Conclusion

1. Monodeuteromethane, tetradeuteromethane, monodeuteroethane, monodeuteropropane-1 and monodeuteropropane-2 have been synthesized and their mass spectra determined on a Nier type and a Consolidated mass spectrometer.
2. A method of calculating the mass spectrum of monodeuteromethane and monodeuteroethane from the corresponding light hydrogen compounds, has been indicated.
3. A method has been given to indicate the position of a deuterium atom in monodeuteropropanes.

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[CONTRIBUTION FROM CHEMICAL LABORATORY, UNIVERSITY OF MISSOURI]

The Quantum Efficiency of the Mercury Sensitized Photochemical Decomposition of Hydrogen

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Introduction

The reaction between mercury atoms excited by absorption of light of λ 2537 Å. and hydrogen molecules to produce hydrogen atoms was reported by Cario and Franck[1] in 1922. The analogous reaction between hydrogen molecules and mercury atoms excited by streaming electrons of controlled energy through the gas mixture has been carried out.[2] These and more recent studies in this laboratory have indicated that the 6^3P_1 state of mercury to which the photochemical reaction is ascribed may play only a slight part, if any, in the electron initiated reaction. The immediate occasion for undertaking the present study is to obtain the necessary reaction rate data to compare the kinetics of the electron and photon activated reactions in the hope that the mechanism of the former will be clarified.

Attention has been devoted by a number of investigators—Stuart, Zemansky, Bates[3] and Evans[4]—to the quenching of fluorescent resonance radiation from Hg^3P_1 atoms by collision of the Hg^3P_1 atoms with added foreign gas molecules. An over-all effective cross section for quenching is obtained through the method but it is not possible to distinguish between processes which may contribute to the quenching. By the method of the present paper it appears possible to determine the effective cross section for a specific process, *i.e.*, the interaction of Hg^3P_1 atoms with hydrogen molecules to cause their removal from the gas phase, presumably through dissociation.

Experimental

The reaction system and light source are shown in Fig. 1. The reaction cell is a cylinder of fused silica which has an internal length of 3.53 cm. and an internal diameter of 2.25 cm. The walls of the cell are lined with a thin cylinder of oxidized copper. The ends of the cylinder are flat polished fused silica windows 2 mm. thick and are fused on. The cell is attached to the rest of the system, which is of Pyrex, by a graded seal. The Pirani gage consists of a 0.0025 cm. platinum filament mounted as shown and immersed in a kerosene filled thermostat which is maintained at 30°. Precaution was taken to prevent a film of kerosene, which was found to absorb λ-2537, from creeping over the entrance window. The system in the thermostat was connected through a U-tube and mercury cut-off to a conventional high vacuum system with mercury condensation pump, McLeod gage, mercury cut-offs, and with no stopcocks in the high vacuum line. Hydrogen was admitted from a gas flame through a palladium tube. The pressure was brought to the desired values, as shown by the McLeod gage, through manipulation of the flame and cut-offs.

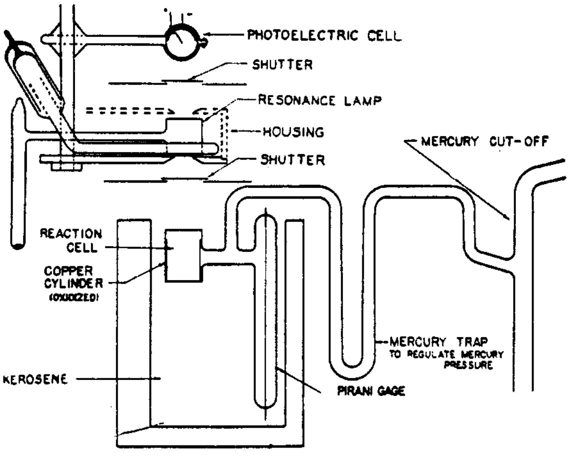

Fig. 1.—Experimental apparatus.

The light source is a monochromatic resonance lamp[5] which operates several degrees above room temperature and gives a very narrow line breadth—about 20% greater than the Doppler breadth at 30°. A fused silica photoelectric cell with a cadmium coated cathode was mounted above the resonance lamp as shown and served as a check on the lamp intensity. The intensity of λ 2537 in this upper position was strictly proportional to that at the reaction cell window when the mercury vapor pressure in the resonance lamp cylinder was kept constant. The procedure in taking data is as follows: The thermostat is replaced by an oven. Oxygen is admitted to the system to about 10 mm. pressure. When the oven temperature becomes sufficiently high the oxygen pressure starts to diminish due to consumption by the copper of

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[1] Cario and Franck, *Z. Physik*, **11**, 155 (1922).

[2] Glockler and Thomas, THIS JOURNAL, **57**, 2352 (1935).

[3] A. C. G. Mitchell and M. W. Zemansky, "Resonance Radiation and Excited Atoms," Cambridge University Press, 1934.

[4] Evans, *J. Chem. Phys.*, **2**, 445 (1934).

[5] Thomas, *Rev. Sci. Inst.*, **12**, 309 (1941).

the cylinder. After the oxygen pressure has diminished about 1 mm. the oxygen is pumped out and the system is baked and flamed while open to the pumps. The thermostat is then replaced, the temperature of a mercury droplet introduced to the U-tube is set at the desired value, hydrogen is introduced to the desired pressure, and the cut-off to the reaction system is closed. After bringing the Pirani gage to balance and bringing the lamp to a steady intensity, the foot-operated shutter below the resonance lamp is opened for a measured time interval. This interval is regulated from four to sixty seconds, depending on the pressures of hydrogen and mercury vapor in the system, to give a Pirani galvanometer excursion of from 10 to 30 scale divisions (readable to 0.1 division), which corresponds to the disappearance of less than 10^{-10} gram of hydrogen. After about five such average exposures the baking-out procedure is repeated. This is necessary because it was found that the observed rates of decomposition began to decrease measurably with total decomposition in excess of this amount. This effect seems to be attributable to the inability of the silica surface to maintain its full capacity for removal of the products of the reaction. All of the data reported in this paper were taken in the initial period after baking out and forming a fresh oxide surface when the reaction rates at a given set of concentration and radiation conditions were quite constant and at a maximum.

The lamp intensity was determined by use of two multiple junction bismuth–silver vacuum thermopiles, one bismuth–(bismuth, 5% tin) vacuum thermopile, two quartz–cadmium photocells, the chloroacetic acid actinometer, and two N.B.S. calibrated lamps along lines described earlier.[6] Ten sets of determinations of the resonance lamp intensity gave 25.6×10^{12} quanta entering the reaction vessel per second for unit (upper position) photocell galvanometer deflection. The absorption (including reflection) of light from the resonance lamp and N.B.S. standard lamps in thermopile and reaction cell windows was measured and the proper corrections were made. As a check on the reliability of the lamp standardization the quantum yield of the chloroacetic acid hydrolysis was run. A quantum yield of 0.29 at 26° was found, which is to be compared with the value 0.33 obtained by Smith, Leighton and Leighton.[7] (The value of 0.342 previously given by Thomas[6] should be revised to 0.29 when correction is allowed for absorption of the radiation of the N.B.S. lamps in the two mm. fused silica ground and polished windows of the thermopiles.)

The absorption for the resonance lamp by the mercury vapor in the reaction cell was calculated from measurements made in a cell similar to the reaction cell but of better optical quality and described with equations used in reference 5. The value of ω (ref. 5, p. 311) was found to be approximately 1.2 and the integral expression with this value of ω and the "l" for the reaction cell of Fig. 1 was used to calculate the absorption in the reaction cell at the various pressures of mercury vapor. This absorption, multiplied by the number of quanta entering the cell per second per unit photocell galvanometer deflection, is plotted in Fig. 2, Curve A.

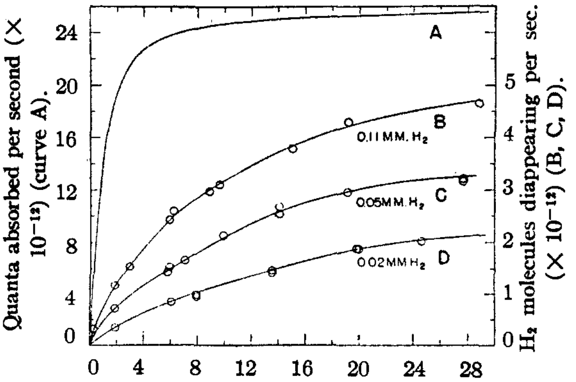

Fig. 2.—Experimental data.

The Experimental Data

The measurements were made at three hydrogen pressures, 0.02, 0.05 and 0.11 mm. over a range of mercury vapor pressures from 0.3×10^{-4} to 30×10^{-4} mm. These data, expressed in hydrogen molecules disappearing per second per unit photocell galvanometer deflection (photocell mounted above resonance lamp), are shown plotted against the pressure of mercury vapor in Fig. 2, Curves B, C, D. Most of the points shown in these curves represent an aggregate of several points so closely placed that they could not be plotted distinctly on a graph of this scale. The data considered in determining the curves are given below in Table I under the column headings I and II, representing, respectively, the mercury vapor pressure in mm. $\times 10^4$ and the rate of removal of hydrogen in molecules per second per unit photocell galvanometer current $\times 10^{-12}$. The number of separate measurements taken to obtain the average value given is indicated by the numbers in parentheses in case of more than one. Column III lists the quanta of λ 2537 ($\times 10^{-12}$) absorbed in the cell per second per unit photocell current over the range of mercury vapor pressures. These are plotted in Curve A, Fig. 2.

TABLE I

REACTION RATE MEASUREMENTS AND LIGHT ABSORPTION IN THE CELL

I, Pressure of Mercury Vapor ($\times 10^4$). II, Hydrogen molecules removed per second per unit photocell current ($\times 10^{-12}$). III, Quanta of λ-2537 absorbed within cell per second per unit photocell current ($\times 10^{-12}$).

0.11 mm. H_2		0.05 mm. H_2		0.02 mm. H_2			
I	II	I	II	I	II	I	III
0.3	0.277	1.85	0.70 (3)	1.85	0.303 (3)	0.0	0.0
1.85	1.22 (5)	1.85	0.694 (3)	1.85	0.3 (3)	1.0	14.3
2.95	1.53 (2)	5.8	1.42 (2)	6.0	0.83 (3)	2.0	19.5
5.8	2.37 (3)	5.9	1.54 (3)	6.1	0.848	4.0	22.8
5.9	2.415 (2)	7.05	1.65 (3)	7.95	0.945 (3)	8.0	24.5
6.2	2.62	9.9	2.14	13.5	1.44 (2)	16.0	25.1
8.7	2.86	14.05	2.60 (3)	19.8	1.91 (2)	24.0	25.4
8.9	2.97	19.15	3.02 (2)	19.95	1.87 (2)		
9.0	3.12	27.7	3.15 (2)	24.6	2.01		
9.6	3.10	27.7	3.20				
15.1	3.78 (3)						
19.15	4.3						
28.8	4.65 (3)						

Discussion

To express the data in more significant form, curves were put through the experimental points (Curves B, C, and D of Fig. 2) and the ordinates of these curves were divided respectively by the ordinates of Curve A, Fig. 2 at corresponding abscissas. The resulting values are plotted in Fig. 3 for each of the hydrogen pressures investigated. The ordinates of these curves are the quantum efficiencies at the various mercury vapor

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(6) L. B. Thomas, THIS JOURNAL, **62**, 1879 (1940).

(7) Smith, Leighton and Leighton, *ibid.*, **61**, 2299 (1939).

pressures. It is seen that the quantum efficiency rises markedly over the mercury pressure range—more than eight-fold at 0.02 mm. hydrogen and 4 fold at 0.11 mm. hydrogen pressure. At the pressure conditions of these experiments the chance that the Hg^3P_1 atoms will radiate is much greater than the chance that they will be quenched. The increasing quantum yield with increasing mercury pressure is due no doubt to the increasing reabsorption of fluorescent λ 2537 within the reaction cell. One of the problems of this paper is to give a quantitative statement of the contribution of this reabsorption process to the reaction kinetics.

The curves of Fig. 3 permit quite definite extrapolation to the axis of zero mercury vapor pressure. The limiting values of the quantum efficiencies at zero mercury vapor pressure are 0.0095 at 0.02 mm. of hydrogen; 0.023 at 0.05 mm. of hydrogen; and 0.045 at 0.11 mm. of hydrogen. These extrapolated values should give the probabilities that single mercury atoms excited to the $^3P_1$ state will react with hydrogen molecules at the specified pressures to cause disappearance of the hydrogen from the gas phase and they should be free from complications resulting from reabsorption of the fluorescent quanta. They may be used to calculate the effective cross section for the process through use of the collision frequency expression: $Z = 5.64 \times 10^5 n_{H_2} \cdot n_{Hg^*} \cdot \sigma^2$ (for hydrogen and mercury at 30°) in which σ^2 is often termed the "effective cross section" for the given process.[3] To apply the present case consider the absorption of one quantum per cc. per second. Then the number of effective collisions per cc. per second, Z, becomes the quantum efficiency, ϕ, and the n_{Hg^*} becomes the product of τ, the average life of the Hg^3P_1 state (1.07×10^{-7} sec.), and $(1 - \phi)$. Substitution of the appropriate values in (1) gives for the intercept with 0.02 mm. of hydrogen:

$$0.0095 = 5.64 \times 10^5 \times 6.42 \times 10^{14} \times 1.07 \times 10^{-7} (1 - 0.0095)\sigma^2$$

From this, $\sigma^2 = 2.45 \times 10^{-16}$ cm.^{2} at 0.02 mm. of hydrogen. Similarly σ^2 is found to be 2.43×10^{-16} and 2.21×10^{-16} at 0.05 mm. and 0.11 mm. of hydrogen, respectively. It appears likely that other quenching processes are competing with that resulting in disappearance of hydrogen. The over-all cross section for quenching of Hg^3P_1 atoms by hydrogen is variously given from 27 to 6.01×10^{-16} cm.^{2} by several investigators.[3,4] The last value of Zemansky,[3] confirmed by Evans[4] using the same apparatus and theory, should be most reliable. The ϕ value used in the $\tau(1 - \phi)$ term to calculate n_{Hg^*} should refer to total quenching rather than to dissociation of hydrogen. In calculating the σ^2 values below, the ϕ in $(1 - \phi)$ is multiplied by the ratio of the σ^2 for quenching (σ_Q^2) to the σ^2 for dissociation of hydrogen (σ_D^2). This gives σ_D^2 values 2.50, 2.50 and 2.37×10^{-16} cm.^{2} for $\sigma_Q^2 = 6.01 \times 10^{-16}$ cm.^{2}, or 2.53, 2.57 and 2.51×10^{-16} cm.^{2} for $\sigma_Q^2 = 8.6 \times 10^{-16}$ cm.^{2} given earlier by Zemansky.[3] The value 2.5×10^{-16} cm.^{2} is selected for σ^2 for the process resulting in disappearance of hydrogen from the intercept measurements.

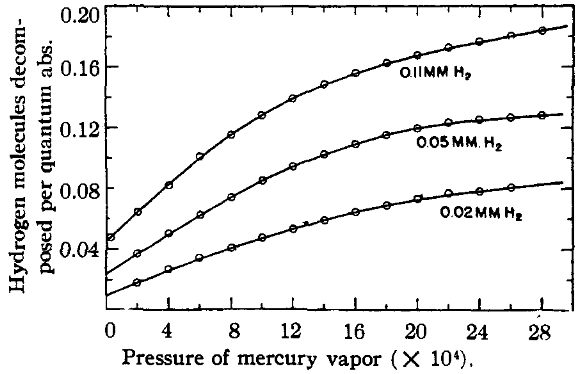

Fig. 3.—Quantum efficiency.

A series of reactions which constitutes the mechanism will be postulated and on the basis of this mechanism the rate constants and the contribution of the reabsorption of fluorescent radiation to the reaction rates will be determined. The reactions postulated are: 1, absorption of λ 2537 quanta by the mercury atoms in the gas mixture; 2, fluorescence of λ 2537 quanta followed by partial reabsorption to an extent depending on the mercury atom concentration; 3, reaction of Hg^3P_1 atoms resulting in dissociation of hydrogen; 4, collision of Hg^3P_1 atoms and hydrogen resulting in quenching of the Hg^3P_1 atoms but not resulting in dissociation of hydrogen. These processes may be written as

(1) $Hg^1S_0 + h\nu\ (\lambda\ 2537) \longrightarrow Hg^3P_1$
(2) $Hg^3P_1 \longrightarrow Hg^1S_0 + h\nu\ (\lambda\ 2537)$
(3) $Hg^3P_1 + H_2 \longrightarrow Hg^1S_0 + 2H + \text{K. E.}$
(4) $Hg^3P_1 + H_2 \longrightarrow Hg^1S_0 + H_2 + \text{K. E.}$

The removal of Hg^3P_1 atoms by Process (2) is greatly modified by reabsorption by the Hg^1S_0 atoms. It is desired that Process (2) represent the net fluorescence, *i.e.*, only those quanta that leave the reacting mixture should be counted as fluorescence. The remainder of the quanta are supplied for repetition of Process (1). It is seen from superficial examination of Fig. 3 that the number of quanta supplied for Process (1) by Process (2) may be of the order of eight times as great as that supplied directly from the lamp. The velocity constant for Process (2) is simply the Einstein "A" coefficient or the reciprocal of the mean life, τ, of the 6^3P_1 state, and this will be modified to represent the net fluorescence by multiplying by a factor which will be designated F (Hg^1S_0). This function of the concentration of Hg^1S_0, *i.e.*, F (Hg^1S_0), will have the characteristic that it approaches unity as the concentration of Hg^1S_0 atoms approaches zero, and it tends toward zero as (Hg^1S_0) becomes large. F(Hg^1S_0) may be defined as the mean probability that a quantum of fluorescent radiation will escape reabsorption within the reaction system. It is of course a function of the size and shape of the reaction vessel as well as the mercury vapor pressure.

Reaction (3) represents the main feature of the Cario and Franck reaction, *i.e.*, a collision of the second kind with utilization of the energy of excitation of mercury atoms to supply the energy of dissociation of hydrogen.

It appears necessary to postulate reaction (4) to take into consideration the above-mentioned variance of σ_Q^2 and σ_D^2, and to develop a proper over-all kinetic expression to fit the data. Reaction (4) represents a process unspecified as to detail whereby mercury atoms lose their excitational energy at a rate proportional to the hydrogen pressure but the process does not result in a pressure decrease as would be expected if dissociation occurred. This proposed process would contribute to the over-all kinetics in somewhat the same manner as would failure of the apparatus to achieve complete clean-up of the H atoms by a factor proportional to the hydrogen pressure but this, as is discussed later, is not thought to be the case. Reaction (4) would, superficially at least, be considered improbable because of the larger (than reaction (3)) amount of kinetic energy developed. However, if the hydrogen molecule comes out of the collision in a high vibrational state, this kinetic energy term would not necessarily be much larger than the 0.3 e.v. of reaction (3).

One can write many other reactions which conceivably could occur under the conditions of this experiment. There is no doubt some production of Hg^3P_0 metastable atoms from collision of Hg^3P_1 atoms with Hg^1S_0 atoms or hydrogen molecules. The possibility was considered that the equivalent of reaction (4) might occur through conversion of Hg^3P_1 atoms to Hg^3P_0 atoms by collision with hydrogen if the Hg^3P_0 atoms were unable to react efficiently with hydrogen to give a pressure decrease. The results of Meyer[8] (which we have confirmed with monochromatic λ 2537) indicate that the Hg^3P_0 atoms can react with hydrogen. The effective cross section for the reaction may be quite low and still give the observed augmented reaction rate with nitrogen added because, with the great excess of nitrogen used, the diffusion time of the Hg^3P_0 atoms (formed by collision of Hg^3P_1 atoms with nitrogen) to the wall would allow a great many collisions with hydrogen. At the pressure conditions of the present work the Hg^3P_0 atoms would mostly reach the wall (if the Hg^3P_0–H_2 cross section were low). However, against this mechanism for reaction (4) is the fact that the first vibrational quantum of hydrogen is approximately 0.5 e.v. which leads one to expect low probability of conversion of Hg^3P_1 to Hg^3P_0 atoms which involves only 0.218 e.v.(see ref. (4), p. 450, or ref. (3), p. 225).

On the basis of Reactions (1) to (4) one obtains an expression for the rate $R = -d(H_2)/dt$ in terms of the constants, concentrations, and I_a, which is the number of quanta absorbed per (cc. × sec.). Noting that the quantum yield, $\phi = R/I_a$, one obtains the expression:

$$\frac{1}{\phi} = \frac{k_2F(Hg^1S_0)}{k_3(H_2)} + \frac{k_3 + k_4}{k_3}$$

If the postulated mechanism fits the reaction, the data of Fig. 3 plotted as $1/\phi$ *vs.* $1/(H_2)$ should give straight lines with slopes $k_2F(Hg^1S_0)/k_3$ and a common intercept of $(k_3 + k_4)/k_3$. Figure 4 shows the data at the three hydrogen pressures plotted for seven values of pressure of mercury vapor. It is seen that the plots do give quite closely a family of straight lines with a common intercept. The intercepts lie between 4.0 and 5.5 with an average about 4.5 for $1/\phi$. Since Curve A, Fig. 4, is for $(Hg^1S_0) = 0$, the value of $F(Hg^1S_0)$ is unity and the slope of this curve, 1.96, is the ratio k_2/k_3. The value of k_2 is the Einstein "A" coefficient for the transition $6^3P_1 \rightarrow 6^1S_0$ and has the value $1/\tau = 1/1.07 \times 10^{-7}$, hence $k_3 = 1/1.07 \times 10^{-7} \times 1.96 = 4.77 \times 10^6$. This is the velocity constant for the reaction (3) in the postulated mechanism and this work constitutes, so far as we are aware, the only attempt at its measurement for this classic reaction. The above constant gives the rate at 30° in molecules of hydrogen per cc. decomposed per second per millimeter of hydrogen pressure per unit concentration of Hg^3P_1 atoms in atoms/cc. If the hydrogen concentration is expressed in molecules per cc. instead of millimeters of pressure, k_3 becomes $4.77 \times 10^6/3.20 \times 10^{16} = 1.49 \times 10^{-10}$. It is of interest to calculate the collision cross section from this constant and to compare with the result obtained previously. In the collision frequency expression Z may be set equal to k_3 when $n_{H_2} = 1$ and $n_{Hg^*} = 1$. The value of σ^2 is found to be 2.64×10^{-16} cm.^{2} as against 2.50×10^{-16} found from consideration of the intercepts of Fig. 3 and published values of σ_Q^2.

It has been pointed out that the intercepts of the lines on Fig. 4 on the $1/\phi$ axis average about 4.5 which is, according to the postulated mechanism, $(k_3 + k_4)/k_3$. The value of k_4/k_3 is 3.5 and $k_4 = 3.5 \times 1.49 \times 10^{-10} = 5.22 \times 10^{-10}$. One would expect so far as the extrapolation to infinite hydrogen pressure, *i.e.*, $1/(H_2) = 0$, is valid that the intercept value, 4.5, would agree with the σ_Q^2/σ_D^2 ratio. It is larger than the ratios obtained using either of the σ_Q^2 values previously mentioned (8.6 and 6.01 × 10^{-16} cm.^{2}) and σ_D^2 (2.64 × 10^{-16}) which give 3.3 and 2.3, respectively. Larger values of σ_Q^2 have been reported but are considered less reliable.[3] This discrepancy, if real, is perhaps explainable on the assumption of a collision-induced emission of λ 2537 (by hydrogen on Hg^3P_1 atoms) with the line sufficiently broadened to allow these quanta to escape reabsorption. These quanta would be quenched from the stand-

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(8) Meyer, *Z. Physik* **37**, 639 (1926).

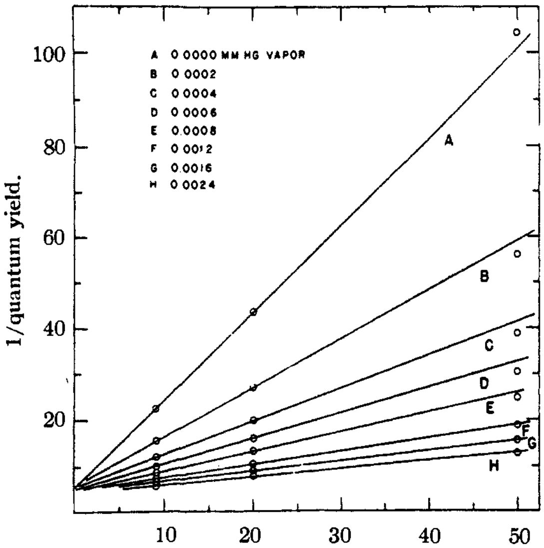

Fig. 4.

point of the present experiment but would show up as fluorescence in the quenching studies.

The ratios of the slopes of the lower lines of Fig. 4 to that of the upper line (A), for which F(Hg^1S_0) is unity, are the values for F(Hg^1S_0) for the various pressures of mercury vapor. These values are plotted in Fig. 5, Curve A. The ordinates of this curve are the probabilities, for the mercury vapor pressures in the particular vessel used, that a quantum of λ 2537 emitted as fluorescent radiation will escape reabsorption within the bounds of the vessel. The quantity [1 − F(Hg^1S_0)] is then the probability that the fluorescent quantum will be reabsorbed, and, since the time spent by a quantum of energy as radiation is negligible compared to τ, the same quantity may be interpreted as the fraction of the quanta of energy, present in the system with the light source on, which are still present at the time, τ, after the light source is cut off. Also $[1 - F(Hg^1S_0)]^n$ is the fraction of quanta still in the system after $n\tau$. This leads to an exponential decay function for the intensity of radiation emitted after excitation is cut off and we may write approximately $I_t/I_0 = [1 - F(Hg^1S_0)]^n = e^{-\beta t}$ in which $t = n\tau$. The values of β calculated from F(Hg^1S_0) are shown in Fig. 5, Curve C. It is possible to estimate β theoretically through a series of methods due to Milne, Zemansky, Samson, Kenty, summarized in reference (3), p. 228 *et seq.* It is necessary to consider a distance, l, through which the radiation must diffuse which we have estimated as 1.125 cm., the radius of the reaction vessel. The values of β so calculated are shown in Curve B, Fig. 5. The experimental values from F(Hg^1S_0) deviate an average of 10% from the calculated values over the range of mercury vapor pressures shown. The agreement is of about the same order as that obtained by comparison of direct measurements of β with the calculated values.[3] Such close agreement must be regarded as fortuitous but the fact that it was possible to arrive, through treatment of the data of this paper, at the F(Hg^1S_0) values which are consistent with existing theory and experiment applied to the "imprisonment" of resonance radiation in the strictly physical (not chemically reacting) system, mercury vapor, seems to support the essential validity of the data and its treatment.

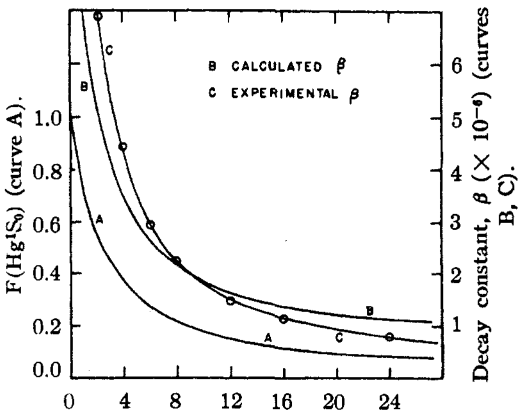

Fig. 5.

We have carried through an application of Milne's theory of the diffusion of "imprisoned" resonance radiation to calculate the number of Hg^3P_1 atoms present in the system and thence the rate of disappearance of hydrogen, *i. e.*, Curve B, C, D, Fig. 2. The expression for the rate involves two effective cross sections, one for reaction (3) of this paper and the other for over-all quenching of Hg^3P_1 atoms by H_2. It is found that rate curves of the general characteristics of B, C, D, Fig. 2 are obtained and that quantitative agreement with experiment is much better if the σ_D^2 and σ_Q^2 values 2.5×10^{-16} from this work and 8.6×10^{-16} cm.^{2} from ref. (3) both are used than if either value is used as the sole cross section involved.

The question arose in conversation with J. Franck as to the possibility that these experiments might be used to distinguish between the two proposed mechanisms involving direct dissociation of hydrogen molecules as against formation of mercury hydride in the process. If one assumes that the hydrogen in the mercury hydride is not cleaned up and is eventually returned as hydrogen to the gas and if one assumes that no other quenching processes than one of the two proposed are involved, a study of the quenching externally and hydrogen removal internally should be able to distinguish between the two mechanisms. One quantum per hydrogen molecule disappearing would be quenched in the first case and two quanta in the second case. Quenching measurements have been made giving an estimated quenching, averaged over the surface of a sphere concentric with and about the cylinder, of

3.5 times the quantum yield observed internally. This is again a measure of σ_Q^2/σ_D^2 and constitutes further confirmation that one or more other quenching processes than that resulting in hydrogen removal is in preponderance. It seems doubtful then that the two mechanisms can be distinguished by this means.

An important assumption upon which the validity of much of the interpretation of the data of this paper rests is that the cleanup of the supposed atomic hydrogen produced is complete. This would be a very difficult assumption to demonstrate conclusively by experiment but we have little doubt of its validity because of the evidence presented below. As mentioned in the **Experimental** section of this paper, all of the data presented were taken at the limiting condition of maximum rate following reoxidation of the copper and thorough outgassing of the vessel. The reproducibility and consistency of the data is in itself strong evidence of the essential completeness of the cleanup. It would be difficult to imagine a kind of adsorption process at the silicon dioxide and cupric oxide surfaces which consistently returned a constant fraction of the reaction products as hydrogen to the gas phase. The following experiment substantiates the assumption of complete clean-up. The reaction was carried out in a fused silica cell without any cupric oxide in it. The rate of reaction as observed on the Pirani gage under constant conditions (except for the inside walls) falls gradually to zero when the walls can no longer remove the products and complete recombination of hydrogen atoms then occurs. The rate becomes practically zero when amounts of hydrogen of the order of 100-fold those used in taking the data of this paper were consumed. When the reaction cell with its cupric oxide lining cylinder is used in a similar attempt to exhaust the capacity for removal of the reaction products it is found that the rate falls off less rapidly than in the former case and becomes flat at a fraction of the initial rate which agrees to within a few per cent. with the fraction of the internal area of the vessel which consists of cupric oxide. (These experiments were carried out with the mercury vapor pressure low in order to spread the reaction more uniformly through the vessel.) (One might be tempted to attribute the sustained behavior with cupric oxide to the steady conversion of hydrogen to water, hence due to the smaller heat conductivity of water, the Pirani gage would show a pressure decrease. However, the accommodation coefficients and C_V values of hydrogen and water are such that in the "free molecule" heat conduction range here applicable, water is 40% more effective than hydrogen in heat conduction from bright platinum.[9]) The interpretation then that we place on the above experiments is that both silicon dioxide and cupric oxide have the same initial efficiencies of removal of the reaction products and this is very unlikely unless both efficiencies are unity. That cupric oxide has sustained, constant efficiency is found in the extensive work done in this laboratory with the electron initiated mercury sensitized decomposition of hydrogen in which the reaction region is more completely surrounded with oxidized copper surface and the initial rates are maintained longer than with the silica, copper oxide cell. The electron work shows constancy of clean-up efficiency with varying reaction rate and with varying mercury pressure, complete quantitative reproducibility of data, and is entirely consistent with the assumption of complete clean-up efficiency.

Lastly, mentioned in connection with completeness of cleanup and general validity of the quantum yield measurements, an independent check was made of four points on Fig. 3. A new vacuum and gas handling system, new Pirani gage and electrical measuring system with new calibrations, new reaction cell with reaction volume more completely surrounded with cupric oxide, and a new photocell were used and the uranyl sulfate–oxalic acid actinometer, following the specifications and general procedures of Leighton and Forbes, was used to determine the lamp intensity. The quantum yields at each hydrogen pressure with mercury at 0° and with hydrogen at 0.11 mm. and mercury at 24° were determined. The four new values of ϕ averaged 1.5% (of ϕ) higher than the four original values with a maximum discrepancy of 5.5%, *i. e.*, a ϕ of 0.036 became 0.038 in the new determination.

Summary

The quantum efficiency of the Cario and Franck mercury sensitized decomposition of hydrogen with λ 2537 has been investigated as a function of mercury and hydrogen pressures. On the basis of the postulated mechanism the velocity constant and the effective cross section are determined for the interaction of Hg^3P_1 atoms and hydrogen resulting in disappearance of hydrogen from the gas phase, presumably through dissociation and removal of the resulting hydrogen atoms on cupric oxide or silicon dioxide walls. The contribution of the reabsorption of fluorescent radiation to the efficiency is singled out and from this the time decay constant of λ 2537 from pure mercury vapor in the reaction vessel after excitation is cut off is calculated and compared with physical theory and measurement. The evidence from several aspects indicates consistently that other quenching processes than that resulting in removal of hydrogen are effective and that the rate of quenching of Hg^3P_1 atom is several times as great as the rate of removal of hydrogen from the gas.

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[9] Thomas and Olmer, THIS JOURNAL, **65**, 1036 (1943).