The Temperature Dependence of the Quenching Rate of the 307.6 nm Zinc Resonance Radiation by Methane and Cyclopropane

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Synopsis. The quenching rate constants of $Zn(^3P_J)$ by methane and cyclopropane at various temperatures were determined on the basis of the Stern-Volmer plots. The activation energy for the quenching by methane was similar to that by cyclopropane. The frequency factor for the quenching-rate constant by cyclopropane was very large.

There has been much evidence to suggest that the mercury-photosensitized decomposition of most alkanes, including cycloalkanes, is initiated by the rupture of a C–H bond with an efficiency close to unity.[1,2] Methane and cyclopropane are, however, apparent exceptions to this behavior. Back and Auwera have pointed out[3] that the primary quenching process of $Hg(^3P_1)$ atoms by methane does not involve the decomposition of methane. Cyclopropane occupies a unique among the reactions of alkanes with $Hg(^3P_1)$ atoms.[1] It is the only hydrocarbon (of the alkanes investigated to date) whose C–C bond appears to be ruptured by the primary process.

In a previous paper,[4] a remarkable dependence of the quenching cross-section of the 307.6 nm zink-resonance radiation by alkane hydrocarbons on the C–H bond strength was reported. The activation energy for the quenching was found to decrease in the following order: primary>secondary>tertiary.[5] It was concluded that hydrogen-atom abstraction from hydrocarbons by excited zinc atoms plays an important role in the quenching of $Zn(^3P_J)$.[4,5]

The C–H bond energies of methane and cyclopropane are larger than that of the primary C–H bond. The quenching cross-section per C–H bond for methane is smaller than that for ethane;[5] this is consistent with the expectation from their C–H bond strengths. The quenching cross-section per C–H bond for cyclopropane, however, is considerably larger than that for ethane.[5] In the present study, the quenching rate constant by methane relative to that by ethane, and the quenching rate constant by cyclopropane relative to that by ethane, were determined over the temperature range of 538—608 K, and from these values the difference in the activation energies and the ratio of the frequency factors for the quenching by methane, ethane, and cyclopropane were estimated.

Experimental

The apparatus and the procedure were the same as those described previously.[4,5]

Cyclopropane (pure-grade; Takachiho Shoji K.K. 99.0%) was freeze-pumped several times and repeatedly subjected to trap-to-trap distillation. Research grade methane (Takachiho Shoji K.K. 99.99%) was used after passing it through a 1-m trap kept at 77 K.

Results and Discussion

When a cell containing zinc vapor was illuminated by the excitation lamp, a resonance radiation at 307.6 nm was observed. When methane–argon and cyclopropane–argon mixtures were added to the zinc vapor, the intensity of the emission at 307.6 nm decreased with the increase in the partial pressures of methane and cyclopropane. The Stern–Volmer plots for the quenching by methane and cyclopropane at various temperatures are shown in Fig. 1, where I° and I are the emission intensities at 307.6 nm in the absence and in the presence of quenchers respectively.

The quenching of the zinc resonance radiation can be

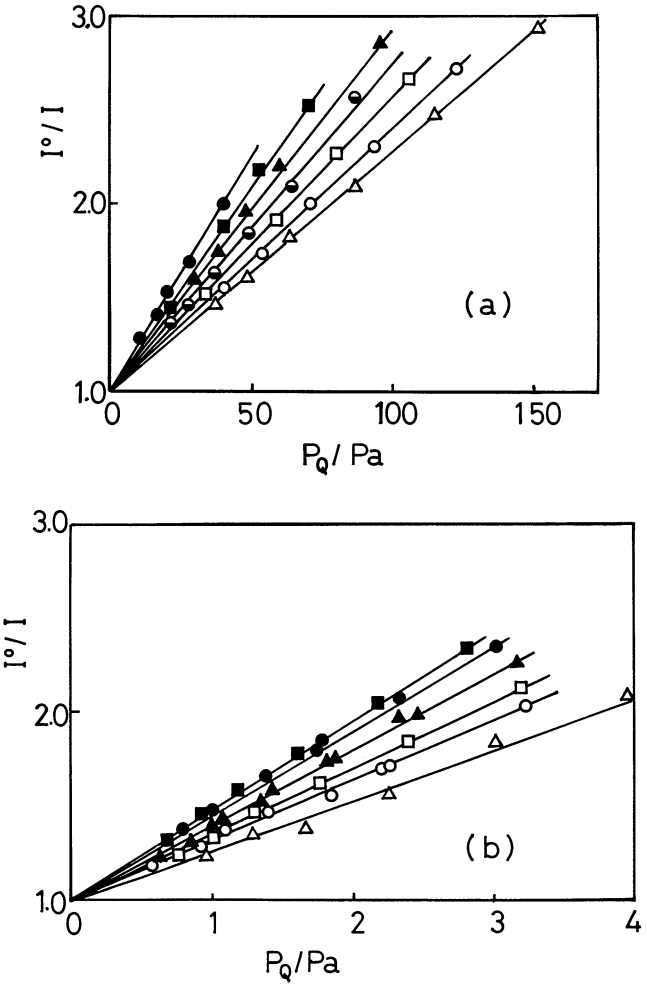

Fig. 1. Stern–Volmer plots for the quenching of $Zn(^3P_J)$ by methane (a) and cyclopropane (b). Total pressure is 5000 Pa. (a); 538 (△), 553 (○), 565 (□), 571 (○), 579 (▲), 591 (■), and 605 K (●). (b); 538 (△), 561 (○), 573 (□), 585 (▲), 597 (●), and 603 K (■).

discussed in terms of this set of reactions:

$Zn(^1S_0) + h\nu(307.6\ nm) \longrightarrow Zn(^3P_1)$	I_a	
$Zn(^3P_1) \longrightarrow Zn(^1S_0) + h\nu(307.6\ nm)$	k_0	
$Zn(^3P_1) + M \rightleftharpoons Zn(^3P_0) + M$	k_1, k_{-1}	(1),(−1)
$Zn(^3P_1) + M \rightleftharpoons Zn(^3P_2) + M$	k_2, k_{-2}	(2),(−2)
$Zn(^3P_0) + Q \longrightarrow$ quenching	k_3	(3)
$Zn(^3P_1) + Q \longrightarrow$ quenching	k_4	(4)
$Zn(^3P_2) + Q \longrightarrow$ quenching	k_5	(5)

Here, M denotes Ar and quenchers, while Q represents quenchers. By assuming the steady-state for $Zn(^3P_0)$, $Zn(^3P_1)$, and $Zn(^3P_2)$, the following equation can be derived:

$$\frac{I^\circ}{I} = 1 + \frac{1}{k_0}\left\{\frac{k_1k_3[M]}{k_{-1}[M] + k_3[Q]} + k_4 + \frac{k_2k_5[M]}{k_{-2}[M] + k_5[Q]}\right\}[Q]$$

If it can be further assumed that, at large argon pressures, the equilibration reactions (1), (−1), (2), and (−2) are always rapid compared to Reactions (3), (4), and (5) under the present experimental conditions, the above equation can be simplified to:

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

where $k_q=(k_1/k_{-1})k_3+k_4+(k_2/k_{-2})k_5$ and $\tau=1/k_0$. From the slopes of the straight lines shown in Fig. 1, the values of $k_q\tau$ were estimated. The quenching rate constants measured are for a nearly statistical equilibrium distribution of $Zn(^3P_0)$, $Zn(^3P_1)$, and $Zn(^3P_2)$. The equilibrated percentages of $^3P_0$, $^3P_1$, $^3P_2$ only change from 26:47:27 to 24:46:30 over the 538—608 K temperature range. Since the populations of the ^3P_J multiplets can be regarded as constant over the present temperature range, the discussion of the temperature dependence using the k_q value seems to be valid.

As has been mentioned in a previous paper,[5] the effective lifetime (τ) of $Zn(^3P_1)$ changes with the temperature (it is lengthened by the radiation imprisonment). It is difficult to estimate the absolute k_q values at high temperatures. In Fig. 2, the ratios of $k_q(CH_4)/k_q(C_2H_6)$ and $k_q(\text{cyclo-}C_3H_6)/k_q(C_2H_6)$ are shown as functions of $1/T$ ($k_q\tau$ values for ethane at various temperatures were measured in this study for comparison; they were found to be consistent with those at some temperatures reported in a previous paper[5]). The differences in the activation energies for $k_q(CH_4)$ and $K_q(C_2H_6)$ and for $k_q(\text{cyclo-}C_3H_6)$ and $k_q(C_2H_6)$ were found to be 10.1±1.5 and 8.0±0.6 kJ mol^{-1} respectively, and the ratio of the frequency factor of k_q for methane to that for ethane and the ratio of the frequency factor for cyclopropane to that for ethane, to be $A(CH_4)/A(C_2H_6)$=2.16±0.53 and $A(\text{cyclo-}C_3H_6)/A(C_2H_6)$=28.2±0.4 respectively. From the values of the differences in the activation energy and the activation energy for a primary C–H bond (16.5±2.5 kJ mol^{-5}), the activation energies for the quenching by methane and cyclopropane were determined to be 26.6±2.5 and 24.5±2.5 kJ mol^{-1}. They are listed as E_a^{obsd} in Table 1.

As has been mentioned in a previous paper,[5] the activation energies of the quenching of excited zinc atoms for the primary, secondary, and tertiary C–H bonds were calculated by the bond-energy-bond-order (BEBO) method by assuming the following model:

Table 1. Activation Energies and Bond Energies

	E_a^{obsd}	E_a^{calcd}	E_b
	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
CH_3–H	26.6±2.5	26.5	440[a]
▷—H	24.5±2.5	29.2	445[b]
Primary	16.5±2.5	15.0	410
Secondary	11.9±2.5	11.1	396
Tertiary	9.0±2.5	8.9	381

a) Ref. 6. b) Ref. 7.

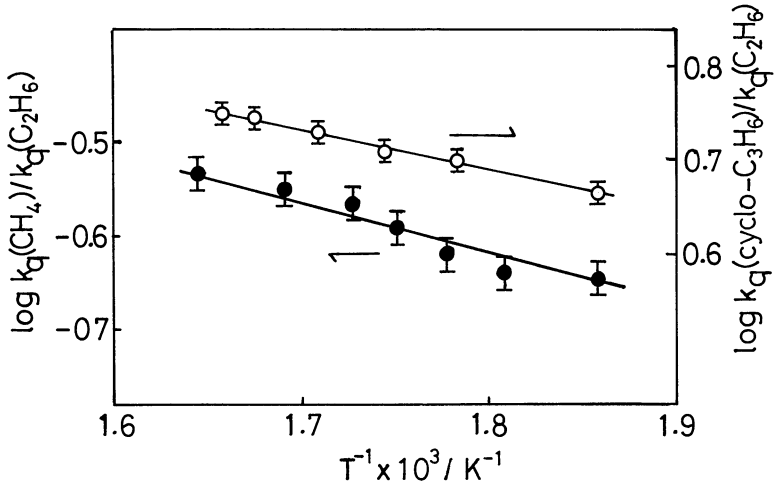

Fig. 2. Arrhenius plots for $k_q(CH_4)/k_q(C_2H_6)$ (●) and $k_q(\text{cyclo-}C_3H_6)/k_q(C_2H_6)$ (○).

$$RH + Zn^* \longrightarrow R \cdots H \cdots Zn \longrightarrow R+HZn$$

It was concluded that the agreement between experimental and calculated activation energies is good. Table 1 gives the activation energies (E_a^{calcd}) for methane and cyclopropane as calculated by the BEBO method (Gilliom's modified method) using the values of the C–H bonds energies (E_b) of methane and cyclopropane shown in Table 1 and the paramenters shown in a previous paper,[5] together with the values for primary, secondary and tertiary C–H bonds.

The experimental activation energies for the quenching of $Zn(^3P_J)$ by methane and cyclopropane are in good agreement with those calculated by the BEBO method. This suggests that, in the initial stage of the zinc-photosensitized reactions of these compounds, the hydrogen-atom abstraction by excited zinc atoms occurs, as has been pointed out previously for other alkane hydrocarbons.[4,5]

As is shown in Table 1, the activation energy for the quenching by methane is very similar to that by cyclopropane, and both activation energies are larger than that by ethane. These findings are in line with the fact that the C–H bond energies in methane and cyclopropane are nearly equal and larger than that in ethane. Similar results have been reported in the hydrogen abstractions by H[8] and Cl[9] from methane and cyclopropane.

Although the activation energy for cyclopropane is considerably larger than that for ethane, the quenching rate constant for the former is larger than that for the latter. The large frequency factor for cyclopropane results in its large quenching rate constant. A possible explanation for the large frequency factor for cyclopropane is that it is due to less steric repulsion in the C–H bond attack by excited zinc atoms.

Strausz et al.[10] studied the mercury-photosensitized reaction of cyclopropane by means of product analysis at room temperature and pointed out that the major primary step is the formation of an electronically excited cyclopropane (possibly the ground state triplet of trimethylene)—that is, the rupture of a C–C bond. As has been mentioned above, in the zinc-phoptosensitized reaction at high temperatures, however, it is concluded that the interaction of the excited zinc atoms with the C–H bonds, resulting in the formation of cyclopropyl radicals and H atoms, is the primary step. The difference in the primary step in the mercury- and zinc-photosensitized reaction of cyclopropane seems to come from the difference in reaction temperature. As has also been mentioned above, the abstraction of a hydrogen atom by excited atoms from alkane molecules has an appreciable activation energy, and at high temperatures it becomes predominant.

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