

# Vibrational Energy Distributions of Reacting $\text{CH}_2(^1\text{A}_1)$ from the 4358, 3660, and 2537 Å Photolyses of $\text{CH}_2\text{N}_2$ and upon Reaction with Cyclobutane. A Chemical Activation Study

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**Abstract:** The decomposition of chemically activated methylcyclobutane formed by the photolyses of ketene and diazomethane in the presence of excess cyclobutane was studied. A model incorporating a distribution of initial energies available to the chemically activated methylcyclobutane and stepwise collisional stabilization was found to satisfactorily describe both the ketene and diazomethane photolysis data. The distribution of chemically activated methylcyclobutane initial energies is the result of a rather narrow thermal Boltzmann distribution for the reactants at 300 K combined with, in the case of diazomethane photolyses, a broad vibrational energy distribution for the reacting  $\text{CH}_2(^1\text{A}_1)$  upon reaction with cyclobutane. An approximate energy level population model for the vibrationally excited  $\text{CH}_2(^1\text{A}_1)$  is developed in order to describe this latter distribution. Chemically activated methylcyclobutane was assumed to be formed with a thermal Boltzmann distribution of initial energies above  $E_{\text{min}}$  in the 3340 Å photolyses of ketene/cyclobutane/oxygen mixtures. The decomposition data for this system were fitted over an extended pressure range by the calculational model with a collisional deactivation step size of  $4 \pm 1$  kcal/mol. Utilizing this 4 kcal/mol step size the calculational model was fitted to the diazomethane photolysis data at 4358, 3660, and 2537 Å by different vibrational energy distributions for the reacting  $\text{CH}_2(^1\text{A}_1)$ . These 4358, 3660, and 2537 Å distributions were represented by "shifted" Gaussians characterized by maxima at 8.4, 10.0, and 1.0 kcal/mol above  $E_{\text{min}}$  and by values of  $4\sigma$  of 5.6, 8.5, and 18.4 kcal/mol, and giving average reacting  $\text{CH}_2(^1\text{A}_1)$  vibrational energies of 8.8, 11.3, and 14.4 kcal/mol, respectively. The differences in these reacting  $\text{CH}_2(^1\text{A}_1)$  vibrational energy distributions for different wavelength photolyses are interpreted as reflecting differences in the initial  $\text{CH}_2(^1\text{A}_1)$  vibrational energy distribution from excess energy partitioning during photodecomposition of diazomethane. No evidence suggesting the participation of  $\text{CH}_2(^1\text{B}_1)$  in the 2537 Å photolysis of diazomethane was found. A brief discussion of the interpretative problems presented to ketene photochemistry by the energetics based on a recent spectroscopic determination of the  $\text{CH}_2(^1\text{A}_1) \leftrightarrow \text{CH}_2(^3\text{B}_1)$  splitting is given.

## Introduction

The decomposition of chemically activated methylcyclobutane has attracted recent attention<sup>2-4</sup> for two reasons: (1) the molecule is the only energized product of the clean reaction of  $\text{CH}_2(^1\text{A}_1)$  with cyclobutane and (2) only a single decomposition path is important.<sup>5</sup> Discrepancies, however, exist among the various reports. Simons et al.<sup>2a</sup> interpreted the results of 4358 and 3660 Å diazomethane photolyses in terms of single-step collisional stabilization of chemically activated methylcyclobutane while Growcock<sup>2b</sup> and McCluskey and Carr<sup>3</sup> found it necessary to interpret their respective results for 3340 Å ketene photolyses with a stepwise collisional deactivation model. Frey and co-workers<sup>4</sup> used a single step collisional stabilization model to interpret their results from the 2062 and 3250 Å photolyses of ketene; however, their 3250 Å results of low pressures seem more consistent with a step-ladder deactivation model. The seemingly anomalous behavior exhibited by these systems is that while the apparently higher energy chemically activated methylcyclobutane systems (diazomethane photolyses and 2062 Å ketene photolysis) appear to follow single-step collisional stabilization, the lower energy systems (3340 and 3250 Å ketene photolyses) require a stepwise collisional deactivation model to adequately describe the observed results. If a stepwise collisional deactivation model applies for a monoenergetic system at low energies, it should apply and become even more apparent for that system at higher energies.

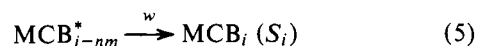
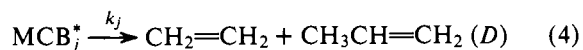
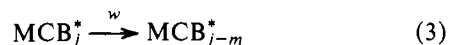
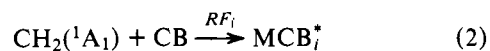
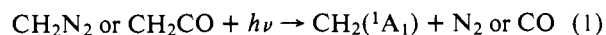
In a previous communication,<sup>6</sup> we reported a possible resolution of this anomaly. Rather than assume an approximately monoenergetic system at the average energy possessed by the chemically activated methylcyclobutane, as had been done previously,<sup>2,4</sup> we included distributions of initial energy states for methylcyclobutane from which decomposition and stepwise stabilization could occur. By combining such distributions of initial energies with the step size for stepwise collisional sta-

bilization determined from the available 3340 Å ketene data, we were able to adequately describe the available 3660 and 4358 Å diazomethane results in terms of the stepladder model.<sup>6</sup>

In this paper, we report the results of a more complete theoretical and experimental study of both the 3340 Å ketene and the 4358 and 3660 Å diazomethane photolysis systems in which more accurate data over extended pressure ranges have been obtained.<sup>7</sup> The results of a study of the 2537 Å photolysis of diazomethane are also presented. These results are of particular interest since absorption of 2537 Å radiation produces a higher excited electronic state of diazomethane which could lead to significantly different partitioning of excess energy into  $\text{CH}_2(^1\text{A}_1)$  and possibly to the formation of a higher excited singlet state,  $\text{CH}_2(^1\text{B}_1)$ .

## Calculational Model

The calculational model used to interpret the experimental results may be derived from the following mechanism for the decomposition and stabilization of chemically activated methylcyclobutane, assuming stepwise collisional stabilization.



$R$  is the total rate of formation of chemically activated meth-

ylcyclobutane, MCB\*, and  $F_i$  is the fraction formed in an arbitrary initial energy level  $i$ , CB is cyclobutane. MCB<sub>*j*</sub>\* is chemically activated methylcyclobutane in an arbitrary energy level  $j$ ,  $w$  is the gas kinetic theory collision frequency,  $k_j$  is the specific rate constant for decomposition of MCB<sub>*j*</sub>\*  $m$  is the average energy removed from MCB\* by a collision with CB, MCB<sub>*i*</sub> is stabilized methylcyclobutane ( $\equiv S_i$ ) formed from MCB<sub>*i*</sub>\*.  $n$  is the largest integer less than  $(E_i - E_0)/m$ , and  $E_0$  is the critical energy for decomposition of MCB.

Any ground state CH<sub>2</sub>(<sup>3</sup>B<sub>1</sub>) produced in the initial photolyses are scavenged by added oxygen.<sup>8</sup> Step 2 occurs for each initial energy level,  $i$ , while steps 3 and 4 occur for every level of energy  $j$ . Step 5 is the special case of step 3 which yields a stabilized methylcyclobutane, i.e., a methylcyclobutane with less internal energy than the critical energy for decomposition.

From steps 3 and 4, it is noted that the fraction of MCB<sub>*j*</sub>\* converted to MCB<sub>*j-m*</sub> is  $w/(w + k_j)$ . Continuing this reasoning, the fraction of stabilized product, from energy level  $i$ , MCB<sub>*i*</sub>, is

$$\frac{S_i}{RF_i} = \prod_{j=0}^n \frac{w}{(w + k_{i-mj})} \quad [1]$$

while summing over all initial energy levels gives

$$\frac{S}{R} = \sum_{i=E_{\min}}^{\infty} F_i \prod_{j=0}^n \frac{w}{(w + k_{i-mj})} \quad [2]$$

where  $E_{\min}$  is the lowest possible initial energy level and is given by the 0 K exothermicity of reaction (1) plus any activation energy for the reaction.

Equations [1] and [2] are equivalent to those presented previously, resulting from the master equation but neglecting up transitions.<sup>9,10</sup>  $R$ , the total number of methylcyclobutane molecules formed in the chemical activation process, is equal to the sum of those molecules which are collisionally stabilized,  $S$ , and those which decompose,  $D$ . Equations [2] and [3] may thus be used to calculate theoretical values of the apparent average rate constant,  $k_a$ , for any choice of an initial energy distribution,  $F_i$ .

$$k_a = w(D/S) = w \frac{1 - S/R}{S/R} \quad [3]$$

The validity of a simple, single step size, stepladder deactivation model is supported by the following considerations. The polyatomic nature of the cyclobutane bath gas and the low temperature, ca. 300 K, minimize the importance of considering activating collision probabilities.<sup>11</sup> Lin and Rabinovitch<sup>12</sup> have presented evidence suggesting that polyatomic bath gases are characterized by a Gaussian distribution of step sizes for collisional energy transfer which are relatively independent of moderate variations in the energy possessed by the activated molecules. These Gaussian distributions of step sizes have been shown to be well approximated by single step sizes at the averages of the distributions.<sup>10,13</sup> Since the step size is only weakly dependent on the excess internal energy of the activated molecule,<sup>12</sup> a step size determined for a system involving one combination of photolysis wavelength and CH<sub>2</sub>(<sup>1</sup>A<sub>1</sub>) precursor should apply to systems involving other combinations of photolysis wavelengths and CH<sub>2</sub>(<sup>1</sup>A<sub>1</sub>) precursors.

The distribution of initial energies,  $F_i$ , of the chemically activated methylcyclobutane is a combination of two reactant distributions: (1) a thermal distribution due to Boltzmann populations of low-lying energy levels of the reactants and (2) a distribution due to the reaction of a thermal cyclobutane with vibrationally excited CH<sub>2</sub>(<sup>1</sup>A<sub>1</sub>) distributed among its vibrational levels. The thermal distribution, denoted  $f_j$ , may be accurately calculated from theory,<sup>14,19</sup> while the CH<sub>2</sub>(<sup>1</sup>A<sub>1</sub>) vibrational energy distribution,  $g_v$ , requires a descriptive

model. That any excess energy of CH<sub>2</sub>(<sup>1</sup>A<sub>1</sub>) at the time of reaction is in its vibrational modes is suggested by the fact that the proportion of unreactive collisions of CH<sub>2</sub>(<sup>1</sup>A<sub>1</sub>) is probably sufficient for complete translational and rotational relaxation but not sufficient for complete vibrational relaxation.<sup>15</sup>

The frequencies of the C-H stretching modes of CH<sub>2</sub>(<sup>1</sup>A<sub>1</sub>) were estimated to be 2800 cm<sup>-1</sup> while the H-C-H bending mode has been reported<sup>16</sup> to be 1353 cm<sup>-1</sup>. These three frequencies, although only approximately commensurate, were assumed to give a set of vibrational energy levels with 4 kcal/mol spacings. The population in each level,  $v$ , is denoted as  $g_v$ , and the energy of level  $v$  is  $4v$  kcal/mol. The largest possible vibrational energy available to the CH<sub>2</sub>(<sup>1</sup>A<sub>1</sub>) is  $4t$ , where  $t$  is the largest integer less than  $E_{xs}/4$ , where  $E_{xs} = h\nu - \Delta H_{rxn}$  is the excess energy of the CH<sub>2</sub>(<sup>1</sup>A<sub>1</sub>) producing reaction (1). The two distributions  $f_j$  and  $g_v$ , contributing to  $F_i$ , combine according to

$$F_i = \sum_{v=0}^t g_v f_{i-4v} \quad [4]$$

where  $f_j$  is represented as populations of energy levels with 1 kcal/mol spacings starting at 0.5 kcal/mol above  $E_{\min}$ . Changing the magnitude of this spacing would not significantly alter the calculated results.

## Experimental Section

**Materials.** Cyclobutane (CB) was prepared in vacuo by the 2537 Å photolysis of cyclopentanone (PCR, Inc.). The fraction distilled from 195 K to 77 K was purified via multiple pass GLC. The final fraction collected was verified by mass spectrometric comparison to authentic cyclobutane.

Diazomethane (DM) was prepared in vacuo by the action of sodium hydroxide on *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Matheson Coleman and Bell) using 1,4-butanediol as a solvent. The fraction condensed at 77 K was transferred to a dibutyl phthalate solution and stored at 77 K for subsequent use.

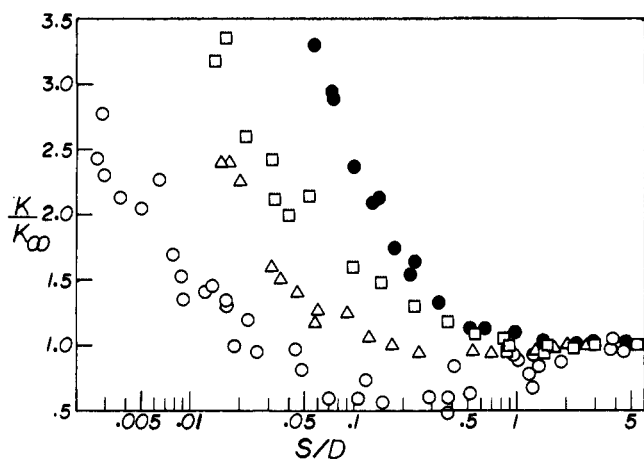
Ketene (K) was prepared by pyrolysis of acetic anhydride in vacuo. The fraction trapped at 77 K was warmed to 113 K to remove ethene. The central portion distilled from 178 K to 77 K was identified as ketene and stored at 77 K for subsequent use.

Oxygen was obtained by passing commercial material through a 195 K trap prior to storage for future use.

**Experiments.** Mixtures of CB-DM-O<sub>2</sub> in the ratio of 10:1:1 and CB-K-O<sub>2</sub> at 10:1:2 were prepared on a standard high-vacuum system featuring greaseless stopcocks in the reactant measuring section. Various total amounts of reactants and various reactor volumes were used to obtain reactor pressures ranging from 0.5 to 150 cmHg. Reaction mixtures containing ketene were photolyzed at 3340 Å, and those containing diazomethane at 4358, 3660, or 2537 Å. The 4358, 3660, and 3340 Å radiations were isolated by a 0.25-m Jarrel Ash monochromator (Model 82-410) with 2-mm slits (66 Å band-pass) following a high-pressure mercury source (Osram HBO 500W). Reactors were of Pyrex, equipped with greaseless stopcocks. Large reactors were of conical construction with a flat Pyrex window at the small end. This permitted optimal use of the diverging beam exiting the monochromator. Photolysis times were varied inversely to the reactor pressure and ranged from 6 to 24 h.

The 2537 Å photolyses were carried out in cylindrical Vycor reactors inserted for about 30 min in a Southern New England Ultraviolet Rayonet source. The reactants were prepared and loaded in a separate mercury free system for this 2537 Å work. *cis*-2-Butene treated to the 2537 Å photolysis procedure resulted in negligible *trans*-2-butene formation; consequently, mercury photosensitization was considered negligible.

**Analysis.** Following photolysis, the portion of the reaction mixture condensable at 77 K was subjected to two passes through a 23-ft column of 30% dibutyl phthalate-dinonyl phthalate (85:15) on 60/100 Chromosorb, at ca. 25 °C, with a flow of 52 mL/min. The first pass permitted removal of approximately 95% of the unreacted cyclobutane. The product of peak height and retention time was determined for both methylcyclobutane and propene from the second pass. The ratio of these two numbers was related to a mole ratio by comparison



**Figure 1.** Comparison of experimental results for chemically activated methylcyclobutane systems: ●, 3340 Å ketene photolysis; □, 4358 Å diazomethane photolysis; ▽, 3660 Å diazomethane photolysis; ○, 2537 Å diazomethane photolyses. The experimental values of  $k_\infty$  using gas viscosity collision cross sections are 3340 Å ketene,  $5.3 \times 10^8 \text{ s}^{-1}$ ; 4358 Å diazomethane,  $2.38 \times 10^9 \text{ s}^{-1}$ ; 3660 Å diazomethane,  $3.69 \times 10^9 \text{ s}^{-1}$ ; 2537 Å diazomethane,  $6.50 \times 10^9 \text{ s}^{-1}$ . The collision diameters (ref 2a) are 5.45, 5.45, 6.49, 6.8, and 3.6 Å for ketene, diazomethane, cyclobutane, methylcyclobutane, and oxygen, respectively. The collisional deactivation efficiency of oxygen was taken as 0.25, for all other gases, 1.0.

to the ratio determined in the same fashion for authentic mixtures of methylcyclobutane and propene of known concentration.

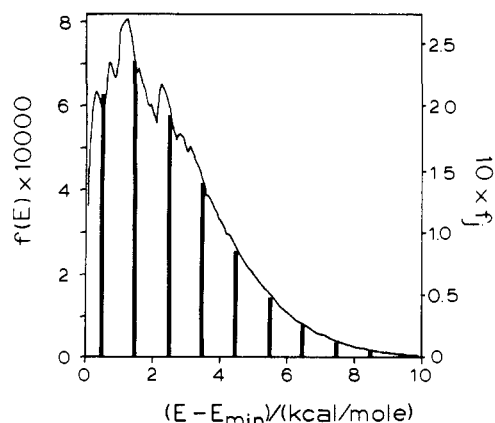
Dark reactions duplicating various experiments gave no observed products of interest.

### Experimental Results

The experimental results are plotted in Figure 1 in terms of the reduced rate constant,  $k_a/k_\infty$ . The value of  $k_\infty$  was taken as the mean of those values of the apparent average rate constant characterized by values of  $S/D$  between 2 and 5. The onset of a sharp turnout in the 3340 Å ketene data at a relatively high  $S/D$  value is indicative of a narrow distribution of MCB\* initial energies, and/or a small collisional energy removal step size while the onset of a more gradual turnout at lower  $S/D$  values for the diazomethane data indicates broader distributions of MCB\* initial energies for the same step size. The small minimum in the 3660 Å data and the pronounced minimum in the 2537 Å data are indicative of broad distributions of MCB\* initial energies for the same step size. The small minimum in the 3660 Å data and the pronounced minimum in the 2537 Å data are indicative of broad distributions in the MCB\* initial energies.

### Calculations

**Thermal Distribution.** The 3340 Å ketene photolysis system provides a possible means of establishing the characteristic energy removing step size for the methylcyclobutane-cyclobutane system since any  $\text{CH}_2(^1\text{A}_1)$  formed from ketene photolyses at 3340 Å are most likely not vibrationally excited, i.e., the excess energy is probably less than the 4 kcal/mol necessary to vibrationally excite  $\text{CH}_2(^1\text{A}_1)$ .<sup>20</sup> As a result, the distribution of initial energies of the chemically activated methylcyclobutane,  $F_i$ , is identical with the thermal distribution function,  $f_j$ . This thermal distribution was determined by constructing an RRKM model for the reverse of the chemical activation step,  $\text{MCB} \rightarrow \text{CH}_2(^1\text{A}_1) + \text{CB}$ . Starting with the methylcyclobutane molecule (see Table II of ref 1), the required activated complex was formed by taking the methyl-ring C-C stretch as the reaction coordinate, retaining the free rotor, and lowering the frequencies of one methyl C-H stretch and the methyl-ring bending modes by a factor of approximately 2. The resulting distribution is depicted in Figure 2. This distribution



**Figure 2.** Thermal distribution function of chemically activated methylcyclobutane at 300 K. The curve represents the distribution,  $f(E)$ , calculated via RRKM theory, the bars represent the integrated population numbers,  $f_j$ , at 1 kcal/mol increments used in the calculational model.

**Table I.** Thermochemistry of the Methylcyclobutane System

Compd	$\Delta H_{f0}^\circ$ <sup>a</sup>	Compd	$\Delta H_{f0}^\circ$ <sup>a</sup>
$\text{CH}_2\text{CO}$ <sup>b</sup>	-10.7	$\text{CH}_2(^1\text{A}_1)$ <sup>d</sup>	$99 \pm 2$
$\text{CH}_2\text{N}_2$ <sup>c</sup>	~60	Methylcyclobutane <sup>f</sup>	6.7
CO	-27.2	Cyclobutane <sup>e</sup>	12.3

<sup>a</sup> Units of kcal/mol. <sup>b</sup> R. L. Nuttall, A. H. Laufer, and M. V. Kilday, *J. Chem. Thermodyn.*, **3**, 167 (1971). <sup>c</sup> A. H. Laufer and H. Okabe, *J. Am. Chem. Soc.*, **93**, 4137 (1971). <sup>d</sup> J. W. Simons and R. Curry, *Chem. Phys. Lett.*, **38**, 171 (1976). <sup>e</sup> S. Kaarsemaker and J. Coops, *Recl. Trav. Chim. Pays-Bas*, **71**, 261 (1952). <sup>f</sup> J. W. Simons, W. L. Hase, R. J. Phillips, E. J. Porter, and F. B. Growcock, *Int. J. Chem. Kinet.*, **7**, 879 (1975).

was represented as populations of energy levels with 1 kcal/mol increments starting at 0.5 kcal/mol above  $E_{\text{min}}$  for use in the calculations.

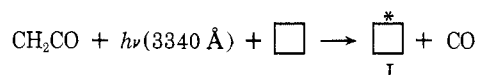
**Decomposition Model.** The decomposition of methylcyclobutane recently has been described by four possible activated complex models,<sup>2,4</sup> based on three different sets of high-pressure thermal Arrhenius parameters.<sup>5,17,18</sup> Comparison of calculated and experimental unimolecular fall-off curves and comparison to high-pressure Arrhenius parameters for the decomposition of other cyclobutanes<sup>19</sup> suggests that model II of Simons et al.<sup>2</sup> is more satisfactory than models I or III, or the model presented by Frey.<sup>4</sup> The reasons for our preference of model II are somewhat different and perhaps stronger than recently suggested by McCluskey and Carr.<sup>3</sup> All calculations here were done with model II, which gives  $A = 4.4 \times 10^{15} \text{ s}^{-1}$  and  $E_a = 62.0 \text{ kcal/mol}$  at 703.2 K.

**Energetics.**  $E_0$ , the critical energy for decomposition of methylcyclobutane, was deduced via activated complex theory from the Arrhenius activation energy given by Pataracchia and Walters<sup>18</sup> utilizing model II. A value of 59.33 kcal/mol was thus obtained.<sup>2</sup>

$E_{\text{min}} = 105.5 \text{ kcal/mol}$  was calculated from the 0 K exothermicity of reaction (1), utilizing the heats of formation in Table I, and adding ~0.9 kcal/mol activation energy for reaction (1). This activation energy is quite likely to be in the range of 0–2 kcal/mol based on the well-known high reactivities of  $\text{CH}_2(^1\text{A}_1)$  without any apparent temperature dependence.<sup>15b</sup> A value of 0.9 kcal/mol was calculationaly convenient.

The heats of formation in Table I are generally accepted values with the exception of  $\Delta H_f^\circ[\text{CH}_2(^1\text{A}_1)]$ . The value of  $\Delta H_f^\circ[\text{CH}_2(^1\text{A}_1)] = 99 \pm 2 \text{ kcal/mol}$  is based on a measured apparent threshold of 84 kcal/mol for the photochemical production of  $\text{CH}_2(^1\text{A}_1)$  from  $\text{CH}_2\text{CO}$ <sup>20</sup> and is consistent with

several other estimates by other indirect photochemical methods.<sup>2,21,22</sup> The same type of photochemical threshold experiment as mentioned above yielded  $\sim 91$  kcal/mol for  $\Delta H_f[\text{CH}_2(^3\text{B}_1)]$ ,<sup>20</sup> in approximate agreement with a value of  $93 \pm 2$  kcal/mol, based on several photoionization and electron impact studies.<sup>23</sup> These photochemical estimates correspond to a  $\text{CH}_2(^1\text{A}_1) \leftrightarrow \text{CH}_2(^3\text{B}_1)$  separation of  $\sim 8$  kcal/mol. Recently a photoelectron detachment study of  $\text{CH}_2^-$  has yielded, in a more direct way, a value of 19.5 kcal/mol for the  $\text{CH}_2(^1\text{A}_1) \leftrightarrow \text{CH}_2(^3\text{B}_1)$  energy splitting<sup>24</sup> which combined with  $93 \pm 2$  kcal/mol for  $\Delta H_f[\text{CH}_2(^3\text{B}_1)]$  yields  $112.5 \pm 2$  kcal/mol for  $\Delta H_f[\text{CH}_2(^1\text{A}_1)]$ . This value combined with  $\Delta H_f(\text{CH}_2\text{CO})$  and  $\Delta H_f(\text{CO})$  predicts a threshold of at least  $97.5 \pm 2$  kcal/mol ( $2930 \pm 60$  Å) for the photochemical production of  $\text{CH}_2(^1\text{A}_1)$  from  $\text{CH}_2\text{CO}$ , which contradicts a substantial quantity of indirect chemical evidence for  $\text{CH}_2(^1\text{A}_1)$  production from the 3340 and 3130 Å photolyses of  $\text{CH}_2\text{CO}$ .<sup>25</sup> For example, the photolyses of ketene at 3340 and 3130 Å in the presence of a radical scavenger such as oxygen and various reactants containing C-H, C=C, and Si-H bonds give the same  $\text{CH}_2$  insertion and addition products, in the same proportions, at high pressures as do diazomethane photolyses under similar conditions.<sup>25</sup> These results in all cases are independent of photolysis wavelength and temperature. The photoproduction and subsequent fast reaction of  $\text{CH}_2(^1\text{A}_1)$  is clearly an attractive explanation of these photochemical results but, in the case of ketene, this interpretation is not consistent with  $\Delta H_f[\text{CH}_2(^1\text{A}_1)]$  as large as 112.5 kcal/mol. A recent suggestion<sup>26</sup> that reactions of an electronically excited molecule,  $\text{CH}_2\text{CO}^*$ , may be responsible for that part of ketene photochemistry at 3340 Å that has previously been attributed to  $\text{CH}_2(^1\text{A}_1)$  would seem to require an unusual coincidence to explain the above similarities in oxygen scavenged ketene and diazomethane photochemical systems. In any case, the 0 K thermochemistry of the reaction



gives for I an  $E_{\min} < 107.6$  kcal/mol. The fraction of the reaction exothermicity partitioned into I is unknown but could be sufficiently large to yield  $E_{\min} = 105.5$  kcal/mol. The internal energy distribution,  $F_i$ , in I from the above reaction would be a combination of the thermal distribution,  $f_j$ , with an unknown product energy partitioning distribution. It is conceivable that  $F_i \sim f_j$ . Thus it is possible that  $E_{\min}$  and  $F_i$  for our 3340 Å ketene photolysis system would not be significantly altered by this  $\text{CH}_2\text{CO}^*$  interpretation. The  $E_{\min}$  for the diazomethane systems, however, would have to be increased by 13.5 kcal/mol to 119.0 kcal/mol assuming that  $\text{CH}_2(^1\text{A}_1)$  is the reactive species in diazomethane photolyses.

This uncertainty in the value of  $\Delta H_f[\text{CH}_2(^1\text{A}_1)]$  and in the resultant interpretation of ketene photochemistry will probably be resolved in the near future but any resolution based on existing evidence would be rather conjectural in nature. The values of the three quantities,  $\Delta H_f[\text{CH}_2\text{CO}]$ ,  $\Delta H_f[\text{CH}_2(^3\text{B}_1)]$ , and  $\Delta E[\text{CH}_2(^3\text{B}_1) \leftrightarrow \text{CH}_2(^1\text{A}_1)]$ , are involved in estimates of  $\Delta H_f[\text{CH}_2(^1\text{A}_1)]$  and the probabilities of significant error in one or more of the current values of these quantities are not vanishingly small. So for the present we will utilize the energetics and interpretations based on  $\Delta H_f[\text{CH}_2(^1\text{A}_1)] \approx 99$  kcal/mol with the obvious reservations required by the above discussion.

**Step Size and Distributions.** Absolute comparison of model II calculations with the high-pressure ( $k_\infty$  values) chemical activation experiments was made after deducing the characteristic collisional energy removal step size for the cyclobu-

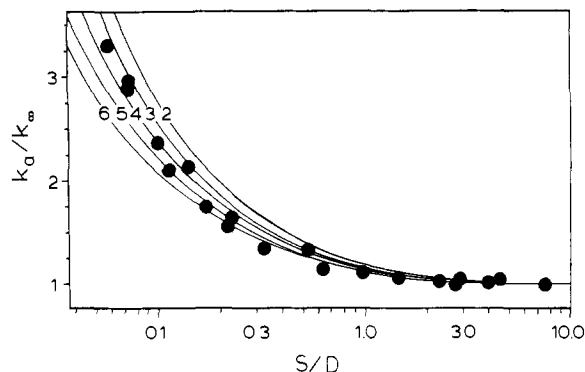


Figure 3. Comparison of the 3340 Å ketene photolysis data with stepladder calculations for various step sizes. The numbers superimposed on the calculated curves are the energies in kcal/mol removed per collision. The curves are calculated according to eq [2] and [3] for a thermal distribution of initial energy levels, i.e.,  $g_0 = 1.0$ ,  $g_{i \neq 0} = 0.0$ ,  $F_i = f_j$ .

tane-methylcyclobutane system. It is important to note that the calculated  $k_a/k_\infty$  vs.  $S/D$  results are virtually identical for all four of the above-mentioned activated complex models.

Since the distribution of  $\text{MCB}^*$  initial energies in the 3340 Å ketene photolysis system was taken to be identical with the thermal distribution,  $f_j$ , the remaining unknown quantity in eq [2] and [3] is the collisional deactivation step size,  $m$ . The 3340 Å ketene data are compared to calculated curves in Figure 3, the curves differing only in the value of the step size used in the calculation. To a precision of about 1 kcal/mol, a step size of 4 kcal/mol adequately fits the entire range of experimental data. It is noted that the 4 kcal/mol step size curve does not exactly match the data over the entire  $S/D$  range. A slightly broadened distribution of initial energies due to the monochromator band-pass might lead to some improvement in this comparison. The deduction of a step size from Figure 3 is facilitated by the pronounced divergence of the calculated curves for various step sizes in the region of  $S/D$  less than 0.3, emphasizing the necessity for obtaining reliable data at small values of  $S/D$ . This value is in moderate agreement with  $6 \pm 2$  kcal/mol used in our preliminary report<sup>6</sup> which was based on the most recent data then available<sup>2b,3</sup> and may be contrasted to Growcock's<sup>2b</sup> estimate of 10 kcal/mol. This early investigation<sup>2b</sup> failed to attain the required low  $S/D$  data; thus the overestimate of the step size was a result of measurements in a region in which the calculated turnover curves did not diverge sufficiently.

A comparison of the RRKM calculated  $k_\infty$  with experiment can now be made. The experimental value of  $k_\infty = 5.3 \times 10^8$  s<sup>-1</sup> was determined for the 3340 Å ketene data using gas viscosity collision cross sections. This  $k_\infty$  value is only 10% higher than the value of  $4.8 \times 10^8$  s<sup>-1</sup> calculated using model II and a 4 kcal/mol step size. This agreement of the theoretical model with the experimental measurements based on a priori values of the gas viscosity collision cross sections is gratifying.

An important result here is that for a given step size, the shape of the calculated turnover curve, relative to the experimental data plotted as  $k_a/k_\infty$  vs  $S/D$ , is only weakly dependent on the value of the minimum energy; only the absolute value of the calculated rate constants vary significantly with  $E_{\min}$  variations within a few kcal/mol range. This permits the determination of a characteristic step size for a chemical activation system with an uncertain thermochemistry. A comparison of calculated to experimental  $k_a/k_\infty$  values over the entire range of  $S/D$  is preferable to a two-point comparison.<sup>3</sup>

With the addition of the collisional energy removing step size to the knowledge of the specific rate constants and the thermal distribution, the results of our 4358, 3660, and 2537

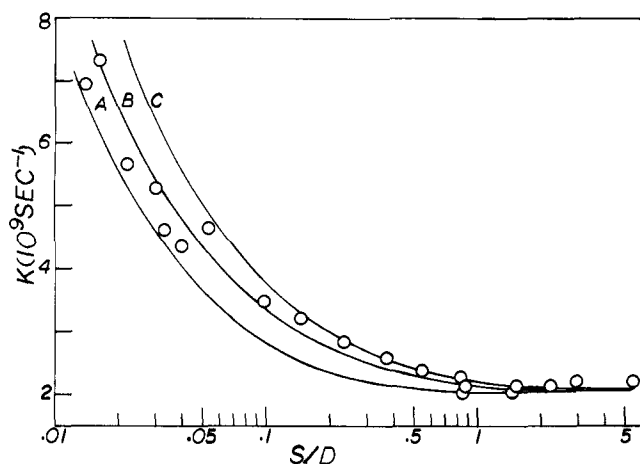


Figure 4. Comparison of 4358 Å diazomethane photolysis data with calculated turnup curves. The Gaussian parameters  $4\eta$  and  $4\sigma$  in kcal/mol, which characterize the  $\text{CH}_2(^1\text{A}_1)$  vibrational energy distributions used to calculate these curves are: curve A, 7.8, 7.0; curve B, 8.4, 5.6; curve C, 9.0, 4.2.

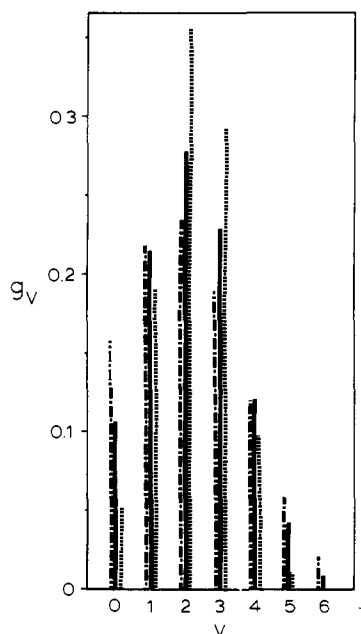


Figure 5. Population fractions,  $g_v$ , of  $\text{CH}_2(^1\text{A}_1)$  vibrational levels used to calculate the turnup curves in Figure 4 for the 4358 Å diazomethane photolysis system. Curve A, ---; curve B, —; curve C, |||||.

Å diazomethane experiments may be analyzed with the intent of determining the vibrational energy distributions of the  $\text{CH}_2(^1\text{A}_1)$  at the time of reaction for each wavelength. The italicized distinction is important since the vibrational energy distribution of the  $\text{CH}_2(^1\text{A}_1)$  at the time of formation may be partially relaxed by collisions at the time of reaction. Our results permit the determination of this partially relaxed distribution by a systematic testing of various distributions in eq [2] and [3]. A Gaussian type function

$$g_{v \geq 0} = \frac{\exp[-(v - \eta)^2 / 2\sigma^2]}{\sum \exp[-(v - \eta)^2 / 2\sigma^2]}, \quad g_{v < 0} = 0 \quad [5]$$

was used to generate various distributions, where  $\eta$  and  $\sigma$  are adjustable and  $v$  represents a vibrational level of the methylene model. The Gaussian parameter,  $\sigma$ , may take any value while  $v$  and  $\eta$  may range from 0 to  $t$ , where  $t$  is the largest integer less than  $E_{\text{xs}}/4$  was described for eq [4]. The criteria for suitability of distribution obtained in this fashion were (1) matching the experimental value of  $k_{\infty}$  as determined by a 10% lowering of

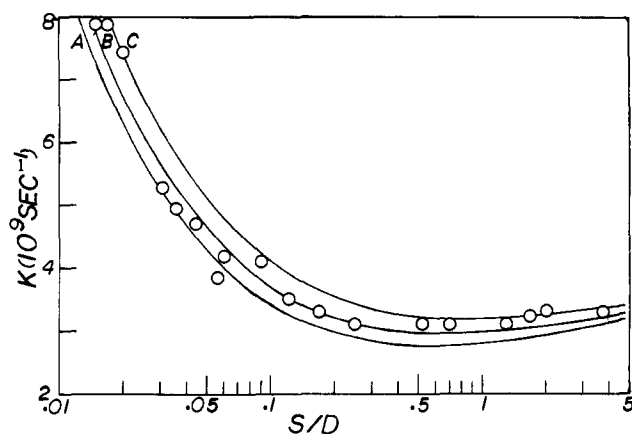


Figure 6. Comparison of 3660 Å diazomethane photolysis data with calculated turnup curves. The Gaussian parameters  $4\eta$  and  $4\sigma$  in kcal/mol which characterize the  $\text{CH}_2(^1\text{A}_1)$  vibrational energy distributions used to calculate these curves are curve A, 9.0, 9.2; curve B, 10.0, 8.5; curve C, 11.0, 7.8.

the gas viscosity based collision cross sections and (2) the fit to the experimental data over the entire  $S/D$  range.

The selection of the values of  $t$  for the diazomethane systems is based on the thermochemistry of these systems. The production of  $\text{CH}_2(^1\text{A}_1)$  from diazomethane is endothermic by no less than 39 kcal/mol, based on the heat of formation of  $\text{CH}_2(^1\text{A}_1)$  of 99 kcal/mol reported by Simons and Curry<sup>20</sup> and the upper limit of 60 kcal/mol for the heat of formation of diazomethane reported by Laufer and Okabe.<sup>27</sup> The difference between this endothermicity and the photon energies of 4358, 3660, and 2537 Å give the maximum values of the excess energy for these diazomethane photolysis systems as 26.6, 39.1, and 73.6 kcal/mol, respectively, resulting in  $t$  values of 6, 9, and 18. The following discussion shows that the highest accessible vibrational levels (large  $v$  values) of our methylene vibrational model, as defined by these excess energies but which would be eliminated by smaller excess energies, are characterized by very small populations. These small populations eliminate the effect on the distributions of a small uncertainty in the maximum excess energy.

The effects of various choices of  $\sigma$  and  $\eta$  for a 4 kcal/mol collisional deactivation step size are illustrated in Figure 4 for the 4358 Å diazomethane system. The methylene vibrational energy distributions which give these calculated curves are depicted in Figure 5. That the shape of the turnup in the experimental data at small  $S/D$  may be explained for a given step size by the breadth of the distribution is seen by an examination of Figures 4 and 5. Turning from this comparison of three rather different distributions, the 3660 Å data are compared to three calculated curves for three rather similar distributions in Figure 6. It is noteworthy that while the distributions responsible for these curves resemble each other, as seen in Figure 7, one of these distributions gives a curve that more adequately fits the entire range of experimental data than the other curves. This observation leads us to conclude that these methylene vibrational energy distributions are well determined by the data, i.e., a rather narrow range of  $\sigma$  and  $\eta$  values gives optimal fit to the experimental results for each photolysis wavelength. It should be noted that the criteria for satisfactory fitting of the data are both the shape of the  $k_a$  vs.  $S/D$  curves as well as the absolute  $k_a$  values.

The average vibrational energy of  $\text{CH}_2(^1\text{A}_1)$  for a particular vibrational energy distributions is given by  $\bar{E}_v = 4 \times \sum v g_v$  kcal/mol. Using this quantity as an invariant, various non-Gaussian type distributions were tested against the 3660 Å data. It was found that only those functions giving sets of  $g_v$  values similar to the "best" Gaussian-like function would

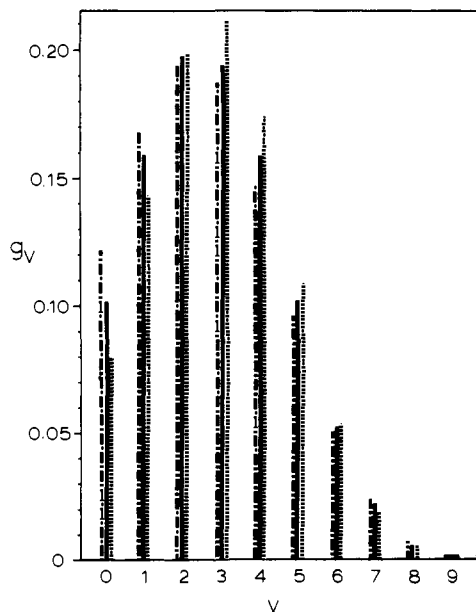


Figure 7. Population fractions,  $g_v$ , of  $\text{CH}_2(^1\text{A}_1)$  vibrational levels used to calculate the turnup curves in Figure 6 for the 3660 Å diazomethane photolysis system. Curve A, ---; curve B, —; curve C, |||11111.

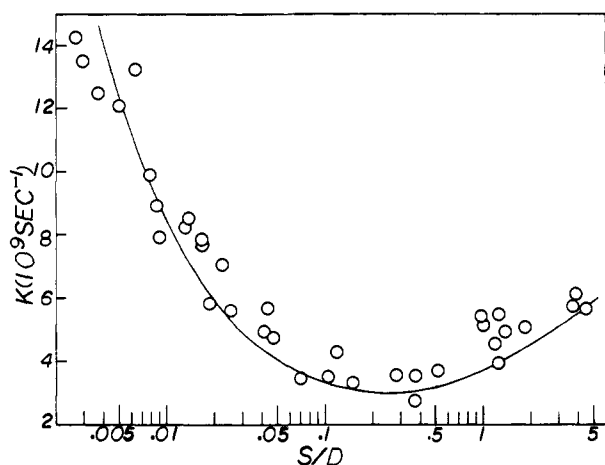


Figure 8. Comparison of 2537 Å diazomethane photolysis data with a calculated curve. The Gaussian parameters  $4\eta$  and  $4\sigma$  in kcal/mol which characterize the  $\text{CH}_2(^1\text{A}_1)$  vibrational energy distribution used to calculate this curve are 1.0 and 18.4, respectively.

satisfactorily fit the entire range of data. Distributions that yield average  $\text{CH}_2(^1\text{A}_1)$  vibrational energies significantly different from that of the "best" Gaussian-like function failed to give absolute  $k_a$  values in agreement with experiment.

The 2537 Å diazomethane photolysis data are presented in Figure 8 along with a calculated curve which adequately fits the data. The prediction of the pronounced minimum at  $S/D \sim 0.2$  is noteworthy. The  $\text{CH}_2(^1\text{A}_1)$  vibrational energy distribution that leads to this calculated curve is depicted in Figure 9. The distribution in Figure 9 is clearly quite different in shape from those fitting the 3660 (Figure 7) and 4358 Å (Figure 5) data. A direct comparison of the "best" fit  $\text{CH}_2(^1\text{A}_1)$  vibrational energy distributions for the 4358, 3660, and 2537 Å diazomethane photolysis data is shown in Figure 10. These distributions peak at  $v = \eta = 2.1, 2.5,$  and  $0.25$  with averages of  $\bar{E}_v = 8.8, 11.3,$  and  $14.4$  kcal/mol for the 4358, 3660, and 2537 Å results, respectively. All three distributions are characterized as "shifted" Gaussians but the 2537 Å distribution is shifted far enough so as to appear to have an almost exponential shape.

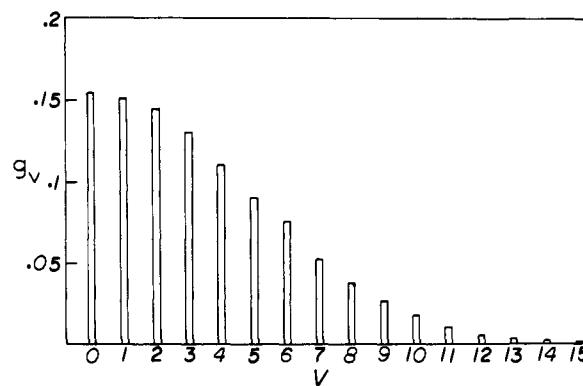


Figure 9. Population fractions,  $g_v$ , of  $\text{CH}_2(^1\text{A}_1)$  vibrational levels used to calculate the turnup curve in Figure 8 for the 2537 Å diazomethane photolysis system.

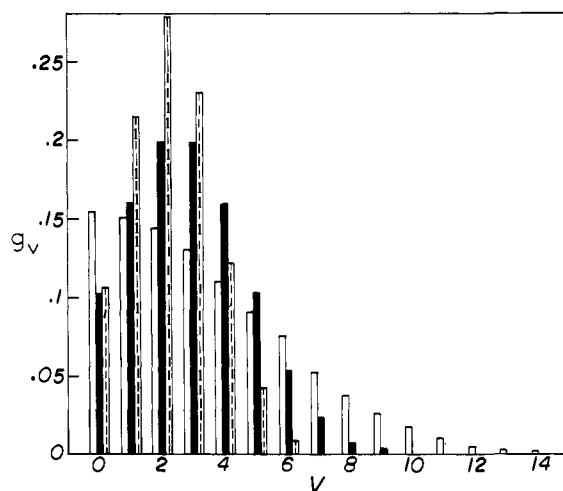


Figure 10. Comparison of the satisfactory methylene vibrational energy distributions for the 4358, 3660, and 2537 Å diazomethane photolysis systems, parameters in kcal/mol. 4358 Å, ---,  $4\eta = 8.4, \sigma = 5.6, \bar{E}_v = 8.8$ ; 3660 Å, —,  $4\eta = 10.4, \sigma = 8.5, \bar{E}_v = 11.3$ ; 2537 Å, □,  $4\eta = 1.0, \sigma = 18.4, \bar{E}_v = 14.4$ .

## Discussion

The photodecomposition reaction (1) for diazomethane results in an initial distribution of vibrational energies,  $n_v$ , of  $\text{CH}_2(^1\text{A}_1)$  which is quite probably partially relaxed via unreactive collisions to  $g_v$ , the distribution of vibrational energies for the reacting  $\text{CH}_2(^1\text{A}_1)$ . The observed increase in  $\bar{E}_v$  and  $4\sigma$  (reflecting the width of the  $g_v$  distribution) with increasing photon energy reflects the intuitively expected qualitative behavior of  $n_v$ . An approximate RRKM statistical calculation of the  $n_v$  for the 4358 and 3660 Å systems, following the method of Lin and Rabinovitch,<sup>28</sup> yielded  $n(v=0)$  values much higher than the experimental  $g(v=0)$  values. A statistical energy partitioning model would not be expected to apply, in any case, since the low-lying diazomethane excited singlet states are probably repulsive with respect to  $\text{CH}_2 + \text{N}_2$ .<sup>29</sup> The 2537 Å absorption by diazomethane produces a different excited electronic state than do the 3660 and 4358 Å absorptions since two distinctly different absorption bands are involved.<sup>29,30</sup> A 2537 Å photon contains sufficient energy to produce  $\text{CH}_2(^1\text{B}_1)$ ,<sup>31</sup> but if this occurs to a great extent, without subsequent relaxation to  $\text{CH}_2(^1\text{A}_1)$ , a quite different  $\text{CH}_2$  vibrational energy distribution than that observed might be expected. A narrow distribution peaked at higher energies would seem more likely.  $\text{CH}_2(^1\text{B}_1)$  formation with relaxation to  $\text{CH}_2(^1\text{A}_1)$  prior to reaction or a small percentage of  $\text{CH}_2(^1\text{B}_1)$  reaction would be consistent with the 2537 Å results. In any

case, the quite different  $g_v$  values at 2537 Å compared to the 4358 and 3660 Å  $g_v$  values can be interpreted to be reflections of quite different  $n_v$  values and hence the fractional partitioning of excess energy into the methylene vibrational modes is significantly different for the excited electronic state of diazomethane produced by 2537 Å photon absorption than for the state produced by 4358 and 3660 Å photon absorption. The possibility of significantly greater collisional relaxation of CH<sub>2</sub> produced in the 2537 Å photolyses compared to the 3660 and 4358 Å photolyses cannot be eliminated and would provide an alternate interpretation. Hopefully, systematic studies with added inert gases, which are known to remove excess energy from CH<sub>2</sub>(<sup>1</sup>A<sub>1</sub>),<sup>21</sup> will aid in establishing the relationship between the  $g_v$  values and  $n_v$  values for a particular system.

As a note of caution, it is emphasized that if the value of  $\Delta H_f[\text{CH}_2(^1\text{A}_1)]$  turns out to be as high as 112.5 kcal/mol, as discussed earlier, the quantitative aspects of this work will be altered but the qualitative features of broadened CH<sub>2</sub>(<sup>1</sup>A<sub>1</sub>) vibrational energy distributions with increased photon energies will remain unchanged.

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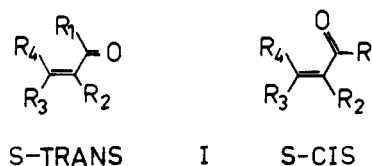
## Conformational Analysis. 128. The Woodward-Fieser Rules and $\alpha,\beta$ -Unsaturated Ketones<sup>1,2</sup>

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**Abstract:** The ultraviolet spectra of a series of alkylated  $\alpha,\beta$ -unsaturated ketones have been calculated using the VESCF method. In particular, nonplanar systems have been examined. The applicability of the Woodward-Fieser rules to such systems has also been examined. According to theory, these rules work as well as they do because of some fortuitous cancellations. A reformulation of the rules increases their general applicability for planar systems. For nonplanar systems the situation is complex. There are two transitions at relatively long wavelengths that must be considered. Both of these vary both in wavelength and in oscillator strength as a function of the dihedral angle about the central bond. These variations are highly dependent on the particular pattern of the alkylation. Generalized predictions about the electronic spectra of these compounds are made.

Conformational effects on the longest wavelength  $\pi \rightarrow \pi^*$  band<sup>4</sup> in the ultraviolet spectra of  $\alpha,\beta$ -unsaturated ketones are most often discussed in terms of intensity changes.<sup>5</sup> Effects on the position of the absorption maxima are usually assumed to be small. The Woodward-Fieser rules,<sup>6,7</sup> which have been widely used for predicting the position of the longest wavelength  $\pi \rightarrow \pi^*$  band of  $\alpha,\beta$ -unsaturated ketones, are well established and have been very successful in correlations between electronic transitions and structures of these compounds. These empirical rules do not take into account any difference in the electronic absorption between s-trans and s-cis forms of the conjugated system. From extensive studies on substituted molecules, the difference in the wavelength of absorption between a cis and a trans diene is well known experimentally and understood theoretically. The main reason for the difference



can be traced to the difference in the 1,4 two-electron repulsion integral, which is considerably larger in the cis conformation than in the trans, due simply to the difference in distance between centers in the two cases.<sup>8</sup> It is qualitatively obvious that the same will hold true for an  $\alpha,\beta$ -unsaturated ketone. Thus calculations on different levels of sophistication consistently predict the s-cis conformation to absorb at longer wavelength than the s-trans conformation, the difference in energy being