

Addition of Peroxyl Radicals to Alkenes and the Reaction of Oxygen with Alkyl Radicals

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Received October 20, 1999

Abstract: The relatively low lying first electronic excited states of peroxyl radicals are suggested to play a direct role in determining the rate of their addition to alkenes, with there being, in the vicinity of the transition state, an unavoided crossing of C_s symmetry of the ground and first excited states. If there is no charge transfer between radical and alkene during the formation of the adduct, then the barrier height is approximately equal to the energy required to excite an isolated peroxyl radical to its first excited state; with charge transfer, the activation energy for the addition is lowered in proportion to the energy released by the charge transfer. It is also suggested that, for the specific case of hydroperoxyl radical addition to ethene, this description is compatible with the generally accepted mechanism for the reaction of ethyl radicals with molecular oxygen whereby the resulting ethylperoxyl radical can decompose to ethene and a hydroperoxyl radical via a cyclic $^2A''$ transition state. Electron affinities, ionization energies, and absolute electronegativities and hardness of acetylperoxyl, hydroperoxyl, methylperoxyl, ethylperoxyl, isopropylperoxyl, and *tert*-butylperoxyl radicals have been calculated at the G2MP2 level.

Introduction

Radical addition to alkenes is a topic of great interest in the fields of radical polymerization, organic synthesis, combustion, and atmospheric chemistry, and there has been much recent work on developing an understanding of the factors that control the rate of reaction.^{1–4} Barrier heights for the addition of radicals to alkenes often show a strong dependence on some property of the isolated reactants. Examination of these structure–activity relationships can have practical use, allowing the prediction of activation energies for reactions of interest,⁵ as well as helping the development of a general understanding of the physical and chemical processes involved in a class of reactions.^{6,7}

The body of work produced over the years by Waddington et al.^{8–16} and Baldwin and Walker et al.^{17–23} on the rate of

reaction of alkenes with hydroperoxyl, acetylperoxyl, and various alkylperoxyl radicals provides an excellent database for the study of the dependence of the rate of reaction on the properties of *both* the alkene and the attacking radical. Thirty-six reactions have been studied in the gas-phase, involving five structurally related radicals attacking seventeen alkenes, and Arrhenius parameters have been determined for most. This class of radical–alkene reaction is also important in the autoxidation of propene to propene oxide, a topic which has been investigated as a possible commercial route for the manufacture of the epoxide.^{24–27} Further, the addition of peroxyl radicals to alkenes can be of significance during the autoxidation of hydrocarbon fuels at relatively low temperatures (below ca. 850 K).²⁸

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The rate of addition of peroxyl radicals to alkenes shows a strong dependence on the alkene ionization energy, with a lower ionization energy correlating to a lower activation energy, identifying the reaction as an electrophilic addition.^{10,18} It has also been understood for some time that the more electrophilic the radical, the faster the reaction rate.^{12,13,15,16} However, lack of data for the electronic properties of peroxyl radicals has prevented the quantification of this dependence. So to facilitate this analysis, relatively high level ab initio calculations of the electron affinities and ionization energies of six relevant peroxyl radicals have been performed.

For the addition of peroxyl radicals to alkenes it has recently been demonstrated that all of the rate constants are strongly correlated to the degree of charge transfer occurring during the reaction.⁵ This dependence has been reevaluated to account for the more accurate peroxyl radical electron affinities and ionization energies reported here. Also, a description of the physical processes involved in the addition of peroxyl radicals to alkenes is suggested, involving low-lying electronically excited states.

The addition of hydroperoxyl radicals to ethene is the simplest reaction of this class, and as such has been investigated by Baldwin and Walker et al.^{20,21} Their proposed mechanism however has been seen as incompatible with the work of particularly Gutman et al.^{29,30} on the reaction of molecular oxygen with ethyl radicals. At high temperatures or low pressure, the resulting ethylperoxyl radicals decompose to ethene and hydroperoxyl radicals, whereas conversely, the reverse the reaction between ethene and hydroperoxyl radicals gives ethene oxide and hydroxyl radicals.^{20,21} The debate has been over both the reaction mechanism and the barrier heights of key steps in the reaction. The reaction of oxygen and ethyl radicals has been extensively studied as being the simplest case of a reaction of oxygen with alkyl radicals that can show decomposition to the conjugate alkene, a topic of paramount importance to the understanding of hydrocarbon combustion in automotive engines.^{28–32} An attempt is made to reconcile the radical addition mechanism reported here with the current understanding of the mechanism for the reaction of oxygen and ethyl radicals.

Ab Initio Calculations

Standard ab initio quantum chemical calculations were performed using GAUSSIAN 94³³ for the anions, radicals, and cations of the peroxyl species for which rates of addition to alkenes have been measured, namely, acetylperoxyl, hydroperoxyl, methylperoxyl, isopropylperoxyl, and *tert*-butylperoxyl. Ethylperoxyl was also investigated to give values for a complete range alkylperoxyl structures. The calculated zero-point-corrected electronic energy at 0 K (E) allowed the determination

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Table 1. Calculated G2MP2 Electron Affinities (A), Ionization Energies (I), Absolute Electronegativities (χ) and Hardness (η), and Energy of the First Excited State ($E(^2A'' \rightarrow ^2A')$)^{40,46} of Acetylperoxyl, Hydroperoxyl, Methylperoxyl, Ethylperoxyl, Isopropylperoxyl, and *tert*-Butylperoxyl (eV)

	A	I	χ	η	$E(^2A'' \rightarrow ^2A')$
CH ₃ C(O)O ₂	2.468	11.37 ^a	6.917	4.449	0.689
HO ₂	1.088	11.50	6.294	5.206	0.872
CH ₃ O ₂	1.205	10.35	5.776	4.571	0.914
C ₂ H ₅ O ₂	1.211	9.994	5.603	4.391	0.941
<i>i</i> -C ₃ H ₇ O ₂	1.196	9.655	5.425	4.230	0.938
<i>t</i> -C ₄ H ₉ O ₂	1.227	9.616	5.422	4.195	0.967

^a Vertical ionization energy.

of the adiabatic electron affinities (A) and ionization energies (I) via

$$A = E_{\text{neutral}} - E_{\text{anion}} \quad (\text{eq 1})$$

$$I = E_{\text{cation}} - E_{\text{neutral}} \quad (\text{eq 2})$$

Structures and energies for HO₂ and CH₃O₂ were determined using the G1,³⁴ G2MP2,³⁵ and G2³⁶ procedures, which are approximations to calculations of the electronic energy at the QCISD(T)-FC/6-311+G(3df,2p)/MP2=full/6-31G(d) level that assume the additivity of various corrective terms that use a larger basis set at lower levels of theory, or vice versa. The electron affinities and ionization energies of hydroperoxyl and methylperoxyl radicals calculated at the more resource efficient G2MP2 level were within 0.03 eV of those found at the G1 or G2 level; this difference is smaller than the typical standard deviation quoted for G2 calculations of ca. 0.04 eV.³⁷ Therefore calculations for the larger species were only performed at the G2MP2 level. Recently, electron affinities have been published for the HO₂, C₂H₅O₂, and CH₃O₂ radicals at the G2MS level,³⁸ which is a density functional equivalent to the G2 level; these values were within 0.015 eV of the G2MP2 calculations reported here.

Geometries were initially optimized at the HF/6-31G(d) level with no symmetry restrictions, to confirm that the lowest energy structure had C_s symmetry ($^2A''$ for the radical or $^1A'$ for the anion or cation). The geometry of the lowest energy conformer was then used (with forced C_s symmetry) for the G2MP2 calculations. Energies calculated at the G2MP2 level and geometries optimized at the MP2(Full)/6-31G(d) level are given in the Supporting Information, while electron affinities, ionization energies, and absolute electronegativities and hardness (χ and η , respectively, defined by eqs 3 and 4) are shown in Table 1.

$$\chi = (I + A)/2 \quad (\text{eq 3})$$

$$\eta = (I - A)/2 \quad (\text{eq 4})$$

Optimizations of the geometry for the acetylperoxyl cation would not converge with O₂ bonded to the acetyl group, with the geometry tending toward isolated O₂ and CH₃CO⁺ fragments. G2MP2 calculations give an energy for the dissociation

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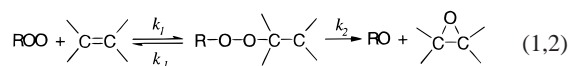
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of $\text{CH}_3\text{C}(\text{O})\text{O}_2$ to $\text{CH}_3\text{CO}^+ + \text{O}_2 + e$ of only 8.539 eV, which is considerably lower than the adiabatic ionization energy for the other peroxy radicals examined. While this value might be valid as an estimate of the adiabatic ionization energy of acetylperoxy, it would seem inappropriate for estimating the charge transfer during the addition of the radicals to alkenes, where the structure of the peroxy group would be expected to be similar to that of the radical. A vertical ionization energy at the G2MP2 level was therefore calculated for this species; this value is given in Table 1 and used in the subsequent analyses.

The calculated G2MP2 electron affinity for hydroperoxy (1.088 eV) is within 1 standard error of the experimental result (1.078 ± 0.017 eV),³⁹ while the calculated electron affinity for *tert*-butylperoxy (1.227 eV) is within 0.03 eV of the measured value (1.20 ± 0.01 eV).⁴⁰ The difference between the hydroperoxy G2MP2 (11.50 eV) and experimental ionization energies (11.35 ± 0.01 eV)⁴¹ of 0.15 eV is less than the typical maximum error quoted for G2MP2 calculations of 0.27 eV.³⁷ For the other peroxy radicals examined, experimental results for the gas-phase electron affinities and ionization energies are not yet available.

The Mechanism of the Addition of Peroxy Radicals to Alkenes

The mechanism by which peroxy radicals add to alkenes has been understood for some time, primarily through studying the reaction of the radicals with *cis*- or *trans*-2-butene. If, for example, *cis*-2-butene is reacted with peroxy radicals, then both *cis*- and *trans*- isomers of the 2-butene epoxide are formed, and in the same ratio as is found if *trans*-2-butene is used instead,¹⁷ demonstrating that the two butene isomers react via a common peroxyalkyl adduct (reactions 1 and 2 show a generic example).⁸



This also demonstrates that the intermediate adduct exists as an independent species for long enough to undergo many rotations around the C–C bond, so that the eventual ring closure and decomposition of the adduct to the *cis*- or *trans*-epoxide has no memory of which isomer of the alkene was reacted. Further, if *trans*-2-butene is reacted, then the dominant products are the epoxide isomers, and not *cis*-2-butene, demonstrating that decomposition of the peroxyalkyl adduct to the epoxide dominates over decomposition back to the alkene ($k_2 > k_{-1}$).^{17,23}

The experiments of Waddington et al. and Baldwin and Walker et al. all involve end product analysis of a reacting gas mixture, with the rate of epoxide formation being compared with the formation rate of a reference compound. As a consequence of the peroxyalkyl adduct predominantly decomposing to the epoxide, measured rate constants and Arrhenius parameters for epoxide formation can also be taken as representative of the initial addition of the peroxy group to the alkene. The mechanistic evidence found from the reactions of 2-butene is not available for the reaction of other alkenes.

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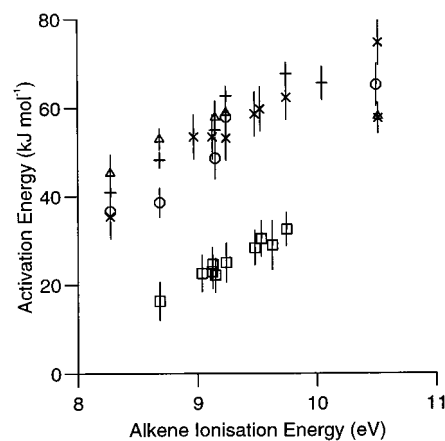


Figure 1. Relationship between alkene ionization energy and the activation energy for the addition to alkenes by acetylperoxy^{9–11} (squares), methylperoxy^{12,13} (circles), isopropylperoxy^{14,15} (horizontal lines), *tert*-butylperoxy¹⁶ (triangles), and hydroperoxy^{18–23} (diagonal crosses) radicals.

However, the mechanism described by reactions 1 and 2 has been assumed to be applicable to all alkenes, because rate data for a particular peroxy radical attacking a series of alkenes all show a strong dependence on the ionization energy of the alkene (Figure 1), suggesting a common underlying mechanism.

The variation in rate of reaction is dominated by variations in the activation energy for the reactions over a fairly wide range, from 16 kJ mol⁻¹ for acetylperoxy + 2-methyl-2-butene¹⁰ to 75 kJ mol⁻¹ for hydroperoxy + ethene²¹ (giving, for example, a range of rate constants of 6 orders of magnitude at 500 K). In comparison, steric factors play a lesser role, with experimentally determined preexponential factors covering a range of only 2 orders of magnitude. Indeed, the *A*-factors for all the reported alkyl and acyl peroxy reactions are essentially the same within experimental error at $\log(A/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = 8.1 \pm 0.5$ (see, for example, ref 5), with those for hydroperoxy being 10–50 times higher.²¹ Therefore, any explanation of reactivity of peroxy radical addition to alkenes is primarily concerned with the factors that determine the activation energy of the reaction.

Previous work has demonstrated that the rate of addition of a peroxy radical to an alkene is strongly dependent on the ionization energy of the alkene, with a lower ionization energy giving a lower activation energy (see, for example, Figure 1).^{10,18} It has also been noted that, for a series of peroxy radicals attacking one alkene, the reaction is faster the higher the electrophilicity of the peroxy radical.^{12,13,15,16} However, in the absence of measurements or calculations of electron affinities, this observation has only been qualitative. The *ab initio* calculations described in the previous section now allow this dependence to be examined quantitatively. Figure 2 shows the correlation between peroxy radical electron affinity and the rate of epoxidation of 2-methylpropene, the alkene which has been most thoroughly examined in this context. The electron affinities of the alkylperoxy and hydroperoxy radicals are all fairly similar to each other, consistent with the activation energies for their addition to a particular alkene also being similar. The electron affinity for acetylperoxy is substantially higher, again consistent with the activation energy for its addition to a particular alkene being much lower than the other peroxy radicals.

The variation of the rate of epoxidation with peroxy electron affinity or alkene ionization energy is usually rationalized by describing the reaction as an electrophilic addition; i.e., the

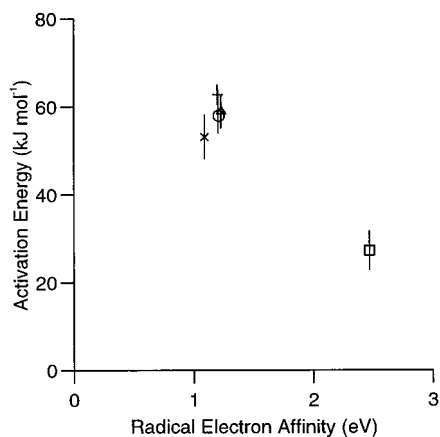


Figure 2. Relationship between radical electron affinity and activation energy for addition to 2-methylpropene by peroxy radicals. See Figure 1 for the key.

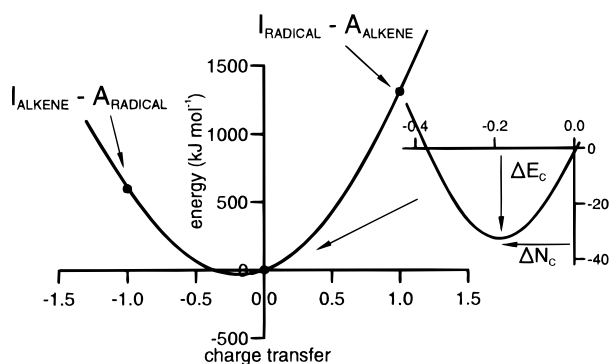


Figure 3. Schematic representation of the parabola model of Pearson and Parr^{42–45} showing the dependence of the energy of the system on the fractional charge on the reactants, for the example of acetylperoxy radical addition to 2-methyl-2-butene.

transition state involves a degree of electron density transfer to the radical.¹⁰ This can be quantified by using the parabola model of Pearson and Parr.^{42–45} Figure 3 shows the energy of the system as electron density is transferred from one species to the other, for the example of $\text{CH}_3\text{C}(\text{O})\text{O}_2$ addition to 2-methyl-2-butene, which is the fastest, most polar epoxidation reaction that has been reported.¹⁰ The energy for integer charge transfer can be estimated from the ionization energies and electron affinities of the isolated species, with the energy at intermediate fractional charge transfers found by fitting a parabola through the three known points $(1, I_{\text{radical}} - A_{\text{alkene}})$, $(-1, I_{\text{alkene}} - A_{\text{radical}})$, and $(0, 0)$.^{42–45} This approximation will be valid insofar as the isolated species retain their identity at the transition state. In this example a charge (ΔN_c) of 0.19 of an electron flows to the acetylperoxy radical, releasing an energy (ΔE_c) of 33 kJ mol^{-1} . This behavior can be expressed quantitatively in terms of the absolute electronegativity (χ) and hardness (η) of the isolated species:^{42–45}

$$\Delta N_c = (\chi_{\text{radical}} - \chi_{\text{alkene}})/2(\eta_{\text{radical}} + \eta_{\text{alkene}}) \quad (\text{eq } 5)$$

$$\Delta E_c = -(\chi_{\text{radical}} - \chi_{\text{alkene}})^2/4(\eta_{\text{radical}} + \eta_{\text{alkene}}) \quad (\text{eq } 6)$$

The energy released (ΔE_c) by the charge transfer can be interpreted as a driving force for the reaction, which suggests

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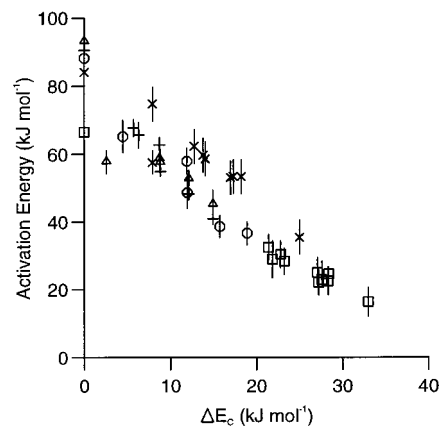


Figure 4. Relationship between activation energy for the addition to alkenes by peroxy radicals and the energy decrease due to the charge transfer in forming the adduct, ΔE_c . See Figure 1 for the key. The energies of the transitions to the first electronically excited states of the peroxy radicals (${}^2A'' \rightarrow {}^2A'$) are shown on the vertical axis of the diagram.

that the best correlation of the rate of reaction should be with ΔE_c , and not necessarily $I_{\text{alkene}} - A_{\text{radical}}$ or ΔN_c . The correlation between ΔE_c and activation energies for all peroxy radical epoxidation reactions that have been measured is given in Figure 4, with the data tabulated in the Supporting Information. It has been reevaluated using previously collated rate data⁵ and the electronegativities and hardnesses reported in Table 1. However, as can be seen from Figure 3, ΔE_c is itself very strongly dependent on ΔN_c or $I_{\text{alkene}} - A_{\text{radical}}$, indeed epoxidation activation energies also show good correlations with $I_{\text{alkene}} - A_{\text{radical}}$ or ΔN_c .⁵

The correlation shown in Figure 4 between epoxidation activation energy and ΔE_c suggests that an addition reaction involving no charge transfer would have an activation energy of ca. 80–90 kJ mol^{-1} , and also that the energy released by the charge transfer lowers the barrier for the addition approximately in proportion. Interestingly, 80–90 kJ mol^{-1} is also the energy required to excite peroxy radicals to their first electronically excited state; these values have been included on the vertical axis of Figure 4 and are given in Table 1.^{40,46} This suggests that the first excited states of the peroxy radical play a role in their addition to alkenes.

This is what would be expected if the radical and alkene approach each other with the peroxy radical and carbons of the double bond in the same plane (C_s symmetry). The ground states of peroxy radicals have the free electron mostly localized in a p-orbital on the terminal oxygen atom that is perpendicular to the plane of the radical (i.e., ${}^2A''$ for radicals with C_s symmetry),⁴⁷ and would therefore give a *doubly filled* antibonding highest occupied molecular orbital for the transition state. However, the peroxy ${}^2A'$ first excited state has the free electron in a p-orbital that is *in* the plane of the radical,⁴⁸ and hence gives a more energetically favourable *singly filled* antibonding orbital (see Figure 5).

If the peroxy radical approaches the vinyl group of the alkene with C_s symmetry, the addition reaction can be described by a surface crossing of the first excited state of the peroxy radical

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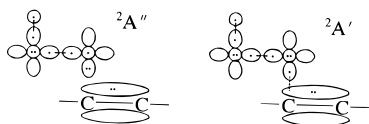


Figure 5. Schematic orbital diagram for the example of the addition of hydroperoxyl radicals to alkenes with C_s symmetry, for the ground ($^2A''$) and first excited ($^2A'$) states.

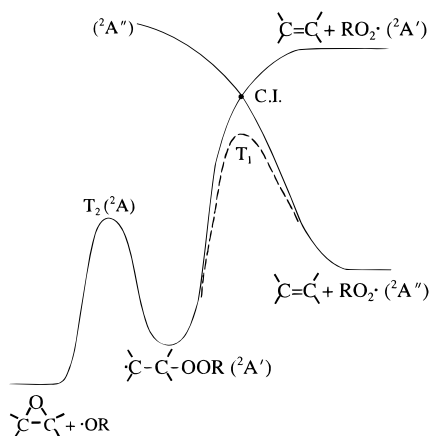


Figure 6. Schematic potential energy diagram for the addition of peroxy radicals to alkenes.

(which correlates with the ground state of the resulting peroxyalkyl radical) with the ground state of the peroxy radical (which correlates with the first excited state of the peroxyalkyl radical). For the case of an addition that involves no charge transfer, the activation energy for the addition appears similar to the energy of the first excited state; therefore, the potential energy surfaces must cross at a value near the first excited state. This implies that the crossing must be unavoided, also known as a conical intersection.⁴⁹ A schematic potential energy diagram is shown in Figure 6.

Unavoided crossings are well known from the photochemistry of polyatomic molecules.⁴⁹ If a system has, say, F degrees of freedom, then the dimension of the subspace in which the two surfaces actually touch is high, at $F - 2$. In the remaining two dimensions (the branching space) the surfaces only touch at a single point, with the surfaces diverging on moving away from this point. The reaction coordinates that define the branching space are one that maintains the high symmetry of the system, and one that lowers the symmetry of the structure.

A preliminary *ab initio* investigation of the addition of HO_2 to ethene was made at the UCIS/6-31(d) level, details are available in the Supporting Information. The calculated geometry of the transition state⁵⁰ deviates from C_s symmetry by having the terminal hydrogen atom on the hydroperoxyl group out of the plane of the CCOO atoms, with a dihedral angle of ca. 90° . Setting this dihedral angle to 0° forces C_s symmetry on the system. The reaction coordinate of the branching space that maintains the high symmetry of the system can be identified as the C–O bond length ($R_{\text{C-O}}$), and with forced C_s symmetry an unavoided crossing was identified at $R_{\text{C-O}} = 2.6 \text{ \AA}$. The symmetry-lowering reaction coordinate of the branching space can tentatively be identified as the dihedral angle for the COO–H bond; increasing this angle from 0° breaks the C_s symmetry of the system and lowers the energy from the conical intersection and toward the (C_1) transition state for the addition.

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It can be argued that the height of the barrier for the addition (T_1 , Figure 6) is determined by being proximate to, and lower than, the conical intersection. In turn, the conical intersection (at least for reactions involving little charge transfer) must be close in energy to that required to excite the isolated peroxy to its first $^2A'$ excited state. The strong effect of charge transfer on the T_1 barrier height must be through either lowering of the conical intersection or increasing the gap between the transition state and the conical intersection; this aspect shall be investigated in future work.

Once the barrier (T_1 , Figure 6) for the addition has been surmounted, the peroxyalkyl adduct (which is $^2A'$ for C_s symmetry, though the lowest energy conformer will be 2A) can decompose via the relatively constrained but low barrier to the epoxide (T_2 , Figure 6), precluding any significant back reaction to re-form the alkene and peroxy radical. That the barrier for decomposition to the epoxide is lower than that for the decomposition back to the alkene is implicit in the good correlations between the epoxide formation and the properties of the reactants, such as alkene ionization energy,¹⁰ and that the hydroperoxybutyl radical formed by $\text{HO}_2 + \text{trans-2-butene}$ decomposes predominantly to the epoxide and not back to *cis*-butene.^{17,23}

It is informative to compare the addition of peroxy radicals to alkenes, which can have a significant barrier for the reaction, with the barrierless addition of hydroxyl radicals.⁵¹ In the ground ($\tilde{X}^2\Pi$) state of the hydroxyl radical, the free electron is also situated in one of two p-orbitals on the oxygen atom. However, for this case the two states have the same energy, at least until the approach of the ethene molecule lifts the degeneracy. The state of the hydroxyl radical that correlates with the $^2A'$ ground state of the hydroxyalkyl adduct decreases in energy on the approach of the alkene, giving, to a first approximation, a barrierless reaction. Therefore, the key factor in determining the difference in reactivity between hydroxyl and hydroperoxyl radicals is that the former has a higher symmetry and that a ground state of the radical correlates with the ground state of the adduct, whereas for the lower symmetry hydroperoxyl radical, an excited state correlates with the ground state of the adduct, necessitating a surface crossing at an energy higher than that of the reactants. It is not necessary to presume that the hydroxyl radical is in any sense inherently more reactive than peroxy radicals to explain their differing reactivities toward alkenes. Indeed, hydroxyl radicals are not unusually electrophilic; the energy released by charge transfer by addition to alkenes (ranging from 19 kJ mol^{-1} for ethene to 40 kJ mol^{-1} for 2,3-dimethyl-2-butene) is comparable with the range found for peroxy radicals ($3\text{--}33 \text{ kJ mol}^{-1}$). Also, the bond formed by OH addition to alkenes is not unusually strong, with the addition being reversible at the relatively low temperature of $500\text{--}600 \text{ K}$.⁵¹

Similarly, radical atoms are known to undergo barrierless addition to alkenes;^{52–54} this is consistent with the above explanation for hydroxyl, as they are of even higher symmetry than OH. The reactions of three other triatomic or larger species with alkenes have been examined extensively (difluoroamino (NF_2),^{55,56} nitrate (NO_3),^{57–59} and ozone (O_3),^{60,61}); they *do* have appreciable activation energies and also show strong correlations

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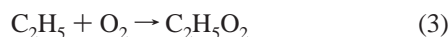
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with the ionization energies of the alkenes, again indicating electrophilic addition. The behavior of these species will be investigated in future work.

Reactions of Alkyl + O₂ and HO₂ + Alkenes

There has been a long-running debate about how the widely accepted mechanism describing the reaction of alkyl radicals with molecular oxygen relates to that for the reaction of hydroperoxyl radicals with alkenes. Experimental work has shown that while at low temperature and high pressure the alkylperoxyl radical is formed from alkyl + O₂ (e.g., reaction 3), at high temperature or low pressure the conjugate alkene and hydroperoxyl radical are the main products (e.g., reaction 4).^{29,30} The discussion has tended to be concentrated on the example of ethyl + O₂, which has been the system most studied.



As there are now many reviews of this problem in the literature,^{20,28–32,40,62–64} this section will only describe the two main, apparently irreconcilable, differences between the mechanisms. The first is that, for the addition of HO₂ to ethene, the work of Baldwin and Walker et al. supports a relatively high barrier for the initial addition, whereas that of Gutman et al.^{29,30} on the reaction of C₂H₅ + O₂ implies that this barrier should be relatively low. The second point of difference is that it was suggested that the products formed from the HO₂•••C₂H₄/O₂•••C₂H₅ system should be independent of which reactants were used, i.e., that the products should be independent of the direction of reaction.³⁰ Therefore, if ethene + HO₂ are the main products from C₂H₅ + O₂, then the expectation was that reacting HO₂ and ethene under the same conditions should give either adducts that decompose back to the reactants, or C₂H₅ + O₂ as the main products, and not ethene oxide and OH as was argued by Baldwin and Walker.^{20,21}

The Mechanism. From the work of particularly Gutman et al.,^{29,30} it appears incontrovertible that reacting oxygen with ethyl radicals leads predominantly to the alkene at higher temperatures; monitoring the formation of the epoxide^{17,65} or the OH radical⁶⁶ confirmed that the fraction of O₂ + ethyl going to the epoxide is only minor. The potential energy surface suggested by Wagner et al.³⁰ for the C₂H₅ + O₂ system is given by the solid line in Figure 7. An important result was that the reaction of C₂H₅ + O₂ was observed to have a negative activation energy,

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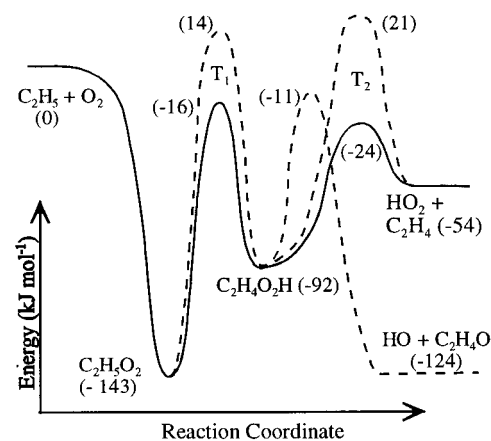


Figure 7. Schematic potential energy diagram for the C₂H₅ + O₂/HO₂ + C₂H₄ system: solid line, Wagner et al.;³⁰ dashed line, barrier heights from Baldwin and Walker et al.^{20,21}

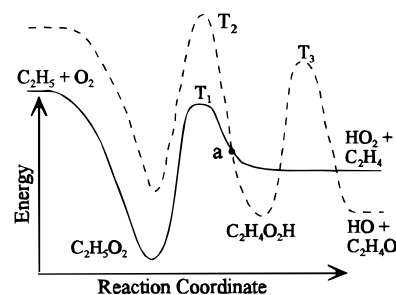
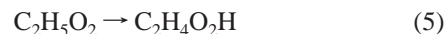
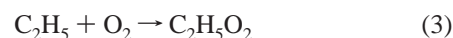


Figure 8. Schematic potential energy diagram for the C₂H₅ + O₂/HO₂ + C₂H₄ system: solid line, Schaefer et al.;^{62–64} dashed line, Robertson et al.³¹

even at higher temperatures where production of the ethene was significant. This precluded direct abstraction of a hydrogen atom by the oxygen molecule, and implied that the ethene must be formed via an adduct. Second, no equilibrium was observed between the reactants C₂H₅ + O₂ and the product C₂H₅O₂,²⁹ which strongly suggested that any barriers to further reaction must be lower in energy than the reactants, the further reactions being isomerization to the hydroperoxyethyl radical (T₁, Figure 7 and reaction 5) and its subsequent decomposition to ethene and hydroperoxyl (T₂, Figure 7 and reaction 6).



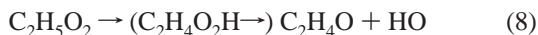
The potential energy diagram for the system as suggested by Baldwin and Walker²⁰ is given by the dashed line in Figure 7 (with C₂H₅ + O₂ as the datum). Their reasons for proposing a relatively high barrier for the addition HO₂ + C₂H₄ and having C₂H₄O₂H decompose to the epoxide have already been described in an earlier section.

There have also been many ab initio studies on the C₂H₅ + O₂ system; the work of Schaefer et al.^{62–64} refined the mechanism of Gutman et al. by suggesting that the transition state for the isomerization of C₂H₅O₂ to C₂H₄O₂H (reaction 5) of C₁ symmetry (T₂, Figure 8) was actually higher in energy than a ²A'' transition state that leads directly to C₂H₄ + HO₂ (T₁, Figure 8). This implied that formation of C₂H₄O₂H and consequently of any epoxide could only be very minor. Therefore, ethyl and oxygen can react on a single, ground-state surface of ²A'' symmetry to form the ethylperoxyl radical, which

if not collisionally stabilized will decompose to $C_2H_4 + HO_2$; a schematic potential energy diagram is given by the solid line in Figure 8. Not shown is a loosely bound complex between C_2H_4 and HO_2 , which is unlikely to greatly affect the kinetics of the system.

Clifford et al.⁴⁰ further discussed the reaction of oxygen with alkyl radicals and commented that the synchronous proton-transfer mechanism described by Quelch et al.⁶² for the decomposition of $C_2H_5O_2$ to $HO_2 + C_2H_4$ would actually correlate the \tilde{X}^2A'' ground state of $C_2H_5O_2$ with an energetically unfavorable highly excited \tilde{B}^2A'' state of HO_2 . They suggested that the $^2A''$ transition state (T_1 in Figure 8) involved mixing of the \tilde{X}^2A'' $C_2H_5O_2$ ground state with an excited $^2A''$ state of $C_2H_5O_2$ that did correlate with the \tilde{X}^2A'' ground state of HO_2 on decomposition, with the latter becoming more significant as the reaction proceeds. Alternatively, they suggested the possibility of the direct decomposition of $C_2H_5O_2$ to $HO_2 + C_2H_4$ via the \tilde{A}^2A' first excited state of $C_2H_5O_2$, but since this would correlate with the energetically unfavorable $^2A'$ first excited state of HO_2 , they suggest a surface crossing of the $^2A'$ and $^2A''$ states to allow the direct formation of the \tilde{X}^2A'' ground state of HO_2 . Like Quelch et al.,⁶² Clifford et al.⁴⁰ also considered the formation of the hydroperoxyethyl radical via an internal hydrogen abstraction reaction by $C_2H_5O_2$ to form the $C_2H_4O_2H$ radical, suggesting that the C_s symmetry is broken at the transition state to allow overlap between the radical orbital on the oxygen and the abstracted hydrogen. Like Quelch et al.⁶² though, Clifford et al.⁴⁰ do not discuss the possible decomposition of the hydroperoxyalkyl radical to the epoxide and OH.

Pilling et al.^{28,31} also recognized the importance of a low-lying electronically excited state in the system and proposed a two-state mechanism to explain the formation of the epoxide, from either $C_2H_4 + HO_2$ or $C_2H_5 + O_2$ (Figure 8). The $^2A''$ surface, describing the reaction of $C_2H_5 + O_2$ to $C_2H_4 + HO_2$, was as suggested by Quelch et al.,⁶³ while a $^2A'$ surface connected the first excited state of O_2 ($^1\Delta_g$) and $C_2H_5O_2$ ($^2A'$), with the ground states of $C_2H_4O_2H$ ($^2A'$) and $C_2H_4O + OH$. The small fraction of $C_2H_5 + O_2$ leading to the epoxide was suggested to be due to occasional intersystem crossing at point "a" in Figure 8, leading to formation of $C_2H_4O_2H$ and subsequently the epoxide. The reaction of $C_2H_4 + HO_2$ was suggested to lead to the epoxide indirectly, via the formation of the ethylperoxyl radical:



The relatively high activation energy for the formation of the epoxide from the reaction of ethene with HO_2 observed by Baldwin and Walker et al.^{20,21} was explained by assuming that decomposition of the ethylperoxyl radical to $C_2H_4 + HO_2$ was the dominant route (i.e., that $k_{-7} \gg k_8$) consistent with Gutman's experimental observations. The rate constant for the overall reaction IX could then be described by the composite expression

$$k_9 = k_8(k_7/k_{-7})$$



The activation energy for the overall reaction can be large by assuming a high barrier for the $^2A'$ decomposition of $C_2H_4O_2H$ to $C_2H_4O + OH$ (T_3 , Figure 8).

This description is capable of rationalizing all the results from the $C_2H_5 + O_2/C_2H_4 + HO_2$ system. However, as demonstrated by Baldwin and Walker, it cannot be valid for describing the

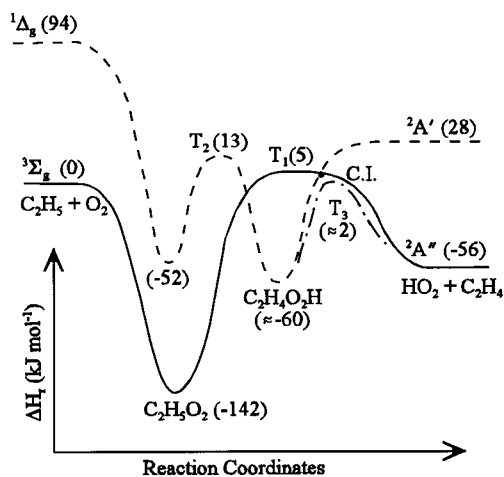


Figure 9. Schematic potential energy diagram for the $C_2H_5 + O_2/HO_2 + C_2H_4$ system: solid line, $^2A''$ state; dashed line, $^2A'$ state; C.I., conical intersection; hatched line, transition state.

addition of hydroperoxyl to 2-butenes or larger alkenes, as, if applicable, reacting HO_2 with *trans*-2-butene would lead to the *sec*-butylperoxyl radical that would mostly decompose back to *cis*-2-butene or *trans*-2-butene, and only occasionally to the epoxides, whereas, experimentally, epoxides of 2-butene are observed to be the main products, not *cis*-2-butene.^{17,23} It is of course possible that HO_2 reacts via a different mechanism with ethene in comparison with 2-butene. However, the structure-activity relations described by Baldwin and Walker and elaborated on in the previous section suggest that the epoxidation of ethene by hydroperoxyl is consistent with other hydroperoxyl epoxidation reactions, and indeed in line with many other peroxy radical addition reactions.

The description of peroxy radical epoxidation given here, which also involves low-lying excited states, can also be combined with the mechanism of Gutman et al.^{29,30} and Schaefer et al.⁶²⁻⁶⁴ in an attempt to reconcile the experimental results of Gutman et al. with those of Baldwin and Walker. From Figure 6, if a hydroperoxyl radical approaches an alkene, with the system having C_s symmetry, then the hydroperoxyl ground $^2A''$ state and the first excited $^2A'$ state intersect at some point at an unavoided crossing (marked C.I.). From Quelch et al.,⁶³ the $^2A''$ hydroperoxyl radical will be directly connected to the $^2A''$ transition state (T_1 , Figure 9) for the decomposition of the alkylperoxyl radical to the alkene, again shown schematically by the solid line in Figure 9.

The $^2A'$ first excited state of the hydroperoxyl radical connects to the $^2A'$ ground state of the hydroperoxyalkyl radical, which in turn connects to the $^2A'$ first excited state of the alkylperoxyl radical, via a 2A transition state (T_2 , Figure 9) as suggested by Quelch et al.⁶³ and Pilling et al.^{28,31} (shown by the dotted line in Figure 9). Also shown is the 2A transition state (T_3) for the addition of HO_2 to the alkene to form the hydroperoxyl radical, which is contiguous with, and necessarily lower than, the conical intersection. For clarity the route for the decomposition of the hydroperoxyalkyl radical to the epoxide is not shown. The $^2A'$ and $^2A''$ states for the system will be described by two reaction coordinates that will be largely independent, and will only coincide at the conical intersection; it is not suggested that there is any surface crossing between T_1 and T_2 .

A conical intersection differs in an important respect from a transition state, in that the behavior of the system depends not only on the coordinates of the nuclei, but also on nuclear motion;⁴⁹ hence, it is necessary to consider the dynamics of the system. The reaction of C_2H_5 and O_2 will produce $C_2H_5O_2$

radicals, which will react further if they have enough energy. Since the lowest energy transition state (T_1) has C_s symmetry, those ethylperoxyl radicals that do react via T_1 will tend to have geometries near to C_s symmetry, particularly at lower temperatures. After crossing the transition state, nuclear motion will carry the radical on the ${}^2A'$ surface toward the conical intersection. At the crossing point, the system is *not* likely to go to the hydroperoxyalkyl radical; nuclear motion will ensure that formation of the conjugate alkene and hydroperoxyl dominates.

However, the reaction in the reverse direction (the addition of HO_2 to alkenes) need not necessarily give the alkylperoxyl radical as a significant product. One reason is that the barrier for the addition (T_3) is necessarily lower than the conical intersection, which in turn is lower than the ${}^2A'$ transition state (T_1) that would give the alkylperoxyl radical. Hence, formation of the hydroperoxyalkyl radical (and subsequent decomposition to the epoxide) will tend to dominate for energetic reasons.

The barrier heights given in Figure 9 are for the specific example of the $C_2H_5 + O_2/C_2H_4 + HO_2$ system and are discussed in the next section. For this system, the height of T_1 is actually sufficiently close to that of T_3 to suggest that a significant proportion of $C_2H_4 + HO_2$ could in fact go to $C_2H_5O_2$ and not $C_2H_4O_2H$. However, this route would not affect the $C_2H_4 + HO_2$ experiments of Baldwin and Walker as only the formation of ethene oxide was monitored,^{20,21} and any $C_2H_5O_2$ formed at the temperatures used (653–773 K) would decompose back to $C_2H_4 + HO_2$. This does not however contradict the experiments of Baldwin and Walker on $HO_2 + trans$ -2-butene,^{17,23} which found the formation of the epoxide and not *cis*-2-butene, since the barrier for the formation of the hydroperoxylbutyl radical (equivalent to T_3 , Figure 9) is ≈ 20 kJ mol⁻¹ lower than for $HO_2 +$ ethene, so at least for the reactions of *trans*-2-butene, the epoxide would still be expected to be the dominant product. This argument could be checked by examining whether HO_2 catalyzed the isomerization of *cis*-dideuterioethene to *trans*-dideuterioethene and did not just form the epoxide.

There is another reason for the addition of HO_2 to alkenes giving the hydroperoxyalkyl radical, and not the corresponding alkylperoxyl radical. Consider an alkylperoxyl radical reacting via T_1 (Figure 9) and approaching the conical intersection on the upper surface; in the two degrees of freedom of the branching space, the conical intersection would tend to act as an attractor and the radical would be funneled toward it. On approaching the bottom of the conical intersection, the radical would transfer to the ground state and carry on to decompose to the alkene and HO_2 . However, approaching the conical intersection on the lower surface (from $HO_2 +$ alkene), the conical intersection acts as a repeller; i.e., if the system was slightly off C_s symmetry, then the symmetry-breaking coordinate (the dihedral angle for the $COO-H$ bond) would increase in magnitude on approaching the conical intersection, preventing the system from passing through the intersection. This would make the formation of the alkylperoxyl radical much less likely to occur, even if energetically possible.

This mechanism is consistent with the work of Baker et al.,¹⁷ who monitored the formation of epoxide and conjugate alkene, and that of Clague,⁶⁶ who monitored the formation of OH radicals, during the reaction of $O_2 +$ alkyl. Both came to the conclusion that their results were best explained by a mechanism in which the conjugate alkene was formed directly from the decomposition of the alkylperoxyl radical, and not via an isomerization to the hydroperoxyalkyl radical. Clifford et al.⁴⁰

recently suggested that the reaction of alkyl radicals with O_2 would lead to a proportion of the resultant chemically activated alkylperoxyl radical being in the first excited state. If not collisionally stabilized, a ${}^2A'$ alkylperoxyl radical with enough energy can isomerize via the 2A internal hydrogen transfer transition state (T_2 , Figure 9) to form the hydroperoxyalkyl radical, which can decompose to the small quantities of epoxide and OH observed by Baker et al.¹⁷ and Clague.⁶⁶

Barrier Heights for the $C_2H_5 + O_2/C_2H_4 + HO_2$ System.

The above description can help explain why the reaction of oxygen with alkyl radicals leads to the formation of the conjugate alkene and HO_2 , while the reverse reaction of hydroperoxyl radical addition to an alkene gives the epoxide. However, the mechanism appears to require that any unavoided crossing should be lower in energy than the heat of formation of alkyl + O_2 .

This requirement can be satisfied by propene or larger alkenes, as they have barriers for HO_2 addition that are comparatively low. However, for ethene itself, it remains difficult to reconcile the high barrier ($E_{-6} = 74.7 \pm 4.5$ kJ mol⁻¹) for $C_2H_4 + HO_2$ found by Baldwin and Walker et al.²¹ with the implication from the work of Gutman et al.^{29,30} that E_{-6} should be lower than the heat of reaction for ethene + HO_2 to ethyl + O_2 ($\Delta H_r(298\text{ K}) = 56.0 \pm 4.6$ kJ mol⁻¹).⁴⁰ Indeed Wagner et al.³⁰ quote a value of $E_{-6} \approx 25$ kJ mol⁻¹, based on thermochemical estimates by Benson,⁶⁷ which in turn were based on a presumed similarity between the addition to alkenes of HO_2 and $O(^1D)$ radicals.

The conclusion that the barrier (E_{-6}) should be lower than 56.0 ± 4.6 kJ mol⁻¹ was largely based on the absence of an observation of an equilibrium for the reaction $C_2H_5 + O_2 \rightleftharpoons C_2H_5O_2$.²⁹ Subsequently though, Gutman et al.⁶⁸ did report a small temperature range (up to 660 K) where an equilibrium *could* be observed. However, in a detailed RRKM kinetic analysis of the system, Wagner et al.³⁰ varied parameters in a four-reaction model to obtain agreement with experiment, and found an optimal value for the barrier height for the rate-determining step in the formation of ethene (T_1 , Figure 7) of 16 kJ/mol *below* $\Delta H(298\text{ K})(C_2H_5 + O_2)$. Further work by Kaiser⁶⁹ determined the apparent activation energy for the reaction $C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$ as 4.6 ± 1.0 kJ mol⁻¹, though again this was interpreted as being consistent with the low barrier for T_1 suggested by Wagner et al.³⁰

It should be noted, however, that in the analysis of Wagner et al.³⁰ the parameters that were floated to obtain an optimum fit were not uniquely determined; it was stated that other combinations of parameters could give an equivalent match between theory and experiment. This raises the possibility that the barrier height of T_1 (Figure 7) could actually be higher than $\Delta H(298\text{ K})(C_2H_5 + O_2)$. This would allow a straightforward explanation of the observation of an equilibrium for the reaction $C_2H_5 + O_2 \rightarrow C_2H_5O_2$. That the equilibrium was not observed above a certain ceiling temperature (660 K) indicates that the barrier height could only be higher than $\Delta H(298\text{ K})(C_2H_5 + O_2)$ by a small margin; at higher temperatures a significant proportion of the population would go straight over the barrier to form ethene, preventing a significant decomposition of $C_2H_5O_2$ back to $C_2H_5 + O_2$. It can be suggested that the small apparent activation energy reported by Kaiser⁶⁹ actually does

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represent the height of the barrier for the rate-determining step in the formation of ethene, T_1 , Figure 9 (i.e., $E_4 \approx 4.6 \pm 1.0$ kJ mol⁻¹).

If this was accepted, it could therefore be argued that the barrier for the addition of hydroperoxyl to ethene (E_{-6}) need only be less than 60.6 ± 4.7 kJ mol⁻¹ to not contradict the findings of Gutman et al. The difference between the value for E_{-6} implied by Kaiser's work and the determination of 74.7 ± 4.5 kJ mol⁻¹ by Baldwin and Walker²¹ is 14.0 ± 6.5 kJ (the error quoted is 1σ ; the 95% confidence limit would be ca. ± 14 kJ mol⁻¹). This difference between these two determinations of E_{-6} would clearly benefit from being addressed by further experimental investigation; however, they do not differ by such a large margin as to be considered fundamentally irreconcilable. The E_{-6} value implied by Kaiser's $E_4 = 4.6 \pm 1.0$ kJ mol⁻¹ is unlikely to be the source of the discrepancy, since even a hypothetical relative error of, say, 50% in the measured value would only give an absolute error of 2–3 kJ mol⁻¹. The E_{-6} value of Baldwin and Walker though, since it is measured from the much lower baseline of the heat of formation of $C_2H_4 + HO_2$, will be more susceptible to error.

Baldwin and Walker's determinations of epoxidation rate constants (along with virtually all other epoxidation rate constants) were determined by a relative rate method. There has however been one reported epoxidation rate constant obtained by more "direct" methods. Arsentiev et al.^{70,71} monitored the total peroxy radical concentration in the gas phase by ESR during the autoxidation of ethene. The rate of production of the ethene oxide was found to correlate well with the product of the peroxy radical and alkene concentrations and was used to derive (effectively, species averaged) rate constants for the epoxidation of the ethene by the peroxy radicals present. For ethene autoxidation at the temperatures used (637–688 K), the dominant peroxy radical present is very likely to be the hydroperoxyl radical, so the rate constant of Arsentiev et al.^{70,71} can be used to give a barrier height for the addition of HO_2 to ethene of $E_{-6} = 56.6 \pm 3.4$ kJ mol⁻¹. This value is consistent with that derived from Kaiser's work of 60.7 ± 4.6 kJ mol⁻¹. Arsentiev's solitary, directly measured value for E_{-6} cannot on its own provide compelling evidence that Baldwin and Walker's value²¹ is too high by ca. 15 kJ mol⁻¹. Nevertheless, it does at least highlight the need for further direct experiments on the $HO_2 + C_2H_4$ reaction.

Baldwin and Walker^{19,21} determined the rate constant for the epoxidation of ethene and propene by competition with the hydroperoxyl radical self-reaction. Subsequent determinations for other alkenes^{18,20,22,23} were by competition with propene or ethene. Hence, if it was suggested that the activation energies for propene and ethene were too high by ca. 15 kJ mol⁻¹, all their other evaluations would also need to be reduced, thus maintaining the excellent correlation between activation energy and alkene ionization energy that they observed. The $\Delta H_f(298$ K) energies quoted in Figure 9 are sourced from: $C_2H_4 + HO_2$,⁴⁰ T_1 ,⁶⁹ T_3 ,^{70,71} $C_2H_4O_2H$,⁶⁴ and T_2 from evaluations of a 1,4p hydrogen transfer reaction³¹ and excited states.⁴⁶

If it were accepted that $E_{-6} \approx 60$ kJ mol⁻¹, and $E_4 \approx 5$ kJ mol⁻¹ and that there was an unavoids crossing of the $^2A''$ and $^2A'$ states of the system in the vicinity of the transition state for the addition of the peroxy radical to the alkene, then the benefits for the understanding of hydrocarbon oxidation are considerable, as it could be contended that the two well-developed mecha-

nisms describing $O_2 + \text{alkyl} \rightarrow \text{alkene} + HO_2$ and HO_2 (or RO_2) + alkene \rightarrow epoxide + OH (or RO) are able to coexist without contradiction.

Conclusions

Ab initio calculations of the electronic properties of selected peroxy radicals have allowed a detailed examination of structure–activity relationships describing their epoxidation of alkenes. A good correlation is found between the activation energy for the initial addition of peroxy radicals to alkenes and the energy released by charge transfer during the formation of the transition state. A physical description of the reaction is suggested whereby if no energy is released by charge transfer, then the activation energy is similar to the energy required to excite the peroxy radical from the ground $^2A''$ state to the first electronically excited $^2A'$ state; with charge transfer, the activation energy for the addition is lowered in proportion to the energy released by the charge transfer. The first electronically excited $^2A'$ state of the peroxy radical correlates with the ground state of the peroxyalkyl adduct, while the ground $^2A''$ state correlates with an excited state of the peroxyalkyl adduct, and it is suggested the surfaces cross at an unavoids crossing of C_s symmetry, which is proximate to, and higher than, the transition state for the addition.

It is suggested that mono- and diatomic radicals can add to alkenes with little or no activation energy because they are of high symmetry and have a ground state that correlates with the ground state of the adduct, in contrast to larger, lower symmetry radicals.

For the specific case of hydroperoxyl addition to alkenes, it is suggested that the presence of an unavoids crossing of high symmetry between the $^2A''$ and $^2A'$ surfaces can help explain the long-standing problem of the apparent irreconcilability of the accepted mechanism for the reaction of oxygen and alkyl radicals forming the conjugate alkene and the hydroperoxyl radical, while the mechanism for the reverse reaction of hydroperoxyl radicals with alkenes yields the epoxide. It appears necessary though to suggest that the currently accepted activation energies for the epoxidation of alkenes by hydroperoxyl radicals have been overestimated by ca. 15 kJ mol⁻¹. Similarly, it is necessary to suggest that the $^2A''$ barrier for decomposition of ethylperoxy radicals to ethene and hydroperoxyl radicals has been underestimated, and it should be ca. 5 kJ mol⁻¹ higher than $\Delta H_f(C_2H_5 + O_2)$. Further experiments are clearly needed to establish whether this is in fact the case.

Acknowledgment. I thank Drs. Darren Chapman, Mark Watkins, and Graham Doggett for advice on GAUSSIAN and quantum mechanics, Dr. Dennis Smith for reviewing the manuscript, and Prof. David Waddington for many helpful discussions and encouragement with this work.

Supporting Information Available: G1, G2, and G2MP2 energies for hydroperoxyl and methylperoxyl radicals, anions, and cations and G2MP2 energies for ethylperoxyl, isopropylperoxyl, *tert*-butylperoxyl, and acetylperoxyl radicals, anions, and cations; compilations of rate constants for the reactions with alkenes of peroxy and calculations of ΔE_c for these reactions; optimized geometries for these species at the MP2(Full)/6-31G(d) level; and details of preliminary ab initio calculations on the addition of HO_2 to ethene at the UCIS/6-31(d) level (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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