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The Quenching of Hg(6^3P_1) Atoms by Molecular Hydrogen as Investigated by ESR Spectroscopy

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The gas phase electron spin resonance technique has been applied to study the quenching efficiency of Hg(6^3P_1) mercury atoms by molecular hydrogen. The concentration of hydrogen atoms produced by the mercury photosensitized decomposition of molecular hydrogen in a flow apparatus was followed as a function of the partial pressure of hydrogen with argon, neon, and hydrogen as carrier gases. The kinetic equations derived from the reaction mechanism proposed was shown to be in agreement with the experimental observations. The total quenching rate k_H was evaluated from the experimental results.

The quenching of excited mercury atoms Hg (6^3P_1) was first observed by Cario and Franck[1] and since that time this process has been the subject of numerous detailed investigations. Several comprehensive reviews of the literature have appeared.[2,3] Most investigators have devoted their attention to studying the quenching of excited Hg($^3P_1$) mercury atoms by hydrogen,[1-9] or hydrocarbons,[2-4,10-13] though many detailed studies have been made of the quenching processes caused by other molecules.[7,12-14] Undoubtedly the reaction of this type which has been most extensively investigated is that of the mercury photosensitized decomposition of molecular hydrogen. These extensive studies have been carried on not only because of the intrinsic importance of the quenching process itself, but because the mercury photosensitized decomposition of molecular hydrogen has proven to be a clean source of hydrogen atoms of considerable importance in the study of hydrogenation processes.

The quenching of excited mercury Hg(6^3P_1) atoms has been measured by both physical and chemical methods. Thus Thomas and Gwinn[5] studied the quenching efficiency of molecular hydrogen by measuring the pressure changes in the reaction cell. Cvetanovic[2] developed a chemical method for the estimation of quenching efficiencies. This method is based on chemical analysis of the reactants. Generally mixtures of nitrous oxide and hydrocarbons were used to quench the excited Hg*(6^3P_1) atoms, and subsequent product analysis enabled relative values for the quenching efficiencies to be estimated. Both physical[12,13] and chemical methods[2,6,10] have been used to study the quenching of excited mercury Hg (6^3P_1) atoms by alkanes and related compounds. The

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[1] G. Cario and J. Franck, *Z. Phys.*, **11**, 161 (1922).

[2] R. J. Cvetanovic, "Progress in Reaction Kinetics" ed. G. Porter, Perganon Press Ltd., Oxford, Vol. **2**, (1964), p. 69.

[3] H. E. Gunning and O. P. Strausz, "Advances in Photochemistry," Interscience Publishers, New York, Vol. **1**, (1962), p. 209.

[4] A. B. Callear and R. G. W. Norrish. *Proc. Roy. Soc.*, **A266**, 299 (1962).

[5] L. B. Thomas and W. D. Gwinn, *J. Amer. Chem. Soc.*, **70**, 2643 (1948).

[6] K. Yang, J. D. Paden, and C. L. Hassell, *J. Chem. Phys.*, **47**, 3824 (1967).

[7] A. B. Callear and R. E. M. Hedges, *Trans. Faraday Soc.*, **66**, 605 (1970).

[8] A. B. Callear and R. E. M. Hedges, *ibid.*, **66**, 615 (1970).

[9] A. B. Callear and J. McGurk, *Nature* **226**, 844 (1970).

[10] K. Yang, *J. Amer. Chem. Soc.*, **89**, 5344 (1967).

[11] A. C. Vikis and H. C. Moser. *J. Chem. Phys.*, **53**, 2333 (1970).

[12] S. Penzes, A. J. Yarwood, O. P. Strausz, and H. E. Gunning, *ibid.*, **43**, 4524 (1965).

[13] S. Penzes, O. P. Strausz, and H. E. Gunning, *ibid.*, *Phys.*, **45**, 2322 (1966).

[14] A. C. Vikis, G. Torrie, and D. J. Le Roy, *Can. J. Chem.*, **48**, 3771 (1970).

flash photolysis technique was first used by Callear and Norrish[4] to investigate mercury photosensitized reactions and in particular to study the role of Hg($^3P_0$) atoms. Callear and Williams[15,16] studied mixtures of mercury vapour and various gases when subjected to a single pulse of uv radiation. A microwave pulse method was developed by Callear and Hedges[7,8] and applied particularly to study the role of HgH as an intermediate in Hg(6^3P_1) photosensitized reactions. More detailed studies of the formation of HgH in the mercury photosensitized decomposition of molecular hydrogen were reported by Callear and McGurk[9]. Many workers have studied the importance of complex formation as an intermediate in the quenching of excited mercury Hg(6^3P_1) atoms by molecules other than hydrogen. Thus Homer and Lossing[18] as the result of studies using a mass spectrometric technique postulated the formation of a HgCO* complex with a life-time of about 3×10^{-5} sec to account for the results of their study of the reaction Hg(6^3P_1) atoms with CO. This same system was studied extensively by Karl, Kruss, and Polanyi[19–21] who recorded the infrared emission of vibrationally excited carbon monoxide to its ground state. The results were also interpreted in terms of the formation of a HgCO* complex. Later, in an extensive physical and chemical study[22] of the Hg/CO system, by London, Vikis, and Le Roy, it was stated that the results failed to yield any substantial additional evidence for the existence of the HgCO* complex.

Recently electron spin resonance spectroscopy has been used to study atom concentrations in reacting systems. In the case of certain reactions it has proved possible to detect atomic hydrogen in the gas phase at concentrations as low as 10^{10}-10^{11} atom/cc, and to estimate the concentrations of such atomic species quantitatively.[23] This method has been applied to the study of the mercury photo-sensitized reaction between hydrogen and oxygen.[24] In this paper we describe a somewhat improved experimental method using electron spin resonance spectroscopy and a flow system to study in greater detail this photosensitized reaction.

Experimental

The pure cylinder hydrogen used in these experiments was further purified by passage through a catalytic deoxygenator unit (Deoxo), and through a cold trap held at liquid nitrogen temperature. The other gases used, namely argon and neon, were obtained from the Matheson Company and were stated to be better than 99.998% pure. Before use these were passed through a cold trap held at liquid nitrogen temperature.

Figure 1 shows a schematic diagram of the experimental arrangement. The gaseous mixtures containing hydrogen were introduced to the reaction vessel after passing through the thermostated mercury saturator. The vapour pressure of the mercury was varied by changing the temperature of the circulating water cooling the saturator. The temperature could readily be controlled to ±0.2°C. After passing the radiation zone the gases entered the ESR cavity operating in a TE_{102} mode. The partial pressure of the gases was determined by measuring the flow rate of each gas which was accurately controlled by needle valves at the inlet and outlet of the system. The capillary flow meters were carefully calibrated before use.

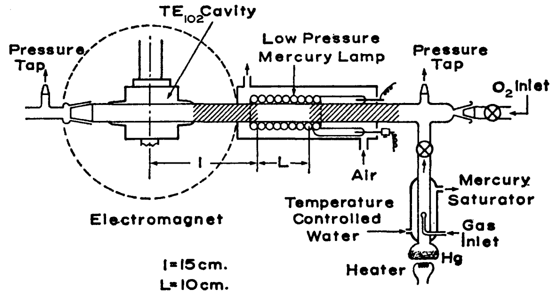

Fig. 1. Diagrammatic sketch of the experimental apparatus.

The irradiations were carried out using a Hanovia low pressure mercury vapour lamp which was spiral in form and having a diameter of 5 cm, and was 15 cm in length. The flow tube was 2 cm o.d. quartz coated on the inside with DuPont Teflon to reduce the rate of recombination of the hydrogen atoms at the surface. It is well known that without such wall coatings it is difficult to observe ESR signals due to H atoms because of high efficiency of the recombination due to wall collisions when uncoated quartz is used. A X-band homodyne ESR spectrometer using a modulating frequency of 100 kHz was used to determine the hydrogen atom concentrations. The H atom concentrations being

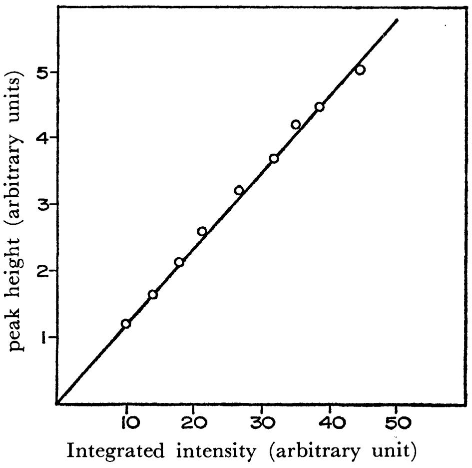

Fig. 2. Relationship between the integrated intensity and peak height of the ESR spectrum of H atoms in a flow system at mean pressures of 0.3 to 0.2 torr.

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[15] A. B. Callear and G. J. Williams, *Trans. Faraday Soc.*, **60**, 2158 (1964).

[16] A. B. Callear, J. A. Green, and G. J. Williams, *ibid.*, **61**, 1831 (1965).

[17] A. B. Callear and J. McGurk, *Chem. Phys. Lett.*, **7**, 491 (1970).

[18] J. B. Homer and F. P. Lossing, *Can. J. Chem.*, **44**, 143 (1966).

[19] G. Karl and J. C. Polanyi, *J. Chem. Phys.*, **38**, 271 (1963).

[20] G. Karl, P. Kruus, and J. C. Polanyi. *ibid.*, **46**, 224 (1967).

[21] G. Karl, P. Kruus, P. C. Polanyi, and I. W. M. Smith, *ibid.*, **46**, 244 (1967).

[22] G. London, A. C. Vikis, and D. J. Le Roy, *Can. J. Chem.*, **48**, 1420 (1970).

[23] A. A. Westenberg and N. de Haas, *J. Chem. Phys.*, **40**, 3087 (1964); **47**, 1393 (1967).

[24] K. Shimokoshi, Y. Mori, and I. Tanaka, This Bulletin, **40**, 254 (1967).

estimated by comparing the integrated intensities with lines in the ESR spectrum of molecular oxygen whose concentrations in the reaction zone was known. The integration was achieved by using two successive operational amplifiers which provided respectively, the first and second integrals of the original derivative spectrum. A plot of the integrated intensity of the atomic hydrogen ESR signal against the peak heights is shown in Fig. 2. These data were obtained at mean pressures of hydrogen of 0.3 to 2.2 torr in the flow system.

Results and Discussion

As will be clear from the above, our experimental technique yields values for the variation of the concentration of the hydrogen atoms as a function of pressure. These data can be used to develop a kinetic analysis of the processes which occur when excited Hg (6^3P_1) atoms are quenched by molecular hydrogen.

When ground state mercury atoms $Hg(6^1S_0)$ absorb radiation of wavelength 2537Å the following initial processes occur:

$$Hg(6^1S_0) + h\nu \xrightarrow{k_1} Hg(6^3P_1) \qquad (1)$$

$$Hg(6^3P_1) \xrightarrow{k_2} Hg(6^1S_0) + h\nu \qquad (2)$$

Collision of the excited $Hg(6^3P_1)$ atoms with molecular hydrogen leads to a number of processes, all of which are of importance in understanding the nature of the complex reactions involved in the overall quenching phenomena.

The first reaction leading to the production of hydrogen atoms which obviously occurs is

$$Hg(6^3P_1) + H_2 \xrightarrow{k_3} HgH + H \qquad (3)$$

Indirect evidence for the formation of HgH was obtained by Thomas and Gwinn.[5] Various workers[6,10,25,26] have discussed the possibility of this process both in terms of studies of potential surfaces correlating the $Hg(6^3P_1)$ atom and molecular hydrogen energy states, and phase-space theory in which reactive scattering is assumed to occur when the relative energy of translation exceeds the hump in the effective interaction potential curve. The observation of the spectrum of HgH in flash spectroscopic studies of mixtures of mercury and H_2, D_2, by Callear and Hedges[7,8], and by Callear and McGurk[9] clearly established that reaction (3) does occur. We should perhaps mention that Callear and McGurk[9] have suggested that the interaction of $Hg(6^3P_1)$ atoms and molecular hydrogen is somewhat more complicated than has been indicated in Eq. (3). They suggested that the following sequence of reactions occur,

$$Hg(6^3P_1) + H_2 \longrightarrow HHgH^* \text{ (insertion)}$$

$$HHgH^* \longrightarrow HHgH \text{ (crossing)}$$

$$HHgH \longrightarrow HgH + H \text{ (dissociation)}$$

In the present studies, however, we are of the opinion that Eq. (3) is an adequate representation of the interaction. The HgH formed in reaction (3) was found[8] to decay in less than 200 μsec.

Various mechanisms have been suggested for the subsequent reactions of the HgH produced in reaction (3). It may for example simply dissociate rapidly as follows

$$HgH + M \longrightarrow Hg(6^1S_0) + H + M$$

since the bond dissociation energy of HgH is only 8.6 kcal mol^{-1}. Another possible reaction is, of course,

$$HgH + H \longrightarrow Hg(6^1S_0) + H_2$$

which was postulated by Thomas and Gwinn[5] and subsequently adopted by a number of workers.[6-9,22]

Apart from reaction (3) there are two other quenching processes which must be considered to be of some importance, namely

$$Hg(6^3P_1) + H_2 \xrightarrow{k_4} Hg(6^3P_0) + H_2 \qquad (4)$$

$$Hg(6^3P_1) + H_2 \xrightarrow{k_5} Hg(6^1S_0) + H_2 \qquad (5)$$

The role of spin-orbit relaxation (reaction (4)) in the quenching of excited mercury (6^3P_1) atoms has been studied in some detail[4,7-9,12-14,22] and it is clear that in the case of hydrogen reaction (4) is an important process. Corresponding processes must occur when a carrier gas is used in the experiments using hydrogen mixtures so we must, in these cases, also include the following processes

$$Hg(6^3P_1) + M \xrightarrow{k_6} Hg(6^3P_0) + M \qquad (6)$$

$$Hg(6^3P_1) + M \xrightarrow{k_7} Hg(6^1S_0) + M \qquad (7)$$

many authers[1-5,7-9,12-14,29,30,32,33] have considered the role of metastable $Hg(6^3P_0)$ atoms in mercury photosensitized reactions. Callear and Hedges[7,8] showed conclusively that both molecular hydrogen and deuterium, in the presence of large excess of nitrogen react with $Hg(6^3P_0)$ atoms in the manner analogous to reaction (3), namely:-

$$Hg(6^3P_0) + H_2 \longrightarrow HgH + H \qquad (3^1\mathrm{H})$$

$$Hg(6^3P_0) + D_2 \longrightarrow HgD + D \qquad (3^1\mathrm{D})$$

and that the yields of HgH (or HgD) were slightly higher from $Hg(6^3P_0)$ than from $Hg(6^3P_1)$ atoms. Earlier, however, Callear and Norrish[4] had shown that the cross-section for quenching of $Hg(6^3P_0)$ by molecular hydrogen is 0.08Å^2, whereas that for $Hg(^3P_1)$ and hydrogen is 6Å^2. More recently London *et al.*[22] and Callear and McGurk[17] have confirmed that the rate of deactivation or reaction of $Hg(6^3P_0)$ atoms by hydrogen is very small. For these reasons it is unlikely that reaction (3^1H) is of any major significance in our case. The only reactions of $Hg(6^3P_0)$ atoms with hydrogen which need be considered are therefore,

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[25] K. J. Laidler, "The Chemical Kinetics of Excited States," Oxford University Press, 1955.

[26] K. J. Laidler, *J. Chem. Phys.*, **10**, 43 (1942).

[27] P. H. Garrett. *Phys. Rev.*, **20**, 779 (1932).

[28] J. E. McAlduff and D. J. Le Roy. *Can. J. Chem.*, **43**, 2279 (1965).

[29] G. H. Kimbell and D. J. Le Roy. *Can. J. Chem.*, **38**, 1714 (1960).

[30] G. H. Kimbell and D. J. Le Roy. *ibid.*, **40**, 1229 (1962).

[31] H. W. Webb and H. A. Messenger, *Phys. Rev.*, **33**, 319 (1929).

[32] A. B. Callear and W. P. D. Pereira, *Trans. Faraday Soc.*, **59**, 2758 (1963).

$$\mathrm{Hg}(6^3P_0) + \mathrm{H}_2 \longrightarrow \mathrm{Hg}(6^1S_0) + 2\mathrm{H} \tag{8}$$

$$\mathrm{Hg}(6^3P_0) + \mathrm{H}_2 \longrightarrow \mathrm{Hg}(6^1S_0) + \mathrm{H}_2 \tag{9}$$

The corresponding reaction to (9) may also occur with a non-chemically reacting atom or molecule, *i.e.*,

$$\mathrm{Hg}(6^3P_0) + \mathrm{M} \xrightarrow{k_{10}} \mathrm{Hg}(6^1S_0) + \mathrm{M} \tag{10}$$

Because the life-time of the $\mathrm{Hg}(6^3P_0)$ atoms is long, the radiative transition to the ground state

$$\mathrm{Hg}(6^3P_0) \longrightarrow \mathrm{Hg}(6^1S_0) + h\nu'$$

is also not likely to be of importance in our case.

The termination reactions involving hydrogen atoms are:—

$$\mathrm{H} + \mathrm{H} + \mathrm{H}_2(\mathrm{M}) \longrightarrow \mathrm{H}_2 + \mathrm{H}_2[\mathrm{M}] \tag{11}$$

$$\mathrm{H}\ (\text{wall}) \longrightarrow \tfrac{1}{2}\mathrm{H}_2 \tag{12}$$

Since the life-time of $\mathrm{Hg}(6^3P_1)$ is quite short and the quenching processes k_3, k_4, and k_5 (and k_2) are fast, we can assume that a steady state concentration of $\mathrm{Hg}(6^3P_1)$ and $\mathrm{Hg}(6^3P_0)$ will quickly be established. Applying the normal steady state approximations we obtain the following equation for the rate of formation of hydrogen atoms:—

$$\begin{aligned}\mathrm{d}[\mathrm{H}]/\mathrm{d}t &= 2k_3[\mathrm{Hg}(6^3P_1)]_{\mathrm{ss}}[\mathrm{H}_2] + 2k_8[\mathrm{Hg}(6^3P_0)]_{\mathrm{ss}}[\mathrm{H}_2] \\ &\quad - k_{12}[\mathrm{H}] - k_{11}[\mathrm{H}]^2[\mathrm{H}_2]\end{aligned} \tag{13}$$

As the total pressure in the flow tube was lower than 5 torr, and the concentration of hydrogen atoms was also so low, the termolecular recombination process (11) can be neglected, particularly as the transit time from the irradiation zone to the cavity is probably only 10^{-3} sec. Equation (13) therefore can be simplified to

$$\mathrm{d}[\mathrm{H}]/\mathrm{d}t = A - k_{12}[\mathrm{H}], \tag{14}$$

where

$$A = \frac{2\mathrm{I}_0[\mathrm{H}_2]}{k_2 + k_{\mathrm{H}}[\mathrm{H}_2] + k_{\mathrm{M}}[\mathrm{M}]}\left\{k_3 + k_8\frac{k_4[\mathrm{H}_2] + k_6[\mathrm{M}]}{k_{\mathrm{H}}{}^\circ[\mathrm{H}_2] + k_{10}[\mathrm{M}]}\right\}. \tag{15}$$

In Eq. (15) we have written k_{H} for $k_3+k_4+k_5$, k_{M} for k_6+k_7, and $k_{\mathrm{H}}{}^\circ$ for k_8+k_9.

Outside the illumination region the rate of formation of H atoms can be neglected so in those regions Eq. (14) has the form

$$\mathrm{d}[\mathrm{H}]/\mathrm{d}t = -k_{12}[\mathrm{H}]. \tag{16}$$

Under our experimental conditions when $[\mathrm{H}_2] \gg [\mathrm{H}]$, then the hydrogen atom concentration $[\mathrm{H}]_{\mathrm{c}}$ in the cavity given by the expression

$$[\mathrm{H}]_{\mathrm{c}} = \frac{A}{k_{12}}\{1 - \exp(-k_{12}L/v)\}\exp(-k_{12}l/v). \tag{17}$$

Where L is the length of the illumination zone, l the distance from the end of the illumination zone to the ESR cavity, and v is the linear flow velocity. The effect of the flow velocity on the hydrogen atom concentration in the cavity $[\mathrm{H}]_{\mathrm{c}}$ at constant pressure of hydrogen of 0.374 torr is shown in Fig. 3. If we assume that $k_{12}L/v$ and $k_{12}l/v$ are both $\ll 1$, then from Eq. (17) we obtain the result

$$[\mathrm{H}]_{\mathrm{c}} = \frac{\mathrm{A}L}{v}\left(1 - \frac{k_{12}l}{v}\right)$$

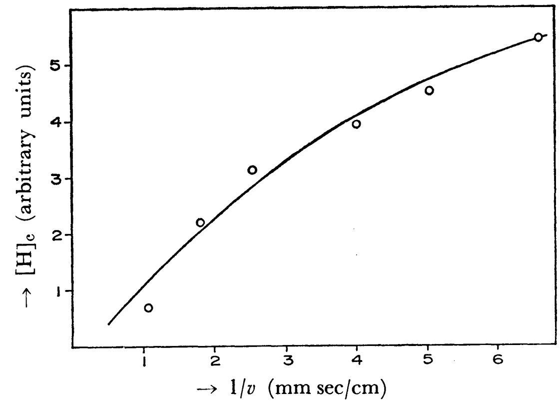

Fig. 3. Plot of hydrogen atom concentration $[\mathrm{H}]_{\mathrm{c}}$ as a function of $1/v$ at pressure of hydrogen of 0.374 torr.

which is in agreement with the experimental results as shown in Fig. 3.

From Eqs. (13)—(17) we can obtain the expression

$$\frac{\mathrm{B}}{[\mathrm{H}]_{\mathrm{c}}} = \left(k_{\mathrm{H}} + \frac{k_2}{[\mathrm{H}_2]} + \frac{k_{\mathrm{M}}[\mathrm{H}]}{[\mathrm{H}_2]}\right) \times \left\{\frac{k_{\mathrm{H}}{}^\circ[\mathrm{H}_2] + k_{10}[\mathrm{M}]}{(k_3k_{\mathrm{M}}{}^\circ + k_8k_4)[\mathrm{H}_2] + (k_3k_{10} + k_8k_6)[\mathrm{M}]}\right\}, \tag{18}$$

where $\mathrm{B} = (2I/k_{12})\{1 - \exp(-k_{12}L/v)\}\exp(-k_{12}l/v)$ which is constant under the conditions of our experiments where L, v, and I were kept constant. To evaluate $k_{\mathrm{H}} = k_3+k_4+k_5$ we proceed as follows. Eq. (18) can be rewritten as

$$\frac{C}{[\mathrm{H}]_{\mathrm{c}}} = \left(k_{\mathrm{H}} + \frac{k_2}{[\mathrm{H}_2]}\right) \tag{19}$$

where $C = Bk_{\mathrm{H}}{}^\circ/(k_3k_{\mathrm{H}}{}^\circ + k_8k_4)$ if we neglect the quenching by inert gases used as carriers. A series of experiments were carried out using Ar, Ne, and H_2 as carrier gases at constant flow rate. Plots of the function $1/[\mathrm{H}]_{\mathrm{c}}$ obtained from the measurements of $[\mathrm{H}]_{\mathrm{c}}$, the hydrogen atom function in the cavity against $1/[\mathrm{H}_2]$ are shown in Figs. 4, 5, and 6. Least squaring the data gave the values of k_{H}/k_2 at 20°C listed in Table 1. The ratio k_{H}/k_2 was evaluated because the method was thought not to be accurate enough to determine the parameters separately.

To evaluate k_{H} we need to have an estimate of k_2

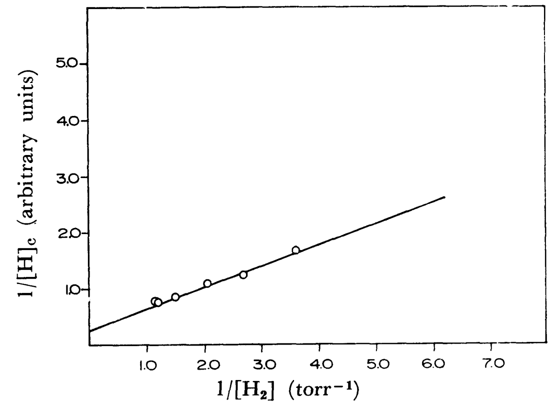

Fig. 4. Plot of $1/[\mathrm{H}]_{\mathrm{c}}$ against $1/[\mathrm{H}_2]$ at total pressure of 1.0 torr with argon as the carrier gas.

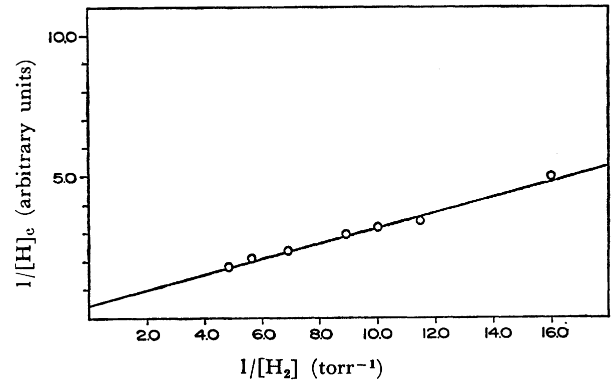

Fig. 5. Plot of $1/[H]_c$ against $1/[H_2]$ at total pressure of 2.0 torr with neon as the carrier gas.

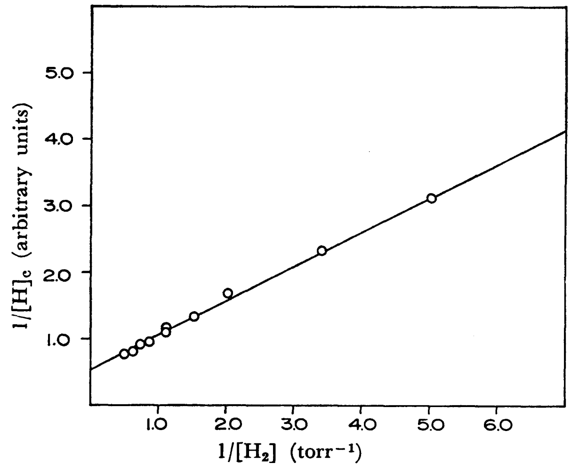

Fig. 6. Plot of $1/[H]_c$ against $1/[H_2]$ with hydrogen as carrier gas.

under the conditions of our experiments. The true lifetime of $Hg(6^3P_1)$ atoms with respect to radiation has been reported by Garrett[27)] as being 1.08×10^{-7} sec. This value may, however, need correction because of the possible imprisonment of the resonance radition, which has the effect of decreasing this value as the mercury vapour pressure is increased. For the range of mercury vapour pressure used in our experiments, we may make use of the expression (20) proposed by McAlduff and LeRoy[28)]

$$k_2=(1-q[\mathrm{Hg}])/\tau \tag{20}$$

when q is a constant. As has been pointed out by many authors[29-31)] radiation imprisonment effects depend on the geometry of the cell as well as the nature of the light source used. Under our experimantal conditions it was difficult to measure the concentration of the mercury atoms with high precision. This difficulty was, however, circumvented to an acceptable degree by the following method. The concentration in the reactor region was assumed to be linearly related to that in the saturator. If we assume there was little change in I_0 then by reducing the concentration of mercury atoms by one half, we carried out a determination of k_H/k_2 with the temperature of the reactor at 12°C at which point the vapour pressure of mercury is one half the value at 20°C. The value of the ratio $(k_H/k_2)_{20^\circ}/(k_H/k_2)_{12^\circ}$ was found to be 0.91, and substituting this value into Eg.(20) we obtain the result that $k_2=1.2/\tau$. This enables us to calculate k_H from the data in column 2 of Table 1. The resulting values of k_H are given in column 3 of Table 1. The only other data available for comparison is given in column 4 which are obtained by a chemical method.[1,22)] The chemical method for determining the kinetic parameters is possibly subject to several inherent errors. The ESR method is more direct and may be more accurate. The agreement between the two sets of values is, however, satisfactory.

Table 1. Summary of the rate constants at 20°C

Carrier gas	k_H/k_2 (torr^{-1})	$10^{-10}\times k_H$ (l mol^{-1} sec^{-1}) this work	Literature values
H_2	1.11±0.20	22.5±4.0	30.7 (Ref. 22)
Ar	1.05±0.41	21.2±8.2	29.0 (Ref. 1)
Ne	0.98±0.33	20.9±5.7	

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