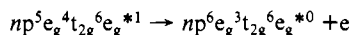


ejection of an electron localized mainly on the ligands. That the e_g^* orbital is a covalent mix of ligand 5σ orbitals with metal nd orbitals provides one conceivable mechanism for this inter-channel coupling. Another consideration is that certain of the MOs giving rise to bands B, though principally ligand in character, have some metal d character as a result of overlap with the 1π and 5σ orbitals. It is noteworthy that in the spectrum of $\text{Mo}(\text{CO})_6$ at the maximum of the $np \rightarrow nd$ resonance ($h\nu = 48 \text{ eV}$; see Figure 2b) the central part of band B seems relatively more intense than it does at nonresonant energies suggesting association of the B resonance with a specific ion state, possibly the 2E_g ion state with a hole in the e_g MO derived from the CO 5σ and Mo $4d$ orbitals, the super-Coster-Kronig decay being represented in this case by



For the Cr and W complexes, such a profile change in the B band is not apparent on visual examination of the spectra. Figure 11 shows branching ratios for each of the four separately integrated components of band B of $\text{Mo}(\text{CO})_6$ as a function of the total B band intensities. It is evident from this figure that the component B_3 shows a reasonable correlation over the $p \rightarrow d$ resonance region with the branching ratios of band A (Figure 10b), whereas the ratios of B_1 , B_2 , and B_4 show no such correlation. The most likely explanation of this is that the ionization band from the e_g orbital is located within the IE region of component B_3 . The e_g band is therefore assigned an IE of 14.8 eV, a value close to the original assignment.^{6a}

The maxima found at 42 eV for the B bands of $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ seem metal independent although this is debatable as a similar maximum is not found for $\text{Cr}(\text{CO})_6$. The value of 42 eV is close to the np ionization thresholds of Mo and W (see Table

I) and may be due to excitation of an np electron to a CO localized level followed by decay and associated ejection of ligand electrons. This would be expected to be a weaker transition than $np \rightarrow nd$ absorption due to the lower overlap of the metal p orbitals with ligand based wave functions.

As is apparent by inspection of Figures 5–7, the maxima in the RPPICS plots of the B bands are considerably smaller than those found for the A bands.

The C band shows a maximum in cross-section at ca. 35 eV followed by a steady decline to higher photon energies similar to the RPPICS of the 4σ band of free CO (see Figure 9); again small resonance features may also be present.

Conclusions

It is clearly possible to distinguish between the strong $np \rightarrow nd$ resonant photoemission shown by the metal d valence bands of the group VI hexacarbonyls and the rather weak structure shown by the ligand bands. Measurement of RPPICS as a function of photon energy over a range in which this excitation occurs thus provides a potential means of assignment of mainly metal d valence bands in the P.E. spectra of gas-phase molecules. The resonance phenomena are also apparent on examination of the branching ratios; indeed, they are so intense that they may be discerned by mere visual inspection of the spectra. In conclusion, it is seen that use of synchrotron radiation to determine RPPICS is likely to provide an invaluable assignment tool in UPS as well as providing crucial information about fundamental photoionization processes.

Acknowledgment. We thank Drs. J. B. West and F. Quinn for their role in setting up the UPS experiment at Daresbury and the SERC for financial support.

The Reactions of Electronically Excited Vinylidene Radicals with Molecular O_2

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Abstract: The rate constant and mechanism for the reaction between electronically excited vinylidene ($\text{H}_2\text{C}=\text{C})({}^3\text{B}_2)$ and molecular oxygen has been examined at 297 K. The vinylidene radicals were produced from the vacuum UV flash photolysis of vinyl chloride. Reactant triplet vinylidene and products CO and formaldehyde were observed, in real time, by their characteristic absorption in the vacuum UV region. The two products were formed in equal amounts, and the reaction probably proceeds through a cyclic intermediate. The rate constants for reaction of $\text{D}_2\text{C}=\text{C}({}^3\text{B}_2)$ with molecular oxygen and $\text{O}({}^3\text{P})$ atoms were $(1.0 \pm 0.25) \times 10^{-13}$ and $(7 \pm 2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. The mechanism of the reaction of unsaturated hydrocarbon radicals with molecular O_2 is discussed.

Chemical reactions of small electronically excited hydrocarbon radicals, aside from those of the low-lying singlet methylene species, have not been extensively studied probably because these species are difficult to prepare and characterize. Methylene and CH, of course, are the smallest of the poorly investigated series of unsaturated hydrocarbon radicals. However, the existence and identification of a long-lived carbene, i.e., the electronically excited vinylidene radical ($\text{H}_2\text{C}=\text{C}$), has been documented in recent work from this laboratory.¹ In these earlier experiments the quenching

of triplet vinylidene to the ground singlet state which in turn is quenched to ground-state acetylene has been examined for a series of nonreactive collision partners. Quenching by H_2 and CH_4 was also investigated. In these two cases there is the possibility of an exothermic abstraction reaction to produce a vinyl radical plus either an H atom or CH_3 radical.² Both reactions are predicted,

(1) Fahr, A.; Laufer, A. H. *J. Phys. Chem.* **1986**, *90*, 5064 and references therein.

(2) $\Delta H_f(\text{H}_2\text{C}=\text{C})({}^3\text{B}_2) = 141 \text{ kcal/mol}$ based upon $\Delta H_f(\text{H}_2\text{C}=\text{C})({}^1\text{A}_1) = 100 \text{ kcal/mol}$ (Davis, J. H.; Goddard, W. A., III; Harding, L. B. *J. Am. Chem. Soc.* **1977**, *99*, 2919) and a $({}^1\text{A}_1)({}^3\text{B}_2)$ splitting of 41 kcal/mol (Osamura, Y.; Schaefer, H. F., III *Chem. Phys. Lett.* **1981**, *79*, 412). $\Delta H_f(\text{C}_2\text{H}_2) = 70.4 \text{ kcal/mol}$, $\Delta H_f(\text{CH}_3) = 35.1 \text{ kcal/mol}$ (McMillan, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493).

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by an empirical BEBO calculation, to have activation energies between 5.5 and 6.3 kcal/mol.³ In neither case could the abstraction be observed, and an upper limit of about 10% of the total process represented by a rate constant of 3×10^{-16} cm³ molecule⁻¹ s⁻¹ was estimated. Possible rapid addition reactions between triplet vinylidene and C₂D₄ and C₂H₄ have been briefly discussed.⁴

It is well-known that ground-state molecular oxygen reacts rapidly with hydrocarbon free radicals, particularly the spin-allowed reactions with triplet moieties. If the excited triplet vinylidene (H₂C=C) has properties similar to that of its methylene analogue then we might expect a relatively rapid reaction with O₂. In the case of triplet CH₂, there are several observed products in the reaction with molecular O₂.⁵ In addition to H₂O and CO₂, CO, which has a very strong absorption in the vacuum ultraviolet region, has been observed. In the work reported here we have carried out a room temperature rate constant and mechanistic investigation of the title reaction by using the flash photolysis of vinyl chloride to produce the excited triplet vinylidene species. Vacuum UV kinetic absorption spectroscopy of CO in its strong Fourth Positive system, acetylene, and formaldehyde were used to monitor product formation from which it was possible to derive the rate constant for the reaction.

Experimental Section

The vacuum UV flash photolysis kinetic spectroscopy apparatus used in the present experiments has been described in previous publications from this laboratory.¹ Very briefly it consists of a Suprasil¹⁸ photolysis cell located in the center of a chamber in which a bank of six capacitors could be discharged through N₂. The energy of the discharge was 2200 J. The 1/e time of the flash was determined to be 6 μs; full width at half-height. The flash output was monitored, in the visible region, by a photomultiplier-oscilloscope combination. The spectroscopic flash, a Garton-type discharge of 2 μs duration and with energy of about 350 J, was triggered at present delays from the photomultiplier-oscilloscope circuit. The output of the analysis flash, from 120–185 nm, was focussed through LiF optics axially through the reaction cell onto the 30 micron entrance slit of a 2-m focal length Eagle mount vacuum spectrograph. Emission lines in the source provided convenient wavelength calibration. The instrumental dispersion is 2.77 Å/mm at the exit plane. Spectra were recorded on Kodak SWR¹⁸ plates. Plate transmission data were obtained by densitometry in conjunction with previously determined characteristic curves of the plate response.

The vinyl chloride was obtained commercially; there were no identifiable impurities, using a flame ionization gas chromatograph, that could be detected following rigorous trap-to-trap distillation. The purified C₂D₃Cl was premixed with ultrahigh purity He (99.99%) and expanded into the reaction vessel. Reactant O₂ was similarly premixed with He and added to the reaction vessel. Additional inert gas diluent, if necessary, was added directly to the reaction cell mixture. In all cases the experiment was delayed to allow for thorough mixing of reactants. Typical sample mixtures of 25 mtorr C₂D₃Cl, 50 mtorr O₂, and 10 torr He were used.

Spectroscopic identification and monitoring of the reactant (³B₂) vinylidene concentration was done at 137 nm. Similarly, product C₂D₂ was monitored near 151 nm, the CO through the (0,0) transition of its strong Fourth Positive system at 154.4 nm, and formaldehyde at 156 nm. The minimum detectable amount of CO was 0.1 mtorr. A search for vibrational excitation in the CO product was also made through the well-characterized Fourth Positive system.⁷ Because of absorption by reactants we were limited to a relatively small range of O₂ and C₂D₃Cl concentrations in our samples before absorption overlap affected the minimum detectable quantities of either product.

Gas chromatographic analysis of the post-flash sample of vinyl chloride/O₂/He did not show any detectable hydrocarbon product other than C₂D₂, even when samples with high concentrations and pressures of reactant were used.

Results and Discussion

The source of triplet vinylidene was the vacuum UV photolysis of vinyl chloride in the presence of He. The processes involved

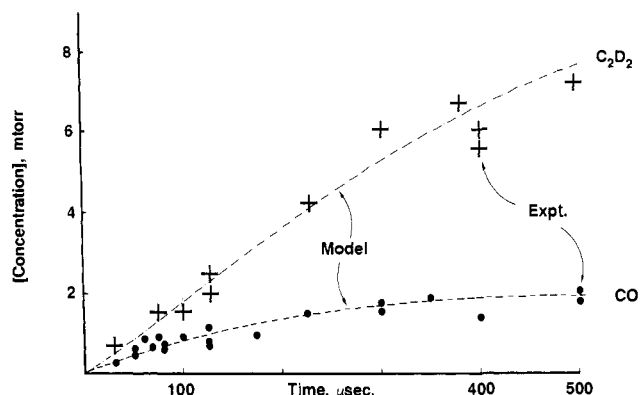


Figure 1. Temporal profile of C₂D₂ and CO production from the reaction of D₂CC(³B₂) in the O₂. Model—see text and Table I.

Table I

reaction	k (cm ³ molecule ⁻¹ s ⁻¹)	ref	contribution to final CO product
(a) C ₂ D ₃ Cl* + He = D ₂ CC + DCI	1.2×10^{-13}	6	
(b) D ₂ CC + He = C ₂ D ₂ + He	1.9×10^{-15}	6	
(c) D ₂ CC + O ₂ = C ₂ D ₂ + O ₂	5.0×10^{-14}	1	
(1) C ₂ D ₂ + O = CD ₂ + CO	1.4×10^{-13}	8	≤5%
(3) D ₂ CC + O ₂ = DCDO + CO	to be estmtd	(see text)	~70%
(5) D ₂ CC + 2O = 2CO + D ₂	to be estmtd	(see text)	~25%
(d) C ₂ D ₃ Cl + O = CO + product	7.0×10^{-13}	12	≤5%

in this system have been previously described,⁶ and the rate constants for quenching of the excited vinylidene triplet to the ground-state singlet have been thoroughly investigated. As noted earlier, the rate constants for collisional quenching of H₂C=C to C₂H₂ by He and other quenchers are significantly faster than the quenching rate of D₂C=C. To ensure more accurate rate measurements with the present apparatus and allow slower quenching of triplet vinylidene to acetylene, the deuterated vinyl chloride analogue was chosen as the source of the vinylidene radical. This permits an improved probability for observation of a chemical reaction between O₂ and triplet vinylidene.

The time history of formation of the reaction products, CO and C₂D₂, is shown in Figure 1. After an observation time of about 500 ms following the incident, the concentrations of CO and C₂D₂ were 2 and 8 mtorr, respectively. As evidenced by the respective product yields, in our mixtures of predominantly He, the major fate of the D₂C=C(³B₂) radicals is physical quenching by He to ultimately produce acetylene. Only a relatively small fraction of the reactive radical actually undergoes chemical reaction to produce CO and formaldehyde.

The majority of the experiments were with He as a quencher molecule. In the presence of Ar, however, the yield of CO was reduced to about half of that observed in the presence of He. The quenching of triplet vinylidene by Ar is about 3.5 times faster than with He.¹ The increase in physical quenching reduces the contribution of a chemical reaction channel and thereby reduces the final concentration of CO.

Since the collisional quenching of H₂C=C with He to acetylene is significantly faster than quenching of D₂C=C, the deuterated vinylidene radicals are chosen for reaction rate measurements with oxygen. We expect no significant differences between the rate data or mechanism for chemical reactions of either isotopically substituted radical with oxygen, because the reactions of interest are involved with C–C bond scission; the C–H bonds are but spectators.

In addition to the title reaction there are, conceptually, several other possible sources of CO product. In a kinetic model, reactions of molecular O₂ as well as O atoms with several C-containing

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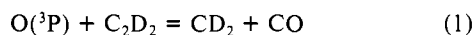
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molecules or radicals present in the post-flash mixture are considered. These processes and corresponding kinetic parameters are given in Table I. Several of the more significant of these processes are discussed in the following sections.

The O(³P) atoms could be generated from the direct photolysis in the Schumann–Runge absorption band of molecular O₂. The concentration of O(³P) atoms produced in the flash, under our experimental conditions, were insufficient to observe in absorption at 130.5 nm. However, when mixtures of O₂/He, at concentrations somewhat higher than the O₂ used in the rate determinations was photolyzed, the characteristic triplet absorption of O(³P) around 130.5 nm was observed. The results indicate that oxygen atoms are indeed a product of the photolysis, and the role of O(³P) atoms had to be considered in kinetic schemes.

Reactions of O(³P) Atoms. A rather obvious choice is the reaction

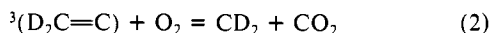


where the C₂D₂ is formed from the rapid collisional quenching of photochemically produced triplet vinylidene to singlet vinylidene followed by its rapid isomerization (Process b in Table I). The overall rate constant for (1) is $1.4 \times 10^{-13} \text{ cm}^3 \text{ molecular}^{-1} \text{ s}^{-1}$ at 298 K.⁸

Several experiments were performed to ascertain the importance of reaction (1) to the overall production of CO. A major channel of (1) is formation of DCCO(ketyl) radicals that may undergo further reaction to produce CO.⁹ Here we are concerned with the net CO production independent of formation mechanism. In the absence of O₂ the yield of C₂D₂ from C₂D₃Cl photolysis was determined by both gas chromatography and absorption spectroscopy. Although C₂D₂ production is expected to show a temporal dependence, the maximum contribution of (1) to CO formation will occur when the initial concentration of C₂D₂ is at its maximum, i.e., its final concentration. Now, blank experiments with the "final" yield of C₂D₂ as reactant in the presence of O₂ are expected to produce CO by reaction 1. As expected, CO was indeed formed but in final quantities that represented less than 10% of product CO formed in photolysis of vinyl chloride–oxygen mixtures. In these experiments, no C₄D₂ (diacetylene) could be observed from the photolysis of acetylene, i.e., products resulting from reaction of C₂D with acetylene were not observed by either absorption spectroscopy or gas chromatography due to the effective competition by reaction with the large excess of molecular O₂ present in the system. The above test provides a method for estimating the oxygen atom yield in the C₂D₃Cl/O₂/He system and is clear indication of an alternate source of CO in addition to reaction 1, as will be discussed latter. However, the total CO observed in the C₂D₂–O₂ system includes, in addition to that from (1), a contribution from the rapid reaction of triplet CD₂ (formed in 1) with O₂ ($k = 1.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)^{5,10} as well as several possible processes involving the ketyl(DCCO) radical.

Reactions of O(³P) with the remaining vinyl chloride in the post-flash mixture and vinylidene radicals are considered in the kinetic model. In our previous studies of the photolysis of vinyl chloride, we had established that nearly 50% of the initial concentration of C₂D₃Cl would remain unreacted and nonphotolyzed.⁶ The importance of the O(³P) + D₂C=C reaction is also examined in the kinetic model, and its rate constant is estimated.

Reactions of Molecular O₂. There are several energetically allowed reaction paths through which excited triplet vinylidene may react with oxygen. The least energetically favorable path can yield CD₂ and CO₂ (reaction 2) with an exothermicity of about



140 kcal/mol.^{2,11} The more favorable paths involve the formation

of CO, viz., reactions 3 and 4. Reactions 3 and 4 are each exothermic by about 193 kcal/mol.



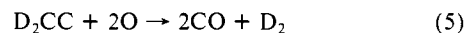
We have looked for the formation of the DCDO through its absorption in the vacuum UV. The absorption spectrum of formaldehyde in the vacuum UV has been examined previously. A series of strong Rydberg transitions of formaldehyde has been observed at 156 nm.¹² Absorption in this region is experimentally quite convenient, but for quantitation it was necessary to determine the extinction coefficient of formaldehyde at that wavelength. Absorption data, in the pressure range of 0.1–1.0 mtorr in several torr of added helium, were fit to the Lambert–Beer equation $I = I_0 \exp(-\epsilon px)$. The value of ϵ , determined from the slope of a plot of $\ln(I_0/I)$ vs. pressure, was $1850 \pm 100 \text{ cm}^{-1} \text{ atm}^{-1}$.

Careful examination of the spectral plates did provide evidence for the formation of DCDO. In fact, within experimental error, the yields of both products were comparable, at short delay times, though the CO yield was about 35% in excess at longer reaction times (CO/D₂CO = 1.55 from experiment). These observations indicate that process 3 is the major source of total CO formation, and all other processes combined are responsible for about 35% of the CO product. Later it will be shown that reaction 4 provides a minor contribution to the overall mechanism.

Considering the rather large exothermicity of (3), we thought it would be reasonable to search for vibrational excitation in the CO product. In fact, the (0,1) absorption in the CO Fourth Positive system at 159.7 nm could be observed while absorption from the second vibrational level (0,2) (absorption at 165.3 nm) could not. The energy difference between the first and second vibrational level in the ground state is about 6 kcal/mol, and the transitions have comparable Franck–Condon factors.⁷ Since there is adequate energy to populate the $v'' = 2$, we conclude the overall dynamics of reaction 3 and do not result in significant vibrational excitation of the reaction products.

Rate Constants of D₂C=C + O₂ and D₂C=C + O(³P). The multiple reaction paths for removal of triplet vinylidene and CO formation preclude isolation of the elementary reaction for direct study. For a more extensive analysis of our data and to estimate rate constants for reaction of vinylidene radicals with O₂ and O(³P) atoms, we have modeled the system by using a numerical integration technique based upon the Gear routine. The reactions and corresponding rate constants are given in Table I. The initial concentration of C₂D₃Cl* is taken to be 50% of the initial concentration of vinyl chloride as was demonstrated in previous studies of the photodissociation of this molecule.⁶ The concentration of D₂CC(³B₂) was determined spectroscopically.¹⁴ The O atom concentration was estimated to be about 2.5% of the initial O₂ concentration. The estimate was based upon a consideration of experiments described earlier, the incident wavelength distribution of the photolysis light, concentration of O₂ in the system, the absorption spectrum of O₂, and assumed applicability of the Lambert–Beer law. The temporal profile of the reaction products was calculated to 1 ms. At times longer than ~500 μs the only process was physical quenching of D₂CC by He.

Rate constants for reactions 3 and 5 were varied, and the calculated temporal profiles of CO and C₂D₂ were compared to the experimental results which are shown in Figure 1. Reasonable



(11) $\Delta H_f(\text{HCHO}) = -27.1 \text{ kcal/mol}$, $\Delta H_f(\text{CO}) = -27.1 \text{ kcal/mol}$, $\Delta H_f(\text{CH}_2) = 93.7 \text{ kcal/mol}$, $\Delta H_f(\text{CO}_2) = -94.0 \text{ kcal/mol}$. Wagman, D. D.; Evans, W. H.; Parker, V. B.; Halow, I.; Bailey, S. M.; Schumm, R. H. NBS Technical Note 270-3, U.S. Government Printing Office: Washington, DC, January 1968.

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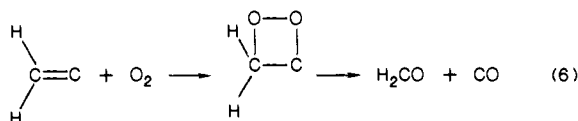
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fits between the model and experimental observations were obtained with $k_3 = 1 \times 10^{-13}$ and $k_5 = 7 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. A 25% error is typical of these measurements.

Reaction 5 is a significant source of CO only at short reaction times (<150 μs) following the incident flash when the concentration of O(³P) is relatively large. At 150 μs reaction 5 is calculated to be the source of about 50% of the CO produced, but its contribution is calculated to be only 25% of the final yield of CO. Modification of the stoichiometry of reaction 5 had minimal effect upon the calculated temporal profiles. With O(2O) atoms, however, the agreement of the model calculation with the experimental product profiles is improved. We are not certain about the mechanism for the atom-radical reaction. Presumably, (5) is a multistep process. Since the overall rate is so fast (7×10^{-11} cm³ molecule⁻¹ s⁻¹), each reaction itself must be quite rapid which effectively eliminates a secondary reaction involving molecular oxygen. For example, the rate constant of triplet methylene, a possible intermediate in reaction 5 with molecular O₂ is about 1×10^{-12} cm³ molecule⁻¹ s⁻¹. In comparison with reaction 5, reaction 3 is significant at longer reaction times and is the source of about 70% of the total CO produced. By difference, reaction 4 can only account for about 5% of the CO production channels.

Products and Mechanism of Reaction. The most likely structure of an intermediate for the reaction of an unsaturated hydrocarbon radical with O₂ has been previously discussed.¹⁵ It was suggested¹⁶ that the reaction proceeds by O₂ addition to one of the carbons of the double bond followed by ring-closure to a four-membered dioxetane ring. In the case of H₂C=C the mechanism for reaction 3 would be



The mechanism predicts the formation of CO and H₂CO by an appropriate ring-scission step.

The mechanism described above involves a simple reaction path for the formation of the formaldehyde and major parts of the observed final CO product. Nevertheless, the structure of the cyclic intermediate cannot be discerned directly from the present study.

The cyclic intermediate, conceptually may dissociate by routes other than a simple ring-scission. Though intuitively unlikely, a 1,2-hydrogen migration may occur prior to ring scission. Now such a scission would lead to two HCO (formyl) radicals which can undergo various disproportionation/combination reactions to produce both CO and H₂CO. The possibility was examined by reaction of a mixture of vinylidenes-*d*₀ and -*d*₂ in the presence of O₂. Vinylidene-*d*₂ leads, in reaction with O₂, to formaldehyde-*d*₂ as observed by its characteristic absorption at 155 nm.¹⁷ In the

vinylidene-*d*₀, -*d*₂ mixtures, the disproportionation of formyl radicals, if present, are expected to produce formaldehyde-*d*₁ to a greater extent than either *d*₀ or *d*₂. Although formaldehyde-*d*₀ and -*d*₂ are indeed observed, there is no spectroscopic evidence for production of formaldehyde-*d*₁ effectively eliminating a mechanism involving radical precursors and confirming reaction 6 as the most likely process.

Conceptually, alternate reaction paths do exist, e.g., the formation of a three-membered closed shell ring compound, with two O atoms in the ring followed by isomerization to an α-lactone type structure that will cleave to form both CO and formaldehyde. Although the strain energy of the three- and four-membered rings are comparable, an "extra" isomerization is required in one of the reaction sequences. Further, the α-lactone intermediate could cleave to form CO₂ and methylene. Though the reverse process has been suggested,¹⁰ there is no chemical evidence for the formation of methylene in the vinyl chloride-O₂ system. We prefer the more direct process, i.e., four-membered ring formation.

The reaction between unsaturated hydrocarbon radicals and molecular O₂ now has been examined for a few radical species. In the case of C₂H and C₂H₃ radicals the reactions have similar rate constants¹⁵ of the order of 5×10^{-12} cm³ molecule⁻¹ s⁻¹. In comparison, an upper limit of 5×10^{-14} and 1×10^{-13} cm³ molecule⁻¹ s⁻¹ for the reaction of allyl(C₃H₅) radicals with O₂¹⁵ and D₂C=C(³B₂) with O₂, respectively, have been obtained at room temperature. In these four cases it is presumed the reaction proceeds by the same mechanism, i.e., addition to the double bond followed by cyclization to a four-membered ring and subsequent molecular fragmentation. The differences in rate constants have been discussed previously in terms of an energy barrier to ring closing that is comparable, in the allyl case, to that for redissociation which would allow the RO₂ adduct to return to reactants.¹⁵ To confirm this concept we have carried out an RRKM calculation of the transition-state dissociation. We assume the addition of the molecular O₂ to the vinylidene (³B₂) occurs without a barrier along the allowed triplet surface at a rate not significantly lower than the collision rate. The overall reaction rate is then totally dependent upon the ratio of ring-closure followed by dissociation to products vs. that for redissociation to reactants. The ring-closure rate, itself, is limited by a potential barrier. In the absence of a barrier to ring-closure every collision "successfully" results in products. We find that to match the overall rate constant a barrier to ring-closure of about 15 kcal/mol is required such that the RO₂ adduct resides in a potential well with an approximately equal barrier to either product or reactant formation. These results suggest the importance of a study of the effect of temperature upon the overall kinetics.

Acknowledgment. This work was supported, in part, by the Planetary Atmospheres Program of NASA. Discussions with Wing Tsang, who also assisted with the RRKM calculations, were most helpful. The possibilities of alternative mechanisms to the one preferred by the authors involved discussion with Joel Liebman (VMD-B.C.) for which the authors are grateful.

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