and olefins, and chain self-condensation of olefins. The formation of propylene dimer and trimer is clearly a self-condensation side reaction and these are rather well established in free radical chemistry. With regard to other side reactions, the decomposition of heptyl radicals can lead to a variety of products—for example, to pentane, butene, hexane and propane.

$$\text{i-}C_7H_{15}\cdot \longrightarrow \text{i-}C_5H_{11}\cdot + C_2H_4 \quad (6)$$

$$C_5H_{11}\cdot + \text{i-}C_4H_{10} \longrightarrow \text{i-}C_5H_{12} + \text{i-}C_4H_9\cdot \quad (7)$$

$$C_2H_4 + C_2H_4 \longrightarrow C_4H_8 \quad (8)$$

$$\text{i-}C_4H_{10} + C_2H_4 \longrightarrow \text{i-}C_6H_{14} \quad (9)$$

$$\text{i-}C_5H_{11}\cdot \longrightarrow C_3H_7\cdot + C_2H_4 \quad (10)$$

$$C_3H_7\cdot + \text{i-}C_4H_{10} \longrightarrow C_3H_8 + \text{i-}C_4H_9\cdot \quad (11)$$

The unexpectedly high selectivity of propane may be partly the result of reaction between propylene and hydrogen and partly from the side reactions discussed above.

In the case of radioalkylation of propylene with isobutane, it can be said that the bulk of the available data can be explained on the basis of what is known of ordinary free radical processes. There does not seem to be a need for attributing to the radiation-induced reaction a mechanism that goes through intermediates, such as ions, peculiar to radiation. However, ionic chain processes could also be postulated and can be made to fit the experimental data. Therefore, the best that can be said is that the available data can be reconciled with rather well established free radical reactions and no new reactions *need* to be postulated. Unfortunately, the question could not be answered unequivocally because the very slow thermal reaction made it difficult to compare the products made with radiation and by the purely thermal reaction at the same conversion of olefin. However, work in this Laboratory on the more reactive propane–ethylene system, which will be published shortly, has shown the products are quite similar when compared at the same conversion of olefin.

The technique of nuclear radiation initiation has made available a new reaction—the chain alkylation of olefins with paraffins. The initial data are not in conflict with ordinary free radical chemistry. However, it remains to be seen whether radiation provides a new and specific chain alkylation reaction or, equally important, a new probe for getting insight into the ordinary thermal chemistry of hydrocarbons.

LINDEN, N. J.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN][1]

Effect of Temperature and Br_2/Ar Ratio on the Rates of Recombination of Br Atoms Produced by Flash Photolysis of Gaseous Br_2

BY WILLIAM G. GIVENS, JR.,[1] AND JOHN E. WILLARD

RECEIVED APRIL 1, 1959

The rate constants k_{Ar} and k_{Br_2} for the reactions $2Br + Ar \rightarrow Br_2 + Ar$ ($d[Br_2]/dt = k_{Ar}[Br]^2[Ar]$) and $2Br + Br_2 \rightarrow 2Br_2$ ($d[Br_2]/dt = k_{Br_2}[Br]^2[Br_2]$) have been determined from atom recombination measurements over a range of Br_2/Ar ratios from 4×10^{-3} to 6×10^{-2} and at cell temperatures from 273 to 418°K. The ratio of the efficiency of Br_2 as the "third body" for the recombination to that for Ar is approximately 100 at these temperatures. CO_2 is about 4 times as efficient as Ar. The apparent activation energy for recombination in Ar, Br_2 or CO_2 over the temperature range studied is in all cases between -1.4 and -2.9 kcal./mole. For all Br_2/Ar ratios above 10^{-2} it was necessary to apply a correction for thermal inhomogeneities which were produced in the cell contents by the flash and which affected the transmission of the analyzing beam.

Introduction

Studies of the recombination of iodine atoms produced by flash photolysis of gaseous I_2 have been reported from four laboratories.[2-5] There is agreement that recombination follows the rate law $d[I_2]/dt = k[I]^2M$, that the rate constant is dependent on the nature of M, the "third body" and that the reaction has a negative temperature coefficient. For the most part the values obtained in different laboratories for the rate constants are in good quantitative agreement. Correlations

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[1] More complete details of this work are available in the Ph.D. thesis of W. G. Givens, Jr., filed with the University of Wisconsin Library in 1959. It may be obtained from University Microfilms, Ann Arbor, Michigan.

[2] (a) M. I. Christie, R. G. W. Norrish and G. Porter, *Proc. Roy. Soc.* (*London*) (Cambridge Papers), **A216**, 152 (1953); (b) M. I. Christie, R. G. W. Norrish and G. Porter, *Disc. Faraday Soc.*, **17**, 107 (1954); (c) M. I. Christie, A. J. Harrison, R. G. W. Norrish and G. Porter, *Proc. Roy. Soc.* (*London*), **A231**, 446 (1955).

[3] K. E. Russell and J. Simons, *ibid.*, **A217**, 271 (1953).

[4] (a) R. Marshall and N. Davidson, *J. Chem. Phys.*, **21**, 659 (1953); (b) D. L. Bunker and N. Davidson, THIS JOURNAL, **80**, 5085 (1958).

[5] R. L. Strong, J. C. W. Chien, P. Graf and J. E. Willard, *J. Chem. Phys.*, **26**, 1287 (1957).

have been made between measurements of the rate of dissociation of I_2 in shock tubes[6] at elevated temperatures and the recombination rates at lower temperatures. Measurements of the recombination of bromine atoms[5] have indicated that the rate constant in argon at room temperature is nearly the same as for iodine and that the temperature coefficients and third body effects are similar to those for iodine. The dissociation of bromine by the shock tube method at elevated temperatures has been studied.[7,8]

For the recombination of I atoms at room temperature k_{I_2}/k_{Ar} has been found to be so great that k_{Ar} cannot be accurately determined from the observed recombination rate when I_2 is flashed, even in a considerable excess of Ar, unless a correction is made for the $I + I + I_2 \rightarrow 2I_2$ reaction. The k_{I_2}/k_{Ar} ratio has been reported as 260[2c] and as 650[4b] at room temperature and as not greater than 30 at 1300°.[6]

No determinations of k_{Br_2} for the $Br + Br + Br_2 \rightarrow 2Br_2$ reaction at room temperature have been reported. The work of the present paper was designed to determine this value, because of its possible importance as a correction factor to the earlier values for k_{Ar}, because of the information which it might give on the existence of a moderately stable Br_3 complex and because of its importance in correlations[2] between the room temperature flash photolysis studies and the shock wave dissociation of Br_2 where k_{Br_2}/k_{Ar} has been reported by one group to be no greater than eight[7] and by another as two.[8] Evaluation of the temperature coefficients of k_{Ar} and of k_{Br_2} from 0 to 145° has been included.

Experimental

Instrumentation and Procedure.—The equipment used in this work was essentially that described previously[5] and so will be outlined only briefly here.

The reaction mixtures were contained in cylindrical Pyrex cells, 10 cm. long and 2.5 cm. diameter, with flat end windows. The cells were filled on a vacuum line and sealed off. Bromine gas (Merck N.F.V., degassed and passed through P_2O_5 on the vacuum line) was metered into the cell. The inert gas (Ohio Chemical Co. "99.6%" argon, or CO_2, dried by passing through P_2O_5) was admitted after the bromine. After sealing off the cell accurate measurements of the bromine concentration were made by measuring its absorbance on a Beckman DU spectrophotometer and using the absorbancy index values determined by Strong[9] for bromine gas in argon.

Runs above and below room temperature were done with the cell in a cylindrical oven that enclosed both the flash lamp and cell. The oven was heated electrically for high temperature runs and was cooled with Dry Ice for those below room temperature. Temperatures were measured with a thermocouple and recording potentiometer, giving results which are thought to be accurate to ±1°.

The system for analyzing the transient changes in bromine concentration in the reaction cell immediately after its exposure to the flask lamp consisted of a 6-v. tungsten filament bulb, a collimating lens system to direct the light through the cell, a monochromator from a Beckman DU spectrophotometer and a 1P21 photomultiplier tube with power supply and cathode follower amplifier. The photomultiplier output was observed with a recording potentiometer which recorded the steady component of the photocurrent and a Tektronix 514A oscilloscope which displayed the varying component. A simple sweep across the oscilloscope screen was used, and this was recorded photographically on 35 mm. film.

The flash lamps used were 17 mm. i.d. quartz tubes with electrodes sealed through Pyrex attached to the lamp with graded seals. The distance between electrodes was 10 cm. The lamps were filled with xenon at 4 to 10 cm. pressure. A capacitance of 9 or 18 microfarads was used, at voltages from 3000 to 8000. Triggering was accomplished with a high voltage pulse from a small ignition transformer applied to a wire around the outside of the lamp tube. A delay circuit which started the oscilloscope sweep and then triggered the lamp after a variable delay was used in all cases. The flash reached peak intensity about 10 μs. after triggering. The width of the light pulse at one-half of peak intensity was about 40 μs. when 18 μf. capacitance was used, but because the measurements of the recombination involve very small changes in light transmission, it was necessary to wait 150 to 200 μs., after triggering the lamp before taking measurements. The lamps were used either singly or with two connected in series and were mounted next to the reaction cell inside the body of the aluminum furnace.

Calculation of Rate Constants.—In this work the monochromator through which the analyzing light passed was set at 5000 Å., a wave length which is absorbed by bromine molecules but not bromine atoms. From Beer's law, the effective absorbancy index determined on the flash photolysis apparatus and the known electrical characteristics of the system, it was possible to determine the bromine molecule concentration at any time, from which the bromine atom concentration could be deduced (after correction for scattered light from the flash and for the thermal effect discussed below).[1,5] This was directly proportional to the corrected oscilloscope deflection. A plot of the reciprocal of this deflection against time gave a straight line, the slope of which was used to determine the second-order rate constant in the expression $R = k_{\text{apparent}}[Br]^2[Ar]$. The values used for the oscilloscope deflections as a function of time for each set of conditions were determined from oscilloscope curves from at least 15 different flashes. The curves were obtained by projecting each photographic negative of an oscilloscope trace onto a piece of graph paper with a photographic enlarger and tracing the image of the curve. Deflections for each of a series of times after the flash were measured for each curve and then averaged for each time to give the curve used to determine the rate.

As in previous studies with iodine,[2c,4b] it was found that k_{app} is dependent on the halogen/argon ratio. This indicates that the recombination occurs by two processes

$$2Br + Ar \longrightarrow Br_2 + Ar \text{ (rate constant } k_{Ar})$$

$$2Br + Br_2 \longrightarrow 2Br_2 \text{ (rate constant } k_{Br_2})$$

The effect of two body recombination[10] of bromine atoms is negligible under our conditions. Since the fractional dissociation of the Br_2 during the time of observation in the experiments reported here was only a few per cent., its concentration was essentially constant and k_{app} is related to the contributing rate constants as

$$k_{app} = k_{Ar} + k_{Br_2}[Br_2]/[Ar]$$

A plot of k_{app} *vs.* $[Br_2]/[Ar]$ should be linear, with intercept k_{Ar} and slope k_{Br_2}, and this relationship was used in the present work for the determination of these constants. The $[Br_2]/[Ar]$ ratio was varied from 4×10^{-3} to 6×10^{-2}, the conveniently usable limits being set by feasible pressure in the reaction cell, the absorbancy index of bromine and thermal effects at high $[Br_2]/[Ar]$ ratios.

Thermal Effects.—Following the flashing of a reaction cell containing Br_2 vapor, the absorbed light energy appears as thermal energy when the atoms which are formed by dissociation of Br_2 recombine. This results in a temperature rise in the gas. During removal of this heat by the walls of the cell the density of the gas near the walls increases, causing an expansion of the gas through which the analyzing light passes in the center portion of the cell. This causes an increase in transmission of the analyzing light, which is not the result of dissociation of bromine molecules into atoms.[2c,4b,5] Since the magnitude of the effect is dependent on the temperature rise, it is most serious at high $[Br_2]/[Ar]$ ratios such as were

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[6] (a) D. Britton, N. Davidson and G. Schott, *Disc. Faraday Soc.*, **17**, 58 (1954); (b) D. Britton, N. Davidson, W. Gehman and G. Schott, *J. Chem. Phys.*, **25**, 804 (1956).

[7] D. Britton and N. Davidson, *ibid.*, **25**, 810 (1956).

[8] H. B. Palmer and D. F. Hornig, *ibid.*, **26**, 98 (1957).

[9] R. L. Strong, Ph.D. thesis, University of Wisconsin, 1954.

[10] H. B. Palmer, *J. Chem. Phys.*, **26**, 648 (1957).

desirable for the evaluation of k_{Br_2} in the work reported here. The apparent recombination rate observed at all $[Br_2]/[Ar]$ ratios above 10^{-2} was slower than the rate predicted from results at lower ratios. When the transmittancy of the reaction cell was observed for longer times after the flash than the few milliseconds required for recombination of the bromine atoms, the oscilloscope trace actually reversed its direction, giving the appearance of a decrease in Br_2 concentration.

The magnitude and variation with time of the fictitious apparent bromine atom concentration attributable to the thermal effect depend on the initial temperature rise in the cell (determined by the light energy absorbed and the amount of inert gas present), the heat conductivity of the gas, the dimensions of the reaction cell, the dimensions of the analyzing beam and the existence of convection currents.

As a basis for correcting the oscilloscope deflection for the thermal effect, we have used the method outlined previously[5] for estimating the magnitude of the effect as a function of time. This method uses the formula for heat conduction in a semi-infinite body of gas initially at a uniform temperature and bounded by a plane surface at a different temperature. The change in temperature distribution with time is approximated with a step temperature profile that advances inward from the walls, dividing the gas between an outer annular volume at the temperature of the walls and an inner cylindrical volume at the warmer temperature. It is assumed that the analyzing beam was entirely contained within the inner warm volume. Since the total heat dissipated in each experiment is less than one calorie, the temperature of the walls does not change appreciably. One curve of Fig. 1 shows the apparent bromine atom concentration due to the thermal effect, calculated for a temperature rise of 50°, in a cell of the dimensions used in this work containing 10 cm. of Ar at a Br_2/Ar ratio of 0.06. The second curve of Fig. 1 shows the *observed* apparent bromine atom concentration as a function of time for a cell flashed under the conditions used in the above calculation. Since the bromine atom recombination was essentially complete in less than 5 milliseconds, most of the observed curve is due to the thermal effect. The step function calculations indicate that the cold annulus would have advanced to fill three quarters of the volume of the cell at about 60 milliseconds. The reversal of the "observed" curve of Fig. 1 at about this time is consistent with the fact that the analyzing beam occupied about one-quarter of the volume of the cell. The fact that the observed curve falls progressively farther below the calculated curve with increasing time after the first few milliseconds may indicate that a portion of the light beam was not included in the central quarter of the cell volume or that some rapid mixing of the gas occurred, or it may reflect the approximate nature of the step function used for the heat conduction calculation. The most serious source of error in the calculated curve at times from a few hundred microseconds to a few milliseconds (the region used for the bromine atom recombination results reported here) was probably the assumption that the cell rises to its maximum temperature at the moment the flash occurs, whereas actually the heat is delivered to the cell over the whole period of atom recombination.

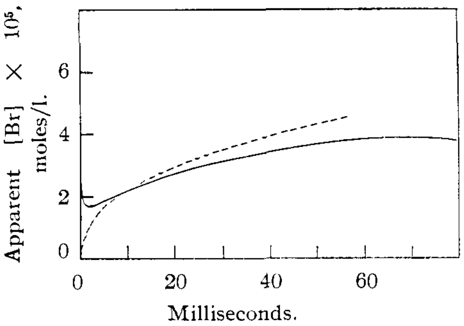

Fig. 1.—Solid line shows experimental values for the apparent bromine atom concentration as a function of time after flashing for a cell with $[Br_2]/[Ar]$ ratio of 6.2 mm./103 mm. = 0.06, in which the temperature rise was 50° and the cell wall temperature 25°. Dashed line shows calculated thermal effect for the same conditions.

In Fig. 2 the reciprocal of the bromine atom concentration, obtained from the oscilloscope trace from the cell described above, is plotted as a function of time, using the uncorrected data for the lower curve and corrected data for the upper. The correction consisted of subtracting a correction curve from the observed curve. The correction curve used was similar in shape to the calculated curve of Fig. 1 but fit the observed data somewhat better. The corrected data give a reasonably good straight line, typical of the second-order atom recombination which has been observed for both iodine and bromine under conditions where the thermal effect is not significant. All of the data reported below for runs at Br_2/Ar ratios sufficiently high to show a measurable thermal effect were corrected in this manner. In each case a calculated curve was matched to the observed deflection at times of two to ten milliseconds and then was used as above to correct the observed short time deflection.

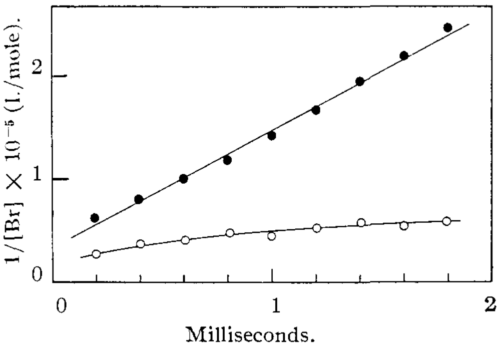

Fig. 2.—Reciprocal of Br atom concentration *vs.* time, with and without application of corrections for thermal effect, same conditions as Fig. 1: ●, corrected; ○, uncorrected.

The temperature rise in each experiment was estimated by extrapolating the apparent bromine concentration, deduced from the oscilloscope deflection after a few hundred microseconds (at which time there was no more scattered light from the flash), back to the time of the flash, and making a calculation on the basis of the energy of the absorbed photons and the heat capacity of the gas, assuming instantaneous recombination. The experiments were done for percentage dissociations ranging from 0.5 to 5% and estimated temperature increases of from 1 to 55°.

Results

Table I shows the values for k_{app} obtained at five Br_2/Ar ratios and over a temperature range from 0 to 166°. Data for a cell in which CO_2 was used as the third body gas are included. Each k_{app} was calculated from a curve obtained from the oscilloscope traces of at least 15 separate flash experiments on the same cell.

For each cell filling the log of the apparent rate constant was plotted against $1/T$ as illustrated in Fig. 3 for one of the argon cells and for the CO_2

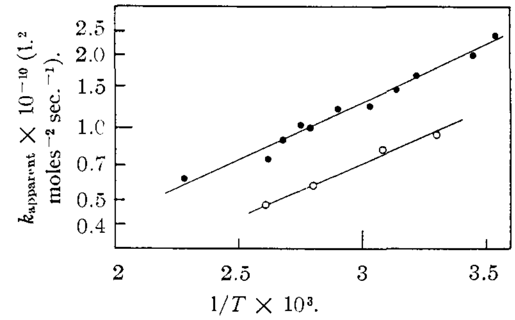

Fig. 3.—Log k_{app} *vs.* $1/T$ for bromine in argon and bromine in CO_2: ●, $[Br_2]/[Ar]$ = 0.060; ○, $[Br_2]/[CO_2]$ = 0.0083.

cell. From the straight line drawn through the log k_{app} *vs.* $1/T$ plot for each $[Br_2]/[Ar]$ ratio, it was possible to read off values of log k_{app} for any desired temperatures. Values so obtained for 300, 350 and 400°K. were used to make the plots of k_{app} *vs.* Br_2/Ar shown in Fig. 4. From the slopes and intercepts of these plots the values of k_{Ar} and k_{Br_2} given in Table II were determined.

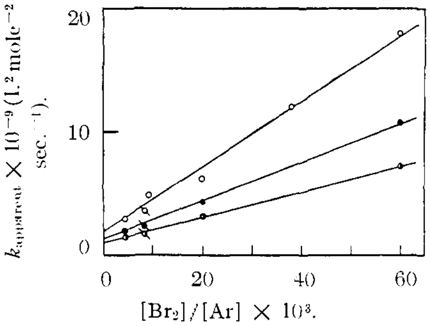

Fig. 4.—k_{app} as a function of $[Br_2]/[Ar]$ ratio and temperature: ○, 300°K.; ●, 350°K.; ◒, 400°K.; ∅, ● and ◌ show data from earlier work.[5]

The values previously reported from this Laboratory[5] for k_{app} for the recombination of bromine atoms in argon agree satisfactorily with the new values at similar Br_2/Ar ratios, as indicated by Fig. 4.

TABLE I

APPARENT RATE CONSTANTS FOR Br ATOM RECOMBINATION AS A FUNCTION OF Br_2/M RATIO AND OF TEMPERATURE

T, °C.[a]	k_{app}[b] (l.^{2} moles^{-2} sec.$^{-1}$)	T, °C.[a]	k_{app}[b] (l.^{2} mole^{-2} sec.$^{-1}$)
$(Br_2)/(Ar)$ = 6.2 mm./103 mm. = 0.060		$(Br_2)/(Ar)$ = 4.9 mm./127 mm. = 0.039	
10	2.46×10^{10}	37	12.7×10^9
17	2.00		
38	1.66		
46	1.44	$(Br_2)/(Ar)$ = 4.44 mm./391 mm. = 0.0113	
57	1.25		
71	1.20	30	4.6×10^9
89	1.00		
101	8.9×10^9		
109	7.4		
166	6.2		
$(Br_2)/(Ar)$ = 4.1 mm./197 mm. = 0.021		$(Br_2)/(Ar)$ = 2.9 mm./700 mm. = 0.0042	
30	5.6×10^9	27	2.9×10^9
63	5.0	45	2.5
112	3.3	72	2.0
154	3.1	103	1.6
$(Br_2)/(CO_2)$ = 4.2 mm./500 mm. = 0.0083		$(Br_2)/(Ar)$ = 0.008[c]	
30	9.3×10^9	27	3.6×10^9
51	8.1	27	2.4
84	5.8	127	1.7
110	4.9		

[a] Temperature of cell walls plus estimated temperature rise in the gas as a result of the flash. [b] These values have been corrected for deflections attributable to scattered light from the flash and thermal effects. [c] Representative values from the work of Strong, Chien, Graf and Willard.[5] Br_2/Ar averaged 0.008 for this work and Ar pressures varied from 500 to 700 mm.

TABLE II

RATE CONSTANTS DETERMINED FROM FIG. 4

T, °K.	k_{Ar}, l.^{2} moles^{-2} sec.$^{-1}$	k_{Br_2}, l.^{2} moles^{-2} sec.$^{-}$
300	2.0×10^9	260×10^9
350	1.4	154
400	1.1	100

The apparent activation energies for the recombination reaction as determined from the slope of plots of the type of Fig. 3 were −2.2 and −1.6 kcal./mole, respectively, for $[Br_2]/[Ar]$ ratios of 6.0×10^{-2} and 4.2×10^{-3}. That for the $[Br_2]/[CO_2]$ ratio of 8.3×10^{-3} was −2.0 kcal./mole.

The values of Table II yield an apparent activation energy of −1.4 kcal./mole for the $2Br + Ar \rightarrow Br_2 + Ar$ reaction and −2.9 kcal./mole for the $2Br + Br_2 \rightarrow 2Br_2$ reaction. Use of the values of k_{Br_2} from Table II to correct for the effect of Br_2 as a third body in the CO_2 experiments indicates that about 22% of the recombination at 300°K. was due to Br_2 and that k_{CO_2} is about 7.8×10^9 l.^{2} moles^{-2} sec.$^{-1}$ No deviation of the oscilloscope trace ascribable to the "thermal effect" occurred in the CO_2 experiments. Since $[Br_2]/[CO_2] = 8.3 \times 10^{-3}$, this is consistent with the observations of thermal effects in the argon cells.

Discussion

The data of Table II indicate that at temperatures in the range of 300–400°K. Br_2 is approximately 100 times as effective as Ar as a third body for the recombination of bromine atoms.[11] This is lower than the two room temperature values in the literature for the corresponding k_{I_2}/k_{Ar} ratio for the recombination of iodine atoms (*i.e.*, 260[2c] and 650[4b]) and, as in the case of the iodine system, is much greater than the ratios found in the high temperature shock wave studies (*i.e.*, = 8 and *ca.* 2).[7,8]

Using the earlier data[5] on the apparent recombination rate constants for Br atoms in argon (converted to dissociation constants with the aid of the equilibrium constant)[13] Palmer and Hornig[8] have shown that a linear relationship between log $k_{Ar(dissoc)}$ and $1/T$ holds over a 10^{27} change in the value of $k_{Ar(dissoc)}$. Figure 5 shows that a similar linearity holds when the values of k_{Ar} and k_{Br_2} obtained in the present work are used in place of the earlier k_{app} values which were uncorrected for the third body effect of Br_2. The dissociation constant plot of Fig. 5 tends to obscure any small variations of rate constant, covering, as it does, a range of 10^{27}, while such variations would be expected to be much more apparent in the plot of the log of the recombination rate constant *vs.* $1/T$ (Fig. 6) where k_{Ar} varies by only 10^1 and k_{Br_2} by only about $10^{2.5}$. In this connection it should

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(11) From measurements over a range of 4 in $[Br_2]/[Ar]$ ratio R. L. Strong and M. R. Basila have obtained values for k_{Ar} and k_{Br_2} at room temperature of 2.7×10^9 and 49×10^9 l.^{2} mole^{-2} sec.$^{-1}$, respectively.[12] These give a ratio of 18 for k_{Br_2}/k_{Ar}. The data reported in the present paper cover a larger change in $[Br_2]/[Ar]$ ratio (15-fold), include corrections for the thermal effect and show somewhat greater internal consistency.

(12) The Flash Photolysis and Recombination of Bromine, M. R. Basila, Ph.D. thesis, Rensselaer Polytechnic Institute, August, 1958.

(13) "Selected Values of Chemical Thermodynamic Properties," Series III, U. S. National Bureau of Standards, Washington, D. C.

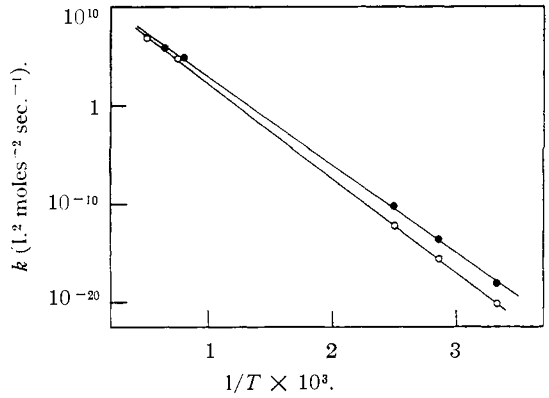

Fig. 5.—Plots of log $k_{Ar(dissoc)}$ (○) and log $k_{Br_2(dissoc)}$ (●) *vs.* $1/T$. Data below 500° are from this work, those above 500° from Palmer and Hornig.[8]

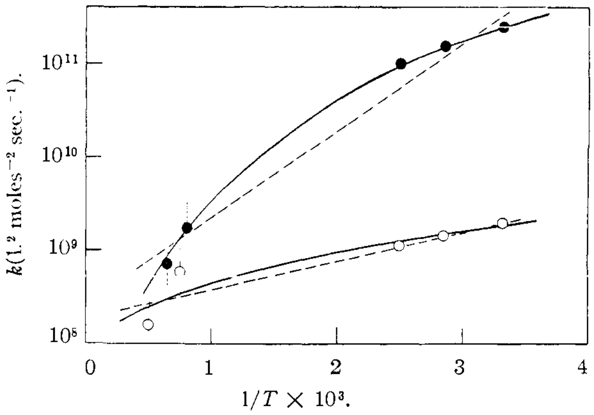

Fig. 6.—Plot of log k_{Ar} (○) and log k_{Br_2} (●) *vs.* $1/T$. Data below 500° are from this work, data above 500° are from the work of Palmer and Hornig.[8]

be noted that determination of temperature coefficients for recombination rates from dissociation data is subject to larger errors than the reverse calculation because the dissociation rates are much more dependent on temperature than the recombination rates and thus relatively small errors in the dissociation temperature coefficient become relatively large errors in the recombination temperature coefficient. The values for the high temperature points of Fig. 6 are taken from solid lines which Palmer and Hornig[8] have determined as the least squares fit to their data for $k_{Ar(dissoc)}$ and $k_{Br_2(dissoc)}$ *vs.* $1/T$ in their Figs. 3 and 5. The vertical lines through the points show a range within which the true values could readily fall, so that it is impossible to say whether the dotted straight lines or the curved solid lines of Fig. 6 give the better representation of the data.

As noted in the work of Palmer and Hornig,[8] it is possible to fit data such as these with different equations which place different emphasis on the contribution of kinetic energy relative to energy stored in additional degrees of freedom. The dashed straight lines in Fig. 6 correspond to the equations

$$k_{Ar} = 1.9 \times 10^8 \exp(1410/RT) \qquad (1)$$

$$k_{Br_2} = 3.0 \times 10^8 \exp(4130/RT) \qquad (2)$$

The exponents are of a magnitude which is plausible if a BrAr complex is involved when Ar serves as a third body, and a Br_3 complex is involved when Br_2 serves as a third body. The pre-exponential factors are reasonable for a 3-body collision mechanism if the three bodies are considered to be in collision if two are within 1 Å. of the third. The collision number for such Br–Br–A collisions is about 5×10^9 at 400°K. if the diameters of the atoms are 3 Å.

The solid lines of Fig. 6 correspond to

$$k_{Ar} = 1.2 \times 10^{-5} T^{1/2} (E_0/RT)^{1.56} \qquad (3)$$

and

$$k_{Br_2} = 5.2 \times 10^2\ T^{1/2} (E_0/RT)^{3.96} \qquad (4)$$

which are related in form to equation 7 below through the equilibrium constant $K = Ce^{-E_0/RT} = k_{(dissoc)}/k_{(recomb)}$. This type of equation represents the data as plotted for k_{Br_2} essentially perfectly, and because it gives an increasing slope at higher temperature would be favored if it were certain that this feature of the plots of Fig. 6 which has also been reported for the recombination of I atoms in argon[4b,6b] were correct.

The lines of Fig. 5 are fitted well by the representation

$$k_{Ar} = 1.1 \times 10^{10}\ T^{1/2} \exp(-43{,}200/RT) \qquad (5)$$

and

$$k_{Br_2} = 1.5 \times 10^{10}\ T^{1/2} \exp(-40{,}400/RT) \qquad (6)$$

The apparent activation energies are not implausible, if the mechanism involves complex formation, since the Br_2 bond energy is 45.5 kcal./mole and complex formation could reduce the necessary energy below this, but the frequency factors are appreciably higher than calculated for Br_2–A collisions with 3 Å. separation of centers ($4.7 \times 10^9\ T^{1/2}$) and Br_2–Br_2 collisions with 3.5 Å. separation of centers ($3.8 \times 10^9\ T^{1/2}$). An equation of the form[14]

$$k_{dissoc} = [AT^{1/2}/(n/2)!](E_0/RT)^{n/2} \exp(-E_0/RT) \qquad (7)$$

should represent the data if n classical square terms in addition to kinetic energy along the line of centers can contribute energy for dissociation and if the energy required is E_0. A is the hard sphere collision number. Using this form the data of Fig. 5 are fitted by the expressions

$$k_{Ar} = 3.4 \times 10^8 T^{1/2} (45500/RT)^{1.56} \exp(-45500/RT) \qquad (8)$$

$$k_{Br_2} = 1.5 \times 10^6 T^{1/2} (45500/RT)^{3.96} \exp(-45500/RT) \qquad (9)$$

The apparent collision numbers $4.8 \times 10^8\ T^{1/2}$ and $3.4 \times 10^7\ T^{1/2}$ correspond to efficiencies of 0.1 and 0.01, respectively, for Ar and Br_2 which are not unreasonable. The exponents of (E/RT) would be lower if the complexes BrAr and Br_3 participate in the act of dissociation and lower the energy necessary. If the energy required for dissociation by Br_2 were 42.5 kcal./mole instead of 45.5 the exponent of (E/RT) in equation 9 would be reduced from 3.96 to 2.6.

It is clear from the above discussion that the data do not furnish a basis for a decision as to whether complexes of appreciable stability are formed. The fact that the large rate constants for I_2 as a third body for I atom recombination and

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[14] Fowler and Guggenheim, "Statistical Thermodynamics," Cambridge University Press, Cambridge, 1952, pp. 495–499.

of Br_2 as a third body for Br atom recombination fall close to the curve of Russell and Simons[3] for the plot of log of the recombination rate constant *vs.* boiling point suggests that the intermolecular attractions which halogen molecules exert on halogen atoms are not of a highly specific chemical type.

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The Entropy of Iodine. Heat Capacity from 13 to 327 K. Heat of Sublimation[1]

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The heat capacity of iodine has been measured from 13 to 327°K. The thermodynamic properties, C_p, S^0, $-(F^0 - H_0^0)/T$ and $(H^0 - H_0^0)/T$ have been tabulated to 330°K. The entropy of the solid at 298.15°K. = 27.76 cal. deg.$^{-1}$ mole^{-1}, the heat of sublimation at 0°K., ΔH_0^0 = 15658 cal. mole^{-1} and the heat of sublimation at 298.15°K. was found to be 14922 cal. mole^{-1}.

The generally accepted value 27.9 cal. deg.$^{-1}$ mole^{-1} for the entropy of solid iodine at 298.15°K. rests less on the rather inadequate heat capacity measurements from which it was calculated, than on its successful use in a calculation[2] of the heat of sublimation of iodine from the vapor pressure data over a temperature range of nearly one hundred degrees. A value based on sufficiently complete heat capacity data will have a greater reliability and the present work was done to provide these data.

Experimental Procedure and Iodine Sample.—Undoubtedly the reason why more complete calorimetric data on the important substance iodine have not become available long ago is that it will react with typical low temperature calorimeters. To avoid this difficulty a special calorimeter was constructed from a 90-cc. Pyrex bottle, blown to fit approximately into a copper cylindrical shell with a diameter of 4.4 cm. and length 9.5 cm. The bottle had a small glass stoppered neck which extended slightly above a small monel neck and collar at the top of the copper shell. The final closure was by means of a copper cap which could be soldered to the monel collar. Monel was used to prevent excessive heat conduction to the calorimeter during the soldering process. As usual, the interior of the calorimeter was filled with helium to improve heat conduction. As would be expected the glass bottle increased the time required for thermal equilibrium and thus caused some increase in the magnitude of the corrections for heat transfer between the calorimeter and its surroundings; however, this involved only a minor decrease in accuracy. In general the calorimetric equipment was similar to that described previously.[3] A gold resistance thermometer-heater was used for high precision temperature measurements and Laboratory Standard Thermocouple No. 105 was used as a temperature reference. The thermocouple was checked for reliability during this work with the following results: 0.02° high at both the triple point (13.94°K.) and the boiling point (20.36°K.) of hydrogen; 0.01° high at the triple point (63.15°K.) and 0.06° high at the boiling point (77.34°K.) of nitrogen.

The sample of iodine was taken from Baker and Adamson Lot No. LO98 (resublimed) and the maximum limits of impurities given were: non-volatile, 0.010% and Cl and Br, 0.005%.

An amount of 253.271 g. *in vacuo* was used for the measurements. 0°C. was taken as 273.15°K. and 1 defined calorie was taken equal to 4.1840 absolute joules.

The Heat Capacity and Thermodynamic Properties of Iodine.—The experimental data are given in Table I and the derived thermodynamic functions are given for C_p, S^0, $(F^0-H_0^0)/T$ and $(H^0-H_0^0)/T$ at even temperature intervals in Table II.

TABLE I

HEAT CAPACITY OF IODINE, CAL. DEG.$^{-1}$ MOLE^{-1}

Cal. deg.$^{-1}$ mole^{-1}			Mol. wt. = 126.91		
T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
13.62	2.143	78.18	10.30	192.96	12.27
15.71	2.644	84.61	10.51	202.06	12.34
18.04	3.322	90.99	10.73	209.66	12.44
20.55	4.018	97.27	10.88	216.84	12.47[a]
23.33	4.754	104.01	11.05	223.32	12.64
26.16	5.359	110.99	11.21	231.05	12.67
29.24	6.051	118.43	11.37	239.68	12.67
32.30	6.510	126.10	11.60	248.58	12.73
36.13	7.051	133.48	11.64	256.85	12.75
39.93	7.549	140.90	11.72	264.96	12.83
44.24	8.043	148.36	11.83	273.32	12.73
49.26	8.520	155.65	11.99	282.02	12.86
54.52	8.891	162.71	12.00	291.14	12.88
60.05	9.361	170.04	12.07	301.22	13.12
65.79	9.757	177.56	12.15	311.19	13.15
71.87	10.044	185.21	12.20	321.93	13.33

[a] This result is uncertain by ±1% due to water vapor in the apparatus and is thus given no weight.

The data of Lange[4] cover the range 9 to 52° K. His measurements deviate from the present work by ± 1% near and somewhat above the boiling point of hydrogen and above 30°K. they are 2 to 4% high.

A Debye extrapolation below 10°K. gives 0.350 cal. deg.$^{-1}$ mole^{-1} as the entropy less the nuclear spin effect at that temperature.

The thermodynamic functions for iodine gas have been given in the Bureau of Standards Tables.[5] We have applied a small correction to convert these values to 0°C. = 273.15°K. instead of 273.16° K. and have also altered the values given for 0 and 25° slightly in addition since these values appear to have been interpolated in the main series without complete accuracy. The only satisfactory method of interpolating such values to 0.001 appears to be a difference plot with a function correspond-

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[1] This work was supported in part by the National Science Foundation.

[2] W. F. Giauque, THIS JOURNAL, **53**, 507 (1931).

[3] W. F. Giauque and C. J. Egan, *J. Chem. Phys.*, **5**, 45 (1937).

[4] E. Lange, *Z. physik. Chem.*, **110**, 343 (1924).

[5] "National Bureau of Standards," Series III, June 30, 1948; March 1, 1954.