

An Evaluation of Vinyl Hydroperoxide as an Isolable Molecule

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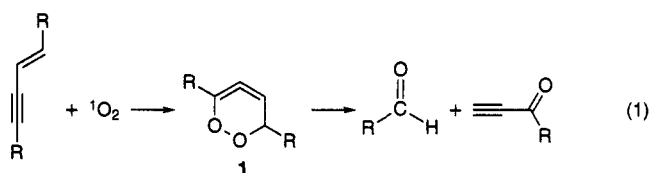
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Ab initio molecular orbital calculations were carried along the reaction surface for the decomposition of vinyl hydroperoxide. Geometry optimizations were obtained at both the 6-31G* and MP2/6-31G* levels for vinyl hydroperoxide, the enol/ α -carbonyl, and hydroxyl radicals, and the transition state structure that leads to these products. Energies for these species were determined by single-point MP4 calculations at the MP2/6-31G* geometry (MP4//MP2/6-31G*). Frequency calculations on these species provide the enthalpy and entropy of reaction and the activation energy at 298 K. From the calculated Arrhenius activation energy of 26.0 kcal/mol and log *A* values of 13.76 and 13.72 at 25 °C and 0 °C, respectively, the lifetimes of vinyl hydroperoxide at these temperatures are estimated to be 58 and 3520 h. These calculations suggest that vinyl peroxides are reactive, but potentially isolable species under proper conditions. Spin density calculations and an analysis of calculated IR frequencies indicate that the odd electron is largely on carbon rather than oxygen in the enol/ α -carbonyl radical.

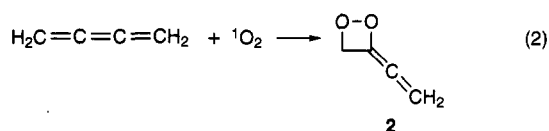
Peroxides are an important class of molecules that are distributed over a variety of environments and have found wide use. There are numerous encounters of peroxides in biological systems.¹ The occurrence of peroxides in biological systems ranges from intermediates in the biosynthesis of prostaglandins which modulate the action of hormones² to chemical signaling in fireflies.³ An unfortunate occurrence of peroxides is found in atmospheric pollution, where peroxides such as peroxyacetyl nitrate (PAN) is implicated in photochemical smog.⁴ Peroxides are a primary concern to the food industry, where for example autooxidation of fats and oils to give peroxide intermediates are involved in rancidity.⁵ The use of peroxides in organic syntheses is well known, such as in olefin oxidation.⁶ There are numerous industrial applications of peroxides as well, a particular noteworthy one is found as initiators in free radical polymerizations.⁷ A wide range of peroxide structural types have been reported,⁸ but seemingly missing categories are vinyl and aryl peroxides.

Sporadic accounts of vinyl and aryl peroxides have appeared, but as yet there are no well-characterized isolable examples to our knowledge. Some examples where these peroxides were reported or suggested as intermediates are shown below. The reaction of an enyne with singlet oxygen gave an aldehyde and an acetylenic ketone where a six-membered ring vinyl peroxide

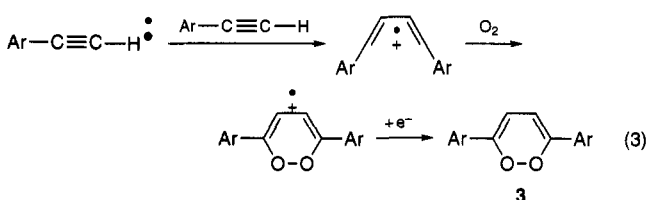
was the suggested intermediate.⁹ Another example of a



proposed vinyl peroxide intermediate from a singlet oxygen reaction is shown in eq 2.¹⁰ Reaction of ground state dioxygen with diene-radical cations was recently



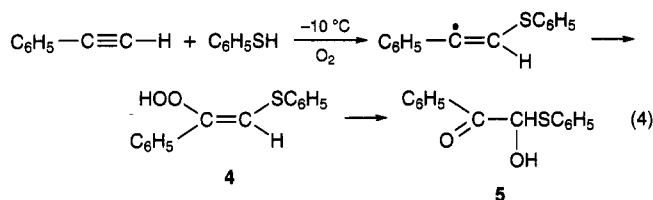
reported to give vinyl peroxides as shown in eq 3.¹¹ The arylacetylene radical cation was generated by electron transfer from the excited state radical cation of 10-methylphenothiazine in acetonitrile at 0 °C. Vinyl peroxide **3** was reported to be isolated and identified by



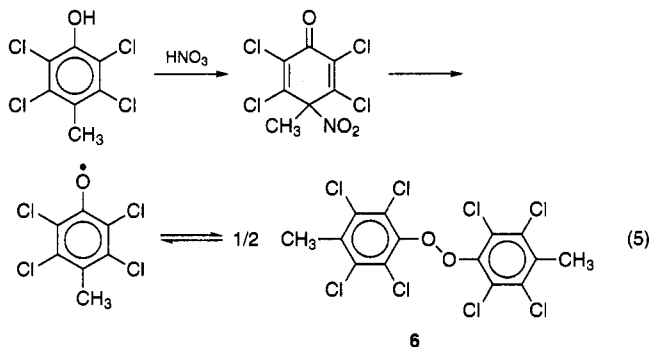
proton NMR and low-resolution mass spectrometry. Attempts to crystallize **3** for high-resolution mass spectrometry resulted in decomposition of the sample. A vinyl hydroperoxide was suggested as a possible intermediate in the radical-chain oxidation of phenylacetylene as shown below.¹² Although the vinyl hydroperoxide **4** was not isolated, such an intermediate appears reasonable, since the final product is the α -hydroxy ketone **5**.

(9) Lee-Ruff, E.; Mileki, M.; Duperrouzel, P.; Lien, M. H.; Hopkinson, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, 346.
 (10) Malcria, M.; Gore, J. *Tetrahedron Lett.* **1979**, 5067.
 (11) Shine, H. J.; Zhao, D.-C. *J. Org. Chem.* **1990**, *55*, 4086.
 (12) Griesbaum, K.; Oswald, A. A.; Hudson, B. E. *J. Am. Chem. Soc.* **1963**, *85*, 1969.

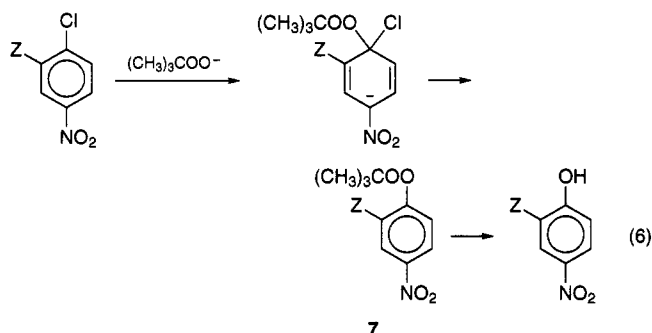
* Abstract published in *Advance ACS Abstracts*, June 1, 1995.
 (1) Niki, E. *Organic Peroxides*; Ando, W., Ed.; Wiley: New York, 1992; p 765.
 (2) Stryer, L. *Biochemistry*, 4th ed.; Freeman: San Francisco, 1995; p 625.
 (3) Shimomura, O. *Chemical and Biological Generation of Excited States*; Adam, W., Cilento, J., Eds.; Academic Press: New York, 1982; p 249.
 (4) Madronich, S.; Calvert, J. G. *J. Geophys. Res. [Atmos.]* **1990**, *95* (D5), 5697.
 (5) Allen, J. C.; Hamilton, R. J. *Rancidity in Foods*, 2nd ed., Elsevier: New York, 1989.
 (6) (a) Smith, M. B. *Organic Synthesis*; McGraw-Hill: New York, 1994; p 263. (b) Carruthers, W. *Some Modern Methods of Organic Synthesis*, 2nd ed.; Cambridge University Press: New York, 1978; p 361.
 (7) O'Driscoll, K. F. *Organic Peroxides*; Swern, D., Ed.; Wiley: New York, 1970; Volume 1, Ch. XI.
 (8) Swern, D., Ed. *Organic Peroxides*; Wiley: New York, 1972; Volumes I-III.



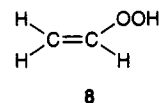
There are reports of aryl peroxides as well which are related to vinyl peroxides by the commonality of the peroxidic oxygen being bonded to an sp^2 carbon atom. Nitric acid oxidation of a phenol was suggested to give an aryl peroxide which was in equilibrium with a phenoxy radical as shown in eq 5.¹³ More recently, an aryl peroxide was proposed as an intermediate in a



nucleophilic aromatic substitution reaction as shown in eq 6.¹⁴ Various electron-withdrawing Z-groups were used to facilitate the first step in the reaction, but the aryl



peroxide **7** was not isolated. From these experimental results it is difficult to ascertain the stability of vinyl and aryl peroxides in a benign environment, since the peroxides may be susceptible to decomposition under the reaction conditions. On the other hand, the apparent instability of vinyl and aryl peroxides could be rationalized on the stability of the developing resonance-stabilized enol/ α -carbonyl or phenoxy radical in the transition state structure. Such resonance stabilization would lower the activation energy relative to simple alkyl peroxides. With the advent of reliable molecular orbital calculations, it is now possible to assess the stability of vinyl peroxides in the gas-phase, a benign environment. For this computational study, the simplest model compound was chosen, vinyl hydroperoxide (**8**). Energy minima and the transition state energy were determined along the reaction surface involving the unimolecular rupture of the peroxide bond.

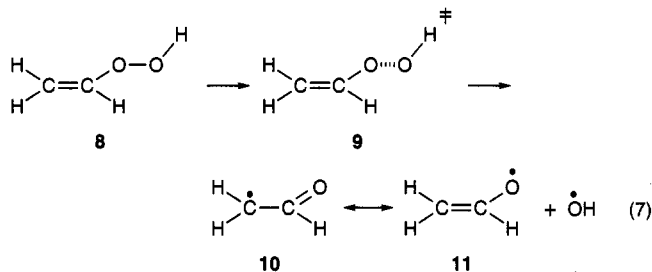


Computational Methods

Ab initio molecular orbital calculations were performed with the Gaussian suite of programs.¹⁵ Geometry optimization was carried out at both the 6-31G* and MP2/6-31G*¹⁶ level of theory. Single point calculations for energies were made with fourth-order Møller–Plesset perturbation theory on the MP2/6-31G* geometry optimized structures (MP4//MP2/6-31G*). The Hartree–Fock (RHF) method was used for vinyl hydroperoxide (**8**), while the unrestricted Hartree–Fock method (UHF) was used for the transition state structure (**9**) and the radical species (**10** and **11**). Frequency calculations were made for all of the species. Negative frequencies were not observed for any of the species except for the transition state structure. Energies of reactions are reported at 0 K with zero-point energy corrections. In addition, enthalpies of reactions at 298 K are calculated where translational, rotational, and vibrational contributions from 0 to 298 K are included.¹⁷ Similarly, entropies are reported at 298 K which contain these contributions. A *PV* work term (0.59 kcal/mol) is included in the overall heat of reaction, since one vinyl peroxide produces two species, an enol/ α -carbonyl radical and a hydroxyl radical.

Results

Energies of the reactant, transition state structure, and products in reaction 7, with zero-point energies at 0 K



are given in Table 1 with the different basis sets. Also, included in this table are the energy barriers (E_b) and energies of the overall reaction (E_r). Spin projected energies (PMP2) are reported in Table 1 at the MP2/UHF/6-31G* level for the enol/ α -carbonyl radical **10** and the hydroxyl radical **11**. Spin contamination is significant for **10** in the UHF wavefunction ($S^2 = 0.886$), but is mostly removed in the projected wavefunction ($S^2(\text{A}) = 0.753$). The UHF wavefunction of the hydroxyl radical shows little spin contamination ($S^2 = 0.755$) and this is eliminated in the projected wavefunction ($S^2(\text{A}) = 0.750$). In Table 2, thermodynamic parameters at 298 K are given for reaction 7, based on electronic energies at the MP4//MP2/6-31G* level and include zero-point and thermal corrections at the MP2/6-31G* level. The IR fre-

(13) Criegee, R. *Methoden der Organische Chemie* (Houben-Weyl), 4th ed.; Muller, E., Ed.; Volume 8, p 8.

(14) Makosza, M.; Sienkiewicz, K. *J. Org. Chem.* **1990**, *55*, 497.

(15) Gaussian 92, Revision C, Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonsalez, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc. Pittsburgh, PA, 1992.

(16) See: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(17) Foresman, J. B.; Frisch, A. *Exploring Chemistry with Electronic Structure Methods*; Gaussian, Inc.: Pittsburgh, PA, 1993; p 114.

Table 1. Energies and Zero-Point Energies for Vinyl Hydroperoxide 8, Transition State Structure 9, Enol/ α -carbonyl Radical 10, and Hydroxyl Radical 11 at 0 K

basis set/ species	E (au) ^a	E_{ZP} (kcal/mol)	E_b (kcal/mol) ^b	E_r (kcal/mol) ^b
6-31G*				
8	-227.6416438	40.65	66.27	-32.38
9	-227.5328140	38.63		
10	-152.3003899	28.30		
11	-75.3822752	5.71		
MP2/6-31G*				
8	-228.2555949	37.59	30.18	17.49, ^c 25.52
9	-228.2037037	35.21		
10	-152.6976955 ^d	27.56		
	-152.6864410			
11	-75.5225720 ^d			
	-75.5210332			
MP4//MP2/ 6-31G*(SDTQ)				
8	-228.3053547		25.58 ^e	22.79 ^e
9	-228.2607999			
10	-152.7285438			
11	-75.5361463			

^a Does not include zero-point energy correction. ^b E_b is the energy barrier and E_r is the overall energy of the reaction and include zero-point energy corrections. ^c Spin projected energies (PMP2) are used for 10 and 11. ^d Spin projected (PMP2) energy. ^e MP2/6-31G* zero-point energies were used.

Table 2. Thermodynamic Parameters at 298 K for the Thermolysis of Vinyl Hydroperoxide (reaction 7) at the MP4//MP2/6-31G* Level

$\Delta H_f^{\circ a}$	$\Delta S_f^{\circ b}$	$\Delta H^{\ddagger c}$	$\Delta S^{\ddagger b}$	$E_a^{a,c}$	$\log A^d$
22.09	38.78	25.40	2.44	26.00	13.76

^a kcal/mol. ^b eu. ^c $E_a = \Delta H^{\ddagger} + RT$. ^d $\log A = \log ekT/h + \Delta S^{\ddagger}/2.303R$.

quencies calculated at the MP2/6-31G* level and corrected by a factor of 0.89¹⁸ are given in Table 3 for vinyl hydroperoxide, the transition state structure, and the enol/ α -carbonyl radical. Assignments were made from the calculated atomic displacements for frequencies above 600 cm⁻¹.

Geometries of the reactant, transition state structure, and products from MP2/6-31G* geometry optimization are given in Figure 1. Structures of vinyl hydroperoxide (8) and the transition state structure 9, generated from optimized coordinates at the MP2/6-31G* level, are given in Figure 2.

Discussion

A careful study of the effect of basis set on energy and geometry of peroxides by Bach and co-workers¹⁹ indicates that geometries are adequately represented at the MP2/6-31G* level and energies with a MP4 single point calculation of this geometry (MP4//MP2/6-31G*). This approach was followed here as well. The necessity for using at least second-order Møller–Plesset (MP) perturbation theory is seen in the large barrier energy (E_b) of 66.3 kcal/mol at 0 K without MP theory (Table 1). Optimization using second-order perturbation theory causes a large decrease in the barrier energy to 30.2 kcal/mol, and a single point MP4 calculation on this optimization geometry causes a further decrease to 25.6 kcal/mol. For comparison, the maximum barrier based on the activation energy for homolysis of a simple dialkyl

Table 3. Corrected Frequencies^a for Vinyl Hydroperoxide Peroxide 8, the Transition State Structure 9, and the Enol/ α -Carbonyl Radical 10 at the MP2/6-31G* Level

	freq, cm ⁻¹	selected assignment ^b
8	3309	O–H stretch
	2979	C–H stretch
	2905	C–H stretch
	2885	C–H stretch
	1531	C–C stretch
	1300	C–H bend
	1246	O–H bend
	1196	C–H bend
	1072	C–H, O–H bend
	887	C–H, O–H bend
	863	C–H bend
	771	O–O stretch
	756	C–H bend
	643	C–H bend
	446	
	308	
	187	
9	95	
	3118	O–H stretch
	2973	C–H stretch
	2869	C–H stretch
	2756	C–H stretch
	1405	C–H bend
	1341	C–H bend
	1232	C–H bend
	1145	C–H bend
	919	C–H bend
	876	C–H bend
	793	C–H, O–H bend
	711	C–H, O–H bend
	556	
	452	
	286	
	280	
208		
-311	imaginary freq: O–O stretch and C–O, O–O twist	
10	3001	C–H stretch
	2886	C–H stretch
	2658	C–H stretch
	1724	C=O stretch
	1344	C–H bend
	1308	C–H bend
	1033	C–C stretch, C–H bend
	959	C–H bend
	860	C–H bend
	600	
	455	
330		

^a Corrected by a factor of 0.89. ^b All frequencies are given, and assignments are made of the higher (greater than 600 cm⁻¹) modes.

peroxide is 38 kcal/mol.²⁰ Some changes in optimized geometry are also effected by the use of perturbation theory. Optimized bond lengths were longer at the MP2/6-31G* level compared to those at 6-31G*. For example, the C–C bonds in 8, 9, and 10 without MP theory and with MP theory (given in parenthesis) are 1.313 (1.334), 1.382 (1.398), and 1.414 (1.458) Å, respectively. Similarly, the O–O bonds in 8 and 9 are longer at the MP2 level: 1.394 (1.477) and 1.940 (2.064) Å, respectively. While the C–O bonds are longer at the MP2 level in 8 and 9, 1.361 (1.379) and 1.245 (1.274) Å, respectively, the C–O bond in 10 is decreased at the MP2 level 1.237 (1.200) Å. Since some of the differences in bond lengths

(18) Reference 9, p 78.

(19) (a) Bach, R. D.; Andres, J. L.; Owensby, A. L.; Schlegel, H. B.; McDouall, J. J. W. *J. Am. Chem. Soc.* **1992**, *114*, 7207. (b) Bach, R. D.; Su, M.-D.; Schlegel, H. B. *Ibid.* **1994**, *116*, 5379. (c) Bach, R. D.; Su, M.-D. *Ibid.* **1994**, *116*, 5392.

(20) O'Neal, H. E.; Richardson, W. H. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds., Elsevier: New York, 1972; Volume 5.

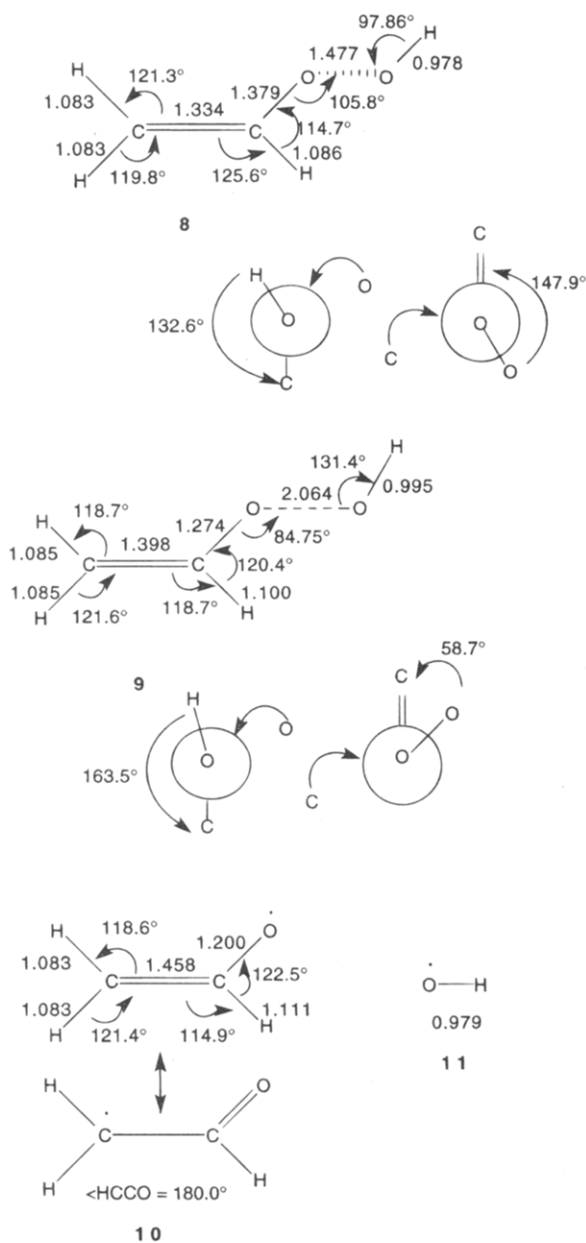


Figure 1. Optimized bond distances (Å) and angles for vinyl hydroperoxide (8), the transition state structure 9 leading to the enol/α-carbonyl radical 10 and hydroxyl radical 11 at the MP2/6-31G* level.

are rather large, the need for geometry optimization at the MP level is apparent.

Energies calculated at the MP4//MP2/6-31G* level and cast in terms of enthalpy at 298 K are shown in Figure 3. Alternative methods for calculating the heat of reaction were explored to see how they compared to the *ab initio* method. An estimate of the heat of reaction (8 to 10 and 11, eq 7), by the Benson group additivity method²¹ ($\Delta H_r^\circ = 22.8$ kcal/mol) is in excellent agreement with the MP4//MP2/6-31G* level value (22.1 kcal/mol). Not all of the groups were available in Benson calculation, so the heat of formation of radical 10 was estimated from reported heats of formation of acetaldehyde,²¹ the hydrogen atom,²¹ and the bond dissociation energy of the H-CH₂CHO bond (92 kcal/mol).²² On the other hand, a semiempirical calculation, using the PM3 method,²³ gave

(21) Benson, S. W. *Thermochemical Kinetic Calculations*; Wiley: New York, 1976.

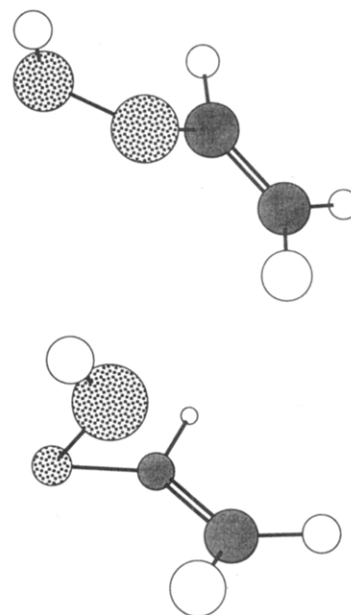


Figure 2. Three-dimensional representation of vinyl hydroperoxide (8) (upper) and the transition state structure 9 leading to the enol/α-carbonyl radical and hydroxyl radical (lower) based on optimizations at the MP2/6-31G* level.

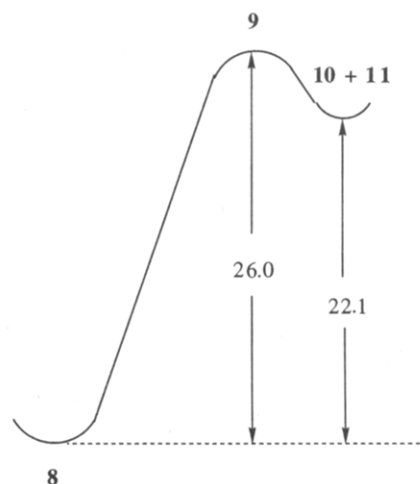


Figure 3. Reaction coordinate diagram for the thermolysis of vinyl hydroperoxide (8) to give the enol/α-carbonyl radical 10 and hydroxyl radical 11 via the transition state structure 9. Enthalpies (kcal/mol) are calculated from single point MP4/6-31G* calculations on structures optimized at the MP2/6-31G* level (*i.e.*, MP4//MP2/6-31G*) and corrected to 298 K.

a lower value of ΔH_r° (6.60 kcal/mol), compared to the *ab initio* calculations.

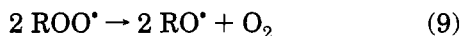
The MP4//MP2/6-31G* estimate of the activation energy is low ($E_a = 26.0$, $\Delta H^\ddagger = 25.4$ kcal/mol at 298 K) compared to experimental values of other types of peroxides. For dialkyl peroxides, the experimental activation energy is 38 kcal/mol, while the value is 32 kcal/mol for peresters.²⁰ It could be argued that a perester, with a one of the peroxy oxygens bound to an sp² carbon atom, is a more reasonable model for vinyl hydroperoxide. Yet, the MP4//MP2/6-31G* activation energy for vinyl hydroperoxide is still 6 kcal/mol below that of a perester.

(22) Holmes, J. L.; Lossing, F. P.; Terlouw, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 1086.

(23) PM3 calculations (Stewart, J. J. P. *Comput. Chem.* **1989**, *10*, 209.) were carried out with the MOPAC 5.0 program.

It can be noted that the E_a value of 26.0 kcal/mol from the *ab initio* calculation neglects tunneling, which could further lower E_a . Tunneling can cause significant decreases in the activation energy compared to the barrier energy when hydrogen atom transfer occurs. Usually tunneling is not considered to be of great importance in reactions involving the transfer of heavy atoms such as in reaction (7), where O–O bond rupture occurs. However, tunneling was proposed to be important in the bond shift automerization reaction of rectangular cyclobutadiene.²⁴ To assess tunneling, the periodic orbit method of Miller²⁵ was used, and this calculation indicated that the tunneling contribution was insignificant.²⁶ The log A value for thermolysis of *tert*-butyl hydroperoxide is reported to be 13.7 in the gas-phase,²⁷ which is in excellent agreement with the calculated value in Table 2 (13.76 at 298 K). *tert*-Butyl hydroperoxide was selected for comparison, since hydroperoxides possessing α -hydrogens can cause experimental problems because of competing reactions.^{20,28}

We can now return to the key question, is vinyl hydroperoxide a stable species? To answer this question, rate constants and lifetimes are evaluated at 25 °C (*cf.*, Table 2) and at 0 °C, where the *ab initio* derived log A values are calculated to be 13.76 and 13.72, respectively. The calculated barrier energy of 26.0 kcal/mol is equated to E_a and rate constants at 25 °C and 0 °C are calculated to be $4.8 \times 10^{-6} \text{ s}^{-1}$ and $7.9 \times 10^{-8} \text{ s}^{-1}$, respectively. The corresponding lifetimes ($\tau = 1/k$) at 25 °C and 0 °C are 58 and 3520 h, respectively. These calculations then suggest that vinyl hydroperoxide would be sufficiently long-lived for spectral characterization, particularly at 0 °C. Once again, these estimates assume that tunneling is unimportant, which seems justifiable. Practical considerations are in order at this point. Hydroperoxides are notorious for induced decomposition,^{20,28} where rupture of the peroxide bond (eq 7) may initiate a chain process (eq 8 and 9). The chain process typically lowers both the activation energy and log A , to increase the rate



of decomposition.²⁰ Additional cyclization processes involving the peroxy radical and the double bond may also occur,²⁹ but eventually a radical would be produced to initiate the decomposition of the hydroperoxide. From an experimental perspective, the preparation and isolation of a vinyl alkyl peroxide, such as vinyl *tert*-butyl peroxide would be a wiser choice in order to avoid chain decomposition. It is expected that aryl peroxides will be even less stable than vinyl peroxides if the phenoxy radical resonance stabilization is substantially reflected in the transition state structure for decomposition. These calculations suggest that reports of isolated aryl peroxides in the range of 0 to 25 °C are particularly suspect.

(24) (a) Carpenter, B. *J. Am. Chem. Soc.* **1983**, *105*, 1700. (b) Dewar, M. J. S.; Merz, K. M., Jr.; Stewart, J. J. P. *Ibid.* **1984**, *106*, 4040.

(25) (a) Miller, W. H. *J. Phys. Chem.* **1979**, *83*, 960. (b) Bicerano, J.; Schaefer, H. F., III; Miller, W. H. *J. Am. Chem. Soc.* **1983**, *105*, 2550.

(26) The tunneling rate calculated by the method of periodic orbits was $8.2 \times 10^{-17} \text{ s}^{-1}$.

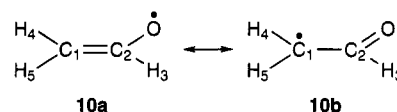
(27) (a) Lossing, F. P.; Tickner, A. W. *J. Chem. Phys.* **1960**, *20*, 907. (b) Birss, F. W.; Danby, C. J.; Hinshelwood. *Proc. Roy. Soc. (London)* **1957**, *A239*, 154.

(28) Hiatt, R. In *Organic Peroxides*; Swern, D., Ed.; Wiley: New York, 1971; Volume 2, Ch. 1.

(29) Carpenter, B. K. *J. Am. Chem. Soc.* **1993**, *115*, 9806.

Turning now to the transition state structure and molecular motions in arriving at the saddle-point, Figures 1 and 2 may be consulted. Progress to the transition state is a rather complex process, in addition to stretching of the O–O bond, rotations occur about the C–O and O–O bonds. Furthermore, the $\angle\text{COO}$ is compressed while the $\angle\text{OOH}$ opened. A fascinating consequence of the rotation about the C–O bond is that the leaving hydroxyl radical is positioned over the enol radical fragment. This description of the transition state structure can be contrasted with the naive picture of departure of the two fragments where the dihedral $\angle\text{O–O–C–C}$ is 90° for maximum overlap of the elongated O–O bond with the $\pi\text{-C–C}$ bond. In fact, if the optimization is begun with $\angle\text{O–O–C–C} = 90^\circ$, this angle decreases and progresses toward the optimized angle of 58.7° (*cf.*, Figure 1). Eventually, the oxygen p-orbital that formally contains the odd electron in the enol/ α -carbonyl radical product should be parallel to the p-orbitals of the carbon atoms or 90° to the σ plane. One measure of the progress of reaction to the transition state is then the approach of the $\angle\text{O–O–C–C}$ dihedral to 90°. Overlap energies are a function of $\cos^2 Q$, where in this instance $Q = \angle\text{O–O–C–C}$ and $\cos^2(1 - Q)$ would be a measure of the progress of the reaction to the transition state *in terms of energy*. For $\angle\text{O–O–C–C} = 58.7^\circ$, calculated for the transition state structure, this simple calculation indicates 73% progress to the transition state *in terms of energy*. Figure 3 graphically displays a one-dimensional reaction coordinate diagram in terms of energy, which qualitatively supports the idea of a late transition state.

The enol radical can be represented by two valence bond structures as shown below. A qualitative weighting



of the two structures can be deduced from the Mulliken atomic spin densities at the UMP2/6-31G* level with SCF spin densities: C₁ (1.14), C₂ (−0.52), O (0.52), H₃ (0.024), H₄ (−0.084), and H₅ (−0.084), where the sum of the spin densities = 1.00. Clearly, structure **10b** is dominant on the basis of the Mulliken spin densities. Another approach to determine the odd electron density distribution is to use the sum of the singly occupied molecular orbital (SOMO) coefficients squared. The fractional distribution of odd electron density at the MP2/6-31G* level based on the SOMO is: C₁ (0.826), C₂ (0.0181), and O (0.156). This analysis again indicates that **10b** is the predominant structure. Bond distances corroborate this assessment, where it is seen that the C–O and C–C bond distances are 1.200 and 1.458 Å, respectively. In comparison, a typical C–O carbonyl bond distance is 1.22 Å,³⁰ while a typical C–C double bond is about 1.33 Å.³¹

Frequency calculations also shed light on the structure of species along the reaction path, but before proceeding to this topic, a few comments on the relative magnitude of the frequencies is in order. The frequencies reported in Table 3 are obtained at the MP2/6-31G* level and corrected by a factor of 0.89.¹⁸ This correction is standard practice for Hartree–Fock wavefunctions, which does not include electron correlation. Considering the O–H stretch-

(30) Reference 8, p 170.

(31) Reference 8, p 167.

ing frequencies as an example, this correction factor gives unusually low O–H stretching frequencies for **8** (3309 cm^{-1}) and especially **9** (3118 cm^{-1}). In comparison, the typical O–H stretching frequency of a peroxide is 3550 cm^{-1} .³² Most likely all of the reported frequencies are somewhat low. Now starting with vinyl peroxide, the calculated IR frequencies of the O–H, C=C, and O–O functionalities are 3309, 1531, and 771 cm^{-1} , respectively (*cf.*, Table 3). Proceeding to the transition state structure, the O–H (3118 cm^{-1}) and composite C–C and C–H (1145 cm^{-1}) are still present, but the C–C bond has weakened. These frequencies are consistent with the development of the enol/ α -carbonyl moiety (*cf.*, **10a** and **10b**). In addition, one imaginary frequency corresponding to passage over the barrier appears at 311 cm^{-1} (at the MP2/6-31G* level and corrected by a factor of 0.89) and includes a stretching of the O–O bond and twisting about the O–O and C–O bonds. It can be noted that the corrected imaginary frequency obtained from a Hartree–Fock wavefunction is at a significantly higher frequency (807 cm^{-1}). Finally, in the enol/ α -carbonyl radical, composite C–C and C–H functionalities are now

found at 1033 cm^{-1} and a new absorption appears at 1724 cm^{-1} , which corresponds to the C=O stretch. These frequencies again point to **10b** as the predominant structure for this radical.

Conclusions

Ab initio molecular orbital calculations at the MP4//MP2/6-31G* level indicate that vinyl peroxides will have activation energies for thermolysis that are considerably lower than those observed for other peroxides. Yet, these calculations offer hope of isolation of vinyl peroxides under benign conditions (*e.g.*, nonpolar aprotic solvents without traces of transition metal ions or acids) at lower temperatures. It should be recognized that with the calculated activation parameters ($E_a = 26.0$ kcal/mol and $\log A = 13.72$) for unimolecular homolysis of vinyl hydroperoxide (**8**), a decrease of 1 kcal/mol in E_a decreases the lifetime of **8** by about 5.5-fold. So some caution is advised in rigorously predicting the conditions for isolation of a vinyl peroxide. Although calculations were not performed on aryl peroxides, it is surmised based on the added stability of phenoxy radical compared to enol radical, that aryl peroxides will most likely not be isolable species at ordinary temperatures.

(32) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Wiley: New York, 1975; p 108.