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Gas Phase Absorption Spectrum and Cross Sections of Vinylperoxy ($C_2H_3O_2$) Radical

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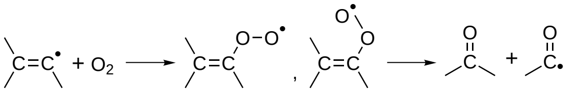
The absorption spectrum and cross sections of vinylperoxy ($C_2H_3O_2$, ethenylperoxy) radical have been determined, for the first time in the gas phase, in the spectral range 220−550 nm. The spectrum exhibits a relatively broad and intense absorption centered at about 232 nm, followed by at least two identifiable and weaker absorptions with maxima at about 340 and 420 nm. The absorption tail persists at longer wavelengths into the visible region. To discern competition between the stabilization of the vinylperoxy isomers and reaction, the effect of pressure on the absorption has been examined. Vinylperoxy radicals in these experiments were produced through photochemical production of vinyl radicals followed by reaction of vinyl radicals with molecular oxygen. Vinyl bromide (C_2H_3Br) photolyzed at 193 nm was used as the precursor of vinyl radicals, and methyl vinyl ketone ($CH_3COC_2H_3$) photolyzed at 193 nm was used as a precursor of both methyl and vinyl radicals. In the latter system identical concentrations of methyl and vinyl peroxy radicals were produced, and by employing comparative methods and using the literature values for methylperoxy absorption cross sections, the absolute absorption cross sections for vinylperoxy were determined. *Ab initio* molecular orbital calculations of CH_3O_2, $C_2H_3O_2$, C_2H_3O, and HCO have been employed to characterize the observed spectrum and to identify the species and assign transitions contributing to the spectrum. These calculations suggest that the observed spectrum can primarily be assigned to two stable isomers (conformations) of the vinylperoxy radical with the O−O bond in a *cis* or *trans* position relative to the C−C bond, with a minor contribution to the absorption spectrum from the vinoxy and formyl radicals. For unsaturated radicals and the weak bonds involved here, accurate geometries are difficult to calculate, but the geometry obtained by gradient optimization using the multiconfiguration self-consistent-field method yields excitation energies that most closely agree with experiment. The relative theoretical oscillator strengths of all relevant vinylperoxy and vinoxy transitions have been evaluated and assist the analysis of the pressure dependence of the absorption spectrum.

I. Introduction

Hydrocarbon peroxy radicals are important species and play major roles in a variety of systems. For example, the small peroxy radicals are known to be important in hydrocarbon oxidation systems, but the vinylperoxy species is unique in that it also has been directly involved in both the identification and study of the parent vinyl radical itself. Several studies of the kinetics and chemistry associated with unsaturated vinyl radical have been accomplished.[1−3] Its reaction with O_2 is one such study.[3]

The reaction between vinyl and O_2 appears to be deceptively simple. The mechanism, initially proposed by Baldwin and Walker[4] to produce HCO and H_2CO in an exothermic reaction, subsequently was confirmed experimentally.[3] The true complexity of the reaction, however, was suggested initially through a quantum RRKM calculation[5] in which a variety of intermediates were proposed.

Recent *ab initio* calculations[6] suggest an extraordinarily complex reactive potential energy surface involving a host of intermediates. Most recently, higher order *ab initio* calculations[7] indicate that as many as 40 separate transition states may be identified on the potential surface. The reaction of C_2H_3 with O_2 is predicted to begin[8] through the formation of a vinylperoxy radical, $C_2H_3O_2$, that may exist in two stable configurations of similar energy:[8] a *trans* and a *cis* form so labeled depending upon the O−O bond geometry with respect to the C−C bond. These isomeric forms are true minima on the potential surface and do not interconvert readily as they are separated by a calculated potential energy barrier of 25.5 kJ/mol.[7]



(1)

When initially formed, the peroxy radical isomers are highly vibrationally excited, and theoretical predictions[7] and recent experiments[9] have noted that, at low pressures and high temperatures, the channel yielding the vinoxy radical and the oxygen atom dominates. At low pressure, the initial internal

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energy of the peroxy radicals obtained in the formation of the C−O bond is not deactivated rapidly enough to stabilize the peroxy radicals with respect to dissociation. Examination of the spectra of the reaction products must therefore consider possible contributions from the two main reaction channels as well as the peroxy radical isomers.

Saturated alkylperoxy radicals generally exhibit a single broad absorption in the near ultraviolet around 235 nm.[10] In contrast, the lowest energy transitions of the intermediate *cis* and *trans* form of the unsaturated vinylperoxy species have been predicted to lie in the visible or near UV regions at about 430 and 383 nm, as a result of the bond conjugation.[11] Solution phase spectra assignable to the $C_2H_3O_2$ radical have been observed in the near ultraviolet and visible regions with broad features centered around 270[12] and 440 nm[12,13] but which are too broad to discern structural information. The observed broad and convoluted solution phase absorption around 440 nm is shifted from those around 383 and 430 nm predicted theoretically *in vacuo*[11] because the excited state is much more polar than the ground state. Substantial charge is transferred during the transition. The energetics and polarity of the UV transition will be examined here.

Only two of the reaction products, vinoxy and formaldehyde, are known to have absorptions that overlap the experimental region. In addition, the hydrocarbon flame bands of HCO are known to extend to beyond 460 nm.[14] Visible transitions have been observed for HCO and are assigned to the ground state $A'(1)$ excitation to $A''(1)$. The latter state is essentially linear in its equilibrium geometry, and absorption bands have been observed from 460 to 860 nm. The far UV absorptions of H_2CO and HCO are to shorter wavelengths below 200 nm, and the absorption of H_2CO in the near ultraviolet with a maximum around 295 nm is not particularly strong.[15] Emission spectra[14] do result from substantial changes in the excited state conformations in both molecules, but that is not relevant here. A number of theoretical predictions of the geometries and excitation energies of the formyl[16] and vinoxy radicals[17−19] have been made that support the experimental observations regarding the structures and absorptions[20,21] but also add considerable detail regarding the shapes of the excited energy surfaces.

In the work reported here the absorption spectrum of vinylperoxy radical was observed in the gas phase. Comparisons of the observed spectra with *ab initio* predictions for both the *cis* and *trans* isomers of vinylperoxy permit assignment of the electronic spectra. The degree of confidence that may be placed upon high-level *ab initio* calculations of open-shell structures and energies is tested in this study. Such calculations for radicals are now increasingly possible[2,11] but still difficult, particularly for unsaturated radicals. The calculated structures, for example, are found to differ between high-level calculations using different electron correlation methods. For the ground states, where the energy varies slowly with geometry, this is not necessarily significant. But for systems with strongly repulsive excited state potential surfaces due to adiabatic correlations that lead to asymptotic degenerate states, small differences in ground state conformations can lead to widely varying absorption predictions. Experimental comparisons are critical to evaluate the accuracy of theoretical predictions, but these predictions provide the pattern of the absorptions and even the appropriate wavelength region important in any assignment.

IIa. Experimental Procedures

The ultraviolet absorption spectra for transient species were obtained employing excimer laser photolysis coupled with UV absorption spectroscopy, a method which has previously been described in detail.[22,23] A brief summary of the experimental method used for these studies is given here.

The output of the excimer laser was expanded by a cylindrical lens and filled the cell side-on through a 2 cm × 10 cm Suprasil[24] flat with minimal variation in light intensity over the cell length. The monitoring light from a 75 W xenon arc lamp was rendered nearly parallel using a condenser and two long focal length lenses. The monitoring light passed through the cylindrical reaction cell, traversed the cell four times, by use of White optics, was deflected by a prism, and focused onto the slit of a monochromator. The photomultiplier signal from the monochromator was fed into a multi-timebase waveform digitizer through a differential comparator. Following pulsed production of the transient absorber, the transient absorption signal was read by the digitizer and then by a computer. At any selected wavelength, up to 300 real-time absorption signals were averaged into the memory. The 0.3 m monochromator was equipped with a 2400 grooves/mm grating blazed at 300 nm. When operated in first order, using slits of 50−75 μm, it was capable of 0.1 nm resolution. For the spectroscopic determinations the maximum absorbances at selected wavelengths, typically in 5 or 10 nm intervals, were determined from the real-time absorption signals. The spectrum was obtained by plotting the maximum absorbance from such absorption signals versus the wavelength. The uncertainties of the absorbance measurements are typically within about 5% in the region of high absorptivity and about 10% in the region of low absorptivity. Total flow rates of about 1.0 l min^{-1} (STP) were used, sufficient to purge the cell contents between each laser pulse at a repetition rate of 0.5 Hz. All the absorption measurements were performed at an ambient temperature of about 298 K.

Vinyl radicals were generated photolytically through 193 nm photolysis of mixtures of either vinyl bromide (C_2H_3Br) or methyl vinyl ketone ($CH_3COC_2H_3$). In the latter photochemical system identical concentrations of methyl and vinyl radicals were simultaneously produced,[25] from which, following reactions with excess oxygen, the corresponding peroxy radicals were generated. The photoreactive cell was operated in continuous flow mode with gases regulated by calibrated mass flow controllers, and the total pressure was controlled and measured with a capacitance manometer. Reagent concentrations were calculated from the total pressure and the calibrated flows. The effect of pressure on the absorption spectra was obtained by adding N_2 to the precursor mixture. Most experiments were performed with low concentrations of vinyl radical precursor in the presence of about 1.33 kPa (10 Torr) O_2. In the experiments involving higher pressure, up to about 6.65 kPa (50 Torr) N_2 was added to the precursor and O_2 mixtures.

As a calibration experiment, the absorption spectrum of methylperoxy radical (CH_3O_2) in the range 220−400 nm was obtained using our apparatus. In these experiments methyl radicals were produced from 193 nm photolysis of acetone. Methyl radicals were then reacted with excess molecular oxygen, yielding the peroxy radical. The observed spectrum attributed to the methylperoxy radical exhibits a broad and strong absorption between 220 and 300 nm with a maximum absorption cross section of about $(4.6 \pm 0.3) \times 10^{-20}$ cm^2 molecule^{-1} at 245 nm. The methylperoxy spectrum and cross sections have previously been reported and critically reviewed by Wallington et al.[10a] and Lightfoot et al.,[10b] who recommend a cross section of 4.4×10^{-20} and 4.6×10^{-20} cm^2 molecule^{-1} at 240 nm, respectively.

In initial experiments involving vinyl radicals it was ascertained that the observed absorption was, in fact, due to a transient species requiring the presence of O_2 and not arising from the vinyl radicals, whose spectra have been previously reported in the visible[26] and in the vacuum ultraviolet.[2a]

IIb. Theoretical Methods

Theoretical analysis of the electronic structure, geometry, and excitation energies of radicals requires consideration of the electron correlation. Theoretical calculations of the CH_3O_2, $C_2H_3O_2$, C_2H_3O, and HCO radicals were performed at the MCSCF level to provide energetics and oscillator strengths calculated at the same level of accuracy for all these systems. A useful analysis of the electronic structure and electronic spectra of the vinylperoxy radical was obtained[11] using the complete active space self-consistent-field (CAS-MCSCF) method as implemented within the GAMESS code.[27] Optimized structures are generated for both ground and excited states with analytic gradients at the MCSCF level, and relevant structures are presented in Table 1. All structures for the vinylperoxy were reported earlier[11] but are tabulated for convenience in comparing properties of the different molecules. The core orbitals are replaced by compact effective potentials used with the concomitant CEP-31G basis.[28] Polarization functions are added to only the heavy atoms. Diffuse functions have a slight effect only on the energies of states in the far UV region. Addition of diffuse s and p functions to the basis for methylperoxy lowers the excitation energy by about 1000 cm^{-1} at 231.3 nm or a shift of 5 nm in the predicted wavelength. Since the half-width at half-maximum intensity for these absorptions is about 50 nm, the neglect of the diffuse functions is warranted in this assignment.

The active space for the MCSCF wave function for the vinylperoxy radical used for the excitation energies was described earlier[11] and adds three valence orbitals to the seven doubly occupied and one singly occupied Hartree–Fock orbitals to distribute 15 electrons among 11 orbitals in the CAS wave function. For the other radicals, three valence orbitals and one open-shell orbital were used in all cases in the active space together with six doubly occupied for methylperoxy but only five for the vinoxy and formyl radicals. The active space for methylperoxy then distributes 13 electrons among 10 orbitals and the vinoxy and formyl radicals distribute 11 electrons among 9 orbitals. These active spaces allow for antibonding σ as well as π orbitals. Although the σ^* orbitals have relatively small natural orbital coefficients, they are necessary to self-consistently interact with the delocalized π orbitals. As a result, bond distances will be a little larger for these MCSCF optimizations than those done with the much smaller active space of five electrons in four orbitals used in all previous studies.[16–19] This is illustrated in Table 1. For methylperoxy only Hartree–Fock (ROHF) and perturbation (MP2) structures have been reported.[8] The excitation energies are obtained by MCSCF calculations based on averaging the second-order density matrices for the relevant states. In the previous work, the relevant transitions were between the ground state, A″(1), and the excited, A″(2), state. Hence, the weighting of the two states was made equal. We are now concerned as well about the absorption to the A″(3) state which is assigned to the far UV transition, so the weight between the ground and excited states is made equal or 0.5 to the ground and 0.25 to each excited state. As a result the energies of the first two excited states will not agree exactly with those reported earlier with a shift of around 500 cm^{-1} in the first excitation energy. In the various MCSCF calculations described here the smallest natural orbital coefficient never exceeds 0.02, showing that the orbital expansion is convergent and describes the ground and excited states well. The smallest natural orbital coefficient obtained for the methylperoxy, for example, is 0.015.

TABLE 1: Geometry of Ground and Excited States of CH_3O_2, $C_2H_3O_2$, C_2H_3O, and HCO

CH_3O_2

	ROHF XA″(1)	MP2 X	MCSCF X	MCSCF A″(2)
C−O	1.426	1.453	1.477	1.433
O−O	1.318	1.312	1.373	1.726
C−H	1.089	1.089	1.087	1.093
H−C−H	110.5	111.0	111.2	107.7, 113.3
H−C−O	110.0	108.9	109.3	106.7
H1−C−O	105.4	105.1	104.5	108.7
C−O−O	110.4	110.2	108.2	100.8

$C_2H_3O_2$, *trans*

	MCSCF[a] XA″(1)	MCSCF[a] A″(2)
C−C	1.363	1.432
C−O	1.388	1.273
O−O	1.369	1.739
C1−H	1.081	1.080
C2−H	1.077	1.081
H−C1−C2	119.0	119.2
C1−C2−H	127.1	121.7
C1−C2−O	118.8	120.5
C2−O−O	110.7	104.7

C_2H_3O

	XA″(1)	A″(2)	X(17)[b]	X(18)	X(19)	exp X(20)	exp X(21)
C1−C2	1.475	1.457	1.405	1.442	1.445	1.405[c]	1.408[c]
C2−O	1.250	1.422	1.275	1.227	1.226	1.272	1.261
C1−H	1.082	1.080					
C2−H	1.099	1.082					
H−C1−H	119.8	120.1					
H−C1−C2	120.8	119.5					
C1−C2−O	123.2	121.9	122.9	122	122.8	121.9	122.4
H−C2−O	120.5	115.9					

HCO

	XA′(1)	A′(2)	X(15)[b]	X(15) exp
C−O	1.209	1.409	1.178	1.175
H−C	1.123	1.146	1.094	1.125
H−C−O	125.2	104.8	124.9	124.9

[a] Reported in ref 11. [b] Reference number is given in parentheses. [c] C−C distance was constrained in experimental analysis to early theoretical value.

III. Results and Discussion

(a) 193 nm Photolysis of $C_2H_3Br/O_2/N_2$ Mixtures: $C_2H_3O_2$ Absorption Spectrum. The laser photolysis–UV absorption spectroscopic experiments were performed to produce vinylperoxy radical and to characterize its absorption spectrum in the spectral range 220–550 nm. In these experiments vinyl radicals were generated initially from 193 nm excimer laser photolysis of mixtures of $C_2H_3Br/O_2/N_2$. The subsequent reaction of vinyl radicals with excess molecular oxygen produced vinylperoxy radicals through the following reaction sequence:[9]

$$C_2H_3Br \xrightarrow{193\ \text{nm}} C_2H_3 + Br \qquad (2)$$

$$C_2H_3 + O_2 \xrightarrow{N_2} C_2H_3O_2 \qquad (3)$$

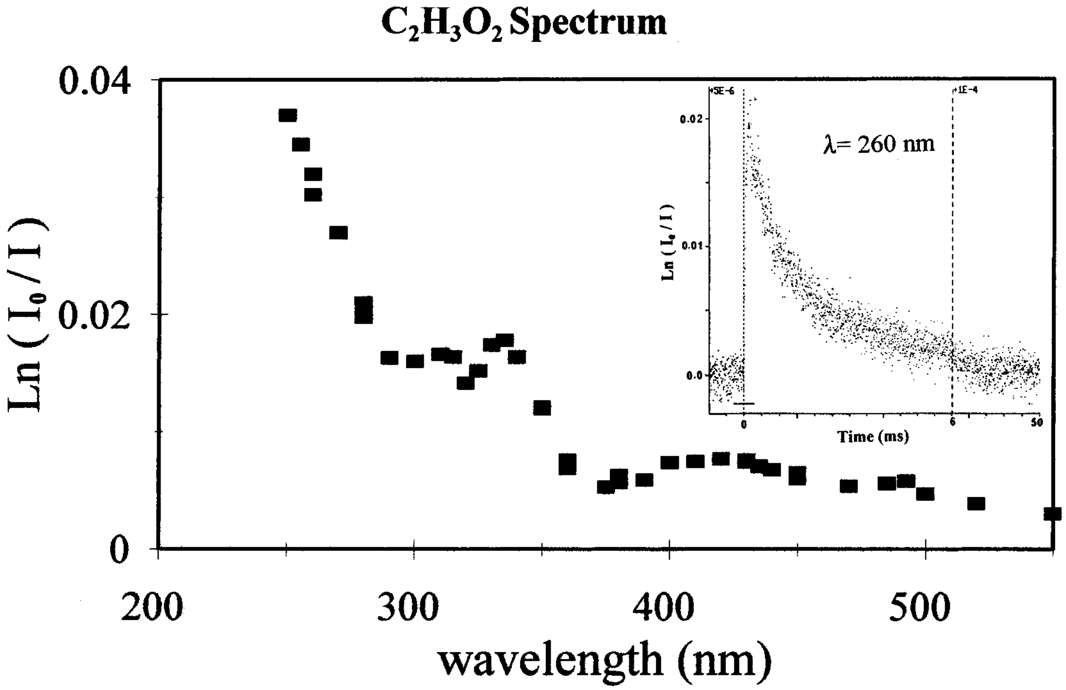

Figure 1. Spectrum derived following the 193 nm photolysis of $C_2H_3Br/O_2/N_2$ mixtures with concentrations of $(5 \times 10^{16})/(1 \times 10^{18})/(1.5 \times 10^{18})$ molecule cm^{-3}, respectively, and a total pressure of about 9.3 kPa (70 Torr). The inset is an example of the real-time absorption signal.

Initial experiments ascertained that the observed absorption was, in fact, due to a transient species requiring the presence of O_2 and not arising from the vinyl bromide, whose absorption has been previously reported, nor to vinyl radicals, whose spectra have been reported in the visible[26] and in the vacuum ultraviolet.[2a] A wide spectral range, in the ultraviolet region, was surveyed for detection of the absorption spectra of vinylperoxy radical and any reaction products. Initial investigations indicated a relatively strong transient absorption at about 230 nm. Real-time absorption signals were then obtained at various wavelengths, in the range 220−550 nm, for flowing mixtures of $C_2H_3Br/O_2/N_2$. The variation of the maximum absorbance (ln I_0/I) was determined as a function of wavelength derived from the real-time absorption signals for mixtures with identical sample composition and pressure. Figure 1 displays the derived spectrum in the wavelength range 220−550 nm. An example of the real-time UV absorption signal is also shown in the inset of Figure 1. Table 2 lists the absorbance versus the wavelength and experimental conditions for these spectral determinations.

The spectrum for vinylperoxy radical exhibits a relatively broad and intense absorption between about 220 and 250 nm, with a maximum at about 230 nm, followed by at least two identifiable and weaker absorptions at about 335 and 420 nm. The tail of the vinylperoxy absorption, in contrast to that of methylperoxy, continues to longer wavelengths and even extends into the visible region. Since absolute absorption cross sections could not be determined from these experiments, alternate approaches were designed and performed to compare the vinylperoxy absorption with that of the known methylperoxy spectrum; thus cross sections for vinylperoxy were estimated.

TABLE 2: Absorbances Following the 193 nm Photolysis of $C_2H_3Br/O_2/N_2$ Mixtures

λ (nm)	ln(I_0/I)	λ (nm)	ln(I_0/I)
230	0.0443	335	0.0178
235	0.0446	340	0.0164
240	0.0425	350	0.0121
245	0.0374	360	0.0076
245	0.0383 ± 0.003[a]	375	0.0053
247.5	0.0363	380	0.0057
250	0.0370	390	0.0059
255	0.0345	400	0.0074
260	0.0302	410	0.0075
270	0.0270	420	0.0077
275	0.0220	430	0.00745
280	0.0184	435	0.00705
280	0.0198	440	0.0068 ± 0.0005[a]
285	0.0175	450	0.0060
290	0.0163	470	0.0054
300	0.0160	485	0.0056
310	0.0161	492.5	0.0058
320	0.0142	500	0.0047
325	0.0152	520	0.0039
330	0.0174	550	0.0031

[a] The uncertainties of the absorbance measurements are typically within about 5% in the region of high absorptivity and about 10% in the region of low absorptivity.

(b) 193 nm Laser Photolysis of $CH_3COC_2H_3/O_2/N_2$ Mixtures: Absorption Cross Sections of $C_2H_3O_2$. Flowing mixtures of methyl vinyl ketone, $CH_3COC_2H_3$, O_2, and N_2 were photolyzed at 193 nm. It has previously been established that 193 nm photolysis of methyl vinyl ketone yields nearly identical concentrations of methyl and vinyl radicals.[22] Rate constants for the reaction of both vinyl[9] and methyl[29] with oxygen are comparable and fast, on the order of 10^{-11} to 10^{-12} cm^3 molecule^{-1} s^{-1}, and therefore titration of methyl and vinyl radicals with excess oxygen would yield nearly identical concentrations of methylperoxy and vinylperoxy radicals through the following reaction sequences:

$$CH_3COC_2H_3 \xrightarrow{193\ \text{nm}} CH_3 + C_2H_3 + CO \qquad (4)$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \qquad (5)$$

$$C_2H_3 + O_2 + M \rightarrow C_2H_3O_2 + M \qquad (3)$$

Composite, real-time absorption signals were obtained in the spectral range from 220 to about 550 nm. The variation of the maximum absorbance with wavelength for mixtures with identical sample composition and pressure was determined and resulted in the spectrum shown in Figure 2. This spectrum is

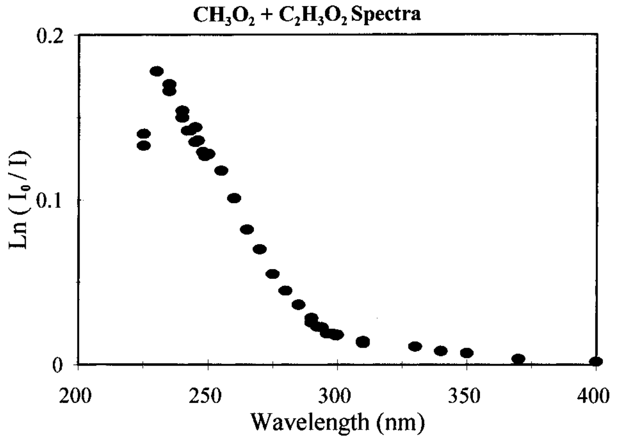

Figure 2. Spectrum derived following the 193 nm photolysis of $CH_3O_2C_2H_3/O_2/N_2$ mixtures with concentrations of about (2 × 10^{16})/(1 × 10^{18})/(1.2 × 10^{18}) molecule cm^{-3} and a total pressure of about 9.1 kPa (68 Torr).

a composite and represents the sum of the absorptions by both CH_3O_2 and $C_2H_3O_2$ radicals with nearly identical concentrations of each. As mentioned earlier, the methylperoxy radical has no significant absorption beyond about 300 nm so that the observed absorption at longer wavelengths, as also seen from results presented in Figure 1, is characteristic of the vinyl/oxygen system. Therefore we can assign the longer wavelength portion of the composite absorption (Figure 2) primarily to the products of the vinyl and molecular oxygen combination reaction with overlapping spectra from vinoxy and vinylperoxy radicals. The pressure dependence of the spectra can be used to distinguish contributions of these radicals to the observed spectrum.

In addition, the contribution of the vinylperoxy absorption to the composite spectra, at wavelengths shorter than about 300 nm, can be evaluated and extrapolated by using the relative absorptions at the short wavelengths ($\lambda < 300$ nm) and long wavelength (here, $\lambda = 420$ nm) using the pure vinylperoxy reaction system (Figure 1 and Table 1). Subtracting the vinylperoxy component of the composite absorption spectrum yields the methylperoxy contribution. Since the concentrations of methylperoxy and vinylperoxy radicals are identical, application of the literature values for methylperoxy absorption cross sections[10] as well as the relative absorption intensities for the two peroxy radicals permits an estimation of the absolute absorption cross sections of vinylperoxy. The vinylperoxy contribution to the composite spectrum at wavelengths shorter than about 300 nm was determined relative to its absorption at 420 nm. Results of this analysis are presented in Figure 3 and Table 3.

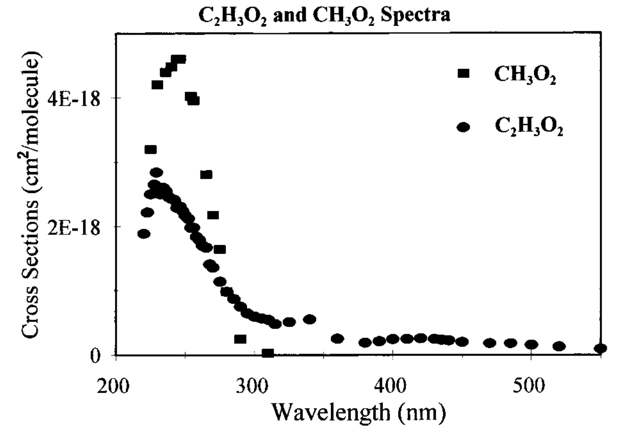

Figure 3. Absorption cross sections of CH_3O_2 and $C_2H_3O_2$ determined through a comparative procedure described in the text.

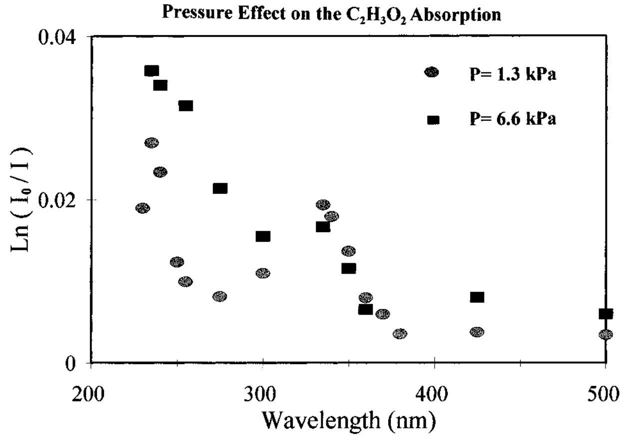

Figure 4. Pressure dependence of the spectra obtained following the 193 nm photolysis of $C_2H_3Br/O_2/N_2$ mixtures with concentrations of C_2H_3Br/O_2 ~(1 × 10^{16})/(3 × 10^{17}) molecule cm^{-3} and a total pressure of 1.33 kPa (10 Torr) and 6.65 kPa (50 Torr).

TABLE 3: Absorption Cross Sections (σ, 10^{-18} cm^2 molecule^{-1}) of $C_2H_3O_2$ and CH_3O_2 at Selected Wavelengths

λ (nm)	$\sigma(C_2H_3O_2)$	$\sigma(CH_3O_2)$	λ (nm)	$\sigma(C_2H_3O_2)$
220	1.90			
225	2.51	3.2	315	0.49
230	2.56	4.2	325	0.52
236	2.56	4.4	340	0.56
240	2.44	4.5 ± 0.3	360	0.26
245	2.30	4.6	380	0.20
250	2.18		390	0.20
255	1.99	3.9	400	0.26
260	1.80		420	0.26
265	1.68	2.8	430	0.25
270	1.37	2.2	435	0.24
275	1.15	1.6	440	0.23 ± 0.02
280	0.99	1.0	450	0.20
285	0.87		470	0.18
290	0.76	0.25	485	0.18
295	0.65		500	0.16
300	0.61		520	0.13
310	0.55	0.03	550	0.10

(c) Pressure Dependence of the $C_2H_3O_2$ Absorption Spectrum. The reaction between C_2H_3 and O_2 to form the vinylperoxy species is exothermic by about 167 kJ/mol,[30] while the C−O bond requires only about 125.5 kJ for dissociation[7] to vinoxy plus an O atom. Although the *cis*- and *trans*-peroxy conformers are true minima on the potential energy surface, the initial excess reaction energy exceeds the barrier to reaction to both the formaldehyde and vinoxy channels. To discern competition between the stabilization of the peroxy isomers and reaction, the effect of pressure on the absorption was examined. In a series of experiments mixtures of C_2H_3Br, O_2, and N_2 were photolyzed at 193 nm. Partial pressures of C_2H_3Br and O_2 were kept constant, and N_2 pressure was varied such that total pressures of 1.3 and 6.7 kPa were achieved. The spectra obtained at two pressures are shown in Figure 4. It is seen that the feature at about 335 nm is not affected by an increase in inert gas pressure, while that at about 420 nm indicates a strengthening of the absorption, i.e., a stabilization of the transient intermediate due to a quenching of the excess reaction energy. The absence of a pressure effect at 335 nm also may be representative of the competition in that both suggested products exhibit absorption in this region. Vinoxy radical absorbs in a broad band to the red of 300 nm,[31,32] and the weak absorption of HCHO is between 290 and 355 nm.[15] The spectral resolution in this type of experiment is not sufficient to observe structure that would allow assignment of the pressure-stabilized absorption at 335 nm to a particular species. The results,

TABLE 4: Excitation Energies, Dipole Moments, and Oscillator Strengths

ground state^a	excited states^a		
	$C_2H_3O_2$		
A″(1)	A″(2)	A″(3)	
trans			
-44.07172^a, 2.41^b	376.1^c, 4.43^b, 0.016^d	238.5^c, 3.26^b, 0.056^d	
cis			
-44.07078^a, 2.48^b	417.1^c, 3.85^b, 0.021^d	228.2^c, 3.89^b, 0.093^d	
	C_2H_3O		
A″(1)	A′(1)	A″(2)	A′(2)
-28.46973^a, 2.90^b	586.7^c, 1.22^b, 0.0002^d	274.4^c, 0.92^b, 0.0067^d	205.7^c, 1.40^b, 0.0002^c
	CH_3O_2		
A″(1)	A″(2)		
ROHF			
$-$, 2.47^b	$207.9,^c$ $-$, 0.060^d		
MP2			
$-$, 2.54	204.0, $-$, 0.060		
MCSCF			
-38.61125^a, 2.76^b	231.3^c, 4.49^b, 0.048^d		
	HCO		
A′(1)	A″(1)	A′(2)	
-21.76542^a, 1.68^b	520.8^c, 1.88^b, 0.0025^d	202.7^c, 1.24^b, 0.0025^d	

^{a} Ground state total energy in au. ^{b} Dipole moment in D. ^{c} Excitation energy or wavelength in nm. ^{d} Oscillator strength for transitions.

however, do suggest that the absorption at 335 nm involves primarily reaction products formaldehyde and vinoxy as well as the *trans* isomer of vinylperoxy.

IV. Theoretical Predictions and Spectral Analysis

The pressure dependence of the spectrum suggests that more than one species contributes to the observed absorption. In order to assign the overlapped absorption bands, theoretical predictions of the excitation energies are required. The calculated energies and dipole oscillator strengths of methylperoxy, vinylperoxy, vinoxy, and formyl are given in Table 4. The known experimental absorptions for the expected reaction products, vinoxy, formyl, and formaldehyde, were compared with theoretical predictions of the absorption wavelengths together with their relative oscillator strengths to assign the observed absorptions.

Ab initio molecular orbital calculations have previously been employed to predict that the first excited state of the isomers of vinylperoxy is in a substantially different region of the spectrum than the first excited state of methylperoxy. In addition, the calculation suggested that the absorption peaks in the near UV can be assigned to two stable conformers of vinylperoxy radical with the O−O bond in the *cis* or *trans* position relative to the carbon−carbon bond. The far UV absorption peaks around 230 nm can only be assigned to the vinylperoxy from the available candidates. Vinoxy, formyl, and formaldehyde all have observed or predicted absorptions much further to the blue around 200−205 nm. In addition, the MCSCF calculations also find the oscillator strengths to these far UV transitions for formyl and vinoxy to be much smaller than the peroxy transitions at 230 nm. The vinylperoxy oscillator strengths range from 0.06 to 0.09, while the oscillator strength is 0.0025 for formyl and an order of magnitude smaller at 0.000 21 for vinoxy. The transition observed with a peak at 230 nm is assigned to a convoluted overlap of the *trans* and *cis* isomers of the vinylperoxy radical. The peak area increases substantially as the pressure increases by a factor of about 5, suggesting that at the higher pressure the vinylperoxy is stabilized as discussed above. This UV transition is assigned to the A″(3) state. The excitation energy to A″(3) is also different for the two isomers, as it was for A″(2), but now the *trans* is lower while the *cis* is higher in energy. Since the transition to A″(3) is to a state whose energy rapidly decreases as the O−O distance increases, small variations in the calculated ground state equilibrium geometry can have substantial effects on the calculated excitation energy. The rapid variation of energy with geometry also leads to a large Franck−Condon progression and a broad absorption band that will encompass both the *cis* and *trans* absorptions even though they are calculated to be separated about 1300 cm^{-1} in energy.[11] At the longer wavelengths this energy separation is more easily resolved, and the isomers can be observed separately in the transition to A″(2). Large variation in the excited state energies with variation of the C−O or O−O distances is also found for the formyl and vinoxy radical and is likely to be a general characteristic of radicals with weak bonds and degenerate asymptotes.

The ground state geometries obtained at the MCSCF level were used to obtain the excitation energy to the A″(3) state of vinylperoxy with good accuracy. This state has been shown to be repulsive, and its energy, to vary rapidly with the O−O distance. The A″(2) state in methylperoxy is also likely to be a repulsive state. As Table 4 shows, the excitation energy calculated at the restricted open-shell Hartree−Fock (ROHF) and second-order perturbation (MP2) levels yields geometries that do not produce accurate excitation energies, but the MCSCF geometry with the larger O−O bond does. The MCSCF geometries for the vinoxy radical are in reasonable agreement with previous calculations and predict an absorption around 206 nm, which is to the blue of the experimental absorption peak. The MCSCF method is appropriate for the calculation of the excited states of these radicals.

The present calculations of the geometries for the formyl and vinoxy radical essentially agree with previous calculations,[16−19] as seen from comparisons in Table 1. However, the small active space used in previous calculations does not incorporate σ antibonding interactions, so the present C−O and C−C distances are about 0.03 Å larger than the results reported earlier with comparable DZP basis sets.[18,19] Experimental analysis had to fix one distance to a calculated value and does not offer a firm comparison.[20,21]

The adiabatic energy difference calculated between A″(1) and A″(2) is 30 300 cm^{-1} in the vinoxy, which has to be compared with a broad maximum at slightly higher energy.[28] The adiabatic excitation energy between the A″(1) and A′(1) states is calculated to be 10 715 cm^{-1}, which is higher than the experimental[28] value of about 8000 cm^{-1}. However, this band is also a very broad transition, with the vertical excitation energy calculated to be 17 040 cm^{-1}. The absorption peaks are not easy to define precisely and we believe the calculations describe the experimental observations to a reasonable accuracy.

The theoretical analysis of the methylperoxy at the MCSCF level has not been presented before and shows again that the geometry for molecules with weak bonds and, ultimately, the excitation energy are sensitive to the level of the calculation. Only structures at the ROHF or MP2 levels have been presented before,[8,33] and these are not adequate to determine the electronic behavior of the peroxy bond. Analysis of the radical geometries is required to interpret the absorption profile. In the lowest energy conformation of the methylperoxy ground and excited states, the $C-O_1-O_2$ bonds define a plane that bifurcates two C−H bonds and mirrors the other. The O_2 atom is directed away from the H atoms. Optimizing the geometry of the A″(2) excited state of methylperoxy shows why the Franck−Condon envelope is so broad. The O−O equilibrium bond length in the excited A″(2) state increases to 1.726 Å from 1.373 Å in the ground state, while the C−O bond distance decreases by about 0.04 Å. There is a much lower A′(1) excited state which is calculated to be only 6585 cm^{-1} above the ground state at the ground state geometry.

Similar increases for the O−O bond distances in the vinylperoxy excited states were determined earlier as well as the observation of surface crossings between excited states that lead to photodissociation in vinylperoxy.[34] For the A″(2) state of vinylperoxy, the O−O bond lengthens to 1.739 Å for the optimized structure restrained to be planar. Relaxing this constraint leads ultimately to energy surface crossings between excited states and dissociation into low-lying or ground state channels.

The increase in the absorption around 225 nm with increasing pressure indicates that absorption due to vinoxy and formaldehyde is being replaced at higher pressure with that arising from the vinylperoxy species. Although the *trans* is slightly more stable than the *cis* isomer, the two are likely to be produced in comparable amounts, indicating a substantial amount of vinoxy and formaldehyde is still present at the higher pressure. The predicted theoretical value of the oscillator strength for vinoxy around 225 nm is 0.0002, and that for formaldehyde is 0.0025. These are very much smaller than the values for vinylperoxy. Around 300 nm the oscillator strength predicted for vinoxy is 0.0067, which exceeds the observed value of 0.0018.[28] The predicted values of the oscillator strengths for the *trans*- and *cis*-vinylperoxy are 0.016 and 0.021, respectively, but at much higher wavelengths. This is suggestive that there are substantial dissociation products contributing in the 300 nm range and the peroxy is still dissociating even at the higher pressures.

At longer wavelengths, a weak but extensive tail is observed that apparently extends beyond 550 nm. This absorption is attributed to HCO, which has a well-known absorption in this region. The absorption is calculated to have a peak around 520 nm and connects the two electronic surfaces that arise from splitting the linear state of HCO upon bending. Optimization of this excited state equilibrium geometry permits an estimate of the adiabatic excitation energy of 837 nm, which is in reasonable accord with the limit of the observed spectrum.

Although the peak around 320 nm is a convolution of the vinoxy, formaldehyde, and *trans*-peroxyl absorptions, it is already obvious that the gas phase peaks around 230 and 420 nm are in reasonable agreement with the theoretical prediction for absorption by vinylperoxy. The 230 nm peak is a convolution of the broad absorptions of the *cis* and *trans* isomers, which are predicted to absorb at 228 and 239 nm, respectively, while 420 nm uniquely corresponds to the *cis* isomer absorption. The dipole moments of both the A″(2) and A″(3) excited states increase substantially over the respective isomeric ground states, leading to a large red shift in water which is observed experimentally.[12,13] A large red shift would be predicted for methylperoxy as well since there is a comparable increase in the excited state dipole moment, as seen in Table 4.

V. Conclusions

The absorption spectrum and cross sections of vinylperoxy ($C_2H_3O_2$) radicals, in the gas phase, have been determined in the spectral range 220−550 nm by employing excimer laser photolysis−UV absorption spectroscopy. Vinylperoxy radicals were produced from reaction of vinyl radicals with molecular oxygen. The composite absorption spectrum for methylperoxy plus vinylperoxy radicals obtained from the 193 nm photolysis of $CH_3COC_2H_3/O_2/N_2$ mixtures was used to determine the absolute absorption cross sections for vinylperoxy radical. We have, for the first time, been able to experimentally identify the absorptions of the theoretically predicted presence of two relatively stable *cis* and *trans* isomers of vinylperoxy radical. The effect of the pressure on the spectral features agrees with a dissociation mechanism of the initially formed vinylperoxy radical into product vinoxy and/or HCHO.

The observation of the broad far UV peak around 230 nm can definitely be assigned to the vinylperoxy radical. The smaller peak around 420 nm is also attributed entirely to the *cis* isomer of this radical. However, the shape and intensity of the 340 nm peak indicates that other species are contributing, which is confirmed by the pressure dependence of the spectrum. The tailing of the 420 nm peak to longer wavelength also is attributed to the absorption of HCO that extends from 460 to 860 nm. The calculation of the oscillator strength finds this transition is much weaker than the neighboring and overlapping transition due to the *cis* isomer of vinylperoxy, suggesting that under the conditions of this experiment the recombination of vinyl and molecular oxygen leads, through formation of the peroxy moiety, to reaction. But the observation of the vinylperoxy is also clear indication that stabilization and dissociation are competitive processes in this system. The peak around 340 nm actually decreases when the pressure is increased, suggesting that stabilization of the intermediate is gaining over the reaction channel yielding the vinoxy plus atomic oxygen. The vinoxy oscillator strength is smaller but closer to that of the *trans* isomer of vinylperoxy. If we assume that the *cis* and *trans* isomers are formed in approximately the same amount, then the relative heights of the 340 and 420 nm peaks suggest that the reaction channels producing either formaldehyde or vinoxy radical are faster than the stabilization of the peroxy radical.

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