

Experimental Determination of the Singlet-Triplet Splitting in Methylene

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Abstract: Singlet methylene is found to be produced collisionlessly when ketene is photolyzed in the 3400–2900-Å region. Its presence is detected by laser-induced fluorescence using the CH₂ ¹B₁–¹A₁ red band system. A study of the appearance of CH₂ ¹A₁(0,0,0) is made as a function of photodissociation wavelength and ketene temperature. When this information is combined with known heats of formation, we are able to place an upper bound of 8.1 ± 0.8 kcal/mol on the methylene singlet-triplet splitting. Arguments are presented that this upper bound is actually close to an equality within the stated uncertainty.

Introduction

For such a small molecule, methylene (CH₂) has been surrounded by a large number of controversies concerning its structural properties.^{1,2} On experimental side, the difficulty of generating a sufficient concentration of this highly reactive intermediate has hindered analysis while on the theoretical side, the fact that methylene is one of the simplest organic species has invited workers to make this molecule a testing ground for ab initio and semiempirical methods of ever increasing sophistication.

Of particular interest is the energy separation between the first two electronic states of methylene, the ground-state triplet, CH₂ ³B₁, and the lowest lying singlet, CH₂ ¹A₁. Despite numerous experiments³ and theoretical calculations,⁴ the singlet-triplet splitting, Δ_{ST} , has remained uncertain. This paper describes the culmination of work begun many years ago to resolve this problem by determining whether singlet methylene is a photofragment of ketene and using this fact to calculate Δ_{ST} from a thermodynamic cycle. The same procedure has been independently carried out by Danon et al.³¹ who reach almost the same conclusion (see Discussion).

Experimental Section

Figure 1 is a schematic diagram of the experimental setup. Acetic anhydride pyrolysis produces the parent molecule, ketene (CH₂CO), which is stored in a liquid-nitrogen-cooled trap and distilled prior to use. Analysis of the ketene by IR, GC, and mass spectrometry showed negligible impurities. The ketene, kept at –77 °C, is admitted to the photolysis chamber through a needle valve. With the fast-flow system employed, the ketene pressure is set and maintained at 0–150 mTorr, as read on an uncalibrated thermocouple gauge.

The dissociating light source is either a Moletron UV 24 nitrogen laser (337.1 nm) or a Chromatix CMX-4 flashlamp-pumped dye laser with a frequency doubler (290–340 nm). The irises used to collimate the N₂ laser beam to a 1-cm spot size reduced the energy available for photodissociation to a maximum of 40 kW of peak power while the dye laser produced 0.1–0.3 kW of peak power. Both an external photodiode and an internal photomultiplier were used to monitor the intensity of the nitrogen laser. The dye laser wavelength was calibrated with a 1-m monochromator, and the power as a function of wavelength was determined with a photomultiplier that had been previously calibrated against a laser calorimeter.

The probe light source was a tunable dye laser (Moletron DL 400) pumped by another nitrogen laser. An external pulse generator provided trigger signals to both N₂ lasers at a 12.5-Hz repetition rate. This permitted the probe laser to be delayed by 0–1 μs with respect to the photodissociation laser (±20-ns jitter). For the 10-Hz tunable photodissociation laser there was a fixed delay of 1.3 μs between the peak of the pump pulse (1-μs fwhm) and the probe pulse. As the probe laser is scanned through a ¹A₁ → ¹B₁ absorption peak, the resulting fluorescence is detected by a photomultiplier (S-20 photocathode), equipped with a filter to block the UV pump laser radiation. The photomultiplier signal is processed by a boxcar averager (PAR Model 162 with Model 164 plug-in) and displayed on a strip chart recorder.

A 30–50-ns delay between the probe pulse and the opening of the 80 ns wide boxcar gate minimized the scattered light contribution while still capturing the bulk of the signal pulse.

Results

Figure 2 shows that singlet methylene is formed by the photolysis of ketene at 337.1 nm. This is an excitation spectrum in which the total fluorescence signal is plotted against the probe laser wavelength. It is taken at 100 mTorr ketene pressure with a delay of 150 ns between the pump and probe laser pulse. The presence of singlet CH₂ is clearly identified by the observed peaks that are assigned by comparison to the CH₂ ¹B₁–¹A₁ absorption spectrum analyzed by Herzberg and Johns.⁵ The vibrational numbering has not been firmly established. Herzberg and Johns assigned this band as the ¹A₁(0,0,0)–¹B₁(0, 16 ± 2, 0); we follow their vibrational numbering although recent ab initio calculations suggest that the numbering will be lowered.^{4s,x,y} The observation of fluorescence excited at wavelengths corresponding to other ¹B₁–¹A₁ bands (see Figure 3) confirms further that singlet methylene is formed from the photodissociation of ketene at 337.1 nm.

The nitrogen laser photon at 337.1 nm carries 84.82 kcal of energy. It is possible that more than this energy is supplied by two-photon absorption, plasma radiation, collisional activation, or thermal excitation of the ketene. The first possibility has been checked by measuring the fluorescence intensity, *I*, as a function of the nitrogen laser intensity. Figure 4 shows that the singlet methylene concentration depends linearly on the laser power, rather than quadratically as would be expected for a two-photon process. It should also be noted that two-photon absorption would provide sufficient energy to produce CH₂ in the ¹B₁ state, giving rise to light emission when only the pump laser is on. We observed no such emission. However, Danon et al.³¹ have reported a quadratic emission dependence in a similar experiment in which they used a higher N₂ laser energy density.

The second possibility, that plasma radiation, particularly the (1,0) band of the N₂ B–A system at 316 nm, is responsible for the formation of ¹A₁ CH₂, is ruled out by the following experiment. A 337.3-nm interference filter (Corion) with a 9.6-nm fwhm bandwidth is inserted in the N₂ laser path. The filter transmits 38% of 337.3-nm light, according to the manufacturer. The observed excitation spectrum is found to be unchanged except for an intensity reduction by about a factor of 4.

Hase and Kelley⁶ have proposed that collisional energy pooling might be responsible for the production of singlet methylene from the photodissociation of ketene. However, we have carried out two experiments that eliminate this possibility under our experimental conditions. First we varied the time

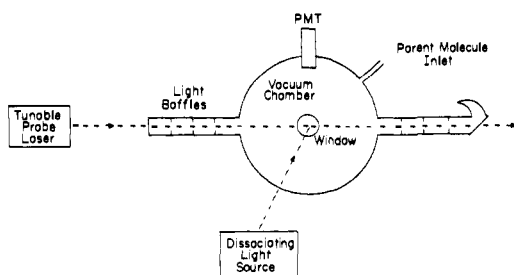


Figure 1. Photolysis apparatus. The dissociating light source is either an N_2 laser or a flashlamp-pumped frequency-doubled dye laser.

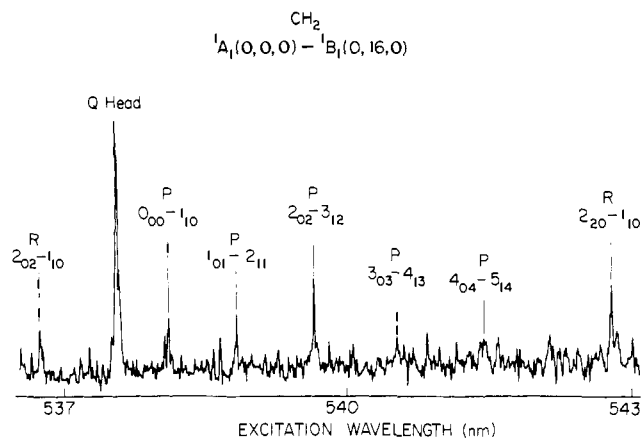


Figure 2. Excitation spectrum of singlet methylene showing the rotational structure in one vibrational band.

delay between the pump and probe laser pulses for a fixed ketene pressure of 100 mTorr. Using 5.5 \AA as the gas kinetic diameter of ketene, the average time between collisions is $0.6 \mu\text{s}$ at this pressure. An energy pooling mechanism would then require an induction period with approximately this build-up time, whereas we find (see Figure 5) that the singlet CH_2 is completely formed within at most 20 ns (our laser jitter). Thus, the singlet methylene concentration $S(t)$ should be related to the ketene concentration K (assumed to be constant) by the differential equation

$$dS(t)/dt = AI_{NL}(t)K - D(t) - k_K S(t)K \quad (1)$$

where $I_{NL}(t)$ is the time dependence of the photolysis laser intensity, A is a proportionality constant, $D(t)$ is the diffusion loss of singlet methylene from the field of view, and k_K is the rate constant for the destruction of singlet methylene by collisions with ketene. In deriving eq 1 we have assumed that $S(t)$ is unaffected by the probe laser. Under our experimental conditions $D(t)$ can be neglected, as the following simple calculation shows. Using a 2.7-\AA diameter of CH_2 , the diffusion coefficient D at 100 mTorr is $1.35 \times 10^3 \text{ cm}^2 \text{ s}^{-1}$ from which we find that a singlet methylene molecule moves an average distance of 0.05 cm in $1 \mu\text{s}$ for one-dimensional diffusion. Equation 1 may be integrated to yield the solution

$$S(t) = C[\exp(-k_K K t) - \exp(-k_{NL} t)] \quad (2)$$

where k_{NL} is the fall rate of the photolysis laser, and C is another proportionality constant. A logarithmic plot of the data in Figure 5 is linear as predicted by eq 2. From this slope and the pressure of ketene measured with an uncalibrated thermocouple gauge, we find $k_K = 4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, which represents the combined rates of collisional intersystem crossing and reactive scattering. This value may be compared with the collisional destruction of the $\text{CH}_2 \text{ } ^1\text{B}_1$ state, which was found³¹ to be $7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$.

The variation of the fluorescence intensity with ketene

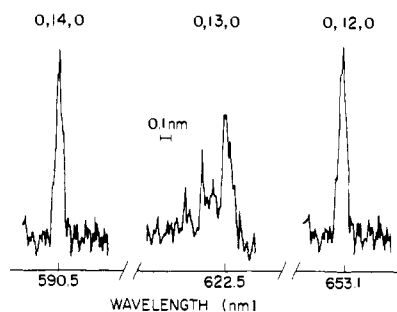


Figure 3. Excitation spectrum of singlet methylene showing some of the more accessible vibrational bands of the $^1\text{B}_1\text{-}^1\text{A}_1$ system.

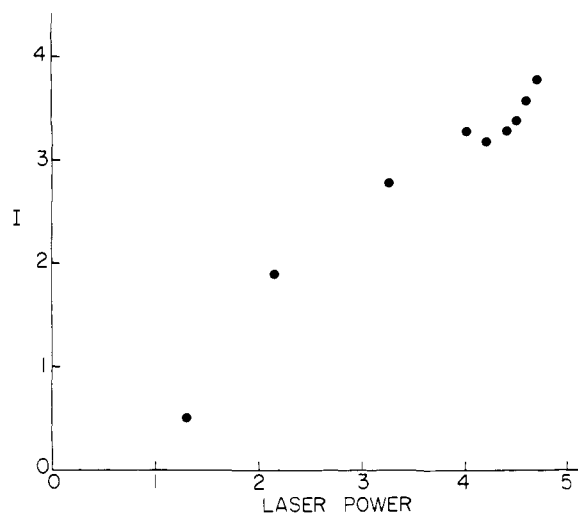


Figure 4. Plot of the singlet methylene fluorescence intensity vs. pump laser power.

pressure (see Figure 6) further corroborates that the $\text{CH}_2 \text{ } ^1\text{A}_1$ comes collisionlessly from the photodecomposition of ketene. A concave-upward dependence would have been anticipated if collisions were responsible for the production of singlet methylene; however, a concave-downward dependence is observed, consistent with the collisional destruction rather than creation of $\text{CH}_2 \text{ } ^1\text{A}_1$.

The pressure-dependent intensity shown in Figure 6 actually contains information about the destruction rate, α , of the $\text{CH}_2 \text{ } ^1\text{B}_1$ state. The data can be fit to the expression

$$I = \frac{CK \exp(-k_K K \Delta)}{(k_{NL} - k_K)(k_{DL} - \alpha)(T_2 - T_1)\alpha} \times [\exp(-\alpha T_1) - \exp(-\alpha T_2)] \quad (3)$$

where Δ is the time delay between the pump and probe pulses, k_{DL} is the probe laser fall rate, T_1 and T_2 are the boxcar gate opening and closing times, and the other symbols have the same meanings as in eq 1 and 2. By extracting a value of α at each ketene pressure, we obtain a quenching rate for the $\text{CH}_2 \text{ } ^1\text{B}_1$ state in fair agreement with that determined by Danon et al.³¹ using a more direct measurement method. The point of this exercise is that the data in Figures 5 and 6 conform to equations based only on collisional destruction processes.

A study was made of the dependence of the $\text{CH}_2 \text{ } ^1\text{A}_1$ concentration on the temperature of the parent molecule. The fluorescence signal is found to increase markedly with temperature, indicating that (1) the photodissociation of ketene dimers cannot be responsible for the observed $\text{CH}_2 \text{ } ^1\text{A}_1$ and (2) there is a contribution from the ketene internal energy to the formation of $\text{CH}_2 \text{ } ^1\text{A}_1$. Figure 7 shows a plot of the logarithm of the $\text{CH}_2 \text{ } ^1\text{A}_1$ fluorescence signal vs. the reciprocal of the absolute temperature. This temperature is that of the ketene

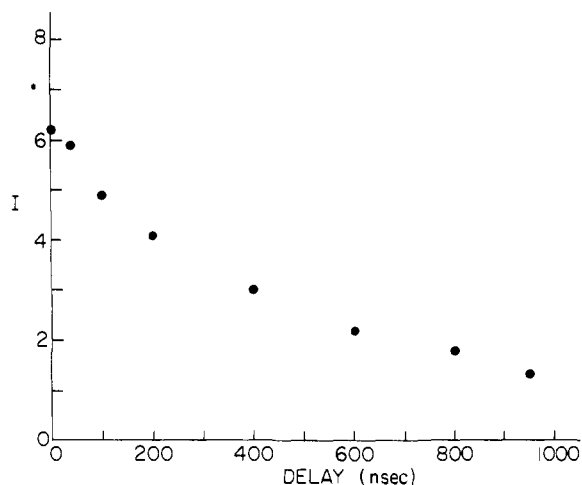


Figure 5. Plot of the singlet methylene fluorescence as a function of the time delay between the pump laser (337.1 nm) and the probe laser (537.5 nm). Each point has a 20-ns uncertainty.

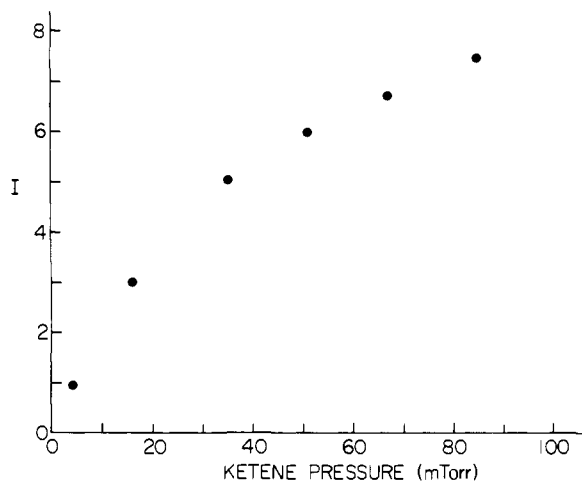


Figure 6. Plot of the singlet methylene fluorescence vs. ketene pressure.

inlet system, a 60 cm long copper tube inside the vacuum chamber.

The slope of the straight line through the data points corresponds to an energy of 516 K or 1.0 kcal/mol. To obtain the threshold for the appearance of $\text{CH}_2^1\text{A}_1(0,0,0)$, we must add this amount of internal energy to the photon energy (84.82 kcal/mol) and subtract the rotational energy ($J = 4$; see Figure 2) of the newborn singlet methylene (0.6 kcal/mol). In this manner we obtain an upper bound of

$$\Delta H_f^\circ(\text{CH}_2\text{CO}) - [\Delta H_f^\circ(\text{CH}_2^1\text{A}_1) + \Delta H_f^\circ(\text{CO})] = -85.2 \pm 0.3 \text{ kcal/mol} \quad (4)$$

to the difference between the heat of formation of ketene and the heats of formation of CH_2^1A_1 and CO. This upper bound would be an equality if at threshold there is negligible rotational energy in CO or recoil energy in the photofragments. Within the experimental uncertainty we believe this to be a reasonable assumption. Using known heats of formation, $\Delta H_f^\circ(\text{CO}) = -27.199 \text{ kcal/mol}$ ⁷ and $\Delta H_f^\circ(\text{CH}_2\text{CO}) = -10.7 \pm 0.4 \text{ kcal/mol}$,⁸ we obtain from eq 4 the heat of formation of singlet methylene:

$$\Delta H_f^\circ(\text{CH}_2^1\text{A}_1) = 101.7 \pm 0.5 \text{ kcal/mol} \quad (5)$$

To obtain another measurement of $\Delta H_f^\circ(\text{CH}_2^1\text{A}_1)$ we investigated the relative concentrations of $\text{CH}_2^1\text{A}_1(0,0,0)$ and $\text{CH}_2^1\text{A}_1(0,1,0)$ as a function of photolysis energy using the tunable pump laser. The data for the appearance of the (0,0,0)

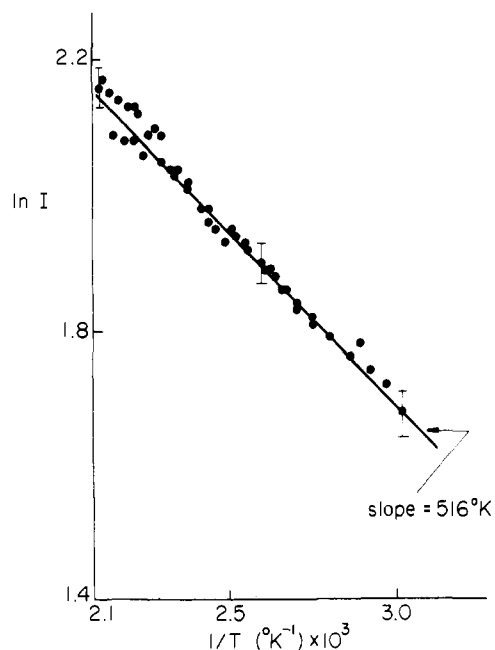


Figure 7. Boltzmann plot of the singlet methylene fluorescence intensity as a function of the ketene temperature.

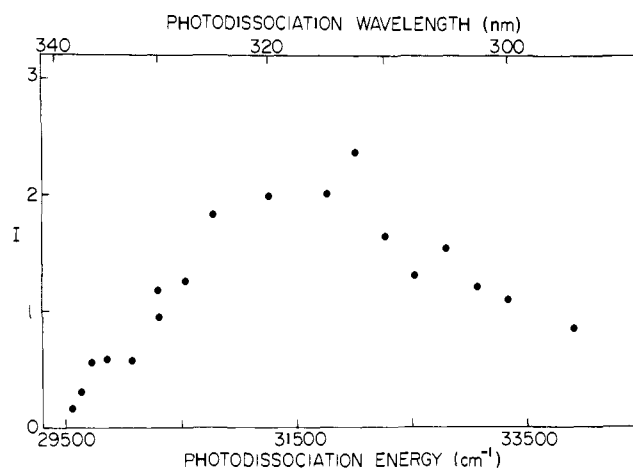


Figure 8. Fluorescence intensity arising from the (0,0,0) level of CH_2^1A_1 as a function of the pump laser energy.

level are presented in Figure 8 from which we obtain an appearance threshold of $84.1 \pm 0.3 \text{ kcal/mol}$. The temperature study in Figure 7 mandates that we correct this value for the internal energy in the ketene. If hot bands had been solely responsible for $\text{CH}_2^1\text{A}_1(0,0,0)$ production, we should have seen a sharp break; instead, the gentle and nearly constant slope toward threshold in Figure 8 supports the interpretation that a more continuous internal energy distribution is involved. McCulloh and Dibeler⁹ found that all three rotational degrees of freedom contributed to the appearance threshold of CH_2^+ from the photoionization of CH_2CO . Assuming a similar classical contribution from rotation, the threshold is raised by $\frac{3}{2}kT$ to $85.0 \pm 0.3 \text{ kcal/mol}$, in agreement with eq 4.

A true threshold for the appearance of the $\text{CH}_2^1\text{A}_1(0,1,0)$ level could not be obtained with the present experimental equipment because of the low light output of the tunable pump laser in the threshold region. Nevertheless, we were able to see this level at 312.5 nm, which places an upper bound on the threshold for $\text{CH}_2^1\text{A}_1(0,0,0)$ production of 87.6 kcal/mol. This additional result encourages us that there is no large systematic error in our measurement of the singlet methylene appearance threshold.

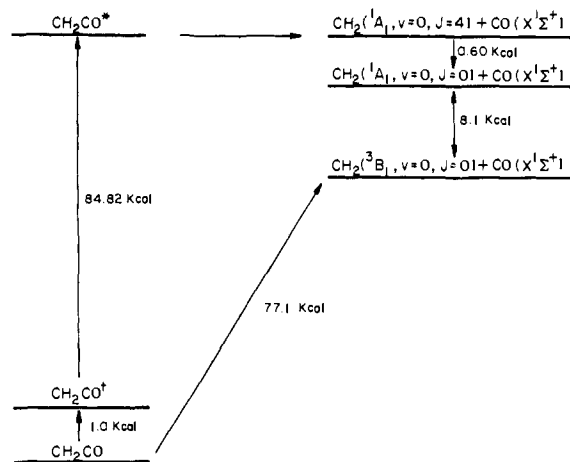


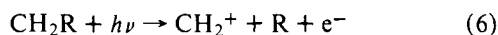
Figure 9. Thermodynamic cycle used in the determination of the methylene singlet-triplet splitting.

Discussion

The $\text{CH}_2\ ^1\text{A}_1\text{-}^3\text{B}_1$ Energy Splitting. To find the value of the methylene singlet-triplet splitting, Δ_{ST} , we must complete the thermodynamic cycle, shown in Figure 9, with the heat of formation of $\text{CH}_2\ ^3\text{B}_1$. This last piece of information cannot be derived from our experiment but is based on the work of others. Fortunately, several independent measurements^{3h,9,10} give essentially the same value for $\Delta H_f^\circ(\text{CH}_2\ ^3\text{B}_1)$.

One method for calculating $\Delta H_f^\circ(\text{CH}_2\ ^3\text{B}_1)$ requires the knowledge of three quantities: (1) the ionization potential for $\text{CH}_2\ ^3\text{B}_1$, (2) the appearance potential of CH_2^+ from the photoionization of some parent compound CH_2R , and (3) the heat of formation of CH_2R . In 1961, Herzberg¹¹ reported the observation of a Rydberg series arising from $\text{CH}_2\ ^3\text{B}_1$ which gave an extrapolated ionization limit of 239.73 ± 0.03 kcal/mol. There was some concern that this spectroscopic limit does not converge to the CH_2^+ ground state, since it was based on what appeared to be vertical transitions from a supposedly linear $\text{CH}_2\ ^3\text{B}_1$, whereas the ground state of CH_2^+ was thought to be bent. Later, EPR results^{12,13} and a reinterpretation of the optical spectrum,¹⁴ however, have shown that $\text{CH}_2\ ^3\text{B}_1$ has a bent structure, firmly establishing its ionization potential.

The appearance threshold for the photoionization process



can differ from the minimum energy required for (6) due to contributions from the internal energy of the CH_2R parent and the excess energy disposed in both translational and internal energy of the fragments. The first contribution may be taken into account by measuring the appearance threshold as a function of temperature and extrapolating to 0 K. However, no corrections can be made directly for the latter contributions, although their size can be estimated by measuring the appearance threshold for a number of different starting compounds. Using the above procedure, McCulloh and Dibeler⁹ obtain $\Delta H_f^\circ(\text{CH}_2) = 93.8 \pm 0.4$ and 93.4 ± 0.4 kcal/mol based on measurements of the CH_2^+ photoionization appearance thresholds using CH_4 and CH_2CO , respectively. These values compare favorably with measurements by Chupka and co-workers of 94.6 ± 0.5 kcal/mol^{10b} using CH_4 , 93.8 ± 0.4 kcal/mol^{10d} using CH_2CO , 91.9 ± 2 kcal/mol^{10a,10d} using CH_3 , and 95.5 ± 3 kcal/mol^{10c,10d} using CH_2CH_2 . The good agreement among all these values supports the contention that the thresholds involve little or no excess energy release.

An alternative procedure for calculating $\Delta H_f^\circ(\text{CH}_2\ ^3\text{B}_1)$ has been provided by Simons and Curry,^{3h} who have measured the long-wavelength limit (377.5 ± 5 nm) for the appearance of CO from the photodissociation of room-temperature ketene.

This corresponds to a threshold for $\text{CH}_2\ ^3\text{B}_1$ production of 75.7 ± 1.0 kcal/mol at 298 K. When this value is corrected for a thermal contribution from the ketene, the threshold measurement yields 92.8 ± 1.0 kcal/mol for $\Delta H_f^\circ(\text{CH}_2\ ^3\text{B}_1)$.

We feel this value for the triplet methylene heat of formation is less accurate than the values based on CH_2^+ appearance thresholds because the photodissociation threshold measurement was not as detailed a study and did not investigate temperature dependence. Nevertheless, the two methods agree within their precision, encouraging us to believe that there is no large systematic error in the determination of $\Delta H_f^\circ(\text{CH}_2\ ^3\text{B}_1)$.

We adopt the value

$$\Delta H_f^\circ(\text{CH}_2\ ^3\text{B}_1) = 93.6 \pm 0.6 \text{ kcal/mol} \quad (7)$$

where the error limit is increased over the precision of each photoionization measurement set to reflect better the spread of values. By subtracting the value of $\Delta H_f^\circ(\text{CH}_2\ ^3\text{B}_1)$ in eq 7 from that of $\Delta H_f^\circ(\text{CH}_2\ ^1\text{A}_1)$ in eq 5 we obtain for the methylene singlet-triplet splitting

$$\Delta_{\text{ST}} = 8.1 \pm 0.8 \text{ kcal/mol} \quad (8)$$

The error estimate in eq 8, which reflects primarily the uncertainty in $\Delta H_f^\circ(\text{CH}_2\ ^3\text{B}_1)$, is based on the precision in the data. The possible presence of systematic errors may cause a doubling of the error in Δ_{ST} .

Comparison with Other Values. Examination of ref 3 and 4 shows a large spread in both the experimental and theoretical determinations of the methylene singlet-triplet splitting. Photochemical studies^{3a-j} attempt to infer the ratio of singlet methylene to triplet methylene based on the different chemistries of these two species. The singlet-triplet splitting is then calculated by assuming that an equilibrium population ratio exists or by measuring the appearance threshold for singlet compared to triplet methylene production. Early work^{3a-c} ignored collisional intersystem crossing whereby singlet methylene is generated from triplet methylene and their values for Δ_{ST} ranged from 1 to 2.5 kcal/mol. Later work^{3d-j} has included this effect and their values for Δ_{ST} range from 7.5 to 9.1 kcal/mol, based upon various assumptions concerning activation energies, branching ratios, and overall rates for singlet and triplet methylene reactions. Recently, it has been suggested that the above determination of Δ_{ST} would be raised appreciably if excited ketene participated in the reaction mechanism.⁶

In contrast to the above indirect determinations, Danon et al.^{3l} and we have directly measured the collisionless production of singlet methylene resulting from the photolysis of ketene. Their value of $\Delta_{\text{ST}} = 6.3 \pm 0.8$ kcal/mol and ours of 8.1 ± 0.8 kcal/mol are in better agreement than might first appear to be the case. Danon et al. used heats of formation at 298 K rather than at 0 K. Hence their value of Δ_{ST} should be raised by 1.2 kcal/mol, making both determinations of Δ_{ST} overlap one another inside each error limit. Moreover, if Danon et al. had made corrections for the internal energies of the reactants and products, the agreement would be even closer.

The most direct measurement of the methylene singlet-triplet splitting by Zittel et al.,^{3k} however, gives $\Delta_{\text{ST}} = 19.5 \pm 0.7$ kcal/mol, based on the photodetachment spectrum of CH_2^- . In this experiment a mass-selected beam of negative methylene ions, generated in a discharge source, is irradiated by an argon ion laser and the resulting electron energy distribution is measured. The photodetachment processes, $\text{CH}_2^- \rightarrow \text{CH}_2\ ^1\text{A}_1 + e^-$ and $\text{CH}_2^- \rightarrow \text{CH}_2\ ^3\text{B}_1 + e^-$, are observed concurrently; by vibrationally assigning the peaks in the electron energy distribution, the methylene singlet-triplet splitting is obtained. As suggested in two recent ab initio studies,^{4w,x} the value of Δ_{ST} derived from the photodetachment spectrum may be too large because of a vibrational mis-

assignment. These two studies, as well as several others^{4h-j,p-t} employing sophisticated computational procedures, also find values of Δ_{ST} in good agreement with our experimental one. However, efforts to check for the presence of hot bands, the supposed cause of the misassignment, have failed so far to detect their existence¹⁵ and the origin of this discrepancy remains unresolved.

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Ground States of Molecules. 50.¹ MNDO Study of Hydroboration and Borohydride Reduction. Implications Concerning Cyclic Conjugation and Pericyclic Reactions

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Abstract: MNDO calculations are reported for the reduction of formaldehyde or methyl formate by borohydride ion and for the reactions of borane with acetone and ketene. Borohydride reduction is predicted to be strongly "forbidden" in the gas phase. The ease of hydroboration is explained in terms of a type of cyclic conjugated system (cruciconjugated) previously recognized in the phosphonitrile chlorides. The analogy between conjugation by $\pi\pi:d\pi$ and $\sigma\sigma:p\sigma$ interactions is pointed out and used to interpret the abnormal ("anti-Hückel"; "Moebius") systems in pericyclic transition states. The inappropriateness of the term "Moebius" in this connection is emphasized.

Introduction

Hydroboration² and the reduction of carbonyl groups by borohydride ion (BH_4^-)³ have become two of the better known

reactions in synthetic organic chemistry. Each formally involves a cycloaddition of a B-H moiety to a double bond, a process which would be classified in Woodward-Hoffman terminology⁴ as a ($\sigma_2s + \pi_2s$) cycloaddition, i.e.