# The Recombination of Iodine Atoms Generated by a C. W. Argon Ion Laser

Naohiko HARADA, Yuji MORI, and Ikuzo TANAKA

*Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo*

(Received September 8, 1970)

The rate constants of iodine-atom recombination in various foreign gases were determined by measuring the relative concentrations of iodine atoms in the photostationary state, through irradiation by a c.w. argon-ion laser at 4880 Å. The relative concentration has been obtained from the absorption intensity for the emission line from an iodine discharge lamp at 1830 Å. The rate constants have been given for the diffusion of iodine atoms and for the second-order recombination of iodine atoms. The values of the diffusion rate constants in various foreign gases have been compared with the calculated values. The logarithmic second-order rate constants in various gases were plotted against their ionization potentials. The plot yielded a straight line, indicating that the formation of the charge-transfer complex between iodine atoms and foreign gas molecules is important in the recombination process, as has been suggested by Porter *et al.*

The gas-phase iodine-atom recombination reaction in the presence of third-body gases has already been studied by several methods. Some of the earliest measurements have been made by Rabinowitch and Wood,[1)] using the photostationary state method, by measuring the change in the absorbance of molecular iodine.

The flash-photolysis technique has been applied to iodine-atom recombination by numerous investigators.[2–12)] Christie, Harrison, Norrish, and Potter,[3)] measuring the decrease of iodine molecules, have pointed out that there is a rapid termolecular reaction, $I+I+I_2 \rightarrow I_2+I_2$.

Porter and Smith[10)] have found that the second-order recombination rate constant for iodine atoms shows a negative activation energy which decreases as the chaperon efficiency increases. This was explained by the existence of intermediate complexes, as has been suggested by Rabinowitch and Wood,[1)] where the complexes resulted not from normal van der Waals-type interactions but from charge-transfer interactions between the third body (M) and the iodine atom.[9,10,13)]

$$I + M \rightleftarrows IM$$

$$IM + I \rightarrow I_2 + M.$$

Strong *et al.*[6)] have observed the same rate of recombination at different wavelengths for photolytic initiation; they have concluded that excited atoms ($^2P_{1/2}$) either recombine at the same rate as ground-state atoms or are deactivated to the ground state ($^2P_{3/2}$) before measurements are made.

The present study has been planned in order to investigate the recombination reaction of iodine atoms, a reaction initiated by the intense light from a c.w. argon-ion laser at 4880 Å. This method enables us to detect the iodine atoms directly by absorption.

In this study the recombination rate was measured by monitoring the concentration of the atomic iodine in the ground state, which absorbs the resonance lines of iodine atoms, not by monitoring the concentration of iodine molecules. Under our experimental conditions, the measurements by the former will be more accurate than those by the latter, because only a very small proportion of iodine molecules decreases upon irradiation.

## Experimental

1. *C. W. Argon-ion Laser.* An argon-ion laser has been constructed in our laboratory. The maximum output power with a single line at 4880 Å was 810 mW at the discharge current of 28 Å and with a magnetic field of about 600 gauss. The output power from the laser was controlled by changing the discharge current.

2. *Reaction Cell and the Optical System for the Detection of Iodine Atoms.* Figure 1 is a schematic diagram of the optical system used in the present measurements. The monochromatic light beam at 4880 Å from the argon-ion laser entered the quartz reaction cell and induced the photodissociation of iodine molecules into atoms. In order to increase the dissociation rate, a concave mirror with a focal length of 80.2 cm was put behind the cell to reflect the laser beam into the cell. The reaction cell had four windows and a small tube at the bottom. The small tube contained a small amount of iodine crystals and was immersed in a water bath at 22°C (iodine vapor pressure was 0.25 Torr at 22°C).

The 1830 Å light beam from an iodine discharge lamp entered the reaction cell, crossed the laser beam at a right angle, and fell on the incident slit of a monochromator after passing through the cell. The iodine lamp, which was powered by microwave. was made of a quartz tube 20 mm in outer-diameter, and had a side arm immersed in a water-ice bath in order to maintain a constant iodine vapor pressure and to give narrow, unreversed lines. The carrier gas of the lamp was 2 Torr He. The monochromator with a 1440 lines/mm grating was set at 1830 Å with a slit width of 0.5

---

1) E. Rabinowitch and W. C. Wood, *J. Chem. Phys.*, **4**, 497 (1936).

2) M. I. Christie, R. G. W. Norrish, and G. Porter, *Proc. Roy. Soc., Ser. A*, **216**, 152 (1953).

3) M. I. Christie, A. J. Harrison, R. G. W. Norrish, and G. Porter, *ibid., Ser. A*, **231**, 446 (1955).

4) R. Marshall and N. Davidson, *J. Chem. Phys.*, **21**, 659 (1953).

5) K. E. Russell and J. Simons, *Proc. Roy. Soc., Ser., A*, **217**, 271 (1953).

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

7) D. L. Bunker and N. Davidson, *J. Amer. Chem. Soc.*, **80**, 5085, 5090 (1958).

8) R. Engelman, Jr., and N. Davidson, *ibid.*, **82**, 4770 (1960).

9) S. J. Rand and R. L. Strong, *ibid.*, **82**, 5 (1960).

10) G. Porter and J. A. Smith, *Proc. Roy. Soc. Ser. A*, **261**, 28 (1961).

11) T. A. Gover and G. Porter, *ibid., Ser. A*, **262**, 476 (1961).

12) G. Porter, Z. G. Szabo and M. G. Townsend, *ibid., Ser. A*, **270**, 493 (1962).

13) G. Porter, *Discuss. Faraday Soc.*, **33**, 198 (1962).

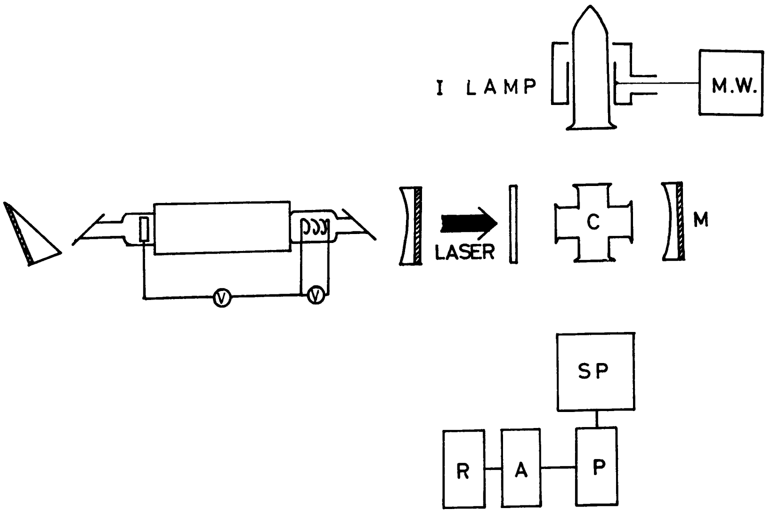


Fig. 1. Schematic diagram of apparatus.

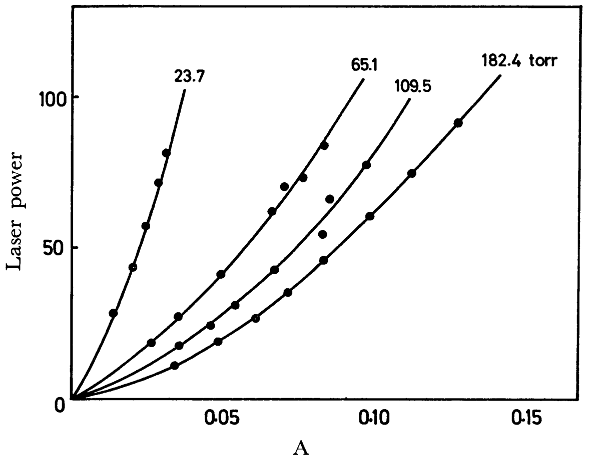


Fig. 2. Plots of the laser output power ($P_0$) to absorbance of iodine atoms ($A$) at various pressure of argon.

mm. The intensity of the exit beam from the monochromator was measured and recorded on a chart paper with a conventional photomultiplier-D.C. amplifier-recorder combination. Since the atmospheric oxygen absorbs the light below 1900 Å, nitrogen streamed between the iodine lamp and the cell, in the monochromator and also in the photomultiplier casing.

3. *Materials.* Commercially-available reagent-grade iodine crystals were used after purification by sublimation three times. The foreign gases used in the present study, He, Ne, Ar, Xe, $H_2$, $N_2$, NO, CO, $CO_2$, and $C_3H_8$, were supplied by the Takachiho Chemical Industry Co. and were used without further purification.

4. *Procedure.* The iodine atoms in the cell were detected by measuring the absorbance for a resonance line of iodine atoms. At first, upon closing the shutter for the laser light, the intensity of the analyzing light at 1830 Å, $I_0$, was measured. Then, the shutter was opened and the intensity, $I$, was measured again. The absorbance at 1830 Å, $\log I_0/I$, gives the relative concentration of iodine atoms.

The absorbance by molecular iodine of the laser light was independent of the laser output power and of the pressure of foreign gases, and it remained constant during the reaction, within the limits of experimental error. Thus, it can be said that the production rate of iodine atoms is proportional to the laser output power and that iodine molecules decompose to only a small extent.

The effect of the light absorption at 1830 Å due to molecular iodine on the determination of the iodine-atom concentration can be ignored because of the weak absorption of molecular iodine. Much care was taken in adjusting the optical system so that the analyzing light beam crossed the laser light beam exactly.

## Results

Figures 2, 3, and 4 illustrate the results obtained in argon as a foreign gas. Figure 2 shows that the laser output power increases with an increase in the absorbance of iodine atoms at 1830 Å, and the slope

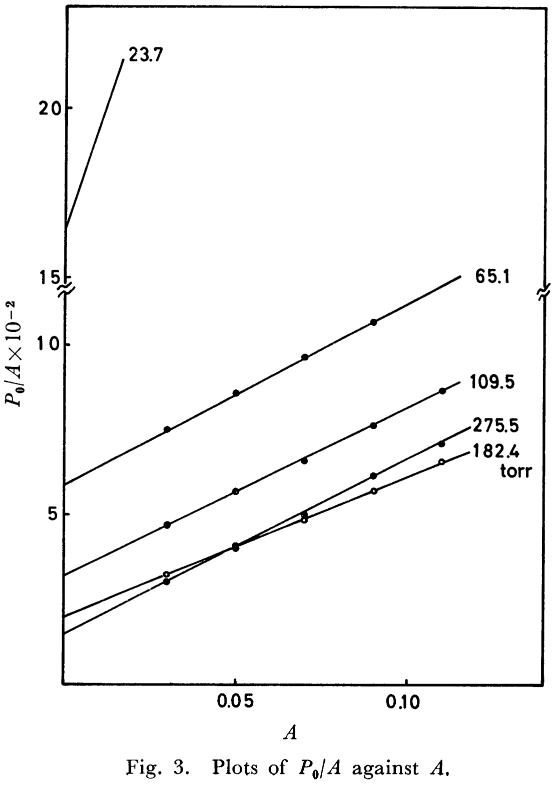


Fig. 3. Plots of $P_0/A$ against $A$.

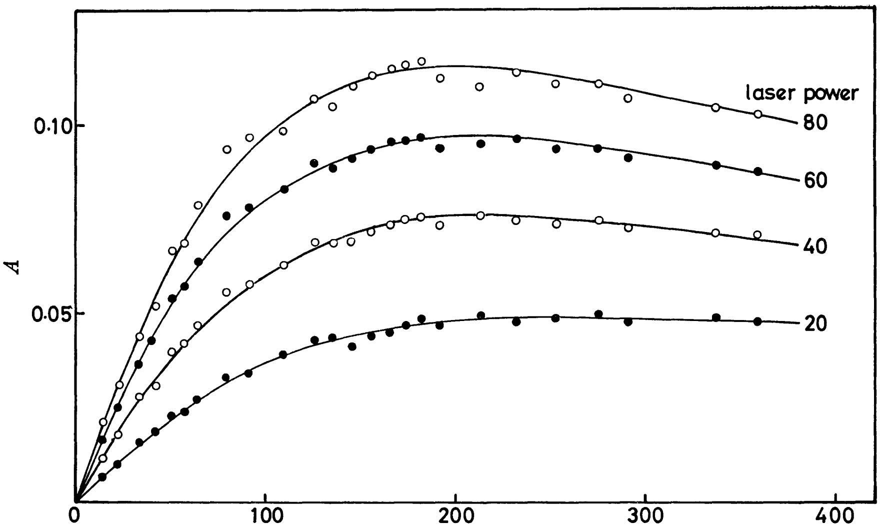


Fig. 4. Variation of absorbance of iodine atoms with the change in argon pressure.

gradually becomes steeper at high absorbances. This is clearly shown in Fig. 3, where the ratio of the laser-output power ($P_0$) to the absorbance at 1830 Å ($A$; relative concentration of iodine atoms) increases linearly with the absorbance. This indicates that the participation of the second-order iodine atom recombination becomes important at high concentrations of iodine atoms. The pressure effect of a foreign gas on the iodine-atom recombination is demonstrated in Fig. 4, where the absorbance at 1830 Å may be seen to increase at low foreign-gas pressures, while at high pressures it decreases with an increase in the foreign-gas pressure after it reaches a maximum. This can be interpreted in terms of the decreasing rate of the diffusion of iodine atoms to the wall at low pressures and by the increasing rate of iodine-atom recombination in the gas phase because of the increased second-order rate constant at high pressures of foreign gases.

The absorption of the laser light at 4880 Å by iodine molecules induces the decomposition of iodine molecules into atoms, a half of the atoms in the ground state ($^2P_{3/2}$) and the rest in the excited state ($^2P_{1/2}$):

$$I_2 + h\nu(4880\,\text{Å}) \xrightarrow{I_a} I(^2P_{3/2}) + I^*(^2P_{1/2}) \qquad (1)$$

The excited iodine atoms are, however, subjected to fast quenching collisions with molecules before recombination[14,15]:

$$I^*(^2P_{1/2}) + M \longrightarrow I(^2P_{3/2}) + M \qquad (2)$$

and have little effect on the recombination reaction.[4]

The mechanisms of the iodine-atom recombination in the gas-phase are believed to involve the following reactions:

1) recombination to form iodine molecules after the diffusion of iodine atoms to the wall of the reaction vessel:

$$I + \text{wall} \xrightarrow[k_3]{\text{(diffusion)}} 1/2\ I_2 + \text{wall} \qquad (3)$$

2) recombination of iodine atoms through collisions with foreign-gas molecules:[1]

$$I + I + M \xrightarrow[k_4]{} I_2 + M \qquad (4)$$

3) recombination of iodine atoms through collisions with iodine molecules:[3]

$$I + I + I_2 \xrightarrow[k_5]{} 2I_2 \qquad (5)$$

Reaction (3) plays an important role in the recombination of iodine atoms at low foreign-gas pressures, while, at higher pressures, reaction (4) predominates over reaction (3). Reaction (5) can not be ignored in spite of the very low concentration of iodine molecules, for the rate constant of reaction (5) has a much larger value than that of reaction (4).[13]

A photostationary-state treatment leads to the next equation for the mechanism of the iodine-atom recombination:

$$\frac{d[I]}{dt} = 2I_a - k_3[I] - (k_4[M] + k_5[I_2])[I]^2 \qquad (6)$$
$$= 0$$

where [I] is the concentration of iodine atoms, which is proportional to the absorbance of iodine atoms at 1830 Å, [M], the concentration of foreign-gas molecules, and [$I_2$], that of iodine molecules. Since $I_a$ is proportional to the laser output power ($P_0$), the next equation can be obtained from Eq. (6):

$$\alpha P_0 = k_3[I] + (k_4[M] + k_5[I_2])[I]^2 \qquad (7)$$

and:

$$\frac{\alpha P_0}{[I]} = k_3 + (k_4[M] + k_5[I_2])[I] \qquad (8)$$

where $\alpha$ is a constant. This equation can explain the linear relationship between $P_0/A$ and $A$ in Fig. 3, because $A$ gives the relative concentration of iodine atoms. The intercept in the figure gives the relative value of $k_3$ for a pressure of a foreign gas, and the slope of the linear plot gives the relative value of $k_4[M]+k_5[I_2]$. Since $k_3$ is inversely proportional to the pressure of a foreign

---

[14] R. J. Donovan and D. Husain, *Nature*, **206**, 171 (1965).
[15] R. J. Donovan and D. Husain, *Trans. Faraday Soc.*, **62**, 11 (1966).

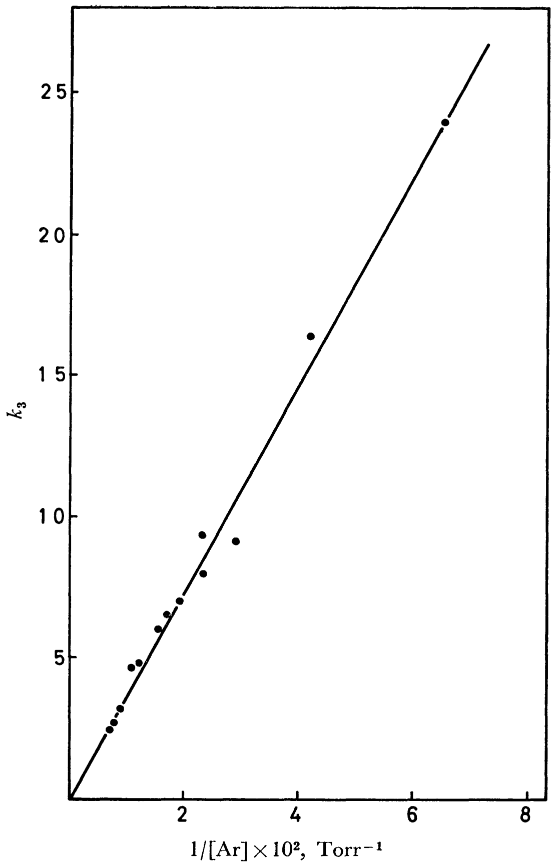


Fig. 5. Plots of $k_3$ against 1/[Ar].

gas, as is shown in Fig. 5, the relative value of the diffusion-rate constant, $\beta$, can be obtained by using the relation:

$$k_3 = \frac{\beta}{[\mathrm{M}]} \tag{8'}$$

The plots of the values of $k_4[\mathrm{M}]+k_5[\mathrm{I}_2]$ for various foreign-gas pressures give the straight line in Fig. 6. From the intercept in the figure, the relative value of the rate constant, $k_5$, can be obtained, while from the slope of the linear plots, the relative value of $k_4$ can be obtained. The relative values of $\beta$ for various foreign gases are listed in Table 1, and those of $k_4$ and that of $k_5$ are listed in Table 2.

TABLE 1. RELATIVE VALUE OF THE DIFFUSION RATE CONSTANT OF IODINE ATOMS IN VARIOUS GASES

| Gas | $\beta$ | $D'$(calculated) |
|---|---|---|
| He | 5.1 | 4.0 |
| Ne | 1.7 | 1.7 |
| Ar | 1 | 1 |
| Xe | 0.81 | 0.52 |
| $H_2$ | 5.1 | 4.8 |
| $N_2$ | 1.2 | 1.2 |
| CO | 0.95 | 1.1 |
| $CO_2$ | 0.95 | 0.92 |
| $C_3H_8$ | 0.80 | 0.60 |

TABLE 2. RELATIVE VALUE OF $k_4$ IN VARIOUS FOREIGN GASES

| Gas | This work | Other work |
|---|---|---|
| He | 0.5 | 0.4[a] |
| Ne | 0.4 | 0.5[a] |
| Ar | 1 | 1 |
| Kr | | 1.3[a] |
| Xe | | 1.6[a] |
| $H_2$ | 0.8 | 1.9[b] |
| $N_2$ | 0.4 | |
| CO | 3.8 | |
| $CO_2$ | 6.8 | 4.5[b] |
| $C_3H_8$ | 27 | |
| $n$-$C_4H_{10}$ | | 12[b] |
| $I_2$ | $4\times10^2$ | 260[a], 530[b] |

a) M. I. Christie *et al.*[3]
b) G. Porter.[13]

## Discussion

*Diffusion-rate Constant.* Helium and hydrogen offer the least resistance to the diffusion of iodine atoms, as is shown in Table 1. Xenon shows the slowest diffusion among rare gases. The rates in carbon dioxide and in propane had to be less accurately measured because of the fast rates of the recombination of iodine atoms in these gases. Since there have been no available data of the diffusion coefficient of iodine atoms in various gases, we have calculated the diffusion-rate constant, which can be compared with $\beta$.

The diffusion coefficient of iodine atoms in a gas is given by the next equation, based on a simple gas kinetic theory:

$$D = \frac{3}{16}\,\frac{1}{p\sigma_{12}^2}\,kT\left(\frac{1}{m_1}+\frac{1}{m_2}\right) \tag{9}$$

where $p$ is the total pressure of the system, $\sigma_{12}$ is the collision diameter between the iodine atom and the molecule, and $m_1$ and $m_2$ are the masses of the iodine atom and the foreign gas molecule respectively. Since this equation involves pressure, we define the diffusion-rate constant by the next expression:

$$D' = \frac{3}{16}\,\frac{1}{\sigma_{12}^2}\,kT\left(\frac{1}{m_1}+\frac{1}{m_2}\right) \tag{10}$$

where the total pressure, $p$, has been approximated by the pressure of a foreign gas. In the calculation, the value of the collision diameter, $\sigma_{12}$, has been obtained as a sum of the radius of iodine atoms and the kinetic collision radius of the molecule. The calculated values of $D'$ for various foreign gases are shown in the right column of Table 1.

The relative values of the diffusion-rate constant observed in various foreign gases are plotted against the relative values of $D'$ in Fig. 7. The relation between $\beta$ and $D'$ is approximately linear; this indicates that the diffusion of iodine atoms can be understood by the usual gas kinetic theory.

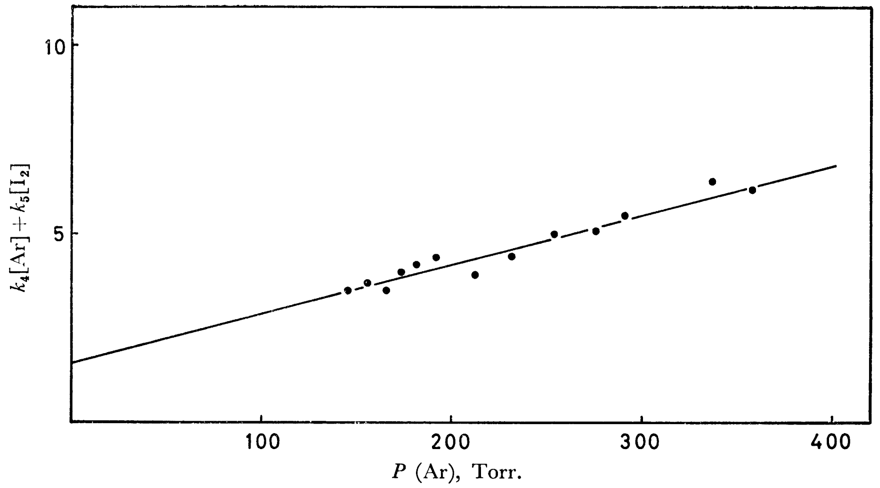


Fig. 6. Plots of $k_4[Ar]+k_5[I_2]$ against [Ar].

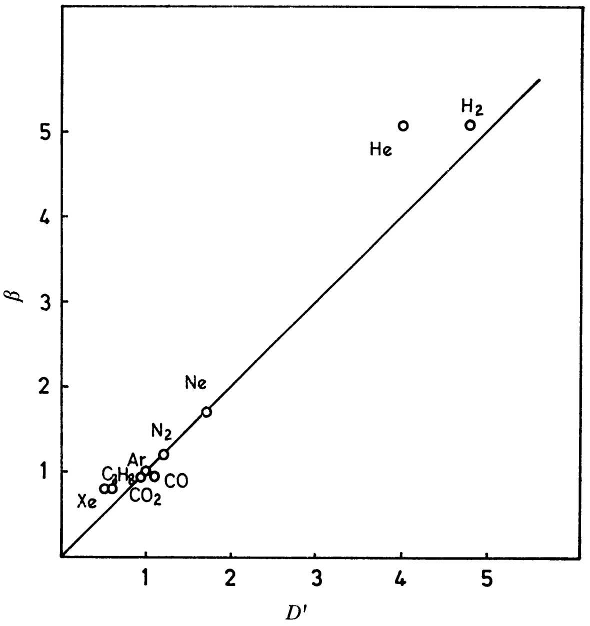
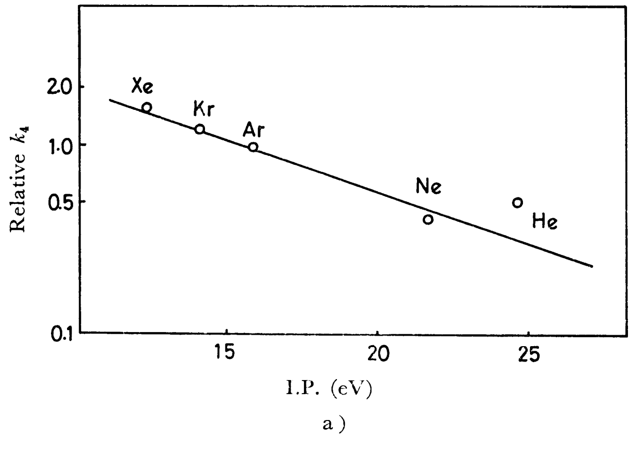
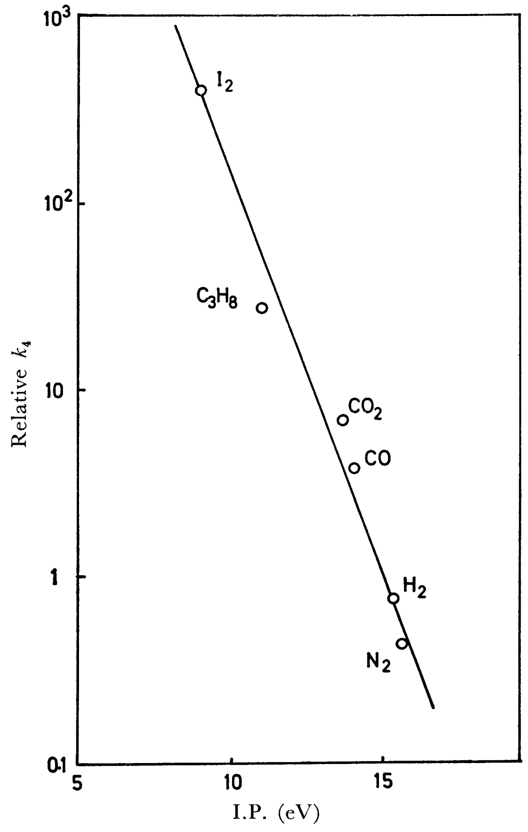


Fig. 7. Relation between β and D'.

*Recombination-rate Constant.* The obtained rate constants, though relative, are found to be qualitatively in good agreement with those obtained by other methods[3,13] (Table 2). The efficiency in the recombination process as a third body is smaller in the case of mono-atomic gases (He, Ne, and Ar) and is larger in the case of polyatomic gases, because the additional degrees of the freedom of internal motion make the energy transfer from the atom to the molecule easier.



a)



b)

Fig. 8a, 8b. Relative values of $k_4$ for various foreign gases as a function of ionization potential of foreign gases.
a) for mono-atomic gases
b) for molecules.

The exceptionally high rate constant in the case of iodine molecules as the third body, which can not be explained by the van der Waals interaction, may imply the formation, and the considerable stability, of the $I_3$ molecule.[3] The complex mechanism may also be applied to the iodine atom decay in propane.

Callear and Wilson[16,17] have suggested the existence of $I...C_3H_8$ as an intermediate complex in the recombination reaction of iodine atoms.

Porter and Smith[10,13] have suggested that a charge-transfer complex is responsible as an intermediate complex and that the recombination rates increase with decrease in the ionization potential of the third-body gas which acts as a donor. We have plotted the logarithmic relative recombination rate constants against the ionization potentials of added gases in Figs. 8a and 8b, where the values for krypton and xenon are those of Cristie *et al.*[3] The plots yield two straight lines, with different slopes, one for rare gases and another for polyatomic gases. The difference in the slope between mono- and poly-atomic gases is due to the stability of IM in the following elementary reactions.

$$I + M \rightarrow IM \tag{11}$$

$$IM + I \rightarrow I_2 + M \tag{12}$$

The intermediate complex, IM, is more stable for the polyatomic gases than for the monoatomic, because, in the case of polyatomic gases, the excess energy in the complexes will be distributed over the increased internal degrees of freedom.

*Detection of* $I^*(^2P_{1/2})$. Attempts to detect iodine atoms in the excited state have met with failure, even in a rare gas, because of the low concentration due to the short life of $I^*(^2P_{1/2})$. The rare gases are inefficient quenchers of excited iodine atoms, but iodine molecules are efficient quenchers of excited iodine atoms. The concentration of iodine molecules in the system is sufficient to quench $I^*(^2P_{1/2})$ in a short time. The life time of excited iodine atoms is estimated to be of the order of $10^{-3}$ sec, using the value of the quenching rate for $I^*(^2P_{1/2})$ by $I_2$, $k_q=3.0\times10^9\ l\ \text{mol}^{-1}\text{sec}^{-1}$.[14] Since the stationary concentration of excited iodine atoms is estimated to be of the order of $10^{14}$ atoms/cm$^3$, the excited iodine atoms can probably be detected with the present apparatus with an improved sensitivity.

We would like to thank Mr. Y. Izumisawa for his assistance with the measurements.

---

16) A. B. Callear and J. F. Wilson, *Trans. Faraday Soc.*, **63**, 1357 (1967).

17) A. B. Callear and J. F. Wilson, *ibid.*, **63**, 1983 (1967).