The Reaction of Singlet Methylene with Methane

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Cyclopropane in an excess of methane was photolyzed at 1470 and 1634 Å. The decomposition rate constants of the resultant vibrationally excited ethane into methyl radicals were found to be 6.0×10^9 s^{-1} and 5.0×10^9 s^{-1} at 1470 and 1634 Å respectively. The following procedure was used in treating the results obtained in our and the other researchers' systems. The statistical calculation was made to estimate the internal energy of singlet methylene, $\bar{\varepsilon}_i$, which is initially acquired in the primary decomposition process. The RRKM theory was then used to estimate the internal energy of the excited ethane. According to these calculations, the fraction of excess photon energy carried into ethane decreases as the energy, $\bar{\varepsilon}_i$, increases.

The chemistry of methylene has received much attention in recent years. The difference in reactivity of the singlet and triplet species is well-known,[1] and the insertion of singlet methylene into C–H bonds of hydrocarbons has been extensively applied to chemical activation techniques.[2] The vibrationally excited ethane is formed by the insertion reaction of singlet methylene with methane;[3–7] it either decomposes into methyl radicals or is deactivated by collision. Ketene,[4,5] diazomethane,[3,7] and methane[6] have been used as the source of methylene.

We have previously reported that cyclopropane is the most suitable molecule to produce methylene in the vacuum ultraviolet region.[8] In this study, we carried out the photolysis of cyclopropane with methane and oxygen (or nitrogen oxide) (cyclo-$C_3H_6/CH_4/O_2$ or NO=1/10/0.1) at 1470 and 1634 Å. The decomposition rate constants of the vibrationally excited ethane were determined and compared with the results obtained from the experiments in which the other molecules were photolyzed to produce singlet methylene with different wavelengths.

Experimental

Most of the experimental procedures used in the present study have been described previously.[8] A synthetic sapphire plate was used as the window of the xenon lamp to cut off the weak 1295 Å line. After irradiation, the products and the remaining reactants were vacuum-distilled at the temperature of solid nitrogen to rid the reaction cell of the excess methane and subsequently collected in a sample tube by means of a Toepler pump. Analyses were made by means of gas chromatography using a 3-m-long charcoal column.

Results and Discussion

In our system, the reaction scheme relating to singlet methylene is as follows:

$$\text{cyclo-}C_3H_6 + h\nu \longrightarrow {}^1CH_2 + C_2H_4, \quad \Delta H = 101\ \text{kcal mol}^{-1}, \tag{1}$$

$${}^1CH_2 + CH_4 \longrightarrow C_2H_6^*, \quad \Delta H = -100\ \text{kcal mol}^{-1}, \tag{2}$$

$$\longrightarrow {}^3CH_2 + CH_4, \tag{3}$$

$${}^1CH_2 + \text{cyclo-}C_3H_6 \longrightarrow \text{removal of } {}^1CH_2, \tag{4}$$

$$C_2H_6^* \xrightarrow{k_d} CH_3 + CH_3, \tag{5}$$

$$\xrightarrow{\Sigma k_s^i(M_i)} C_2H_6. \tag{6}$$

Reaction 1 is the major primary process in the photolysis of cyclopropane.[8] Singlet methylene reacts with methane to form vibrationally excited ethane, Reaction 2, or to be deactivated to the triplet, Reaction 3. The rate constants for Reactions 2 and 3 were found to be $(1.9\pm0.5)\times10^{-12}$ and $(1.6\pm0.5)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} respectively from a flash photolysis study.[5] The energized ethane should be accompanied by decomposition to methyl radicals, Reaction 5, unless it is collisionally deactivated to a stable ethane molecule, Reaction 6. Both triplet methylene and methyl radicals will be removed by the added radical scavenger, oxygen or nitrogen oxide.[9]

A steady-state treatment of Reaction 1—6 leads to:

$$\frac{(C_2H_4)}{(C_2H_6)} = C \times (1+k_d\omega^{-1}), \tag{I}$$

$$C = 1 + \frac{k_3}{k_2} + \frac{k_4}{k_2}\frac{(\text{cyclo-}C_3H_6)}{(CH_4)}, \tag{II}$$

and

$$\omega = \sum_i k_s^i(M_i), \tag{III}$$

where C is constant under our experimental conditions of $(\text{cyclo-}C_3H_6)/(CH_4)=1/10$, and ω is the effective collision frequency of bath gas with the energized ethane. The collisional deactivation efficiencies (β) were taken to be 0.61 and 0.83 for methane and cyclopropane respectively.[10] The collision diameters of $\sigma_{C_2H_6}=4.38$ Å, $\sigma_{CH_4}=3.81$ Å, and $\sigma_{\text{cyclo-}C_3H_6}=4.92$ Å were used to calculate the collision frequencies (Z). The effective collision frequencies of bath gases in units of s^{-1}, $\omega=\beta Z$, are as follows: $\omega_{CH_4}=0.90\times10^7\ P_{CH_4}$ (Torr) and $\omega_{\text{cyclo-}C_3H_6}=1.20\times10^7\ P_{\text{cyclo-}C_3H_6}$ (Torr). The k_d values were determined from plots of $(C_2H_4)/(C_2H_6)$ *vs.* ω^{-1} at both wavelengths; these plots are illustrated in Fig. 1. We obtained $k_d=6.0\times10^9$ s^{-1} and $C=3.2$ at 1470 Å photolysis and $k_d=5.0\times10^9$ s^{-1} and $C=3.2$ at 1634 Å photolysis. The high-pressure intercept of 3.2, combined with $k_3/k_2=0.8$,[5] gives $k_4/k_2=14$ and leads to a value for the relative reactivity of methane and cyclopropane of $k_4/(k_2+k_3)=7.8$.

The k_d values are listed in Table 1, together with those obtained from the experiments in which ketene, diazomethane, and methane were used as the source of methylene. The variation in k_d apparently reflects the internal energy of methylene which is originally acquired in the primary decomposition process to form methylene. We tentatively used the following procedure to elucidate the dependence of k_d on the

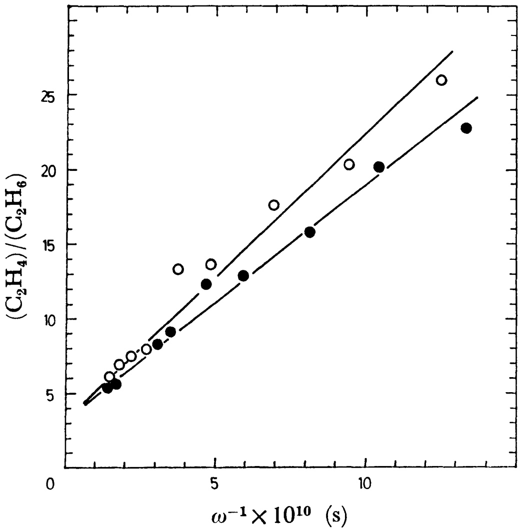

Fig. 1. Plot of $(C_2H_4)/(C_2H_6)$ *vs.* ω^{-1} at the 1470 and 1634 Å photolysis of cyclo-$C_3H_6/CH_4/O_2$ (or NO) mixtures.

○, 1470 Å Photolysis; ●, 1634 Å photolysis.

Table 1. Decomposition rate constants of $C_2H_6^*$ formed by the $^1CH_2 + CH_4$ reaction[a)]

Source of methylene	$P_{1/2}$[c)] (Torr)	k_d (s^{-1})	Ref.
CH_2CO (3130Å)[b)]	240	2.6×10^9	4)
CH_2N_2 (4358Å)[b)]	320	4.2×10^9	7)
cyclo-C_3H_6 (1634Å)	560	5.0×10^9	This work
cyclo-C_3H_6 (1470Å)	670	6.0×10^9	This work
CH_4 (1236 and 1048—1067Å)[b)]	770	6.9×10^9	6)

a) Bell and Kistiakowsky[3)] photolyzed CH_2N_2/CD_4 mixtures, from which a value for k_d of $\sim 2\times10^9\,s^{-1}$ was deduced by Setser and Rabinovitch[11)] after correcting for isotope effects, and Braun *et al.* flash-photolyzed CH_2CO/CH_4 mixtures, from which $k_d = 4\times10^9\,s^{-1}$ was obtained. However, these values are not listed because their photolytic lamp was not monoenergetic. b) The following effective collision frequencies in units of s^{-1}, $\omega = \beta Z$, were used: $\omega_{CH_4} = 0.90\times10^7\,P_{CH_4}$ (Torr), $\omega_{C_3H_8} = 1.22\times10^7\,P_{C_3H_8}$ (Torr), $\omega_{CH_2N_2} = 1.61\times10^7\,P_{CH_2N_2}$ (Torr), and $\omega_{iso\text{-}C_4H_{10}} = 1.90\times10^7\,P_{iso\text{-}C_4H_{10}}$ (Torr). c) The pressure at which the half of $C_2H_6^*$ is stabilized.

internal energy of methylene. First, the average internal energy of methylene, $\bar{\varepsilon}_i$, which is initially present in the primary decomposition process was estimated on the basis of the statistical model proposed by Campbell and Schlag.[12)] Second, the average internal energy of methylene, $\bar{\varepsilon}_f$, which is carried into the insertion product (ethane) was calculated from the ordinary RRKM model.

Estimation of $\bar{\varepsilon}_i$. The methylene-forming processes besides Reaction 1 in Table 1 are:

$$CH_2CO + h\nu \rightarrow {}^1CH_2 + CO,\ \Delta H = 86\ \text{kcal mol}^{-1}, \quad (7)$$

$$CH_2N_2 + h\nu \rightarrow {}^1CH_2 + N_2,\ \Delta H = 52\ \text{kcal mol}^{-1}, \quad (8)$$

$$CH_4 + h\nu \rightarrow {}^1CH_2 + H_2,\ \Delta H = 117\ \text{kcal mol}^{-1}. \quad (9)$$

The maximum energy available for methylene can be obtained by means of:

$$\varepsilon_{\max} = E_p - \Delta H, \quad (IV)$$

where E_p is the energy of the photon and ΔH, the heat of the reaction of each methylene-forming process. The energy, $\varepsilon_{\max}$, may either be partitioned among each degree of freedom of methylene and the partner fragment more or less statistically or appear as the non-statistical kinetic energy of fragments.[13)] To simplify the treatment, we neglected the non-statistical energy and assumed all the vibrational modes to be active. The fraction of methylene which retains a vibrational energy, ε, out of the maximum available energy, $\varepsilon_{\max}$, can be written[12)] as:

$$f(\varepsilon) = \frac{N_{CH_2}(\varepsilon)N_R(\varepsilon_{\max}-\varepsilon)}{\sum N_{CH_2}(\varepsilon_j)N_R(\varepsilon_{\max}-\varepsilon_j)}, \quad (V)$$

where $N_{CH_2}(\varepsilon)$ is the energy-level density of the methylene part of the molecule used as the source of methylene, and $N_R(\varepsilon_{\max}-\varepsilon)$, that of the remaining part. The energy-level densities were calculated by means of Eq. IX; all the vibrational frequencies for ethylene and methylene are given in the Appendix. The average energy, $\bar{\varepsilon}_i$, was derived from:

$$\bar{\varepsilon}_i = \int \varepsilon f(\varepsilon)\mathrm{d}\varepsilon. \quad (VI)$$

The resultant values are listed in Table 2. If methylene, with the internal energy of $\bar{\varepsilon}$, is inserted into the C–H bond of methane, the average internal energy of energized ethane, $\bar{E}$, is:

$$\bar{E} = \bar{\varepsilon} + \varepsilon_{\text{thermal}} - \Delta H \quad (VII)$$

where $\varepsilon_{\text{thermal}}$ is the thermal energy (≈ 2 kcal mol^{-1}) and ΔH, the heat of reaction of Reaction 2. The experimental values for k_d are plotted as a function of $\bar{E}(=\bar{\varepsilon}_i + \varepsilon_{\text{thermal}} - \Delta H)$ is Fig. 2. This plot may represent the dependence of k_d on the internal energy of ethane, assuming that all of $\bar{\varepsilon}_i$ is carried into the insertion product without any energy loss. In case singlet methylene without any internal energy is inserted into methane, the energized ethane possesses internal energies of 102 kcal mol^{-1}, corresponding to $\bar{\varepsilon}=0$ in Eq. VII. We obtained $k_d = 1.7\times10^9\,s^{-1}$ at $\bar{E} = 102$ kcal mol^{-1} in Fig. 2.

Estimation of $\bar{\varepsilon}_f$. The specific rate constant, k_E, of the decomposition of ethane with an internal energy of E can be given by the RRKM theory[14,15)]

Table 2. Internal energy of singlet methylene[a)]

Source of methylene	$\varepsilon_{\max}$[b)] (kcal mol^{-1})	$\bar{\varepsilon}_i$[c)] (kcal mol^{-1})	$\bar{\varepsilon}_f$[d)] (kcal mol^{-1})	$\bar{\varepsilon}_f/\bar{\varepsilon}_i$
CH_2CO (3130 Å)	5	3	2	0.67
CH_2N_2 (4358 Å)	13	8	4	0.50
cyclo-C_3H_6 (1634)	74	14	5	0.37
cyclo-C_3H_6 (1470 Å)	93	17	6	0.35
CH_4 (1236 Å)	114	83	7	0.08
CH_4 (1048—1067 Å)	≈ 153	≈ 113	7	0.06

a) $\Delta H_f^\circ(^1CH_2) = 101$ kcal mol^{-1} was assumed. b) Maximum energy carried by methylene to form $C_2H_6^*$. c) Average energy of methylene calculated by means of $f(E)$. d) Calculated from the RRKM model.

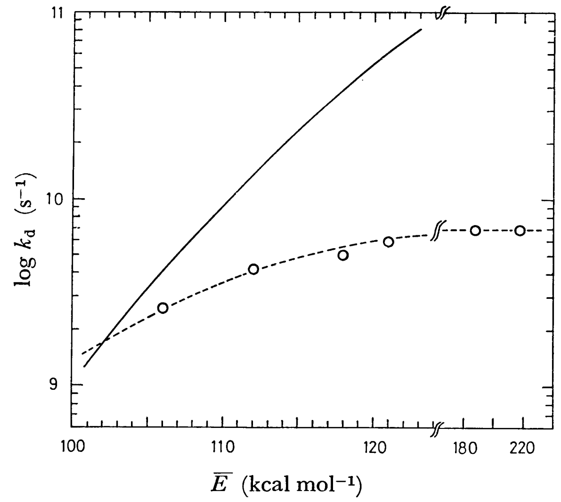

Fig. 2. Variation of k_d with $\overline{E}(=\bar{\varepsilon}_i+\varepsilon_{thermal}-\Delta H)$. Solid line represents the specific rate constant calculated from the RRKM treatment.

as follows:

$$k_E=\frac{1}{h}\frac{\sigma}{\sigma^\dagger}\left(\frac{I_A{}^\dagger I_B{}^\dagger I_C{}^\dagger}{I_A I_B I_C}\right)^{1/2}\frac{\sum P(E-E_0)}{N(E)}, \quad \text{(VIII)}$$

where σ and $\sigma^\dagger$ are the symmetry numbers of the ethane molecule and the activated complex respectively. $N(E)$ is the energy level density for the ethane molecule at the energy of E, $\sum P(E-E_0)$, the energy-level sum for the activated complex, and E_0, the critical energy required for the decomposition of energized ethane into methyl radicals (85 kcal mol^{-1}).[15] In the absence of an internal free rotation, $N(E)$ and $\sum P(E-E_0)$ can be approximated by:

$$N(E)=\frac{(E+aE_z)^{s-1}}{\Gamma(s)\Pi h\nu_i}, \quad \text{(IX)}$$

and:

$$\sum P(E-E_0)=\frac{(E-E_0+a^\dagger E_z{}^\dagger)^{s\dagger}}{\Gamma(s^\dagger+1)h\nu_i{}^\dagger}, \quad \text{(X)}$$

as proposed by Whitten and Robinovitch.[16] In Eqs. IX and X, s and $s^\dagger$ are the numbers of the vibrational degrees of freedom, E_z and $E_z{}^\dagger$ are the zero point energies, and ν_i and $\nu_i{}^\dagger$ are the vibrational frequencies of ethane and the activated complex respectively. We assumed that $a=1$ and $a^\dagger=0.8$.[17] Our structural parameters for ethane are given in Table 3. The model used was similar to that adopted by Hase[18] except that we did not set the torsional mode (ν_4) at a free rotor in the activated complex. The frequency for $\nu_4{}^\dagger$ was taken to be 39 cm^{-1} because the model gave $k_E=1.7\times10^9$ s^{-1} at $E=102$ kcal mol^{-1} corresponding to $\varepsilon=0$. The calculated values for k_E are plotted as a function of the internal energy of ethane in Fig. 2 (solid line). The two curves in the figure apparently show different dependences on the energy, which implies that the internal energy, $\bar{\varepsilon}_f$, carried by methylene into the insertion product differs to a great extent from the energy, $\bar{\varepsilon}_i$, originally acquired in the methylene-forming process. We estimated the value for $\overline{E}(=\bar{\varepsilon}_f+\varepsilon_{thermal}-\Delta H)$ corresponding to each k_d value by virtue of the calculated curve for k_E. The average internal energy of singlet methylene which is carried into ethane, $\bar{\varepsilon}_f$, was calculated by introducing the average internal energy of energized ethane, $\overline{E}(=\bar{\varepsilon}_f+\varepsilon_{thermal}-\Delta H)$, into Eq. VII; the values for $\bar{\varepsilon}_f$ are listed in Table 2.

Table 3. Structure parameters for ethane

	Molecule	Activated complex
Frequency (cm^{-1})	2915	2915
	955	—
	1388	1388
	260	39
	2915	2915
	1370	1370
	2950 (2)	2950 (2)
	1460 (2)	1460 (2)
	1190 (2)	273 (2)
	2974 (2)	2974 (2)
	1469 (2)	1469 (2)
	822 (2)	188 (2)
Zero-point energy (kcal mol^{-1})	45.1	38.9
r_{C-C} (Å)	1.54	3.6
Moment of inertia		
I_A =	10.8×10^{-40}	10.8×10^{-40}
$I_B=I_C$ =	42.0×10^{-40}	185.5×10^{-40}
(g cm^2)		
Number of symmetry	6	6

The ratios of $\bar{\varepsilon}_f$ to $\bar{\varepsilon}_i$ are also given in Table 2. The results show that only a fraction of $\bar{\varepsilon}_i$ (or ε_{max}) is carried into chemically activated ethane and that this fraction rapidly decreases as $\bar{\varepsilon}_i$ (or ε_{max}) becomes larger. The most likely explanation of this result is that singlet methylene suffers a number of inelastic collisions before reacting with methane and loses a considerable amount of the internal energy originally acquired in the primary decomposition process. In fact, a flash photolysis study[5] suggested that singlet methylene would undergo hundreds of collisions prior to insertion. The probability of the insertion reaction occurring, however, would be large to such an extent that the internal energy of singlet methylene is not fully thermalized before insertion.

Appendix

The vibrational frequencies of ethylene are taken[19] to be 3000, 1600, 1350, 1000, 3100, 1250, 950, 950, 3100, 800, 3000, and 1450 cm^{-1} for ν_1 to ν_{12}.

The vibrational frequencies of methylene are estimated to be 2850, 1450, and 2925 cm^{-1} for ν_1, ν_2, and ν_3, respectively.

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