

The Quenching of Excited Zinc(3P_J) Atoms by Alkane Hydrocarbons

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The intensities of the 307.6 nm resonance line of zinc were measured at different pressures of alkane hydrocarbons, and the quenching-rate constants were determined on the basis of the Stern-Volmer plots. A remarkable dependence of the quenching cross-section on the C–H bond strength was observed, and the relative decrease in the quenching cross-section with an increase in the C–H bond strength was interpreted in terms of the semiempirical bond-energy-bond-order(BEBO) method.

Recently, Breckenridge and Renlund have measured the quenching cross-sections of $\text{Cd}(^3P_J)$ by the use of several alkane hydrocarbons.¹⁾ They have then compared their values with those for the quenching of $\text{Hg}(^3P_0)$ and $\text{Hg}(^3P_1)$. They summarized the important aspects of their results as follows: (1) The $\text{Cd}(^3P_J)$ quenching-rate constants are remarkably small for alkane hydrocarbons. (2) There is a slight increase in the quenching cross-section in the order of primary, secondary, and tertiary C–H bonds. (This is in contrast to the fact that there is a remarkable dependence of the quenching cross-section on the C–H bond strength in the case of $\text{Hg}(^3P_{0,1})$). (3) The direct abstraction of a hydrogen atom to form CdH appears to be a major quenching pathway for all the alkanes studied, with the possible exception of methane. (4) The quenching of $\text{Cd}(^3P_J)$ by alkane hydrocarbons differs substantially from the quenching of $\text{Hg}(^3P_1)$. (They suggested that the difference in the quenching behavior between $\text{Cd}(^3P_J)$ and $\text{Hg}(^3P_1)$ can be understood if the mechanistic pathway for $\text{Hg}(^3P_1)$ is merely energetically inaccessible to the low-energy $\text{Cd}(^3P_J)$ atom.

Since the excitation energy of $\text{Zn}(^3P_J)$ lies between those of $\text{Cd}(^3P_J)$ and $\text{Hg}(^3P_1)$, we expected that the study of the quenching of $\text{Zn}(^3P_J)$ would give further detailed information about the mechanism. The present paper will deal with the quenching of $\text{Zn}(^3P_J)$ by several alkane hydrocarbons.

Experimental

The apparatus was the same as that previously described,²⁾ except for the use of a zinc-resonance lamp made of Pyrex. This lamp emits only resonance line, at 307.6 nm, which gives rise to $\text{Zn}(^3P_1)$ atoms. The reaction cell and the zinc lamp were kept in a furnace at $305 \pm 2^\circ\text{C}$ for most of the measurements. The light intensity from the cell was measured by means of a Hitachi spectrophotometer, Model 139. The pressures of the gases were measured by means of a Bourdon pressure gauge (W & T model 62-075, Nagano Keiki Co.). The low pressures of the quenching gases were measured using calibrated expansion volumes.

The zinc metal used was high-purity zinc (99.9999%) manufactured by Osaka Asahi Metal Co. The ethane, propane, ethylene, and propylene (Gasukuro Kogyo Co., Ltd.), and cyclopropane (Santetsu Kagaku Kogyo Co., Ltd.) were freeze-pumped several times. The isobutane and neopentane (Tokyo Kasei Kogyo Co., Ltd., E. P. grade) and other alkanes (Tokyo Kasei Co., Ltd., G. R. grade) were freeze-pumped several times and repeatedly subjected to trap-to-trap distillation. Pure-grade argon (Daido Sanso Co., 99.999%) was used without further purification.

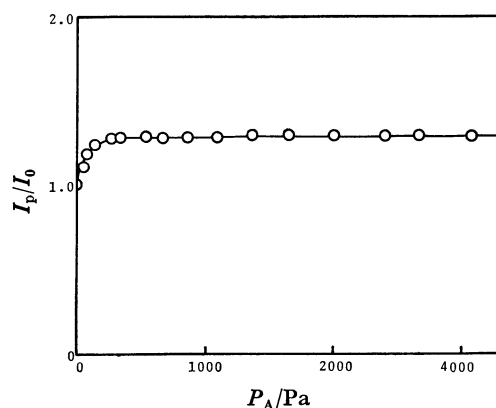


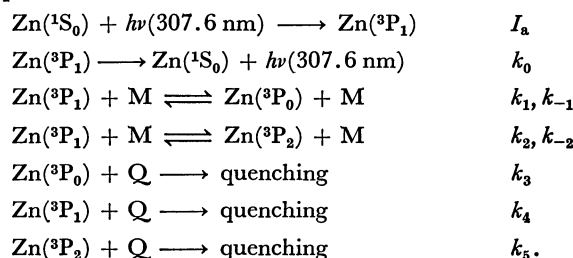
Fig. 1. Intensity of resonance line at 307.6 nm as a function of argon pressure.

Results

Pressure Dependence of the Emission Intensity at 307.6 nm.

When a cell containing zinc vapor was illuminated by the exciting lamp, a resonance line was observed at 307.6 nm. Upon the addition of argon, the intensity of the line increased with the increase in the pressure, as is shown in Fig. 1. This was attributed to the increase in the light intensity absorbed by zinc atoms as a result of the pressure broadening of the absorption line.²⁾ In order to minimize such pressure dependence of the absorption of the resonance line, quenchers were diluted with a large amount of argon (total pressures 1000–3000 Pa).

Quenching of the 307.6 nm Resonance Line. In a previous paper,²⁾ the following reaction scheme was proposed:



Here, M denotes Ar and/or quenchers. As before, the ratio of the emission intensities in the absence and in the presence of quenchers can be given as:

$$\frac{I_{307.6}^0}{I_{307.6}} = 1 + \frac{1}{k_0} \left(\frac{k_1}{k_{-1}} k_3 + k_4 + \frac{k_2}{k_{-2}} k_5 \right) [\text{Q}]. \quad (1)$$

Some typical Stern-Volmer plots for the quenching of the resonance line by several alkanes are shown

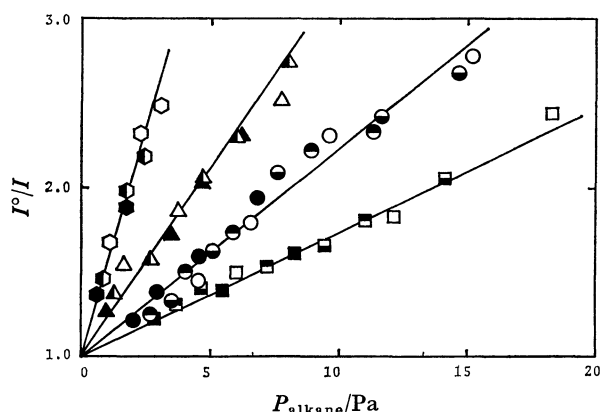


Fig. 2. Stern-Volmer plots for quenching of resonance line at 307.6 nm by alkanes diluted with argon 1) ethane: Total pressures are 2800 (■), 2100 (□), 1700 (▣), and 1300 Pa (●). 2) Propane: 2800 (○), 2100 (◐), 1700 (◑), and 1300 Pa (●). 3) Butane: 2800 (△), 2100 (▲), and 1700 Pa (▴). 4) Cyclopentane: 2800 (○), 2100 (◐), and 1700 Pa (●).

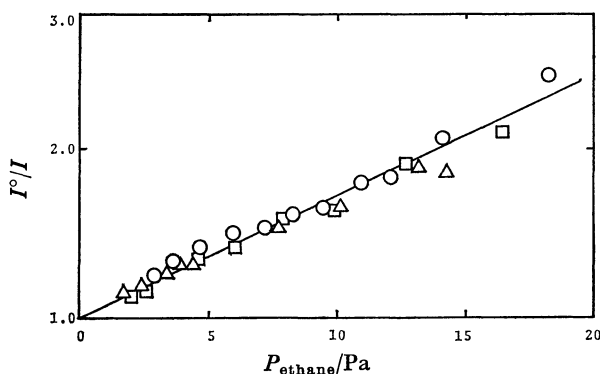


Fig. 3. Stern-Volmer plots for quenching of resonance line at 307.6 nm by ethane at various temperatures. 1) 290 °C (△), 2) 300 °C (○), 3) 320 °C (□).

in Fig. 2, where I° and I are the intensities of the resonance line in the absence and in the presence of quenchers respectively. Similar plots were obtained for other alkanes and alkenes. These Stern-Volmer plots are accounted for by Eq. 1.

As the f -value of the zinc 307.6 nm line is about one-tenth that of the cadmium 326.1 nm line,³⁾ the absorption of the 307.6 nm line by the zinc vapor (0.36 Pa at 305 °C) seems to be too small to cause any significant radiation trapping. If the lengthening of the effective radiation lifetime of $\text{Zn}(^3\text{P}_1)$ caused by radiation imprisonment is not negligible, the effective lifetime must be dependent on both the zinc pressure and the total pressure. In Fig. 3, the values of I°/I obtained for propane at various temperatures and at various total pressures are plotted as functions of the partial pressure of propane. The points lie on a straight line, and no dependence of the zinc pressure (from 0.25 Pa at 290 °C to 0.77 Pa at 320 °C) or the total pressure (1300–2700 Pa) can be seen. This suggests that the effective lifetime of the $\text{Zn}(^3\text{P}_1)$ is not lengthened by the radiation imprisonment under the present conditions. Therefore, k_0 can

TABLE 1. QUENCHING OF $\text{Zn}(^3\text{P}_J)$ BY ALKANES AND ALKENES

Gas	$10^{11} k_q$	$10^{18} \sigma_q$
	$\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	cm^2
H_2	106.6 ± 7.2	42.7 ± 2.8
D_2	64.1 ± 4.5	35.5 ± 2.5
CH_4	0.50 ± 0.01	0.50 ± 0.03
C_2H_6	2.88 ± 0.06	3.74 ± 0.06
C_3H_8	4.74 ± 0.09	6.94 ± 0.13
$c\text{-C}_3\text{H}_8$	12.8 ± 0.2	18.4 ± 0.4
$n\text{-C}_4\text{H}_{10}$	9.14 ± 0.21	14.5 ± 0.9
$i\text{-C}_4\text{H}_{10}$	5.02 ± 0.12	8.70 ± 0.20
$n\text{-C}_5\text{H}_{12}$	11.9 ± 0.2	21.8 ± 0.4
$i\text{-C}_5\text{H}_{12}$	8.53 ± 0.12	14.3 ± 0.21
$neo\text{-C}_5\text{H}_{12}$	4.45 ± 0.10	7.41 ± 0.22
$c\text{-C}_5\text{H}_{10}$	22.5 ± 0.4	41.1 ± 0.7
$c\text{-C}_6\text{H}_{12}$	34.5 ± 0.6	60.0 ± 1.0
C_2H_4	121.7 ± 2.4	153.9 ± 3.1
C_3H_6	89.7 ± 1.2	129.7 ± 1.9

be taken as the reciprocal of the natural lifetime of $\text{Zn}(^3\text{P}_1)$ ($\tau_0 = 2.0 \times 10^{-5} \text{ s}$).⁴⁾

From the slope of the Stern-Volmer plots, the composite rate constants for the quenching, $(k_1/k_{-1})k_3 + k_4 + (k_2/k_{-2})k_5$, were estimated. Since the three triplet states are in equilibrium, $k_1/k_{-1} = (1/3)\exp(2300/RT)$ and $k_2/k_{-2} = (5/3)\exp(-4730/RT)$, and at 305 °C k_1/k_{-1} and k_2/k_{-2} are 0.54 and 0.62 respectively. The quenching rate constants, $k_q (= 0.54k_3 + k_4 + 0.62k_5)$, and the corresponding quenching cross-sections for equilibrated $\text{Zn}(^3\text{P}_{0,1,2})$ calculated by means of:

$$\sigma_q = k_q \left[\frac{8RT}{\pi} \cdot \frac{M_{\text{Zn}} + M_q}{M_{\text{Zn}} \cdot M_q} \right]^{-1/2}, \quad (2)$$

are listed in Table 1.

As may be seen in Table 1, because the quenching cross-sections for alkanes determined here are considerably smaller than those for hydrogen and alkenes, it is important to discuss the possible effects on these measurements of very small amounts of impurities in the gases. Any hydrogen initially present in these gases would have been removed by many careful freeze-pump cycles performed. The alkanes used were at least 99.5% pure, except for neopentane (96% pure). Most of the impurities are thought to be other alkanes, and these alkane impurities at this level would not be sufficient to cause any considerable error in the measurements. For example, a 0.5% cyclopentane impurity causes about a 1% error in the cross-section for butane. On the other hand, alkenes have large cross-sections, and if the propane used contain 0.1% propylene, it would cause about a 1.8% error. This error is, however, within the limits of experimental error. Therefore, it is thought that, for alkanes except for neopentane, the errors attributable to possible impurity contents are negligibly small. As neopentane has a little larger amount of impurities, we regard the k_q value obtained for neopentane as the upper limit.

TABLE 2. COMARISON OF QUENCHING CROSS-SECTIONS AND CORRELATION OF THOSE CROSS-SECTIONS WITH C-H BOND STRENGTHS OF ALKANE HYDROCARBONS

Gas	Quenching cross-section			C-H bond strength ^{a)}	
	$10^{16}\sigma_q$ cm ²			kJ mol ⁻¹	
	Zn(3P_J)	Cd(3P_J) ^{b)}	Hg(3P_1) ^{c)}	Weakest	Average
CH ₄	0.50	0.0041	0.3	435	435
C ₂ H ₆	3.74	0.016	0.5	410	410
C ₃ H ₈	6.94	0.0082	7.2	395	406
<i>c</i> -C ₃ H ₈	18.4	—	5.0	423	423
<i>n</i> -C ₄ H ₁₀	14.5	—	18	396	404
<i>i</i> -C ₄ H ₁₀	8.73	0.011	22	381	407
<i>n</i> -C ₅ H ₁₂	21.8	—	42	396	403
<i>i</i> -C ₅ H ₁₂	14.3	—	53	381	405
<i>neo</i> -C ₅ H ₁₂	7.44	—	6.6	416	416
<i>c</i> -C ₅ H ₁₀	41.1	—	60	398	398
<i>c</i> -C ₆ H ₁₂	60.0	0.19	63	393	393

a) W. H. Breckenridge and O. K. Malmin, *J. Chem. Phys.*, **74**, 3307 (1981); J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York (1966). b) Ref. 1. c) Includes quenching to Hg(3P_0). Ref. 5.

Discussion

The reaction and quenching of Hg($^3P_{0,1}$) by alkane hydrocarbons have been very thoroughly studied,⁵⁻⁹⁾ and several mechanistic schemes have been proposed to explain the large body of data. In the case of Hg($^3P_{0,1}$), a remarkable dependence of the quenching rate on the C-H bond strength was observed. On the other hand, there is virtually no dependence in the case of Cd(3P_J), and the cross-sections for methane, propane, and isobutane can be fit by assuming an additive cross-section of 0.0010×10^{-16} cm² for each C-H bond, irrespective of the type of bond.¹⁾

Table 2 compares the quenching cross-sections of Zn(3P_J), Cd(3P_J), and Hg(3P_1) by alkanes; the C-H bond strength is also shown. It may be noted that the quenching cross-section of Zn(3P_J) depends greatly on the C-H bond strength, and that the dependence is very similar to that of Hg(3P_1). Since the quenching cross-sections of such alkanes as methane, ethane, and neopentane, which contain neither secondary nor tertiary C-H bonds, are considerably smaller than those of alkanes which do contain secondary and/or tertiary C-H bonds, it is plausible that, in the latter case, the weaker secondary and tertiary C-H bonds are predominantly ruptured in the primary quenching act. An inspection of Table 2, however, shows that the quenching cross-section of Zn(3P_J) by alkanes is more closely correlated with the average C-H bond strength than with the weakest C-H bond strength. The correlation between the average quenching cross-section per C-H bond and the average C-H bond strength for Zn(3P_J), Cd(3P_J), and Hg(3P_1) is shown in Fig. 4. In general, the cross-sections increase with a decrease in the C-H bond strength for Zn(3P_J) and Hg(3P_1), but those for Cd(3P_J) are almost constant. This figure also shows that the cross-sections increase more regularly for Zn(3P_J) than for Hg(3P_1). In the latter case, the plots are somewhat scattered. The

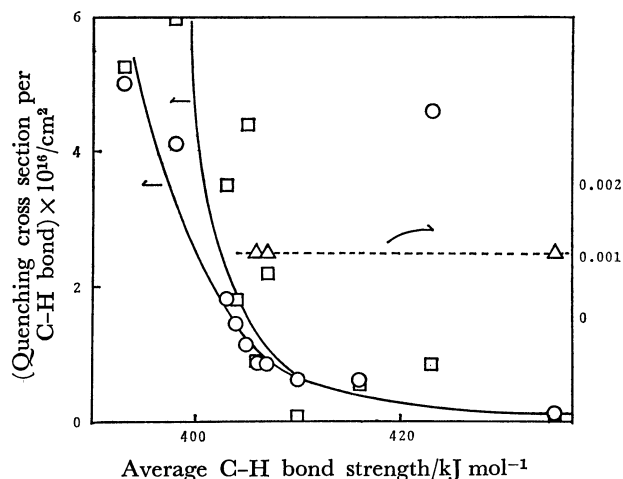


Fig. 4. The quenching cross section per C-H bond plotted against average C-H bond strength. Zn(3P_J) (O), Cd(3P_J) (Δ), and Hg(3P_1) (□).

good correlation shown indicates that the excited zinc do not attack only the weakest C-H bond, but all kinds of C-H bonds, with efficiencies which depend on the bond strength.

The quenching cross-section, σ_q , of a certain molecule is defined as the sum of the quenching cross-section, σ_i , for each individual quenching site (C-H bond):

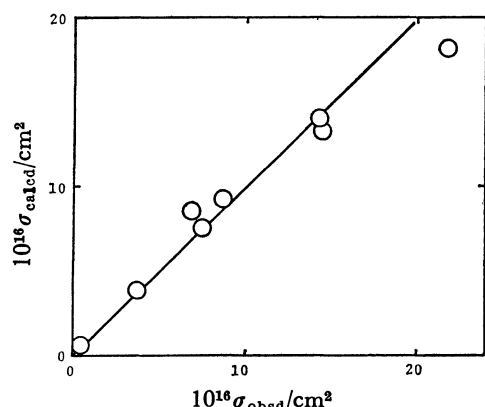
$$\sigma_q = \sum \sigma_i. \quad (3)$$

Conversely, from the obtained quenching cross-section, σ_q , an effective cross-section, σ_i , for each C-H bond can be calculated. The effective cross-section per C-H bond in methane and that per primary C-H bond are obtained by:

$$\sigma_i(\text{CH}_3\text{-H}) = \sigma_q(\text{CH}_4)/4$$

$$\sigma_i(\text{primary}) = \sigma_q(\text{C}_2\text{H}_6 \text{ or } \text{neo-C}_5\text{H}_{12})/(\text{number of C-H bonds}).$$

The effective cross-sections per secondary or tertiary

Fig. 5. Relationship between σ_{calcd} and σ_{obsd} .

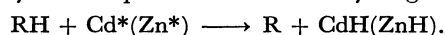
C-H bond are estimated by means of:

$$\begin{aligned} \sigma_1(\text{secondary}) &= \frac{\sigma_q(\text{C}_3\text{H}_8, n\text{-C}_4\text{H}_{10}, \text{ or } n\text{-C}_5\text{H}_{12}) - 6\sigma_1(\text{primary})}{\text{number of secondary C-H bonds}}, \\ \sigma_1(\text{tertiary}) &= \sigma_q(i\text{-C}_4\text{H}_{10}) - 9\sigma_1(\text{primary}) \\ &= \sigma_q(i\text{-C}_5\text{H}_{12}) - 9\sigma_1(\text{primary}) \\ &\quad - 2\sigma_1(\text{secondary}). \end{aligned}$$

The values of σ_1 thus obtained are given in Table 3. The average values of σ_1 for primary, secondary, and tertiary C-H bonds are 0.62, 2.4, and 3.6 respectively, corresponding to a ratio of 1:3.9:5.8. These values are different from those of 1:65:350 for $\text{Hg}(^3\text{P}_1)$ quenching.¹⁰⁾ In Fig. 5, the cross-sections, σ_{calcd} , calculated by summing the cross-sections, σ_1 , for primary, secondary, and tertiary C-H bonds shown in Table 3 are plotted against the observed cross-section, σ_{obsd} . This figure shows that the quenching cross-sections for alkanes can be reproduced fairly well by summing the σ_1 -values.

As is shown in Tables 2 and 3, the cross-sections for cyclopentane and cyclohexane are quite high. These high cross-sections for cycloalkanes were also observed in the cases of $\text{Cd}(^3\text{P}_j)$ and $\text{Hg}(^3\text{P}_1)$.⁵⁾ The higher cross-sections for cyclopentane and cyclohexane could be due to less steric repulsion in the cycloalkane C-H bond attack by excited atoms.

Table 4 shows the estimated enthalpies of reaction for the abstraction of a hydrogen atom by $\text{Zn}(^3\text{P}_j)$, $\text{Cd}(^3\text{P}_j)$, and $\text{Hg}(^3\text{P}_1)$ atoms from various types of C-H bonds in the alkane hydrocarbons. In the $\text{Cd}(^3\text{P}_j)$ - and $\text{Zn}(^3\text{P}_j)$ -photosensitized decomposition of alkanes, the major primary step is thought to be the C-H bond cleavage, which becomes energetically feasible only if the process is a true hydrogen transfer:



The formation of CdH in the course of the reaction can be readily detected spectroscopically.^{11,12)} In the case of the $\text{Hg}(^3\text{P}_1)$ -photosensitized decomposition, however, the direct cleavage of C-H bonds without the intermediate formation of HgH is also energetically possible; the enthalpy of reaction for this process is shown in Table 4. It seems interesting that the dependence of the quenching cross-section on the C-H bond strength decreases in this order: $\text{Hg}(^3\text{P}_1) >$

TABLE 3. EFFECTIVE CROSS-SECTION, σ_1 , FOR EACH C-H BOND

		$10^{16}\sigma_1$ cm ²
CH ₃ -H		0.13
	Primary	0.62
	Average	0.62
Secondary		1.6
		2.7
	Average	2.4
Tertiary		3.2
		3.9
	Average	3.6

TABLE 4. ENTHALPY OF REACTION FOR THE ABSTRACTION OF A HYDROGEN ATOM BY EXCITED METAL ATOMS

	$\frac{\Delta H}{\text{kJ mol}^{-1}}$			
	$\text{Zn}(^3\text{P}_1)$	$\text{Cd}(^3\text{P}_1)$	$\text{Hg}(^3\text{P}_1)$	$\text{Hg}(^3\text{P}_1)^a)$
CH ₃ -H	-38	0	-77	-37
Primary				
C ₂ H ₅ -H	-63	-25	-102	-62
(CH ₃) ₂ CH ₂ -H	-57	-19	-96	-56
Secondary				
(CH ₃) ₂ CH-H	-78	-40	-117	-77
Tertiary				
(CH ₃) ₃ C-H	-92	-54	-131	-91

$\text{Zn}(^3\text{P}_j) > \text{Cd}(^3\text{P}_j)$. This order is consistent with the order of the decrease in the enthalpy of reaction for the abstraction of a hydrogen atom.

In the case of $\text{Hg}(^3\text{P}_1)$, several workers⁵⁻⁸⁾ have proposed mechanism in which the initial step is the formation of a weak complex between $\text{Hg}(^3\text{P}_1)$ and the alkane quencher. The resulting complex can decompose (if there is sufficient energy) by surmounting a potential barrier, the height of which is dependent on the type of C-H bond. Such a general model was originally proposed by Yang,⁶⁾ and the rate of passage over the barrier has been estimated by the use of Kassel,⁶⁾ RRKM,⁷⁾ and BEBO⁸⁾ treatments. All of these theories would predict large variations with the C-H bond strength in quenching cross-sections for lower-energy $\text{Cd}(^3\text{P}_j)$ and $\text{Zn}(^3\text{P}_j)$. As has been mentioned above, however, the variation for $\text{Zn}(^3\text{P}_j)$ is considerably smaller than that for $\text{Hg}(^3\text{P}_1)$, and there is virtually no dependence on the C-H bond strength in the quenching of $\text{Cd}(^3\text{P}_j)$ by alkanes. Therefore, it is obvious that previous models based on $\text{Hg}(^3\text{P}_1)$ quenching data are not directly applicable for $\text{Zn}(^3\text{P}_j)$ and $\text{Cd}(^3\text{P}_j)$.

Recently, Breckenridge and Renlund have pointed out that the mechanistic pathways which have been proposed for $\text{Hg}(^3\text{P}_{0,1})$ quenching are not energetically accessible for $\text{Cd}(^3\text{P}_j)$ quenching and have proposed

a possible mechanism which is consistent with several observations in the $\text{Hg}(^3P_1)$ -alkanes system and explains the small variation of $\text{Cd}(^3P_J)$ quenching cross-sections among the alkane hydrocarbons studied.

In this paper, it is shown that the $\text{Zn}(^3P_J)$ -photosensitized decomposition of alkanes can be considered as a simple hydrogen-atom transfer reaction; consequently, it is possible to calculate the relative potential energies of activation of these reactions by a modified BEBO method.¹³⁾

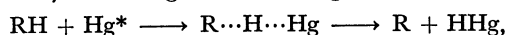
In the BEBO method, the potential energy of activation for hydrogen-atom abstraction by a radical as a function of the bond order, n , of the bond being broken is given by:

$$V = E_b(1-n^p) - E_t(1-n)^q + V_{tr}, \quad (4)$$

where E_b and E_t are the single-bond energies of the bond being broken and formed, V_{tr} is the triplet repulsion term, and p and q are the bond-energy indices defined by the expression:

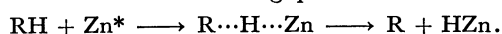
$$p \text{ or } q = \frac{0.26 \ln(D_0/\epsilon_x)}{r_x - r_e}, \quad (5)$$

in which ϵ_x and r_x are the potential depth and the equilibrium internuclear distance of the analogous diatomic noble gas cluster, while D_0 and r_e are the bond dissociation energy and the equilibrium internuclear distance of the bond in question. Strausz *et al.*⁹⁾ calculated the potential energies of activation for the mercury-photosensitized decomposition of alkanes by assuming the following model:



and by neglecting the repulsive triplet term, V_{tr} . They described since the model assumed is somewhat oversimplified, only the relative values are significant.

In the case of $\text{Zn}(^3P_J)$, we could not obtain information about the bond-energy index (q). Therefore, we estimated only the relative potential energy of activation for the following process:



If it can be assumed that the bond order, n , for the transition state and the bond-energy index, q , are constant, irrespective of the type of C-H bond being broken, the activation energy referred to that for $\text{CH}_3\text{-H}$ is expressed by the following equation:

$$\Delta V = E_b(1-n^p) - E_b^{\text{CH}_3}(1-n^{p_0}), \quad (6)$$

where $E_b^{\text{CH}_3}$ and p_0 are the bond energy of $\text{CH}_3\text{-H}$ and the p -value for the $\text{CH}_4\text{-Zn}^*$ system. If $p=p_0$, as was assumed for the alkane- Hg^* system by Strausz *et al.*, the above equation becomes:

$$\Delta V = (E_b - E_b^{\text{CH}_3})(1-n^p). \quad (7)$$

The cross-section, σ_1 is expressed by the following equation:

$$\sigma_1 \propto k_1 = A \exp(-V/RT). \quad (8)$$

Therefore, $\sigma_1/\sigma_1^{\text{CH}_3}$ can be expressed as follows:

$$\ln \sigma_1/\sigma_1^{\text{CH}_3} = -\Delta V/RT. \quad (9)$$

From Eqs. 7 and 9, the following equation is obtained:

$$\ln \sigma_1/\sigma_1^{\text{CH}_3} = -\frac{(1-n^p)}{RT}(E_b - E_b^{\text{CH}_3}). \quad (10)$$

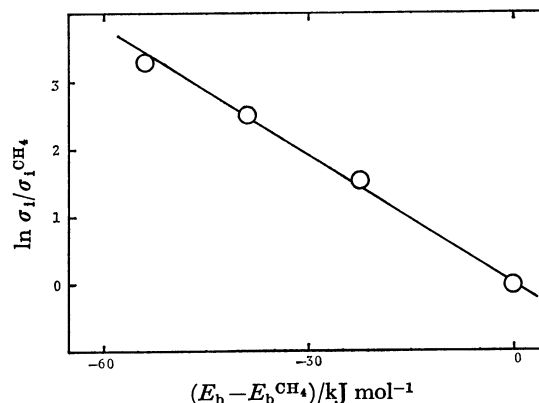


Fig. 6. Relationship between $\ln \sigma_1/\sigma_1^{\text{CH}_3}$ and $E_b - E_b^{\text{CH}_3}$.

In Fig. 6, $\ln \sigma_1/\sigma_1^{\text{CH}_3}$ is plotted as a function of $E_b - E_b^{\text{CH}_3}$. From the slope of the straight line in Fig. 6, the value of $(1-n^p)/RT$ can be estimated to be 0.063 mol/kJ . If we used the same p -value as that used for the alkane- $\text{Hg}(^3P_1)$ system, a bond order, n , of about 0.7 is obtained. This value is almost the same as that obtained for the alkane- $\text{Hg}(^3P_1)$ system and so may be thought to be valid.

By the BEBO method, the relative values of the cross-section of the $\text{Zn}(^3P_J)$ quenching by alkanes can be explained. As was mentioned above, however, it is difficult to explain the difference in the variations with the C-H bond strength in quenching cross-sections between those obtained for $\text{Zn}(^3P_J)$ and for $\text{Hg}(^3P_1)$ by means of the BEBO method.

Strausz *et al.* calculated the potential energy of activation for the $\text{Hg}(^3P_1)$ -photosensitized decomposition of alkanes and described the BEBO calculation predicts the observed trends. By using the values of the potential energy of activation obtained by them, and by assuming that the relative quenching cross-sections of the various types of C-H bonds are governed only by the difference in the activation energy, the relative quenching cross-sections for primary, secondary, and tertiary C-H bonds can be calculated. These calculated values of 1:8:43 are considerably smaller than the observed values. The temperature at which the $\text{Hg}(^3P_1)$ -photosensitized reaction was carried out was lower than that for the $\text{Zn}(^3P_J)$ -photosensitized reaction; therefore, the selectivity appears to be somewhat emphasized for the former. However, it seems to be impossible to explain the large variation with the C-H bond strength in the quenching cross-section for higher-energy $\text{Hg}(^3P_1)$ in terms of the same mechanism as that used for $\text{Zn}(^3P_J)$.

In the case of $\text{Hg}(^3P_1)$, the quenching by alkanes appears to result in a direct cleavage of the C-H bonds without the intermediate formation of HgH , as was pointed out by Breckenridge and Renlund.¹⁾ The cleavage with the formation of hydride, as in the $\text{Zn}(^3P_J)$ -photosensitized decomposition, involves a transition state in which the Zn-H bond is partly formed. The formation of the Zn-H bond somewhat lowers the potential energy and seems to make the $\text{Zn}(^3P_J)$ quenching less sensitive to the C-H bond strength.

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