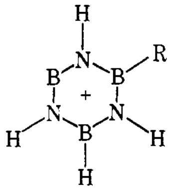
that are probably more stable are



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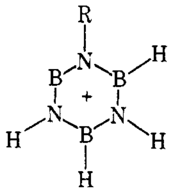
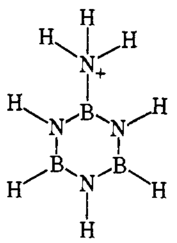


These correspond to the parent − 1 ion of the *B*-alkylborazine or *N*-alkylborazine, respectively.

The species $(NH_3)H_2B_3N_3H_3^+$ observed in the NH_3–borazine system is most probably the protonated form of *B*-monoaminoborazine formed by the reaction

$$NH_4^+ + H_3B_3N_3H_3 \longrightarrow (NH_3)H_2B_3N_3H_3^+ + H_2 \quad (8)$$

A reasonable structure for the product is



In this case it is unlikely that a proton is transferred to the borazine ring.

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Lowest Excited States of Ketene[1]

Allan H. Laufer* and Richard A. Keller*

Contribution from the National Bureau of Standards,
Washington, D. C. 20234.
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Abstract: Analysis of the vibrational progression evident in the absorption spectrum of ketene suggests the absorption is due to a singlet–singlet transition and indicates the energy of the lowest singlet state is less than 61 kcal/mol (2.65 eV) above the ground state. Reasonable singlet–triplet energy splittings place the energy of the lowest triplet at less than 55 kcal/mol (2.39 eV). This conclusion is in agreement with recent results which demonstrate that ketene quenches the triplet state of biacetyl. Attempts to directly observe the triplet state of ketene by a variety of spectroscopic methods, including gas- and liquid-phase absorption spectroscopy, oxygen enhancement techniques, and triplet ← triplet absorption spectroscopy, were unsuccessful.

Recent spectroscopic data from our laboratory in combination with a reinterpretation of the published results of other workers[2] have led us to conclude that the lowest excited singlet level of ketene is below 61 kcal/mol (2.65 eV) and the lowest triplet level is below 55 kcal/mol (2.39 eV). The values are *much* lower than the commonly accepted values[2] of E_S = 74 kcal/mol (3.21 eV) and E_T = 61 kcal/mol (2.65 eV).

Ketene has been widely used as a photochemical source of triplet and singlet methylene radicals. Recent evidence, primarily based upon product analysis and quenching data, has suggested that both spin states of methylene are formed by photolysis of ketene at all wavelengths less than 3660 Å.[3,4] Spin conservation requires the postulating of triplet ketene as the precursor to triplet methylene. Direct evidence for triplet ketene is sparse, but a spectroscopic investigation has positioned the lowest triplet state of ketene at 61 kcal/mol (2.65 eV) above the ground state.[2] Using the sensitized phosphorescence of triplet biacetyl as a test for triplet ketene, Grossman, *et al.*,[2a] observed that ketene quenched rather than enhanced emission from biacetyl.

A recent redetermination of $\Delta H_f°(CH_2CO)$ = -11.4 ± 0.4 kcal/mol,[5] together with $\Delta H_f°(CH_2) \leqslant 94$ kcal/mol,[6] and $\Delta H_f°(CO) = -27.2$ kcal/mol,[7] suggests a bond dissociation energy in the neighborhood of 78 kcal/mol (3.38 eV). This value is in agreement with the fact that only photons with energy in excess of 3.38 eV photodissociate ketene and suggests that predissociation is not important in excited states of energy less than 3.38 eV. This is in contrast to the results of Dixon and Kirby,[2b] who have suggested the triplet state of ketene is predissociated, setting an upper limit for the bond dissociation energy of ketene as 61 kcal/mol. Interest in our laboratory in the mechanism of photodissociation and the thermodynamic values of ketene has prompted us to reinvestigate the absorption spectrum of this molecule. Our studies included (a) gas- and liquid-phase absorption spectra, (b) search for absorption from metastable states following flash photolysis, and (c) investigation of the oxygen-intensification technique which is known to enhance weak singlet–triplet transitions.[8]

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[1] Work supported in part by the United States Atomic Energy Commission.

[2] (a) M. Grossman, G. P. Semeluk, and I. Unger, *Can. J. Chem.*, **47**, 3079 (1969); (b) R. N. Dixon and G. H. Kirby, *Trans. Faraday Soc.*, **62**, 1406 (1966).

[3] A. N. Strachan and D. E. Thornton, *Can. J. Chem.*, **46**, 2353 (1968), and references therein.

[4] M. A. Voisey, *Trans. Faraday Soc.*, **64**, 3058 (1968).

[5] R. L. Nuttall, A. H. Laufer, and M. V. Kilday, *J. Chem. Thermodyn.*, in press.

[6] (a) W. A. Chupka, J. Berkowitz, and K. M. A. Refaey, *J. Chem. Phys.*, **50**, 1938 (1969); (b) V. H. Dibeler, M. Krauss, R. M. Reese, and F. N. Harllee, *ibid.*, **42**, 3791 (1965).

[7] D. D. Wagman, *et al.*, NBS Technical Note 270-3, Jan 1968.

[8] D. F. Evans, *Nature (London)*, **178**, 534 (1956).

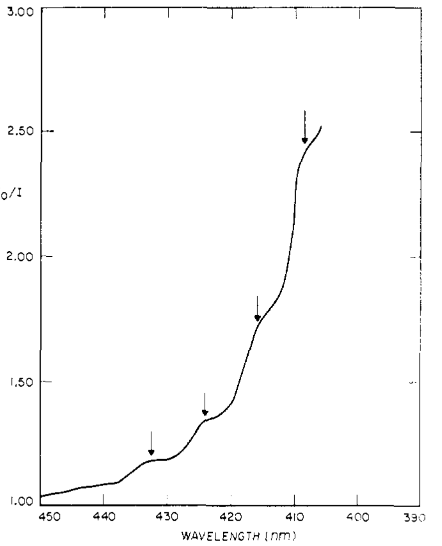

Figure 1. Absorption spectrum of ketene showing diffuse structure.

Experimental Section

Ketene was prepared by pyrolysis of acetic anhydride vapor[9] and purified as previously described.[5] Gas chromatographic analysis indicated the presence of less than 0.1% C_2H_4 and C_2H_6. A CO_2 impurity of less than 0.2% was the only other detectable impurity. The ketene was stored at −196° in the dark.

The liquid-phase absorption measurements were performed with a Cary 12[10] spectrophotometer. Ketene was distilled into the side arm of a quartz absorption cell and kept at −196°. The cell was immersed into an ethyl alcohol bath, the bottom of which had two quartz windows. The bath was cooled *via* conduction by Dry Ice to −78°. This apparatus was placed inside another chamber, also equipped with quartz windows, and evacuated to prevent condensation on the windows. Removal of the liquid N_2 trap resulted in the distillation of the ketene into the bottom of the absorption cell where it remained as a quiescent liquid. Absorption cell path lengths varied from 0.1 mm to 1.0 cm.

The gas-phase absorption spectrum of ketene in the region from 4500 to 3800 Å was measured using a multiple-pass 2-m cell.[11] Path lengths up to 48 m and ketene pressures to 55 Torr were used. The exit beam was imaged on the entrance slit of a 0.5-m scanning grating monochromator. The monochromator output was observed by a 1P28 photomultiplier and a recorder. Hg resonance lines were used to calibrate the instrument. At shorter wavelengths, a 10-cm absorption cell and pressures to 150 Torr were used in conjunction with the Cary 12.[10] At these pressures, dimerization was negligible within the time required for an experiment.

Gas-phase absorption studies using the oxygen-intensification technique were taken at room temperature with up to 100 atm of O_2 pressure in a high-pressure optical cell whose light path was 10 cm. Ketene pressures of about 150 mm were used and the spectrum was recorded on a Cary 14[10] over the wavelength region from 7500 to 3300 Å.

The 18-kV flash photolysis apparatus used to search for T ↔ T absorption has been previously described.[12] Wavelengths <3600 Å were removed by a (1 cm) solution filter of (2.0 × 10^{-6} *M*) 1,4-diphenylbutadiene-1,3 in C_2H_5OH circulated concentrically around the reaction vessel. Pressures of ketene as high as 550 Torr were used in this portion of the work.

Results and Discussion

The gas-phase absorption spectrum of ketene consists of diffuse bands superimposed upon a broad continuum. No detailed structure was observed under any experimental condition. A typical portion of the spectrum is shown in Figure 1. From data such as these, band maxima were located and differences between adjacent bands calculated. These results, along with those of other workers, are listed in Table I and plotted in Figure 2. The measured frequencies agreed quite well with previous data.[2b,13] Dixon and Kirby ob-

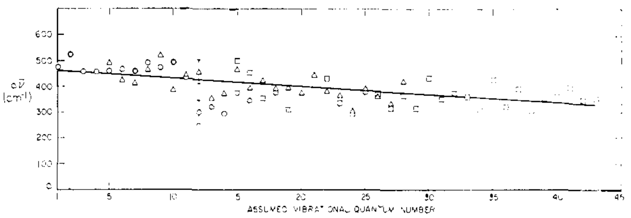

Figure 2. Vibrational spacings between adjacent bands: □, ref 2b; ○, ref 13; △, this work. For clarity, typical error bars have been shown for only two points.

Table I. Band Maxima in the Absorption Spectrum of Ketene

λ_{air}, nm			ν_{vac}, cm^{-1}	$\Delta\nu_{vac}$, cm^{-1}
a	*b*	This work		
	260.7			
	263.1			
	265.5			
	268.3			
	270.9			
	273.5			
	275.8			
	278.8			
	281.3			
	284.7			
	287.2			
	290.2			
	293.4			
	296.9			
	301.2			
	304.1	303.8	32,906	416
	307.5	307.7	32,490	335
	310.5	310.9	32,155	358
	314.1	314.4	31,797	389
	317.9	318.3	31,408	303
	320.9	321.4	31,105	364
	324.4	325.2	30,741	382
	329.0	329.3	30,359	445
		334.2	29,914	372
	338.8	338.4	29,542	396
	342.4	343.0	29,146	394
	347.4	347.7	28,752	423
	351.7	352.9	28,329	396
357.5	357.4	357.9	27,933	468
362.0	363.9	364.0	27,465	372
367.0	370.0	369.0	27,093	355
371.0		373.9	26,738	457
375.5				
379.8		380.4	26,281	449
386.2		387.0	25,832	387
393.7		392.9	25,445	521
401.2		401.1	24,924	469
409.3		408.8	24,455	412
417.2		415.8	24,043	426
425.5		423.3	23,617	491
434.0		432.3	23,126	
442.8				
452.0				
463.0				
473.5				

[a] Dixon and Kirby, ref 2. [b] Norrish, *et al.*, ref 13.

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(9) A. D. Jenkins, *J. Chem. Soc.*, 2563 (1952).

(10) Certain commercial instruments and materials are identified in this paper in order adequately to specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the instruments or materials identified are necessarily the best available for the purpose.

(11) J. U. White, *J. Opt. Soc. Amer.*, 32, 285 (1942).

(12) E. F. Zalewski and R. A. Keller, *J. Luminescence*, 1, 143 (1970).

served that the mean spacing of the bands corresponded to 475 ± 20 cm^{-1} at lower energies (lower vibrational numbers) and to 365 ± 50 cm^{-1} at higher energies. They interpreted this change in spacing as indicative of two different progressions corresponding to two different electronic transitions, singlet and triplet ketene. This alone is the only experimental evidence upon which the value of 61 kcal/mol for the energy of the lowest triplet state of ketene is based. In fact, the vibrational spacings show a *continuous* trend toward smaller spacing with decreasing wavelength. A least-squares fit of the existing data plus that of the present work also is shown as the solid line in Figure 2. Assuming that the progression belongs to a single transition, the intercept, corresponding to the mean spacing at the onset of absorption,[14] is 459 cm^{-1}, and as previously suggested,[2b] probably represents an upper-state skeletal bending vibration. The slope, −3.08, represents an effective anharmonicity constant of −1.54 cm^{-1}.

The smoothed gas-phase extinction coefficient is shown in Figure 3 along with the extinction coefficient (ϵ) for liquid-phase ketene at −78°.[15] The entire absorption spectrum shown in Figure 3 probably is the result of a transition to one excited singlet state, since there are no apparent sudden intensity changes. The low energy of this excited state indicates considerable interaction between the two double bonds. The assignment of the transition to specific orbitals, however, awaits detailed molecular orbital calculations. If these bands are truly diffuse, as indicated by Dixon and Kirby, serious doubt is cast upon the thermodynamic value for the heat of dissociation of ketene. Truly diffuse bands can only result from predissociation. However, the bands may be only apparently diffuse, resulting from an inherently complex rotational structure which is strongly coupled to a pseudo-continuum of bound electronic states. The observable onset of this transition (4735 Å) fixes the energy of the lowest singlet state as <61 kcal/mol.[16] There was no indication of a banded system over the complete liquid-phase absorption spectrum. Absorption at the long-wavelength end of the spectrum increases substantially in going from the liquid to the gas phase. This type of behavior can be attributed to the difference in temperature between the two samples.

O_2 pressures up to 100 atm had no visible effect on the observed absorption except to smooth the diffuse banded structure, and no new bands attributable to ketene on top of the continuum were observed in the region from 7500 to 3300 Å. The fact that O_2 does not enhance any portion of the observed spectrum is in agreement with our conclusion that the spectrum results from spin-allowed transitions.

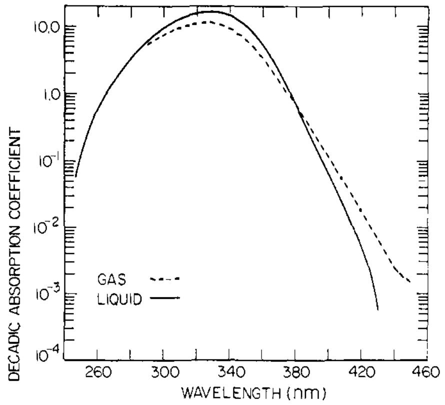

Figure 3. Absorption spectrum of ketene. Ordinate values in l. mol^{-1} cm^{-1}.

The final series of experiments involved a search for triplet–triplet absorption using flash photolysis–kinetic spectroscopy techniques. Here we searched for discrete absorption arising from metastable species in the region from 3700 to 6200 Å; none was observed under all experimental conditions. If triplet ketene was formed either through direct absorption, intersystem crossing, or collisional quenching, then its absorption is completely continuous without any evidence for discrete structure.

An estimation of the energy of the lowest triplet state can be made by observing that the separation between the lowest excited singlet state and the lowest triplet state in similar molecules is approximately 0.25 eV.[17] This would suggest that the lowest point of the ketene triplet manifold is ≦54 kcal/mol, in agreement with the observed quenching of the biacetyl triplet (55 kcal/mol[18]). The reason that direct absorption from the ground state to this triplet state was not detected, even at high O_2 pressures or in a 1-cm path of liquid ketene, is probably that the Franck–Condon-accessible region of the spectrum is at much higher energy than the 0–0 transition. This means that the $T_1 \leftarrow S_0$ absorption could easily be hiden under the $S_1 \leftarrow S_0$ absorption.

Acknowledgment. Special thanks are due Joseph J. Ball for his help in assembling the multiple-pass absorption cell and to M. Krauss and J. T. Hougen for helpful comments.

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(13) R. G. W. Norrish, H. G. Crone, and O. Saltmarsh, *J. Chem. Soc.*, 1533 (1933).

(14) There is little reason to suspect that the 0–0 band corresponds to 4735 Å (the onset of absorption),[2b] although longer wavelength absorption has not been observed.

(15) Obtaining a value for ϵ(liquid) necessitated a density measurement for which a value of 0.758 g/cm^3 at −78° was obtained. This value is probably correct to ±10%.

(16) If indeed the absorption represents a long progression to the first excited singlet state, the mirror-image relationship between absorption and fluorescence would dictate that the peak of the fluorescence emission curve would occur around 7000 Å. Fluorescence has never been reported from this molecule, perhaps because it was never searched for in this spectral region. See also R. Holroyd, Ph.D. Thesis, University of Rochester, 1955.

(17) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969.

(18) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964).