BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47 (11), 2768—2774 (1974)

# Quenching of Excited Mercury Atoms($6^3P_1$ and $6^3P_0$) in Molecular Collisions

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(Received May 22, 1974)

The lifetime of Hg($6^3P_0$) in a gaseous mixture of Ar and $N_2$ with quenching molecules(Q) was measured by monitoring the decay of the Hg($6^3P_0$) concentration following the excitation of Hg by pulsed 253.7 nm radiation. The lifetime in the absence of Q was reduced with the increase in the $N_2$ pressure, being inversely proportional to the total pressure. This can be attributed to the deactivation by impurities involved in the gas and that by collision on the wall of the reaction cell. Deactivation due to impurities is dominant at a total pressure higher than 50 Torr. With quenchers in the mixture, the lifetime measurement gave the quenching cross-section of Hg($6^3P_0$). In addition, the measurement of the stationary concentration of Hg($6^3P_0$) made it possible to determine the rate for each of the processes $6^3P_1 \rightarrow 6^3P_0$ and $6^3P_1 \rightarrow 6^1S_0$. Based on the observed ratio, $\alpha = \sigma^2(6^3P_1 \rightarrow 6^1S_0)/\sigma^2(6^3P_0 \rightarrow 6^1S_0)$, quenching molecules are classified into three groups. The first group consists of $N_2O$, $O_2$, $C_2H_4$, $C_3H_6$, and $C_2H_2$ with $\alpha = 1.2$. These molecules deactivate Hg($6^3P$) to form their triplet states. The second group (CO, NO, $H_2$, $C_3H_8$, *i*-,*n*-$C_4H_{10}$, and $C(CH_3)_4$) in which $\alpha \approx 4$ makes the quenching *via* a short-lived complex (Hg–Q)*. The last group ($CH_4$ and $C_2H_6$) has a value of $\alpha$ larger than 100. This is caused by a weak interaction between potential surfaces of Hg($6^3P$)+Q and Hg($6^1S$)+Q.

In contrast to the Hg($6^3P_1$) state, transition from the Hg($6^3P_0$) to the ground state ($6^1S_0$) is weakly allowed by the spin-orbit interaction. The probability calculated by Garstang¹⁾ is $0.18\ s^{-1}$. Thus, the radiative process would be negligible in the deactivation of Hg($6^3P_0$) atoms. The lifetime in $N_2$ has been measured by means of several methods.²⁻⁵⁾ Callear and Norrish⁴⁾ suggested that the main quenching process was the collisional deactivation by ground state Hg atoms. However, a very small cross-section (0.03—0.1 Å²) for the $6^3P_1$ quenching by Hg($6^1S_0$) was estimated by Waddell and Hurst,⁶⁾ and the more recent data of Callear and McGurk⁵⁾ indicated that the deactivation was caused mostly by impurities in $N_2$ gas. The quenching cross-sections of Hg($6^3P_0$) by other species were measured by Callear and Williams,⁷⁾ who found very small cross-sections and concluded a metastable character of the Hg($6^3P_0$) state. However, they later observed a cross-section larger by an order of magnitude than the previous value with use of a new flash device.⁵⁾ Their result is consistent with our former measurements.⁸⁾

In this paper we report on the direct measurement of the lifetime of Hg($6^3P_0$) in a medium of Ar+$N_2$ mixture together with cross-sections of various molecules for quenching Hg($6^3P_0$). The method proposed in the previous paper⁹⁾ has been also applied for the measurements of the rates of the processes $6^3P_1 \rightarrow 6^3P_0$ and $6^3P_1 \rightarrow 6^1S_0$. The difference between the collisional processes of $6^3P_1 \rightarrow$ and $6^3P_0 \rightarrow 6^1S_0$ has been discussed.

## Experimental

The apparatus and procedure were the same as those described previously,⁹⁾ except for the use of pulsed 253.7 nm radiation to excite Hg atoms and to follow a time history of Hg($6^3P_0$) concentration. A schematic diagram of the apparatus is shown in Fig. 1. An exciting lamp was a germicidal lamp (Toshiba, 30 W), operated in a pulsed mode. The filament electrodes of the lamp were heated for several minutes by connecting A with B in the switch, which was then moved to the other side. At the final position of the switch, three thyratrons (2D21) made a short circuit between the two electrodes. In this way, the lamp was turned on for a short interval (10—40 ms) during which the connection of B with A changed to that with C, and was turned off in less than 40 μs. The light pulse thus obtained was monitored by a photomultiplier through an interference filter transmitting 253.7 nm radiation, and its out-put was used as a trigger pulse for an oscilloscope (Iwasaki, SS-5004). For the measurement of Hg($6^3P_0$) concentration, the 404.7 nm light beam from a low pressure mercury lamp was passed through a reaction cell, whose length and diameter were 100 and 4 cm, respectively. The light beam was fed into a grating monochromator, whose out-put was recorded on the oscilloscope.

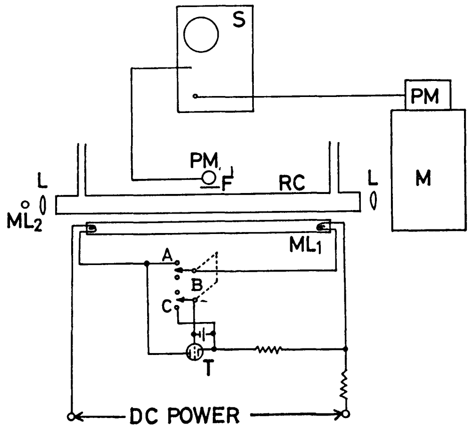

Fig. 1. Schematic diagram of the apparatus.
$ML_1$: low pressure Hg lamp for 253.7 nm radiation, $ML_2$: low pressure Hg lamp as a source of 435.8 and 404.7 nm lines, L: quartz lens, RC: reaction cell, M: monochromator, PM: photomultiplier, F: optical filter for 253.7 nm line, S: oscilloscope, T: thyratron.

Figure 2 shows a typical example of the oscilloscope record. After the exciting lamp is turned on, the intensity of the 404.7 nm line is reduced following an increase of 253.7 nm radiation due to the formation of Hg($6^3P_0$) atoms. Turning off of the lamp causes a gradual recovery of the 404.7 nm intensity. The concentration of Hg($6^3P_0$) was calculated as described previously. The decay of the Hg($6^3P_0$) concentration is exponential against time as seen from Fig. 3,

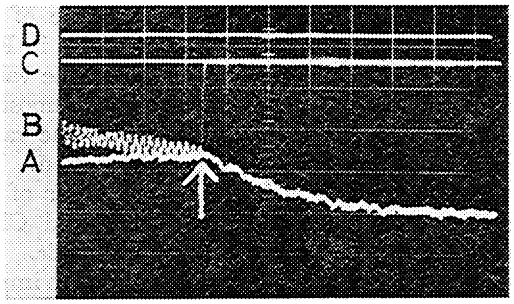

Fig. 2. Oscilloscope trace of the absorption of Hg($6^3P_0$) at 404.7 nm after the pulsed irradiation of 253.7 nm radiation into the mixture of $p(NH_3)=1.2\times10^{-2}$, $p(N_2)=0.2$, $p(Ar)=9.8$, and $p(Hg)=1.9\times10^{-4}$ Torr. A: intensity of 404.7 nm line, B: intensity of 253.7 nm radiation (the arrow shows the turning off of the lamp), C: zero for 253.7 nm intensity, D: zero for 404.7 nm intensity, sweep velocity: 5 ms/div.

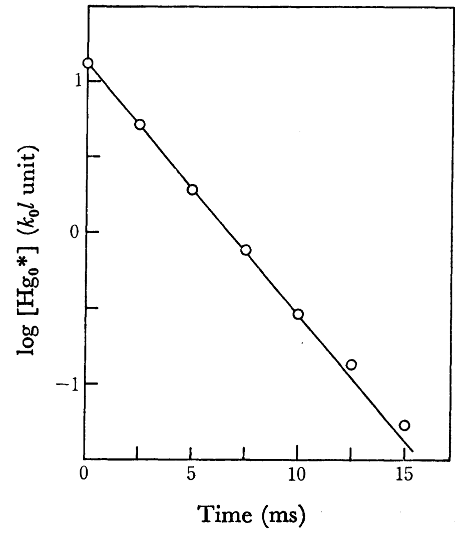

Fig. 3. Decay of the Hg($6^3P_0$) concentration obtained from the data given in Fig. 2.

and the lifetime can be defined.

Sample gases employed were commercial. Ar, CO and NO were purified in the same procedure as reported previously. In order to eliminate a trace of $O_2$, $N_2$ gas was passed through a U-shaped glass tube packed with small tips of copper at 350 °C. The nominal purity of other gases was: 99.9% for $CH_4$ and $i$-$C_4H_{10}$, 99.7% for $C_2H_6$, $C_3H_8$ and $n$-$C_4H_{10}$, 99.99% for $CO_2$, and 99.5% for $NH_3$. These gases were purified by trap-to-trap distillation in vacuum at liquid nitrogen temperature, their purity being found by gas chromatography to exceed 99.9%. The total pressure of the system was kept constant by adding Ar gas as a diluent to avoid the pressure broadening effect of spectral lines, where Ar could be assumed as a very poor quencher of excited Hg atoms.

## Results and Discussion

*Lifetime of Hg($6^3P_0$) in $N_2$ and Ar.* Hg($6^3P_0$) atoms are formed by the reactions:

$$\text{(i)}\quad Hg + h\nu\,(253.7\text{ nm}) \longrightarrow Hg_1^*,$$

$$\text{(ii)}\quad Hg_1^* \longrightarrow Hg + h\nu\,(253.7\text{ nm}),$$

$$\text{(iii)}\quad Hg_1^* + N_2 \longrightarrow Hg + N_2,$$

$$\text{(iv)}\quad Hg_1^* + N_2 \longrightarrow Hg_0^* + N_2,$$

where Hg, $Hg_1^*$ and $Hg_0^*$ represent Hg atoms of $6^1S_0$, $6^3P_1$, and $6^3P_0$ states, respectively. As reported previously, the rate for Reaction (iii) is negligibly small. Therefore, in a $N_2$-rich system, all $Hg_1^*$ atoms formed by the 253.7 nm radiation are converted into $Hg_0^*$ atoms. Possible processes for the deactivation of $Hg_0^*$ atoms in a mixture of $N_2$ and Ar are as follows;

$$\text{(v)}\quad Hg_0^* + N_2 \longrightarrow Hg + N_2,$$

$$\text{(vi)}\quad Hg_0^* + N_2 \longrightarrow Hg_1^* + N_2,$$

$$\text{(vii)}\quad Hg_0^* + M \longrightarrow Hg + M + h\nu,$$

$$\text{(viii)}\quad Hg_0^* + Hg \longrightarrow 2Hg,$$

$$\text{(ix)}\quad Hg_0^* + Hg \longrightarrow Hg_2^* \longrightarrow 2Hg + h\nu,$$

$$\text{(x)}\quad \left\{\begin{array}{l} Hg_0^* + Hg + M \longrightarrow Hg_2^* + M, \\ Hg_2^* \longrightarrow Hg_2 + h\nu\,(335.0\text{ nm}), \\ Hg_2^* + M \longrightarrow Hg_2 + h\nu\,(485.0\text{ nm}), \end{array}\right.$$

where M stands for $N_2$ or Ar. Among these processes, Reactions (viii)—(x) cannot be dominant, since the observed lifetime of $Hg_0^*$ is independent of the mercury pressure, as seen from Table 1. Callear and Norrish[4)] proposed the cross-section of 18 Å$^2$ for Reaction (viii). This results in a lifetime shorter than 0.1 ms at $p(Hg)=1.4\times10^{-3}$ Torr, and this is not the case in this experiment. Since their experiment was carried out in a system of atmospheric pressure, there might be a contribution from a termolecular process like Reaction (x). In order to check this possibility, the lifetime was observed under pressures up to 655 Torr. The lifetime is reduced with the increase in the total pressure of the system, and is independent of the mercury pressure in the range of $10^{-4}$—$10^{-3}$ Torr. The former fact is due to impurities in the sample gas, and the latter to a small contribution of a termolecular process. The poor efficiency of quenching by $Hg_0^*$–Hg collisions indicates that potential surfaces of $Hg_0^*$+Hg and Hg+Hg cross each other at a small internuclear distance where the potential energy is high.[10)] Since the radiative transition from the excited state of $Hg_2(^30_u^-)$ to the ground state is forbidden, Reaction (ix) is impossible. The only possibility is that the excited $Hg_2$ formed by a collision with a third body makes a spontaneous or a collision-induced transition, *i.e.*, Reaction

TABLE 1. LIFETIME (in ms) OF Hg ($6^3P_0$) IN THE MIXTURE OF Ar+$N_2$

| Total pressure (Torr) | $p$(Hg) (Torr) | | |
|---|---|---|---|
| | $1.7\times10^{-5}$ | $1.9\times10^{-4}$ | $1.4\times10^{-3}$ |
| 1 | 2.6$^{a)}$ | 2.8$^{d)}$ | 2.6$^{e)}$ |
| 5 | 6.6$^{b)}$ | 6.7$^{d)}$ | 7.0$^{e)}$ |
| 10 | 10.8$^{c)}$ | 10.0$^{d)}$ | 10.5$^{e)}$ |
| 50 | — | 5.0$^{f)}$ | — |
| 150 | — | 1.3$^{g)}$ | 1.4$^{g)}$ |
| 400 | — | 0.8$^{h)}$ | 0.9$^{h)}$ |
| 655 | — | 0.54$^{i)}$ | 0.57$^{i)}$ |

Partial pressure of $N_2$ (Torr): a) 1.05, b) 1.26, c) 0.52, d) 0.08, e) 0.026, f) 0.05, g) 0.22, h) 4.0, i) 10.0.

(x). However, the spontaneous radiation and the collision-induced radiation rates of $Hg_2(^3 0_u^-)$ are $20\ s^{-1}$ and $2.1\times10^{-31}$ atom$^{-2}$ cm$^6$ s$^{-1}$, respectively.[11] Thus the rate of Reaction (x) is too small to be measured in the present experiment.

Reaction (vii) for the case of $M=NH_3$ was proposed by Freeman *et al.*,[12] who found that the decay rates of $Hg_0$ concentration and of luminescence at 347.0 nm were the same. Koskikallio *et al.*[13] found a termolecular mechanism for the deactivation of $Hg_0{}^*$ by $NH_3$. This suggests a long-lived complex $Hg\text{–}NH_3{}^*$ emitting the luminescence. However, a luminescence of a similar kind has not been found in $N_2$, and this suggests that the interaction between $N_2$ and $Hg_0{}^*$ may not be strong enough to form a complex with a long lifetime.

The first experimental evidence for Reaction (vi) was reported by Samson.[14] He found a slow decay of 253.7 nm fluorescence after the pulsed irradiation of 253.7 nm light into the $N_2$–Hg mixture, and attributed the decay to Reaction (vi). More recently, Callear and McGurk[5] also observed a slow decay of fluorescence which they interpreted to be a tracer of $Hg_0{}^*$ atoms. After the flash excitation of Hg atoms, a quasi-stationary condition for $[Hg_1{}^*]$ can be assumed since the radiative lifetime of $Hg_1{}^*$ is very short as compared with the time scale of observation. Then, we get the relation

$$[Hg_1{}^*]/[Hg_0{}^*] = k_6[N_2]/(k_2+k_4[N_2]), \qquad (1)$$

where Reaction (iii) and the quenching of $Hg_1{}^*$ by impurities are disregarded. Assuming that this relation holds, the lifetime of $Hg_0{}^*$ atom can be formulated as

$$1/\tau = [k_2k_6[N_2]/(k_2+k_4[N_2])] + k_5[N_2] + k_Q[Q], \qquad (2)$$

where $k_Q[Q]$ represents the contribution of quenching molecules or impurities in a sample gas to the deactivation of $Hg_0{}^*$. If we assume a detailed balancing for Reaction (iv) and (vi), the first term in Eq. (2) can be calculated from our previous result for the rate of Reaction (iv). The result is shown in Fig. 4.

The experimental relation of the lifetime of $Hg_0{}^*$ with the partial pressure of $N_2$ is shown also in Fig. 4. The reciprocal of the lifetime, from which the value of the first term in Eq. (2) is subtracted, is almost proportional to $[N_2]$, its linear slope giving the rate 85 Torr$^{-1}$ s$^{-1}$ or $1.7\times10^{-4}$ Å$^2$ of the cross-section. However, this cross-section is larger by an order of magnitude than that observed by Berberet and Clark,[3] who used the $N_2$ gas made from sodium azide. Since $N_2$ has a very small quenching cross-section, an impurity in the gas which is less pure than the Ar gas may contribute dominantly to the quenching. If an impurity molecule has a quenching cross-section of 10 Å$^2$, the purity of $N_2$ should exceed 99.9999% in order to eliminate the impurity effect. Therefore, the value of $1.7\times10^{-4}$ Å$^2$ for the cross-section should be assumed as an upper limit.

In Fig. 4 also seen is the increase of the lifetime with the increase in the total pressure. This means that $Hg_0{}^*$ atoms are deactivated by collisions with the

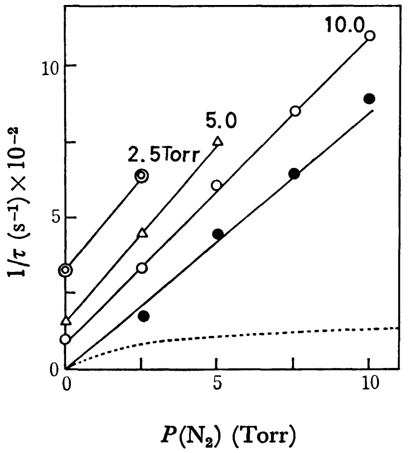

Fig. 4. The reverse of the lifetime of $Hg(6^3P_0)$ in the Ar+$N_2$ mixture against the $N_2$ pressure.
Total pressure is 10 Torr for ○, 5 for △, 2.5 for ◎ with the Hg pressure of $1.9\times10^{-4}$ Torr, and the dashed line is calculated from Eq. (2). The point ● shows the data at 10 Torr from which the calculated value (dashed line) and the one in the absence of $N_2$ are subtracted.

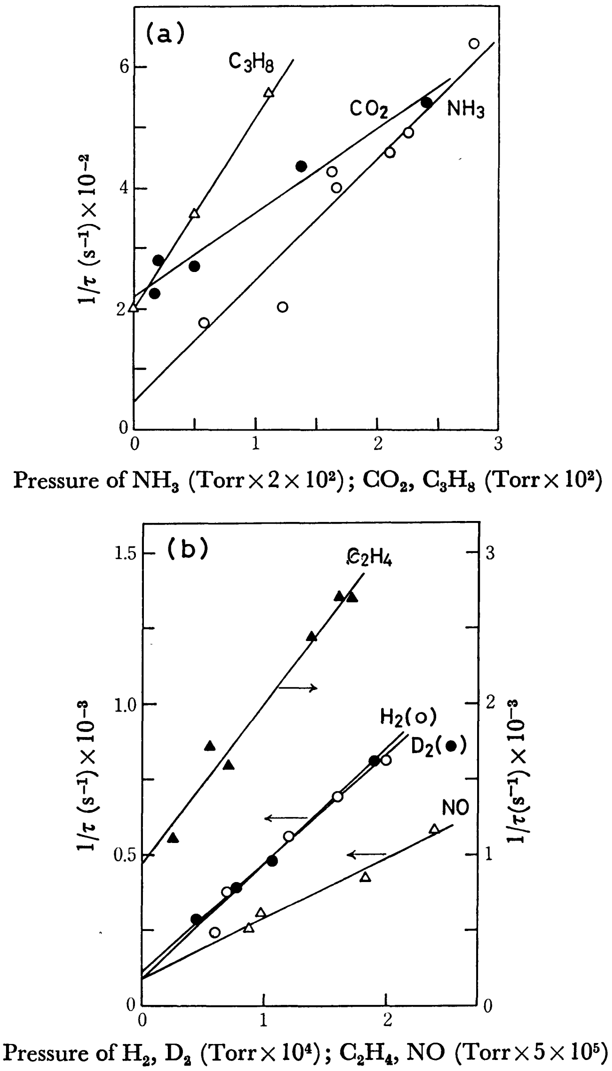

Fig. 5. The reverse of the lifetime of $Hg(6^3P_0)$ against a pressure of quencher. The experimental condition except for $NH_3$, $C_2H_4$ and NO: $p(N_2)=0.2$, $p(Ar)=9.8$, and $p(Hg)=1.9\times10^{-4}$ Torr; for $NH_3$: $p(Ar)=10.0$; for $C_2H_4$: $p(N_2)=4.8$, $p(Ar)=5.8$, for NO: $p(N_2)$ 1.3, $p(Ar)=8.7$ Torr.

TABLE 2. QUENCHING CROSS-SECTIONS ($\sigma^2$ in Å$^2$) OF Hg($6^3P_0$)

| Quencher | This work | Callear & McGurk[5)] | Freeman *et al.*[15)] |
|---|---|---|---|
| $N_2$ | $<2\times10^{-4}$ | — | — |
| $CH_4$ | $1.4\times10^{-4}$ | $2.70\times10^{-4}$ | — |
| $C_2H_6$ | $2.0\times10^{-3}$ | $5.73\times10^{-3}$ | $2.9\times10^{-2}$ |
| $NH_3$ | 0.016 | 0.015 | 0.016 |
| $CO_2$ | 0.032 | 0.033 | — |
| CO | 0.69 | 0.655 | 2.5 |
| NO | 8.0 | 16.2 | 13 |
| $H_2$ | 2.1 | 0.956 | 1.6 |
| $D_2$ | 2.9 | — | — |
| $C_3H_8$ | 0.073 | 0.033 | — |
| $n$-$C_4H_{10}$ | 0.93 | — | — |
| $i$-$C_4H_{10}$ | 1.4 | — | — |
| $C(CH_3)_4$ | 0.11 | — | — |
| $N_2O$ | 14 | 8.48 | 4.4 |
| $O_2$ | 16 | 12.0 | 18 |
| $C_2H_4$ | 41 | 26 | — |
| $C_3H_6$ | 50 | — | — |
| $C_2H_2$ | 36 | — | — |

TABLE 3. OBSERVED RATE ($k_{12}$ IN cm$^3$ molecules$^{-1}$ s$^{-1}$) FOR THE SPIN-ORBIT RELAXATION OF $6^3P_1\rightarrow6^3P_0$.

| Colliding molecule | Partial pressure (Torr) | $[Hg_0^*]/[Hg_1^*]_0$[a)] | $k_{12}$ | $\sigma^2(6^3P_1\rightarrow 6^3P_0+6^1S_0)$ (Å$^2$) |
|---|---|---|---|---|
| $CH_4$ | 0.27 | 10 | $2.1\times10^{-13}$ | 0.08[b)] |
| | 0.35 | 12 | 2.1 | |
| | 0.47 | 13 | 1.8 | |
| $C_2H_6$ | 0.48 | 36 | $2.1\times10^{-12}$ | 0.57[b)] |
| | 0.68 | 48 | 3.1 | |
| $NH_3$ | 0.012 | 36 | $2.3\times10^{-11}$ | 4.05[b)] |
| | 0.018 | 40 | 2.2 | |
| | 0.021 | 43 | 2.3 | |
| | 0.025 | 55 | 2.8 | |
| | 0.033 | 59 | 3.1 | |
| CO | 0.0020 | 3.8 | $6.3\times10^{-11}$ | 6.91[c)] |
| | 0.0031 | 5.6 | 8.4 | |
| | 0.0049 | 6.6 | 9.0 | |
| | 0.010 | 8.0 | 11.0 | |
| NO | 0.00037 | 0.5 | $7.6\times10^{-11}$ | 35.3[d)] |
| $C_3H_8$ | 0.018 | 12 | $1.6\times10^{-11}$ | 2.23[b)] |
| | 0.032 | 13 | 1.6 | |
| $n$-$C_4H_{10}$ | 0.0051 | 3.5 | $4.3\times10^{-11}$ | 5.67[b)] |
| $i$-$C_4H_{10}$ | 0.0046 | 2.9 | $5.3\times10^{-11}$ | 9.3[e)] |
| $C(CH_3)_4$ | 0.058 | 12 | $1.7\times10^{-11}$ | 1.9[f)] |

a) $[Hg_1^*]_0$ is the Hg($6^3P_1$) concentration in the absence of colliding molecules. All the measurements were carried out in the mixture with Ar at 10 Torr, b) the data of Zemansky[17)] multiplied by 1.379 as a correction factor, c) the data of Deech *et al.*,[16)] d) the value recommended by Cvetanović,[21)] e) the value calculated from $\sigma^2$ ($i$-$C_4H_{10}$)/$\sigma^2$($n$-$C_4H_{10}$) determined by Darwent,[19)] f) the data of Kang Yang.[18)]

wall of the reaction cell, and that diffusion to the wall is the rate-determining step. However, at a total pressure higher than 50 Torr, the reduction of the lifetime is found to be due to the deactivation by impurities.

*Quenching Rate of Hg($6^3P_0$) with Various Molecules.* The lifetime of $Hg_0^*$ was measured in a gaseous mixture of $N_2$ and Ar with a small amount of a quenching gas (Q). The reciprocal of the observed lifetime is plotted as a function of a partial pressure of Q in Fig. 5. The experimental data satisfy the Stern-Volmer relation, and the slope of the line gives the deactivation rate of $Hg_0^*$,

$$\text{(xi)}\quad Hg_0^* + Q \longrightarrow Hg + Q.$$

The results are summarized in Table 2 together with the data of Callear and McGurk[5)] and Freeman *et al.*[15)] to show the general agreement.

*Rates for the Processes of $6^3P_1\rightarrow6^3P_0$ and $6^3P_1\rightarrow6^1S_0$.* A method was given to obtain the rate constant for each of the two processes from the $6^3P_1$ state,

$$\text{(xii)}\quad Hg_1^* + Q \longrightarrow Hg_0^* + Q,$$

$$\text{(xiii)}\quad Hg_1^* + Q \longrightarrow Hg + Q,$$

based on the measurement of a stationary concentration of $Hg_0^*$.[9)] This method was applied to the system of Ar and various quenchers. In the previous work, we also measured the stationary concentration of $Hg_1^*$ as a function of a partial pressure of Q, and determined the total quenching rate of $Hg_1^*$. However, a weak absorption of the 435.8 nm line made the observed rate unreliable. In addition, a high pressure of Hg ($1.9\times10^{-4}$ Torr) caused an imprisonment of 253.7 nm resonant radiation, so that it is difficult to estimate the effective lifetime of $Hg_1^*$ accurately. Hence, we adopted the total quenching rate observed by others in this work. Deech *et al.*[16)] measured directly the lifetime of $Hg_1^*$ excited by a pulsed radiation. The quenching rate determined through this procedure does not depend on the radiative lifetime. Therefore, their data should be more reliable than those determined by the fluorescence method. For the rates which have not been measured by Deech *et al.*, correction factors are sought by comparing the results of Zemansky,[17)] Kang Yang,[18)] Darwent,[19)] and Campbell *et al.*[20)] with those of Deech *et al.*, since it would be reasonable to assume that the relative magnitude of cross-sections determined by the fluorescence method in one laboratory is more reliable.

Based on Eq. (6) of the previous paper, the rate for either of Reaction (xii) and (xiii) can be calculated. The results are summarized in Table 3. In this experiment, $Hg_0^*$ was detected faintly in NO, and not in $CO_2$, $H_2$, $D_2$, $N_2O$, $O_2$, $C_2H_4$, $C_3H_6$, and $C_2H_2$, for which upper limits of the rates are given from the detection limit of $Hg_0^*$. It is seen that the rate constant $k_{12}$ of CO depends on its partial pressure; a larger CO partial pressure results in a larger value of $k_{12}$. This is due to disregard of the reverse reaction of (xii). At room temperature, the rate for this reaction is quite small because of its endothermicity. However, it is probable that Reaction (xii) causes the vibrational excitation of a quenching molecule. If the deactivation rate of a vibrationally excited species is not large like that of $N_2$ or CO, a population in the excited level increases to more than that in the equilibrium state. Thus, the reverse of Reaction (xii) is accelerated since a large endothermicity is covered by

TABLE 4. CROSS-SECTIONS ($\sigma^2$ in Å$^2$) OF VARIOUS MOLECULES FOR QUENCHING Hg($6^3P_1$ and $6^3P_0$)

| Group | Quencher | $6^3P_1 \rightarrow 6^1S_0$ | $6^3P_1 \rightarrow 6^3P_0$ | $6^3P_0 \rightarrow 6^1S_0$ | $\sigma^2(6^3P_1 \rightarrow 6^1S_0)/\sigma^2(6^3P_0 \rightarrow 6^1S_0)$ ours | $\sigma^2(6^3P_1 \rightarrow 6^1S_0)/\sigma^2(6^3P_0 \rightarrow 6^1S_0)$ V and M[a)] |
|---|---|---|---|---|---|---|
| I | $N_2O$ | 22—20 | <2 | 14 | 1.6—1.3 | — |
| | $O_2$ | 19—17 | <2 | 16 | 1.2—1.1 | — |
| | $C_2H_4$ | 48—43 | <5 | 41 | 1.2—1.0 | — |
| | $C_3H_6$ | 57—52 | <5 | 50 | 1.1—1.0 | — |
| | $C_2H_2$ | 43—39 | <4 | 36 | 1.1—1.0 | — |
| II | CO | 3.0 | 3.9 | 0.69 | 4.3 | — |
| | NO | 30 | 5 | 8.0 | 3.8 | — |
| | $H_2$ | 7.8 | <0.1 | 2.1 | 3.7 | — |
| | $D_2$ | 7.2 | <0.1 | 2.9 | 2.5 | — |
| | $C_3H_8$ | 1.0 | 1.2 | 0.073 | 14 | 2.6 |
| | $n$-$C_4H_{10}$ | 2.1 | 3.6 | 0.93 | 2.3 | 3.1 |
| | $i$-$C_4H_{10}$ | 4.8 | 4.5 | 1.40 | 3.4 | 1.5 |
| | $C(CH_3)_4$ | 0.3 | 1.6 | 0.11 | 2.8 | 49 |
| III | $CH_4$ | 0.07 | 0.01 | $1.4 \times 10^{-4}$ | 500 | 860 |
| | $C_2H_6$ | 0.40 | 0.17 | $2.0 \times 10^{-3}$ | 200 | 6.6 |
| | $NH_3$ | 2.75 | 1.3 | 0.016 | 170 | — |
| | $CO_2$ | 3.2 | <0.02 | 0.032 | 100 | — |

a) calculated by Vikis and Moser[24)] based on the RRKM theory.

the vibrational energy of a quenching molecule, and the lifetime of $Hg_0^*$ is reduced by the process in which $Hg_0^*$ changes to $Hg_1^*$ through the reverse of Reaction (xii) and $Hg_1^*$ makes a spontaneous transition to the ground state. We therefore adopt a value of $k_{12}$ for CO by the extrapolation to zero pressure of CO. For other gases except $N_2$, the rate of the vibrational relaxation is so large that an equilibrium state in the system may be assumed.

The final results of the quenching cross-sections are summarized in Table 4 for each of the processes $6^3P_1 \rightarrow 6^1S_0$, $6^3P_1 \rightarrow 6^3P_0$, and $6^3P_0 \rightarrow 6^1S_0$.

*Correlation between the Cross-Sections for Processes $6^3P_1 \rightarrow 6^1S_0$ and $6^3P_0 \rightarrow 6^1S_0$.* In Fig. 6, the cross-sections of various quenching molecules for the process $6^3P_1 \rightarrow 6^1S_0$ are plotted as a function of the corresponding cross-sections for that of $6^3P_0 \rightarrow 6^1S_0$. It is concluded that quenching molecules can be classified into three groups, each of which has a constant ratio,

$$\sigma^2(6^3P_1 \rightarrow 6^1S_0)/\sigma^2(6^3P_0 \rightarrow 6^1S_0) = \alpha. \quad (3)$$

Though this classification is made empirically, one group with the same $\alpha$ can be characterized by a collision mechanism.

In the first group which consists of $C_3H_6$, $C_2H_4$, $C_2H_2$, $O_2$, and $N_2O$, $\alpha \approx 1.2$, and their lowest triplet energy levels are lower than those of the $6^3P_1$ and $6^3P_0$ states. Thus, in this group of molecules, a mechanism is suggested to be the electronic-to-electronic energy transfer such as

$$\text{(I)}\ Hg_{1,0}^* + Q \longrightarrow Hg + Q^T.$$

Burton and Hunziker[22)] found the formation of the triplet benzene or naphthalene by collisions with excited Hg atoms. This provides a direct evidence for mechanism (I). The collision process occurs through a non-adiabatic crossing from the potential surface of $Hg^* + Q$ to that of $Hg + Q^T$. The crossing is very efficient due to the strong interaction of the 6p electron of Hg with the $\pi^*$ orbit of quenching molecule. The cross-section is thus close to its gas kinetic one for quenching either of $6^3P_1$ and $6^3P_0$ states. The potential surface is schematically given in Fig. 7 together with cases for groups II and III.

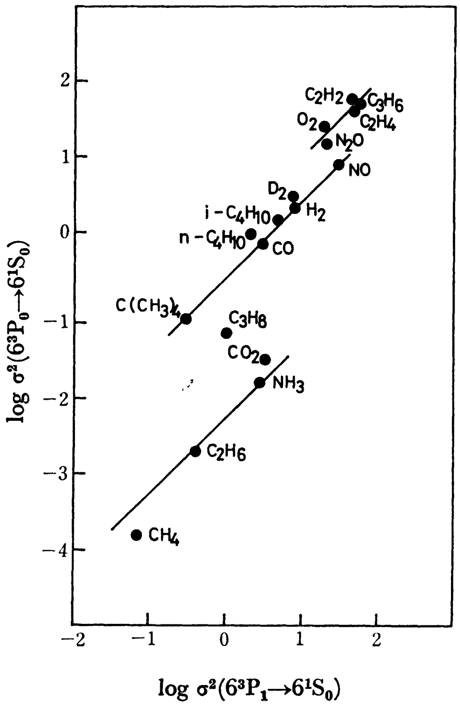

Fig. 6. Correlation of $\sigma^2(6^3P_1 \rightarrow 6^1S_0)$ to $\sigma^2(6^3P_0 \rightarrow 6^1S_0)$ in Å$^2$.

In the second group which involves $H_2$, $D_2$, NO, CO, $i$-$C_4H_{10}$, $n$-$C_4H_{10}$, $C(CH_3)_4$, and $C_3H_8$, $\alpha$ is about 4, and their lowest triplet energy levels are higher than or close to that of the $6^3P_1$ state. For hydrocarbon

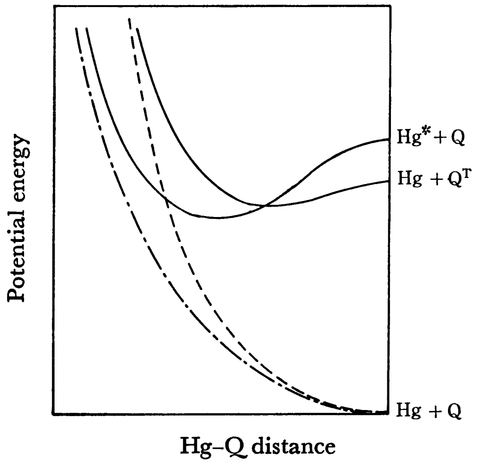

Fig. 7. Schematics of potential surfaces between Hg and Q.

molecules in this group, the quantum yield of $H_2$ formation is large in the Hg-photosensitized reaction, and the Hg*–CO or –NO collision affords the vibrational excitation of a colliding molecule.[23)] This suggests a process *via* a short-lived intermediate:

$$\text{(II)}\quad \mathrm{Hg}^* + \mathrm{Q} \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} (\mathrm{Hg\text{-}Q})^* \begin{array}{l} \overset{k_b}{\nearrow}\ \text{decomposition of Q,} \\ \underset{k_c}{\searrow}\ \text{vibrational excitation of Q.} \end{array}$$

Based on this mechanism, the cross-section should be explained as $k_a[(k_b+k_c)/(k_{-a}+k_b+k_c)]$. A large quantum yield of the C–H bond scission of a paraffin hydrocarbon leads to the fact that $k_c \approx 0$ due to a small bond energy of C–H. Assuming the complex (Hg–Q)*, Vikis and Moser[24)] applied the RRKM theory to calculate the rate of hydrogen abstraction by excited Hg atoms. The calculated value of the cross-section is larger by an order of magnitude than the present value, but the ratio of α is in agreement for molecules in the second group except neopentane. This means that the difference between the $6^3P_1$ and $6^3P_0$ quenching is explained simply by the energy content of the complex (Hg–Q)*. In this case, the potential surface between Hg* and Q is weakly attractive, and is crossed by the strongly repulsive surface of Hg+Q as shown in Fig. 7. In the course of sliding down on the latter surface, Q is excited vibrationally or undergoes a decomposition by a mechanism similar to the unimolecular reaction.

The ratio of the quenching cross-section for a hydrocarbon molecule to that of a D-substituted one is of a measurable magnitude. The experimental ratio of $\sigma^2(CH_3CH_2CH_3)$ to $\sigma^2(CH_3CD_2CH_3)$ was determined by Kang Yang[18)] as 3.0—8.0, which agreed well with the calculated one by Vikis and Moser based on the RRKM theory. This supports the energy dissipation through the unimolecular decomposition of (Hg–Q)*. However, the situation seems different for $H_2$ and $D_2$ because of its small isotope effect. If scheme II is assumed, the rate-controlling step is not the dissociation of (Hg–Q)* for $H_2$ or $D_2$, *i.e.*, the rate would be $k_a$ since $k_{-a} \ll k_b$ and $k_c \ll k_b$. The process is a non-adiabatic transition from Hg*+Q to Hg+Q*, and this does not show a large isotope effect. Callear and McGurk[25)] proposed two possible mechanisms for quenching Hg* by $H_2$: an electronically adiabatic route and a non-adiabatic one after H–Hg–H complex was formed by a sideway attack of Hg*.

The third group is characterized by a large ratio of α and by a small cross-section for quenching $Hg_1^*$ except $NH_3$ and $CO_2$. It is thus probable that there is no crossing between two surfaces of Hg*+Q and Hg+Q, or the crossing point is in an energy region higher than the excitation energy of Hg. Callear and McGurk[5)] pointed out a steric hindrance of Hg* inserting into a C–H bond to be the cause of inefficiency of quenching by a simple hydrocarbon such as $CH_4$ or $C_2H_6$.

In the quenching of $Hg_0^*$ by $NH_3$, the emission which originated from $(Hg\text{–}NH_3)^*$ was found by Freeman *et al.*[26)] The rate constant for the radiative process

$$\mathrm{Hg}(6^3P_0) + \mathrm{NH_3} \longrightarrow (\mathrm{Hg\text{-}NH_3})^* \longrightarrow \mathrm{Hg}(6^1S_0) + \mathrm{NH_3} + h\nu$$

was determined to be $3.2 \times 10^{-13}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$. This agrees with our result $3.1 \times 10^{-13}$. Hence, most of the $6^3P_0$ quenching process should be the radiative one. In contrast, $\sigma^2(6^3P_1 \rightarrow 6^3P_0 + 6^1S_0)$ is of the same order of magnitude as that of a molecule in group II, and the quantum yield of the decomposition of $NH_3$ at a low pressure is close to 1.[27)] Thus, the quenching of $Hg_1^*$ by $NH_3$ should be categorized into group II.

Since the dissociation energy of $CO_2$ is much larger than the excitation energy of Hg, the reaction scheme for the $6^3P_1$ quenching is a triplet formation. The triplet level of $CO_2$ is uncertain, but the experiment of the thermal decomposition[28)] suggests a level near that of the $6^3P$ state. If this is the case, a small cross-section of the $6^3P_0$ quenching may be explained by the fact that the triplet level lies between those of the $6^3P_1$ and $6^3P_0$ states.

*Quantum Yield of Hg($6^3P_0$).* The quantum yield

TABLE 5. QUANTUM YIELD OF Hg ($6^3P_0$)

| Collision partner | This work | Callear and McGurk[5)]* | Vikis *et al.*[29)] |
|---|---|---|---|
| $CH_4$ | 0.13 | 0.11(0.11) | — |
| $C_2H_6$ | 0.30 | 1.21(0.67) | 0.64 |
| $NH_3$ | 0.32 | 0.64(0.64) | 1.05 |
| $CO_2$ | <0.006 | ~0.02(0.02) | <0.01 |
| CO | 0.56 | 0.57(0.90) | 0.88 |
| NO | 0.14 | <0.10(<0.10) | — |
| $H_2$ | <0.01 | <0.03(<0.03) | — |
| $D_2$ | <0.01 | — | — |
| $C_3H_8$ | 0.54 | 0.12(0.21) | 0.14 |
| $n$-$C_4H_{10}$ | 0.63 | — | 0.11 |
| $i$-$C_4H_{10}$ | 0.48 | — | 0.05 |
| $C(CH_3)_4$ | 0.84 | — | 0.58 |
| $N_2O$ | <0.09 | <0.10(<0.10) | — |
| $O_2$ | <0.10 | <0.10(<0.10) | — |
| $C_2H_4$ | <0.10 | <0.10(<0.10) | — |
| $C_3H_6$ | <0.09 | — | — |
| $C_2H_2$ | <0.09 | — | — |

*Uncorrected values in parentheses.

of $Hg_0$* defined as $\sigma^2(6^3P_1 \rightarrow 6^3P_0)/\sigma^2(6^3P_1 \rightarrow 6^1S_0+6^3P_0)$ are given in Table 5. The results are compared with those reported by Callear and McGurk.5) Their data are corrected by using the total cross-sections of the $6^3P_1$ quenching that are adopted in this work. The agreement is within a factor of 2 except $C_2H_6$. As stated already, the process $6^3P_1 \rightarrow 6^3P_0$ has a possibility to cause the vibrational excitation of a colliding molecule. However, there seems to be no distinct correlation between the cross-section and the resonance energy defect. The quantum yield is large for a molecule in group II and III except $H_2$, $D_2$, and $CO_2$. This suggests that the state mixing between the $6^3P_1$ and $6^3P_0$ states in the (Hg–Q)* complex may result in the transition to the $6^3P_0$ state, and that the production of $Hg(6^3P_0)$ is not efficient if there is a large probability of transition from the Hg*+Q surface to the Hg+Q, *i.e.*, the condition $k_{-a}>k_b+k_c$ in scheme (II) is necessary for a large quantum yield.

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