on distilling a basic aqueous solution of NH_4Cl and KCN containing the radioactive hot atom products. However, no peak corresponding to radioactive NH_3 was found in the gas chromatograms; consequently it was concluded that the small amount of activity found probably was due to small amounts of nitrogen gas being carried over into the distillate.

[CONTRIBUTION NO. 2545 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIFORNIA]

Some Iodine Atom Recombination Rates by Flash Photolysis[1]

BY ROLF ENGLEMAN, JR.,[2] AND NORMAN R. DAVIDSON[3]

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The rate constants of the homogeneous gas-phase iodine atom recombination have been measured by flash photolysis in the presence of several third body gases. Hydrogen, helium, benzene and methyl iodide have been studied as third body gases at several temperatures between 323 and 548°K., and their third order rate constants are $1.41 \times 10^9 (298/T)^{0.80}$, $4.93 \times 10^9 (298/T)^{1.48}$, $1.00 \times 10^{11} (298/T)^{2.53}$ and $1.50 \times 10^{11} (298/T)^{3.24}$ l.^{2} moles^{-2} sec.$^{-1}$, respectively. Ethyl iodide, hydrogen iodide and carbon monoxide were used at 323°K. and yielded 2.38×10^{11}, 2.81×10^{10} and 5.42×10^9 l.^{2} moles^{-2} sec.$^{-1}$, respectively. Limited experiments were made with nitric oxide as a third body gas. The recombination rate was apparently too fast to measure with this apparatus, but an apparent lower limit of 4.8×10^{14} l.^{2} moles^{-2} sec.$^{-1}$ was established.

The homogeneous gas-phase iodine atom recombination in the presence of a third body gas has been studied by several methods and many investigators. Some of the earliest measurements were made by Rabinowitch and Wood[4] using a photostationary state method. Shock tube measurements have been used to study the rate of iodine dissociation in the presence of a third body gas at high temperatures (1000–1600°K.).[5]

The flash photolysis technique has been applied to iodine atom recombination by numerous investigators,[6–13] and this paper is a continuation of earlier measurements in this Laboratory.[8,12] The over-all simple recombination reaction and rate equation are

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

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

where M is the third body gas. The third order rate constant, $k(M,T)$, specifies the third body gas and the temperature, and it will be given here in units of l.^{2} moles^{-2} sec.$^{-1}$. The extensive measurements of Russell and Simons[7] give the rate constant for recombination in helium as much larger than predicted by the "intermediate complex" treatment of Bunker and Davidson.[14] Their measurements give relatively large rate constants for recombination in benzene and ethyl iodide, presumably due to complex formation with iodine atoms. In an attempt to clarify and confirm these results, helium, hydrogen, benzene and methyl iodide have been used as third body gases at various temperatures. In addition, limited measurements were made at a single temperature on recombination in ethyl iodide, hydrogen iodide, carbon monoxide and nitric oxide. The experiments recently reported by Porter and Smith[13] were directed towards the study of essentially the same questions that interest us.

Experimental

The apparatus used in this study was essentially that described by Bunker and Davidson.[12] The measurements with helium and hydrogen were made with a Dumont 304-H oscilloscope as described previously. The other measurements were made with a Tektronix 535 oscilloscope with a 53/54D amplifier plug in unit. The sweep of the Tektronix oscilloscope was triggered manually to give a base line from which to measure deflections. At a preselected point on the sweep, the oscilloscope generates a delayed trigger pulse which causes a 2D21 thyratron to discharge and generate a 200 volt pulse. This pulse is applied to the control grid of a 5C22 hydrogen thyratron and the resulting breakdown allows a $4\mu f$ condenser bank to discharge through the flash lamp. A high voltage power supply was used to charge the condenser bank to between 10 and 16 kv., depending on the flash intensity desired.

Materials.—Reagent grade iodine crystals were used after at least one sublimation. Linde argon (99.9%), Linde hydrogen (99.9%) and Ohio Chemical Company helium (99.9%) were used directly after passage through a Dry Ice or liquid nitrogen trap. Matheson C.P. carbon monoxide was used without further purification. Baker and Adamson reagent benzene was used after freezing and degassing. A freshly opened bottle of Matheson C.P. methyl iodide was degassed by pumping and freezing and was stored in the dark over a piece of copper wire. The methyl iodide remained almost colorless throughout the experiments. Matheson C.P. ethyl iodide was used after a similar treatment.

Matheson C.P. nitric oxide was purified as described by Huffman.[15] Condensed nitric oxide was twice distilled from a methylpentane-bath at about −150° to a liquid nitrogen bath. This process changed the nitric oxide from a multicolored solid to a very light blue liquid or a light blue icelike solid. This solid was stored at liquid nitrogen temperature.

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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 R. E. to the California Institute of Technology, 1959.

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[13] G. Porter and J. A. Smith, *Nature*, **184**, 446 (1959).

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[15] R. E. Huffman and N. Davidson, *ibid.*, **81**, 2312 (1959).

Hydrogen iodide was prepared by the method suggested in Henderson and Fernelius.[16] A slight excess (over the calculated stoichiometric quantity) of red phosphorus was mixed with iodine crystals and some clean dry sand in a flask. The vacuum tight system was flushed with argon at atmospheric pressure and then distilled water was slowly added to the mixture. The liberated hydrogen iodide was passed through an ice-cooled trap filled with Pyrex wool to remove some water and iodine vapor. The hydrogen iodide was collected in a liquid nitrogen trap after passing through a drying tube containing phosphorous pentoxide on glass beads. The hydrogen iodide was dark colored, but two bulb to bulb distillations afforded a light yellow solid. This was stored in a Dry Ice trap in the dark and it did not discolor during the several days of experimentation.

Procedure.—Before a typical experimental run was started, the gas cell was filled with the desired pressure of third body gas, and the electronics and monitor light were turned on. The U-tube containing the iodine was kept at a temperature somewhat less than that corresponding to the desired vapor pressure of iodine. The gas was circulated through the U-tube for 0.5 to 3 hours by means of the heater on the side arm. After the optical density of the gas cell became and remained relatively constant, the heater was turned off and the actual run was started. The condenser bank was charged, the Polaroid camera shutter was opened and the measurement sequence was started by manually triggering the oscilloscope sweep. Between 5 and 7 such recombinations were recorded over a period of about 15 minutes. Since there was some drift in the system, the photomultiplier d.c. output voltage was recorded between each recombination measurement. At the end of a run, the cell was pumped out, a Dry Ice bath was placed on the U-tube and the new photomultiplier d.c. output voltage was measured so that the iodine concentration could be calculated. A scattered light and noise test was then made by discharging the flash lamp in the same sequence as for a recombination measurement but with the gas cell evacuated.

The Kinetic Effect.—For the idealized kinetic system resulting from the flash photolysis of iodine vapor in excess third body gas, M, the recombination reactions and rate equation are

$$\mathrm{I} + \mathrm{I} + \mathrm{M} \xrightarrow{k_1} \mathrm{I}_2 + \mathrm{M} \qquad (2)$$

$$\mathrm{I} + \mathrm{I} + \mathrm{I}_2 \xrightarrow{k_2} 2\mathrm{I}_2 \qquad (3)$$

$$\mathrm{I} + \mathrm{I} + \mathrm{I} \xrightarrow{k_3} \mathrm{I}_2 + \mathrm{I} \qquad (4)$$

$$-\,\mathrm{d}[\mathrm{I}]/\mathrm{d}t = 2k_1[\mathrm{I}]^2[\mathrm{M}] + 2k_2[\mathrm{I}]^2[\mathrm{I}_2] + 2k_3[\mathrm{I}]^3 \qquad (5)$$

The last equation can be integrated between appropriate limits to give

$$t = \frac{1}{a}\left\{\frac{1}{[\mathrm{I}]} - \frac{1}{[\mathrm{I}]_0}\right\} - \frac{b}{a^2}\ln\left|\frac{(a + b[\mathrm{I}]_0)[\mathrm{I}]_0}{(a + b[\mathrm{I}])[\mathrm{I}]}\right| \qquad (6)$$

where $a = 2\,k_1[\mathrm{M}] + 2\,k_2[\mathrm{I}_2]_\infty$, $b = 2\,k_3 - k_2$, $[\mathrm{I}]_0$ = initial iodine atom concentration and $[\mathrm{I}_2]_\infty$ = total iodine molecule concentration. If iodine atoms can be considered as "inert gas" atoms, the last reaction (equation 4) might be expected to have a rate constant about twice that of the first reaction (equation 2) with M = xenon. There is no direct experimental evidence on k_3, although it has been found[12] that the observed recombination kinetics are independent of the initial iodine atom comcentration, and this fact tends to exclude any relatively large value for k_3.

The second reaction (equation 3) can become important when k_1 is small, since k_2 is quite large at lower temperatures. If the initial degree of dissociation is small, the I_2 concentration can be considered constant and included as part of the third body gas. Assuming that k_3 is relatively small and $[\mathrm{I}_2]_0 >> [\mathrm{I}]_0$, equation 6 reduces to

$$t = \frac{1}{2k_1[\mathrm{M}] + 2k_2[\mathrm{I}_2]_\infty}\left\{\frac{1}{[\mathrm{I}]} - \frac{1}{[\mathrm{I}]_0}\right\} \qquad (7)$$

Equation 7 was used to analyze all kinetic data in this paper.

Equation 6 predicts that the slope of a 1/[I] *vs.* time plot will increase as time increases. This effect could be important for third body gases which have small rate constants and fulfill the condition, $k_1[\mathrm{M}] \approx k_2[\mathrm{I}_2]$. Helium at 50° and 200 mm. pressure was chosen as a case where this "kinetic effect" should be most severe and should cause the most deviation from equation 7. This deviation from the simple third order kinetics is just the second term of equation 6. If the experimental helium and iodine rate constants and typical iodine concentrations are substituted, the second term gives a rate constant about 4% too large. Since this is probably within the experimental error and the other third body gases give even smaller errors, no corrections were made for this "kinetic effect."

The Thermal Effect.—The temperature increase in the gas mixture during a recombination experiment will give rise to nonuniform iodine concentrations, which can cause relatively large errors. This thermal effect may be minimized by the use of a large excess of third body gas and by utilizing a small initial degree of dissociation. The method of Bunker and Davidson[12] was used to calculate the expected thermal effect for helium under identical conditions as considered under "The Kinetic Effect." This gave a maximum error of − 6% in the rate constant. All other conditions and gases used gave much smaller negative errors. The kinetic and thermal effect cause errors in the opposite directions and tend to partially cancel.

Treatment of Data.—A typical recombination trace photograph starts with a base line which is y_0 above d.c. zero. This base line ends immediately after the thyratons are triggered and the flash causes a spike due to scattered light entering the photomultiplier. Starting at time t_0, the actual recombination trace is observed. The total deflection at time t is called y_t, and the quantity, $\Delta y_t = y_0 - Fy_t$, was measured at about ten different times following t_0. Since y_0 and a were measured in volts and y_t was in grid units of the scope screen, it was necessary to determine a scale conversion factor, F. The actual position of t_0 (usually about 200 microseconds after the flash) was located where scattered light was essentially zero, as determined by evacuated gas cell flash experiments. With the gas cell evacuated, the photomultiplier d.c. output voltage was also measured and denoted as a. The iodine atom and molecule concentrations are then given by

$$[\mathrm{I}]_t = (2/\epsilon L)\log_{10}(\Delta y_t/y_0) \qquad (8)$$

$$[\mathrm{I}_2] = (1/\epsilon L)\log(a/y_0) \qquad (9)$$

where ϵ is the decadic extinction coefficient[12] and L is the cell length. The third body concentration was calculated by assuming it to be an ideal gas.

The observed rate constant, $k(\text{obsd.}) = k(\mathrm{M},T) + k(\mathrm{I}_2,T)([\mathrm{I}_2]/[\mathrm{M}])$, can now be calculated by applying equation 7. The values of $1/[\mathrm{I}]_t$ are plotted against t and yield a straight or slightly curving line, the slope of which is k(obsd.). From the intercept of this line at the time the flash occurs, the initial iodine atom concentration may be calculated and generally corresponded to about 10% dissociation. The slopes of the kinetic plots were taken near t_0 to minimize errors in slope due to measurement of small deflections.

An Electrodata 205 digital computer was used to reduce the experimental data to kinetic information. A weighted least squares straight line was calculated for $1/[\mathrm{I}]_t$ *vs.* t and the results were used to calculate k(obsd.), $[\mathrm{I}_2]_0/[\mathrm{M}]$ and their probable errors. $[\mathrm{I}_2]_0$ is the iodine molecule concentration corrected for the degree of dissociation at t_0. For each gas sample there were obtained 5 to 7 rate measurements which were averaged and then plotted against their corresponding $[\mathrm{I}_2]_0/[\mathrm{M}]$. The points of this plot were fitted to a straight line by least squares and the slope, the intercept and their probable errors were found. The intercept, at $[\mathrm{I}_2]_0/[\mathrm{M}] = 0$, is then $k(\mathrm{M},T)$ and the slope is $k(\mathrm{I}_2,T)$. The calculated $k(\mathrm{I}_2,T)$ should be the same for all third body gases at a given temperature, although it is subject to considerable experimental error, particularly at higher temperatures.

Results

All rate constants are for the rate equation, $\mathrm{d}[\mathrm{I}_2]\mathrm{d}t = k[\mathrm{I}]^2[\mathrm{M}]$ and are reported in units of mole^{-2} l.^{2} sec.$^{-1}$. A summary of our results is presented in Table I. A few comments on the special features of the different experiments and comparison with previous work with the same apparatus[12] are made here.

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[16] W. E. Henderson and W. C. Fernelius, "Inorganic Preparations," McGraw-Hill Book Co., New York, N. Y., 1935, p. 72.

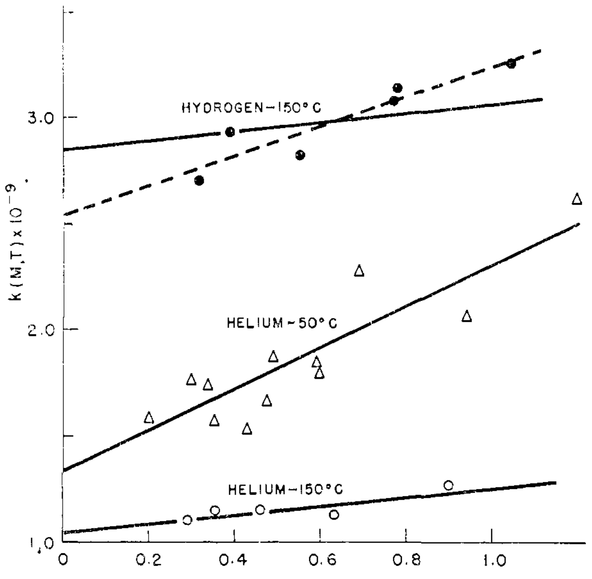

Fig. 1.—Plots of k(obsd.) *vs.* $[I_2]/[M]$ for helium and hydrogen.

Argon.—A few runs were made to check technique with the previous work on the same apparatus. The values in Table I compare well with the values of $k(Ar, 50°) = (2.99 \pm 0.13) \times 10^9$ and $k(Ar, 150°) = (1.66 \pm 0.05) \times 10^9$ obtained by Bunker and Davidson.[12]

Helium.—Plots of the average observed rate constant *vs.* $[I_2]_0/[He]$ for each run are given in Fig. 1 along with the least squares straight line. At 50° as much as half of the observed rate can be due to molecular iodine and this may account for much of the scatter in points, since the observed rate will be quite sensitive to error in iodine concentration as well as error in gas temperature. The slope of this least squares fit (Table I) compares favorably with $k(I_2, 50°) = (1.07 \pm 0.18) \times 10^{12}$ obtained by Bunker and Davidson[12] from recombination in argon. At 150° the slope compares with their value of $k(I_2, 150°) = (1.43 \pm 0.38) \times 10^{11}$. Due to the small contribution of molecular iodine to the rate at 275°, Bunker and Davidson's[12] value of $k(I_2, 275°) = 1.23 \times 10^{11}$ in argon was used to correct the observed rates.

Hydrogen.—Measurements were made on hydrogen at 150 and 275°, since good results have been obtained at 50°[12] on essentially the same apparatus. A least squares fit of the 150° runs (Fig. 1, dashed line) gave $k(H_2, 150°) = 2.54 \times 10^9$ and $k(I_2, 150°) = 7.06 \times 10^{11}$. This latter rate constant is three times greater than the corresponding rate constant obtained from helium measurements. If the observed rate constants are corrected for $k(I_2, 150°)$ from the helium measurements, the average rate constant is $k(H_2, 150°) = 2.84 \times 10^9$ (Fig. 1, solid line) which is considered a more reliable value.

It is possible but not likely that formation of hydrogen iodide may be causing some systematic errors. The rate of homogeneous thermal formation of HI can be shown to be negligible under prevailing conditions, but the contribution of heterogeneous and photochemical reactions is not known. If the photolysis flashes were producing HI, the rates would tend to increase during a series of measurements on the same gas sample, but this was not observed. A gas sample which had been heated at 275° and illuminated for 4 hr. showed no absorption at 4.33 μ (fundamental vibrational frequency of HI). The influence of hydrogen iodide cannot be completely settled from this evidence, since only 1% conversion to HI will result in about 10% change in observed rate.

Table I

Rate Constants for Iodine Atom Recombination

Gas	No. of expts.	T, °C.	$k(M,T) \times 10^{-9}$ mole^{-2} l.^{2} sec.$^{-1}$	$k(I_2,T) \times 10^{-11}$ mole^{-2} l.^{2} sec.$^{-1}$
Ar	2	50	3.15	12.0
	2	150	1.84	1.90
He	15	50	1.33 ± 0.06	9.73 ± 1.0
	5	150	1.04 ± .03	2.27 ± 0.53
	3	275	0.87 ± .10	1.23[a]
H_2	6	150	2.84 ± .10	2.27[b]
	2	275	2.03 ± .13	1.23[a]
C_6H_6	3	50	81.2 ± 4.4	10.7[a]
	3	100	57.2 ± 3.8	4.42[a]
	3	200	31.0 ± 1.3	0.96[a]
CH_3I	3	50	118 ± 5	10.7[a]
	3	100	69.7 ± 2.9	4.42[a]
	3	200	34.0 ± 2.1	0.96[a]
C_2H_5I	2	50	238 ± 23	10.7[a]
CO	2	50	5.42 ± 0.16	10.7[a]
HI	3	50	28.1 ± 1.8	10.7[a]
NO	3	50	$>4.8 \times 10^5$(?)	....

[a] Assumed values from Bunker and Davidson's argon data. [b] Assumed values from the helium data.

Only two of the hydrogen runs at 275° were considered successful. These rates were corrected for $k(I_2, 275°)$ and then averaged.

Benzene.—Recombination measurements were made in benzene at 50, 100 and 200°. Since the contribution of $k(I_2,T)$ to the observed rates is small for benzene (*ca.* 5% at 50°), the observed rates were corrected by using $k(I_2,T)$ as derived from recombination in argon.[12] The resulting values of $k(C_6H_6,T)$ were averaged and the probable errors found. Due to the thermal effect and the vapor pressure of benzene, a pressure range of 50 to 70 mm. was used. Three runs were pressurized with about 150 mm. pressure of argon to check for the presence of the thermal effect. The argon–benzene runs gave the same average rate constants as the benzene only runs, after correction was made for the contribution to the rate by the added argon.

Methyl Iodide.—Methyl iodide was used as a third body gas over the pressure range of 75 to 225 mm. and at 50, 100 and 200°. A pressurized run with 150 mm. pressure of argon did not differ significantly when corrected for the argon, thus showing the thermal effect to be small. As with benzene, the observed rates were corrected for $k(I_2,T)$.

Ethyl Iodide.—Two runs were made at 50° and the observed rates corrected for $k(I_2, 50°)$. Both runs were made with 65 mm. pressure of ethyl iodide, but one run was pressurized with about 200 mm. of argon. The average corrected rates were within 10% of each other.

Hydrogen Iodide.—Three good runs were made with hydrogen iodide at 50° and pressures of 65, 118 and 220 mm. Some uncertainty was encountered in measuring pressures since HI slowly attacks mercury and the colored mercuric iodide tends to obscure the mercury manometer level. One run was made with no mercury in the system and the pressure was determined by the known vapor pressure at solid CO_2 temperature. The observed rates were corrected for $k(I_2, 50°)$ and the resulting average rate constants had a spread of less than 10%. Hydrogen iodide will decompose during an experimental run, but at 50° the homogeneous thermal reaction is not fast enough to cause error. If extensive decomposition has occurred, there should have been a decrease in pressure during the run, but this was not observed. Since hydrogen is only one-sixth as efficient as hydrogen iodide, 1% decomposition will only change the observed rate by about the same amount.

Nitric Oxide.—To fill the gas cell with nitric oxide, the vacuum line and gas cell were filled with atmospheric pressure argon and then re-evacuated. This was followed by the same treatment with 20 mm. pressure of pure nitric oxide. Then the cell was filled with the desired pressure of nitric oxide mixture. This procedure was an attempt to eliminate any oxygen or nitrogen dioxide. Three runs were made at 50° using pressures of 442 mm. of NO, 27 mm. of NO–146 mm. of argon mixture and *ca.* 1 mm. of NO–110 mm. of argon mixture. A single run was made at 200° with 26 mm. of NO–122 mm. of argon mixture. The oscilloscope traces of the recombination for all four runs appeared to be essentially identical with the traces from scattered light with an evacuated gas cell.

There are several ways of interpreting these results, but a simple third order recombination will be assumed. The typical flash duration is about 200 microseconds, and it will be assumed that at that time, at least 19/20 of the iodine atoms have already disappeared. Using the concentrations of $[I]_0 = 2 \times 10^{-6}$ mole/l. and $[NO] = 5.0 \times 10^{-5}$ mole/l., substitution into equation 7 gives $k(NO, 50°) = 4.8 \times 10^{14}$. This large rate is a lower limit and is about 270 times larger than $k(I_2, 50°)$.

Discussion

Temperature Coefficients.—The negative temperature coefficients of the rate constants can be conveniently fitted either to an expression of the form F/T^n (which as a matter of calculational convenience, we write as $A(298/T)^n$), or of the form $B \exp(\Delta E/RT)$ (or as a variation of the latter, $B'T \exp(\Delta E/RT)$[13]). There is no good theoretical or experimental reason for preferring one representation over the other. The results of the present investigation are contained in Table II. These results in the exponential form are plotted in Fig. 2. A plot of log k *vs.* log T suggested by the representation, $k = F/T^n$, looks equally good.

Comparison with Other Results.—Russell and Simons[7] measured recombination rate constants in helium and other gases before the high efficiency of I_2 was realized. Their rate constants have been roughly corrected for $k(I_2,T)$ and will be called "corrected Russell and Simons" rates (CRS).

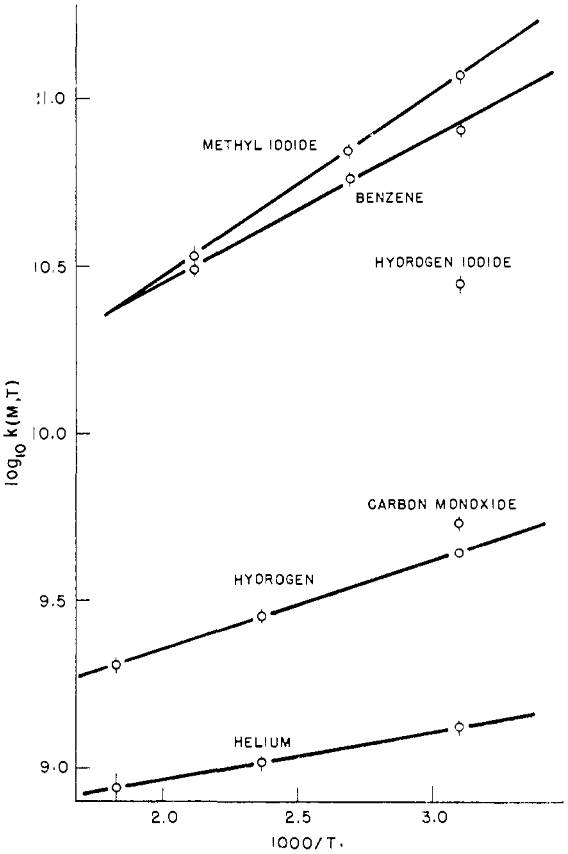

Fig. 2.—Temperature dependence of $k(M,T)$ in the form suggested by the representation, $k = B \exp(\Delta E/RT)$.

The CRS values for He are $k(20°) = 1.38 \times 10^9$, $k(127°) = 0.82 \times 10^9$; whereas we measure 1.47×10^9 and 1.08×10^9, respectively. Porter and Smith[13] gave $k(20°) = 1.5 \times 10^9$, and $k(He,T) = 4.7 \times 10^7\ T \exp(1400/RT)$, which predicts $k(127°) = 1.1 \times 10^9$. In the temperature range of interest, our equations and that of Porter and Smith gave about the same temperature coefficient, although this similarity is obscured by the different functional forms used. The shock tube value of Britton, *et al.*,[5] at 1400°K. is 1.8×10^8, whereas our equation, $k = 1.4 \times 10^9 (298/T)^{0.80}$, predicts 2.6×10^8 at 1400°K. Thus the shock tube data favor a slightly higher temperature coefficient or an increasing curvature at higher temperature.

TABLE II

TEMPERATURE COEFFICIENTS OF RECOMBINATION RATE CONSTANTS

Substance	A,[a] mole^{-2} l.^{2} sec.$^{-1}$	n[a]	B,[b] mole^{-2} l.^{2} sec.$^{-1}$	ΔE,[b] kcal.
He	1.41×10	0.80(±0.04)	4.8×10^8	0.662(±0.003)
H_2	4.93×10^9	1.48(± .07)	6.6×10^8	1.22 (± .01)
C_6H_6	1.00×10^{11}	2.53(± .07)	3.9×10^9	1.97 (± .09)
CH_3I	1.50×10^{11}	3.24(± .11)	2.3×10^9	2.55 (± .01)

[a] $k = A(298/T)^n$. [b] $k = B \exp(\Delta E/RT)$.

For C_6H_6, the CRS values are 1.04×10^{11} (20°) and 4.75×10^{10} (127°) whereas we get 8.75×10^{10} and 2.7×10^{10}. Porter and Smith gave $k(20°) = 7.9 \times 10^{10}$, and $k = 4.3 \times 10^6\ T \exp(2400/RT)$, which again gives essentially the same temperature coefficient as obtained by us.

For C_2H_5I, we have $k(50°) = 2.4 \times 10^{11}$; the CRS value at 20° is 2.5×10^{11}; Porter and Smith give $k(20°) = 2.8 \times 10^{11}$, $k = 4.3 \times 10^6\ T\ \exp(3{,}400/RT)$, so that $k(50°) = 1.7 \times 10^{11}$.

Interpretation.—There are some discrepancies in quantitative detail, but in the semi-quantitative features, the present work and that of Porter and Smith are in good agreement. They support the generalization suggested by Bunker and Davidson[12] that the magnitude of the negative temperature coefficient increases with the efficiency of the third body as a recombination catalyst at low temperatures.

There is considerable activity in the further development of ideas as to the mechanism of recombination reactions just now, and it does not appear to be profitable to comment on our results in detail.[13,17,18]

Several simple points however should be made. Bunker and Davidson[12] developed a detailed theory of the collision stabilized IM complex in thermal equilibrium, assuming a Van der Waal's interaction between I and M. In the reaction mechanism

$$I + M \rightleftarrows IM \tag{10}$$

$$IM + I \longrightarrow I_2 + M \tag{11}$$

the negative temperature coefficient is attributed to the increasing degree of dissociation of the IM complex with temperature. It has now been emphasized that, even for argon,[18] this theory predicts too low a rate constant. The van der Waals interaction of H_2 and He with an iodine atom would be very weak, and this theory is unable to account for the magnitude of the rate constant or for the negative temperature coefficient for these substances. Porter and Smith[13] have now advanced the ingenious suggestion that a charge transfer complex between an iodine atom and a third body provides a stronger interaction than the van der Waals interaction.

It is of course also conceivable that the theory of the deactivation mechanism[17,18]

$$I + I \rightleftarrows I_2^* \tag{12}$$

$$I_2^* + M \longrightarrow I_2 + M \tag{13}$$

when completely developed will turn out to explain the negative temperature coefficients for the simple third bodies such as He and H_2.

The large magnitude of the rate constants and of the negative temperature coefficients for such third bodies as methyl and ethyl iodides, benzene, mesitylene[13] and iodine strongly support the IM hypotheses for these third bodies and it is plausible that there are "charge transfer" complexes of atomic iodine with these molecules similar to the complexes of molecular iodine with them. Indeed there is now direct experimental evidence for an iodine atom benzene complex in the liquid phase.[19]

The experiments with NO indicate that this substance is a very efficient third body. The mechanism of this reaction is presumably similar to the

$$I + NO \rightleftarrows INO \tag{14}$$

$$INO + I \longrightarrow I_2 + NO \tag{15}$$

I_3 mechanism in recombination catalysis by iodine molecules.[12] It is not likely that there is a small concentration of NOI in this system before the flash, and the iodine atoms produced by the flash react rapidly according to (15), since this would result in an increase in the total I_2 concentration after the flash. It is then probable that a small amount of NOI is formed rapidly after the flash according to reaction 14 and disappears by reaction with the excess of free iodine atoms. The lower limit on k(NO, 50°) quoted in Table I indicates that the equilibrium constant for reaction 14 is greater than 10^4 l. mole^{-1}.

Acknowledgment.—One of us (RE) is indebted to the Shell Oil Company for a fellowship.

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