January, 1979] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (1), 15—20 (1979)

# Chemiionization of Excited Mercury Atom with 253.7 nm Irradiation in the Presence of $N_2$ and $CH_4$

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(Received April 1, 1978)

Chemiionization of excited mercury atom with 253.7 nm irradiation was studied. Results on the system Hg–$N_2$ previously reported were further confirmed. It was found that $CH_4$ can also induce chemiionization of Hg atoms with 253.7 nm irradiation. The dependence of ionization current on $CH_4$ pressure and light intensity was investigated, the ionization current being found to be proportional to the square of light intensity and to increase with increase in $CH_4$ pressure up to 30 Torr, reaching a constant value. $N_2$ and $CH_4$ are considered to show a similar behavior in ionization current against pressure and light intensity, and other substances such as $H_2$, He, CO, NO, Ar, $C_2H_4$, and 1-butene to give no appreciable ionization current. Thus the mechanism in which chemiionization proceeds through the collision of $Hg(^3P_1)$ with $Hg(^3P_0)$ is further confirmed.

Ionization of mercury atoms excited with 253.7 nm irradiation was first reported by Steubing in 1909,[1)] the history of studies in this field being surveyed in detail by Fontijn.[2)] An extensive study on this reaction was carried out by Berberet and Clark,[3)] the following mechanism being proposed:

$$Hg(^3P_1) + N_2 \longrightarrow Hg(^3P_0) + N_2,$$

$$Hg(^3P_1) + Hg(^3P_0) + N_2 \longrightarrow Hg_2^* + N_2,$$

$$Hg_2^* \longrightarrow Hg_2^+ + e^-.$$

In the present study we attempted to further clarify the mechanism of the chemiionization.

## Experimental

*Apparatus and Procedure.* Vacuum line and gas handling system are conventional ones. For irradiation of 253.7 nm light a commercial germicidal lamp (Toshiba 10 W) was used. The reaction cell and optical arrangement are schematically shown in Fig. 1. A fused quartz reaction cell was furnished with three windows of 20 mm$\phi$, two Pt plane electrodes (5×10 mm) for ion collection being placed inside parallel to each other 10 mm apart. Exciting light was focussed with a fused quartz condensor lens through a 5 mm$\phi$ hole defined by Al foil in front of the reaction cell to prevent exposure of the electrodes from 253.7 nm radiation. Photoionization in the Hg–$N_2$ system is due to neither ejection of photoelectrons by direct irradiation nor impact of metastable mercury atoms ($Hg(^3P_0)$) on the electrode surface, provided Pt electrodes are used.[2)] We have also confirmed that no appreciable ionization current thought to be caused by direct irradiation of the electrode surface was detected in the absence of $N_2$.

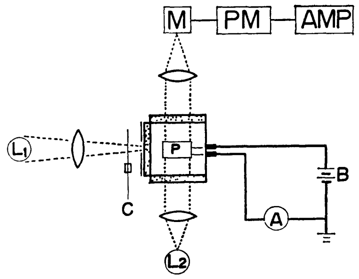

Fig. 1. Schematic view of photoionization cell.
$L_1$: Lamp for excitation, $L_2$: lamp for absorption photometry, B: battery, C: chopper, P: platinum electrode, M: monochromator, PM: photomultiplier, A: amplifier for ion current measurement, AMP: lock-in amplifier. For the ion current measurement, chopper is removed.

Ion current was measured either by a vibrating reed electrometer (Yanagimoto GCF 101) or a micro-voltmeter (Okura Denki AM 1001) as a voltage across 4.7 kΩ external resistor, no difference being observed in the values of ionization current measured by the two methods. For determination of concentration of $Hg(^3P_0)$, absorption photometry was carried out at 404.7 nm by modulation technique. The exciting light from a low pressure mercury lamp operated by DC power was chopped with a sector at 8 Hz. The light for absorption photometry was obtained from a lamp of the same type as that used for excitation. Two Vycor lenses, focal length 10 cm, were used, one to make the incident light flux parallel through the reaction cell and the other to focus the light at the position of a slit of monochromator (Fig. 1). The light at 404.7 nm was isolated from the transmitted light by a monochromator (Ritsu MC 10, grating: 600 grooves per mm). Its intensity was determined with a photomultiplier (RCA 1P 21) and a lock-in amplifier (PAR Model 186) using the chopped exciting light as time reference. Since the effective lifetime of $Hg(^3P_0)$ is in the order of ms under the present experimental condition, it can be assumed no phase delay takes place between the exciting light of 8 Hz and the transmitted light at 404.7 nm for photometry. The light for absorption photometry contains 253.7 nm DC component, but we can assume that it does not affect the modulation photometry.

*Materials.* Two kinds of $N_2$ (stated purity 99.999% from a glass bottle; stated purity 99.9% from a cylinder) were used. The latter was used after passing through a molecular sieve column cooled at liquid nitrogen temperature. Neither of these $N_2$ shows appreciable difference in ionization current in the experiments under comparable conditions. Other gasses ($CH_4$, Ar, $H_2$, He, CO, NO, $C_2H_4$, and 1-butene) were used from commercial glass bottles without further purification.

## Results and Discussion

### 1. *Collection Efficiency of Ionization Current.*

The relationship between photoionization current and ion collecting voltage has been studied by many workers, its main feature being summarized by von Engel.[4)] At an insufficient voltage the recombination process of the ion pair formed competes with the ion collecting process at electrodes, resulting in incomplete ion collection. With increase in voltage, the collecting efficiency of ions increases, approaching a saturated plateau value. In the plateau region, all the ions formed in the effective electric field can be collected without appreciable recombination, and the total rate of ion formation under the present experimental setup, $R_{\mathrm{exp}}$ (in number of ions per s) is expressed by the simple formula

$$R_{\mathrm{exp}} = i/e,$$

where $i$ is the total ion current in A measured at the saturated voltage, and $e$ is elementary charge in C.

We measured the ionization current, DC voltage being varied from 10 to 150 V, keeping the pressure of $N_2$ constant (3.2 and 23 Torr). Saturation of current is established when 80—120 V is applied, and a higher voltage is required for a higher $N_2$ pressure. Under the present experimental conditions, the multiplication effect of electrons can be neglected, since the first Townsend coefficient is extremely small (approximately $7\times10^{-8}$ at $N_2$ pressure of 1 Torr and applied voltage 100 V).[4]

*2. Ionization Current and Concentration of Hg($^3P_0$) against $N_2$ Pressure and Quantum Yield of Ionization.* Since it has been pointed out[2,3,5] that the ionization of Hg is closely related with the formation of Hg($^3P_0$), we attempted the determination of ionization current and concentration of Hg($^3P_0$) (denoted as $N_0$ hereafter) under the same experimental conditions varying the pressure of $N_2$. As Fig. 2 shows, the variations of ionization current and $N_0$ *vs.* $N_2$ pressure behave in a similar way. The $N_2$ pressure dependence of ionization current would not be expected to be completely the same as that of $N_0$ (Sec. 6). It was confirmed that the application of DC voltage across electrodes does not affect $N_0$.

Under the present conditions we can assume that all the input photons of 253.7 nm light are absorbed by mercury atoms in the reaction cell, and determine the quantum yield of ionization by actinometry. Actinometry was carried out in the system Hg–$N_2O$ (100 Torr)–$C_2H_6$(60—100 Torr), the total number of input photons per s (described as $Ia_{\mathrm{exp}}$ hereafter) being found to be $5.0\times10^{14}\,\mathrm{s}^{-1}$. The quantum yield of ionization ($\phi = R_{\mathrm{exp}}/Ia_{\mathrm{exp}}$) is thus in the range $10^{-6}$—$10^{-4}$, depending on the pressure of $N_2$.

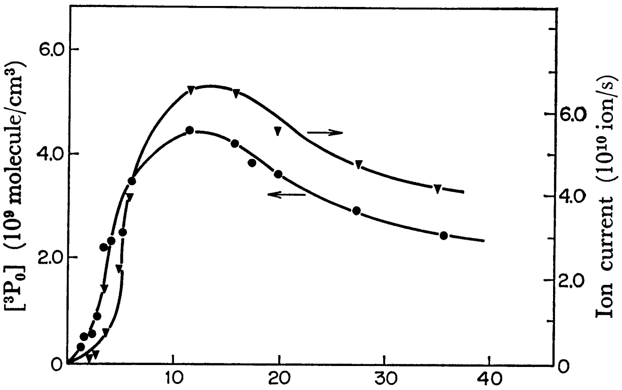

Fig. 2. Simultaneous determination of ion current and concentration of Hg($^3P_0$) *vs.* $N_2$ pressure in $N_2$–Hg system.

*3. Relationship between Ionization Current and Light Intensity in the $N_2$–Hg System and the Effect of Hg Pressure.* Ionization current was measured varying light intensity with neutral density filters of fused quartz in the range 39—100% at pressures of 1, 5, and 9 Torr of $N_2$. The ionization current was found to be proportional to the square of light intensity (Fig. 3), in line with the results reported by Houterman,[5] and Berberet and Clark.[3]

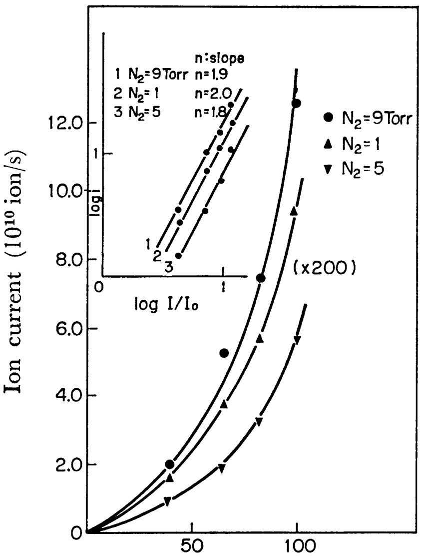

Fig. 3. Plots of ion current *vs.* light intensity in $N_2$–Hg system. Inserted figure is log-log plot for the same quantities.

Dependence of ionization current on Hg pressure was studied only semiquantitatively, since the actual pressure of Hg in the reaction cell was not measured. We measured the ionization current keeping the mercury reservoir at 0 °C (reported Hg pressure, $1.85\times10^{-4}$ Torr), room temperature 24—25 °C (Hg pressure: $1.7\times10^{-3}$ Torr at 24 °C) and $N_2$ pressure 10 Torr. The observed ionization current at 0 °C of mercury reservoir is about one third of that at room temperature. We may interpret this decrease of ionization current at 0 °C in terms of the decrease of radiation imprisonment due to the decrease of Hg pressure.

*4. Chemiionization of Excited Mercury Atom in the System $CH_4$–Hg.* In the proposed mechanism of chemiionization it has been assumed that the ionization takes place through the collision of Hg($^3P_1$) with Hg($^3P_0$). If this is valid, $CH_4$ could also induce chemiionization of mercury atom, since $CH_4$ has a relatively large rate constant to produce Hg($^3P_0$) from Hg($^3P_1$), and a small rate constant to quench Hg($^3P_1$) and Hg($^3P_0$) to ground state (Table 1).[6] Actually we find $CH_4$ gives an ionization current under 253.7 nm irradiation, the magnitude being 1/50—1/100 as compared with that for $N_2$. Dependence of ionization current on the pressure of $CH_4$ has a feature similar to that for $N_2$(Fig. 4), its dependence on light intensity being of second order. We also investigated $H_2$, CO, NO, Ar, $C_2H_4$, and 1-butene–Hg systems. However, none of them gave any appreciable ionization current in the experimentally detectable limit (less than $10^{-11}$ A) under conditions similar to the cases of $N_2$ and $CH_4$.

5. *Effect of $NiSO_4$ Solution Filter.* The problem is whether radiation other than 253.7 nm light might participate in the chemiionization in view of the finding that the ionization current is proportional to the square of light intensity. An experiment was carried out with irradiation of 253.7 nm isolated from total radiation of the low pressure mercury lamp using a $NiSO_4$ solution filter.[7] Reduction of ionization current to 33% was observed, but it is due to the absorption of light at 253.7 nm by the filter. The pressure dependence of current is similar to that without filter. We may conclude that no direct radiation other than 253.7 nm light contributes to the chemiionization.

6. *Reaction Mechanism of Chemiionization.* The fact that the ionization current is proportional to the square of light intensity is a strong support for the assumption that two excited mercury atoms(Hg($^3P_0$) and Hg($^3P_1$)) are involved. Since only $N_2$ and $CH_4$ are known to induce chemiionization, and both have relatively large cross sections to generate Hg($^3P_0$) from Hg($^3P_1$), it is certain that one atom of Hg($^3P_0$) is at least involved in the ionization. The pressure dependence of ionization current is closely related to that of $N_0$ in the case of $N_2$. Simultaneous determination of ionization current and $N_0$ *vs.* $CH_4$ pressure was not possible for the case of $CH_4$, since $N_0$ is too small. However, the general feature of pressure dependence of ionization current is similar to that for Hg–$N_2$ system (Fig. 4).

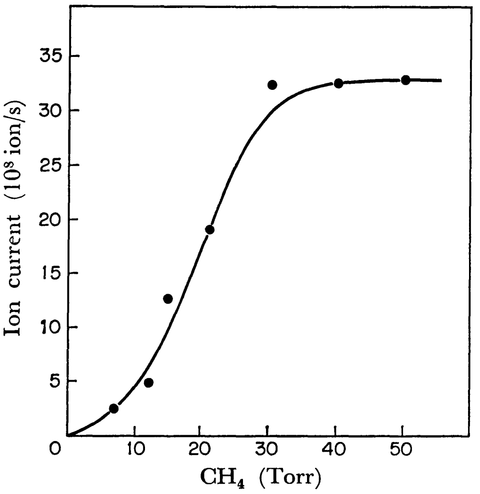

Fig. 4. Plot of ion current *vs.* $CH_4$ pressure in $CH_4$–Hg system.

The steady state concentrations of Hg($^3P_1$) and Hg($^3P_0$) are expressed in respective rate constants according to the following reaction schemes:

$$\mathrm{Hg}(^1S_0) + h\nu(253.7\,\mathrm{nm}) \xrightarrow{Ia} \mathrm{Hg}(^3P_1),$$

$$\mathrm{Hg}(^3P_1) \xrightarrow{k_f} \mathrm{Hg}(^1S_0) + h\nu_f,$$

$$\mathrm{Hg}(^3P_1) + \mathrm{M} \xrightarrow{k_1} \mathrm{Hg}(^3P_0) + \mathrm{M}, \tag{1}$$

$$\mathrm{Hg}(^3P_1) + \mathrm{M} \xrightarrow{k_2} \mathrm{Hg}(^1S_0) + \mathrm{M}, \tag{2}$$

$$\mathrm{Hg}(^3P_0) + \mathrm{M} \xrightarrow{k_3} \mathrm{Hg}(^1S_0) + \mathrm{M}, \tag{3}$$

$$\mathrm{Hg}(^3P_0) \xrightarrow[\text{(at wall)}]{k_4} \mathrm{Hg}(^1S_0), \tag{4}$$

$$\mathrm{Hg}(^3P_0) \xrightarrow[\text{(very small)}]{k_5} \mathrm{Hg}(^1S_0), \tag{5}$$

where $Ia$ is the number of photons absorbed per $cm^3$ s, $k_f$ is effective radiative decay constant of Hg($^3P_1$); $k_1$, $k_2$, $k_3$, are quenching rate constants of excited atoms by M, $k_4$ is diffusion rate to wall at unit pressure (1 Torr) and $k_5$ is the disappearing rate of Hg($^3P_0$) by quenching by impurity and/or radiative decay. We can express $N_1$ (steady state concentration of Hg($^3P_1$)) and $N_0$ by the steady state treatment as follows, neglecting the disappearance process of the excited mercury atoms by chemiionization, since the quantum yield of chemiionization is very small:

$$N_1 = Ia/(k_f + (k_1 + k_2)[\mathrm{M}]), \tag{I}$$

and

$$N_0 = N_1 k_1 [\mathrm{M}]/(k_3[\mathrm{M}] + k_4/P + k_5), \tag{II}$$

where $P$ is the total pressure in Torr.

As Berberet and Clark[3] assumed, we may assume the following two step ionization mechanism, if the chemiionization takes place through the collision between Hg($^3P_1$), Hg($^3P_0$), and M,

$$\mathrm{Hg}(^3P_1) + \mathrm{Hg}(^3P_0) + \mathrm{M} \xrightarrow{k_6} \mathrm{Hg_2}^* + \mathrm{M}, \tag{6}$$

$$\mathrm{Hg_2}^* \xrightarrow{k_7} \mathrm{Hg_2}^+ + e^-, \tag{7}$$

and the rate of ion formation, $R$(in number of ions $cm^{-3}\,s^{-1}$) is given by

$$\begin{aligned} R &= \phi Ia = k_6 N_1 N_0 [\mathrm{M}] \\ &= k_1 k_6 [\mathrm{M}]^2 Ia^2/(k_f + (k_1 + k_2)[\mathrm{M}])^2 (k_3[\mathrm{M}] + k_4/P + k_5). \end{aligned} \tag{III}$$

Berberet and Clark assumed the two step mechanism, considering the fact that the lifetime of $Hg_2^*$ is of the order of ms. The pressure dependence of $i$ is almost similar to that of $N_0$ in the system $N_2$–Hg(Fig. 2). However, Eq. III indicates that $i$ is proportional to $N_1$ and the concentration of third body as well as $N_0$. In the case $k_f \gg (k_1 + k_2)[N_2]$, $N_1$ would be independent of the concentration of $N_2$, and the behavior of $i$ may be similar to that of $N_0$.

Under the high concentration of $N_2$, $R \approx k_1 k_6 Ia^2/(k_1 + k_2)^2 (k_3[\mathrm{M}] + k_4/P + k_5)$, and we may expect a linear relationship between $1/R$ and the concentration of M.

In order to evaluate the approximate ratio of the ionization current in the presence of a certain substance M to that for $N_2$, we derive the following equation from Eq. III, assuming $k_{6,\mathrm{M}}$ is equal to $k_{6,\mathrm{N_2}}$,

$$\begin{aligned} i_{\mathrm{M}}/i_{\mathrm{N_2}} = &\left(\frac{k_{1,\mathrm{M}}[\mathrm{M}]}{k_{1,\mathrm{N_2}}[\mathrm{N_2}]}\right)^2 \left(\frac{k_f + (k_{1,\mathrm{N_2}} + k_{2,\mathrm{N_2}})[\mathrm{N_2}]}{k_f + (k_{1,\mathrm{M}} + k_{2,\mathrm{M}})[\mathrm{M}]}\right)^2 \\ &\times \left(\frac{k_{3,\mathrm{N_2}}[\mathrm{N_2}] + k_4/P + k_5}{k_{3,\mathrm{M}}[\mathrm{M}] + k_4/P + k_5}\right). \end{aligned} \tag{IV}$$

Table 1. Ratios of ionization current calculated by Eq. IV and used quenching rate constants[6] of $Hg(^3P_1)$ and $Hg(^3P_0)$ by several gases

| | Ratio of ionization current,[a] $i_M/i_{N_2}$ | Quenching rate constants (cm$^3$/molecule s) | | |
|---|---|---|---|---|
| | | $k_1(^3P_1 \rightarrow {}^3P_0)$ | $k_2(^3P_1 \rightarrow {}^1S_0)$ | $k_3(^3P_0 \rightarrow {}^1S_0)$ |
| $N_2$ | (1.0) | $3.9 \times 10^{-12}$ | $1.5 \times 10^{-13} >$ | $1.0 \times 10^{-15} >$ |
| $CH_4$ | $0.18 >$ | $1.0 \times 10^{-13}$ | $4.6 \times 10^{-13}$ | $2.7 \times 10^{-15}$ |
| $C_2H_6$ | $0.03 >$ | $3.3 \times 10^{-12}$ | $2.0 \times 10^{-12}$ | $2.6 \times 10^{-14}$ |
| $C_3H_8$ | $5.0 \times 10^{-4} >$ | $1.3 \times 10^{-11}$ | $4.2 \times 10^{-12}$ | $6.3 \times 10^{-13}$ |
| $NH_3$ | $4.5 \times 10^{-4} >$ | $2.2 \times 10^{-11}$ | $1.7 \times 10^{-11}$ | $2.4 \times 10^{-13}$ |
| $CO_2$ | $7.8 \times 10^{-5} >$ | $8.0 \times 10^{-13}$ | $1.3 \times 10^{-11}$ | $3.9 \times 10^{-13}$ |
| CO | $6.4 \times 10^{-6} >$ | $1.1 \times 10^{-10}$ | $1.5 \times 10^{-11}$ | $9.1 \times 10^{-12}$ |
| NO | $4.6 \times 10^{-8} >$ | $3.4 \times 10^{-11}$ | $1.5 \times 10^{-10}$ | $1.7 \times 10^{-10}$ |
| $H_2$ | $1.9 \times 10^{-8} >$ | $5.4 \times 10^{-12} >$ | $1.4 \times 10^{-10}$ | $1.1 \times 10^{-10}$ |
| $C_2H_4$ | $9.9 \times 10^{-9} >$ | $8.1 \times 10^{-11} >$ | $2.4 \times 10^{-10}$ | $6.5 \times 10^{-10}$ |

a) Since $k_{2,N_2}$ and $k_{3,N_2}$ are given as upper limits, all the calculated ratios should be understood as upper limits.

In calculating the ratios, we used the values of the rate constants given in Table 1, $2 \times 10^5$ s$^{-1}$ for $k_f$(calculated according to the Milne-Samson formula[8]), 26 Torr s$^{-1}$ for $k_4$ and 100 s$^{-1}$ for $k_5$. The value of $k_5$ is not definite, but it would not cause serious errors in calculating the ratios since the magnitude of $k_5$ is small as compared with that of $k_{3,M}[M]$. The calculated upper limit of the ratio, $i_{CH_4}/i_{N_2}$ is 0.18, while the experimental value of $i_{CH_4}/i_{N_2}$ at 10 Torr is 0.005, no measurable ionization current being observed for the other compounds($H_2$, He, CO, NO, $C_2H_4$, Ar, and 1-butene). From Table 1 we may expect $C_2H_6$ to induce the chemiionization current in a measurable amount.

We observed the decrease of ionization current in the system $N_2$–Hg at 0 °C as compared with that at room temperature. We have estimated the ratio of ionization current at 0 °C to that at room temperature (24 °C) using Eq. III. We assume that $[N_2]$ and the rate constants defined above except $k_f$ are almost the same at 0 °C and 24 °C, and interpret the decrease of ionization current at 0 °C in terms of the decrease of effective radiative decay lifetime($1/k_f$) of $Hg(^3P_1)$, *viz.*, the decrease of radiation imprisonment. The calculated values of $k_f$ at 0 °C and 24 °C are $2 \times 10^6$ and $2 \times 10^5$ s$^{-1}$ respectively. We obtain $N_1$ and $N_0$ at two temperatures as follows; $N_1$: $1.5 \times 10^8$ at 0 °C and $3.4 \times 10^8$ atom cm$^{-3}$ at 24 °C, and $N_0$: $4.3 \times 10^{11}$ at 0 °C and $9.5 \times 10^{11}$ atom cm$^{-3}$ at 24 °C. Using these values of $N_1$ and $N_0$ with Eq. III, we obtain the ratio of the ionization current at 0 °C to that at 24 °C to be 0.2, while its experimental value is 0.3. In this calculation, we assumed $Ia$ in Eq. III to be the number of total incident photons at 253.7 nm in the reaction cell, which was determined by actimometry carried out at room temperature.**

*7. Chemiionization of $N_2$–$CH_4$–Hg System and Estimation of the Rate Constant of Excimer Formation.* Since $N_2$ and $CH_4$ are the only substances known to induce chemiionization of Hg, we studied the behavior of ionization current in a mixture of $N_2$ and $CH_4$. Since $N_2$ has a large rate constant to produce $Hg(^3P_0)$ from $Hg(^3P_1)$ and $CH_4$ has a large rate constant to quench $Hg(^3P_0)$ (more than three times as large as that of $N_2$), we expect that $N_2$ mainly produces $Hg(^3P_0)$ and $CH_4$ quenches $Hg(^3P_0)$ in the mixture (Table 1). For the sake of confirmation we measured the ionization current in the mixture system varying the pressure of $CH_4$ keeping the $N_2$ pressure constant. The total pressure $(N_2+CH_4+Ar)$ which may affect the absorption line profile of Hg atoms and the diffusion rate of $Hg(^3P_0)$ to wall was also kept constant. Two series of experiments were carried out, (a) $N_2$, 3 Torr and total pressure, 10 Torr; (b) $N_2$, 6 Torr and total pressure, 20 Torr. If we take reciprocals of both sides of Eq. III, we may expect a Stern-Volmer type linear relation between $1/R$ and $CH_4$ pressure at constant $N_2$ and total pressures, noting $k_{1,N_2} \gg k_{1,CH_4}$ and $k_{2,CH_4}$, as follows:

$$1/R = (X/k_6 P I a^2)(k_{3,N_2}[N_2] + k_{3,CH_4}[CH_4] + k_4/P + k_5), \quad \text{(V)}$$

where

$$X = (k_f + (k_{1,N_2} + k_{2,N_2})[N_2] + (k_{1,CH_4} + k_{2,CH_4})[CH_4])^2 / (k_{1,N_2}[N_2] + k_{1,CH_4}[CH_4])^2 \sim \text{constant}.$$

Figure 5 shows that the linear relation holds. From the empirical values of either slope or intercept, we can calculate $k_6$ if we substitute the values of other rate constants for $N_2$ and $CH_4$ and of $Ia$ into Eq. V. We are aware of the accumulated large errors caused by using many rate constants ($k_f$, $k_{1,N_2}$, $k_{1,CH_4}$, $k_{2,N_2}$, $k_{2,CH_4}$, $k_{3,N_2}$, $k_{3,CH_4}$) in calculation. Our estimation of $k_6$ from slope gives the values of $9.6 \times 10^{-29}$ cm$^6$ molecules$^{-2}$ s$^{-1}$ (series (a)) and $8.3 \times 10^{-29}$ (series (b)). The rate constant of the ternary collision ($k_6$) obtained here may be compared with that of an excimer formation ($Hg_2(1_u) \xleftarrow{k_{1_u}} Hg(^3P_0) + Hg(^1S_0) + N_2$). Phaneuf *et al.*[9] gave the values of the rate constant($k_{1_u}$) reported by several workers. They are in the range $10^{-30}$—$10^{-29}$ cm$^6$ molecule$^{-2}$ s$^{-1}$, differing from that by McAlduff *et al.*[10] which was exceptionally large ($1.33 \times 10^{-27}$ cm$^6$ molecule$^{-2}$ s$^{-1}$). The value of $k_6$ obtained here is several times larger than $k_{1_u}$, but we consider it reason-

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** The authors acknowledge the referee's suggestion on the interpretation of the effect of Hg pressure on the ionization current.

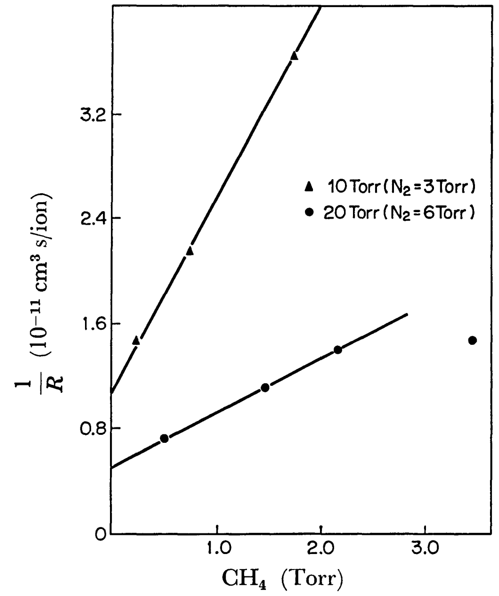

Fig. 5. Plots of reciprocals of rate of ion formation ($R$) *vs.* $CH_4$ pressure in the mixture of $N_2$, $CH_4$, and Hg for 10 Torr and 20 Torr of total pressure.

Table 2. Rate constants of ternary collision ($k_6$) in the systems $N_2$–Hg and $CH_4$–Hg ($cm^6$ $molecule^{-2}$ $s^{-1}$)

| Pressure (Torr) | 3 | 6 | 10 |
|---|---|---|---|
| $N_2$ | $3.4\times10^{-29}>$ | $2.8\times10^{-28}>$ | $4.9\times10^{-28}>$ |
| $CH_4$ | $1.8\times10^{-29}$ | $2.3\times10^{-29}$ | $4.0\times10^{-29}$ |

able.

The rate constant ($k_6$) can be also calculated by means of Eq. III instead of Eq. V using the reported rate constants and our experimental results in the system $N_2$–Hg or $CH_4$–Hg. The results, given in Table 2, increase with pressure. For the interpretation of this pressure effect and the difference of magnitudes of $k_6$ among $N_2$–Hg, $CH_4$–Hg, and $N_2$–$CH_4$–Hg systems we might speculate more complex mechanism in the ionization, but we feel better to refrain from further discussions on this matter, because many pressure terms are included in Eq. III. In the case of $N_2$, the value of $k_3$ which is considered to be the most important in the determination of $k_6$ is known only as an upper limit. Thus the values of $k_6$ in the system $N_2$–Hg should be taken as upper limits.

*8. Other Possible Mechanisms of Ionization and Energetic Consideration.* Since we have found that the ionization current is proportional to the square of light intensity, and that at least one atom of Hg($^3P_0$) is involved, the following two mechanisms might also be considered. (1) To assume the participation of one more Hg($^3P_0$) atom instead of Hg($^3P_1$). If two atoms of Hg($^3P_0$) are involved in chemiionization, the reciprocal of ionization current would be proportional to the square of pressure of $CH_4$ in the mixture experiment of $N_2$–$CH_4$. However, this is not compatible with our result (Fig. 5). In addition, the energy requirement for ionization is less favorable with the deficiency of 0.22 eV. (2) Ionization proceeds through the absorption of another 253.7 nm photon by an excimer formed by the collision between Hg($^3P_0$) and ground state Hg. The formation of such an excimer ($1_u$) has been confirmed.[9] However, it is not probable from energetic consideration (Fig. 6) that this excimer can be ionized by absorption of another 253.7 nm photon. Furthermore, the absorption of 253.7 nm photon by the excimer is less likely, since the absorption of 253.7 nm photon by ground Hg would be much stronger.

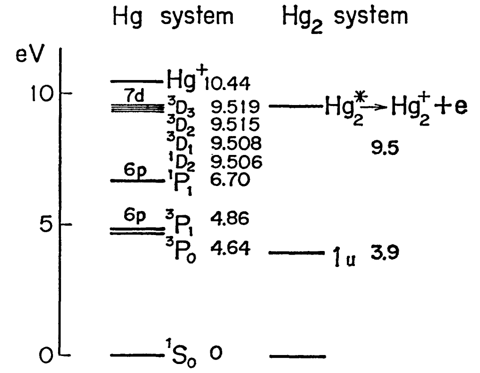

Fig. 6. Energy level diagram for Hg and $Hg_2$ systems.

Since the ionization potential of mercury atom is 10.44 eV, the sum of energy of Hg($^3P_1$) and Hg($^3P_0$) (4.86+4.64=9.50 eV) is not enough to give Hg atomic ion. It has been assumed[3] that the formation of molecular ion $Hg_2^+$ is more likely. Arnot and Milligan[11] observed mass-spectrometrically the formation of $Hg_2^+$ in the electron impact of dense mercury vapor, and determined its appearance potential to be 9.5 eV. They presumed that its formation proceeds through the collision of Hg($^1D_2$) generated by electron impact with Hg in ground state, since the energy level of Hg($^1D_2$) is 9.506 eV above ground state and is close to the appearance potential of $Hg_2^+$. In the optical excitation experiments, the formation of Hg($^1D_2$) is not possible, and the collision of Hg($^3P_1$) with Hg($^3P_0$) is an acceptable process for the formation of $Hg_2^+$ from energetic consideration. Berberet and Clark assumed the formation of an excimer $Hg_2^*$ as a precursor of $Hg_2^+$, considering the decay of ionization current after switch-off of exciting light to be very slow. They estimated the lifetime of the excimer to be of the order of ms. So far we know nothing about the electronic state of the excimer. However we presume that such an excimer is in a highly excited Rydberg state, since the energy level of the excimer should be very close to its ionization level.

From energetic consideration, we should not discard the possibility of mercury ion pair formation by the collision of Hg($^3P_1$) with Hg($^3P_0$), if electron affinity of Hg is 1.53 eV exoergic.[12] If this is acceptable, the total energy balance of ion pair formation

$$Hg(^3P_1) + Hg(^3P_0) \longrightarrow Hg^+ + Hg^-$$

would be 0.59 eV exoergic. However, Makita *et al.*[13] pointed out that the value is not based on reliable experimental measurement. They estimated it to be 0.19±0.3 eV endoergic. When we adopt this value, mercury ion pair formation by the collision of Hg($^3P_1$) with Hg($^3P_0$) is not possible.

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