KETENE PHOTOCHEMISTRY. RELATIVE  $CH_2(^1A_1)$  quantum yields at 3130, 3340 and 3660 Å

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The photochemistry of ketene has been studied at 3130, 3340 and 3660 Å. A chemical trapping technique was used to determine the relative singlet methylene quantum yields. At a pressure of  $\approx 120$  torr the 3130:3340:3660 Å CH<sub>2</sub>(<sup>1</sup>A<sub>1</sub>) quantum yield ratio is 1.0:0.16:< 0.0006. One of the major implications of this result is that the fraction of methylenes which are singlets at 3660 Å is smaller than reported previously.

The photolysis of ketene in the 2600-3700 Å wavelength region yields both singlet ( ${}^{1}A_{1}$ ) and triplet ( ${}^{3}B_{1}$ ) methylene radicals [1-5]. Ethylene and carbon monoxide are the principal products and the following mechanism is consistent with quantum yields measurements of their formation [6-8]

$$CH_2CO + h\nu \rightarrow CH_2CO^+,$$
 (1)

 $CH_2CO^+ \rightarrow CH_2 + CO,$  (2)

$$CH_2 + CH_2CO \rightarrow C_2H_4 + CO.$$
(3)

The species  $CH_2CO^+$  represents all the electronic states which could participate in the photodecomposition of ketene and  $CH_2$  represents both the singlet and triplet methylenes.

Previous studies of ketene photochemistry in the 2600–3700 Å region [2–8] have established that: (1) the primary quantum yield of ketene photodissociation is equal to one half the quantum yield of carbon monoxide formation,  $\Phi_{CO}$ ; (2) the variation of  $\Phi_{CO}$  is dependent on both temperature and wavelength; (3) the zero pressure  $\Phi_{CO}$  is found to increase from 0.04 at 3660 Å to unity as the wavelength is decreased; and (4) the fraction of the methylenes which are triplets (<sup>3</sup>B<sub>1</sub>) increases as the wavelength increased. In addition to the above, it has been suggested that some of the CH<sub>2</sub>(<sup>1</sup>A<sub>1</sub>) radicals are formed via an oxirene inter-

mediate [9]. It is also thought that photoexcitation in the 2600–3700 Å wavelength region initially produces the first excited singlet state of ketene  $({}^{1}A_{2})$ [10,11].

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These results suggest that the photochemistry of ketene is quite complicated. Determining the specific electronic states involved in the photochemical mechanism and their relative importance will not be an easy task. Another complication is that no fluorescence or phosphorescence has been observed [12] and a measurement of the energy dependence of the non-radiative rate cannot be made to help deduce the photochemical mechanism [13]. However, measurements of the individual quantum yields of  $CH_2({}^1A_1)$  and  $CH_2({}^3B_1)$ formation as a function of photon energy would provide considerable insight into the microscopic photodissociation mechanism. In this paper we describe an experimental technique for measuring the  $CH_2(^{I}A_1)$ quantum yield as a function of energy and present some preliminary results.

The experimental technique we employ is based on the observation that  $CH_2({}^1A_1)$  radicals inset into both the C-H and Si-H bonds of alkylsilanes [14,15] while  $CH_2({}^3B_1)$  radicals preferentially abstract the H-atoms from Si-H bonds [14,16]. In this study mixtures of dimethylsilane (DMS) and ketene with and without oxygen were photolyzed at 3130, 3340 and 3660 Å. Oxygen molecules are efficient scavengers for triplet methylene and any doublet radicals [14-16]. The relative quantum yield of  $CH_2({}^1A_1)$  formation was determined by measuring the quantum yield of methylethylsilane (MES).

Ketene was prepared by acetic anhydride pyrolysis at 540°C and purified by trap to trap distillation. Dimethylsilane (DMS) was prepared in vacuo by the reaction of dimethyldichlorosilane with LiAlH<sub>4</sub> in dibutyl ether. The photolysis system consisted of a 200-W super pressure mercury arc lamp (HBO-200, Osram) and a 0.25 meter Jarrell-Ash monochromator with 2000  $\mu$  slits (66 Å resolution). In addition to the monochromator, Corning filters # 7380 and # 5860 were used for the 3660 Å photolyses to ensure the exclusion of the 3130 Å and 3340 Å mercury lines since the ketene photodissociation rates [6-8] and extinction coefficients are larger at 3130 Å and 3340 Å than 3660 Å<sup>°</sup>. For the 3660 Å photolyses no emission was observed at 3130 Å, and the emission intensity at 3340 A was four orders of magnitude smaller than that at 3660 Å. The emission intensity at 3600 Å and 3700 Å was more than three orders of magnitude smaller than that at 3660 Å. A 20.1 cm<sup>3</sup> cylindrical quartz vessel with two flat suprasil end windows of 2.5 cm o.d. was used for all photolyses. Relative light intensity was measured with a 1P28 photomultiplier tube. The products methylethylsilane (MES) and trimethylsilane (TMS) were analyzed by glpc on an 11 ft., 1/4'' o.d. column packed with 30% di-n-butylphthalate on chromosorb P (60/80) operated at room temperature. The relative amounts of TMS and MES were measured in terms of their retention times and peak heights. The TMS/MES relative sensitivity was determined by fitting a previous measurement of TMS/MES [15]. The photolysis of ketene was less than 1% for all experiments. All experiments were performed at room temperature, ≈.23°C.

Methylene radicals produced by ketene photolysis can undergo the following important reactions with dimethylsilane and ketene:

 $\operatorname{CH}_2(^1A_1) + \operatorname{DMS} \to \operatorname{TMS},$  (4)

 $CH_2(^1A_1) + DMS \rightarrow MES,$  (5)

$$CH_2(^{1}A_1) + CH_2CO \rightarrow C_2H_4 + CO,$$
 (6)

$$CH_2({}^{3}B_1) + DMS \rightarrow CH_3 + SiH(CH_3)_2,$$
(7)

$$CH_{2}({}^{3}B_{1}) + CH_{2}CO \rightarrow C_{2}H_{4} + CO.$$
 (8)

The measurements of TMS/MES and relative MES quantum yields ( $\Phi_{MES} \times \text{constant}$ ) are given in table 1. At 120 torr both TMS and EMS are collisionally stabilized [16]. No attempt was made to measure CO,  $C_2H_4$  or other possible products. The values of  $\Phi_{MES}$ are insensitive to variations in the DMS/CH<sub>2</sub>CO ratio, which is in agreement with previous measurements of singlet methylene relative reactives [17,18]. A very important result is the absence of any MES formation at 3660 Å. The limiting values given at 3660 Å are based upon the sensitivity of the gas chromatograph.

The ratio of TMS/MES resulting from singlet methylene reaction is  $2.3 \pm 0.1$  [15]. Ratios higher than this are evidence for triplet methylenes, since recombination of CH<sub>3</sub> and SiH(CH<sub>3</sub>)<sub>2</sub> radicals from reaction (7) yield TMS. At 3130 Å the TMS/MES ratio is independent of the amount of O<sub>2</sub> added. This result is indicative of a small CH<sub>2</sub>(<sup>3</sup>B<sub>1</sub>) quantum yield at 3130 Å. In contrast, at 3340 and 3660 Å the TMS/MES ratio is dependent upon the amount of O<sub>2</sub> added, which indicates the presence of triplet methylenes at these wavelengths.

As shown in table 1, varying the per cent  $O_2$  may effect the MES quantum yield. No effect is seen at 3130 or 3660 Å. However, at 3340 Å the MES quantum yield increases as the percentage of  $O_2$  is decreased. The result at 3660 Å is understandable since no MES is formed. Oxygen can quench the excited singlet state of ketene by intermolecular singlet energy transfer [19]. That oxygen effects the 3340 Å but not the 3130 Å MES quantum yield, agrees with the longer lifetime for ketene relative to photodissociation at 3340 Å compared to 3130 Å [7].

The most striking result in table 1 is the dramatic change in the MES quantum yield as a function of wavelength. The 3130:3340:3660 MES quantum yield ratio without O<sub>2</sub> added is 1.0:0.16:<0.0006. We may equate the MES quantum yield to the CH<sub>2</sub>(<sup>1</sup>A<sub>1</sub>) quantum yield,  $\Phi_1$ , if DMS only traps singlet methylenes and therefore does not induce intersystem crossing,

$$CH_2(^1A_1) + DMS \rightarrow CH_2(^3B_1) + DMS.$$
(9)

<sup>\*</sup> The ketene extinction coefficients were measured on a Cary-14 spectrophotometer. They are 11.1, 11.7 and 2.89 2 mole<sup>-1</sup> cm<sup>-1</sup> at 3130, 3340 and 3660 Å, respectively.

Table 1

Photolysis <sup>a)</sup> time (hours)	P <sub>DMS</sub> b)	P <sub>CH2</sub> CO	<i>P</i> <sub>O2</sub>	TMS MES	$\Phi_{MES}$ X constant	
And a second	3130 Å photolyses				ere zam er kulturen en e	**************************************
0.25	104	20	17	2.34	1.04	
0.25	102	22	11	2.35	0.98	
0.50	101	20	1	2.26	0.99	
0.5	100	23	0	2.30	0.98	
				average	1.00	
	3340 Å photolyses				• •	*
1.5	95	27	22	2.30	0.132	
2.0	99	22	18	2.30	0.134	
1.0	100	18	18	2.25	0.141	
3.0	105	13	15	2.34	0.128	
1.5	102	14	14	2.26	0.130	
2.0	99	12	12	2.34	0.131	
3.0	99	20	9	2.26	0.140	
				average	0.134	
3.5	98	22	1	2.56	0.154	
4.5	101	21	· 0	2.88	0.160	
2.0	102	20	0	2.99	0.163	
	3660 A photolyses <sup>c</sup> )					
4.0	102	26	36	4	< 0.0030	
25.0	98	35	17		< 0.00036	
24.0	96	20	1	> 37	< 0.00066	,
24.0	99	22	0	> 85	< 0.00060	

Relative quantum yields of trimethylsilane and methylethylsilane

a) The quantum yields at a particular wavelength are accurate to within ≈ 10%.
b) Pressures are expressed in torr.

c) No MES was formed during any of the 3660 A photolyses. TMS/MES and  $\Phi_{MES} \times constant$  values are limits determined by the sensitivity of the gas chromatograph. For experiments with TMS/MES given by - neither TMS or MES were formed.

However, in relating relative MES quantum yields to relative  $CH_2(^1A_1)$  quantum yields all that is required is that the ratio of the rate of reaction (9) to reaction (5) is the same at all wavelengths. Previous measurements of relative rates of collision induced  $CH_2(^1A_1)$  $\rightarrow$  CH<sub>2</sub>(<sup>3</sup>B<sub>1</sub>) intersystem crossing [20,21] and relative rates of  $CH_2(^1A_1)$  insertion [18,22,23] indicate that there is no wavelength dependency for the relative rates of reactions (5) and (9). Therefore, it seems valid to equate the relative  $CH_2({}^1A_1)$  quantum yields to the relative MES quantum yields. It should be noted that the independence of the TMS/MES ratio at 3130 Å with per cent  $O_2$  indicates that the concentration of  $CH_{1}({}^{3}B_{1})$  radicals is small and that reaction (9)

may be unimportant relative to (5).

In contrast to the relative  $CH_2({}^{I}A_1)$  quantum yields measured here, the absolute quantum yields for ketene dissociation at 120 torr are 0.70, 0.36 and 0.006 for photolysis at 3130, 3340 and 3660 Å, respectively [7]. Qualitatively, this shows that the  $CH_2({}^{3}B_1)$  photodissociation quantum yield,  $\Phi_3$ , is not as energy dependent as that for  $CH_2({}^1A_1)$ . If we make the approximate assumption that 120 torr of our DMS-CH<sub>2</sub>CO mixture is equivalent to 120 torr of CH<sub>2</sub>CO we can use the ketene dissociation quantum yields to calculate the relative fraction of the methylenes formed by photodissociation which are singlets,  $\Phi_1/(\Phi_1 + \Phi_3)$ . Thus, we find the 3130:3340:3660 ratio for the relative values

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## of $\Phi_1/(\Phi_1 + \Phi_3)$ is 1.0:0.31:<0.07.

Previous determinations of the fraction of singlet methylene versus wavelength have involved measurements of both singlet and triplet methylene products without doing relative quantum yield studies [1-5]. These earlier results are in general agreement with ours; i.e., they show a decrease in the singlet methylene fraction with increase in wavelength. However, those studies do not show nearly as large a change in the singlet methylene fraction with wavelength as does our result. These earlier studies also indicated that a significant fraction of the methylenes were singlets at 3660 Å. For example, DeGraff and Kistiakowsky [3] report the per cent methylenes which are singlets at 2900, 3160, 3340 and 3660 Å as 67, 59, 39 and less than 40%, respectively. Carr and Kistiakowsky [2] found the per cent singlet methylenes to be 85, 85, 70 and 60% at 2800, 3130, 3340 and 3660 Å. Using propane to monitor singlet and triplet methylene products, Ho and Noyes [4] found the percentages of singlet methylenes to be 80% at 2800 Å and 23% at 3800 Å. With trans-2-butene as a methylene monitor, Ho and Noyes [4] find the singlet methylene percentages to be 87%at 2800 Å and 42% at 3800 Å. In the most recent study of this type, Ede: and Carr [5,24] find that 13% and 71% of the methylenes are singlets at 3500 and 3130 Å, respectively. Our results are in considerable disagreement with all these studies except that of Eder and Carr.

There are several possible explanations for the differences between our measurement of the relative values of  $\Phi_1/(\Phi_1 + \Phi_3)$  and the earlier measurements of per cent singlet methylene versus wavelength. As has been pointed out previously [25],  $CH_2(^1A_1) \rightarrow$  $CH_2({}^{3}B_1)$  collision induced intersystem crossing may be important in studies of ketene photochemistry. If this is the case, yields of triplet and singlet methylene products would not reflect the singlet and triplet methylene photodissociation quantum yields. Also, because of the large decrease in singlet methylene formation at 3660 Å relative to 3340 and 3130 Å, it is necessary to exclude the 3130 and 3340 Å radiation if meaningful measurements are to be obtained at 3660 Å. The previous reports of high fractions of singlet methylenes at 3660 Å may have been due to the lack of monochromaticity in the photolysis system<sup>\*</sup>. As discussed above, near monochromatic radiation was achieved for our 3660 Å photolyses. Finally, a comparison of our



Fig. 1. Energetics for CH<sub>2</sub>CO photodissociation.

study with the previous ones is inherently difficult due to the different pressures and bath gases used. Inelastic collisions with the excited ketene molecules will lower their average energy from that when they are formed initially. Therefore, measurements of  $\Phi_1$  and  $\Phi_3$  at pressures greater than zero will not represent the quantum yields for the initially excited ketene molecules. The difference between the measured quantum yields and those at zero pressure will depend upon the pressure and the ability of the moderating gas to de-energize the excited ketene molecules.

An explanation for the wavelength dependency of  $\Phi_1/(\Phi_1 + \Phi_3)$  is given by the energetics of ketene photochemistry, as shown in fig. 1. The <sup>1</sup>A<sub>2</sub> state of ketene,  $S_1$ , is though to be  $\leq 61$  kcal/mole above the ground state,  $S_0$  [11]. If the <sup>1</sup>A<sub>2</sub> and <sup>3</sup>A<sub>2</sub> separation in ketene is close to that of similar molecules, the  $T_1 - S_0$  separation is  $\leq 55$  kcal/mole [11]. Using measured values for heats of formation, the separation between  $S_0$ [CH<sub>2</sub>CO(<sup>1</sup>A<sub>1</sub>)] and CH<sub>2</sub>(<sup>3</sup>B<sub>1</sub>) and CO is 79 kcal/

<sup>\*</sup> The difficulty in achieving monochromatic rediztion at 3660 A is also discussed in ref. [20].

mole [11,17]. The  $CH_2({}^1A_1)-CH_2({}^3B_1)$  separation is placed at 9 kcal/mole. This agrees with both quantum mechanical [26–28] and photochemical [29] determinations of this separation. As shown in fig. 1, a vibrationally excited  $S_1$  state is formed at each of the wavelengths. However, the probability that the excited state contains sufficient energy, including thermal energies, to ultimately form  $CH_2({}^1A_1)$  radicals decreases as the wavelength is increased. Therefore, the decrease in  $\Phi_1/(\Phi_1 + \Phi_3)$  with increasing wavelength seems to reflect the CH<sub>2</sub> singlet-triplet splitting. However, a complete understanding of our observed increase in  $\Phi_1/(\Phi_1 + \Phi_3)$  with excitation energy requires knowledge of the rates and energy dependence of the non-radiative paths which form the singlet and triplet methylenes, and the effect of inelastic collisions on the initially excited  $S_1$  molecules.

We are currently extending this study to different pressures and wavelengths to determine the exact shape of the singlet methylene quantum yield as a function of energy, the rates of singlet methylene formation, and the zero pressure singlet methylene quantum yields. The results should be very useful in deducing the important nonradiative processes involved in ketene photochemistry.

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<sup>\*</sup> In ref. [30] CH<sub>2</sub>CO was photolyzed at 3130 Å, and the dissociation rate of  $C_2H_6$ , formed by  $CH_2(^1A_1) + CH_4$  insertion, was measured. The rate constant was analyzed using the RRKM theory and a value of 2.5 kcal/mole deduced for the  $CH_2({}^{1}A_1)-CH_2({}^{3}B_1)$  splitting. However, the critical configuration used by Halberstadt and McNesby in their RRKM calculation will not fit the thermal rate of  $C_2H_6$  dissociation. A re-analysis of the rate constant measured by Halberstadt and McNesby using a critical configuration which fits the thermal rate of ethane dissociation shows their data is consistent with a  $CH_2({}^{1}A_1) - CH_2({}^{3}B_1)$  splitting of 9 kcal/mole [31]. Carr et al. [24], suggest a lower CH2('A1)  $-CH_2(^3B_1)$  splitting of 1-2 kcal/mole. This value is deduced by associating  $\Phi_1$  and  $\Phi_3$  to measurements of singlet and triplet methylene products and assuming the dissociation of excited ketene to form  $CH_2({}^{1}A_1)$  and  $CH_2({}^{3}B_1)$ can be described by Arrhenius equations with similar A-factors for singlet and triplet methylene formation.

## References

- [1] J.W. Simons and B.S. Rabinovitch, J. Phys. Chem. 68 (1964) 1322.
- [2] R.W. Carr Jr. and G.B. Kistiakowsky, J. Phys. Chem. 70 (1966) 118.
- [3] B.A. DeGraff and G.B. Kistiakowsky, J. Phys. Chem. 71 (1967) 3984.
- [4] S. Ho and W.A. Noyes Jr., J. Am. Chem. Soc. 89 (1967) 5091.
- [5] T.W. Eder and R.W. Carr Jr., J. Phys. Chem. 73 (1969) 2074.
- [6] A.N. Strachan and W.A. Noyes Jr., J. Am. Chem. Soc. 76 (1954) 3258.
- [7] B.T. Connelly and G.B. Porter, Can. J. Chem. 36 (1958) 1640;
  G.B. Porter and B.T. Connelly, J. Chem. Phys. 33 (1960) 81;
  G.A. Taylor and G.B. Porter, J. Chem. Phys. 36 (1962) 1353.
- [8] A.N. Strachan and D.E. Thornton, Can. J. Chem. 46 (1968) 2353.
- [9] D.C. Montague and F.S. Rowland, J. Am. Chem. Soc. 93 (1971) 5381;
   R.L. Russell and F.S. Rowland, J. Am. Chem. Soc. 92 (1970) 7508.
- [10] J.W. Rabalais, J.M. McDonald, V. Scherr and S.P. McGlynn, Chem. Rev. 71 (1971) 73.
- [11] A.H. Laufer and R.A. Keller, J. Am. Chem. Soc. 93 (1971) 61.
- [12] G.B. Kistiakowsky and B.H. Mahan, J. Am. Chem. Soc. 79 (1957) 2412.
- [13] S.F. Fischer, A.L. Stanford and E.C. Lim, J. Chem. Phys. 61 (1974) 582;
   J.C. Hsieh, C. Huang and E.C. Lim, J. Chem. Phys. 60 (1974) 4345.
- [15] C.J. Mazac and J.W. Simons, J. Am. Chem. Soc. 90 (1968) 2484.
- [15] W.L. Hase, W.G. Brieland and J.W. Simons, J. Phys. Chem. 73 (1969) 4401.
- [16] W.L. Hase, W.G. Brieland, P.W. McGrath and J.W. Simons, J. Phys. Chem. 76 (1972) 459.
- [17] K. Dees and D.W. Setser, J. Phys. Chem. 75 (1971) 2240.
- [18] W.L. Hase and J.W. Simons, J. Chem. Phys. 54 (1971) 1277.
- [19] E.K.C. Lee, M.W. Schmidt, R.G. Shortridge Jr. and G.A. Haninger Jr., J. Phys. Chem. 73 (1969) 1805.
- [20] T.W. Eder and R.W. Carr Jr., J. Chem. Phys. 53 (1970) 2258.
- [21] R.A. Cox and K.F. Preston, Can. J. Chem. 47 (1969) 3340.
- [22] A.K. Dhingra and R.D. Koob, J. Phys. Chem. 74 (1970) 4490.
- [23] P.M. Kelley, W.L. Hase and J.W. Simons, J. Phys. Chem., to be published.
- [24] R.W. Carr Jr., T.W. Eder and M.G. Topor, J. Chem. Phys. 53 (1970) 4716.
- [25] J.A. Bell, J. Phys. Chem. 75 (1971) 1537.

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- [26] P.J. Hay, W.J. Hunt and W.A. Goddard III, Chem. Phys. Letters 13 (1972) 30.
- [27] C.F. Bender, H.F. Schaefer, D.R. Franceschetti and L.C. Allen, J. Am. Chem. Soc. 94 (1972) 6888.
- [28] M.J.S. Dewar, R.C. Haddon and P.J. Weiner, J. Am. Chem. Soc. 96 (1974) 253.
- [29] W.L. Hase, R.J. Phillips and J.W. Simons, Chem. Phys. Letters 12 (1971) 161;

R.J. Phillips, M.S. Thesis, New Mexico State University, Las Cruces, New Mexico.

- [30] M.L. Halberstadt and J.R. McNesby, J. Am. Chem. Soc. 89 (1967) 4317.
- [31] W.L. Hase, J. Chem. Phys. 57 (1972) 730;
   F.B. Crowcock, W.L. Hase and J.W. Simons, Intern. J. Chem. Kinetics 5 (1973) 77.