230. Qualitative tests showed the presence of Si–H bonding in the new bromo and the new iodo compounds.

Careful treatment of 5.40 g. of $(C_2H_5)_2SiHI$ with 7-, then 5- and then 3-ml. portions of water, with removal of the acid layer each time, finally yielded 2.58 g. of a liquid of density less than 1.00. Fractional distillation under 49 mm. pressure resulted in the rejection of 0.65 g. of b.p. 90–91.5°, followed by collection of 1.75 g. of b.p. 91.5–92.0°, while 0.20 g. of residue remained undistilled. This largest fraction of $(C_2H_5)_2Si(H)O(H)Si(C_2H_5)_2$ had these observed properties: b.p. 170.6° under 760 mm.; $n^{20}$ $1.416_2$; $d^{20}{}_4$ 0.820; *R* 58.95 (calcd., 58.72).[6] *Anal.* Calcd. for $(C_2H_5)_2Si(H)O(H)Si(C_2H_5)_2$: Si, 30.2; mol. wt., 192.54. Found: Si, 29.9; mol. wt. (camphor), 201. Also, Si–H bonding was present according to a test with alcoholic $AgNO_3$, or to the great care needed in the addition of concd. $HNO_3$ in analysis. This oxide had very little odor.

These last two preparative methods differ from those used with $(CH_3)_2SiHI$, b.p. 92°, and $(CH_3)_2Si(H)OSi(H)(CH_3)_2$, b.p. 73°, both b.p.s being extrapolated values.[7]

**Other Reactions of $(C_2H_5)_3SiH$ Tried.**—In the same procedure as in Table I $(C_2H_5)_3SiH$ failed to react appreciably in 15 minutes reflux with any of the compounds: HgO, $KMnO_4$, $HgI_2$, $SnCl_2$, $TiCl_4$, $K_2PtCl_6$, $n$-$C_3H_7COCl$ (without $AlCl_3$), $GeBr_4$ or $C_6H_5SO_2Cl$. However, $CF_3COOH$ in reflux appeared to give an ester at about 4%/hour; $SbF_3$ gave a small amount of $(C_2H_5)_3SiF$ evidently. In contrast to all these, AgF reacted vigorously with $(C_2H_5)_3SiH$ to give $(C_2H_5)_3SiF$ and at least $(C_2H_5)_2SiF_2$. Similarly, $(C_2H_5)_2SiH_2$ failed to react with $K_2PtCl_6$.

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[6] A. I. Vogel, *J. Chem. Soc.*, 607 (1948); A. I. Vogel and others, *J. Phys. Chem.*, **58**, 174 (1954).

[7] H. J. Emeleus and L. E. Smythe, *J. Chem. Soc.*, 609 (1958).

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[CONTRIBUTION NO. 2206 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

# A Further Study of the Flash Photolysis of Iodine[1]

BY DON L. BUNKER AND NORMAN DAVIDSON[2]

RECEIVED MARCH 15, 1958

The rate of the third-order homogeneous gas-phase recombination of iodine atoms in the presence of argon has been remeasured by a flash photolysis technique. The data at 298°K., obtained in this Laboratory and two others, are now in substantial agreement. Measurements have been extended to 548°K. for comparison with shock tube results. The rate constant for the reappearance of $I_2$, over the full temperature range 298–1600°K., can be represented by $k = 2.98 \times 10^9 (298/T)^{1.83}$ $l.^2$ $mole^{-2}$ $sec.^{-1}$. If the third body is $n$-butane rather than argon, the measured rate constant from 298 to 493°K. is $3.5 \times 10^{10} (298/T)^{2.16}$. The third-body efficiencies of $H_2$ and $D_2$ were compared at 326°K. and found to be nearly equal. In the course of the above measurements the rate of the recombination reaction in which the third body is $I_2$ itself was determined. The ratio $k_{I_2}/k_{Argon}$ is 600 near 300°K. and decreases markedly with increasing temperature. The rate constant $k_{I_2}$ is given by $10^{4.65}T^{3/2}e^{5320/RT}$. A calculation of the effect of temperature inhomogeneity in a recombining system has been made; errors from this source were found to be negligible under our conditions.

The third-order homogeneous combination of iodine atoms has been extensively investigated in the gas phase by the method of flash photolysis. The over-all reaction may be written

$$I + I + M \longrightarrow I_2 + M \qquad (1)$$

$$d[I_2]/dt = k(M,T)[I]^2[M]$$

in which M represents any third body. The notation adopted for the rate constant indicates that it is a function of both the temperature and the nature of the third body M.

Early attempts to measure $k(A,T)$ by the flash photolysis of iodine in the presence of excess argon[3–5] produced somewhat misleading and contradictory results. The source of error was traced to the unexpectedly high efficiency of $I_2$ as a third body and to insufficient attention to thermal effects arising from the irradiation of the sample by the high energy flash.[6] This Laboratory and two others[7,8] have undertaken independent remeasurements of the room temperature rate of recombination in the presence of argon. The results of these three measurements are compared in this paper. We shall refer to references 7 and 8 as SCGW and CHNP, respectively.

Values of the same recombination rate have been obtained from measurements of the rate of dissociation of $I_2$ at 1000-1600°K. in a shock tube.[9] The results reported here include measurements in argon from room temperature to 548°K., which, when combined with the shock tube investigation and the high temperature data of SCGW, provide a fairly complete picture of the temperature dependence of this reaction. In the course of the temperature dependence investigation we have also carried out measurements at various temperatures in which $n$-butane, hydrogen or deuterium replaced argon as third body.

## Experimental

The experiments were carried out in a horizontally mounted cylindrical furnace constructed by winding resistance wire over asbestos on an 18 inch length of 6 inch aluminum pipe. The temperature inside was spatially uniform and could be controlled to within 1°. The furnace was divided into two compartments by a horizontal layer of Corning

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[1] (a) This work was supported by the Office of Naval Research. (b) Further experimental details may be found in the Ph.D. thesis submitted by D. B. to the California Institute of Technology, 1957. (c) Presented in part before the Division of Physical and Inorganic Chemistry, National Meeting of the American Chemical Society, New York, September 11, 1957.

[2] To whom inquiries concerning this paper should be addressed.

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[8] M. I. Christie, A. J. Harrison, R. G. W. Norrish and G. Porter, *Proc. Roy. Soc.* (*London*), **A231**, 446 (1955).

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No. 3486 glass filters, which transmit light above 520 mμ. The upper compartment contained the flash lamp and the lower, the reaction cell.

The cell was cylindrical, 32 cm. long and 5 cm. in diameter. It was provided with a side arm at each end; the side arms connected to an exterior U-tube and to a conventional vacuum line. A portion of the external tubing was provided with a heater, so that gas mixtures could be prepared by thermal siphoning of the "third body" gas over $I_2$ contained in the U-tube. A 500 watt projection lamp, operated from 120-volt storage batteries, was the light source employed in concentration measurements. The light passed through a condensing lens, along the axis of the cylindrical cell, through an iris diaphragm, a converging lens and a layer of filters and impinged on the cathode of a 931-A photomultiplier tube. The filters were a Bausch and Lomb interference filter (H-486) and a Corning No. 3387 yellow filter. The combination transmitted about 28% at its maximum, 481 mμ, with a half-width of 8 mμ. 0.5 μamp. or less primary photocurrent was generated; the tube was operated at a gain near 1500. The signal to shot noise ratio was always greater than 1000.

The photomultiplier was operated from a regulated (drift and ripple <0.01%) d.c. power supply. It was found that linearity corrections (see below) were appreciable unless a separate collecting voltage was employed. Also, in order to allow the output to be d.c. coupled to the vertical input of the DuMont 304-H oscilloscope, a means of measuring and adjusting the DC signal level was required. A circuit found satisfactory for these purposes is shown in Fig. 1. With this arrangement, if the photomultiplier output is adjusted to zero oscilloscope deflection, the signal level may be read directly from the potentiometer dial.

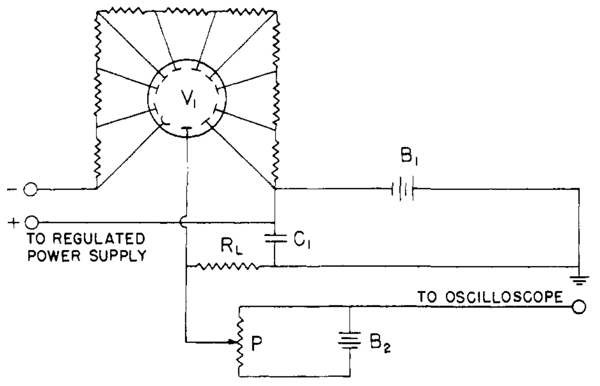

Fig. 1.—Photomultiplier circuit: $V_1$, 931-A; $R_L$, 100 KΩ; other resistances, 15 KΩ; $C_1$, 1 μF.; $B_1$, 90 V. collecting battery; $B_2$, 45 V. bucking battery; P, 50 KΩ Helipot precision potentiometer.

The flash lamp was constructed of Pyrex tubing, 36 cm. × 13 mm. i.d. The two electrodes were nickel cylinders attached to tungsten leads. The lamps were filled to 50 mm. pressure with xenon; a lamp so constructed and filled will break down spontaneously on the application of >10 Kv. across the electrodes. The flash lamp leads were connected across a 4 μF. capacitor, *via* a 5C22 thyratron to serve as on-off switch. The capacitor could be charged to 16 Kv. from an external power supply.

Operation of the equipment was initiated by a 12-volt signal synchronized, for improved noise control, to the local 60 cycle wave form. The signal triggered the oscilloscope single sweep and a time delay generator described previously.[6] After the selected delay a 200 volt positive pulse was applied to the grid of the 5C22, resulting in the connection of the charged 4 μF. capacitor to the flash lamp. The flash lamp discharge commenced within a few μsec. thereafter. The observed scattered light from the discharge (with the reaction cell evacuated) became comparable with shot noise in 200–400 μsec. The oscillographic optical density measurements which constitute an experiment began at this point and continued for 1/2 to 5 msec.

Timing was accomplished on a separate trace with a Tektronix type 181 time mark generator. A DuMont Polaroid type camera was employed in trace photography.

**Materials.**—Reagent grade $I_2$ was resublimed twice before use. The gases used were Linde argon, 99.99% pure and passed over drierite; Linde hydrogen, 99.9% pure; and deuterium supplied at >99.5% purity by the Stuart Oxygen Company. A liquid sample of 99% pure *n*-butane (impurity mostly isobutane) was kindly provided by the Chemical Engineering Department of the California Institute. It was redistilled in the course of transfer to the vacuum line.

**Procedure.**—In an experiment, the instruments and light source were allowed to warm up for at least 1 hour, in order to attain stability and particularly to fatigue the photomultiplier to the point where further sensitivity change was slow. After the chosen pressure of "third body" gas was admitted to the cell, the U-tube, containing $I_2$, was warmed to a temperature corresponding approximately to the pressure of $I_2$ desired. The gases were then mixed to constant optical density by thermal siphoning and the photomultiplier output adjusted to match the d.c. zero of the oscilloscope. Photographs (usually 7) were then taken of oscilloscope traces during actual flash photolysis experiments initiated as described above. About 10% of the $I_2$ was dissociated by each flash. The gases were then rapidly removed from the cell, by pumping and freezing. The d.c. signal level before and after doing so was recorded for use in determining initial $I_2$ concentration. Pictures of scattered flash lamp light and of time marks were taken with the cell thus emptied. A measurement of the ratio of potentiometer units to inches oscilloscope deflection was made during each run.

At a particular temperature between 5 and 20 samples of gas were examined in this way. Gas pressures were chosen to cover the range of $[I_2]/[M]$ between the limits set by excessively fast recombination at high pressures and the onset of thermal errors at low pressures.

**Treatment of Data.**—The oscilloscope deflections in any convenient units (potentiometer dial, volts or oscilloscope inches) are designated as follows: $a$ = amplitude with cell empty; $y_i$ = amplitude with cell filled, *i.e.*, signal level after sweep initiation but before lamp firing; $y_t$ = amplitude at time $t$ during the experiment. The concentrations are given by the Beer's law expressions

$$[I]_t = (2/\epsilon L)\log_{10}(y_t/y_i);\quad [I_2] = (1/\epsilon L)\log_{10}(a/y_i)$$

L is the cell length in cm. and ε the decadic extinction coefficient of $I_2$. $[I_2]_i$ is the concentration before the flash. A convenient integrated form of eq. 1 is

$$(1/[I]_t) - (1/[I]_0) = 2k(M,T)[M](t - t_0)$$

The subscript 0 indicates the time at which measurement is started, dictated by the decay time of the flash lamp.

For each picture $1/[I]_t$ was calculated for 10 or more values of $t$ and plotted *vs.* $t$, yielding a straight line whose slope was determined by eye and equated to $2k_{\text{obsd.}}[M]$. Thus for each gas sample 7 measurements of $k_{\text{obsd.}}$ were obtained, grouped in a narrow range of $[I_2]_0/[M]$. The small spread in this ratio was due to slight differences in the initial degree of dissociation. The $k_{\text{obsd.}}$ values for an individual gas sample had a range of about 5%.

For a particular temperature, all the observed rate constants were plotted *vs.* $[I_2]_0/[M]$ in order to separate the effects of $I_2$ and M as third bodies. These plots, for M = A, $C_4H_{10}$ and $H_2$ or $D_2$, are shown in Fig. 2, 3 and 4, respectively. The intercept gives the final value of $k(M,T)$ for that temperature, and the slope is a measure of $k(I_2,T)$. The lines were determined by least squares.

**Extinction Coefficients.**—The extinction coefficient of $I_2$, for the combination of lamp, filters and photomultiplier described, was determined in the apparatus. If only $I_2$ was present in the cell, a

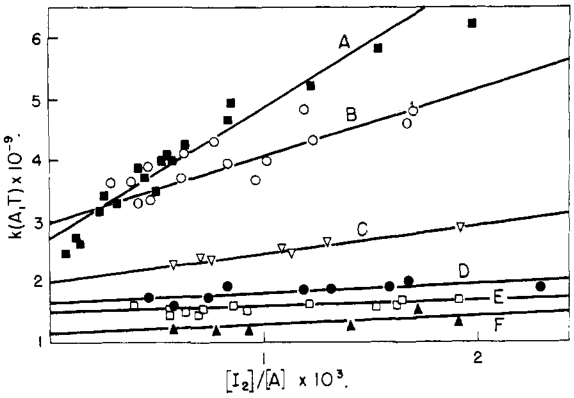

Fig. 2.—Variation of recombination rate in argon with $[I_2]/[A]$: A, 29°; B, 50°; C, 100°; D, 150°; E, 200°; F, 275°.

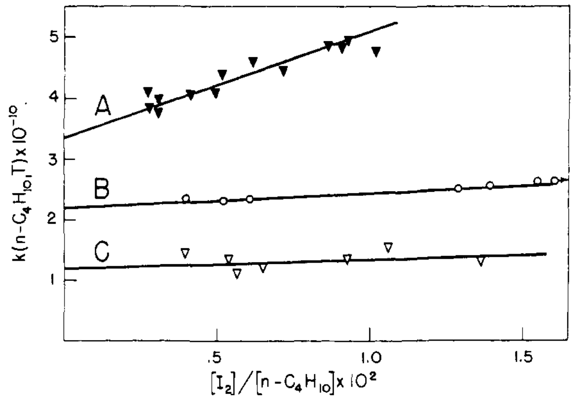

Fig. 3.—Variation of recombination rate in *n*-butane with $[I_2]/[n\text{-}C_4H_{10}]$: A, 32°; B, 100°; C, 220°.

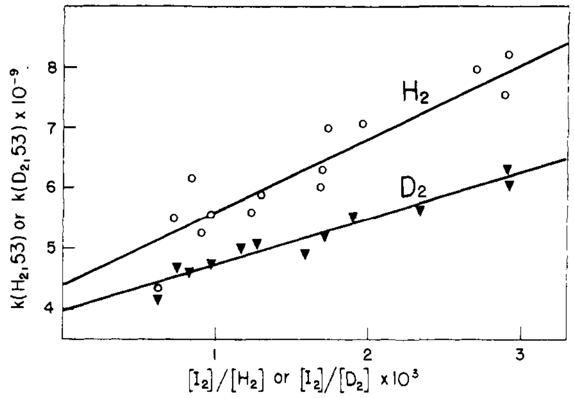

Fig. 4.—Variation of recombination rate in hydrogen and deuterium with $[I_2]/[H_2]$ or $[I_2]/[D_2]$, at 53°.

known concentration could be maintained by controlling the U-tube temperature; ε was then determined by noting the change in light transmission when the cell was suddenly evacuated. This method of concentration measurement was supplemented by some chemical determinations in which the $I_2$ was frozen down, removed from the cell and titrated in KI solution with standard $Na_2S_2O_3$. The latter procedure was also applicable to mixtures of $I_2$ and inert gas. The results of the two methods coincided.

With ε established in this way at room temperature, its temperature dependence could be measured by varying the temperature of the furnace. A double beam arrangement was constructed for this purpose, employing for the reference light source another projection lamp operating from the same battery bank as the first. The extinction coefficient was found to decrease with increasing temperature as shown by the solid line in Fig. 5. The curve shown was very reproducible; it agrees with the data of Britton, Davidson, Gehman and Schott,[9] which are also shown. ε was not found to vary significantly with total pressure at any temperature in the range indicated. This indicates that very little light of wave length greater than the $I_2$ convergence limit (499.5 mμ) reached the photocathode.

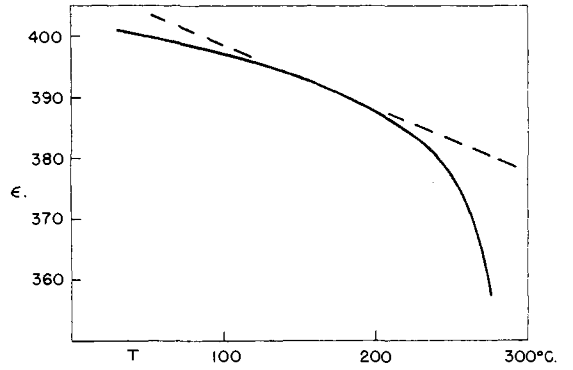

Fig. 5.—Observed variation of extinction coefficient ε(l. mole$^{-1}$ cm.$^{-1}$) with temperature: solid line, this investigation; dashed line, Britton, Davidson, Gehman and Schott (extrapolated).

**Photomultiplier Linearity.**—If a photomultiplier circuit is assembled in the usual way, *i.e.*, to have a single regulated voltage impressed across ten dividing resistors from photocathode to last anode, its response is not necessarily linear. This is because the voltage across the final or collecting stage, in which no amplification occurs, is diminished when an appreciable amplified photocurrent flows. The regulation then requires that the voltage across the earlier stages increase in order to maintain a constant total value, and a corresponding increase in sensitivity is observed. The device of placing a capacitor in parallel with each resistor is not applicable in our case because it delays recovery of the tube from the pulse of scattered light from the flash lamp.

Initially, in this investigation, only five stages of multiplication were employed, in order to allow a higher interdynode voltage to be used. This was supposed to minimize defocussing by disturbances radiated from the flash lamp circuit. After half the measurements were completed, it was discovered that for some reason the use of the sixth dynode as collector greatly intensifies the nonlinearity of the tube—the sensitivity increase upon illumination may be ten times greater than that predicted on the basis of the preceding paragraph.

The seriousness of this unfortunate error was mitigated by the fact that all the affected measurements were obtained under similar instrumental conditions, so that a blanket correction could be made to the rate constants. The corrections were obtained by exhaustive calibration of photomultiplier tubes, using a weak chopped light signal to observe the sensitivity in the presence or absence of a strong d.c. light source; they amounted to +13% for $k(\mathrm{M} \neq \mathrm{I}_2,T)$ and +32% for $k(\mathrm{I}_2,T)$. The increased uncertainty in the rate constants is not very large, and the corrected values fit smoothly with later rate constants which did not require correction.

The conditions leading to non-linearity were removed by reconstruction of the photomultiplier circuit as shown in Fig. 1.

**Thermal Effects.**—In our experiments the initial degree of dissociation is relatively small, and the heat capacity added to the system by the third body M is sufficient to confine the temperature rise during the recombination to about 1°. The major problem to be anticipated in connection with the appearance of translational energy during the recombination is, therefore, of the type described by CHNP,[8] arising from the fact that the concentration distribution in the cell may be expected to become non-uniform as the reaction proceeds. This effect is due to the cooling by heat conduction and consequent contraction of the outer layers of gas while the reaction is proceeding; an explicit correction is necessary under the CHNP experimental conditions. A further explanation of this process, and a calculation showing that it is unimportant in our work, are given in the Appendix.

**Miscellany.**—The usual tests of the kinetic order of the reaction were performed. The data were found to be invariant to a four-fold decrease in initial degree of dissociation, and to a threefold range of total pressure. The latter range was restricted by the limited vapor pressure of $\mathrm{I}_2$. Under optimum noise and thermal conditions a linear kinetic plot extending to 5–6 half-lives could be obtained; however, in a typical experiment, only 1 half-life was followed. Long-term variations in the storage battery voltage were not large enough to affect the extinction coefficients. No test for possible non-uniform illumination by the flash lamp was made; in the previous investigations of this kind non-uniform illumination has not been found to be important. Since the optical density of the cell and its contents, viewed from the side, is small, most of the flash light passes through the cell again and again before absorption. If, in spite of this, there is an initially non-uniform distribution of I atoms, its effect on the measured rate constant would be expected to be small.[7]

## Results

**Measurements in Argon.**—In the discussion of $k(\mathrm{A},T)$ accompanying the shock tube results[9] two methods of presenting temperature dependence data were employed. Similar ones are used here. In Fig. 6 log $k(\mathrm{A},T)$ is plotted[10] against log $T$ and in Fig. 7 log $k(\mathrm{A},T)$ *vs.* $1000/T$ is shown. The shock tube results also are displayed. The flash photolysis data extend from 302 to 548°K. and the shock tube data cover the range 1080-1570°K. It will be noted that neither representation completely reconciles the high and low temperature results. This circumstance will be explained in the accompanying paper.[11] In the figures the recent results of SCGW are included; the range shown has as its extremes the equivalent "high" and "low" values arising in their investigation. The difference between these is neither very large nor very serious for present purposes. The agreement between our results and those of SCGW is remarkably good. The straight lines were calculated by least squares using only our results, except in the log-log plot where the shock tube investigation was regarded as a single point $k(\mathrm{A},1285°\mathrm{K.}) = 10^{8.665}$. The functional relations so obtained are

$$k(\mathrm{A},T) = 10^{8.67}\, e^{1130/RT} \quad \mathrm{l.}^2\ \mathrm{mole}^{-2}\ \mathrm{sec.}^{-1} \quad (2)$$

$$k(\mathrm{A},T) = 2.98 \times 10^{9}(298/T)^{1.33}\ \mathrm{l.}^2\ \mathrm{mole}^{-2}\ \mathrm{sec.}^{-1} \quad (3)$$

**Measurements in *n*-Butane.**—These measurements, carried out at 305, 373 and 493°K., can be treated in the same way as those in argon, and an equally good fit to either form of temperature law is found.

$$k(n\text{-}\mathrm{C_4H_{10}},T) = 10^{9.36}\, e^{1650/RT} \text{ or}$$
$$3.5 \times 10^{10}\,(298/T)^{2.16} \quad \mathrm{l.}^2\ \mathrm{mole}^{-2}\ \mathrm{sec.}^{-1} \quad (4)$$

**Measurements in Hydrogen and Deuterium.**—The third-body efficiencies of $\mathrm{H}_2$ and $\mathrm{D}_2$ were compared at a single temperature, 53°. The quantity of interest (see following paper[11]) is the ratio $k(\mathrm{H}_2,53)/k(\mathrm{D}_2,53) = 1.1$, as obtained from the intercepts in Fig. 4. Some difficulty was encountered in these measurements with misbehavior of the furnace controller, and it is likely that the divergence of slopes in Fig. 4 reflects a difference in furnace temperature of about 5°. If the temperature dependence of $k(\mathrm{H}_2,T)$ and $k(\mathrm{D}_2,T)$ resembles that for $k(\mathrm{A},T)$ the above ratio should be reduced to 1.04. For discussion purposes the value 1.05 ± 0.05 will be adopted.

**$\mathrm{I}_2$ as Third Body.**—Each experimental point shown in Fig. 6 or 7 is accompanied by a measurement of $k(\mathrm{I}_2,T)$; the major purpose of the *n*-butane series was to check the $k(\mathrm{I}_2,T)$ determined in argon. In Fig. 8 the collection of $k(\mathrm{I}_2,T)$ determined with all four gases is displayed in the form $\ln[k(\mathrm{I}_2,T)/T^{3/2}]$ *vs.* $1000/T$. This representation is selected for later convenience[11]; it will be of interest to factor the rate constant into the product of a collision number and equilibrium constant which in pressure units is of the form $Ae^{E/RT}$, with $A$ and $E$ more or less constant. The rate constants are found to be insensitive to the nature of the added gas. A weighted least squares treatment leads to

$$k(\mathrm{I}_2,T) = 10^{4.65}\,T^{3/2}e^{5320/RT}\ \mathrm{l.}^2\ \mathrm{mole}^{-2}\ \mathrm{sec.}^{-1} \quad (5)$$

**Comparison with Other Results.**—The negative temperature coefficients of recombination reactions, first noted by Russell and Simons,[4] and the extreme third-body efficiency of $\mathrm{I}_2$ proposed by Christie, Norrish and Porter[6] are confirmed by our results.

From eq. 3 and 5, the values of $k(\mathrm{A},25°)$ and $k(\mathrm{I}_2,25°)$ may be computed for comparison with CHNP[8] and SCGW.[7] This comparison is dis-

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(10) In Fig. 6–8, the probable error of the observation is indicated by the height of the experimental point.

(11) D. Bunker and N. Davidson, THIS JOURNAL, **80**, 5090 (1958).

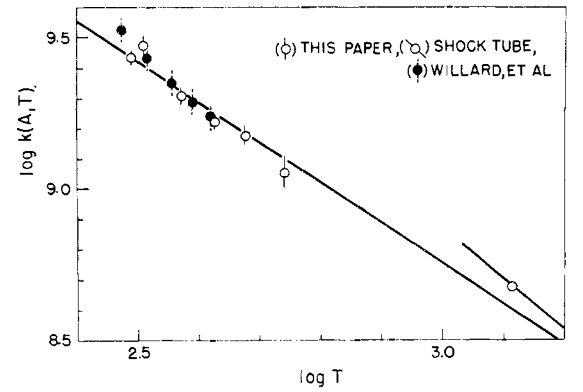

Fig. 6.—Variation of recombination rate in argon with temperature; log-log representation.

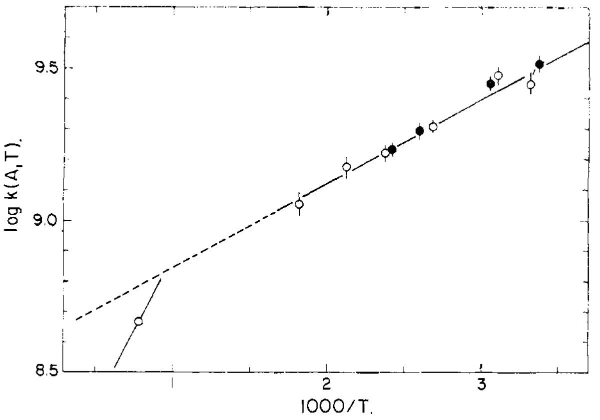

Fig. 7.—Variation of recombination rate in argon with temperature; Arrhenius representation.

played in Fig. 9. Our results are: $k(\mathrm{A},25°) = 2.9\ (\pm.3) \times 10^9\ \mathrm{l.}^2\ \mathrm{mole}^{-2}\ \mathrm{sec.}^{-1}$, $k(\mathrm{I}_2,25°) = 1900\ (\pm200) \times 10^9$. CHNP give, near 21°, $k(\mathrm{A}) = 3.34 \times 10^9$, $k(\mathrm{I}_2) = 850 \times 10^9$. Thermal effects are larger in the CHNP experiments than in ours; if greater weight were given to their points at lower $[\mathrm{I}_2]/[\mathrm{A}]$ ratios, the agreement for $k[\mathrm{A}]$ and $k(\mathrm{I}_2)$ would be still better. There is thus fairly good agreement with CHNP as to the values of $k(\mathrm{A})$ and $k(\mathrm{I}_2)$ and with SCGW as to $k(\mathrm{A})$ and its temperature coefficient.

The interpretation of the combined results of our investigation and those of SCGW and CHNP, as well as that of a number of other recombination rate measurements, is discussed in the accompanying paper.[11]

**Acknowledgment.**—One of us (DB) is indebted to the National Science Foundation and the General Electric Company for fellowships.

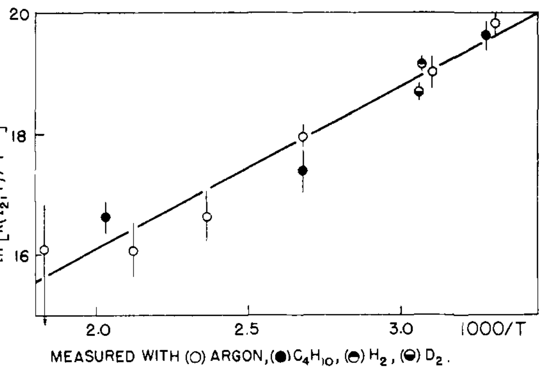

Fig. 8.—Variation of rate of $\mathrm{I} + \mathrm{I} + \mathrm{I}_2$ with temperature.

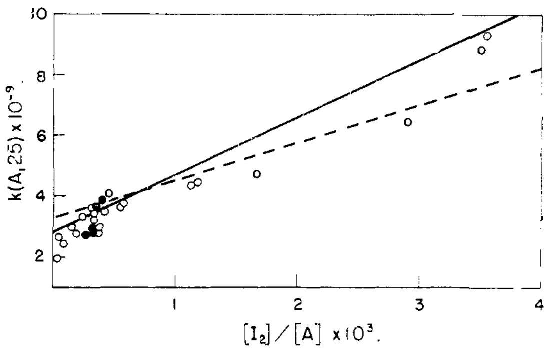

Fig. 9.—Comparison of various measurements of rate of recombination in argon, at 25°: solid line, this investigation; dashed line and open circles, CHNP; solid circles, SCGW.

## Appendix

An approximation which is suitably pessimistic for our purposes and which serves to illustrate the nature of the thermal problem is that all the radiant energy absorbed appears as translation immediately after the flash. Actually, in our case, up to 20 kcal. of translational energy appears almost immediately as a consequence of the induced predissociation which leads to formation of the two $^2P_{3/2}$ iodine atoms. The model, then, is one of a cylindrical cell of radius $r$ with its interior initially at $T + \Delta T$ and its boundaries at $T$. If it is considered that the mean distance from the boundary into the cell which will have cooled significantly at some time $t$ after the flash is $\delta r = g(Dt)^{1/2}$, where $D$ is a heat diffusivity of the order of magnitude of the ordinary diffusion coefficient and $g$ is a small number between 1 and 3, then the thermal errors can be represented as arising from the pressure equilibrium between a cylindrical annulus of thickness $\delta r$ at temperature $T$ and the rest of the cell at $T + \Delta T$. The result will be that as the annulus enlarges the concentration of $\mathrm{I}_2$ at the center of the cell will be depleted; since a small variation in the $[\mathrm{I}_2]$ in the light path gives rise to a large error in measured [I], the consequences for a rate measurement may under some conditions become serious.

In our case $\delta r << r$. Then the fractional volume cooled to $T$ is

$$V_0/V = 2\delta r/r = 2g(Dt)^{1/2}/r \qquad (6)$$

The fractional concentration change at the center is

$$-(V_0/V)(\Delta T/T) = y = -2g(Dt)^{1/2}\,\Delta T/rT \qquad (7)$$

$y$ is the fractional loss of $\mathrm{I}_2$ from the light path and is related to concentrations by $y = ([\mathrm{I}_2]_{\mathrm{app}} - [\mathrm{I}_2])/[\mathrm{I}_2]$. On the concentration brackets "app" means "apparent," and the absence of a subscript implies the concentration that would have prevailed in the absence of heat diffusion effects. For the small degree of dissociation employed here, it is easily shown that

$$[\mathrm{I}]^{-1}_{\mathrm{app}} = [\mathrm{I}]^{-1}\,(1 + 2y[\mathrm{I}_2]/[\mathrm{I}]) \qquad (8)$$

We define the *second-order* rate constants, for a particular M

$$k_{\mathrm{app}} = \mathrm{d}[\mathrm{I}]^{-1}{}_{\mathrm{app}}/\mathrm{d}t \text{ and } k = \mathrm{d}[\mathrm{I}]^{-1}/\mathrm{d}t \qquad (9)$$

The fractional corrections calculated for these will be the same as for the customary third order constant. Differentiating eq. 8 with $[\mathrm{I}_2]$ approximately constant leads to

$$k_{\mathrm{app}} = (1 + 4y[\mathrm{I}_2]/[\mathrm{I}])k + 2([\mathrm{I}_2]/[\mathrm{I}]^2)\mathrm{d}y/\mathrm{d}t \qquad (10)$$

For convenience this is rewritten

$$k_{\mathrm{app}} = k(1 + c_1 + c_2) \qquad (11)$$

where $c_1 = 4y[\mathrm{I}_2]/[\mathrm{I}]$ and $c_2 = (2[\mathrm{I}_2]/k[\mathrm{I}]^2)\mathrm{d}y/\mathrm{d}t$.

To evaluate the $c$'s, a series of dimensionless parameters is introduced: $C\Delta T = \alpha\phi\Delta H$; $\Delta T/T = h\alpha\phi$; $h = \Delta H/CT$. $\phi$ is $[\mathrm{I}_2]/[\mathrm{M}]$; $\alpha$, initial degree of dissociation; $\Delta H \cong 60$ kcal./mole; and $C$ is a heat capacity of M between $C_{\mathrm{v}}$ and $C_{\mathrm{p}}$. $y$ is then given by $-2gh\alpha\phi(Dt)^{1/2}/r$. The extent of recombination is described by a variable $\beta = [\mathrm{I}]_0/[\mathrm{I}]$, where $[\mathrm{I}]_0$ is the atom concentration just after the flash. Time can then be replaced by $t = (\beta - 1)/[\mathrm{I}]_0\,k$. Substitution of these quantities into the definition of $c_1$ results in

$$c_1 = (8gh\alpha\phi[\mathrm{I}_2]/r[\mathrm{I}])(D_1\{\beta - 1\}/Pk[\mathrm{I}]_0)^{1/2} \qquad (12)$$

wherein $D$ has been made pressure-dependent, $D_1$ being the heat diffusivity at 1 atm. Use of $\alpha[\mathrm{I}_2] = (1/2)[\mathrm{I}]_0$ in eq. 12 reduces it to

$$c_1 = -(4gh\beta\phi/r)(D_1\{\beta - 1\}/Pk[\mathrm{I}]_0)^{1/2} \qquad (13)$$

The estimation of $c_2$ starts from

$$\mathrm{d}y/\mathrm{d}t = -gh\alpha\phi(Dt)^{1/2}/rt$$

$$c_2 = -2[\mathrm{I}_2]gh\alpha\phi(Dt)^{1/2}/rkt[\mathrm{I}]^2 \qquad (14)$$

If $t$ is written in terms of $\beta$ and $\alpha$ eliminated as before, and the result compared with eq. 13, it is revealed that

$$c_2 = (c_1/4)\beta/(\beta - 1) \qquad (15)$$

This allows the correction eq. 11 to be written in the form

$$k_{\mathrm{app}}/k = 1 - [\beta(5\beta - 4)/4(\beta - 1)^{1/2}]x$$

where

$$x = (4gh\phi/r)(D_1/Pk[\mathrm{I}]_0)^{1/2} \qquad (16)$$

In eq. 16, $x$ is a number characterizing the experimental conditions, and the $\beta$ bracket is a universal time factor applicable to all experiments. $x$ was evaluated for our argon measurements, with the values $C = 4$ cal./mole, $h = 50$, $g = 2.5$ and $r = 2.5$ cm., and found to be between $5 \times 10^{-2}$ and $3 \times 10^{-3}$, with the higher value only rarely attained. Our $\beta$ runs from 1.1 to, at most, 3, with the rate constant obtained from the slope of the second-order plot at $\beta = 1.1$; the value of the $\beta$ bracket ranges from 1.3 to about 6 in this interval. Appreciable deviation from linearity seldom was found and would not be expected on the basis of the above treatment. Under our experimental conditions the error in the measured rate constant, due to thermal effects, is probably less than 1%.

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# On the Interpretation of Halogen Atom Recombination Rates[1]

BY DON L. BUNKER AND NORMAN DAVIDSON[2]

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A theory for the rate of recombination of halogen atoms, X, in the presence of various third bodies, M, is developed. The theory assumes the formation of an equilibrium concentration of MX complexes. It is furthermore assumed that the recombination reaction, $\mathrm{MX} + \mathrm{X} \rightarrow \mathrm{M} + \mathrm{X}_2$, takes place only when MX is in a bound state, with internal kinetic energy less than the binding energy. For the case of chemically inert M's, a Lennard-Jones potential between M and X is used and an *a priori* statistical calculation gives good agreement with the measured rate constants and their temperature coefficients. The theory does not explain the cases, $\mathrm{M} = \mathrm{H}_2$, $\mathrm{D}_2$ and He, however. In the special case that the third body is $\mathrm{I}_2$ (in I atom recombination) the intermediate complex is chemically bound and its thermodynamic properties may be estimated from the recombination rate. The present data give, for the reaction $\mathrm{I}_2 + \mathrm{I} \rightarrow \mathrm{I}_3$, $\Delta H^0 = -5.3$ kcal., $\Delta S^0 = -20$ e.u.

There is now available a considerable amount of kinetic data pertaining to recombination of halogen atoms in the gas phase. Christie, Harrison, Norrish and Porter,[3] Strong, Chien, Graf and Willard[4] and the present authors[5] have all recently studied various aspects of the recombination rate of iodine atoms in the presence of argon and a few other added gases. Russell and Simons[6] have compiled a great deal of useful data relating the third-body efficiencies of various gases in this reaction. The reverse dissociation process had been studied above 1000°K. in the shock tube for iodine[7] and for bromine.[8,9] Room temperature measurements of the recombination rate of bromine atoms have been reported.[4]

As a result of these investigations, several general features of the recombination reactions have emerged.

(a) The termolecular rate constants have a small negative temperature coefficient

(b) There is a wide variation in effectiveness among the various gases which may be added as

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