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# Infrared Spectrum of the Propargyl Peroxyl Radical, $\text{HC}\equiv\text{C}-\text{CH}_2\text{OO } \tilde{\text{X}}^2\text{A}''^{\dagger}$

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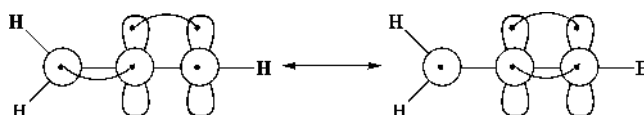
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When the propargyl radical,  $\text{HCCCH}_2$ , and  $\text{O}_2$  are codeposited onto a cold argon matrix, a chemical reaction ensues; infrared absorption spectra reveal the formation of the propargyl peroxy radical:  $\text{HC}\equiv\text{C}-\text{CH}_2\tilde{\text{X}}^2\text{B}_1 + \text{O}_2 \rightarrow \text{trans-HC}\equiv\text{C}-\text{CH}_2\text{OO } \tilde{\text{X}}^2\text{A}$ . We do not observe the isomeric adduct,  $\text{CH}_2=\text{C}=\text{CHOO } \tilde{\text{X}}^2\text{A}''$ . The propargyl radicals are produced by a hyperthermal nozzle while a second nozzle alternately fires bursts of  $\text{O}_2/\text{Ar}$  at the 20 K matrix. The absorption spectra of the radicals are measured using a Fourier transform infrared spectrometer. We observe 13 of the 18 fundamental infrared bands of the propargyl peroxy radical in an Ar matrix at 20 K. The experimental frequencies ( $\text{cm}^{-1}$ ) of  $\text{trans-HC}\equiv\text{C}-\text{CH}_2\text{OO } \tilde{\text{X}}^2\text{A}''$  are assigned. The  $\text{a}'$  modes are  $\nu_1 = 3326$ ,  $\nu_2 = 2960$ ,  $\nu_3 = 2148$ ,  $\nu_4 = 1440$ ,  $\nu_5 = 1338$ ,  $\nu_6 = 1127$ ,  $\nu_7 = 982$ ,  $\nu_8 = 928$ ,  $\nu_9 = 684$ , and  $\nu_{10} = 499 \text{ cm}^{-1}$ , while the  $\text{a}''$  modes are  $\nu_{14} = 1218$ ,  $\nu_{15} = 972$ , and  $\nu_{16} = 637 \text{ cm}^{-1}$ . Linear dichroism spectra were measured with photo-oriented  $\text{HCCCH}_2\text{OO}$  radical samples to establish the experimental polarizations of several vibrational bands. The experimental frequencies ( $\nu$ ) for the propargyl peroxy radical are compared to the anharmonic frequencies ( $\nu$ ) resulting from electronic structure calculations. We have used CBS-QB3 electronic structure calculations to estimate the peroxy bond energies:  $\Delta H_{298}(\text{trans-HC}\equiv\text{CCH}_2-\text{OO} \rightarrow \text{CH}_2\text{CCH } \tilde{\text{X}}^2\text{B}_1 + \text{O}_2) = 19 \pm 1 \text{ kcal mol}^{-1}$  and  $\Delta H_{298}(\text{trans-CH}_2=\text{C}=\text{CH}-\text{OO} \rightarrow \text{CH}_2\text{CCH } \tilde{\text{X}}^2\text{B}_1 + \text{O}_2) = 21 \pm 1 \text{ kcal mol}^{-1}$ . The experimental thermochemistry for  $\text{C}_3\text{H}_3$  reacting with oxygen has been reanalyzed as  $\Delta_{\text{rxn}}H_{298}(\text{HCCCH}_2 + \text{O}_2 \rightarrow \text{CH}_2=\text{C}=\text{O} + \text{HCO}) = -83 \pm 3 \text{ kcal mol}^{-1}$ ;  $\Delta_{\text{rxn}}H_{298}(\text{HCCCH}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{CO} + \text{CO}) = -111 \pm 3 \text{ kcal mol}^{-1}$ ;  $\Delta_{\text{rxn}}H_{298}(\text{HCCCH}_2 + \text{O}_2 \rightarrow \text{CH}_2\text{CHO} + \text{CO}) = -106 \pm 4 \text{ kcal mol}^{-1}$ ;  $\Delta_{\text{rxn}}H_{298}(\text{HCCCH}_2 + \text{O}_2 \rightarrow \text{HCHO} + \text{HCCO}) = -67 \pm 4 \text{ kcal mol}^{-1}$ ;  $\Delta_{\text{rxn}}H_{298}(\text{HCCCH}_2 + \text{O}_2 \rightarrow \text{CH}_2\text{CH} + \text{CO}_2) = -105 \pm 3 \text{ kcal mol}^{-1}$ .

## Introduction

The propargyl radical ( $\text{HCCCH}_2$ ) is an important species in combustion.<sup>1,2</sup> This species is produced<sup>2</sup> in flames by H abstraction from either  $\text{CH}_3\text{C}\equiv\text{CH}$  or  $\text{CH}_2=\text{C}=\text{CH}_2$  or by the addition of  $\text{CH}_2 \tilde{\text{a}}^1\text{A}_1$  to  $\text{HC}\equiv\text{CH}$ . Propargyl is a delocalized hydrocarbon radical and is classically written<sup>3</sup> as  $[\text{HC}\equiv\text{C}-\text{CH}_2 \leftrightarrow \text{HC}=\text{C}=\text{CH}_2]$ . The spin-delocalization on  $\text{HCCCH}_2$  has been measured and it has been shown that there is a significant amount of spin density on either side of the propargyl molecule. An EPR spectrum of propargyl revealed a “doublet of triplets” in its hyperfine splitting pattern, indicating comparable spin densities [ $(\text{spin})(\text{atom})^{-1}$ ] on the (1,3) carbons.<sup>4</sup> CCSD(T)/ANO spin density calculations<sup>5</sup> based on coupled-cluster theory find 35% of the spin on C(3) and 65% on C(1). The  $\text{HCCCH}_2$  radical

is a doublet and can be represented by  $\text{HC}\equiv\text{C}-\text{CH}_2\tilde{\text{X}}^2\text{B}_1$  corresponding to the generalized valence bond (GVB) diagrams<sup>6</sup> in eq 1.



From hydrocarbon thermochemistry<sup>7</sup> one can show that the delocalized propargyl radical is stabilized<sup>5</sup> by approximately 11  $\text{kcal mol}^{-1}$  (the “resonance energy”). And it has already been emphasized<sup>2</sup> that  $\text{HCCCH}_2$  forms weak bonds with oxygen since  $\text{O}_2$  addition destroys the resonance. Weakly bound  $[\text{C}_3\text{H}_3\text{OO}]^*$  adducts do not readily rearrange to produce oxidized bimolecular products and are not stabilized by collisions. Many of the  $[\text{C}_3\text{H}_3\text{OO}]^*$  dissociate back to  $\text{O}_2 + \text{C}_3\text{H}_3$ . Consequently propargyl radicals begin to reach high concentrations in flames and react with themselves<sup>2,8</sup> to form aromatic species:  $\text{HCCCH}_2 + \text{HCCCH}_2 \rightarrow \text{C}_6\text{H}_6 \rightarrow (\text{benzene})$ .<sup>8–12</sup>

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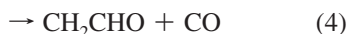
<sup>||</sup> California Institute of Technology.

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Although dimerization may be the dominant loss channel for propargyl radicals in flames, reactions with oxygen will certainly play a crucial role as well.<sup>2,10,13,14</sup> Possible reaction channels for propargyl and oxygen are



In a pioneering study, the kinetics and mechanism of the reaction of  $\text{C}_3\text{H}_3$  with  $\text{O}_2$  were investigated<sup>13</sup> from 293 to 900 K using a tubular reactor coupled to a photoionization mass spectrometer (PIMS). The flow reactor was a 1.05 cm-id heatable quartz tube with  $\text{N}_2$  buffer gas at pressures of 0.9–1.8 Torr. From 293–333 K, the reaction is a simple, reversible addition:  $\text{C}_3\text{H}_3 + \text{O}_2 \rightleftharpoons \text{C}_3\text{H}_3\text{OO}$ . Between 380 and 430 K the equilibrium was clearly observable and the equilibrium constant was measured as a function of temperature. The binding energy of oxygen to propargyl,  $\Delta H_{298}(\text{C}_3\text{H}_3-\text{OO})$ , was deduced<sup>13</sup> to be  $18.9 \pm 1.4$  kcal mol<sup>-1</sup>. A mechanism change was observed as the temperature rises. Above 350 K,  $\text{CH}_2=\text{C}=\text{O} + \text{HCO}$  are observed as reaction products and remain important as the temperature increases.

Laser photolysis (193 nm) and cavity ring-down spectroscopy were used<sup>10</sup> to produce and monitor the propargyl radical. The oxygen termolecular association rate coefficients for the propargyl radical were measured at 295 K at total pressures between 2.25 and 100 Torr in Ar, He, and  $\text{N}_2$  buffer gases. The association reaction  $\text{C}_3\text{H}_3 + \text{O}_2$  was found to lie in the falloff region between linear and saturated pressure dependence for each buffer gas (Ar, He, and  $\text{N}_2$ ). A fit of these data derived the high-pressure limiting rate coefficient  $k_\infty(\text{C}_3\text{H}_3 + \text{O}_2) = (2.3 \pm 0.5) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

In addition to the earlier<sup>13</sup> flow tube/PIMS study, the reaction dynamics of propargyl radical with  $\text{O}_2$  was studied at low pressures by time-resolved Fourier transform infrared (FTIR) spectroscopy.<sup>14</sup> A gas mixture of  $\text{HCCCH}_2\text{Br}$  (0.3 Torr) and  $\text{O}_2$  (0.2 Torr) was flowed through a reaction chamber. The  $\text{HCCCH}_2$  radical was produced by laser photolysis of  $\text{C}_3\text{H}_3\text{Br}$  at 248 nm and the reaction of propargyl radical with  $\text{O}_2$  was observed. Emission of infrared radiation was observed from the nascent vibrationally excited products  $\text{HCO}^*$ ,  $\text{CO}_2^*$ , and  $\text{CO}^*$  after 5  $\mu\text{s}$  following laser triggering by time-resolved FTIR spectroscopy. Observation of these products led to the conclusion that reactions 2, 3, and 6 are the dominant channels for  $\text{HCCCH}_2$  reacting with  $\text{O}_2$ .

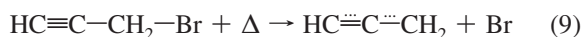
Hahn et al.<sup>2</sup> carried out a theoretical study of the temperature and pressure-dependent kinetics of the reaction of propargyl radical with molecular oxygen. They calculated the stationary points on the potential energy surfaces for the addition of  $\text{O}_2$  with  $\text{HC}\equiv\text{C}\cdot\text{CH}_2 \tilde{X}^2\text{B}_1$  by a combination of electronic structure theory, transition state theory, and the time-dependent master equation. The stationary points on the potential energy surface were located with B3LYP density functional methods. QCISD(T,full)/6-311++G(3df,2pd) energies were obtained at these stationary points.

An important question is the nature of the initial addition complex because there are two isomeric adducts possible.



QCISD(T) electronic structure calculations<sup>2</sup> find there is a lower barrier for the addition of  $\text{O}_2$  to the methylenic side of the radical to form  $\text{HC}\equiv\text{CCH}_2-\text{OO}\cdot$  [ $E_a(8) = 3.7$  kcal mol<sup>-1</sup>] than to the acetylenic end to produce the more stable<sup>2</sup>  $\text{CH}_2=\text{C}=\text{CH}-\text{OO}\cdot$  [ $E_a(7) = 7.1$  kcal mol<sup>-1</sup>] adduct. Those barriers suggest that molecular oxygen would preferentially react with propargyl radicals to form  $\text{HC}\equiv\text{CCH}_2\text{OO}\cdot$  rather than  $\text{CH}_2=\text{C}=\text{CH}-\text{OO}\cdot$ . The order of these barriers,  $E_a(8) < E_a(7)$ , reflects the spin densities on the propargyl radical in eq 2.

More than a decade ago it was demonstrated that a hyperthermal nozzle could decompose propargyl bromide to produce intense beams of the radical.<sup>15</sup>

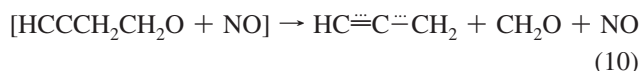
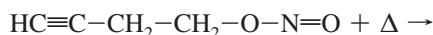


Using such a hyperthermal nozzle we have produced an intense beam of propargyl radicals and measured their vibrational spectra when deposited upon a cold (20 K) argon matrix using an FTIR spectrometer.<sup>5</sup> Polarizing 248 nm light from a KrF excimer laser enabled us to record linear dichroism spectra of photooriented samples, thus establishing the experimental polarizations of most of the vibrational bands. Of the 12 fundamental vibrational modes of propargyl, 9 were observed.

Our earlier study<sup>16</sup> shows that it is possible to combine  $\text{CH}_3$  radicals with  $\text{O}_2$  in an Ar matrix to produce the methylperoxyl radical,  $\text{CH}_3\text{OO}$ . Because of this earlier success, we have codeposited samples of  $\text{HCCCH}_2$  and  $\text{O}_2$  in a cryogenic matrix. Infrared absorption spectroscopy has been used to identify reaction products. The IR spectra reveal that the reaction product of  $\text{HCCCH}_2 \tilde{X}^2\text{B}_1$  with  $\text{O}_2$  in a 20 K Ar matrix is the propargyl peroxy radical, *trans*- $\text{HC}\equiv\text{C}-\text{CH}_2\text{OO}\cdot \tilde{X}^2\text{A}''$ . We find no evidence for the isomeric allenyl peroxy radical,  $\text{CH}_2=\text{C}=\text{CH}-\text{OO}\cdot \tilde{X}^2\text{A}''$ .

## Experimental Section

**Radical Beam and Infrared Spectroscopy.** We use a hyperthermal nozzle to produce intense beams of propargyl radical.<sup>5</sup> Briefly, the nozzle consists of a resistively heated 1-mm diameter SiC tube at the output of a pulsed solenoid Parker General Valve (Series 9). The hyperthermal nozzle can be heated up to 1800 K to thermally dissociate an appropriate precursor. Because the radical's residence time in the hyperthermal nozzle is approximately 65  $\mu\text{s}$ , few radical–radical byproducts are observed. Upon exiting the nozzle the hot molecules undergo a supersonic expansion since they are entrained by the Ar buffer gas. Two different propargyl radical precursors were used in this work:  $\text{HC}\equiv\text{CCH}_2\text{Br}$  and  $\text{HC}\equiv\text{CCH}_2\text{CH}_2\text{ONO}$ . The propargyl bromide precursor was purchased from Aldrich Chemical Co., while 1-butyne-4-nitrite ( $\text{HC}\equiv\text{CCH}_2\text{CH}_2\text{ONO}$ ) was synthesized.<sup>5</sup> The nitrite is a convenient source of propargyl radical because the hyperthermal nozzle fragments the nitrite at a lower temperature than  $\text{HC}\equiv\text{CCH}_2\text{Br}$ . An estimate<sup>17</sup> for the bond energy is  $\Delta H_{298}(\text{HCCCH}_2\text{CH}_2\text{O}-\text{NO})$  roughly 42 kcal mol<sup>-1</sup>.



The hyperthermal nozzle was optimized for propargyl radicals by use of a combination of photoionization mass spectrometry and infrared spectroscopy.<sup>5</sup>

The hyperthermal nozzle was mounted to the vacuum shroud of an APD two-stage closed-cycle helium cryostat, approximately 2.5 cm away from the cryogenic CsI sample.<sup>18</sup> Room temperature gas mixtures were created by seeding the degassed vapor of the precursor in argon. The hyperthermal nozzle was operated with an approximate 150  $\mu\text{s}$  pulse width and a stagnation pressure of 1.2 atm. The pressure drop in the stagnation reservoir (1.2 L) was measured using a capacitance monometer to determine the gas throughput.

Propargyl peroxy radicals were produced by mixing  $\text{O}_2$  and propargyl radicals in the matrix, in a similar fashion to the technique used by Nandi et al.<sup>16</sup> to create the methylperoxy radical,  $\text{CH}_3\text{OO}\cdot$ . The method consists of first depositing propargyl radicals from the pyrolysis nozzle. A second Parker General Valve Series 9 pulsed solenoid valve then introduces the  $\text{O}_2/\text{Ar}$  gas mixture to the matrix. This second valve mounts to the same APD vacuum shroud, positioned  $45^\circ$  from the pyrolysis nozzle and also approximately 2.5 cm away from the cryogenic CsI substrate. One beam was dosed at a time onto the 20 K window; by depositing alternating monolayers of reactants a multilayer sandwich matrix is created. Both valves were fitted with 100  $\mu\text{m}$  circular output orifices.

The infrared spectrum of the sample was measured after dosing the matrix substrate for approximately one hour using a Nicolet Magna 550 Fourier transform infrared spectrometer with a mercury/cadmium/telluride (MCT-A or B) detector. The APD cryostat is equipped with a pair of CsI side windows that are traversed by the IR beam. For depletion and linear dichroism experiments a KrF excimer laser and a plate polarizer were used to produce polarized 248 nm light to create an aligned matrix of trapped propargyl peroxy radicals. Subsequently the differ-

ence in the IR signal was obtained with the light first polarized horizontally and then vertically. This yields the linear dichroism spectrum of the matrix. Polarized IR light is generated with a Molelectron wire grid IR polarizer.

**Electronic Structure Calculations.** The vibrational assignments were facilitated using harmonic frequencies calculated from electronic structure methods. The equilibrium geometry and harmonic frequencies of  $\text{HCCCH}_2\text{OO}$  and  $\text{CH}_2\text{CCHOO}$  species were calculated using a commercial computer program that employs the B3LYP functional which is a combination of exchange from Becke's 3-parameter HF/DFT hybrid exchange functional<sup>19</sup> (B3) with the dynamical correlation functional<sup>20</sup> of Lee, Yang, and Parr (LYP).

To estimate the bond energies of  $\text{HCCCH}_2-\text{OO}$  and  $\text{CH}_2\text{CCH}-\text{OO}$ , we have used the complete basis set (CBS) methods developed by Petersson et al.<sup>21,22</sup> These compound models employ modest basis sets for the geometry and frequency calculations, large basis sets for a single point SCF calculation, medium basis sets for the MP2 correction with extrapolation to the CBS limit, and small basis sets for higher levels of correlation. The CBS-QB3 method<sup>22</sup> uses the CBS-Q model chemistry that has been modified to use B3LYP hybrid density functional geometries and harmonic frequencies  $\{\omega\}$  and has a characteristic accuracy of  $\pm 1$  kcal mol<sup>-1</sup>.

Coupled-cluster theory,<sup>23-26</sup> while more expensive than DFT methods, provides a nearly quantitative treatment of electron correlation in most cases and can therefore provide accuracy beyond that achievable with DFT. Accordingly, we have used another package<sup>27</sup> (CFOUR) to calculate the equilibrium geometry, anharmonic force field, and dipole moment function for propargyl peroxy using the CCSD(T) method<sup>28,29</sup> with the atomic natural orbital (ANO) basis set.<sup>30</sup> The anharmonic force field  $\{v\}$  was calculated by numerical differentiation of analytical CCSD(T) second derivatives<sup>31</sup> using a general approach described elsewhere.<sup>32</sup> Care was taken to ensure that the numerical precision of the frequencies (harmonic and anharmonic) quoted in Table 1 is roughly 1 cm<sup>-1</sup>. The core molecular orbitals corresponding to the 1s carbon atomic orbitals were excluded from the correlation treatment. For propargyl peroxy,

**TABLE 1: Calculated *trans*-H-C $\equiv$ C-CH<sub>2</sub>-OO  $\tilde{X}^2A''$  Vibrational Modes CCSD(T) Calculation of Harmonic ( $\omega$ ) and Anharmonic ( $v$ ) Vibrational Frequencies and Intensities for *trans*-H-C $\equiv$ C-CH<sub>2</sub>-OO  $\tilde{X}^2A''$  Using the ANO0 Basis Set<sup>a</sup>**

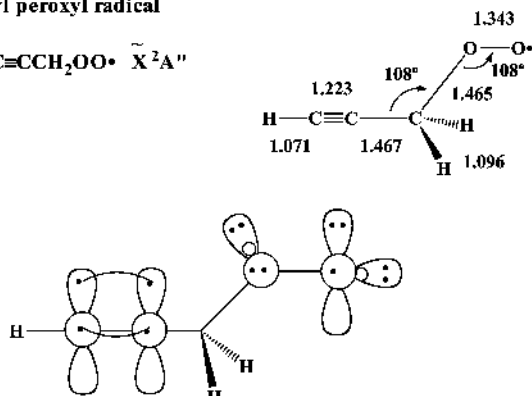
mode	local mode	$\omega$ (cm <sup>-1</sup> )	$v$ (cm <sup>-1</sup> )	$v-\omega$ (cm <sup>-1</sup> )	$A(\omega)$ (km mol <sup>-1</sup> )	$A(v)$ (km mol <sup>-1</sup> )	$v$ (adj)	$A$ (adj)
a'								
1	C-H st	3466	3332	-134	50	45	3337	44
2	sym CH <sub>2</sub> st	3092	2961	-131	7	7	2951	7
3	C $\equiv$ C st	2169	2126	-43	6	4	2144	5
4	CH <sub>2</sub> scissors	1490	1453	-37	3	1	1445	2
5	CH <sub>2</sub> wag	1374	1339	-35	50	41	1336	42
6	O-OCH <sub>2</sub> CCH st	1086	1072	-14	26	10	1130 <sup>b</sup>	20 <sup>b</sup>
7	C-C st	986	967	-19	18	16	973	20
8	O-C st	976	933	-43	27	50	943	65
9	C $\equiv$ C-H in-plane bend	667	652	-15	31	31	678	32
10	O-C-C bend	499	487	-12	3	2	496	2
11	O-O-C bend	418	416	-2	9	9	424	9
12	C-C $\equiv$ C in-plane deformation	157	155	-34	1	1	163	1 <sup>c</sup>
a''								
13	asym CH <sub>2</sub> st	3155	2994	-161	4	4	2980	5
14	CH <sub>2</sub> twist	1231	1197	-34	1	1	1189	1
15	CH <sub>2</sub> rock	1002	977	-25	4	4	973 <sup>d</sup>	4 <sup>d</sup>
16	C $\equiv$ C-H out-plane bend	623	608	-15	40	40	633	42
17	C-C $\equiv$ C out-plane deformation	293	296	3	6	7	309	7
18	O-O-CH <sub>2</sub> -C torsion	79	72	-7	0	0	73	0

<sup>a</sup> "Adjusted" values in the rightmost columns are based on the CCSD(T)/ANO1 harmonic force field (see the section Electronic Structure Calculations) and represent the best estimates from theory. <sup>b</sup> After treatment of  $\nu_6 \approx \nu_9 + \nu_{11}$  resonance. <sup>c</sup> After treatment of  $\nu_{12} \approx 2\nu_{18}$  resonance. <sup>d</sup> After treatment of  $\nu_{15} \approx \nu_9 + \nu_{17}$  resonance.

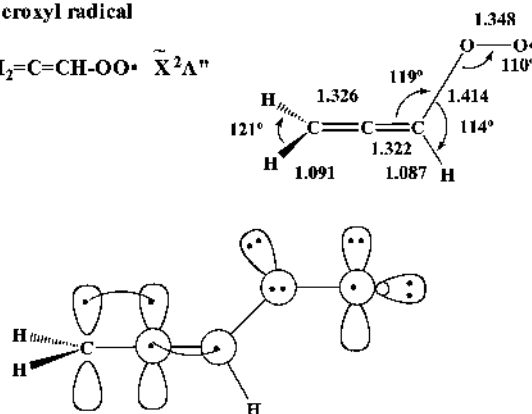
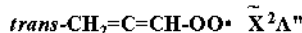


## ROHF/CCSD(T)/ANO0 structures (Å) and GVB formulae

## propargyl peroxy radical



## allenyl peroxy radical

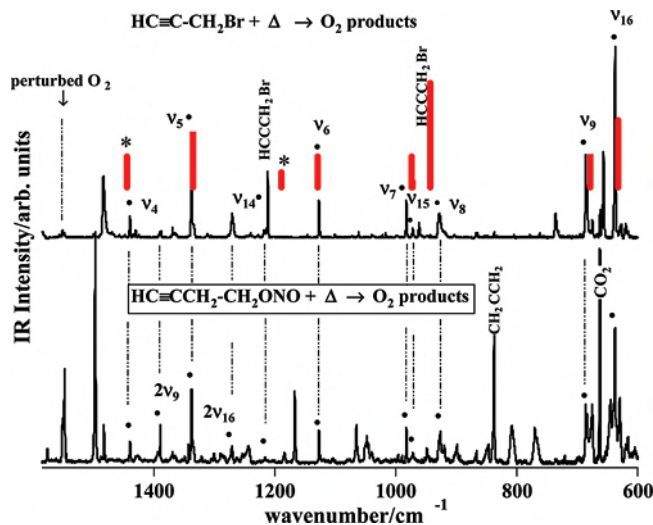


**Figure 1.** Minimized  $\text{C}_3\text{H}_3\text{OO}$  geometries found resulting from an ROHF/CCSD(T)/ANO0 calculation. The two minimum structures are the *trans*-propargyl peroxy radical,  $\text{HC}\equiv\text{C}-\text{CH}_2\text{OO}\cdot \tilde{X}^2A''$ , and the *trans*-allenyl peroxy radical,  $\text{CH}_2=\text{C}=\text{CH-OO}\cdot \tilde{X}^2A''$ . All distances are in Å and angles are in degrees. GVB structures<sup>6</sup> are shown as well.

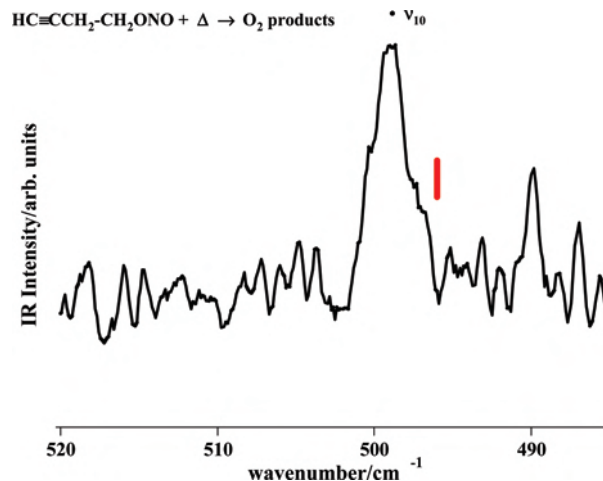
the harmonic force field was obtained with both the 4s2p1d (on H)/4s3p2d1f (on C) contraction known as ANO1 and the somewhat smaller 2s1p (H)/3s2p1d (C) contraction called ANO0. The anharmonic force field was determined only with the smaller basis, and the fundamental levels were calculated with second-order vibrational perturbation theory (VPT2) using the ANO1 harmonic force field in conjunction with cubic and quartic constants obtained with CCSD(T)/ANO0.

## Results

One anticipates several isomers of the  $\text{C}_3\text{H}_3\text{OO}$  radical: *cis*- and *trans*- $\text{HC}\equiv\text{CCH}_2\text{OO}$  as well as *cis*- and *trans*- $\text{CH}_2=\text{C}=\text{CHOO}$ . Both peroxy radicals have  $\tilde{X}^2A''$  ground states; Figure 1 shows the GVB structures.<sup>6</sup> To determine the structure and energy of the  $\text{C}_3\text{H}_3\text{OO}$  product, electronic structure calculations were performed using the B3LYP/6-311G(d,p) and CCSD(T)/ANO methods. Four isomers of  $\text{C}_3\text{H}_3\text{OO}$  were calculated: *cis*- and *trans*- $\text{HC}\equiv\text{CCH}_2\text{OO}$ , as well as *cis*- and *trans*- $\text{CH}_2=\text{C}=\text{CHOO}$ . The *trans*- $\text{CH}_2=\text{C}=\text{CHOO}$  isomer was identified as the most stable conformation, while *cis*- $\text{HC}\equiv\text{CCH}_2-\text{OO}$  never converged as a stable minimum but to a *gauche* structure located more than 2 kcal mol<sup>-1</sup> below the *cis* conformer. For all structures the CCC angle was nearly 180°. Minima for both *cis* and *trans* conformations were found for the  $\text{CH}_2=\text{C}=\text{CHOO}$  peroxy, as well as *trans*- and *gauche*- $\text{HC}\equiv\text{C}-\text{CH}_2\text{OO}$ . Anharmonic frequencies for  $\text{HC}\equiv\text{C}-\text{CH}_2\text{OO}$



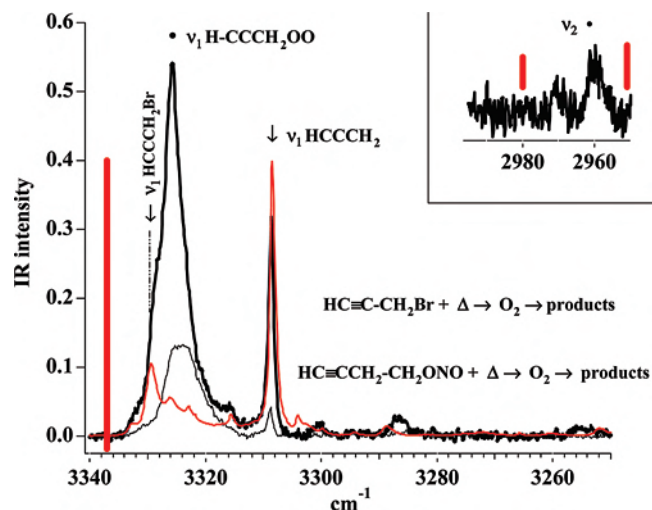
**Figure 2.** IR spectra of the propargyl peroxy resulting from addition of  $\text{HCCCH}_2$  radicals to  $\text{O}_2$  in an Ar matrix at 20 K. Propargyl radicals are produced from two different precursors. The top spectrum is propargyl peroxy radical generated by using  $\text{HC}\equiv\text{C}-\text{CH}_2\text{Br}$  as a precursor for propargyl radicals, while the bottom spectrum is a spectrum of propargyl peroxy radical using  $\text{HC}\equiv\text{C}-\text{CH}_2\text{CH}_2\text{ONO}$  as a precursor. The calculated CCSD(T)/ANO anharmonic frequencies  $\{\nu\}$  are shown as sticks in red while the experimental frequencies  $\{\nu\}$  are marked by bullets (•). Peaks common to both spectra are attributed as being due to the  $\text{C}_3\text{H}_3\text{OO}$  adduct, unless otherwise noted.



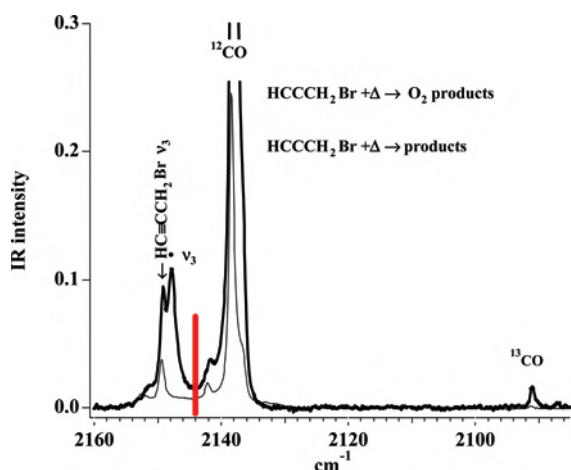
**Figure 3.** The  $\text{OO}-\text{CH}_2-\text{CCH}$  bending mode ( $\nu_{10}$ ) of  $\text{HC}\equiv\text{CCH}_2\text{OO}$  radical that results for addition of  $\text{HCCCH}_2$  radical to oxygen. Propargyl radicals are generated by thermal cracking of  $\text{HC}\equiv\text{C}-\text{CH}_2\text{CH}_2\text{ONO}$ .

were calculated from the optimized geometry in Figure 1 and are summarized in Table 1.

Figure 2 shows the fingerprint region of the  $\text{C}_3\text{H}_3\text{OO}$  radical, 1600–600 cm<sup>-1</sup>. The bottom trace represents  $\text{C}_3\text{H}_3\text{OO}$  formed by condensing  $\text{O}_2$  with  $\text{HCCCH}_2$  produced by decomposition of  $\text{HC}\equiv\text{C}-\text{CH}_2\text{CH}_2\text{ONO}$  (bottom trace) and  $\text{HC}\equiv\text{C}-\text{CH}_2\text{Br}$  (top trace). Common bands exhibiting similar relative intensity patterns are assigned to the  $\text{HC}\equiv\text{CCH}_2\text{OO}$  radical. These assignments are guided by the anharmonic frequencies predicted by the CCSD(T) calculation in Table 1. The computed *trans*- $\text{HC}\equiv\text{CCH}_2-\text{OO}$  stick spectrum, shown in red, closely resembles the experimental spectrum. The only  $\text{C}_3\text{H}_3\text{OO}$  peak observed below 600 cm<sup>-1</sup> was generated from  $\text{HC}\equiv\text{C}-\text{CH}_2\text{CH}_2\text{ONO}$  and is shown in Figure 3. Figure 4 depicts the CH stretching region while Figure 5 shows the  $-\text{C}\equiv\text{C}-$  region. Figures 6, 7, and 8 display the remaining low frequency bands. In all of these



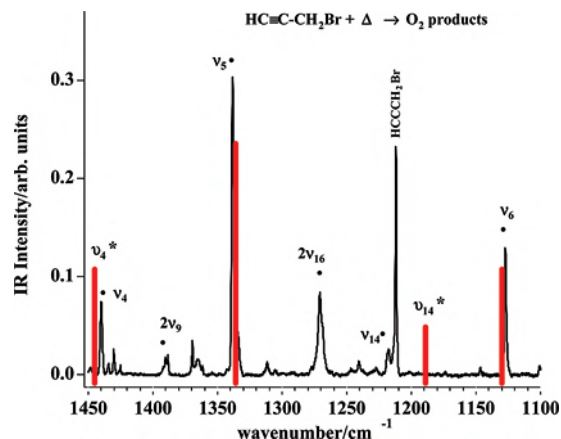
**Figure 4.** The two black traces are IR spectra (of the CH stretching region) resulting from combination of propargyl radicals with O<sub>2</sub> in a cryogenic matrix. The top black trace uses HCCCH<sub>2</sub>Br as the propargyl precursor and the bottom trace uses HCCCH<sub>2</sub>CH<sub>2</sub>ONO to generate propargyl radical. The red trace is the IR spectrum that results from the thermal cracking of HC≡C-CH<sub>2</sub>Br. The red spectrum provides us with ν<sub>1</sub>(H-CCCH<sub>2</sub>Br) and ν<sub>1</sub>(H-CCCH<sub>2</sub>). The intense red stick is the predicted CCSD(T)/ANO anharmonic transition, ν<sub>1</sub>. The in-set at the top of the figure shows the weak CH<sub>2</sub> absorption at 2960 cm<sup>-1</sup> resulting from reaction of propargyl radical (from HCCCH<sub>2</sub>Br) and oxygen. The red stick is the predicted CCSD(T)/ANO ν<sub>2</sub> at 2951 cm<sup>-1</sup>.



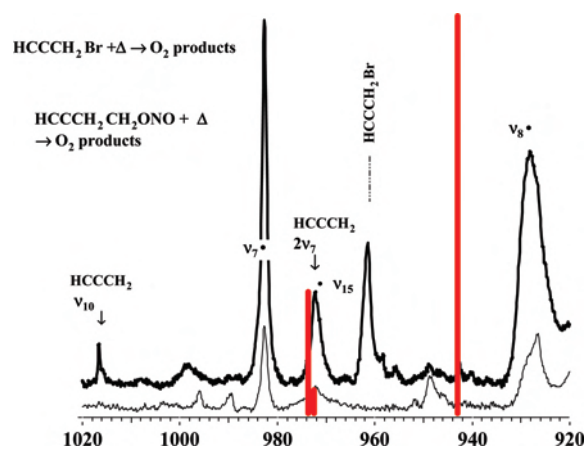
**Figure 5.** A scan through the -C≡C- stretching region of the IR spectrum following the addition of HCCCH<sub>2</sub> to O<sub>2</sub>. The top black trace uses HCCCH<sub>2</sub>Br as the propargyl precursor together with addition of O<sub>2</sub>. The bottom trace is of HCCCH<sub>2</sub>Br and the HCCCH<sub>2</sub> radical by themselves; no oxygen is present. The intense red stick is the predicted CCSD(T)/ANO anharmonic transition, ν<sub>3</sub>(HC≡CCH<sub>2</sub>OO).

figures, the predicted CCSD(T) anharmonic modes {*v*} from Table 1 are plotted as red sticks.

Linear dichroism spectra were also measured to aid in the assignment of vibrational bands. The electronic structure of all alkyl peroxy radicals should be somewhat similar, because their electronic transitions tend to be localized on the terminal oxygen atoms. For both HOO and CH<sub>3</sub>OO the ground state<sup>33,34</sup> is  $\tilde{X}^2A''$ . The low lying  $\tilde{A}^2A'$  excited states of a handful of peroxy radicals have been extensively studied, with the  $\tilde{A}^2A' - \tilde{X}^2A''$  transitions lying in the near IR.<sup>35-39</sup> Alkyl peroxy radicals also possess a second, dissociative, excited state with broad electronic transitions usually in vicinity of 260 nm ( $\tilde{B}^2A'' - \tilde{X}^2A''$ ). Consequently the transition matrix element  $\langle \tilde{B}^2A'' | \mu | \tilde{X}^2A'' \rangle$



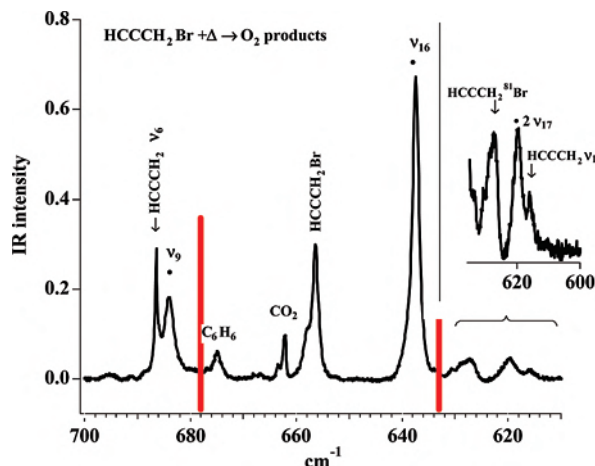
**Figure 6.** The IR spectrum resulting from addition of O<sub>2</sub> to propargyl radical (generated from HCCCH<sub>2</sub>Br). The intense red sticks are the predicted bands: ν<sub>4</sub>, ν<sub>5</sub>, ν<sub>14</sub>, and ν<sub>6</sub>. The calculated anharmonic modes, 4 and 14, are have low intensity (see Table 1) and have been scaled by a factor of 10 to show up in this figure. The scaled bands are marked by an asterisk, ν<sub>4</sub>\* and ν<sub>14</sub>\*.



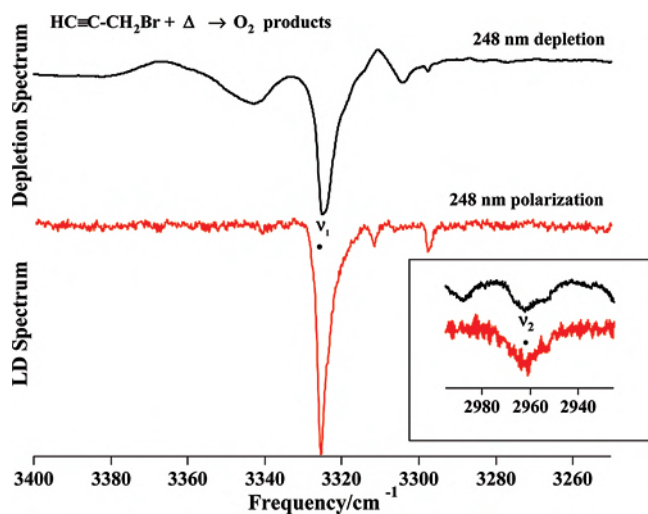
**Figure 7.** A scan through fingerprint region of the IR spectrum following addition of HCCCH<sub>2</sub> to O<sub>2</sub>. The top black trace uses HCCCH<sub>2</sub>Br as the propargyl precursor and the bottom trace uses HCCCH<sub>2</sub>CH<sub>2</sub>ONO to generate propargyl radical. The intense red sticks are the predicted CCSD(T)/ANO anharmonic transitions. The calculated modes, ν<sub>7</sub> and ν<sub>15</sub> are accidentally degenerate at 973 cm<sup>-1</sup>. For display purposes, we have plotted (ν<sub>7</sub>, ν<sub>15</sub>) split by 1 cm<sup>-1</sup>.

yields the symmetry of the transition moment to be A'. As a first step the initially isotropic distribution of propargyl peroxy radicals trapped in the matrix is selectively depleted using polarized 248 nm light until roughly 75% of the identified HCCCH<sub>2</sub>-OO IR fundamental lines are bleached. Because the laser is polarized horizontal with respect to the laboratory frame, Z, any propargyl peroxy molecule with a significant projection of its transition dipole moment,  $\mu$ , parallel to the depleting laser light is destroyed because of excitation to the broad  $\tilde{B}^2A''$  dissociative state (200–300 nm). The remaining propargyl peroxy radicals are therefore oriented with their transition dipole moments perpendicular to the depleting laser light and the molecules in the matrix are aligned. Depletion spectra are shown as the black traces in Figures 9 and 10.

Linear dichroism spectra are then collected with polarized IR light generated using a Molelectron wire grid IR polarizer. The difference in the two polarized spectra collected with the light parallel and perpendicular with respect to the laboratory frame ( $I_z - I_y$ ) yields the LD spectrum of the aligned matrix species, shown as the red traces in Figures 9–11.



**Figure 8.** A scan of the low frequency portion of the IR spectrum resulting from addition of O<sub>2</sub> to propargyl radical (generated from HCCCH<sub>2</sub>Br). The inset at the top of the figure shows the weak overtone of HCCCH<sub>2</sub>OO, 2ν<sub>17</sub>.

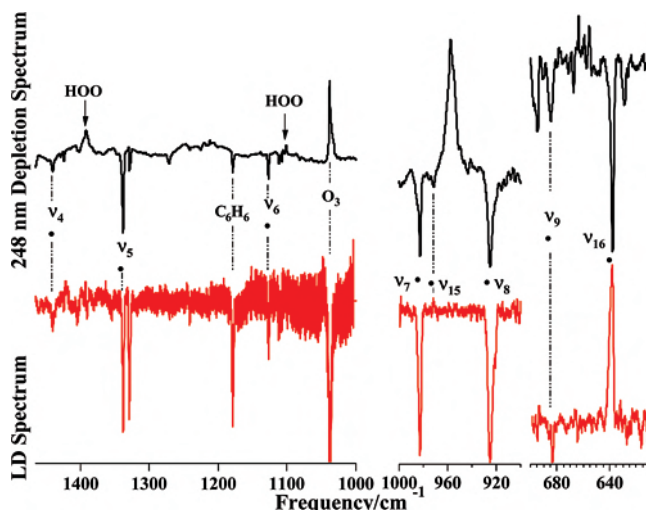


**Figure 9.** At the top, in black, is an infrared spectrum showing the depletion of matrix isolated propargyl peroxy radicals in the CH stretching region upon bombardment by 248 nm laser light. On the bottom, in red, is a linear dichroism spectrum of the propargyl radical following matrix depletion by polarized 248 nm light. IR bands of propargyl peroxy that are a' polarized will have a negative dichroism while IR features that are a'' polarized will have a positive dichroism. The infrared fundamentals of the propargyl peroxy radical are marked by bullets (•). An inset figure shows the weakly polarized peak for ν<sub>2</sub>.

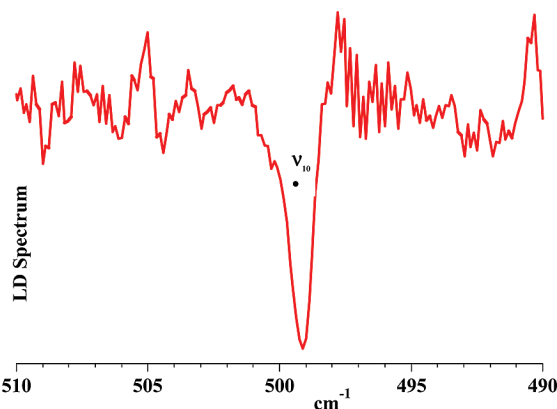
## Discussion

We believe that the propargyl radical is reacting with oxygen in the cryogenic matrix to produce a peroxy radical, C<sub>3</sub>H<sub>3</sub>-OO•. The simplest alkylperoxy radical, CH<sub>3</sub>-OO•, has four vibrational fundamentals<sup>16,40</sup> that are characteristic peroxy modes: ν<sub>5</sub>(CH<sub>3</sub> rock + OO stretch) = 1180 cm<sup>-1</sup>, ν<sub>6</sub>(CH<sub>3</sub> rock - OO stretch) = 1109 cm<sup>-1</sup>, ν<sub>7</sub>(CO stretch) = 902 cm<sup>-1</sup>, ν<sub>8</sub>(COO bend) = 492 cm<sup>-1</sup>. Consequently if we are producing a C<sub>3</sub>H<sub>3</sub>-OO• radical, we anticipate the presence of comparable ROO• bands: an O-O stretch between 1100 and 1200 cm<sup>-1</sup>, a C-O• stretch at approximately 900 cm<sup>-1</sup>, and a C-O-O• bend at roughly 500 cm<sup>-1</sup>.

We observe that addition of molecular oxygen to the matrix destroys the propargyl radical. The IR spectra in Figure 2 with characteristic ROO• modes strongly suggests that the HCCCH<sub>2</sub> radical has combined with oxygen to produce a peroxy radical,



**Figure 10.** At the top, in black, is an infrared spectrum showing the depletion of matrix isolated propargyl peroxy radicals, in the fingerprint region upon exposure to 248 nm laser light. On the bottom, in red, is a linear dichroism spectrum of the HCCCH<sub>2</sub>OO radical following matrix depletion by polarized 248 nm light. IR bands of propargyl peroxy that are a' polarized will have a negative dichroism while IR features that are a'' polarized will have a positive dichroism. The infrared fundamentals of the propargyl peroxy radical are marked by bullets (•).



**Figure 11.** The linear dichroism spectrum of the HCCCH<sub>2</sub>OO following matrix depletion by polarized 248 nm light. The OO-CH<sub>2</sub>-CCH bending mode, ν<sub>10</sub>, is polarized A'.

C<sub>3</sub>H<sub>3</sub>OO•. In Figures 2 and 3, bands at 1127, 928, and 499 cm<sup>-1</sup> were observed in spectra derived from two different precursors. Guided by the CCSD(T) anharmonic frequencies, these are assigned (Table 1) as ν<sub>6</sub>(O-O stretch), ν<sub>8</sub>(C-OO stretch), and a mixed bending mode (ν<sub>10</sub>) that has substantial C-O-O bending character.

We must decide if the peroxy radical is H-C≡CCH<sub>2</sub>-OO• or CH<sub>2</sub>=C=CHOO• (or both). One way to differentiate between these two peroxy radicals is to search for a high frequency CH stretch (>3300 cm<sup>-1</sup>) which is characteristic of an acetylenic mode (H-C≡C-). The CH portion of the IR spectrum is shown in Figure 4. The bottom portion of this figure shows three different spectra. The two black traces result from addition of the HCCCH<sub>2</sub> radical [prepared from HCCCH<sub>2</sub>Br (top) or HCCCH<sub>2</sub>CH<sub>2</sub>ONO (bottom)] to O<sub>2</sub>. The red trace corresponds to the HCCCH<sub>2</sub> radical as produced from propargyl bromide and shows the two H-C≡C bands for propargyl bromide (ν<sub>1</sub>, H-C≡CCH<sub>2</sub>Br, 3329 cm<sup>-1</sup>) and the propargyl<sup>5</sup> radical (ν<sub>1</sub>, H-C≡C-CH<sub>2</sub>, 3308 cm<sup>-1</sup>). In both spectra when HCCCH<sub>2</sub> radical is combined with O<sub>2</sub>, a new band grows in between



TABLE 2: *trans*-HC≡C-CH<sub>2</sub>-OO  $\tilde{X}^2A''$  Vibrational Modes

mode	local mode description	Ar matrix IR/20 K		calculated ROHF/CCSD(T)/ANO0 anharmonic	
		$\nu$ (cm <sup>-1</sup> )	polarization	adjusted $\nu$ (cm <sup>-1</sup> )	adjusted $A$ (km mol <sup>-1</sup> )
a'					
1	C-H st	3326 ± 3	—	3337	44
2	sym CH <sub>2</sub> st	2960 ± 3	—	2951	7
3	C≡C st	2148 ± 1	na	2144	5
4	CH <sub>2</sub> scissors	1440 ± 1	—	1445	2
5	CH <sub>2</sub> wag	1338 ± 1	—	1336	42
6	O-OCH <sub>2</sub> CCH st	1127 ± 1	—	1130 <sup>a</sup>	20
7	C-C st	982 ± 1	—	973	20
8	O-C st	928 ± 3	—	943	65
9	C≡C-H in-plane bend	684 ± 1	—	678	32
10	O-C-C bend	499 ± 1	—	496	2
11	O-O-C bend	na	na	424	9
12	C-C≡C in-plane deformation	na	na	163 <sup>b</sup>	1 <sup>b</sup>
a''					
13	asym CH <sub>2</sub> st	na	na	2980	5
14	CH <sub>2</sub> twist	1218 ± 1	na	1189	1
15	CH <sub>2</sub> rock	972 ± 1	+	973 <sup>c</sup>	4 <sup>c</sup>
16	C≡C-H out-plane bend	637 ± 1	+	633	42
17	C-C≡C out-plane deformation	na	na	309	7
18	O-O-CH <sub>2</sub> -C torsion	na	na	73	0

<sup>a</sup> After treatment of  $\nu_6 \approx \nu_9 + \nu_{11}$  resonance. <sup>b</sup> After treatment of  $\nu_{12} \approx 2\nu_{18}$  resonance. <sup>c</sup> After treatment of  $\nu_{15} \approx \nu_9 + \nu_{17}$  resonance.

$\nu_1(\text{H}-\text{C}\equiv\text{CCH}_2\text{Br})$  and  $\nu_1(\text{H}-\text{CCCH}_2)$ . This new band observed at 3326 cm<sup>-1</sup> only appears when O<sub>2</sub> is added to the matrix and is assigned as the acetylenic H-C stretch,  $\nu_1(\text{H}-\text{C}\equiv\text{CCH}_2-\text{OO}\cdot)$ . The CCSD(T)/ANO prediction for  $\nu_1$  is 3337 cm<sup>-1</sup> and is plotted as the bold red stick in Figure 4. The inset at the top of Figure 4 shows the weak  $\nu_2$  symmetric CH<sub>2</sub> absorption at 2960 cm<sup>-1</sup>; the predicted CCSD(T)/ANO  $\nu_2$  is 2951 cm<sup>-1</sup>. The antisym CH<sub>2</sub> stretching mode,  $\nu_{13}$ , could not be located. The CCSD(T) calculations in Table 1 predict  $\nu_{13} = 2980$  cm<sup>-1</sup> and  $A_{13} = 5$  km mol<sup>-1</sup>, slightly less than  $A_2$ .

If the carrier of the signal is HCCCH<sub>2</sub>OO $\cdot$ , we expect a -C≡C- stretch to appear in the IR spectrum. The predicted CCSD(T)/ANO  $\nu_3$  is 2144 cm<sup>-1</sup> and is plotted as a red stick in Figure 5. There are two black traces in this figure showing the spectra resulting from addition of HCCCH<sub>2</sub> (produced from HCCCH<sub>2</sub>Br to O<sub>2</sub> (top trace) and the spectrum resulting from HCCCH<sub>2</sub>Br and propargyl radical by themselves. Intense features for <sup>12</sup>CO and <sup>13</sup>CO are identified, and a new band at 2148 cm<sup>-1</sup> grows in to the red of the  $\nu_3(\text{HC}\equiv\text{CCH}_2\text{Br})$  signal. We assign  $\nu_3(\text{HC}\equiv\text{CCH}_2\text{OO}\cdot)$  to this new feature.

The clear presence of acetylenic features,  $\nu_1(\text{H}-\text{CCCH}_2\text{OO})$  and  $\nu_3(\text{HC}\equiv\text{CCH}_2\text{OO})$ , identifies the C<sub>3</sub>H<sub>3</sub>OO adduct as the propargyl peroxy radical. The HC≡C-CH<sub>2</sub>OO $\cdot$   $\tilde{X}^2A''$  radical has 12 a' ⊕ 6 a'' vibrational modes and we are able to assign most of the major bands. Four fundamental bands, two a' and two a'', are predicted to lie outside the detection region of the MCT detector used (4000–450 cm<sup>-1</sup>).

Four fundamentals are shown in Figure 6. A pair of modes,  $\nu_5(\text{CH}_2 \text{ wag})$  and  $\nu_6(\text{O}-\text{OCH}_2\text{CCH st})$ , are intense and thus easy to identify. The other two fundamentals,  $\nu_4(\text{CH}_2 \text{ scissors})$  and  $\nu_{14}(\text{CH}_2 \text{ twist})$ , are weaker. Two features are identified as the overtones  $2\nu_9$  and  $2\nu_{16}$ . The predicted CCSD(T)/ANO levels ( $\nu_4$ ,  $\nu_5$ ,  $\nu_{14}$ ,  $\nu_6$ ) are plotted as red sticks in Figure 6. The calculated intensities for  $\nu_4$  and  $\nu_{14}$  are small and have been scaled by a factor of 10 (marked by an asterisk (\*) in the figure) so they will be visible.

The spectra in Figure 7 show intense bands assigned to the HCC-CH<sub>2</sub>OO $\cdot$  stretch ( $\nu_7 = 982$  cm<sup>-1</sup>) and the HCCCH<sub>2</sub>-OO $\cdot$  stretch ( $\nu_8 = 928$  cm<sup>-1</sup>). The CH<sub>2</sub> rocking mode ( $\nu_{15} = 972$  cm<sup>-1</sup>) is very weak and is blended with the  $2\nu_7$

overtone of propargyl radical. Figure 2 shows the ( $\nu_7$ ,  $\nu_{15}$ ) pair better. The calculated CCSD(T)/ANO  $\nu_7$  and  $\nu_{15}$  modes are accidentally degenerate at 973 cm<sup>-1</sup> but are plotted as red sticks split by 1 cm<sup>-1</sup> in Figure 7. The OCH<sub>2</sub>CC≡C-H bending modes,  $\nu_9 = 684$  and  $\nu_{16} = 637$  cm<sup>-1</sup>, are shown in Figure 8. At the top right is an inset which shows a feature at 620 cm<sup>-1</sup>; this is assigned as the overtone of C-C≡C out-plane deformation,  $2\nu_{17} = 620$  cm<sup>-1</sup>.

Figures 9–11 depict the depletion and linear dichroism spectra for the H-C≡CCH<sub>2</sub>-OO $\cdot$  radical. In the CH stretching region  $\nu_1$  and  $\nu_2$  demonstrate negative dichroism at  $3326 \pm 6$  and  $2961 \pm 8$  cm<sup>-1</sup> characteristic of a' modes (Figure 9). Seven additional propargyl peroxy bands demonstrated negative LD (Figure 10) and are assigned as a' modes:  $\nu_4$ ,  $\nu_5$ ,  $\nu_6$ ,  $\nu_7$ ,  $\nu_8$ ,  $\nu_9$ , and  $\nu_{10}$ . Vibrations  $\nu_{15}$  and  $\nu_{16}$  have positive LD, and are thus a'' modes. The weak OCH<sub>2</sub>CC≡CH mode ( $\nu_3$ ) and the CH<sub>2</sub>-twisting mode ( $\nu_{14}$ ) were not detected in an LD experiment. To collect such spectra, IR signals are first depleted by as much as 75%. The wire grid polarizers tend to attenuate signals even further, thus making weaker signals difficult to observe over the noise.

The H-C≡C-CH<sub>2</sub> radicals are reactive radicals and can dimerize. IR signals from benzene were clearly observed in some of the matrix spectra (for example, Figure 8). In previous work<sup>5</sup> we observed propargyl radical chemistry by observing (CH<sub>2</sub>=C=CH<sub>2</sub>, HC≡C-CH<sub>3</sub> and benzene) in both matrix IR spectra and in gas phase photoionization mass spectra. Their presence in both experiments indicates that radical/radical dimerization and H-abstraction reactions are occurring in the hyperthermal nozzle.

The final set of matrix assignments for *trans*-H-C≡CCH<sub>2</sub>-OO $\cdot$  are collected in Table 2. We have adopted the half-full-width at half-maximum ( $1/2$  fwhm) intensity as a measure of the uncertainty for the matrix frequency. These uncertainties are somewhat subjective because we have little understanding of the complex line shapes that are observed. An additional difficulty is that several of the HCCCH<sub>2</sub>OO modes are blended with other peaks in the spectrum.



**TABLE 3: Comparison of CH<sub>3</sub>OO  $\tilde{X}^2A'$  Matrix vs Gas-Phase Vibrational Modes**

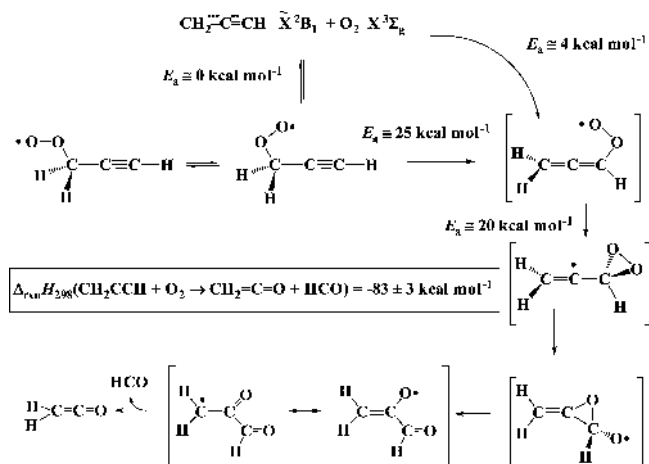
		matrix <sup>16</sup> (cm <sup>-1</sup> )	gas phase <sup>40</sup> (cm <sup>-1</sup> )
a'			
$\nu_1$	CH <sub>3</sub> symmetric stretch	3032	3033 ± 1
$\nu_2$	CH <sub>3</sub> total symmetric stretch	2954	2954 ± 1
$\nu_3$	CH <sub>3</sub> deformation	1448	1453 ± 2
$\nu_4$	CH <sub>3</sub> umbrella	1410	1408 ± 1
$\nu_5$	CH <sub>3</sub> rock+OO stretch	1180	1183 ± 1
$\nu_6$	CH <sub>3</sub> rock+OO stretch	1109	1117 ± 2
$\nu_7$	CO stretch	902	na
$\nu_8$	COO bend	492	na
a''			
$\nu_9$	CH <sub>3</sub> asymmetric stretch	3024	3020 ± 2
$\nu_{10}$	CH <sub>3</sub> asym. deformation	1434	1441 ± 1
$\nu_{11}$	CH <sub>2</sub> wag	na	na
$\nu_{12}$	CH <sub>3</sub> torsion	na	na

It would be helpful to estimate a complete set of internally consistent, reliable vibrational frequencies for the gas-phase HCCCH<sub>2</sub>OO radical. There are no gas-phase observations of the propargyl peroxy radical. Jacox has reviewed the matrix shifts for a large number of diatomic and small polyatomic free radicals and ions trapped in Ne and Ar matrices.<sup>41,42</sup> She concluded that for polyatomic free radicals in Ar matrices the frequency shift is generally less than 1% and usually to the red.

In an earlier study of the allyl radical,<sup>43</sup> we observed the five CH stretching modes of CH<sub>2</sub>CHCH<sub>2</sub>. High resolution laser spectroscopy<sup>44-46</sup> subsequently also detected all five as well. For allyl radical, CH<sub>2</sub>CHCH<sub>2</sub>, the shifts (gas-matrix) are  $\Delta\nu_1$  (25 cm<sup>-1</sup>),  $\Delta\nu_2$  (18 cm<sup>-1</sup>),  $\Delta\nu_3$  (4 cm<sup>-1</sup>),  $\Delta\nu_{13}$  (4 cm<sup>-1</sup>), and  $\Delta\nu_{14}$  (0 cm<sup>-1</sup>). A similar result was found for the phenyl radical, C<sub>6</sub>H<sub>5</sub>. Almost a decade ago a hyperthermal nozzle was used<sup>47</sup> to deposit phenyl radical in a matrix, and 24 of 27 total vibrational modes were observed. Recent tunable-difference-frequency laser studies<sup>48</sup> of jet-cooled C<sub>6</sub>H<sub>5</sub> radicals have reported  $\nu_{19}(\text{C}_6\text{H}_5) = 3071.8904 \pm 0.0010$  cm<sup>-1</sup>. Consequently for phenyl radical, the gas-to-matrix shift is  $\Delta\nu_{19}$  (0.9 cm<sup>-1</sup>).

An earlier IR study of the methyl peroxy radical<sup>16</sup> produced the CH<sub>3</sub>OO radical by condensation of CH<sub>3</sub> with O<sub>2</sub> in a cryogenic matrix. Recently it has become possible to assess the gas-matrix shifts of the CH<sub>3</sub>OO radical. A step-scan Fourier-transform spectrometer coupled with a multipass absorption cell was employed<sup>40</sup> to record time-resolved IR absorption spectra of reaction intermediates resulting from addition of CH<sub>3</sub> to O<sub>2</sub>. That paper observed rotationally resolved bands for several modes of the CH<sub>3</sub>OO\* radical. A comparison of the matrix values versus the gas-phase assignments is shown in Table 3. Most of the matrix values are within a few cm<sup>-1</sup> of the gas-phase modes; the biggest discrepancy is 8 cm<sup>-1</sup> for  $\nu_6$ . Consequently we believe that all of the matrix frequencies for the propargyl radical are within  $\leq 1\%$  of the true, gas phase frequencies.

What are the likely pathways for HCCCH<sub>2</sub> to react with O<sub>2</sub>? The thermochemistry of reactions 2–6 has been considered earlier but should be slightly revised. Table 4 lists the experimental enthalpies for reaction of HCCCH<sub>2</sub> with O<sub>2</sub>. For most channels, the  $\Delta E_{\text{calcd}}$  values<sup>2</sup> are close to the range spanned by the  $\Delta_{\text{rxn}}H_{298}$  uncertainties. It is also encouraging that the CBS/QB3 “semi-empirical” calculations correctly predict  $\Delta H_{298}(\text{HCCCH}_2\text{—OO})$  to be  $19 \pm 1$  kcal mol<sup>-1</sup> in good agreement with the flow tube results. The QCISD(T,full)/6-311++G(3df,2pd) calculations correctly predict that the activation barriers for O<sub>2</sub> addition to HCCCH<sub>2</sub> favor the propargyl peroxy radical,  $E_a(8) < E_a(7)$ . The QCISD(T,full) estimate for

**Figure 12.** A possible mechanism for the reaction,

This composite figure is based on previous electronic structure calculations.<sup>2,49,50</sup> The thermochemistry is from Table 4.

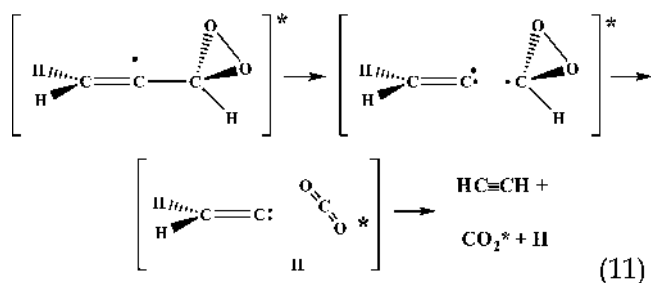
**TABLE 4: Experimental Thermochemistry of the HCCCH<sub>2</sub> + O<sub>2</sub> Reaction**

reaction	$\Delta_{\text{rxn}}H_{298}$ (kcal mol <sup>-1</sup> )	reference
HCCCH <sub>2</sub> + O <sub>2</sub> → HC≡CCH <sub>2</sub> OO	-19 ± 1	13
HCCCH <sub>2</sub> + O <sub>2</sub> → CH <sub>2</sub> =C=O + HCO	-83 ± 3	51–54
HCCCH <sub>2</sub> + O <sub>2</sub> → CH <sub>3</sub> CO + CO	-111 ± 3	53, 55
HCCCH <sub>2</sub> + O <sub>2</sub> → CH <sub>2</sub> CHO + CO	-106 ± 4	53, 56–58
HCCCH <sub>2</sub> + O <sub>2</sub> → HCHO + HCCO	-67 ± 4	53, 59
HCCCH <sub>2</sub> + O <sub>2</sub> → CH <sub>2</sub> CH + CO <sub>2</sub>	-105 ± 3	54, 60
HCO → H + CO	15.6 ± 0.1	52

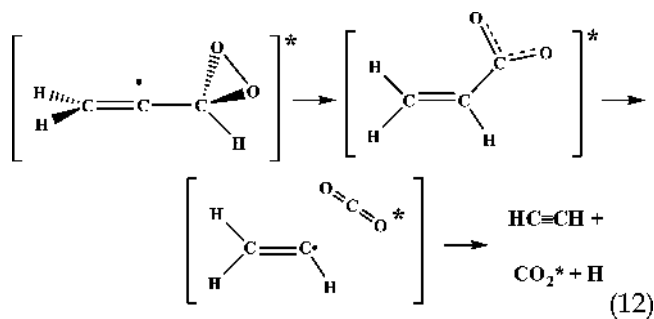
$E_a(8)$  is 3.7 kcal mol<sup>-1</sup> but Hahn et al. empirically<sup>2</sup> reduced  $E_a(8)$  to -0.2 kcal mol<sup>-1</sup>. Our experimental findings agree with this revision. The HC≡CCH<sub>2</sub>OO radicals in Figures 2–11 are produced by addition of HCCCH<sub>2</sub> radicals with O<sub>2</sub> in an Ar matrix at 20 K. Exothermic bimolecular reactions at such low temperatures cannot have non-negligible activation barriers. Even though the CBS/QB3 calculations predict  $\Delta H_{298}(\text{CH}_2=\text{C}=\text{CH—OO})$  to be  $21 \pm 1$  kcal mol<sup>-1</sup>, we find no experimental evidence for the formation of the allenyl peroxy radical. This is consistent with the prediction of Hahn et al.<sup>2</sup> that  $E_a(7) > 0$ .

On the basis of the theoretical results, earlier experimental findings, and this work, we can produce a plausible reaction mechanism for the reaction of HCCCH<sub>2</sub> and O<sub>2</sub>; this is shown in Figure 12. At low temperatures, propargyl radical reversibly adds to oxygen to produce the HC≡CCH<sub>2</sub>OO radical. At higher temperatures above 350 K, propargyl radicals combine with oxygen to produce chemically activated allenyl peroxy radicals, (CH<sub>2</sub>=C=CH—OO)\*. On the basis of the calculations of Hahn et al.<sup>2</sup> and Carpenter's insights to dioxiranyl radicals,<sup>49,50</sup> a mechanism for reaction 2 producing CH<sub>2</sub>=C=O + HCO is sketched in Figure 12. Ketene and the formyl radical were the only products detected by Slagle and Gutman<sup>13</sup> but their PIMS spectrometer could not detect CO or CO<sub>2</sub>. Dong et al. clearly observed IR emission signals<sup>14</sup> for HCO\*, CO<sub>2</sub>\*, and CO\* from the reaction of HCCCH<sub>2</sub> with O<sub>2</sub> at low pressures (0.3 Torr). The addition of 2 Torr Ar buffer gas completely quenched signals from CO<sub>2</sub>\*. All of these products can be rationalized by Figure 12. Table 4 shows  $\Delta_{\text{rxn}}H_{298}(\text{HCCCH}_2 + \text{O}_2 \rightarrow \text{CH}_2\text{CO} + \text{HCO}) = -83 \pm 3$  kcal mol<sup>-1</sup>. Consequently it is likely that the products CH<sub>2</sub>=C=O\* and HCO\* are chemically activated. Because  $\Delta H_{298}(\text{H—CO})$  is only  $15.6 \pm 0.1$  kcal mol<sup>-1</sup>, it seems

likely that much of the CO\* could be derived from HCO\*. The intermediate dioxiranyl radical is a possible source for the CO<sub>2</sub>\* detected by Dong et al.



Equation 11 is consistent with the observation<sup>14</sup> that increasing the buffer gas pressure suppresses emission from CO<sub>2</sub>\*. The dioxiranyl radical in eq 11 was computed to be an important intermediate by Dong et al. (designated IM2 in Figure 4 of ref 14). The pathways in Figure 4 in ref 14 are the result of UB3LYP/6-31+G(d,p) electronic structure calculations. These calculations argue that the <sup>2</sup>A' dioxiranyl radical rearranges to the vinyl oxycarbonyl radical (designated IM7 in Figure 4 of ref 14) that decarboxylates to the vinyl radical. The CH<sub>2</sub>=CH radical could decompose to acetylene and a H atom.



The differences between the pathways in eq 11 and 12 are based on the observation that alkyloxycarbonyl radicals, RCO<sub>2</sub>, are not bound species. They spontaneously fragment carbon dioxide: RCO<sub>2</sub> → R + CO<sub>2</sub>. The HCO<sub>2</sub>, CH<sub>3</sub>CO<sub>2</sub>, and C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub> radicals have been studied by photodetachment: RCO<sub>2</sub><sup>-</sup> + ħω<sub>266 nm</sub> → RCO<sub>2</sub> + e<sup>-</sup>. The only oxycarbonyl radical that has been isolated is the oxybenzoyl radical, C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>, which was observed by EPR in a low temperature crystal. It is unlikely that the UB3LYP/6-31+G(d,p) calculations will properly characterize RCO<sub>2</sub> radicals and we think that eq 11 is a more likely path for the production of CO<sub>2</sub>\* observed by Dong et al.<sup>14</sup>

## Conclusions

Propargyl radicals have been produced through the use of a supersonic hyperthermal nozzle. These radicals were able to combine with O<sub>2</sub> in a cold Ar matrix, indicating that the reaction between propargyl radical and O<sub>2</sub> occurs without a barrier. Vibrational bands characteristic of all R-OO species were positively identified for the new species, confirming its identity as a peroxy radical. The high frequency acetylenic stretch detected in the experiment shows that the addition product is the propargyl peroxy (HC≡CCH<sub>2</sub>-OO) conformer. No peaks corresponding to the allenyl peroxy radical (CH<sub>2</sub>=C=CH-OO) have been detected. Although previous calculations<sup>2</sup> have found allenyl peroxy to be >5 kcal mol<sup>-1</sup> more stable than propargyl

peroxy, we find no prominent spectroscopic evidence for the CH<sub>2</sub>CCHOO peroxy radical.

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