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Reaction of Singlet Methylene with Cyclopropane

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Ketene in excess of cyclopropane containing enough O_2 to eliminate its reactions with CH_2 ($^3B_1$) was photolyzed, using a monochromator and suitable filters, at four different wavelengths, 214, 277, 313, and 330 nm. The lifetimes of the resultant "hot" methylcyclopropane prior to isomerization into butenes were found to be 2.55, 3.92, 5.40, and 6.29 × 10^{-10} sec, increasing with decreasing photolyzing energy. The RRKM theory was used to estimate the internal energy of the excited methylcyclopropane and the energies so obtained ranged from 104 kcal/mol at 330 nm to 110 kcal/mol at 214 nm. According to these calculations the fraction of excess photon energy carried into methylcyclopropane rapidly decreases as the photon energy increases.

Methylene has been used extensively in chemical activation studies.[1] Butler and Kistiakowsky (BK) photolyzed both ketene and diazomethane at several wavelengths and reacted the resulting CH_2 with propene or cyclopropane to produce vibrationally excited methylcyclopropane (MCP).[2] The excited MCP either isomerized to form isobutene, 1-butene, and *cis*- and *trans*-2-butene or was deactivated by collision. Their work was done before the importance of CH_2 ($^3B_1$) as a reactant distinct from CH_2 ($^1A_1$), but present along with CH_2 ($^1A_1$) in the methylene systems was recognized; consequently no effort was made to prevent the CH_2 ($^3B_1$) from reacting with the hydrocarbons. BK's main conclusion that the distribution of energy in the MCP produced from cyclopropane does not differ from that produced from propene is unaffected by the knowledge that two distinct electronic states of CH_2 were present in the reaction system. However, one would expect the lifetimes of the MCP to be shorter when there is more vibrational energy brought to it by the methylene, as might be the case when shorter photolyzing wavelengths are used. The results of BK's experiments were not consistent with these expectations since they found that photolyses in their ketene system at 310 nm produced MCP with shorter lifetimes than photolyses at 260 nm did. Now one might suspect that this inconsistency was the result of some complicating reactions of the CH_2 ($^3B_1$), except that the reaction of CH_2 with cyclopropane is quite slow.[3] CH_2 ($^3B_1$) undoubtedly was significant in their ketene–propene system.

Dorer and Rabinovitch[4] also studied the reaction of CH_2 with propene using both ketene and diazomethane as a source of CH_2. In some of their experiments, they used the well-known technique of adding O_2 to scavenge the CH_2 ($^3B_1$), but they photolyzed ketene at one wavelength only and consequently could not investigate the lifetime of MCP as a function of the photolyzing wavelength. Strachan and Thornton[3] studied the photolysis of ketene and cyclopropane in the presence of O_2 but used their results only to determine at what cyclopropane/ketene ratio the reactions of CH_2 ($^3B_1$) and CH_2 ($^1A_1$) with ketene become negligible compared to their reactions with cyclopropane.

We repeated BK's experiments and photolyzed ketene and cyclopropane at four different wavelengths. Although CH_2 ($^3B_1$) is not expected to react extensively with cyclopropane,[3] we added a small amount of O_2 (5% of the total

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(1) See, for example, the reviews by H. M. Frey, *Prog. React. Kinet.*, **2**, 131 (1964); B. S. Rabinovitch and M. C. Flowers, *Quart. Rev., Chem. Soc.*, 122 (1964).

(2) J. N. Butler and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, **82**, 759 (1960).

(3) D. E. Thornton and A. N. Strachan, *J. Phys. Chem.*, **71**, 4583 (1967).

(4) F. H. Dorer and B. S. Rabinovitch, *J. Phys. Chem.*, **69**, 1952, 1964, 1973 (1965).

mixture) to ensure that the only methylene species reacting with cyclopropane was singlet CH_2.

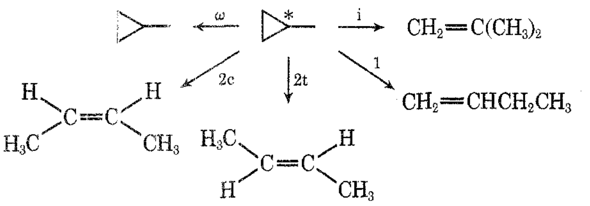
Experimental Section

Mixtures containing cyclopropane, ketene, and oxygen in the ratio of 20:1:1 were photolyzed at 330 , 313, and 277 nm using an Osram HBO 500-W mercury lamp with a Bausch and Lomb monochromator and at 214 nm using a 25-W Phillips zinc lamp with a Baird-Atomic 214-nm standard line filter. The total pressure of the photolysis mixture was varied between 30 and 700 Torr with at least three different pressures within this range being used at each wavelength. In each photolysis, only 2–5% of the ketene was decomposed. The condensable products were transferred using liquid nitrogen to a gas chromatograph equipped with a flame ionization detector. The products were then separated on a 10 ft, 0.25-in. o.d. column filled with two parts of Porapak Q and one part of Porapak Q-S (both 50–80 mesh) operated at 80° with a carrier (helium) flow rate of 100 cc/min. Isobutene and 1-butene were not resolved from each other on this column, but the separation of these two products was not necessary to determine the lifetimes of MCP. Ketene was prepared by the pyrolysis of acetic anhydride.[5] The cyclopropane used was Matheson's CP grade which contained 0.3% propene as its major impurity. Air Reduction Co. research grade O_2 was used. Further details are discussed in ref 6 and 7.

Results and Discussion

CH_2 ($^1A_1$) inserts into the C–H bonds of cyclopropane to form excited MCP whose fate is decided according to the reaction shown in Scheme I.[2,3,8,9] The overall rate constant for the isomerization of MCP, $k_a = k_i + k_1 + k_{2c} + k_{2t}$, is equal to the collision frequency, ω, multiplied by the ratio of the sum of concentrations of olefin products, D, to the concentration of the stabilized MCP, S

Scheme I



$$k_a = \omega(D/S) = \omega[\text{butenes}]/[\text{MCP}]$$

The k_a values were determined from plots of [butenes]/[MCP] *vs.* $1/\omega$ or 1/total pressure at each wavelength, and these plots are shown in Figure 1. The dashed line in Figure 1 represents BK's average of both the 260- and 310-nm experiments. The scatter of individual points in BK's experiments is much larger than in ours. In direct contrast to BK,[2] the lifetimes of the MCP, $1/k_a$, became shorter as the photolyzing energy was increased.

The ratios of *trans*-2-butene to *cis*-2-butene and that of the 2-butenes to isobutene and 1-butene were about 1.0 and varied somewhat with pressure,[6] in agreement with other workers.[2,8] Dorer and Rabinovitch[4] studied further reactions of 1-butene resulting from the isomerization of "hot" methylcyclopropane and found that in the pressure range employed in the present work butene was overwhelmingly stabilized by collisions. We felt justified therefore in using the plots of Figure 1 to evaluate k_a.

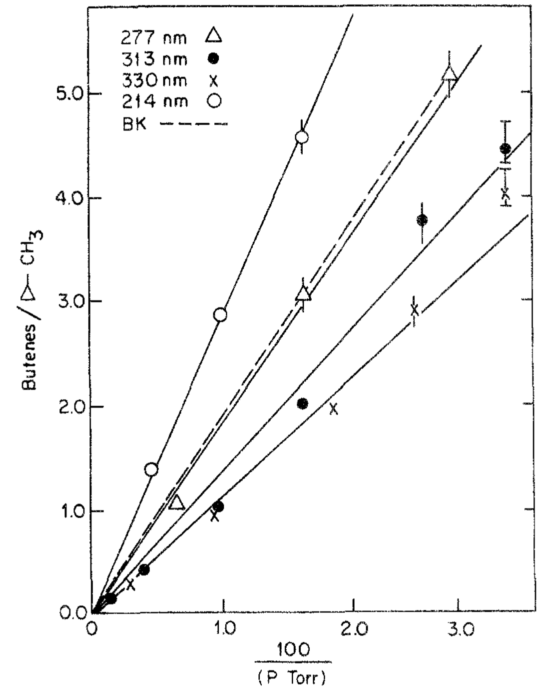


Figure 1. Plot of butene/MCP *vs.* 100/*P* (Torr).

The usual RRKM treatment which used models very similar to those developed by Dorer and Rabinovitch[4] was applied to models for MCP isomerization in order to estimate the average vibrational energies of the MCP molecules produced at several wavelengths. The best models so determined for the activated complex and the molecule are given in Table I. The average energies of the excited molecules for each photolyzing wavelength are given in Table II. For comparison, the average energy and the rate of decomposition of MCP formed by the reaction of propene and CH_2 ($^1A_1$) produced from the photolysis of ketene at 320 nm[4] are included in this table. However, it should be noted that Dorer and Rabinovitch[4] used unfiltered light from a GE AH-6 super pressure lamp and, on the basis of other work,[10] estimated that 320 nm is the effective photolyzing wavelength and so this wavelength is not as well defined as those in our present work are.

The unmistakable difference in lifetime, and hence in internal energies, $\langle E \rangle$, of MCP produced by radiation of different wavelengths reflects the differences in energies carried into MCP by the CH_2 ($^1A_1$). Several specific RRKM models tried by us gave somewhat different values of $\langle E \rangle$ for the hot MCP molecules, so that the numbers shown as $\langle E \rangle$ in Table II should be regarded as uncertain to a very few kcal. All these RRKM models show, how-

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(5) A. D. Jenkins, *J. Chem. Soc.*, 2563 (1962).
(6) B. B. Saunders, Ph.D. Thesis, Harvard University, 1972.
(7) B. A. DeGraff and G. B. Kistiakowsky, *J. Phys. Chem.*, 71, 3984 (1967).
(8) D. W. Setser and B. S. Rabinovitch, *J. Amer. Chem. Soc.*, **86**, 564 (1964); E. Jakubowski, H. S. Sandhu, and O. P. Strauz, *ibid.*, **93**, 2610 (1971).
(9) J. P. Chesick, *J. Amer. Chem. Soc.*, **82**, 3277 (1960).
(10) D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 1425 (1962).

TABLE I: Models for Methylcyclopropane (Molecule and Best Complex)[a]

	Molecule	Complex
C–H stretch	3015 (8)	3015 (7)
"Breathing," ring	1202	1082
CH_2 bend	1047	884
	889	747
CH_2 twist	1111	570
CH_2 rock	911	890
CH_2 bend	983	730
CH_2 rock	1016	790
CH_2 twist	810	815
	756	421
Methyl ring torsion	0	0
CH_3 and CH_2 H bends	1436 (6)	1436 (6)
Skeletal bend	320 (2)	320 (2)
CCH methyl bends	1046 (2)	1046 (2)
E_0		62.5 kcal/mol

[a] Values given in cm^{-1}. σ = 5.4 Å for collisions of methylcyclopropane and cylopropane.

TABLE II: Average Energies and the Rates of Decomposition

Photolysis system	$\langle E \rangle_{max}$,[a] kcal/mol	$\langle E \rangle$,[b] kcal/mol	k_a,[c] sec^{-1}
320 nm + propene[d]	104.5	99.6 ± 1.4	0.72×10^9
330 nm + cyclopropane	109.4	104.2 ± 0.7	1.59×10^9 ± 12%
313 nm + cyclopropane	114.2	105.1 ± 0.8	1.85×10^9 ± 12%
277 nm + cyclopropane	126.0	107.2 ± 0.1	2.55×10^9 ± 3%
214 nm + cyclopropane	156.8	110.5 ± 0.6	3.92×10^9 ± 8%

[a] $\langle E \rangle_{max}$ assumes that the entire photon energy in excess of that needed for the decomposition of ketene appears as internal energy of the hot methylcyclopropane. [b] Calculated from RRKM model. [c] Measured. [d] Reference 4.

TABLE III: Heats of Formation

$\Delta H_f°$ at 298°K, kcal/mol	Substance
92.2[a]	CH_2
12.7	Cyclopropane
5.7	Methylcyclopropane
−11.4[b]	Ketene
−27.2[c]	CO
4.9	Propylene
−3.7	Isobutene
0	1-Butene
−1.7	*cis*-2-Butene
−2.7	*trans*-2-Butene

[a] W. A. Chupka, and C. Livshitz, *J. Chem. Phys.*, **48**, 1109 (1968). [b] R. L. Nuttal, A. H. Laufer, and M. V. Kilday, *J. Chem. Thermodyn.*, **3**, 167 (1971). [c] D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, *Nat. Bur. Stand. (U. S.), Tech. Note*, No. 270–3 (1968). All other values are taken from S. W. Benson, "Thermodynamics of Gas Reactions," Wiley, New York, N. Y., 1968.

ever, that only a fraction of the excess photon energy is carried into the MCP and that this fraction rapidly decreases as the wavelength gets shorter and the photon energy larger.

The excess photon energy is divided in an unknown manner as internal energies of CH_2 and CO and as their translational energies in the 2:1 ratio. We consider it highly improbable that the $\langle E \rangle$ values shown in Table II are the measure of the total energy received by CH_2 in the decomposition process, for this would mean that CO receives a rapidly increasing fraction as the total energy becomes larger. The more likely explanation is that CH_2 ($^1A_1$) suffers several inelastic collisions before reacting with cyclopropane. In fact, it has been estimated[4] that the rate of this reaction is slower than that of its reaction with propene by a factor of 10. It would be consistent with the theories of collisional energy transfer to expect that the energy loss would be greater when the total energy is greater. The reaction probability, however, is large enough that CH_2 ($^1A_1$) does not become fully thermalized before reaction. This we consider definitely proven by this work, the earlier results of BK having been undoubtedly distorted by the presence of CH_2 ($^3B_1$). It might be further noted that irradiation of ketene by the 214-nm wavelength induces a $\pi \rightarrow \pi^*$ transition and probably produces methylene in the excited $^1B_1$ state. The estimated internal energies of hot methylcyclopropane, Table II, indicate that the electronic excitation energy of CH_2 ($^1B_1$) is not carried into the reaction with cyclopropane.

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