THE THRESHOLD FOR PHOTODISSOCIATION OF KETENE INTO $CH_2(\tilde{a} \ ^1A_1)$ AND THE $CH_2(\tilde{a} \ ^1A_1 - \tilde{X} \ ^3B_1)$ ENERGY SEPARATION

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The photodissociation of ketene has been measured in the threshold region of the process $CH_2CO(\tilde{X}^1A_1) + h\nu \rightarrow CH_2(\bar{a}^1A_1) + CO$ between 310 and 355 nm. The ketene has been dissociated by the tunable light from a frequency doubled dye laser. The singlet $CH_2(\bar{a}^1A_1)$ in its vibrational ground state (0,0,0) and first excited (0,1,0) state has been detected by laser induced fluorescence. A threshold energy for the dissociation of ketene into $CH_2(\bar{a}^1A_1)$ of (85.4 ± 0.3) kcal/mole has been determined. From this an upper limit for the singlet-triplet energy separation $CH_2(\bar{a}^1A_1 - \tilde{X}^3B_1)$ of (9.8 ± 1.5) kcal/mole can be determined using published thermodynamic data.

1. Introduction

The energy separation between the triplet ground state $\tilde{X}^{3}B_{1}$ and the lowest singlet state $\tilde{a}^{1}A_{1}$ of the CH₂ radical has been the subject of many experimental [1-9] and theoretical [10-15][†] studies during the last years. The results of recent calculations [10-16] show a tendency to converge to an energy of (11 ± 3) kcal/mole. Experimental photolysis studies with product analysis have yielded values around 8 kcal/mole, whereas in a recent work [8] using photoelectron spectroscopy an energy of (19.5 ± 0.7) kcal/mole has been determined. Reinterpretations of the latter results have been proposed [13-15] to lower this high value.

In a recent experiment [9] we have observed the laser induced fluorescence of singlet CH_2 produced when ketene was irradiated with the 337 nm light from a nitrogen laser. Using thermodynamic data an upper limit of $(6.3 \pm 0.8 \text{ kcal/mole})$ for the energy separation could be obtained. In deriving this value, the thermal energy of the ketene molecules was not taken into account. In the present work we have investigated the $CH_2(\tilde{a} \ ^1A_1)$ production by photodissociation of ketene as a function of the wavelength.

The $CH_2(\tilde{a}^{1}A_1)$ has again been observed by laser induced fluorescence (LIF).

2. Experimental

The experimental set-up is shown schematically in fig. 1. The ketene has been prepared from $(CH_3CO)_2O$ in the same way as previously described. The dissociation was carried out by the frequency doubled output of a tunable dye laser. The doubling was performed in a KDP crystal. The dye laser was pumped by a frequency doubled YAGlaser and consisted of a pressure tuned oscillator and three amplifier stages. The wavelength region used in these experiments ranged from 310 to 355 nm.



Fig. 1. Schematic diagram of the apparatus.

[†] Ref. [10] gives a compilation of results up to 1973.

The dye laser was operated in this region at powers up to 100 kW using Rh 640 and a mixture of Rh 640 and nile blue. The repetition rate, pulse duration and bandwidth were 10 Hz, 10 ns and 0.01 nm, respectively. Details of the laser system will be given elsewhere [17]. The beam diameter of the dissociation laser was about 1 mm in the centre of the Juorescence cell.

The light from a flash lamp pumped dye laser used for the LIF detection of $CH_2(\tilde{a}^{1}A_1)$ traversed the fluorescence cell in the opposite direction with a beam diameter of about 5 mm. The peak power, bandwidth and pulse duration of the LIF laser were 5 kW, 0.1 nm and 1 μ s, respectively.

The beam diameters and positions of the laser beams were controlled by apertures. The wavelengths of the lasers were measured with an accuracy of better than \pm 0.01 nm with a 3/4 m Spex grating spectrometer. Laser powers were measured with calorimetric detectors (Scientec 336) in front of the cell. Both lasers were synchronized by a trigger unit in such a way that the peak of the detectionlaser pulse was delayed with respect to the dissociation laser pulse by 1 μ s. The pulses were monitored by the same photodiode as shown in fig. 1.

Light from the centre of the fluorescence cell was viewed at right angles to the laser beams through suitable combinations of interference, cut-off and neutral density filters, using as detector an RCA



Fig. 2. Excitation spectrum of the $\Sigma - \Pi$ subband of the $CH_2(\vec{b}^1 B_1(0, 14, 0) \leftarrow \vec{a}^1 A_1(0, 0, 0))$ transition. The arrows I and II indicate the excitation wavelength, used to determine the wavelength dependences for dissociation.



Fig. 3. Excitation spectrum of $CH_2(\tilde{b}^1B_1(0,15,0) \leftarrow \tilde{a}^1A_1(0,1,0))$ transitions.

C31034 photomultiplier tube. The pulses from the multiplier were amplified and accumulated in a gated counter for a preselected number of laser shots. The gate was opened by a trigger from the dissociation laser pulse with a delay of 0.5 μ s to this pulse, for 5 μ s. Under typical experimental conditions the background signal, measured without ketene or without UV laser light in the cell was of the order of 1 count per 20 shots.

3. Experimental results

3.1. Excitation spectra of $CH_2(\widetilde{a} A_1)$

The $CH_2(\tilde{b}-\tilde{a})$ transition exhibits an open spectrum of many discrete lines extending from the visible region to the infrared. The dissociation of ketene was found to produce $CH_2(\tilde{a}^{-1}A_1)$ in the ground vibrational level (0,0,0) and also in the first excited level (0,1,0). Excitation spectra were taken to identify the rovibronic levels of the a state. The visible dye laser was scanned in steps of about 0.04 nm, and the count rates accumulated for 10 laser shots at each wavelength were stored in a multichannel analyser. Fig. 2 shows a small portion of the excitation spectrum in the region of the Σ - Π subband of the $\tilde{b}(0,14,0) \leftarrow \tilde{a}(0,0,0)$ transition[†]. It was taken at a dissociation laser wavelength of 335 nm and a ketene pressure of 5 mtorr. The fluorescence was observed through an interference filter (643 nm

[†] We used the vibrational numbering of ref. [18] for the $\vec{b}^{I}B_{1}$ state.

centre wavelength, 15 nm fwhw) and a cut-off filter (Scott, OG 615) which isolated the emission from (0,14,0) to the (0,1,0) vibronic levels of the $\tilde{a}^{1}A_{1}$ state. For quantitative measurements calibrated neutral density filters were added when necessary to prevent the counting system from being saturated.

Fig. 3 shows an example of an excitation spectrum in the region of the $\tilde{b}(0,15,0) \leftarrow \tilde{a}(0,1,0)$ transition. In this case the fluorescence from $\tilde{b}(0,15,0)$ to $\tilde{a}(0,0,0)$ was observed, using an interference filter of 559 nm centre wavelength and 15 nm fwhm in front of the photomultiplier.

3.2. Wavelength dependence

The wavelength dependence of the $CH_2(\tilde{a}^{I} A_1)$ yield in the (0,0,0) level was measured at two wavelength positions in the excitation spectrum, marked by I and II in fig. 2. At I (591.2 nm) the fluorescence represents a resolved excitation line from the rotational level 1₁₀ in the lower state, \tilde{a} (0,0,0), to the level 0₀₀ in the upper state, \tilde{b} (0,14,0). The measurement at this wavelength refers accordingly to the population and thus production yield of $CH_2(\tilde{a}^{I}A_1)$ in this 1₁₀ level. The position II in the excitation spectrum includes the fluorescence of a few unresolved Q branch lines with rotational levels J'' =1-4 in the \tilde{a} (0,0,0) state. Measurements at this wavelength are accordingly not purely state selective.

Figs. 4a and 4b show the $CH_2(\tilde{a}^1 A_1)$ yield as obtained with the detection laser set at the wavelengths I and II, respectively. To obtain these curves, the fluorescence signals were determined at a constant dissociation laser intensity. In order to diminish the influence of the power fluctuation that both lasers showed, the fluorescence intensity was measured as a function of laser intensity at every dissociation laser wavelength used. To improve the precision further the number of laser shots per experimental point was chosen such that signals were accumulated to levels such that the statistical error was of comparable magnitude at each dissociation laser intensity. The number of laser shots per experimental point was 200 to 1600 depending on the fluorescence signal.

An example of an intensity dependence measurement is shown in fig. 5 for a dissociation laser wavelength of 335 nm and probe laser wavelengths at I and II. As in this example least squares fitting by



Fig. 4. The wavelength dependences of 1 CH₂ photoproduction from ketene. (a) Dissociation laser power 10 kW, pressure 5 mtorr: XCH₂ in the \bar{a}^{1} A₁(0,0,0) 1₁₀ level, \circ CH₂ in the \bar{a}^{1} A₁(0,1,0) state. (b) CH₂ in the 1₁₁, 2₁₂, 3₁₃, 4₁₄ levels of the \bar{a}^{1} A₁(0,0,0) state. The lines are drawn to guide the eye. The fluorescence signals are not normalized with respect to each other.

straight lines was employed to determine the value for 10 kW which is given in figs. 4a and 4b.

The pressure dependence of the fluorescence was checked in the range between 1 and 15 mtorr of ketene. No foreign gas was added. Fig. 6 shows as an example the pressure dependence of the fluorescence excited from $CH_2(\tilde{a}^{-1}A_1)$ in the (0,0,0) level. The fluorescence increases at first practically linearly and tends to level off at higher pressure, as expected from the quenching effect. The measurements of the $CH_2(\tilde{a}^{-1}A_1)$ yield were made at pressures of 1-5 mtorr, where quenching was obviously still



Fig. 5. Fluorescence signal as a function of the UV laser intensity. I and II correspond to the two excitation wavelengths, see fig. 2 and text.

negligible. The wavelength dependence is determined for 5 mtorr ketene pressure.

The wavelength dependence of the production of $CH_2(\tilde{a}^1A_1)$ in the (0,1,0) level, as shown in fig. 4a by the dashed curve (circles), was obtained in a slightly different way. At the given wavelengths an excitation spectrum was taken and the points plotted in the figure were derived from the height of the peak of the $Q_{2,N}$ branch indicated in fig. 3. This peak includes a number of unresolved lines from different rotational levels. Again, the fluorescence intensity was normalized to 10 kW dissociative laser power.

The fluorescence signals of the two curves in fig. 4a are shown in arbitrary units. They are not normalized with respect to each other, because the



Fig. 6. Pressure dependence of the fluorescence signal.

relative strengths of the transitions involved are unknown.

3.3. Two-photon excited fluorescence

In our previous study [9] we have observed fluorescence in the visible wavelength region when the ketene was irradiated with 337 nm only, i.e. without using the probe laser. This fluorescence was appreciable only at relatively high laser light power (above 30 kW/pulse), and it was found to depend quadratically on the power. The occurrence of this fluorescence was confirmed in the present experiments at different wavelengths of the dissociation laser. Also the quadratic dependence was obtained.

The likely production mechanism for the fluorescence (see fig. 7) is two-photon dissociation of CH₂CO into excited CH₂-radicals, possibly in the \tilde{c} ¹A₁ or in the \tilde{b} ¹B₁ state. Another mechanism, namely dissociation of CH₂CO to CH₂(\tilde{a} ¹A₁) in the first step and excitation of the fragment by a second UV photon, may be largely excluded since



Fig. 7. Simplified schematic energy diagram and transitions induced, observed or discussed in the text. hv_1 photons from the UV dissociation laser, hv_2 photons from the visible excitation laser, hv_f fluorescence detected.

on the one hand the fluorescence was obtained with various UV laser wavelengths, whereas on the other hand the excitation of $CH_2(\tilde{a} \, {}^1A_1)$ is a selective process. Fig. 7 shows the pathways of these two mechanisms. With respect to the present experiments, the fluorescence excited by the dissociation laser was of no consequence here, because the quadratic dependence made it possible to keep its intensity low compared to the fluorescence obtained with the detection laser on. At dissociation laser powers below 30 kW the fluorescence signal caused by two UV photons was less than 5% of that produced with the probe laser. The experiments were accordingly performed at powers less than 30 kW.

4. Discussion

4.1. The dissociation mechanism

Fig. 7 shows an energy level diagram of CH₂CO and CH₂ with transitions relevant in this work. The dissociation mechanism is not established in detail, though previous work indicates that at the wavelengths employed in this work the dissociation proceeds into two branches; one yielding CH₂ in the electronic ground state, $\tilde{X}^{3}B_{1}$, and the other in the $\tilde{a}^{1}A_{1}$ state.

According to the spin conservation rule the $CH_2(\tilde{a}^{1}A_1)$ formation should occur through an excited singlet state of CH_2CO . In previous work an excited $^{1}A_2$ state has been assigned in the region of the diffuse ketene absorption spectrum [19-21] A recent calculation by Harding and Goddard [22] has yielded a vertical excitation energy of 3.69 eV $\triangleq 29762 \text{ cm}^{-1}$ for the $^{1}A_2$ state. This is consistent with experiments by Frueholz et al. [23] who have measured the electron impact energy loss spectrum and identified the state at 3.7 eV.

No fluorescence has been observed from ketene [24] indicating that the ${}^{1}A_{2}$ state is strongly predissociated yielding CH₂($\tilde{a}^{-1}A_{1}$) + CO($\tilde{X}^{-1}\Sigma$). On the other hand Del Bene [25] has correlated the ${}^{1}A_{2}$ state of ketene with states of the separated fragments, CH₂ + CO, with an energy much higher than the CH₂($\tilde{a}^{-1}A_{1}$) state, which would not allow the ${}^{1}A_{2}$ state to directly decay into the observed products. Zabransky and Carr [24] have proposed a dissociation path from the ${}^{1}A_{2}$ state via an internal conversion to the ketene ${}^{1}A_{1}$ ground state potential from which then the fragments fly apart. Other suggestions have been the formation of an oxirene intermediate, dissociating after rearrangement [26] and adduct formation [7].

Whereas previously employed indirect techniques cannot exclude interference of the dissociation by collisional processes, $CH_2(\tilde{a}\,^1A_1)$ observed here was produced by direct photodissociation. Referring to a pressure of for instance 1 mtorr and using the gas kinetic collision cross section, the average time between collisions is of the order of 10^{-4} s as compared to the time interval between production and detection of 1×10^{-6} s in our experiment. The observed linear pressure dependence at low pressures (fig. 6) is consistent with this. The primary steps can thus be summarized as

$$CH_{2}CO(\widetilde{X}^{1}A_{1}) + h\nu_{1} \rightarrow CH_{2}CO(^{1}A_{2}) , \qquad (1)$$

$$CH_{2}CO(^{1}A_{2}) \rightarrow \ldots \rightarrow CH_{2}(\widetilde{a}^{1}A_{1}) + CO(\widetilde{X}^{1}\Sigma^{+}) , \qquad (2)$$

where the dots in reaction (2) simply indicate that we cannot specify a distinct decay process.

4.2. Wavelength dependence

The curves shown in fig. 4 represent the wavelength dependence of the dissociation yield, or the cross section for the formation of $CH_2(\tilde{a}^{-1}A_1)$ in the corresponding levels. The two curves I and II that refer to the ground vibrational state (0,0,0) in the selected 1_{10} sublevel (I) and the unresolved levels $1_{11}, 2_{12}, 3_{13}, 4_{14}$ (II) are practically the same within the experimental uncertainty, both starting with a gradual increase followed by a rather steep maximum slope, a peak and a pronounced decrease at shorter wavelengths. The wavelengths of the maximum slope and the peaks are 335 and 330 nm, respectively, with approximately ± 1 nm uncertainty.

The 1_{10} level lies 31 cm^{-1} above the rotational zero level, and the J'' = 1-4 levels have energies of up to 170 cm^{-1} . If the higher J levels were predominantly populated one might expect in principle a corresponding shift between curves I and II with II being on the shorter wavelength side which, however, does not show up in these curves.

A dependence of the production yield on various J levels was qualitatively observed in the well resolved P branch. Taking excitation spectra with

different dissociation laser wavelengths the relative fluorescence intensity of lines from high J levels in the (0,0,0) ground state systematically decreased with increasing dissociation laser wavelength. This behaviour is to be further investigated quantitatively.

The dissociation cross section for the production of $CH_2(\tilde{a}^{-1}A_1)$ in the (0,1,0) vibrational state (fig. 4a) exhibits a shift towards shorter wavelengths. Since the fluorescence intensities of the curves in fig. 4 are not normalized to each other, the determination of the shift between the curves is not quite unambiguous. It is, however, of the order of the (0,1,0) vibrational energy, which has been determined by Herzberg and Johns [18] and confirmed by us [27] to be 1350 cm⁻¹. As to the dependence of the dissociation on the rotational energy of $CH_2(a^{-1}A_1)$;(0,1,0) it was also found that the J levels died out with increasing dissociation laser wavelength the earlier the higher the J value.

4.3. Dissociation energy and threshold

The dissociation energy D_0 is given by the energy between the zero energy level of the CH2CO molecule and the zero energy levels of the fragments CH($\tilde{a}^{1}A$) and CO($\tilde{X}^{1}\Sigma^{+}$) (see fig. 7). In general the measurement of the wavelength dependence of the dissociation will not show a step-wise onset of the product yield but rather an asymptotic kind of dependence at long wavelengths. The measurement can yield upper limits only, where the limit in general cannot precisely be determined. The threshold behaviour is determined by the individual shapes of the upper and lower potentials and by the details of the energy distribution of the fragments. In the present case the observation of $CH_2(\tilde{a}^{1}A_1)$ leaves open the internal energy carried by the other fragment, $CO(\tilde{X}^{1}\Sigma^{+})$, and the kinetic energy of the fragments.

Another influence to be considered is the effect of the internal energy of the parent molecule. At room temperature, where the present experiments have been carried out, a relatively small fraction ($\leq 10\%$) of the CH₂CO molecules is vibrationally excited, and their dissociation may contribute to the long wavelength tail of the yield curves. The effect of rotation on the dissociation wavelength dependence cannot be determined in detail either. But it should not contribute to a long wavelength tail because angular momentum should be conserved in the first step (1) of the dissociation process.

In our case an additional uncertainty arises from the unknown dissociation mechanism discussed above. The determination of an experimental dissociation threshold thus remains ambiguous to some degree. Choosing the steepest slopes of curves I and II thus yields a wavelength of (335 ± 1) nm or (29850 ± 100) cm⁻¹.

For comparison, Simons and Curry [6] have reported a threshold value of (340 ± 2.5) nm \triangleq (29400 ± 200) cm⁻¹. They obtained the singlet CH₂ production wavelength dependence from ketene by using chemical means to probe for the radical formation. Their measurements have yielded a linear increase of the singlet-CH₂ formation beginning with an extrapolated threshold at 340 nm. The difference to the present experiments with a distinct non linear wavelength tail may be due to the few wavelength points covered in their experiments. Also, the present observations refer to selected levels of the CH₂ product whereas their experiments have not been level specific.

4.4. The $CH_2(\tilde{a}^{I}A_1 - \tilde{X}^{3}B_1)$ energy separation

An upper limit of the energy of the singlet CH₂level can be derived from the experimental threshold of the CH₂($\tilde{a}^{1}A_{1}$);(0,0,0) production and the thermodynamic values of the heat of formation of CH₂CO, CO and ground state CH₂($\tilde{X}^{3}B_{1}$). Using the values ΔH_{0} (CH₂CO) = (-10.7 ± 0.4) kcal/mole [28,29], ΔH_{0} (CO) = (-27.2 ± 0.04) kcal/mole [30] and ΔH_{0} (CH₂($\tilde{X}^{3}B_{1}$)) = (92.07 ± 1.0) kcal/ mole [31] we obtain with the threshold D_{th} = (29850 ± 100) cm⁻¹ \triangleq (85.4 ± 0.3) kcal/mole the energy separation ΔE = (3425 ± 500) cm⁻¹ or (9.8 ± 1.5) kcal/mole, where the quoted uncertainty mainly arises from the thermodynamic values*.

The recent theoretical results and also the recent photochemical results are within the limits of error in agreement with this result.

^{*} Three additional theoretical papers came to our knowledge after the formulation of this paper [32-34]. They all give values of the singlet-triplet energy separation within the above mentioned range.

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