

CROSS-SECTION FOR QUENCHING OF Hg (3P_1) BY HD USING MEASUREMENTS OF LYMAN ALPHA ABSORPTION*

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SUMMARY

The Hg (3P_1) quenching cross-sections of H₂ and HD have been measured at pressures of Hg approximately in the range 23.2 to 95.4 μ Torr by measuring the Lyman α absorption of the product H atoms produced. The quenching cross-section so measured for H₂ was 0.100 ± 0.004 nm² and for HD was 0.109 ± 0.012 nm². Experimental values for radiation imprisonment lifetimes in Hg are shown to be consistent with those obtained by earlier workers.

INTRODUCTION

The study of the quenching of Hg (3P_1) atoms by small molecules is fundamental to the development of a theory by which electronic energy is transferred to a receptor molecule. Consequently, a number of investigations have focused on the measurement of the quenching cross-section of the Hg (3P_1) and H₂ reaction¹⁻⁵ since the early discovery by Cario and Franck⁶ that hydrogen decomposition occurred. While considerable attention has been devoted to H₂, measurements involving either HD or D₂ are surprisingly sparse. The first study which encompassed isotopic hydrogen was reported by Evans⁷ using the techniques developed by Zemansky¹ and Bates⁸. He reported the quenching cross-section for D₂ to be greater than that of H₂, contrary to observations made when D was substituted for H in saturated hydrocarbons. Yang⁹, using both the physical and chemical methods, re-investigated the isotopic hydrogens and showed that H₂, HD, and D₂ had essentially the same quenching cross-sections within his experimental error and, if anything, the order of quenching cross-sections was HD > H₂ > D₂. Deech *et al.*¹⁰ measured the decay of Hg (3P_1) following pulse excitation and confirmed

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that D_2 has a smaller quenching cross-section than H_2 . Callear and McGurk¹¹ have recently confirmed the relative quenching cross-sections of Yang by observing the product HgH and HgD by kinetic flash spectrometry and explained their measurements in terms of an insertion reaction mechanism. Since the technique of Lyman alpha photometry which detects the other quenching products, H atoms, had been successfully applied to H_2 by Michael and his co-workers⁵, it seemed desirable to make use of this completely different technique to establish the validity of the quenching cross-section for HD, especially in view of the preferred formation of HgD from HD reported by Callear and McGurk.

EXPERIMENTAL

Materials

HD obtained from Merck, Sharp and Dohme, Ltd., Canada, was determined to contain 0.76% H_2 and 0.4% D_2 by mass spectrometry (C.E.C. 21-103C Mass Spectrometer, calibrated daily with n-butane) and was used without further purification. Matheson Company hydrogen and deuterium were purified by passing them through a palladium thimble at 500°C and stored for later use. The H_2 and D_2 so treated contained less than 0.08% HD as the only impurity. Research grade Ne and Ar were obtained from J. T. Baker Company and contained no detectable impurities by mass spectrometry. Matheson Company NO was purified by bulb-to-bulb distillation (from -160°C to -195°C) and contained 0.32% CO_2 as the only impurity. Oxygen was passed through a liquid nitrogen trap to remove trace water contamination. Triple distilled Hg was used without further purification.

Apparatus

A schematic diagram of the apparatus is given in Fig. 1. Light from the Lyman alpha lamp, A, was produced by a conventional discharge through H_2 . It was filtered in a chamber B containing flowing O_2 after passage through a LiF window, W_1 , and admitted to the reaction chamber through a LiF window, W_2 . Unabsorbed Lyman alpha radiation passed through the LiF window, W_3 , and was detected in the region D by photoionization of 1% NO in an atmosphere of Ar. All chambers except B, which was a flow filter of O_2 , was protected from back diffusion of water vapor by liquid nitrogen traps, L.T., in Fig. 1. The hydrogen lamp has been described elsewhere¹²⁻¹⁴ as has the ionization detector¹⁵. The vapor pressure of Hg in zone C, the reaction chamber, was varied from 95.4 to 23.2 μ Torr by surrounding the cold finger containing the Hg beneath the reaction vessel with various coolants. A low pressure Hg lamp, Model SL 2537, was reproducibly located about 2 cm from the Vycor window, V_2 , and monitored through V_1 . The flux of O_2 filtered Lyman alpha radiation before (I_0) and after admission of hydrogen (I), was assumed to be proportional to the current produced in the detector

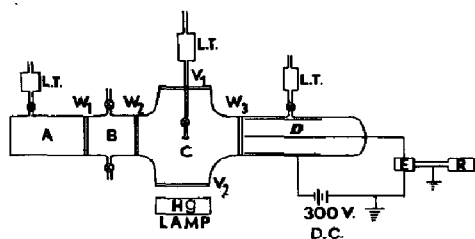


Fig. 1. Schematic diagram of the apparatus.

and measured using a Keithley Model 610C Electrometer, E, and recorded using a Keithley Model 370 recorder, R.

Procedure

A known pressure of reactant gas [H_2 , HD or D_2 , in these experiments], measured using a calibrated oil manometer, was slowly introduced through the liquid nitrogen trap after the apparatus had been switched on and allowed to reach a stationary state for measurement of I_0 . [D_2 was used only as a check on the sharpness of the Lyman alpha line; no absorption by D atoms was detected.] The reaction vessel was isolated from the cold trap and sufficient time was permitted to elapse for convective mixing with the Hg vapor and the equilibration of the latter with the cooled Hg liquid in the cold finger. The attenuated Lyman alpha flux, I , was then measured. The observed transmittance, T , was defined as follows: $T = I/I_0$.

RESULTS

The absolute cross-sections for H atom production from $Hg(^3P_1) + H_2$ and $Hg(^3P_1) + HD$ were measured under identical experimental conditions by monitoring the attenuation of the Lyman alpha beam reaching the detector. The Hg

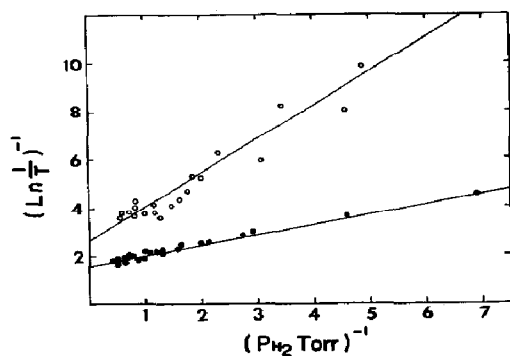


Fig. 2. Graph of $[\ln(1/T)]^{-1}$ vs. $P_{H_2}^{-1}$. ●, $P_{Hg} = 8.1 \times 10^{-5}$ Torr; ○, $P_{Hg} = 2.32 \times 10^{-5}$ Torr.

vapor was varied as stated earlier and the entire apparatus was at room temperature, 18°C, unless otherwise stated. At constant mercury vapor pressure, graphs of $[\ln(1/T)]^{-1}$ vs. $(P_{\text{H}_2 \text{ or HD}})^{-1}$ gave straight lines with positive slopes as illustrated in Figs. 2 and 3. The data extracted from these experiments, including the slope to intercept ratios, are given in Table 1.

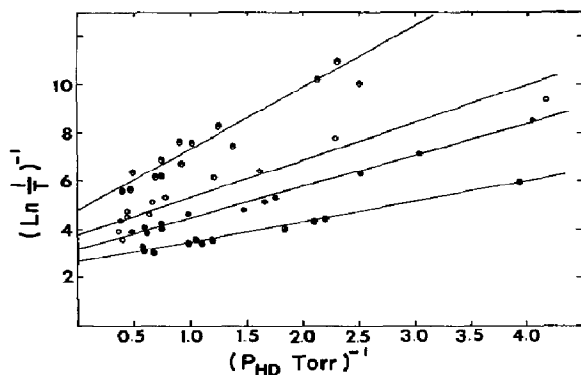


Fig. 3. Graph of $[\ln(1/T)]^{-1}$ vs. P_{HD}^{-1} , \oplus , $P_{\text{Hg}} = 9.54 \times 10^{-5}$ Torr; \bullet , $P_{\text{Hg}} = 6.9 \times 10^{-5}$ Torr; \circ , $P_{\text{Hg}} = 4.81 \times 10^{-5}$ Torr; \ominus , $P_{\text{Hg}} = 2.45 \times 10^{-5}$ Torr.

TABLE 1

QUENCHING CROSS-SECTIONS OF HYDROGEN AND HYDROGEN DEUTERIDE BY LYMAN ALPHA ABSORPTION TECHNIQUE

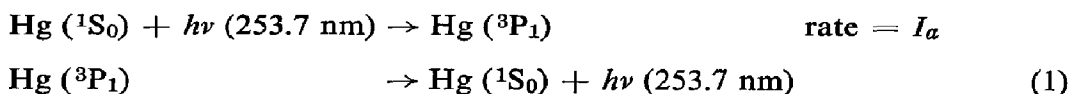
| Compound | $S/I \times 10^4$ (mol/l) | $(\text{Hg}) \times 10^{-12} \times l$ (atom cm^{-2}) | τ/τ_0 | k_1 (or k'_1) $\times 10^8$ (s^{-1}) | $k_0 \times 10^{14}$ ($1 \text{ mol}^{-1} \text{ s}^{-1}$) | σ^2 (nm^2) |
|----------------|------------------------------|--|---------------|---|---|---------------------------------|
| HD | 0.16 ± 0.01 | 7.3 | 1.80 | 4.87 | 3.15 ± 0.23 | 0.117 ± 0.007 |
| | 0.17 ± 0.03 | 7.14 | 1.80 | 4.87 | 2.91 ± 0.44 | 0.105 ± 0.016 |
| | 0.22 ± 0.01 | 4.98 | 1.50 | 5.85 | 2.65 ± 0.16 | 0.097 ± 0.006 |
| | 0.23 ± 0.03 | 3.69 | 1.30 | 6.74 | 3.04 ± 0.43 | 0.112 ± 0.015 |
| | 0.28 ± 0.04 | 1.84 | 1.00 | 8.78 | 3.15 ± 0.39 | 0.115 ± 0.014 |
| H ₂ | 0.16 ± 0.01 | 6.5 | 1.71 | 5.12 | 3.35 ± 0.14 | 0.10 ± 0.005 |
| | 0.28 ± 0.03 | 1.84 | 1.00 | 8.78 | 3.24 ± 0.4 | 0.097 ± 0.004 |

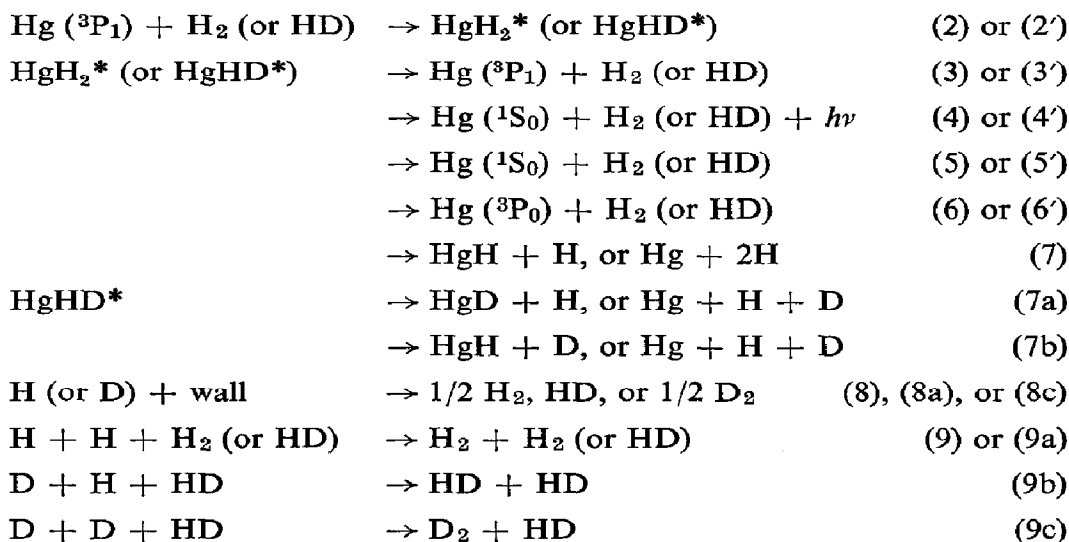
$$\sigma^2_{\text{O}_{\text{HD}}} \text{ (average)} = (0.109 \pm 0.012) \text{ nm}^2.$$

$$\sigma^2_{\text{O}_{\text{H}_2}} \text{ (average)} = (0.100 \pm 0.004) \text{ nm}^2.$$

DISCUSSION

The general mechanism for the interaction of hydrogen and Hg, appropriately modified to include the special case of HD, has been proposed⁵ as follows:





The complex HgH_2^* (or HgHD) has been postulated by Gunning *et al.*¹⁶ in systems containing hydrogen and is included here. It may be the insertion complex, H-Hg-H or H-Hg-D of Callear and McGurk¹¹. Regardless of its structure, it need be observed that the u.v. monitor located outside of V_1 showed no change when either H_2 or HD was admitted to the reaction zone suggesting that collision-induced fluorescence, *i.e.* reactions (4) and (4') are negligible. Reaction (6) has been shown to be negligible in kinetic flash photolysis experiments^{17,18} and is neglected in subsequent considerations. Reactions (7) and (7a) and possibly (7b) are believed to be the principal sources of H atoms in these experiments. The H (or D) atoms so produced may be removed by either reactions (8) or (9) or some combination of both. The three body recombination rate constant has been recently reported for reaction (9) as $8.3 \pm 0.4 \times 10^{-33} \text{ cm}^6 \text{ s}^{-1} \text{ molecule}^{-1}$ at room temperature in the pressure range 2 to 12 Torr¹⁹. This suggests that reaction (9) may be neglected when compared with reaction (8), since $k_8 = 5 \text{ s}^{-1}$ was reported by Michael and Osborne²⁰ for a reaction system of almost identical geometry in their study of the effect of added H_2 and Hg concentration on the H atom decay time. Therefore, reactions (9)–(9c) will be neglected in the subsequent discussion of these experiments. The rate constant k_8 is taken to be independent of pressure, in accordance with direct experimental determinations made in this laboratory (Jane-huey Hong, Ph. D. thesis).

Assuming a photostationary state for the intermediates $\text{Hg } (^3P_1)$, HgH_2^* , and H, the following equation can be derived for the system containing H_2 :

$$(\text{H})_{\text{ss}} = [k_7/k_8] [k_2\tau I_a (\text{H}_2)/k_1 + k_2 (\text{H}_2) - k_2k_3\tau(\text{H}_2)]$$

where $(\text{H})_{\text{ss}}$ is the steady state H atom concentration, τ is the lifetime of HgH_2^* , $(1/k_3 + k_5 + k_7)$, (H_2) is the concentration of molecular hydrogen, and the k 's refer to the specific rate constants for the reactions subscripted. For small absorp-

tion of the Lyman alpha radiation, Beer's law may be assumed to be valid and the following equation derived:

$$[\ln(1/T)]^{-1} = [k_8 - k_3 k_8] / \epsilon I_a k_7 + k_1 k_8 / \epsilon I_a k_2 k_7 \tau(\text{H}_2)$$

where all the terms have been previously defined except ϵ , the extinction coefficient for H atoms, and l , the optical path length of the Lyman alpha radiation. Therefore, a graph of the left-hand side of the above equation vs. $1/P_{\text{H}}$ is predicted to be linear as observed in Fig. 2 provided the vapor pressure of Hg is constant. Furthermore, the ratio of the slope to the intercept, leads to $S/I = k_1/k_2 f = k_1/k_Q$, where f is the fraction of HgH_2^* which leads to deactivation of the Hg ($^3\text{P}_1$), and k_Q is the sought after quenching rate constant. Finally k_Q may then be related to the quenching cross-section, σ^2 , by:

$$k_Q = \sigma^2 [8\pi RT(M_{\text{Hg}} + M_Q)/M_{\text{Hg}}]^{1/2}$$

where the M 's are the molecular weights of Hg and quencher, respectively, and the other terms have their usual definitions. Using identical reasoning it may be shown that similar equations apply to the situation when HD is substituted for H_2 and the ratio, $S/I = k_1/k'_Q$. Therefore, an exact knowledge of k_1 is necessary for the accurate calculation of k_Q and k'_Q .

In order to obtain k_1 , the *effective* rate of emission of resonance radiation by Hg ($^3\text{P}_1$), it is necessary to make a correction for imprisonment of the radiation. This is done by taking the ratio of the ratios of slopes to intercepts, *i.e.* $[(S/I)_{\text{Hg}=0} / (S/I)_{\text{Hg} \neq 0}] = (k_1)_0 / k_1 = \tau / \tau_0$, where τ_0 is the lifetime of an isolated Hg ($^3\text{P}_1$) atom, $1.14 \times 10^{-7} \text{ s}^{18}$. Since measurements of (S/I) were made at a variety of known pressures of Hg, it was possible to calculate τ / τ_0 values, plot them against the parameter $[(\text{Hg}) \cdot l]$, where $l = 2.31 \text{ cm}$ for this geometry, and compare the results with those obtained by other investigators. The results, shown in Fig. 4, compare very well with

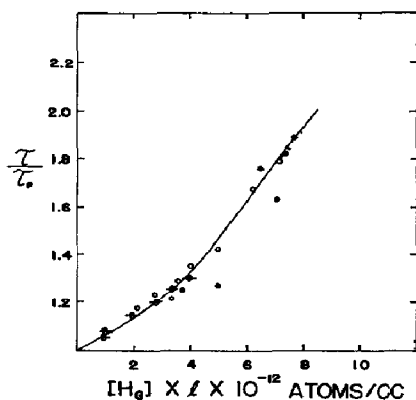


Fig. 4. Ratio of the imprisonment lifetime to the natural lifetime as a function of opacity. O, Michael and coworker's work; ●, this work; ◐, Yang's work.

earlier studies and support the technique as a valid method of determining k_Q and the quenching cross-sections.

Inspecting the data reported in Table 1, a variation in (S/I) of almost a factor of two is observed for both H_2 and HD in the range of Hg pressures studied and is directly attributable to radiation imprisonment. To within the accuracy of the measurements k_Q is identical for both H_2 and HD. When corrected to the same scale, Yang's cross-sections for H_2 and HD, *i.e.* 0.091 and 0.099 nm², compares well with the average cross-sections of Table 1, *i.e.*, 0.100 and 0.109 nm² and is in agreement with the observations of Callear and McGurk. Thus, regardless of whether variations in σ^2 are attributed to the qualitatively electrophilic character of excited mercury atoms in the (3P_1) state²¹, or quantitatively to the strength of the bonds being broken and made through a "bond energy-bond order" empirical computation²², the fact must be faced that any H_2 /HD isotope effect for quenching of Hg (3P_1) is either non-existent or beyond the precision of the current measurements. The data, in fact, support Callear and McGurk's postulate that reaction (2) is an insertion reaction resulting in a very unstable and energetic H-Hg-H molecule in its triplet state. The isotope effects found by Callear and McGurk for reactions (7a) and (7b) for HD are not inconsistent with the data reported here (direct measurement of the H atoms produced in the primary quenching act) or with the data obtained by Yang using a physical method (attenuation of fluorescence) and a "chemical" method (comparison of stable product yields) when the much higher pressures employed in the flash photolysis experiments are taken into consideration.

There remains some uncertainty concerning the mechanism of removal of HgH.

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