Electronic States of Methylene from Ketene Photodissociation between 214 and 313 nm

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Abstract: The photolysis of ketene in the presence of *cis*-2-butene was studied at a series of wavelengths from 313 to 250 nm of the ketene $^1A'' \leftarrow {}^1A_1$ transition, and at 214 nm in the $^1B_2 \leftarrow {}^1A_1$ transition. The effects of pressure and absorbed intensity at 285 and 214 nm were examined, and the effect of small amounts (~5 mol %) of O_2 was determined. The hydrocarbon reaction products formed between 250 and 313 nm are consistent with the presence of two reactive electronic states of methylene during photolysis, the ground state, $X\ ^3B_1$, and first excited state, $\bar{a}\ ^1A_1$. Furthermore, the two states appear to be formed in approximately constant relative proportion over this wavelength region. At 214 nm an increase in the nonstereospecificity of the methylene addition to the double bond in *cis*-2-butene can be attributed to the presence of the second excited state, $CH_2(\bar{b}\ ^1B_1)$. If $\bar{b}\ ^1B_1$ is postulated to be formed from ketene at 214 nm, the results require that it react more rapidly with oxygen than with *cis*-2-butene, and also indicate that the $X\ ^3B_1$ and $\bar{a}\ ^1A_1$ states of methylene are simultaneously present.

The photolysis of ketene between about 270 and 350–360 nm results in the formation of two electronic states of methylene, the $^3B_1$ ground state and the $^1A_1$ first excited state.[1-4] At shorter wavelengths higher excited states of methylene are possible, and changing product yields at 249 nm have been suggested to provide evidence for participation of $CH_2(^1B_1)$, the second excited state.[5] Experiments on ketene photolysis at 213.9 nm have been inconclusive concerning whether the reactive states of methylene are only the ground and first excited state, or whether $CH_2(^1B_1)$ is also involved.[6,7]

In this paper we report the results of a wavelength study of ketene photolysis in the presence of *cis*-2-butene between 200 and 313 nm. Hoffmann has predicted that $CH_2(^1B_1)$ should add nonstereospecifically to olefins.[8] Since *cis*-2-butene lacks a symmetry axis along the carbon–carbon double bond, and since its reactions with $CH_2(^3B_1)$ and $CH_2(^1A_1)$ have been extensively studied,[9] it was selected as the substrate in this work. Harrison[10] has recently reviewed experimental and theoretical work on the low-lying electronic states of methylene.

Experimental Section

Apparatus. A conventional Pyrex vacuum apparatus, capable of 10^{-5} to 10^{-6} Torr, was used. Teflon-glass valves were employed in all portions where reaction products were handled. The 142-cm^3 cylindrical reactor had planar Ultrasil quartz end windows, was 18.3 cm long, and had a 3.1 cm i.d. Ketene-*cis*-2-butene mixtures were photolyzed with three different light sources. (1) The emission from a medium pressure Zn arc was filtered with 4 cm of Cl_2 (1 atm) to block radiation above 290 nm. (2) Emission from a 1000 W dc Xe arc lamp was passed through a Bausch and Lomb High Intensity grating monochromator, permitting selection of desired wavelength regions between 250 and 313 nm. The slits were set to pass a 5.0-nm band centered on the selected wavelength. (3) A high-pressure Hg arc, Osram HBO 500, was used with a three-compartment chemical filter containing a 2.5-cm path of a 55.2 g $NiSO_4{\cdot}6H_2O$/100 cm^3 H_2O solution and a 5-cm path of Cl_2 at 1 atm, for which the transmitted actinic wavelength was 265 nm. A higher intensity at 265 nm was possible with this arrangement than with the Xe arc. Transmission spectra of arc-filter and arc-monochromator combinations were recorded photoelectrically with a 0.5-m Ebert-mounting scanning spectrometer, using 10 μ slits. Reactor absorbance was measured with an RCA 935 photocube.

Reactants. Ketene was prepared by acetic anhydride pyrolysis, as previously described.[3] After several trap-to-trap distillations from −78 to −196 °C, and being pumped on at −127 °C, it contained only trace (<0.1%) C_2 impurities. Phillips research grade *cis*-2-butene with a 99.91% stated purity was used. GC detectable impurities were *trans*-2-butene (0.05–0.06%) and *n*-butane. UHP grade O_2 was taken directly from an NCG cylinder. Airco Ar of 99.995% stated purity was used without further treatment.

Experimental Methods. Products were quantitatively determined by gas chromatography with flame ionization detection. A 0.25-in. o.d. three-part column, which has been previously described,[11] was used at 20 °C for the complete separation of all products observed except ethane and ethylene, which were measured as a common C_2 fraction. Calibration of the detector was done with mixtures of authentic samples of known composition. Mixtures of CH_2CO and *cis*-2-C_4H_8 were prepared in a 1-l. blackened storage vessel for periods never exceeding 10–14 days since a slow dark reaction between CH_2CO and *cis*-2-C_4H_8 usually accumulated detectable products, many of which were identical with the photoproducts, by the end of a 2-week period. It was necessary to periodically clean the reactor because a solid film, presumably a polymer, slowly formed on the inside of the reactor entrance window. While the film absorbed part of the incident radiation it did not affect the wavelength distribution of transmitted light. The film formed more rapidly at wavelengths below 300 nm, and particularly at 213.9 nm, than at 313 nm, where it is not troublesome. Appreciable cis → trans isomerization of 2-butene was observed in experiments immediately following reactor cleansing, and a few experiments were needed to condition the reactor.

Results

Reaction Products. The following were obtained at all wavelengths and pressures: *cis*-1,2-dimethylcyclopropane (CDMC), *trans*-1,2-dimethylcyclopropane (TDMC), *cis*-2-pentene (C2P), *trans*-2-pentene (T2P), 2-methyl-2-butene (2M2B), 3-methyl-1-butene (3M1B), 2-methyl-1-butene (2M1B), *n*-pentane (nP), ethane, ethylene, and methane. Small yields (~0.5%) of 1-pentene were observed in a few experiments at 280 and 265 nm. When oxygen was present, propylene was a product, 3M1B was absent, and some other product yields showed significant changes; compare Figures 1 and 2.

Effect of Wavelength. Figures 1 and 2 show product yields, relative to total C_5 hydrocarbon yields, vs. wavelength at 200 Torr total pressure for CH_2CO-*cis*-2-butene = 1:7 mixtures and CH_2CO-*cis*-2-butene-O_2 = 1:7:0.04, respectively.

Data taken near 1 atm at 213.9 and 280 nm are included to indicate the existence of pressure effects. Details of a pressure study of this system will be reported separately. The major product yields in Figure 1 appear independent of wavelength except for TDMC, which increases with increasing photon energy. The minor products, 3M1B and T2P, go through a shallow minimum near 280 nm, and the

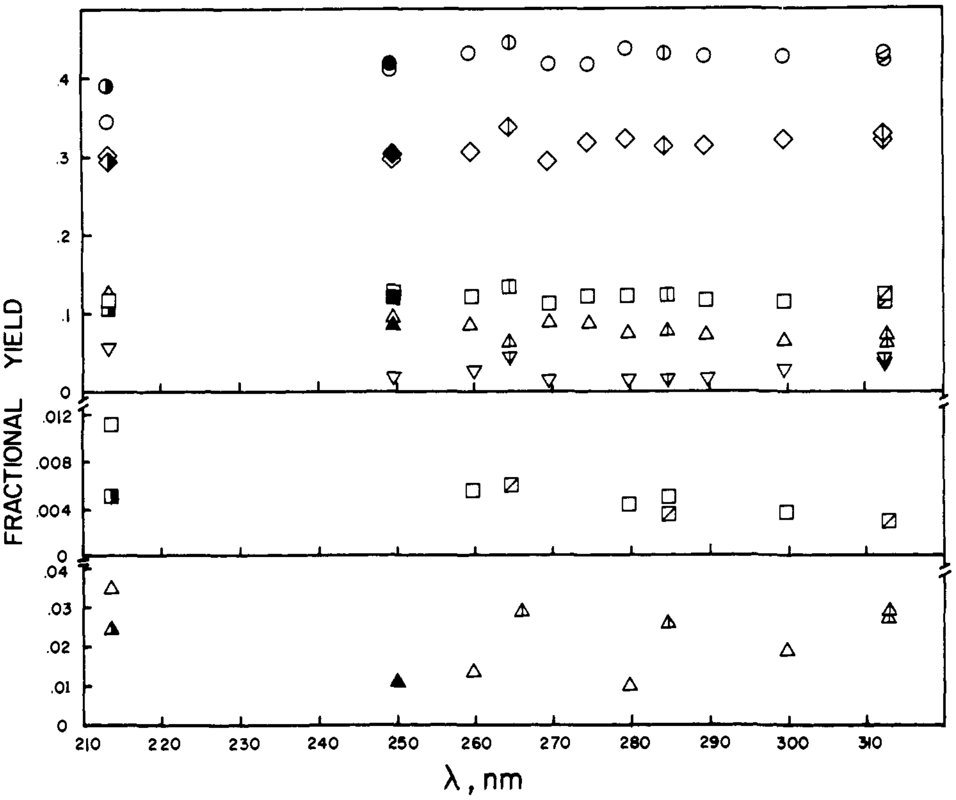


Figure 1. Fractional yields of reaction products from 1:7 ketene-*cis*-2-butene experiments. Top frame: (○) CDMC; (◇) C2P; (△) TDMC; (▽) T2P; (□) 2MB2. Middle frame: (□) 2MB1. Bottom frame: (△) 3MB1. Open symbols, 200 Torr; half-shaded symbols, 478 Torr; full-shaded symbols, 760 Torr; crossed symbols, 200 Torr with Hg arc source.

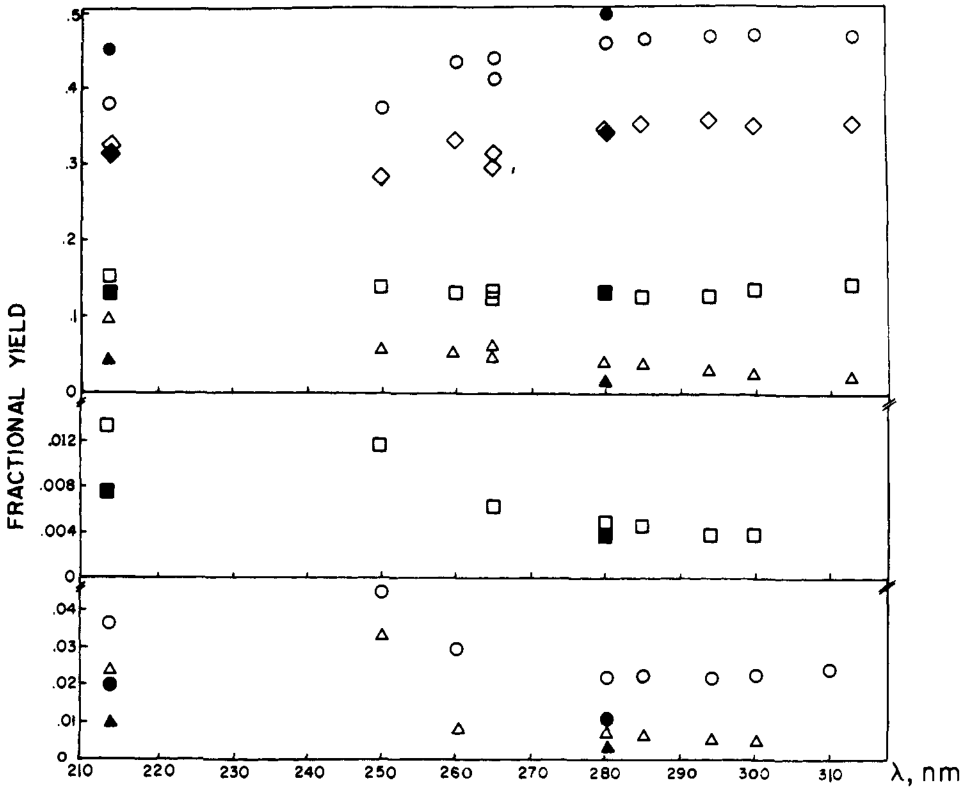


Figure 2. Fractional yields of reaction products from 1:7:0.04 ketene-*cis*-2-butene-O_2 experiments. Top frame: (○) CDMC; (◇) C2P; (□) 2MB2; (△) TDMC. Middle frame: (□) 2MB1. Bottom frame: (○) propylene; (△) T2P. Open symbols, 200 Torr; full-shaded symbols, 760 Torr.

yield of 2M1B increases with increasing photon energy. The yields of CH_4, C_2's, and n-P showed no discernible wavelength dependence, and their average values are 0.085, 0.126, and 0.03, respectively.

With O_2 present, Figure 2, the yields of CDMC and T2P decrease below 2700 Å, 3M1B and CH_4 are no longer detected, C_2 yields are roughly halved, and *n*-P yields are reduced by about a factor of 10. The yields of TDMC, T2P,

Table I. Effect of Reactor Size

		Fractional product yields									
Reactor	*P*, Torr	CH_4	$C_2H_4 + C_2H_6$	3M1B	TDMC	2M1B	T2P	C2P	CDMC	2M2B	CDMC/ TDMC
1250 cm^3 Pyrex sphere 13.5 cm D; $S/V = 0.45$	165	0.017	0.14	0.042	0.070	0.003	0.048	0.34	0.41	0.086	5.9
250 cm^3 Pyrex sphere 7.8 cm D; $S/V = 0.77$	200	0.016	0.13	0.039	0.067	0.003	0.041	0.35	0.41	0.092	6.2
10 cm^3 Pyrex sphere $S/V = 2.4$	200	0.012	0.11	0.035	0.065	0.003	0.037	0.34	0.43	0.094	6.6

2MB1, and propylene all show increases with decreasing wavelength.

Light Intensity. The effect of light intensity on the relative product yields resulting from photolysis of 1:7 ketene-*cis*-2-butene mixtures at 213.9 and 285 nm was investigated over a 30-fold change in absorbed intensity. The data appear in the microfilm edition of this issue.[12] At each wavelength it was found that the yields of T2P and 3M1B and the C_2 fraction, relative to total C_5 yield, decreased with decreasing light intensity, while CH_4 and n-C_5H_{12}, relative to total C_5 yield, increased with decreasing light intensity. All other relative product yields were independent of intensity within the limits of experimental error.

Reactor Size. Three spherical Pyrex reactors having surface/volume ratios of 0.45 (1250-cm^3 bulb), 0.77 (250-cm^3 bulb) and 2.4 (10-cm^3 bulb) were used for photolysis of 1:7 mixtures of ketene-*cis*-2-butene by an unfiltered Hg arc. The average effective wavelength was 320 nm. Relative product yields from these experiments are given in Table I, from which it can be seen that a fivefold change in S/V results in small decreases of CH_4, C_2's, 3M1B, and T2P, all other product yields not being detectably changed.

Discussion

Accessible Electronic States of CH_2. The low-lying electronic states of CH_2 in order of increasing energy are $X(^3B_1)$, $\tilde{a}(^1A_1)$, $\tilde{b}(^1B_1)$, and $\tilde{c}(^1A_1)$. The enthalpy change for CH_2CO dissociation to $CO(X^1\Sigma)$ and $CH_2(^3B_1)$, $\Delta H°_{298} = 80 \pm 1$ kcal/mol,[13] corresponds to λ 356 ± 4 nm. This lies above the 0-0 band of the $CH_2CO(^1A'') \leftarrow CH_2CO(^1A_1)$ transition,[14] and is consistent with the observation that approximately 90% of the methylenes formed from photodissociation of CH_2CO in the vicinity of 350 nm are in the ground state.[2,3] The excitation energy of the first excited state, $\tilde{a}\ ^1A_1$, is uncertain. Recent values of about 2 kcal/mol,[15,16] and in the 6-11 kcal/mol range, have been reported.[17-21] It is only necessary to note that the threshold wavelength for $^1A_1$ formation from CH_2CO must lie between 345 and 312 nm, and that $^1A_1$ is known to be present during CH_2CO photolysis at 350, 334, and 313 nm.[1-4]

An analysis of the red absorption bands of CH_2 by Herzberg and Johns[22] placed the (0,0,0)-(0,0,0) band of $\tilde{b}\ ^1B_1 \leftarrow \tilde{a}\ ^1A_1$ at 7400 ± 500 cm^{-1}. This places the minimum wavelength for $^1B_1$ formation from CH_2CO in the 275 to 250 nm range, where the uncertainty is due to uncertainty in the $\tilde{a}\ ^1A_1 \leftarrow X\ ^3B_1$ excitation energy. Hay, Hunt, and Goddard[20] suggested that the lowest observed transition in the red bands of CH_2, which occurs at 10 767.6 cm^{-1},[22] is the $\tilde{b}\ ^1B_1(000) \leftarrow \tilde{a}\ ^1A_1(000)$ transition. This would place the minimum wavelength for $^1B_1$ formation from CH_2CO between 252 and 234 nm. However, the difference in H-C-H bond angle, 105° for $^1A_1$ vs. 135° for $^3B_1$, makes it seem unlikely that the 0-0 band of the bending frequency would be observed in an optical transition. Furthermore, the 30.8 kcal/mol $^1B_1$-$^1A_1$ energy difference resulting from this interpretation is significantly larger than all but one of the other published ab initio computations of this quantity,[23] which are by and large in agreement with the assignment made by Herzberg and Johns.[22] The $\tilde{c}\ ^1A_1$ state (hereafter labeled $^1A_1{}^*$ to distinguish it from $\tilde{a}\ ^1A_1$) has received little attention. From observations of the CH_2 middle uv absorption bands,[22] Herzberg[24] has given the $^1A_1{}^* \leftarrow {}^1A_1$ energy difference as less than or equal to 79 kcal/mol, and Chu, Siu, and Hayes[25] computed the value 44 kcal/mol for the adiabatic excitation energy. Using the lower value, $^1A_1{}^*$ production might be expected from ketene photolysis at wavelengths as long as 201 to 226 nm.

Mechanism. As a basis for discussion at shorter wavelengths, the mechanism at 313 nm will be discussed first. The only accessible states of CH_2 at 313 nm are the $^3B_1$ and $^1A_1$ states, and both are produced at this wavelength. Investigations of the mechanisms of their reactions with olefins, carried out in several laboratories, show that these two electronic states react with the 2-butenes by completely different mechanisms. A good discussion has recently been given by Kirmse.[9] The accumulated evidence leaves no doubt that $^1A_1$ addition to double bonds occurs stereospecifically, while the $^3B_1$ addition occurs nonstereospecifically. The reactions of $^1A_1$ with *cis*-2-butene are stereospecific addition to the double bond, and insertion into C-H bonds.

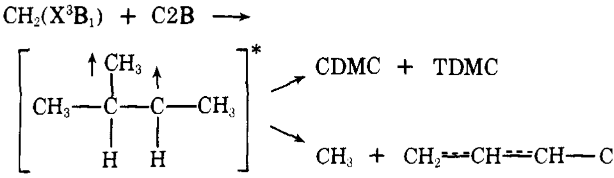
$$CH_2(^1A_1) + cis\text{-2-B} \rightarrow CDMC^* \qquad (1a)$$

$$CH_2(^1A_1) + cis\text{-2-B} \rightarrow T2P^* \qquad (1b)$$

$$CH_2(^1A_1) + cis\text{-2-B} \rightarrow 2M2B^* \qquad (1c)$$

The asterisk represents chemically activated species (~100 kcal/mol). However, at 313 nm, about 200 Torr of a polyatomic heat bath (collision partner) is enough to suppress virtually all isomerization and decomposition of these species.[1]

Nonstereospecific addition of $^3B_1$ proceeds via the 1,2-dimethyltrimethylene triplet biradical:



$$CH_2(X^3B_1) + C2B \longrightarrow \left[CH_3{-}\overset{\uparrow CH_3}{\underset{H}{C}}{-}\overset{\uparrow}{\underset{H}{C}}{-}CH_3 \right]^* \begin{matrix} \nearrow CDMC + TDMC \\ \searrow CH_3 + CH_2{=\!=}CH{=\!=}CH{-}CH_3 \end{matrix} \qquad (2)$$

The vibrationally excited biradical may cyclize competitively with rotation about the central C-C bond to yield both CDMC and TDMC, or may decompose to methyl plus methallyl.[11] Finally $^3B_1$ may abstract hydrogen from C2B at either the allyl or vinyl position, with the former predominating. The remainder of the

$$CH_2(^3B_1) + C2B \rightarrow CH_3 + CH_2{=\!=}CH{=\!=}CH{-}CH_3$$
$$\rightarrow CH_3 + CH_3{-}CH{=}\dot{C}{-}CH_3$$

products observed at 313 nm are easily explained by expect-

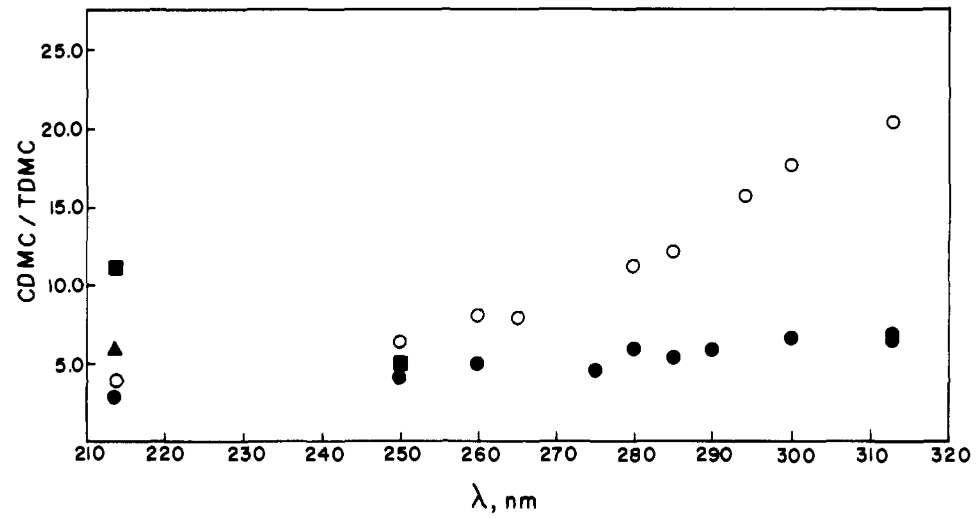


Figure 3. CDMC/TDMC as a function of wavelength. Open circles, from O_2-containing experiments at 200 Torr. Full-shaded symbols, from O_2-free experiments at 200 Torr. ▲, 480 Torr, O_2 added. ■, 760 Torr, O_2 added.

ed reactions of methyl and butenyl radicals,

$$CH_3 + CH_3CH{=}\dot{C}CH_3 \rightarrow 2M2B$$

$$\begin{aligned} CH_3 + CH_2{=}CH{=}CHCH_3 &\rightarrow 3M1B \\ &\rightarrow T2P \\ &\rightarrow C2P \\ &\rightarrow CH_4 + 1{,}3\text{-butadiene} \end{aligned} \tag{3}$$

$$2CH_3 \rightarrow C_2H_6$$

$$CH_3 + C2B \rightarrow CH_4 + CH_2{=}CH{=}CHCH_3$$

$$CH_2(^1A_1) \text{ or } CH_2(^3B_1) + CH_2CO \rightarrow C_2H_4 + CO \tag{4}$$

and the attack of CH_2CO by either CH_2 spin state. Since the retention time of 1,3-butadiene occurred during the tail of the C2B peak, it could not be routinely detected.

With 5% O_2 present, products formed by reactions involving $^3B_1$ are suppressed, leaving only those products due to $^1A_1$ reactions. Russell and Rowland[26] have shown that $^3B_1$ reacts with O_2 to produce CO and CO_2.[26]

$$CH_2(^3B_1) + O_2 = H + CO + OH \qquad \Delta H°_{298} = -60 \text{ kcal/mol}$$

$$CH_2(^3B_1) + O_2 = 2H + CO_2 \qquad \Delta H°_{298} = -85 \text{ kcal/mol}$$

Propylene formation can be explained as a result of H atoms, which are simultaneously formed in these reactions, adding to 2-butene. The chemically activated *sec*-butyl radicals which result from the expected predominantly terminal addition may decompose at the pressures of the present experiments provided the H atoms receive a significant amount of the exothermicity of the methylene oxidation as translational energy.[27]

$$H + cis\text{-}CH_3CH{=}CH{-}CH_3 = CH_3CH_2\dot{C}HCH_3^*$$

$$CH_3CH_2\dot{C}HCH_3^* + M = CH_3CH_2\dot{C}HCH_3$$

$$CH_3CH_2\dot{C}HCH_3^* = CH_3 + CH_3CH{=}CH_2$$

Propylene yields increase with decreasing pressure at 213.9 nm, in agreement with the predictions of this mechanism.

The relative product yields obtained at 313 nm, both in the presence of O_2 and in its absence, are in good agreement with previous investigations at this wavelength,[1,28] and corroborate the evidence that both the $^3B_1$ and $^1A_1$ states of methylene are formed and react with 2-butene.

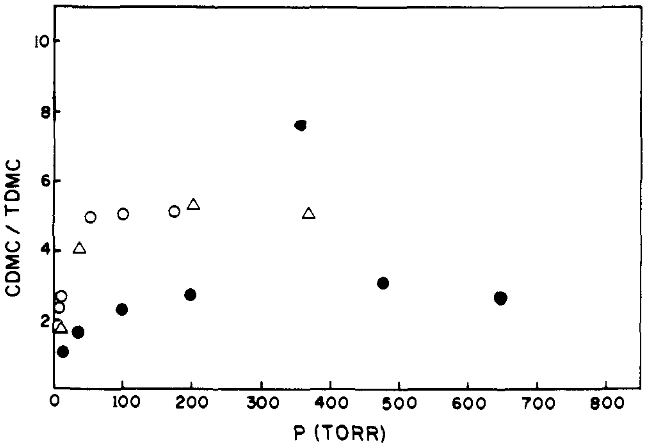


Figure 4. CDMC/TDMC as a function of pressure: (●) 214 nm; (▲) 285 nm; (○) 320 nm, from ref 1. All O_2 free.

Surface Effect. The low reactivity of $CH_2(^3B_1)$ raises the question of whether loss of these species, or of any of the other free-radical intermediates, by heterogeneous processes, can occur to an appreciable extent. Table I shows that a fivefold increase in *S/V* causes some decreases (~20%) in the yields of products arising as a result of $^3B_1$ or free-radical reactions, but products formed either predominantly or exclusively by $CH_2(^1A_1)$ are unaffected. In addition to providing corroborating evidence for the mechanism, the data show that the product yields are a weak function of *S/V*, and that they are being affected in only a minor way by the walls.

200–300 nm. In this wavelength region, the formation of higher excited states of methylene, namely the $^1B_1$ and $^1A_1{}^*$ states, as discussed above, is possible. If higher states are able to react with 2-butene before electronic relaxation some changes in the product distribution might be expected. Although Figures 1 and 2 show only minor changes in percentage yields as a function of wavelength, and reveal no new products, Figures 3 and 4 reveal significant changes in the ratio, CDMC/TDMC. The 200-Torr data from O_2-scavenged runs (Figure 3) clearly indicate an increase in the nonstereospecificity of dimethylcyclopropane with increasing photon energy, and also shows that the nonstereospecificity can be at least partially restored at higher pressures. A plot of TDMC/CDMC vs. reciprocal pressure at 213.9 nm revealed that TDMC/CDMC → 0 as $p \rightarrow \infty$, and constitutes evidence that with O_2 present the only source of nonsterospecificity is geometrical isomerization of chemically activated dimethylcyclopropanes, reaction 5.

$$\text{CDMC}^* \rightleftharpoons \text{TDMC}^* \quad (5)$$

Although at 313 nm 200 Torr of 2-butene is sufficient to collisionally quench all but about 4% of the isomerization, the trend with wavelength indicates that at higher photon energies the energy of activated dimethylcyclopropane is greater, requiring higher pressures for virtually complete stabilization. Since the energy of activated dimethylcyclopropane is composed primarily of the exothermicity of methylene addition to 2-butene plus any nonequilibrium amounts of energy received by methylene during photolysis that has not been removed by unreactive collisions, Figure 3 shows that energy partitioning into those methylenes that react with 2-butene in O_2-scavenged systems is a continuous function of photon energy. Also, the relative yields of the major products, 2M2B, the sum of C2P and T2P, and the sum of CDMC and TDMC are independent of wavelength in O_2-scavenged systems, and are identical with previously reported values[1-4] for work with C2B and T2B at 313 nm and longer wavelengths where they arise through insertion and addition reactions, respectively, of $^1A_1$. Thus, the $^1A_1$ state of CH_2 is present during CH_2CO photolysis at *all* wavelengths studied in the 200–300 nm region, corroborating and extending the conclusions from previous work at 213.9,[6] 280,[3,29] and 265 nm,[2-30] and is the only state capable of reacting with C2B when O_2 is present.

Figure 3 also shows that in the absence of oxygen the methylene addition is appreciably more nonstereospecific over the entire wavelength range than when O_2 is present, and that the nonstereospecificity increases with decreasing wavelength. Figure 4 distinguishes pressure-dependent nonstereospecificity from pressure-independent nonstereospecificity at 285 and 213.9 nm for non-O_2-scavenged runs, where the decrease of CDMC/TDMC at lower pressures again shows the existence of geometrical isomerization of chemically activated dimethylcyclopropane. The high-pressure region, however, shows a pressure-independent source of nonstereospecificity which is wavelength dependent. At 285 nm, CDMC/TDMC $\simeq$ 5 at high pressures (Figure 4), which is about the same as previously reported at 313 nm,[1] but about twice the value at 213.9 nm. At 313 nm the high-pressure nonstereospecificity must be attributed to $^3B_1$, which forms the excited biradical, reaction 2, and this must also be the case at 285 nm, which is just beneath the minimum predicted threshold for $^1B_1$ formation. The approximately equal amounts of nonstereospecificity at these wavelengths is in good accord with reports that approximately equal amounts of $^3B_1$ (~30% of total methylenes) are formed from CH_2CO at these two wavelengths.[1,3,28,29] It is clear from Figure 4 that the high-pressure nonstereospecificity at 213.9 nm is not due to isomerization of a chemically activated intermediate, such as reaction 5.

The increased high-pressure nonstereospecificity at 213.9 nm (CDMC/TDMC ~ 2.5) almost certainly constitutes evidence for a higher electronic state of methylene, rather than a greater proportion of the $^3B_1$ state. Hoffmann's[8] extended Hückel calculations predict that addition of $^1B_1$ to double bonds should be nonstereospecific. In this connection it should be noted that at 213.9 nm the high-pressure yields of 3M1B and T2P, which at longer wavelengths are diagnostic of $^3B_1$ reactions, are about equal to their yields at 313 nm.[31] Furthermore, the decrease in T2P and 3M1B yields with decreasing incident light intensity at constant pressure is evidence that these products are formed by radical combination reactions (reactions 3) at 213.9 nm,[12] as they are at 280[12] and 313 nm.[3] Assuming that at 213.9 nm T2P and 3M1B are formed by the sequence of (2) followed by (3), it follows from the approximate equality of their yields with those at 313 nm that CDMC/TDMC $\simeq$ 5 would be expected if the $^1A_1$ and $^3B_1$ states of CH_2 were the only reactive states of CH_2 present. Vibrationally hot $^3B_1$, from either the primary process or electronic relaxation of $^1B_1$ or vibrationally excited $^1A_1$, cannot explain the results, since enhancement of biradical decomposition resulting in increased T2P and 3M1B yields, contrary to experiment, would be the required outcome. Also, in view of the low reactivity of $^3B_1$,[32-35] much of its excess energy should be collisionally removed before reaction. Furthermore, CDMC/TDMC ~ 2.5 would require roughly equal proportions of $^1A_1$ and $^3B_1$ in a two-state scheme, clearly incompatible with the results as well as data from CH_2CO-n-C_4H_{10} experiments at this wavelength.[6] The results can be explained by assuming that in addition to the $^1A_1$ and $^3B_1$ states of methylene, the $^1B_1$ state is also formed at 213.9 nm and reacts with C2B in the nonstereospecific manner predicted by Hoffmann.[8]

Table II. Nonstereospecificity in CH_2CO–*cis*-2-Butene Photolysis

λ, nm	*P*, Torr	CDMC/TDMC	Ar/(C2B + CH_2CO)
250	200	4.2	
250	761	5.0	
265	199	7.2	
265	199	4.6	
265	400	4.9	
265	636	4.8	
265	638	5.9	14.6
265	608	5.1	6.6
213.9	650	2.5	9.6
213.9	562	2.2	19

Examination of Table II shows that CDMC/TDMC at pressures near 1 atm remains at about 5 at wavelengths down to 250 nm. It was not feasible to carry out experiments closer to the short wavelength limit of the middle uv band because of the combined effect of rapidly decreasing arc luminosity and decreasing extinction coefficient. Thus no evidence could be obtained for $^1B_1$ production in this region. Even if $^1B_1$ is formed in the 250-275 nm region, it is likely that the yields are small and would go undetected in this type of experiment. For this reason the results at 250 nm cannot be construed to be at variance with Rowland and Russell's observations at 249 nm.[5]

Added Ar. Table II contains the CDMC/TDMC ratios obtained with Ar present. The experiments were done in an attempt to test the sensitivity of the $^1B_1$ state to collisional electronic relaxation. At 265 nm a slight increase in stereospecificity was observed, but experiments at 213.9 nm do not show this trend. It is most likely that if the $^1B_1$ state is being deactivated by Ar, the final state is $^3B_1$ rather than $^1A_1$. It was not meaningful to make comparisons of T2P and 3M1B yields in Ar with yields in the absence of Ar to corroborate this, because these are pressure-dependent products, and the relative collisional deactivation efficiency of the hot triplet 1,3-biradical by Ar and C2B is unknown.

While the experiments described above show evidence for the presence of various methylene electronic states during photolysis, they should not be construed to provide evidence on the mechanism of their formation. While $^1B_1$ may be formed directly via dissociation of electronically excited ketene at 213.9 nm the possibility also exists that $^1A_1{}^*$ is the primary fragment and that $^1B_1$ results from relaxation of $^1A_1{}^*$. Similarly, the $^1A_1$ and $^3B_1$ states may result either from the ketene primary process, or from electronic relaxation of higher excited states of methylene. Recent work at 313 nm shows that all the $^1A_1$ and 85% of the $^3B_1$ at 313 nm results directly from dissociation of ketene, and 15% of the $^3B_1$ is formed by collisional deactivation of $^1A_1$.[36]

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Supplementary Material Available: Discussion of intensity effects, and three figures (5 pages). Ordering information is given on any current masthead page.

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The Inversion Barrier in AH_3 Molecules

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Abstract: A one-electron approach is used to rationalize the trends in the inversion barriers of AH_3 molecules as the central atom is varied. The large increase in the barrier as A is changed from a second- to a third-row element and the substituent electronegativity effect upon the height of the barrier can be traced to a single MO interaction which obtains in AH_3 molecules.

In the AH_3 isoelectronic series with eight valence electrons, the barrier to inversion increases dramatically as the central atom is changed from a second-row to a third-row element.[1] For example, the inversion barrier of NH_3 is 5.78 kcal/mol,[2] while the inversion barrier of PH_3 is 37.2 kcal/mol,[3] the difference indicating an effect of extremely large magnitude. The experimentally determined barriers to inversion for several other molecules are shown in Table I. While the preferred pyramidal geometry of AH_3 molecules is adequately rationalized by simple MO theory, one can confidently state that no theoretical explanation of the relationship between the electronic nature of the central atom and the magnitude of the barrier has been advanced. In this paper, we present a one-electron MO approach that is capable of rationalizing the observed trend of the magnitude of the inversion barrier in the AH_3 isoelectronic series.

First, we shall briefly review the factors which seem to be responsible for the nonplanar geometry of AH_3 molecules.[4] The correlation diagram for the planar and pyramidal forms of a typical AH_3 molecule is shown in Figure 1. Since the system has eight valence electrons, the highest occupied MO (HOMO) in either the planar or pyramidal form is a "lone pair" MO. Upon bending, the lowest valence MO(A_1) is changed little in energy and its effect on geometry preference is negligible. On the other hand, the energy of the degenerate pair of MO's (E) increases, and this increase has been ascribed to two effects: first, there is a decrease in the in-phase (bonding) overlap between the central atoms p AO's and the 1s atomic orbitals of the hydrogen, and, secondly, there is an increase in the out-of-phase (antibonding) overlap of any two hydrogens as they are moved closer together. Finally, the energy of the HOMO of the planar AH_3 molecule decreases considerably upon pyramidalization due to its mixing with the lowest unoccupied MO (LUMO) which is a σ^*-type MO. Since the energy lowering of the lone pair MO is greater than twice the energy increase of one of the degenerate MO's, the molecule assumes a nonplanar geometry. *The extent of interaction between the HOMO and LUMO in these molecules determines not only the geometry but also, as we shall see, the inversion barrier.*

Perturbation theory[5] provides a convenient framework for discussing orbital interactions. If there is no degeneracy

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