Mechanism and Rate Constant of the Reaction between Methylene and Methyl Radicals

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The chemistry of the reaction between methyl and triplet methylene radicals has been examined by means of flash photolysis of azomethane and ketene followed by gas chromatographic analysis of the hydrocarbon products. Using the combination rate constant of triplet $CH_2 = 5.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ and the combination of $CH_3 = 9.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, a value of $1.0 \pm 0.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ for the reaction ${}^{3}CH_2 + CH_3 \rightarrow C_2H_5^* \rightarrow C_2H_4 + H$ has been determined.

Introduction

Bimolecular reactions between alkyl radicals have been studied extensively and been the subject of numerous review articles.^{1a,b} The reactions between alkyl and carbene radicals have been examined only infrequently^{1c} and rate data for these reactions are not available. Recent work indicates that the reactivity of ${}^{3}CH_{2}{}^{2}$ with hydrocarbon molecules is sufficiently low that the CH₂ may react with other radicals present in the system.^{1c}

Lee et al.^{1c} have shown the reaction between the simplest carbene and alkyl, ${}^{3}CH_{2}$ and CH_{3} , results in ethylene plus an H atom:

$${}^{3}\mathrm{CH}_{2} + \mathrm{CH}_{3} \rightarrow \mathrm{C}_{2}\mathrm{H}_{5}^{*} \rightarrow \mathrm{C}_{2}\mathrm{H}_{4} + \mathrm{H}$$
(1)

If the rate constants of the competing reactions 2 and 3 are known

$$CH_3 + CH_3 \rightarrow C_2H_6 \tag{2}$$

$${}^{3}\mathrm{CH}_{2} + {}^{3}\mathrm{CH}_{2} \rightarrow \mathrm{C}_{2}\mathrm{H}_{2} + (\mathrm{H}_{2} \text{ or } 2\mathrm{H})$$

$$(3)$$

we may calculate k_1 using standard computer techniques. We have determined the rate constant of (1) and attempted to elucidate the chemistry of the CH₃-CH₂ system by utilizing flash photolysis of azomethane-ketene mixtures combined with gas chromatographic analysis of the hydrocarbon products.

Experimental Section

The vacuum-ultraviolet, flash-photolysis, gas-chromatographic analysis system and the procedures utilized in these experiments have been described previously in detail.^{3,4} Briefly, the quartz reaction cell was placed inside a 3000-J flash chamber. The photoflash, through N_2 , had a 1/e decay time of ~5 µsec. Following the flash, samples for chromatographic analysis were obtained by rapid withdrawal from the center of the reaction vessel. In any given experiment, milliTorr quantities of azomethane and ketene were, after thorough mixing, flash photolyzed both individually and as a mixture in the presence of quenching gas, and the products were subsequently analyzed.^{3,4a} Several such experiments were done so as to ascertain accurately the product distribution. Yields of products were determined absolutely by comparison against known quantities of calibrating mixtures which included each product.

Azomethane, obtained commercially, was used as the source of CH_3 . Ketene, for which the preparation has been described previously,⁵ was used as the source of CH_2 . Reac-

tion products (C₁-C₄ hydrocarbons) were separated on a 7-m. long 6-mm o.d. stainless steel column packed with 30% (W/W) squalane on Chromosorb-P maintained at 35°.

He, Ar, and N_2 used as quenching gases were ultrapure grade which had less than 10 ppm impurities, according to the manufacturer's specifications. Research grade propylene and ethylene were used without further purification.

Results and Discussion

Chemistry. The reactions and processes involved in the flash photolysis of ketene have been discussed in detail.^{4a} Briefly, the CH₂ produced as a result of photolysis is presumed to be in a singlet state which, upon collision with inert gas molecules, is quenched to the ground triplet state. ³CH₂ reacts principally according to reaction 3, but a small fraction of the ³CH₂ may react with the product, C₂H₂, viz.

$${}^{3}\mathrm{CH}_{2} + \mathrm{C}_{2}\mathrm{H}_{2} \rightarrow \mathrm{C}_{3}\mathrm{H}_{4} \tag{4}$$

Further, some C_2H_4 is produced as a result of ${}^{1}CH_2$ reacting with parent ketene:

$${}^{1}\mathrm{CH}_{2} + \mathrm{CH}_{2}\mathrm{CO} \rightarrow \mathrm{C}_{2}\mathrm{H}_{4} + \mathrm{CO}$$

$$\tag{5}$$

Similarly, the processes involved in the flash decomposition of azomethane have been described.^{3,4b} The products formed, in the presence of helium, are C_2H_4 , CH_4 , and C_2H_6 in the approximate ratio of 1:3:15. C_2H_6 is formed by reaction 2, and CH_4 is produced from the reaction of CH_3 with H atoms:

$$CH_3 + H + M \rightarrow CH_4 + M \tag{6}$$

 C_2H_4 is formed through reaction 1.

In a mixture of azomethane and ketene, the yields of C_2H_6 and C_2H_2 decrease and an associated increase in C_2H_4 is observed.³ This increase is attributed to reaction 1. A requisite for the calculation of k_1 is a knowledge of the precursors to the final hydrocarbon products so that a determination of the concentration of radical species at t = 0 may be made. We must consider, therefore, all plausible reactions which may lead to CH_4 , C_2H_2 , C_2H_4 , or C_2H_6 . These are the principal hydrocarbon products in the system. In addition, very small quantities of propylene are formed.

The major paths by which the hydrocarbon products are formed in the mixture have been described above and are due to reactions 6, 3, 1, and 2 for CH₄, C_2H_2 , C_2H_4 , and C_2H_6 , respectively.

TABLE I: Thermochemical Values

	$\Delta H^{\circ} a$		
Species	kcal/mol	Ref	
Н	51.63	Ь	
CH	142.1	c	
CH_2	93.5	d	
CH_3	34.0	b	
CH_4	-15.97	b	
C_2H_2	54.32	b	
C_2H_4	14.52	b	
C_2H_6	-16.52	b	
C_3H_6	8.47	е	

^a 1 kcal/mol = 4.184 kJ/mol. ^b D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, *Natl. Bur. Stand., Tech. Note*, No. 270-3 (1968). ^c A. H. Laufer and H. Okabe, J. Am. Chem. Soc., 93, 4137 (1971). ^d V. H. Dibeler and K. E. McCulloh, IV International Conference on Vacuum U.V. Radiation Physics, Hamburg, 1974. ^e F. D. Rossini et al., API Research Project 44, Carnegie Press, Pittsburgh, Pa., 1953.

Although the prime source of C_2H_2 is reaction 3, it is thermochemically possible for the C_2H_4 produced in (1) to undergo further dissociation to C_2H_2 (reaction 7). Using the heats of formation listed in Table I

$$C_2H_4 \rightarrow C_2H_2 + H_2 \tag{7}$$

reaction 1 is 61.3 kcal/mol exothermic. The endothermicity of (7) is 39.8 kcal/mol which allows it to proceed if the energy resulting from (1) is primarily in the C_2H_4 moiety. The importance of (7) was examined by varying the CH_3/CH_2 ratio. In the limit of a high CH_3/CH_2 ratio, virtually all the CH_2 will react with CH_3 in which case reaction 3 becomes unimportant. It may be shown by calculation, neglecting reaction 7, that at a ratio of $CH_3/CH_2 = 15$, less than 10% of the CH_2 present at t = 0 [$(CH_2)_0$] results in C_2H_2 . The remainder reacts to produce C_2H_4 . Experiments at high CH_3/CH_2 as a function of pressure confirm the trial calculations that the yield of C_2H_2 is no greater than anticipated, and we conclude that (7) is not important in our system and that the product C_2H_2 arises solely via (1).

We have mentioned the formation of small quantities of C_3H_6 as a product of the $CH_2 + CH_3$ reaction. A suggested mechanism leading to C_3H_6 might involve the reaction of ${}^{3}CH_2$ with product C_2H_4 :

$${}^{3}\mathrm{CH}_{2} + \mathrm{C}_{2}\mathrm{H}_{4} \rightarrow \mathrm{C}_{3}\mathrm{H}_{6} \tag{8}$$

It is known⁶ that reaction 8 produces cyclopropane in addition to propylene, with the ratio of the two products dependent upon the pressure. Careful examination of the products of the CH₂-CH₃ system indicates that cyclopropane is present at concentrations of less than 3% of the propylene which suggests C_2H_4 is not the precursor. In addition to the negative mechanistic argument, calculations indicate that a value of $k_8 \simeq 8.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ is required to account for the yield of propylene assuming ${}^{3}CH_{2}$ as the precursor. To examine this possibility, we redetermined k_8 by photolysis of CH_2CO in the presence of C_2H_4 and 700 Torr of helium. Relative to $k_3 = 5.3 \times 10^{-11}$ cm³ molecule⁻¹ sec⁻¹, we obtain $k_8 \le 3 \times 10^{-14}$ cm³ molecule⁻¹ sec^{-1} , or several orders of magnitude slower than is required to account for C₃H₆ production in the CH₃-CH₂ system. The redetermined value of k_8 agrees well with previous values of the collision efficiency of 10^{-52} and 10^{-47}

for reaction 8. These measurements preclude (8) as the mode of formation of C_3H_6 .

Perhaps a less obvious possible precursor of propylene involves CH. CH(X²II) is known to react with alkanes with rate constants approaching 1×10^{-10} cm³ molecule⁻¹ sec^{-1 8} to produce C₂H₄ and an alkyl radical, the latter dependent upon the alkane involved⁹ as in

$$H(X^{2}\Pi) + R - CH_{3} \rightarrow C_{2}H_{4} + R$$
(9)

However, methyne inserted into ethane is also capable of producing $propylene^{10}$

$$CH(X^2\Pi) + C_2H_6 \rightarrow C_3H_7^* \rightarrow C_3H_6 + H$$
(10)

While the C_2H_4 produced in (9) is not distinguishable from that produced via (1), the propylene is unique. Reaction 10 is exothermic by 65.5 kcal/mol, and though reaction 9 is favored on energetic grounds, reaction 10 has been observed. Reaction 10 is analogous to the addition of CH to ethylene to yield an allyl radical.¹¹ In fact, addition of C_2H_4 in quantities of between 70–100 times greater than either CH₂ or CH₃ does result in a noticeable increase in allene yield, presumably as the result of the loss of an H atom from the intermediate allyl radical reaction

$$CH(X^{2}\Pi) + C_{2}H_{4} \rightarrow CH_{2} + CHCH_{2} \rightarrow CH_{2} = C = CH_{2} + H \quad (11)$$

While the involvement of CH may be attractive to explain the formation of propylene, we must now consider the mode of formation of the methyne radical. The obvious mode of production of CH is disproportionation of CH_2 and CH_3 , viz.

$${}^{3}\mathrm{CH}_{2} + \mathrm{CH}_{3} \rightarrow \mathrm{CH} + \mathrm{CH}_{4} \tag{12}$$

We have already mentioned that (1) is exothermic by 61.3 kcal/mol while (12) is only exothermic by 1.4 kcal/mol, as written. In addition to examining the products for evidence of CH, another approach would be to determine if CH₄ is formed from (12). The other source of CH_4 , reaction 6, may be eliminated by removal of CH₃ radicals which would also diminish the importance of reaction 12. Alternatively, we may reduce the relative importance of reaction 6 by removal of H atoms. Experiments were attempted to scavenge the H atoms by addition of several Torr of either ethylene or propylene to the mixture. Photodecomposition of the additive was minimized by use of a double-walled reaction vessel, the outer compartment of which could be filled with a fluid to serve as a light filter. These experiments, while indicating the importance of H atoms in the system, were not entirely successful as we were unable to separate CH₄ production into fractions arising separately from either reaction 6 or 12. However, if we assume the product propylene arises from (10) and further that it represents only half the total CH (the remainder would react with C2H4 with which its rate constant is about the same as with alkanes⁸), we can estimate as an upper limit that about 10% of the reaction between $CH_2 + CH_3$ proceeds through a disproportionation mechanism.

Rate Constant of ${}^{3}CH_{2} + CH_{3}$. In addition to understanding the chemistry of the system, the computation of the rate constant requires knowledge of the product distribution as well as of the values of the rate constants for the competing reactions. For the latter we use $k_{2} = 9.5 \times 10^{-11}$ cm³ molecule⁻¹ sec⁻¹³ and $k_{3} = 5.3 \times 10^{-11}$ cm³ molecule⁻¹ sec^{-1,13} The rate constant was calculated by using

TABLE II: Product Distribution

	7	Pres-		Pres-	Product, mTorr					$h = am^3 m^{-1}c$
	Inert sure, gas Torr ^a	re, cr ^a Reactant	sure, mTorr	CH ₄	C_2H_2	$\mathbf{C}_{2}\mathbf{H}_{4}$	C_2H_6	CH_3/CH_2	k, cm ⁵ mole- cule ⁻¹ sec ⁻¹	
. II.	Не	700	Azomethane (AM) Ketene (K) Mixture	20 35	0.31 0.08 0.68	0.71 0.29	0.09 0.06 0.69	1.06 0.66	2.1	1.5×10^{-10}
			AM K Mixture	20 35	0.28 0.07 0.62	0.67 0.27	0.09 0.06 0.54	0.99 0.59	2.1	1.2×10^{-10}
			AM K Mixture	15 70	0.17 0.12 0.56	0.98 0.64	0.05 0.12 0.51	0.66 0.27	0.9	1.1×10^{-10}
			AM K Mixture	10 80	0.08 0.08 0.52	1.08 0.91	0.05 0.18 0.63	1.02 0.05 0.39	0.7	1.0 × 10-10
		500	AM K Mixture	15 60	$0.12 \\ 0.08 \\ 0.40$	0.88 0.53	$0.04 \\ 0.06 \\ 0.43$	0.52 0.10 0.24	0.9	0.90×10^{-10}
		300	AM K Mixture	15 60	0.11 0.09 0.39	0.94 0.48	0.04 0.06 0.50	0.55 0.28	1.0	0.90×10^{-10}
		100	AM K Mixture	15 60	$0.07 \\ 0.07 \\ 0.25$	0.79 0.50	$0.04 \\ 0.06 \\ 0.45$	0.52 0.30	0.9	0.90 × 10 ⁻¹⁰
		50	AM K Mixture	10 80	0.08 0.08 0.20	1.08 0.64	0.05 0.18 0.36	$1.02 \\ 0.05 \\ 0.23$	0.6	0.81 × 10-10
	Ar	500	AM K Mixture	15 70	$0.29 \\ 0.15 \\ 0.64$	0.68 0.70	$0.03 \\ 0.04 \\ 0.55$	0.47	0.9	1.2 × 10 ⁻¹⁰
		200	AM K Mixture	15 70	0.15 0.21 0.34	0.98	0.03 0.06 0.38	0.41 0.01 0.21	0.7	0.90×10^{-10}
		50	AM K Mixture	10 70	0.05 0.08 0.18	0.91 0.62	$0.02 \\ 0.10 \\ 0.31$	$\begin{array}{c} 0.27 \\ 0.04 \\ 0.19 \end{array}$	0.5	0.80×10^{-10}
	N ₂	700	AM K Mixture	15 60	$0.27 \\ 0.04 \\ 0.43$	0.65 0.33	$0.03 \\ 0.05 \\ 0.42$	0.49 0.22	1.2	1.3×10^{-10}
		150	AM K Mixture	15 60	$0.11 \\ 0.06 \\ 0.30$	0.53 0.40	$0.04 \\ 0.06 \\ 0.47$	0.54 0.27	1.0	1.1×10^{-10}
		50	AM K Mixture	15 60	0.08 0.03 0.20	0.74 0.46	$0.04 \\ 0.07 \\ 0.44$	0.55 0.30	1.1	1.0 × 10 ⁻¹⁰

^a Pressure in units of milliTorr except where noted; 1 Torr = 133.3 N m⁻².

the product distribution of the four major products CH_4 , C_2H_2 , C_2H_4 , and C_2H_6 for which the time-dependent equations are based upon reactions 6, 3, 1, and 2, respectively.

$$d(CH_3)/dt = -k_1(CH_2)(CH_3) - 2k_2(CH_3)^2 - k_6(CH_3)(H)$$
(A)
$$d(CH_2)/dt = -k_1(CH_2)(CH_3) - 2k_3(CH_2)^2$$
(B)

 $\begin{array}{ll} d(CH_4)/dt = k_6(CH_3)(H) & (C) \\ d(C_2H_2)/dt = k_3(CH_2)^2 & (D) \\ d(C_2H_4)/dt = k_1(CH_2)(CH_3) & (E) \end{array}$

 $d(C_2H_6)/dt = k_2(CH_3)^2$ (F)

The method used to evaluate k_6 has been described in detail.^{4b} Briefly, we have used a value for $k_{6\infty} = 3.44 \times 10^{-10}$

 cm^3 molecule⁻¹ sec⁻¹ and corrected it for both the pressure in the system and identity of quenching gas. Relative to the photolysis of either substrate, the mixture photolysis of the mixture resulted in decreased C₂H₂ and C₂H₆ with an increase in both C_2H_4 and CH_4 , the latter due to enhanced production of H atoms by reaction 1. Preliminary calculations indicate the lack of sufficient H atoms to account for the observed CH_4 yield. Therefore, to compute the yield of CH_4 it is necessary to assume that reaction 3, the production of C_2H_2 , results in two H atoms and not molecular H_2 . The Runge-Kutta numerical integration technique was used to solve the simultaneous differential equations. The step size was varied from 0.5 to 2.0 μ sec without any change in predicted product distribution.

The data were fitted by prediction, initially, of the product distribution of the pure components. With the previously mentioned assumptions, we were able to calculate k_1 such that the final calculated product distribution of the mixed system agrees with experimental observation. The data from which the calculations were performed and the results are shown in Table II. The rate constant k_1 , expressed as the average of 14 determinations and standard deviations of the mean, is $1.0 \pm 0.1 \times 10^{-10}$ cm³ molecule⁻¹ \sec^{-1} . The rate constant is independent of added inert gas (Ar, N_2 , or He) over the pressure range from 50 to 700 Torr. The rate constant, k_1 , was also independent of the ratio of CH_3/CH_2 which was varied from 2.1 to 0.5. In a few experiments, CH₃/CH₂ was as high as 15 without any apparent effect on k_1 . This value for k_1 specifically excludes any consideration of the disproportionation mechanism as we did not compute k_1 based upon the disappearance of either CH_2 or CH_3 but rather upon the product C_2H_4 .

The yield of CH₂ and CH₃ in the mixed photolysis should be simply the sum of the CH_2 and CH_3 produced in the photolysis of the separate precursor. Nevertheless, a discrepancy between the separate and mixed systems is the apparent loss of CH_2 with an increase in CH_3 in the mixed systems. We cannot account for this quantitatively but it may be due, in part, to the combination of ${}^{3}CH_{2}$ with an H atom resulting in CH₃ radicals. Another possible explanation is the reaction between ³CH₂ and azomethane to produce CH_3 by abstraction. The system would then appear to lose CH_2 and gain CH_3 . We have examined this and the results indicate that although reaction between CH₂ and azomethane does occur, as measured by increasing C_2H_4 in the presence of azomethane, the rate constant for this reaction is $\sim 3 \times 10^{-13}$ cm³ molecule⁻¹ sec⁻¹ which indicates that less than 5% of the CH_2 reacts with substrate.

The computation indicates that the reaction time is limited by loss of CH₃ radicals. This is not surprising since CH_3 may react by more paths than CH_2 ; in addition, the rate constant for self-combination of CH3 is about twice that for self-combination of CH_2 , the most important loss mechanism for either species. The sensitivity of k_1 to computation error was determined by varying the value of k_2 . If k_2 is changed by a factor of 2, then the computed value of k_1 would change in the same direction by about 30%. At the same time, however, the value of k_6 would require a change by the same 30% to permit prediction of the observed product distribution. Thus, the final value of k_1 is probably accurate to within 30% since only gross errors in both k_2 or k_3 would be required to change k_1 by more than 30%.

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References and Notes

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- ³CH₂ refers to the ground triplet state of $CH_2(X^3\Sigma_g^{-1})^3B_1$ and ¹CH₂ to the lowest singlet state of $CH_2(a)^1A_1$. (2)
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