It is exceedingly likely that the pyrolysis and oxidation are similarly complex systems, and we feel that they could be profitably reexamined in the light of the results of this work.

Acknowledgment. The authors wish to express their thanks to other members of the Department of Thermochemistry and Chemical Kinetics for helpful and stimulating discussion of this work.

The Absolute Rate of the Reaction between Excited Mercury Atoms ($^3P_1$) and Ethylene, and the Role of Imprisonment of Resonance Radiation in Fluorescence Experiments

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Abstract: The rate constant (k) of an energy-transfer reaction, $Hg(^3P_1) + {}^1C_2H_4 \rightarrow Hg(^1S_0) + C_2H_4^*$, is determined by measuring the decrease in the intensity of fluorescence, $Hg(^3P_1) \rightarrow Hg(^1S_0) + h\nu$, as a function of ethylene pressure. Quenching data are extrapolated to zero pressure of mercury to eliminate the effect of the imprisonment of resonance radiation. At 25°, k_q is found to be 2.48×10^7 mm^{-1} sec^{-1}, corresponding to a quenching cross section of 48.2 A^2. When mercury pressure, p (mm), is appreciable, the mean life, τ, of the excited state, estimated by using the Stern–Volmer equation, increases with increasing p according to the relation, $\tau = \tau_0(1 + 0.25 \times 10^4 p\rho)$ ($p \lesssim 4 \times 10^{-4}$), where τ_0 ($= 1.08 \times 10^{-7}$ sec) is the mean life of an isolated atom and ρ is the distance in centimeters from the irradiated slab of mercury to the emerging surface of a cell. A diffusion model for the transport of resonance radiation yields the relation $\tau = \tau_0(1 + 0.28 \times 10^4 p\rho)$, which agrees well with experiments.

The quenching of $Hg(^3P_1)$ atoms by various gases plays an important role in the elucidation of structural factors which govern the efficiency of electronic energy transfer.[1] The rates of this quenching can be determined by using the Stern–Volmer equation[2]

$$\frac{Q}{Q_0} = \frac{1}{1 + \tau k_q[M]} \tag{1}$$

where Q and Q_0 denote the intensity of fluorescence, $Hg(^3P_1) \rightarrow Hg(^1S_0) + h\nu$, in the presence and absence of M, and τ is the mean life of the excited state.[3] Quenching data provide τk_q, from which k_q can be estimated, if τ is known. Essentially, this is the method used in the past to determine absolute quenching rates. It is called a physical method, to distinguish it from a chemical method[4] which is often used to determine relative quenching rates. The mean life, τ_0, of an isolated atom is 1.08×10^{-7} sec. In practice, however, appreciable mercury vapor is always present and this greatly complicates the estimation of τ to be used in (1).

The ground-state atoms have a very high absorption coefficient for resonance radiations.[5] For this reason, a photon emitted as fluorescence usually undergoes several absorption–emission processes before it reaches the emerging surface of a cell. Since a photon can be quenched as long as it resides within a cell, the net effect of the above phenomenon, known as imprisonment, is to prolong τ. Thus τ depends both on mercury pressure and on cell geometry. Several theories[6] have been advanced to treat the imprisonment, and the resulting theoretical τ is then used to evaluate k_q from quenching data.[7] Therefore, various assumptions and approximations involved in the theory of imprisonment are inevitably incorporated in presently accepted k_q values.

The major source of error in the theoretical estimation of τ seems to be the idealization of cell geometry. A typical experiment for the investigation employs a flat disk of thickness 1.3 cm and of diameter 5.1 cm. In the theory, such a cell is assumed to be an infinite slab so that the transport equation can be reduced to one dimension. Theoretical τ values estimated on the basis of this idealization agree with experiments only in the order of magnitude.[5,8]

To obtain reliable quenching rates and also to test the theory of imprisonment as applied to the quenching rate calculations, then, it is highly desirable to determine k_q without using a theoretical τ value. This is attempted in the present work.

Since the imprisonment prolongs τ, τk_q estimated from (1) should increase with increasing pressure, p, of

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(1) For example, see (a) A. C. G. Mitchell and M. W. Zemansky, "Resonance Radiation and Excited Atoms," The Cambridge University Press, Cambridge, 1961; (b) R. J. Cvetanović, *Progr. Reaction Kinetics*, **2**, 39 (1964); (c) H. E. Gunning and O. P. Strauz, *Advan. Photochem.*, **1**, 209 (1963).

(2) O. Stern and M. Volmer, *Z. Physik*, **20**, 183 (1919); also see ref 1a.

(3) More properly, τ here should be called an "apparent" or "imprisonment" lifetime. The meaning of τ will be further clarified in the subsequent discussion.

(4) R. J. Cvetanović, *J. Chem. Phys.*, **23**, 1208 (1955).

(5) T. Holstein, *Phys. Rev.*, **72**, 1212 (1947).

(6) For a review, see ref 5.

(7) M. W. Zemansky, *Phys. Rev.*, **36**, 919 (1930).

(8) Actually, the quantity concerned in the investigation of the imprisonment is the decay time of imprisoned resonance radiation, after the exciting beam is cut off. Under experimental conditions commonly used in quenching experiments, where the Stern–Volmer equation is approximately valid, the decay time and τ are the same; hence no attempt is made in the present paper to distinguish between them.

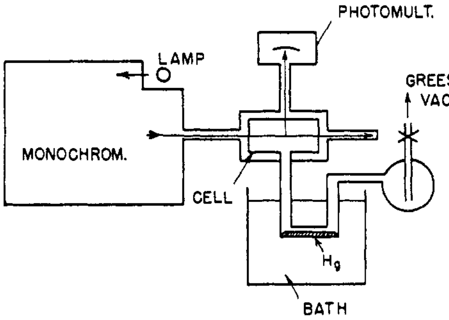

Figure 1. Apparatus used in the investigation of the quenching of fluorescence at different mercury pressures.

mercury. This is confirmed as shown by the following empirical equation.

$$\tau k_q = \tau_0 k_q + \text{constant} \times p \quad (p \lesssim 4 \times 10^{-4}\ \text{mm})$$

Extrapolation to zero p yields $\tau_0 k_q$ which does not contain any contribution from the imprisonment. In this manner, k_q for ethylene at 25° is found to be $2.48 \times 10^7\ \text{mm}^{-1}\ \text{sec}^{-1}$.

Experimental Section

The experimental arrangement is depicted in Figure 1. The 2537-A resonance line from a low-pressure mercury lamp (Pen-ray type, UV Products Inc., San Gabriel, Calif.) was isolated and collimated using a Beckman DU monochromator. The light emerging from a 2-mm slit entered a cell made by fusing two Suprasil disks (2.54-cm diameter) to the ends of a Suprasil tube (4.0 cm long). The cell was placed in a light-tight aluminum block, maintained at 25 ± 1°. Fluorescent light emerging at right angles to the exciting beam was measured by using an IP 28 photomultiplier tube. Mercury vapor pressure was changed by varying the temperature of the mercury reservoir immersed in an ethylene glycol bath. The lowest temperature employed was −16.4° (±0.05°) which was the slurry temperature of ethylene glycol (containing some water as an impurity). Other temperatures, with a maximum deviation of ±0.1°, were obtained by using a refrigerating coil and a heater connected to a temperature controller (Bayley Instrument Co., Danville, Calif.). To reduce the disturbance of mercury vapor pressure at the time of ethylene introduction, a buffer volume of 500 cc saturated with mercury vapor at a given temperature was added in the system. After introduction of ethylene, at least 1 hr was allowed before reading fluorescence intensity. Phillips research grade ethylene, thoroughly degassed by repeated pumping, was used.

Results

Table I. The Quenching of Mercury Fluorescence by Ethylene at Various Temperatures of Mercury Reservoir. Q'/Q_0' is the Ratio of Photocurrent in the Presence and Absence of Ethylene

	Q'/Q_0'		
p, mm	−13.7°	−1.3°	+11.5°
1.03	0.297	...	0.138
0.789	...	0.283	...
0.399	0.502	0.409	0.267
0.199	0.646	0.583	0.407
0.133	0.737	0.655	0.509
0.0998	...	0.744	0.578

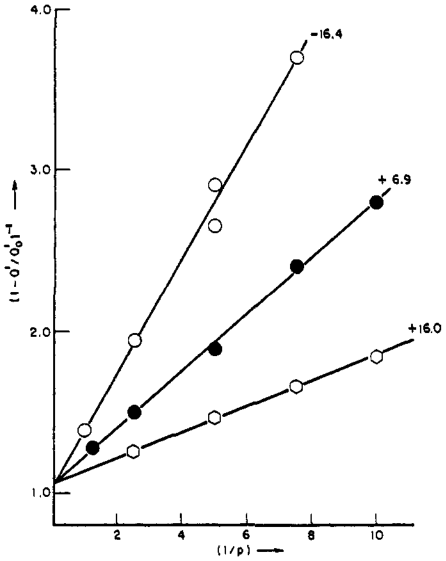

Figure 2. Quenching data plotted according to a modified Stern–Volmer formula (eq 3 in the text).

Examples of experimental data are summarized in Table I. At a given pressure of ethylene, more light is quenched at a higher temperature of mercury reservoir. This agrees with the expected prolonging of τ with increasing p. Experimentally determined photocurrents, Q' and Q_0', where subscript "0" denotes the absence of ethylene, contain contributions from scattered light coming from the sources other than the fluorescence. Error due to this cause is eliminated as follows. When the relations

$$\begin{aligned} Q' &= Q + \Delta \\ Q_0' &= Q_0 + \Delta \end{aligned} \tag{2}$$

where Δ denotes the scattered light are substituted in (1), a modified Stern–Volmer formula results

$$(1 - Q'/Q_0')^{-1} = \alpha + \beta[\text{H}_2]^{-1} \tag{3}$$

where $\alpha = (1 - \Delta/Q_0')^{-1}$ and $\beta = (\tau k_q \alpha)^{-1}$; α/β gives τk_q values free from the contribution from scattered light.[9]

According to (3), the plot of $(1 - Q'/Q_0')^{-1}$ *vs.* $[\text{C}_2\text{H}_4]^{-1}$ should be a straight line. Some examples of this linearity are shown in Figure 2. Table II summarizes τk_q estimated by the least-squares method, the standard deviations being calculated using an approximation

$$\sigma_{\alpha/\beta} = \beta^{-1}[\sigma_\alpha^2 + \sigma_\beta^2(\alpha/\beta)^2]^{1/2}$$

Table II. τk_q Values in the Quenching of Hg($^3P_1$) Atoms by Ethylene at Various Pressures of Mercury[a]

Reservoir temp, °C	Hg pressure, mm × 10^4	τk_q,[b] mm^{-1}
−16.4	0.283	2.98 ± 0.35
−13.7	0.393	3.01 ± 0.14
−7.8	0.779	3.74 ± 0.63
−1.3	1.62	3.59 ± 0.48
+3.1	2.54	4.88 ± 0.26
+6.9	3.65	5.78 ± 0.24
+9.5	4.69	7.26 ± 0.21
+11.5	5.63	7.67 ± 0.05
+14.0	7.06	12.17 ± 0.50
+16.1	8.53	13.40 ± 0.28

[a] τ is the mean life of excited atoms, while k_q is the rate constant of quenching. [b] Error ranges in standard deviations.

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[9] K. Yang, *J. Am. Chem. Soc.*, **87**, 5294 (1965).

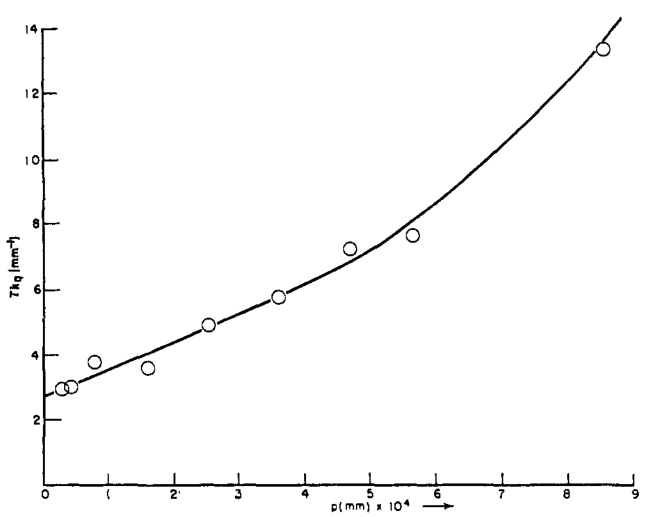

Figure 3. The increase of τk_q (τ = mean life, k_q = rate constant of quenching) with increasing vapor pressure of mercury.

The vapor pressure of mercury given in Table II is estimated from the graphical interpolation of data given in Lange's "Handbook of Chemistry," using the assumption that the pressure of mercury in the cell is the same as the equilibrium vapor pressure at the temperature of the mercury reservoir. As shown in Figure 3, τk_q increases with increasing p. When $p \lesssim 4 \times 10^{-4}$ mm, the increase is linear

$$\tau k_q = (2.68 \pm 0.09) + (0.85 \pm 0.05) \times 10^4 p \quad (4)$$

In the estimation of coefficients in (4) by the least-squares method, τk_q values were properly weighted with standard deviations given in Table II. The value of 2.68 mm^{-1} represents τk_q at negligible mercury pressure in the cell and is equal to $\tau_0 k_q$ ($= 1.08 \times 10^{-7} k_q$). Hence $k_q = 2.48 \times 10^7$ mm^{-1} sec^{-1}. By definition, quenching cross section σ^2 is related to k_q as follows

$$k_q = \sigma^2[8\pi RT/\mu]^{1/2}$$

where the symbols have the usual meanings. For ethylene at 25°, k_q (mm^{-1} sec^{-1}) = $0.515 \times 10^6 \sigma$ (A^2); thus, $\sigma^2 = 48.2$ A^2.

Discussion

(A) Absolute Quenching Rates. The existing literature value[10] of $\sigma^2(C_2H_4)$, obtained by using a theoretically estimated τ with Samson's equivalent opacity,[11] is 37 A. This is 30% lower than the present value. As pointed out before,[9] the quenching rates obtained by the past physical method, reported in different papers, differ considerably. It is thus not certain whether the 30% discrepancy can be attributed to the error in the theoretical estimation of τ or whether it is within experimental error ranges of the past physical method. In any case, the present value is preferable in discussing the absolute quenching rates.

The relative quenching cross section, $\sigma^2(N_2O)/\sigma^2(C_2H_4)$, estimated by the chemical method, is 0.57.[4] Hence $\sigma^2(N_2O)$ = 27 A. An often-used value is $\sigma^2(N_2O)$ = 12.6 A. In view of the present results, quenching cross sections estimated by using this latter value should be multiplied by 2.1.

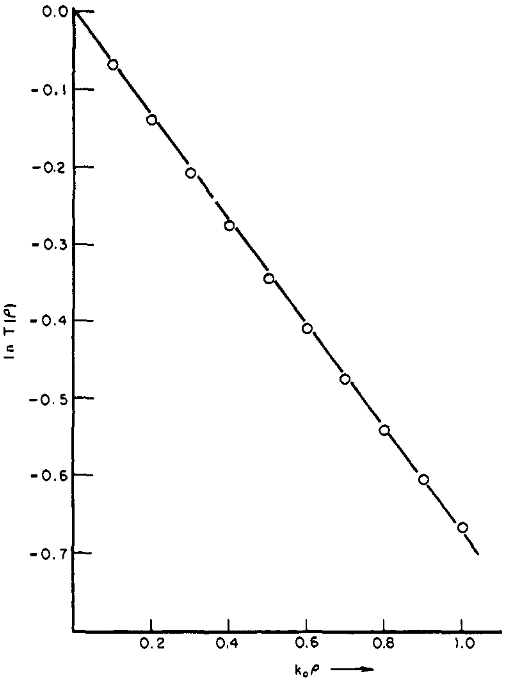

Figure 4. The logarithmic decrease of $T(\rho)$ with increasing opacity: ○, estimated from the numerical integration of eq 7; ———, least-squares line, $T(\rho) = \exp(-0.675 k_0 \rho)$.

(B) Imprisonment and Lifetime. With increasing p, τ first increases linearly, then more rapidly than the first power of p. The liner portion is explainable using a simple diffusion model. In fluorescence, only those photons escaping the cell are counted as not quenched. The mean life is thus the time elapsed between the time of absorption from the exciting beam and the time a photon reaches an emerging surface. It takes τ_0 sec for the first emission from the time of light absorption. Before reaching the surface, the photon undergoes the absorption–emission process $k\rho$ times, where k is the average distance the photon traverses per absorption–emission process and ρ is the distance to the surface. The time of flight between atoms is negligible; hence the photon requires $k\rho\tau_0$ sec to reach the surface following the first emission. Thus

$$\tau = \tau_0(1 + k\rho) \quad (5)$$

Since k in (5) is an average absorption coefficient, the probability, $T(\rho)$, of the photon traversing a distance ρ is

$$T(\rho) = \exp(-k\rho) \quad (6)$$

For monochromatic light (6) is strictly valid. In the present case, however, the line is Doppler-broadened, and $T(\rho)$ must be averaged over an appropriate frequency distribution[5]

$$T(\rho) = \int_{-\infty}^{+\infty} \frac{1}{\pi^{1/2}} e^{-x^2} \exp[-k_0 \rho e^{-x^2}]dx \quad (7)$$

where $x = [(\nu - \nu_0)/\nu_0](c/\nu_0)$ and $\nu_0 = (2RT/M)^{1/2}$; here, ν_0 is the frequency at the center of the line, c is the velocity of light, M is the molecular weight of mercury, and k_0 is the absorption coefficient at the center of the line. The behavior of $T(\rho)$ at low opacities is investigated by numerical integration. The result summarized in Figure 4 indicates that the relation

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[10] B. de B. Darwent, M. K. Phibbs, and F. G. Hurtubise, *J. Chem. Phys.*, **22**, 859 (1954); also see ref 1b.

[11] E. W. Samson, *Phys. Rev.*, **40**, 940 (1932); also see ref 1a.

$$T(\rho) = \exp(-0.675k_0\rho)$$

is a reasonable approximation. Hence, $k\rho$ in (5) is equal to $0.675k_0\rho$. The absorption coefficient at the center of the line is

$$k_0 = {}^1/_5(g_2/g_1)(n\lambda_0{}^3/8\pi^{3/2}\nu_0\tau_0)$$

where g_1 and g_2 are the statistical weights of the ground and excited states, λ_0 is the wavelength at the center of the line, and n is the number of mercury atoms per cc.[5] Hence, k_0 (cm^{-1}) = 0.420×10^4p (p in mm) at 25°. Thus the present diffusion model gives

$$\tau = \tau_0(1 + 0.284 \times 10^4p\rho)$$

In the present experiment, the distance from the slab of irradiated mercury to the emerging surface of the cell facing the photomultiplier tube is 1.27 cm. With this ρ, and using (4), the experimental relation becomes

$$\tau = \tau_0(1 + 0.25 \times 10^4p\rho)$$

which agrees well with the above estimation.

At a higher opacity, various complications arise. First $T(\rho)$ fails to decrease exponentially with opacity, and the mean absorption coefficient loses its significance. In addition, not only the mercury slab in the exciting beam (and facing the photomultiplier tube) but also the slabs in other volume elements contribute to photocurrents; hence the value of ρ to be used in the estimation of opacity becomes uncertain. In spite of these complications, the qualitative behavior of τ at a higher opacity can be deduced from Milne's treatment of radiation transport.[12] Since τ is a mean life, the decay of excited atoms in the absence of a quencher after the exciting beam is cut off should follow the first-order law

$$n^*(t) = n^*(0)\exp(-t/\tau) \tag{8}$$

Milne's one-dimension diffusion model gives τ in (8) in the form

$$\tau = \tau_0[1 + (k_0\rho)^2/\delta^2]$$

where δ is the positive root of $\tan x = k_0\rho/x$ which lies between 0 and $\pi/2$. At a low opacity $\delta \simeq k_0\rho$, and eq 5 results. At a high opacity, $\delta \simeq \pi/2$ and

$$\tau = \tau_0[1 + 4(k_0\rho)^2/\pi^2]$$

Since k_0 is proportional to p, τ now increases with the second power of p. This is in qualitative agreement with the present result (Figure 3) where τ is found to increase more rapidly than the first power of p at higher opacities.

Acknowledgment. Dr. W. H. Harwood and Mr. C. L. Hassell offered valuable discussion, and Mr. J. D. Reedy helped with experimental work. The author gratefully acknowledges this assistance.

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[12] E. A. Milne, *J. London Math. Soc.*, **1**, 1 (1926).

Chemiluminescence from the Reduction of Rubrene Radical Cations

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Contribution from the Department of Chemistry and
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Cambridge, Massachusetts 02139. *Received May 18, 1966*

Abstract: It has been demonstrated that reduction of aromatic hydrocarbon cation radicals can produce chemiluminescence when electron donors other than the corresponding anion radical are used. Such reactions have been studied in detail for rubrene radical cations, using dimethylformamide, water, *n*-butylamine, and triethylamine as electron donors. Spectral studies showed that the chemiluminescence emission was identical with hydrocarbon fluorescence. Studies of a number of experimental variables are reported including the effects of concentration, water, oxygen, and repetitive scans on the chemiluminescence emission. Also, it was observed that solvent oxidation products quenched chemiluminescence emission when dimethylformamide was used as solvent, and that products of the reaction between rubrene cation and water-quenched light emission.

Recently a number of reports have appeared describing production of chemiluminescence in aromatic hydrocarbon systems. Chemiluminescence has been observed by alternating current electrolysis of hydrocarbons in nonaqueous solvents[1-3] and by chemical oxidation of hydrocarbon anions,[4] and a report has described excimer formation in the electrochemically produced chemiluminescence.[5]

The chemiluminescence observed during alternating current electrolysis has been interpreted as resulting from an annihilation reaction between positive and negative hydrocarbon radical ions produced during electrolysis. The mechanism for this reaction has been postulated to be an electron transfer from the negative to the positive radical ion to produce an excited singlet state. The observation of excimer emission[5] in such systems tends to support this point of view. Observation of chemiluminescence by chemical oxidation of

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(1) D. M. Hercules, *Science*, **143**, 808 (1964).

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(5) E. A. Chandross, J. W. Longworth, and R. E. Visco, *ibid.*, **87**, 3259 (1965).