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The Temperature Dependence of the Quenching Rate of the 307.6 nm Zinc Resonance Line by Some Alkane Hydrocarbons

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The intensities of the 307.6 nm resonance line of zinc were measured as a function of the alkane pressure at various temperatures between 556 and 696 K, and the quenching rate was determined on the basis of the Stern-Volmer plots. Assuming that the quenching rate constant, k_Q, of a certain alkane is equal to the sum of the quenching-rate constant, k_i, for each C-H bond, the ratios of k_s/k_p and k_t/k_p (k_p, k_s, and k_t are the quenching-rate constants for primary, secondary, and tertiary C-H bonds) were estimated from the ratios of the quenching rates of butane, isobutane, and neopentane. The differences in the activation energies for the quenching for primary, secondary, and tertiary C-H bonds were obtained from the temperature dependence of the ratios of k_s/k_p and k_t/k_p and were interpreted in terms of the modified bond-energy-bond-order (BEBO) method.

In a previous paper,[1] a remarkable dependence of the quenching of the cross section of the 307.6 nm zinc resonance line by alkane hydrocarbons on the C-H bond strength was reported. It was pointed out that the quenching cross-section of a certain alkane can be estimated as the sum of the quenching cross-section for each individual quenching site (C-H bond). The above findings show that the excited zinc atoms attack not only the weakest C-H bond, but all kinds of C-H bonds, with efficiencies which depend on the bond strength, and it was concluded that hydrogen-atom abstraction from hydrocarbons by means of excited zinc atoms plays an important role in the quenching of $Zn(^3P_J)$.

In this study, relative quenching-rate constants for butane, isobutane, and neopentane were determined over the temperature range of 556—696 K, and from these values the ratios of k_s/k_p and k_t/k_p (k_p, k_s, and k_t are quenching-rate constants for primary, secondary, and tertiary C-H bonds) were estimated at various temperatures.

Experimental

The apparatus and the procedure were the same as those described previously.[1,2]

The zinc metal used was high-purity zinc (99.9999%) manufactured by the Osaka Asahi Metal Co. The ethane, butane, isobutane, and neopentane (Tokyo Kasei Kogyo 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.

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 argon pressure. 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.[1,2] In order to minimize this effect of the pressure broadening of the absorption line, quenchers were diluted with a large amount of argon (total pressures: 1333—2666 Pa).

Results and Discussion

In a previous paper, the following reaction scheme was proposed for the quenching of $Zn(^3P_J)$[1,2]

$$\begin{array}{ll}
Zn(^1S_0) + h\nu(307.6\,\text{nm}) \longrightarrow Zn(^3P_1) & I_a \\
Zn(^3P_1) \longrightarrow Zn(^1S_0) + h\nu(307.6\,\text{nm}) & k_0 \\
Zn(^3P_1) + M \rightleftharpoons Zn(^3P_0) + M & k_1, k_{-1} \\
Zn(^3P_1) + M \rightleftharpoons Zn(^3P_2) + M & k_2, k_{-2} \\
Zn(^3P_0) + Q \longrightarrow \text{quenching} & k_3 \\
Zn(^3P_1) + Q \longrightarrow \text{quenching} & k_4 \\
Zn(^3P_2) + Q \longrightarrow \text{quenching} & k_5 .
\end{array}$$

Here, M denotes Ar and quenchers, and Q represents quenchers. By assuming the steady state for $Zn(^3P_{0,1,2})$, the following equation can be derived:

$$\frac{I^\circ}{I} = 1 + \frac{1}{k_0}\left(\frac{k_1}{k_{-1}}k_3 + k_4 + \frac{k_2}{k_{-2}}k_5\right)[Q]. \qquad (1)$$

where I° and I are the intensities of the resonance line in the absence and in the presence of quenchers respectively. Stern-Volmer plots for the quenching by butane at various temperatures are shown in Fig. 1.

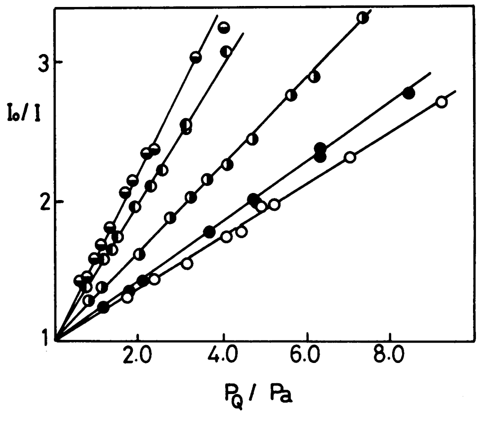

Fig. 1. Stern-Volmer plots for the quenching of Zn(^3P_J) by butane at various temperatures.
556 (○), 605 (●), 636 (◑), 666 (◐), and 696 K (◒).

Table 1. $k_Q\tau$ Values in the Quenching of $Zn(^3P_J)$ Atoms by Butane, Isobutane, and Neopentane at Various Temperatures

T		$k_Q\tau$ Pa^{-1}	
K	Butane	Isobutane	Neopentane
556	0.188±0.003	0.127±0.003	0.105±0.002
578	0.194±0.003	0.133±0.003	0.112±0.003
605	0.208±0.003	0.144±0.003	0.125±0.003
636	0.317±0.005	0.219±0.004	0.195±0.003
666	0.500±0.008	0.350±0.006	0.320±0.006
696	0.798±0.013	0.559±0.009	0.518±0.009

Table 2. Quenching Rate Constants of Neopentane and Ethane

T	$k_Q\tau$	k_Q'	k_Q''
K	Pa^{-1}	10^{-12} cm^3 molecule^{-1} s^{-1}	10^{-12} cm^3 molecule^{-1} s^{-1}
Neopentane			
548	0.095±0.002	3.00±0.08	2.97
556	0.105±0.002	3.36±0.08	3.33
567	0.107±0.002	3.50±0.08	3.43
578	0.112±0.003	3.74±0.12	3.60
588	0.119±0.003	4.03±0.12	3.80
596	0.124±0.003	4.27±0.13	3.92
605	0.125±0.003	4.35±0.13	3.85
636	0.195±0.003	7.14±0.13	4.64
666	0.320±0.006	12.3 ±0.2	4.22
696	0.518±0.009	20.8 ±0.3	3.37
Ethane			
553	0.063±0.001	4.02±0.04	3.98
563	0.065±0.001	4.18±0.04	4.14
568	0.068±0.002	4.45±0.08	4.36
573	0.073±0.002	4.80±0.08	4.62
588	0.076±0.002	5.13±0.08	4.84
599	0.081±0.002	5.57±0.08	5.11
613	0.094±0.003	6.62±0.13	5.76

Similar plots were obtained for other quenchers. From the slope of the straight lines, the values of $k_Q\tau$ ($k_Q=(k_1/k_{-1})k_3+k_4+(k_2/k_{-2})k_5$ and $\tau=1/k_0$) were estimated; they are listed in Tables 1 and 2.

As has been mentioned above, k_Q is the composite rate constant for the quenching of $Zn(^3P_0)$, $Zn(^3P_1)$, and $Zn(^3P_2)$. Since the three triplet states are in equilibrium, $k_1/k_{-1}=(1/3)\exp(2.30\ \mathrm{kJ\ mol^{-1}}/RT)$ and $k_2/k_{-2}=(5/3)\exp(-4.70\ \mathrm{kJ\ mol^{-1}}/RT)$,[2] k_1/k_{-1} and k_2/k_{-2} are temperature-dependent. As these equations show, k_1/k_{-1} decreases slightly, and k_2/k_{-2} increases with an increase in the temperature, but their changes are small.

The quenching rate constant, k_Q, can be rewritten as follow:

$$k_Q = k_4\left(\frac{k_1}{k_{-1}}\frac{k_3}{k_4} + 1 + \frac{k_2}{k_{-2}}\frac{k_5}{k_4}\right) \qquad (2)$$

Since the excitation energy increases in this order: $Zn(^3P_0)$, $Zn(^3P_1)$, and $Zn(^3P_2)$, the activation energies for k_3, k_4, and k_5 decrease in that order. Therefore, k_3/k_4 increases, and k_5/k_4 decreases, with the temperature. Since the changes in k_1/k_{-1} and k_2/k_{-2} are compensated for by the changes in k_3/k_4 and k_5/k_4, the temperature-dependence of the value in parentheses in Eq. 2 seems to be very small. It can be said that k_Q is approximately proportional to k_4.

In Fig. 1, the Stern-Volmer plots at various temperatures for butane are shown. The slope of the line increases with the temperature. A similar temperature-dependence was observed for the quenching by isobutane and neopentane.

As has been mentioned above, the value of $k_Q\tau$ can be obtained from the slope of the Stern-Volmer plots. These values for butane, isobutane, and neopentane are shown in Fig. 2 as a function of the temperature. As is shown in Fig. 2, the value of $k_Q\tau$ slightly increases with the temperature below about 606 K, while the $k_Q\tau$ value increases more rapidly at temperatures higher than 606 K. This indicates that the effective lifetime (τ) of $Zn(^3P_1)$ may be hardly lengthened at all by the radiation imprisonment below 606 K. However, the effect of imprisonment can not be neglected at temperatures higher than 606 K.

Therefore, the quenching rate constant, k_Q, can be calculated from the slope by using the natural lifetime (2.0×10^{-5} s)[3] as τ below 606 K, but not at higher temperatures. Only the relative rate constant can be estimated from the slope at higher temperatures.

The ratios of the imprisonment lifetime to the natural lifetime at various temperatures were calculated by the use of the following equation, given by Milne for infinite slab geometry:[4]

$$\tau/\tau_0 = 1 + (kl/\lambda)^2, \tag{3}$$

where k is the absorption coefficient at the line center, l is the thickness of the slab, and λ is the root between 0 and $\pi/2$ of the equation:

$$\tan y = kl/y. \tag{4}$$

Samson[5] has modified Milne's theory so that an equivalent opacity $\bar{k}\,l$ is used in Eqs. 3 and 4 instead of kl, the opacity at the line center. The equivalent opacity for the Doppler line-shape is defined by :

$$\exp(-\bar{k}l) = \frac{\int_{-\infty}^{\infty}\exp(-\omega^2)\exp[-kl\exp(-\omega^2)]d\omega}{\int_{-\infty}^{\infty}\exp(-\omega^2)d\omega}, \tag{5}$$

where $\omega=[2(\nu-\nu_0)/\Delta\nu_D](\ln 2)^{1/2}$ ($\Delta\nu_D$ is the Doppler breadth). k can be estimated by means of this equation:

$$k = (2/\Delta\nu_D)(\ln 2/\pi)^{1/2}(\lambda_0{}^2/8)(g_2/g_1)([\mathrm{Zn}]/\tau_0) \tag{6}$$

where g_2 and g_1 are the degeneracies of the upper and lower states respectively, λ_0 is the wavelength at the center of the atomic line, and τ_0 is the natural lifetime of an excited atom. The values of $\bar{k}\,l$ for the Doppler case were obtained by the interpolation of the values given by Zemansky[6] and Blickensderfer et al.[7]

The values of τ/τ_0 calculted by Samson's method are shown in Table 3. As Table 3 shows, the imprisonment effect can be nearly neglected below 605 K, but it becomes significant at higher temperatures. This finding is in agreement with the tendency observed above.

In Fig. 3, the ratios of k_Q(butane)/k_Q(neopentane) and k_Q(isobutane)/k_Q(neopentane) are shown as a function of $1/T$. These plots give curves. This can be explained by considering that butane and isobutane have two types of reaction sites (the former has primary and secondary C–H bonds, while the latter

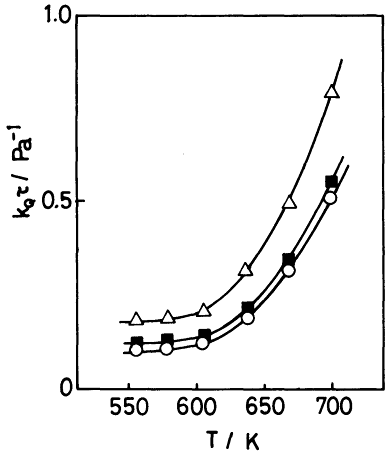

Fig. 2. Temperature dependence of $k_Q\tau$.
Butane (△), isobutane (■), and neopentane (○).

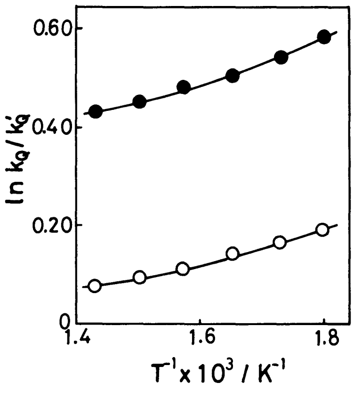

Fig. 3. Temperature dependence of rate constant ratio.
k_Q(butane)/k_Q(neopentane) (●) and k_Q(isobutane)/k_Q(neopentane) (○).

Table 3. $k_Q\tau$ Values in the Quenching of Zn(^3P_J) Atoms by Neopentane and the Imprisonment Lifetime at Various Temperatures

T	P_{Zn} a)	k b)	$k_Q\tau$	τ
K	Pa	cm^{-1}	Pa^{-1}	τ_0
548	0.045	0.016	0.095±0.002	1.01
556	0.070	0.024	0.105±0.002	1.01
567	0.124	0.041	0.107±0.002	1.02
578	0.217	0.069	0.112±0.003	1.04
588	0.353	0.110	0.119±0.003	1.06
596	0.515	0.157	0.124±0.003	1.09
605	0.779	0.233	0.125±0.003	1.13
636	2.96	0.822	0.195±0.003	1.54
666	9.57	2.48	0.320±0.006	2.91
696	27.99	6.79	0.518±0.009	6.15

a) $\log(133.33P_{Zn}/\mathrm{Pa})=-7198/T+9.664$: J. D. McKinley and J. E. Vance, *J. Chem. Phys.*, **22**, 1120 (1954). b) The absorption coefficient at the center of the Doppler-broadened line.

has primary and tertiary C–H bonds) and that the activation energies for the rates of quenching by these C–H bonds are not equal to each other.

In a previous paper,[1] we reported that the quenching cross section for any C_1—C_5 alkanes can be calculated by the following equation:

$$\sigma_Q = \sum n_i \sigma_i \tag{7}$$

where n_i is the number of the C–H bond of Type i (CH_3–H, primary C–H, secondary C–H, and tertiary C–H) and where σ_i is the cross section for each C–H bond of Type i. If a similar additivity can be applied for the quenching rates by butane, isobutane, and neopentane at every temperature examined, the following equations must hold:

$$\frac{k_Q(\text{butane})}{k_Q(\text{neopentane})} = \frac{6k_p + 4k_s}{12k_p} = \frac{1}{2} + \frac{1}{3}\frac{k_s}{k_p} \tag{8}$$

$$\frac{k_Q(\text{isobutane})}{k_Q(\text{neopentane})} = \frac{9k_p + k_t}{12k_p} = \frac{3}{4} + \frac{1}{12}\frac{k_t}{k_p} \tag{9}$$

Therefore, the following equations can be obtained:

$$\frac{k_s}{k_p} = \{ \frac{k_Q(\text{butane})}{k_Q(\text{neopentane})} - \frac{1}{2} \} \times 3 \tag{10}$$

$$\frac{k_t}{k_p} = \{ \frac{k_Q(\text{isobutane})}{k_Q(\text{neopentane})} - \frac{3}{4} \} \times 12 \tag{11}$$

From the experimental values for k_Q(butane)/k_Q(neopentane) and k_Q(isobutane)/k_Q(neopentane) shown in Fig. 3, the ratios of k_s/k_p and k_t/k_p at various temperatures can be calculated. In Fig. 4, the Arrhenius plots for k_s/k_p and k_t/k_p are shown. These Arrhenius plots give straight lines. The differences in the activation energies for k_s and k_p and for k_t and k_p were found to be 4.6±0.4 and 7.5±0.5 kJ mol^{-1} respectively.

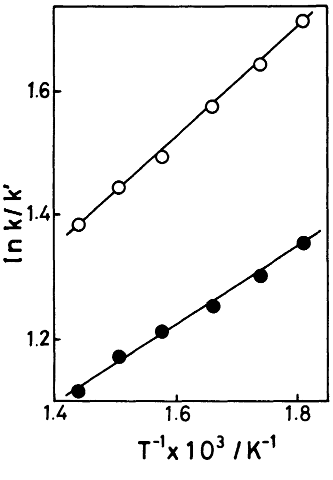

Fig. 4. Arrhenius plots for k_s/k_p (●) and k_t/k_p (○).

Since the imprisonment effect is nearly neglected below 606 K, as has been mentioned above, the quenching-rate constant, k_Q, can be calculated from the $k_Q\tau$ value using the natural lifetime as τ. In Table 2, the quenching-rate constants(k_Q') per C–H bond for neopentane and ethane, which have only primary C–H bonds, are shown. The optimized expressions for the rate constants(k_Q'), in the units cm^{3}molecule^{-1}s^{-1}, are:

$$k_Q'(\text{neopentane}) = (1.9 \pm 0.3) \times 10^{-10} \times \exp\{(-18.7 \pm 1.6)\text{kJ mol}^{-1}/RT\} \tag{12}$$

$$k_Q'(\text{ethane}) = (2.5 \pm 0.3) \times 10^{-10} \times \exp\{(-19.0 \pm 2.0)\text{kJ mol}^{-1}/RT\} \tag{13}$$

The activation energies for neopentane and ethane are in good agreement with each other. The activation energy for a primary C–H bond is determined to be 18.9±1.8 kJ mol^{-1}. The ratio (1.32) of the frequency factors of k'_Q for ethane and neopentane is approximately equal to the ratio (1.29) of the relative velocities for Zn*+ethane and Zn*+neopentane. This is in agreement with the prediction from the simple collision theory. Equations 12 and 13 show that the quenching cross-sections per C–H bond for neopentane and ethane are in agreement with each other at every temperature.

As has been mentioned above, the imprisonment effect below 605 K is very small and was neglected in the above treatment. If the imprisonment effect is taken into account, that is, if the effective lifetime of the excited zinc atoms shown in Table 3 is used, somewhat smaller quenching rate constants (k_Q'') are obtained from the $k_Q\tau$ values (Table 2). The activation energies calculated from these rate constants below 636 K are a little smaller (13.1±1.8 kJ mol^{-1} for neopentane and 14.8±1.8 kJ mol^{-1} for ethane) than those obtained using the natural lifetime.

Since the rate constant for neopentane calculated using the effective lifetime shown above decreases with the temperature above 636 K, and since the difference in the activation energies obtained from k_Q'' for ethane and neopentane is larger than that obtained from k_Q', and since the ratio of the frequency factors (1.8) of k_Q'' for ethane and neopentane is considerably larger than that predicted from the simple collision theory, the imprisonment lifetime shown in Table 3 does not seem to be precise (it may be too large at higher temperatures). The above estimation of the imprisonment lifetime may include some uncertainty because of the effect of collision broadening, the presence of the isotopes of the zinc atom, and the difference in the experimental conditions from the ideal conditions of infinite slub and uniform external excitation. Therefore, the activation energies calculated from k_Q'' seem to be lower limits, whereas those estimated from k_Q' (by neglecting the imprisonment effect) are upper limits. The activation energy for the

Table 4. Potential Energies of Activation as Calculated by the BEBO Method

Parameter	V_a/kJ mol^{-1}		
	Primary	Secondary	Tertiary
Old	7.5	4.9	3.7
Old modified[a]	18.4	14.6	12.0
Gilliom's	6.4	3.9	2.3
Gilliom's modified[a]	15.0	11.1	8.9
Experimental	16.5±2.5	11.9±2.5	9.0±2.5

a) The correction for zero-point energy is made using the calculated frequencies of the transition state and the stretching frequency of the reactant (Ref. 12).

primary C–H bond was concluded to be 16.5±2.5 kJ mol^{-1}. From this value and the values of the differences in the activation energies for k_p, k_s, and k_t shown above, the activation energies for secondary and tertiary C–H bonds were calculated; they are listed in Table 4.

Strausz et al.$^{8)}$ calculated the potential energies of activation for the mercury-photosensitized decomposition of alkanes by the BEBO method by assuming the following model:

$$\mathrm{RH} + \mathrm{Hg}^* \longrightarrow \mathrm{R{-}{-}H{-}{-}Hg} \longrightarrow \mathrm{R} + \mathrm{HHg}.$$

Since the repulsive triplet term was neglected, they pointed out that their calculation was somewhat oversimplified and that only the relative values were significant.

We have also applied the BEBO method to the quenching of excited zinc atoms by alkane by assuming the following model:

$$\mathrm{RH} + \mathrm{Zn}^* \longrightarrow \mathrm{R{-}{-}H{-}{-}Zn} \longrightarrow \mathrm{R} + \mathrm{HZn}.$$

We could thus qualitatively interpret the relative decrease in the quenching cross section with an increase in the C–H bond strength.$^{1)}$

In the BEBO formulation, the value of the potential energy of activation, V_a, is obtained by finding the value of n, the bond order of the breaking C–H bond, that causes V to reach its maximum value, subject to the constraint that the sum of the bond orders of the forming Zn–H bond and of the breaking C–H bond is unity.$^{9)}$

$$V = D_{\mathrm{DH}}(1-n^p) - D_{\mathrm{ZnH}}(1-n)^q + C_1 D_{\mathrm{ZnC}} B(n-n^2)^\gamma\{1+B(n-n^2)^\gamma\} \tag{14}$$

where:

$$B = C_2 \exp\{-\beta(R_{\mathrm{CH}} + R_{\mathrm{ZnH}} - R_{\mathrm{ZnC}})\} \tag{15}$$

$$\gamma = C_3\beta \tag{16}$$

The BEBO parameters p and q are given by:

$$p = C_3 \ln(D_{\mathrm{HC}}/D_{\mathrm{HeNe}})(R_{\mathrm{HeNe}} - R_{\mathrm{HC}}) \tag{17}$$

$$q = C_3 \ln(D_{\mathrm{ZnH}}/D_{\mathrm{KrHe}})/(R_{\mathrm{KrHe}} - R_{\mathrm{ZnH}}) \tag{18}$$

In these expressions, C_1 is the factor of the anti-Morse function (the old, C_1=1, old-modified, C_1=2, as suggested by Mayer and Schieler,$^{10)}$ Gilliom's, C_1=1 and Gilliom's modified parameters, C_1=2,$^{11)}$ were used) C_2 is 0.5 for the old BEBO method and is 0.45 for the Gilliom's method, C_3 is the Pauling constant (Gilliom recommended C_3=0.28 rather than the older value of 0.26), β is the Morse-function parameter for ZnC, and D and R are the normal single-bond energy (corrected for zero-point energy) and the distance for the indicated molecule respectively.

Table 4 gives the potential energies of activation as calculated by the BEBO method using the parameters shown above. Table 4 shows that the old modified and Gilliom's modified methods, which are generally used for the hydrogen-atom abstraction by such triplet species as O(^{3}P), give activation energies which are almost within the limits of experimental error.

Gilliom$^{11)}$ compared the activation energies calculated by the BEBO method with the experimental values for about 100 reactions and pointed out that the BEBO method in its original form gives an average error of 6.4 kJ mol^{-1}, while his method affords an average error of 5.4 kJ mol^{-1}. Thus, the agreement between experimental and calculated activation energies for the present study seems to be good considering the experimental error and the empiricism of the BEBO method.

As has been mentioned above, the experimental activation energies for the quenching of Zn(^3P_J) by alkanes are in good agreement with those calculated by the BEBO method by assuming this model: RH+Zn*→R--H--Zn→R+H-Zn. This strongly suggests that, in the initial stage of zinc-photosensitized reaction of alkanes, the hydrogen-atom abstraction by excited zinc atoms from alkane molecules occurs. In order to make sure of this point, further studies are in progress of the isotope effect on the quenching rate and of the zinc-photosensitized decomposition of ethane and propane based on product analysis.

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