# The Quenching of Mercury ($^3P_1$) Atoms by Isotopic Hydrogen Molecules

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The isotope effect in the quenching of Hg($^3P_1$) by isotopic hydrogen molecules is investigated by chemical and physical methods. The chemical method utilizes a competition between the reactions

$$N_2O + Hg^* \longrightarrow N_2 + O + Hg$$
$$H_2 + Hg^* \longrightarrow 2H + Hg, \text{ etc.}$$
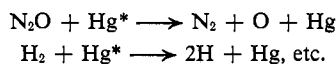
The quenching rate is deduced from the dependence of the quantum yield of nitrogen on $[H_2]$, $[HD]$, or $[D_2]$. Propane or ethylene is added in the system to avoid the occurrence of the reaction $N_2O + H \rightarrow N_2 + OH$. In the physical method, the intensity of fluorescence, Hg($^3P_1$) $\rightarrow$ Hg($^1S_0$) $+ h\nu$, is measured at different $[H_2]$, $[HD]$, or $[D_2]$, and the quenching rate is calculated on the basis of Stern-Volmer mechanism. The concentration of quencher is kept sufficiently low so that the collision broadening of absorption line may be neglected. Even at $0°$, the vapor pressure of mercury is found to be high enough to cause severe imprisonment of the resonance radiation. Error due to this cause is corrected by an empirical method. Relative quenching cross sections estimated by the two methods are given. A previous report on the reverse isotope effect between the collision efficiency of H_2 and D_2 is not confirmed. In the quenching by paraffins, D-substitution at the quenching site drastically reduces collision efficiency. Such a drastic reduction is not present in the collision involving isotopic hydrogen molecules. This difference is explained by supposing that the quenching by hydrogen molecules proceeds by the formation of a cyclic complex, while in the quenching by paraffins the formation of such a complex, involving the bond to be broken, encounters a high potential barrier.

I. Introduction

The collision of the second kind between atoms

$$A^* + B \longrightarrow A + B^*$$
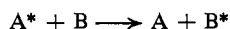
is most efficient when the following rules are satisfied[1]; (a) the total spin before and after collision is the same (spin conservation rule)[2] and (b) the least energy is converted to kinetic energy (resonance energy rule).[3] For example, in helium–neon discharge, the spin-allowed transitions are about 1000 times more effective than spin-forbidden transitions,[4] showing the validity of the spin-conservation rule; in the mercury-sensitized

fluorescence of sodium, sodium terms lying close to Hg($^3P_1$) or Hg($^3P_0$) terms are preferentially excited,[5] demonstrating the applicability of the resonance energy rule.

In atom–molecule collisions, the spin-conservation rule is still valid, as is seen in the reaction

$$Hg(^3P_1) + N_2O \longrightarrow N_2 + O + Hg(^1S_0)$$

where the oxygen atoms are produced in a triplet state.[6] The resonance energy rule, however, seems to break down completely. A good example is the isotope effect in the quenching of Hg($^3P_1$) by paraffins, leading to C–H or C–D bond ruptures. Since the excitation energy (113 kcal.) is larger than C–H or C–D bond strength, the resonance energy rule demands deuterated paraffins to have larger cross sections. Experimentally, the reverse is observed.[7] For example, the quenching cross section of $CH_3CH_2CH_3$ is seven times that of $CH_3CD_2CH_3$. In view of this and other evidence, the resonance energy rule is usually discarded in the discussion of quenching involving molecules.[8] There is a puzzling datum in this connection. In the quenching of Hg($^3P_1$), deuterium is reported to have a larger cross section (8.41 Å.^{2}) than hydrogen (6.01 Å.^{2}).[9] Originally, this reversal in isotope effect was explained by invoking the resonance energy rule. It is, however, not clear why the resonance energy rule works in atom–diatomic molecule collisions but not in atom–paraffin collisions. The isotope effect in C–H and C–D quenching is explained[8] by the use of the absolute rate theory according to which the major contribution comes from the difference in the zero-point energies of the two bonds. Evidently, this argument does not apply in the quenching by isotopic hydrogen molecules. Further research leading to the proper understanding of these contradictions may provide an important insight concerning the mechanism of energy transfer in atom–molecule collisions.

Two different methods have been employed in the determination of quenching rates. The first is the physical method in which the decrease in mercury fluorescence caused by quenching is determined.[10] The second is the chemical method in which the decrease in the quantum yield of N_2 in the mercury-sensitized decomposition of nitrous oxide is determined at various concentrations of an additional quencher.[11] The hydrogen isotope effect was investigated by the first method, while the second method was used in the investigation of the paraffin isotope effect. The relative quenching cross sections obtained by the physical

(1) G. Herzberg, "Atomic Spectra and Atomic Structure," Dover Publications, New York, N. Y., 1944, pp. 231, 232.
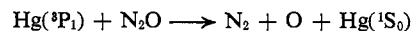
(2) K. J. Laidler, "The Chemical Kinetics of Excited States," Oxford at the Clarendon Press, London, 1955, pp. 32, 114.

(3) For the review of the experimental supports for the resonance energy rule, see (a) A. C. G. Mitchell and M. W. Zemansky, "Resonance Radiation and Excited Atoms," The Cambridge University Press, Cambridge, 1961, pp. 66–69. For the theoretical justification of the resonance energy rule, see (b) T. Holstein and I. B. Bernstein, *Phys. Rev.*, **83**, 201 (1951); (c) E. C. G. Stueckelberg, *Helv. Phys. Acta*, **5**, 369 (1933); (d) H. Kallmann and F. London, *Z. Physik*, **B2**, 207 (1929).

(4) J. T. Massey, A. G. Schulz, B. F. Hochmeimer, and S. M. Cannon, *J. Appl. Phys.*, **36**, 658 (1965).

(5) H. Beutler and B. Josephy, *Z. Physik*, **53**, 747 (1929).

(6) R. J. Cvetanović, *Progr. Reaction Kinetics*, **2**, 39 (1964).

(7) Y. Rousseau and H. E. Gunning, *Can. J. Chem.*, **41**, 465 (1963).

(8) H. E. Gunning and O. P. Strauz, *Advan. Photochem.*, **1**, 209 (1963).

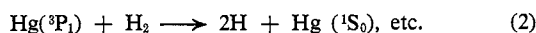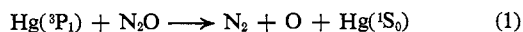(9) M. G. Evans, *J. Chem. Phys.*, **2**, 445 (1934).

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

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

method reported in different papers differ considerably. For example, $\sigma^2(n\text{-}C_4H_{10})/\sigma^2(C_3H_8) = 2.3\text{-}3.2$.[6,12-14] Thus, the reported reverse isotope effect can be within the experimental error range of this method. In view of this and also considering the important implication of the reverse isotope effect on the mechanism of energy transfer, we decided to reinvestigate the isotope effect by both chemical and physical methods, taking extra care to obtain accurate relative quenching efficiency. For the present purpose, it is necessary to introduce some modifications in both methods, and these are discussed in the next section.

II. Chemical and Physical Method

A. Chemical Method. Supposing a competition between the following two reactions

$$\text{Hg}(^3P_1) + N_2O \longrightarrow N_2 + O + \text{Hg}(^1S_0) \qquad (1)$$

$$\text{Hg}(^3P_1) + H_2 \longrightarrow 2H + \text{Hg}\ (^1S_0),\ \text{etc.} \qquad (2)$$

we obtain the rate equation

$$\phi^{-1} = 1 + (k_2/k_1)[H_2]/[N_2O] \qquad (\text{E-1})$$

where ϕ denotes the quantum yield of nitrogen and k_i is the rate constant of the ith reaction. This type of rate equation applies in various systems, such as N_2O–paraffins and N_2O–olefins.[6] In the N_2O–H_2 system, we encountered difficulties. At the ratio $[H_2]/[N_2O]$ higher than about 2, the plot of ϕ^{-1} vs. the ratio gives an apparent straight line, but the intercept at the ϕ^{-1} axis is consistently higher than unity. In addition, the quenching cross section estimated from the slope is only $^1/_6$ of the value obtained by the physical method.[15] These difficulties are attributed to the occurrence of the reaction

$$N_2O + H \longrightarrow N_2 + OH \qquad \Delta H = -59\ \text{kcal.}$$
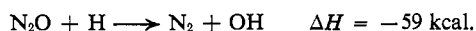
A hydrogen atom scavenger M is then added to avoid the above reaction. The rate equation then becomes

$$\phi^{-1} = 1 + (k_2/k_1)\,[H_2]/[N_2O] + (k_3/k_1)[M]/[N_2O] \quad (\text{E-2})$$

where k_3 is the rate constant of the reaction

$$\text{Hg}(^3P_1) + M \longrightarrow \text{Hg}(^1S_0) + \text{product} \qquad (3)$$
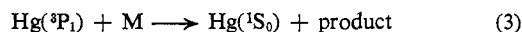
A good part of the present paper is devoted to show that (E-2) is valid in spite of the fact that (E-1) is not valid.

B. Physical Method. We suppose that the concentration of quencher is sufficiently low so that the radiative transition

$$\text{Hg}(^3P_1) \longrightarrow \text{Hg}(^1S_0) + h\nu \qquad (4)$$
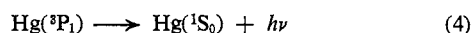
can compete with quenching reaction (2). The steady-state condition for [Hg*] then gives the following rate equation (Stern–Volmer formula[16])

$$\frac{Q}{Q_0} = \frac{1}{1 + (k_2/k_4)[H_2]} \qquad (\text{E-3})$$

where Q_0 and Q are, respectively, the intensity of

fluorescence in the absence and presence of quencher. In the use of (E-3), two precautions should be exercised. First, the pressure of quencher must be kept sufficiently low so that the collision broadening of the absorption line can be neglected; otherwise, the amount of the light absorbed by mercury vapor depends on the concentration of quencher in a complicated manner,[17] and (E-3) is no longer valid. The second has to do with the imprisonment of resonance radiation.

Under most experimental conditions, the light emitted by an excited atom is very likely reabsorbed by another ground-state atom before it reaches the emerging surface of the enclosure. This is because the absorption coefficient $\kappa(\nu)$ (ν = frequency) for the resonance line is very high, and the concentration of mercury in most experiments is appreciable. The net effect of this imprisonment is to prolong the lifetime of excited state; thus k_4 in (E-3) is reduced. An approximate treatment of the imprisonment by Gaviola[18] indicates that (E-3) is still valid, provided k_4 is replaced by Ck_4, where $C(\leq1)$ depends on the geometry of experimental arrangement and the concentration of mercury but not on the concentration of quencher. For some idealized geometry of enclosure, it is possible to estimate theoretically the contribution from the imprisonment to the Stern–Volmer formula. Zemansky[10] solved this problem for the case of an infinite slab, and presently accepted quenching rates come from his work. Zemansky used the Milne[19] theory of the diffusion of imprisoned radiation in which the following important approximation is incorporated.

$$\int \kappa(\nu)d\nu = \kappa\Delta\nu \qquad (\text{E-4})$$

This implies a uniform absorption through a line breadth, $\Delta\nu$. Various attempts[20] have been made to define the average κ, a well-known example being the equivalent absorption coefficient used by Samson.[21] The transport of radiation by the process of emission–absorption–emission resembles the process of diffusion, and (E-4) presumes the existence of mean-free path $(1/\kappa)$ in such radiation diffusion. A detailed investigation,[20] however, demonstrates that, because of the functional form of the dependence of $\kappa(\nu)$ on ν, it is impossible to define the mean-free path precisely; consequently, the radiation transport cannot be described by the Milne's diffusion-type equation.[20] In the present work, no attempt is made to calculate C. Instead, we accept the conclusion of Gaviola on the independence of C on the concentration of quencher and determine k_2/Ck_4 from a quenching curve. C is then empirically evaluated from the known quenching rate of a quencher. The extent of error introduced in the presently accepted quenching rate, coming from the use of (E-4), is not known, and this uncertainty is also inherent in the present work.

In the Zemansky method for the determination of the quenching rate, it is necessary to measure the intensity of fluorescence as the difference between the total light

(12) J. R. Bates, *J. Am. Chem. Soc.*, **52**, 3825 (1930); **54**, 569 (1932).

(13) B. de B. Darwent, *J. Chem. Phys.*, **18**, 1532 (1950).

(14) B. de B. Darwent and M. K. Phibbs, *ibid.*, **22**, 110 (1954).

(15) These difficulties are not discussed in a recent paper: H. Niki, Y. Rousseau, and G. J. Mains, *J. Phys. Chem.*, **69**, 45 (1965). The major conclusions of this paper are, however, not affected by the breaking down of (E-1) in the N₂O-H₂ system, because the rate equation (E-1) plays there only a minor role; also see ref. 6.

(16) O. Stern and M. Volmer, *Z. Physik*, **20**, 183 (1919); also see ref. 3a, pp. 192, 193.

(17) For example, see K. Yang, *J. Am. Chem. Soc.*, **86**, 3941 (1964), and various references quoted there.

(18) E. Gaviola, *Phys. Rev.*, **34**, 1049 (1929). In his notation, $C = 1 - q(1 - f)$.

(19) E. A. Milne, *J. Lond. Math. Soc.*, **1**, 1 (1926).

(20) For example, see reference quoted in T. Holdstein, *Phys. Rev.*, **83**, 201 (1957).
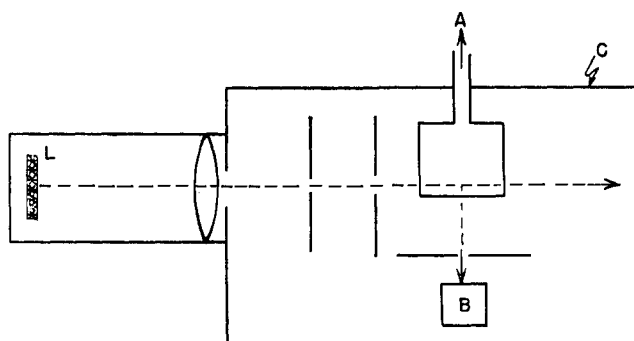
(21) E. W. Samson, *ibid.*, **40**, 940 (1932).

Figure 1. The equipment used in the determination of the intensity of fluorescence: L, low-pressure mercury lamp; B, photomultiplier; C, black, light-tight box.

H_2, torr	Time, min.	N_2, torr	ϕ, molecule/ photon
50	10	0.675	0.680
100	15	0.787	0.529
150	15	0.648	0.435
200	15	0.562	0.378
250	15	0.479	0.321
300	20	0.562	0.283
400	25	0.566	0.228

[a] Intensity = 0.0993 torr/min. (= 3.83 μeinsteins/min.).

(fluorescence light plus the light passing through unabsorbed) and the unabsorbed light. As seen later, the scattered light is measured directly in the present experiment; thus the present method, though it does not yield an absolute quenching rate, is expected to provide more accurate relative rates.

III. Experimental Section

A. Chemical Method. Matheson's nitrous oxide was passed through a water solution of ferrous sulfate to remove nitric oxide; potassium hydroxide and activated charcoal traps then followed to remove water spray. The resulting nitrous oxide was degassed by repeated evacuation and subjected to one-stage, trap-to-trap distillation, discarding a good portion of initial distillate. Phillips' research grade hydrocarbons were purified as described before.[17] Hydrogen and deuterium were obtained from Air Products and Chemicals, Inc. (Oklahoma City, Okla.), and hydrogen deuteride was purchased from Merck Sharp and Dohme Co. Ltd. (Montreal, Canada); these gases were purified by passing through a molecular sieve, or activated charcoal column, immersed in a liquid nitrogen trap.

Nitrogen was determined chromatographically. A molecular sieve column (Linde 5A, 30/60) effectively separated nitrogen from other possible interfering gases, such as O_2 and CH_4. It absorbed, however, nitrous oxide irreversibly. A charcoal column was put in ahead of the molecular sieve column. After the determination of nitrogen, nitrous oxide, which still resided in the charcoal column, was flushed out of the column by reversing the flow of carrier gas. Linde hydrogen, purified by passing through an activated charcoal column at room temperature, was used as a carrier gas. The plot of nitrogen pressure (in a 25-cc. sample loop) *vs.* the peak height was a good straight line passing through origin.

The reaction cell was made of a Vycor cylinder (5.1 cm. in diameter, 20 cm. long). Both ends of the cell were connected to an all-glass gas circulating pump, supported on two Teflon bearings. Mercury was introduced in a flat cylinder (2 cm. high, 7.5 cm. in diameter) and connected to the circulating system outside of the cell. The mercury surface stayed clean throughout experiments. Gases were thoroughly mixed by circulation, and irradiation was carried out (with a Hanovia low-pressure mercury lamp) while the reactant was being circulated. The plot of $[N_2]$ *vs.* time was an excellent straight line passing through origin. The

total volume, reaction cell plus pumping system, was 781 cc. Intensity was determined by supposing that ϕ in the N_2O–C_3H_8 system approaches unity as $[C_3H_8]$ becomes zero. All experiments were carried out at $24 \pm 1°$. An example of experimental data is shown in Table I.

B. Physical Method. The equipment depicted in Figure 1 was used to determine the intensity of fluorescence. The cell was made by fusing two optically flat quartz windows of 2.5-cm. diameter at the ends of a 5-cm. long Vycor cylinder. A collimated beam of the resonance light from a low-mercury lamp (Pen-ray type, UV Products Inc., San Gabriel, Calif.) illuminated a narrow slab of mercury vapor 0.4 cm. thick and lying parallel to the window. The distance from the center of the slab to a window was 1.2 cm. The mercury reservoir was kept at $0°$, and proper precautions were taken to ensure vapor equilibration. The intensity of fluorescence was monitored at right angles to the exciting beam with an IP 28 photomultiplier coupled with a galvanometer.

The pressure of quencher did not exceed 1 torr; hence the collision broadening of the absorption line can be neglected. The line shape of the fluorescence (which governs the imprisonment process) emitted at right angles to the exciting beam is independent of the shape of the exciting line.[22,23] Thus the shape of the exciting line does not affect the present work in spite of the fact that the intensity of the absorbed light critically depends on it. For a more refined treatment of quenching than that presented here, however, information on the shape of exciting line may be required. For this reason, the line shape is photographed by using a Jarrell ash spectrograph with a 15,000 lines/in. grating at 24th order. The result is given in Figure 2, where five hyperfine components can be clearly seen. The modification of the line by self-reversal seems to be negligible, and the whole line can be considered as a supposition of five Doppler-broadened lines.

With the present equipment, there was some photocurrent even in the absence of mercury vapor. This light, to be denoted Δ, presumably came from the fluorescence of the cell material. Experimentally determined photocurrent is then

$$Q' = Q + \Delta$$
$$Q_0' = Q_0 + \Delta$$
(E-5)

where the subscript "0" denotes the absence of

(22) W. Orthmann and P. Pringsheim, *Z. Physik*, **43**, 9 (1927).
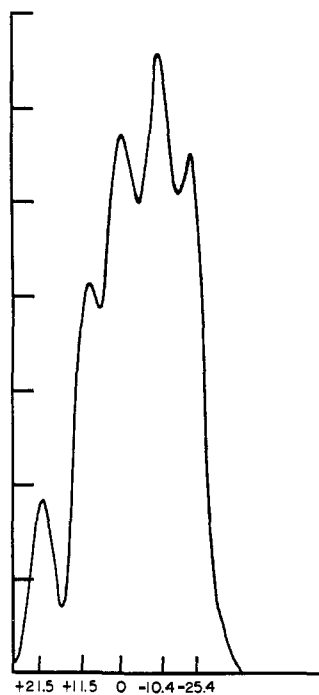(23) W. Prokofjew and G. Gamow, *ibid.*, **44**, 887 (1927).

Figure 2. The hyperfine structure of the 2537-Å. resonance line used to excite fluorescence. No attempt was made to locate the position of each component; the separation between peaks given in mÅ. was taken from ref. 3a, p. 38.

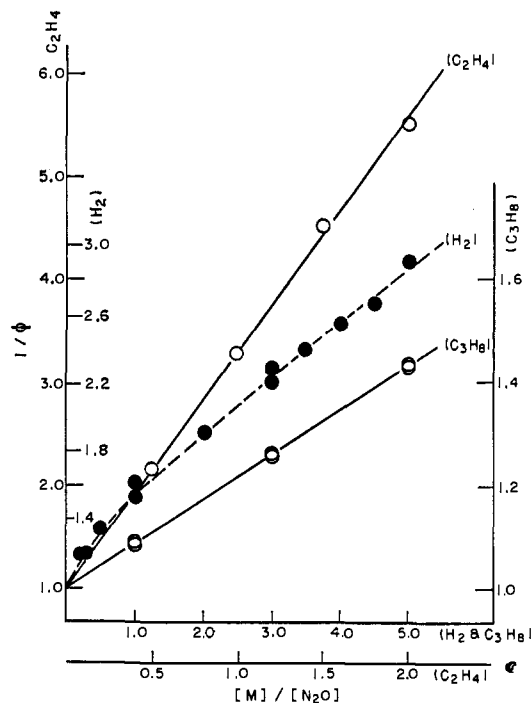Figure 3. The dependence of the quantum yield of nitrogen on concentration ratios in the systems of N_2O-C_3H_8 (600 torr total pressure), N_2O-C_2H_4 (600 torr total pressure), and N_2O-H_2 (300 torr total pressure).

quencher. Replacing k_4 by Ck_4 and also using (E-5), (E-3) becomes

$$\frac{1}{1 - (Q'/Q_0')} = \alpha + \beta[H_2]^{-1} \qquad \text{(E-6)}$$

where $\alpha = (1 - \Delta/Q_0')^{-1}$ and $\alpha/\beta = k_2/(Ck_4)$. The quenching data, an example of which is shown in Table II, are treated using (E-6).

Table II. The Quenching of Fluorescence by Hydrogen[a]

H_2, torr	Q_0'	Q'
0.125	9.35	6.70
0.125	9.50	6.95
0.167	9.70	6.55
0.167	9.43	6.32
0.250	9.58	5.53
0.500	9.60	4.00
1.00	9.45	2.80

[a] Q' and Q_0' denote the photocurrent in an arbitrary unit in the presence and absence of the quencher.

IV. Results

A. The Chemical Method. Two-Component Systems. In the mixtures of N_2O-C_3H_8 and N_2O-C_2H_4, the plot of ϕ^{-1} vs. the concentration ratio gives a good straight line, as shown in Figure 3. The slopes give $k_2/k_1 = 0.0871$ for propane and $k_2/k_1 = 2.17$ for ethylene. By definition, a quenching cross section, σ^2, and a rate constant, k, are related to themselves as

$$k = \sigma^2\left[8\pi RT\left(\frac{1}{M_1} + \frac{1}{M_2}\right)\right]^{1/2}$$

where the symbols have their usual meanings. If $\sigma^2(N_2O)$ is taken[6] to be 12.6 Å.^{2}, then $\sigma^2(C_3H_8) = 1.3$

and $\sigma^2(C_2H_4) = 23$. These values agree with the results of other laboratories: $\sigma^2(C_3H_8) = 1.2$,[7] and $\sigma^2(C_2H_4) = 22$.[11] An attempt is also made to determine the dependence of ϕ in the C_3H_8-N_2O system on total pressure, but within 100–900 torr, no variation is found.

In the N_2O-H_2 system, the plot of ϕ^{-1} vs. the concentration ratio gives an apparent straight line, provided the ratio exceeds about 2. The intercept, however, is larger than unity. Presuming at the moment the validity of (E-1), the slope gives $k_2/k_1 = 0.32$, which corresponds to $\sigma^2(H_2) = 0.95$. This is too low compared with $\sigma^2(H_2) = 6.01$ determined by physical method. These abnormalities led us to investigate ϕ at ratios less than unity. The results are given in Figure 3, where the nonlinearity of the plot is clearly seen; thus (E-1) is not applicable in the N_2O-H_2 system.

For (E-1) to be applicable, the added quencher must react readily with oxygen atoms formed in (1); otherwise, oxygen atoms react with mercury atoms and lead to various complications.[6] The reaction

$$H_2 + O \longrightarrow OH + H$$
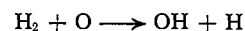
with a thermalized oxygen atom is slightly endothermic ($\Delta H \simeq +3$ kcal.); hence, it is expected to proceed very slowly at room temperature. In the present experiment, oxygen is not formed unless the ratio $[H_2]/[N_2O]$ becomes less than about 0.2. The absence of oxygen at higher ratios indicates that oxygen atoms are efficiently removed by reacting with hydrogen. It may be that oxygen atoms formed in the quenching are slightly hot. In the present case, more nitrogen is formed than one would expect from the $\sigma^2(H_2)$ value of 6.01. This excess nitrogen is likely to come from the highly exothermic reaction of H atoms with N_2O
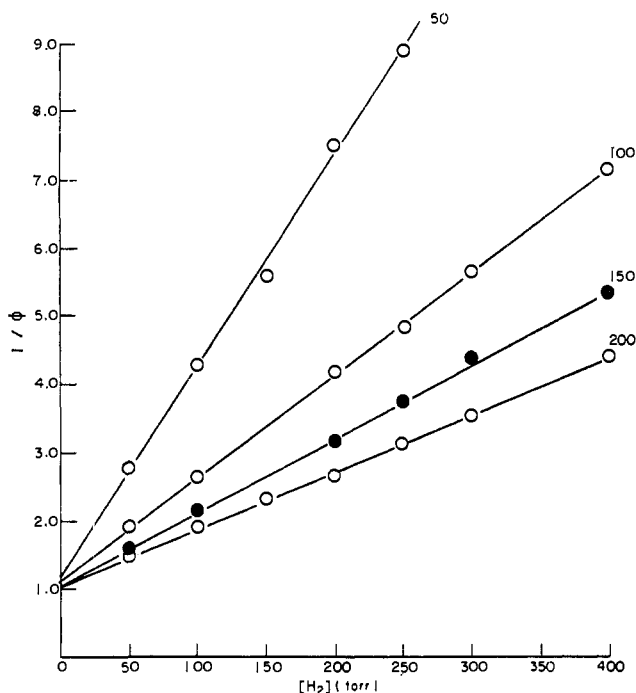
Figure 4. The quantum yield of nitrogen at various [H₂] and at constant [C₃H₈] (= 100 torr) and [N₂O]; [N₂O] in each series of experiments is indicated along the line.

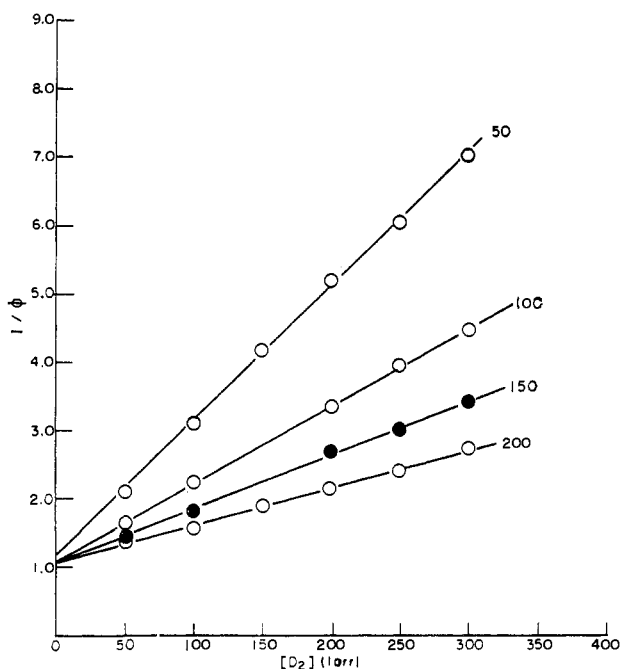Figure 5. The quantum yield of nitrogen at various [D₂] and at constant [C₃H₈] (= 100 torr) and [N₂O]; [N₂O] in each series of experiments is indicated along the line.

producing N_2 and OH. This view is further supported by experimental data given in the next section.

B. The Chemical Method. Three-Component Systems. In the presence of propane or ethylene, the formation of nitrogen from the reaction, $H + N_2O \rightarrow OH + N_2$, may be neglected. In this case, (E-2) should be applicable. When [M] (propane or ethylene) and [N₂O] are kept constant and [H₂] is varied, (E-2)

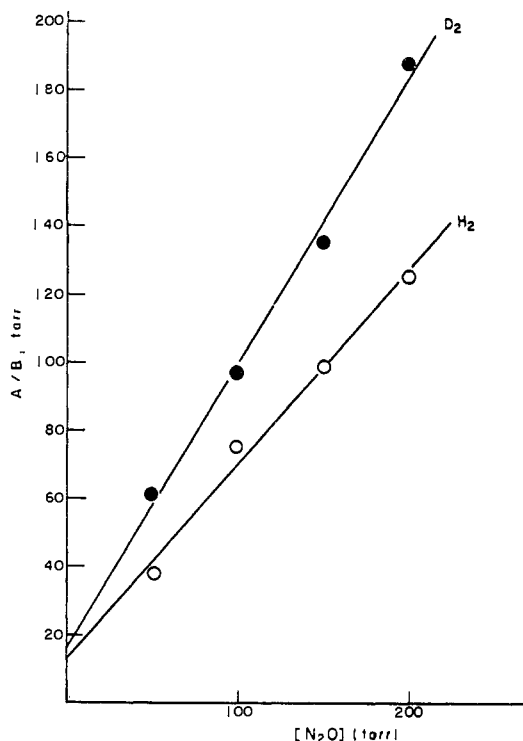Figure 6. A test of the relation $A/B = (k_1/k_2)[N_2O] + (k_1/k_3)\cdot[C_3H_8]$ at constant [C₃H₈] (= 100 torr).

becomes

$$\phi^{-1} = A + B[H_2] \qquad \text{(E-7)}$$

where A and B are constants. Experimental tests of (E-7) are given in Figure 4 for hydrogen and in Figure 5 for deuterium. In all experiments, [C₃H₈] is 100 torr; [N₂O] in each series of experiments is indicated along the plot of ϕ^{-1} vs. [H₂]. Straight lines clearly demonstrate the validity of (E-3). Table III summarizes two constants, A and B, in (E-7) estimated by the least-squares method.

Table III. Constants A and B in the Rate Equation, $\phi^{-1} = A + B[H_2 \text{ or } D_2^{-1}]$ at [C₃H₈] = 100 Torr

N₂O, torr	A		B, torr⁻¹ × 100	
	H₂	D₂	H₂	D₂
50	1.17	1.19	3.08	1.95
100	1.13	1.09	1.50	1.13
150	1.06	1.06	1.08	0.784
200	1.04	1.04	0.830	0.553

Experimental error in the determination of intensity affects A and B individually but not the ratio A/B. From (E-2) and (E-3)

$$\frac{A}{B} = \frac{k_1}{k_2}[N_2O] + \frac{k_3}{k_2}[M] \qquad \text{(E-8)}$$

Since [M] is kept constant, the plot of A/B vs. [N₂O] should give a straight line. This linearity is demonstrated in Figure 6. The reciprocal of the slope gives k_2/k_1; hence, $\sigma^2(H_2)$ and $\sigma^2(D_2)$ relative to $\sigma^2(N_2O)$ (= 12.6) may be evaluated. The results are summarized in Table IV.
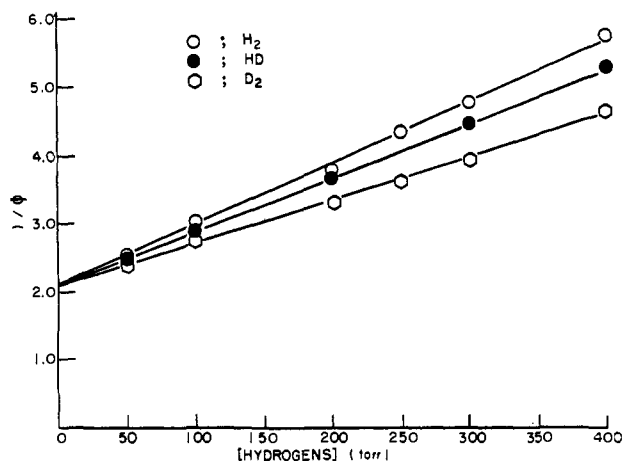
Figure 7. The quantum yield of nitrogen at various [H₂], [HD], or [D₂] at constant [N₂O] (= 200 torr) and [C₂H₄] (= 100 torr).

Still another test of (E-2) is that k_2/k_1 should be independent of the nature of M, provided M reacts readily with hydrogen atoms. To test this, ethylene is used as M, and ϕ is determined at constant [M] and [N₂O]

Table IV. Relative Rates and Quenching Cross Sections Determined by Using Different Hydrogen Atom Scavengers[a]

	k_2/k_1		σ^2, Å.[2]	
	P	E	P	E
H₂	1.8	1.8	5.3	5.3
HD	...	1.6	...	5.8
D₂	1.2	1.3	5.0	5.4

[a] Namely propane (denoted P) and ethylene (denoted E).

and at various [H₂], [HD], or [D₂]. Straight lines in Figure 7 show that (E-2) is also applicable in these systems. As summarized in Table IV, the slope of the lines gives the σ^2, which agrees well with the result obtained with propane.

C. The Physical Method. In Figure 8, the quenching data for H₂, HD, and D₂ are presented according to (E-6). Straight lines demonstrate that the modified Stern–Volmer formula is applicable in the present system. The slope and intercept give $k_2/(Ck_4)$ = 5.19 (torr)$^{-1}$ for the quenching by H₂. Since k_4 = (1.08 × 10⁻⁷)$^{-1}$ and $\sigma^2(H_2)$ = 5.3 Å.[2], we estimate C = 0.200. This indicates that the imprisonment increases the apparent lifetime five times, even though the mercury reservoir is at 0°. Quenching cross sections estimated with this C value are summarized in Table V.

Table V. Constants α and β (torr) in the Modified Stern–Volmer Formula[a]

	α	β	$k_2/(Ck_4)$	σ^2, A.[2]
H₂	1.09	0.210	5.19	5.3[b]
HD	1.13	0.246	4.59	5.7
D₂	1.10	0.319	3.45	5.0

[a] (E-6) in the text. [b] Assumed value.

$\sigma^2(HD)$ and $\sigma^2(D_2)$ agree well with the results of the chemical method.

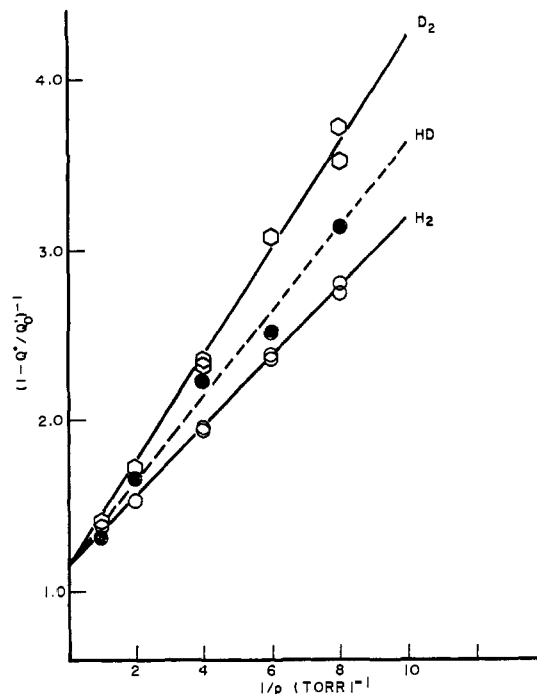Figure 8. The quenching data plotted according to (E-6); Q' and Q_0 denote, respectively, photocurrent in the presence and absence of quencher.

V. Discussion

The relative collision efficiency estimated by the two methods is

	H₂	HD	D₂
Chemical method	1.0	1.1	0.98
Physical method	1.0	1.1	0.94

As compared to $\sigma^2(H_2)$, $\sigma^2(HD)$ is higher, but $\sigma^2(D_2)$ is slightly lower. These small differences may be within experimental error range. In any case, the following two conclusions can be drawn. First, the reported reverse isotope effect between $\sigma^2(H_2)$ and $\sigma^2(D_2)$ is not confirmed. Second, the sharp decrease in collision efficiency observed in hydrocarbons by replacing H by D at the quenching site is not present in the collision involving hydrogen molecules. In the discussion below, the implication of these conclusions in the mechanism of energy transfer is considered.

A. The Resonance Energy Rule in the Atom–Molecule Collisions. The present result indicates that the resonance energy rule breaks down even in atom–hydrogen molecule collisions. This rule was criticized as having no theoretical justification in atom–molecule collisions, because here the restriction to the crossing of potential curves caused by a failure of levels to fit is slight.[24] The latter conclusion is reached by applying the Zener–Laundau formula for the crossing of potential curves.[25,26] A recent investigation demonstrates, however, that the Zener–Laundau formula leads to a serious error when electrons other than s electrons are involved, and the transition probability

(24) K. J. Laidler, *J. Chem. Phys.*, **10**, 43 (1942).

(25) J. L. Magee, W. Shand, and H. Eyring, *J. Am. Chem. Soc.*, **63**, 677 (1941).

(26) For a review, see S. Glasstone, K. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 301–316.
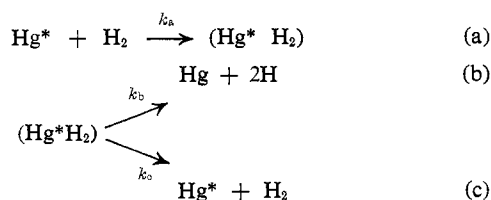
is not very small.[27] Since the past works deal with p electrons and with large transition probability, the above criticism on the resonance energy rule is based on uncertain conclusions.

The reason for the violation of the rule can be understood by considering an intuitive, classical interpretation of the rule.[28] In the collision of the second kind, such as (1), the forward and backward processes have the same collision efficiency[29]; thus one may employ either of these processes in the discussion. If B* approaches A with a smaller relative kinetic energy, B* then spends more time at the A–B* distance at which the transition occurs; hence the transition probability is large, as required by the rule. In atom–molecule collisions, a complication arises because the reaction coordinate is not the distance between the center of mass of two colliding partners. Considering the quenching

$$-\overset{|}{\underset{|}{C}}-H + Hg^* \longrightarrow -\overset{|}{\underset{|}{C}}--H--Hg^* \longrightarrow -\overset{|}{\underset{|}{C}}\cdot + H + Hg \quad (5)$$
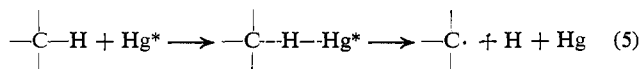
we note that, for the same reason as in atom–atom collisions, the probability of Hg* being at the transition point is the largest when the least energy is converted to kinetic energy. For the transition to occur, however, a hydrogen atom must also be at the transition point. This requires the C–H bond to be in a stretched state. The probability of such an event is likely to be governed by the strength of the bond, a bond with a higher strength having a lower probability, but not by the energy to be converted to kinetic energy. If this latter event governs the over-all transition, then σ^2 for a stronger bond can be small. This is contrary to the rule but is in agreement with observations. The above argument shows how the rule could break down, but it does not provide any answer for the difference in isotope effect of paraffin and hydrogen quenching.

B. The Structure of Activated Complex. The quenching of electronically excited species is often discussed in terms of the nonadiabatic crossing of potential curves. The processes involved may be schematically represented as

$$Hg^* + H_2 \xrightarrow{k_a} (Hg^* \ H_2) \quad (a)$$

$$(Hg^*H_2) \xrightarrow{\ \ k_b \ \ } Hg + 2H \quad (b)$$
$$\xrightarrow{\ \ k_c \ \ } Hg^* + H_2 \quad (c)$$

Here (Hg^*H_2) denotes the system at the crossing point, and the process c implies that the system recedes without the crossing of the curves. The quenching rate constant becomes

$$k_q = \xi \cdot k_a; \quad \xi = \frac{k_b}{k_b + k_c}$$

where ξ is the transmission coefficient. For a qualitative discussion, k_a may be taken as the number of collisions per second per unit concentrations. Taking the collision diameters[30] of H_2, C_3H_8, and Hg to be,

respectively, 2.9, 5.0, and 2.9 Å., and also using the information $\sigma^2(H_2) = 5.3$ and $\sigma^2(C_3H_8) = 1.3$, we obtain the following results: ξ for the quenching by H_2 = 0.63; ξ for the quenching by C_3H_8 = 0.083. The quenching by hydrogen is eight times more efficient. When ξ is close to unity, as it is in the quenching by hydrogen, the isotope effect in σ^2 is expected to be negligible because then the quenching rate is governed by the collision number, and σ^2 becomes equal to the square of collision diameter, which does not depend on isotopic substitution. We thus believe that the marked isotope effect observed in the quenching by paraffins and the fact that $\xi \ll 1$ in these quenchings are very closely related phenomena.

In the reaction involving p electrons, the cyclic activated complex (I) is more stable than a linear struc-

$$\begin{array}{c} Hg^* \\ \diagup \quad \diagdown \\ H\text{------}H \\ I \end{array}$$
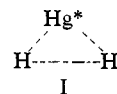
ture.[31] If such a complex is to form in the quenching by paraffins, then it must involve the carbon atom which is sterically hindered (II). The formation of the

$$\begin{array}{c} Hg^* \\ \diagup \quad \diagdown \\ -\overset{|}{\underset{|}{C}}\text{------}H \\ II \end{array}$$
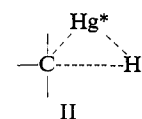
C–Hg bond here is likely to encounter a highly repulsive potential barrier, and the complex is likely to be forced to assume an open structure[32] (III). It is reasonable to

$$-\overset{|}{\underset{|}{C}}\text{---}H\text{---}Hg^* \cdot$$
$$III$$
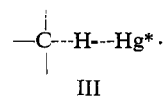
suppose that, with respect to the decomposition to the excited mercury and the quencher (which corresponds to process c), the cyclic complex is more stable than the open complex. On this basis, a much smaller value of ξ in the paraffin quenching is explainable. For a qualitative discussion of the isotope effect, we employ a crude model that the activated complex is an excited molecule, with the total energy of E ($\sim$113 kcal.), to which two decomposition paths, namely (b) and (c), are open. Classically, the rate constant of the decomposition of such an excited molecule is given as[33]

$$k = \nu\left(1 - \frac{E_0}{E}\right)^{n-1}$$

where ν is the frequency factor, n is the number of effective oscillators, and E_0 (for the present purpose)

(27) D. R. Bates, *Proc. Roy. Soc.* (London), **A257**, 22 (1960).

(28) For example, see ref. 3a, pp. 56–59.

(29) D. R. Bates, "Quantum Theory I. Elements," D. R. Bates, Ed., Academic Press Inc., New York, N. Y., 1961, pp. 259–261.

(30) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 1110–1112.

(31) J. L. Magee, *J. Chem. Phys.*, **8**, 687 (1940).

(32) The cyclic complex may involve atoms not bound to the bond to be broken (see ref. 8). For the formation of a cyclic complex, a good portion of electron cloud, originally in the stable C–H bond, must be relocalized in the Hg–H or Hg–C regions. This is expected to occur more readily with the bond to be broken; hence we presume that the cyclic structure involving atoms not bound to the reactive bond is less stable than the cyclic structure with the reactive bond. For the present purpose, then, the former complex plays the same role as the open structure; also see J. P. Chesick, *J. Am. Chem. Soc.*, **86**, 3597 (1964).

(33) N. B. Slater, "Theory of Unimolecular Reactions," Cornell University Press, Ithaca, N. Y., 1959.

may be considered as the strength of the bond to be broken, measured from the zero-point energy level; thus, k decreases with increasing E_0. The substitution by D reduces both k_b and k_c because the zero-point energies of both C–H and H–Hg bonds in the open structure are reduced. In the present case, the difference in the zero-point energies is governed by the force constant of the bond to be broken; hence, if we make a reasonable assumption that at the transition point the C–H bond is stronger than H–Hg, then the D substitution affects k_b more strongly than k_c. This leads to the decrease in ξ in agreement with the observed trend in σ^2. The same argument applies also in the quenching by H_2; but in this case, because of the stability of the cyclic complex, k_c is still quite small and ξ is close to unity. The isotope effect in σ^2 should be thus negligible.

Reactions of Energetic Carbon Atoms with Ammonia.   II[1,2]

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Carbon atoms react with gaseous ammonia to give methane, methylamine, and methylenimine. Methylenimine and part of the methylamine are formed in reactions between carbon atoms with excess kinetic energy ("energetic") and ammonia. Most of the methane is formed in thermal reactions. Evidence for the formation of formaldoxime from the reaction between carbon atoms and ammonia–oxygen mixtures is presented. Facile radiolytic reduction of methylenimine and methylamine has been demonstrated. The formation of hydrogen cyanide or any derivative thereof was not demonstrable under the reaction conditions.

Introduction

Until the ammonia system was first studied,[2] no system in which energetic carbon atoms were produced and allowed to react to give organic compounds had lent itself to a study of product distribution encompassing a complete determination of the chemical fate of all the carbon atoms produced in the system. The carbon atoms[2] were made *in situ* by using the nuclear reaction $N^{14}(n,p)C^{14}$, and the products were determined by identifying the carbon-14 containing compounds. The most significant feature of this study was the fact that all the activity was accounted for as gaseous products. It had not been until the demonstration by Hornig, Levey, and Willard[4] that "hot" iodine-128 atoms could react with gaseous methane to give methyl iodide-I^{128} that it was deemed possible for an atom with a large excess of kinetic energy to react in the gas phase. It had been assumed until that time that the amount of energy contained in the intermediate or complex would

be too great to allow stabilization in any other than the liquid or solid states.

Methane-C^{14} accounted for nearly all of the carbon-14 produced under the conditions used in the experiments of Yang and Wolf.[2] Traces of methylamine-C^{14} were also found. It was explicitly stated that the effect of the high extraneous radiation field accompanying hot carbon atom production in the nuclear reactor was difficult to evaluate. Further investigation was clearly needed to determine the effects of radiation chemistry on the distribution of carbon-14 in the products observed. The absorbed dose in the carbon-14 work was between 0.4 and 1.2 e.v./molecule.

Suryanarayana and Wolf[5] pointed out that energetic carbon-11 atoms could be made with considerably lower accompanying radiation dose. The nuclear reactions available for producing carbon-11 are numerous, and one in particular, the $N^{14}(p,\alpha)C^{11}$ reaction, is ideally suited for studies involving nitrogen-containing systems. Radiation doses accompanying the production of the hot atom could be varied from about 10^{-4} to 10 e.v./molecule. In addition the use of the carbon-11 technique[5] allows greater flexibility in experimental conditions so that gas, liquid, and solid phases and a wider variety of mixtures involving ammonia as the substrate could be studied.

The study of the reactions of energetic carbon atoms[6-8] is of primary interest. Nevertheless the mechanisms of these reactions cannot be studied until the role of the accompanying radiation damage is understood. A quantitative determination of the effect of the concomitant radiation on the spectrum of reaction products obtained by allowing energetic carbon atoms to react with ammonia was delineated in a

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Paper I: J. Y. Yang and A. P. Wolf, *J. Am. Chem. Soc.*, **82**, 4488 (1960).

(3) Visiting Scientist at B.N.L., 1961–1962, from Centro Chimica Nucleare, University of Rome, Italy.

(4) J. F. Hornig, G. Levey, and J. E. Willard, *J. Chem. Phys.*, **20**, 1556 (1952).

(5) B. Suryanarayana and A. P. Wolf, *J. Phys. Chem.*, **62**, 1369 (1958).

(6) A. P. Wolf, *Ann. Rev. Nucl. Sci.*, **10**, 259 (1960). This review details primarily the synthetic aspects of carbon atom reactions.

(7) See A. P. Wolf, *Advan. Phys. Org. Chem.*, **2**, 202 (1964), for a discussion of mechanism in carbon atom chemistry.

(8) See R. Wolfgang, *Progr. Reaction Kinetics*, in press.