8296 *J. Phys. Chem. A* **1997,** *101,* 8296−8301

Epoxidation of Alkenes by Peroxyl Radicals in the Gas Phase: Structure−Activity Relationships

Moray S. Stark[†]

Department of Chemistry, University of York, York, YO1 5DD, U.K.

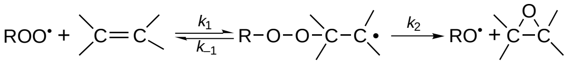
Received: June 24, 1997[⊗]

The epoxidation of alkenes by peroxyl radicals in the gas phase is examined, and it is demonstrated that the activation energies for 36 epoxidation reactions between 17 alkenes and 5 peroxyl radicals correlate well to the charge transfer, or the corresponding energy decrease, in forming the peroxyalkyl adduct, or the difference between the ionization energy of the alkene and the electron affinity of the peroxyl radical. These correlations have been used to estimate five previously unmeasured epoxidation rate constants relevant to propene autoxidation.

Introduction

Alkenes and peroxyl radicals are, respectively, significant primary products and important chain carriers of the oxidation of alkanes in the gas phase at relatively low temperatures,[1] below ca. 850 K. The study of the addition of peroxyl radicals to alkenes is therefore necessary for a good understanding of hydrocarbon combustion in the cool flame regime. Furthermore, the resulting epoxides are high-value chemical products, and their formation via the noncatalytic, gas-phase autoxidation of alkenes has been of considerable recent interest.[2−5]

It has been understood for some time that the addition of peroxyl radicals to alkenes is the rate-determining step in the formation of the epoxide ($k_2 \gg k_{-1}$),[6] and that for a peroxyl radical attacking a series of alkenes, the activation energy for the overall reaction correlates well with the ionization energy of the alkene (Figures 1 and 2).[6,7]



(R1, R2)

It would also be of practical use to be able to relate the rate of epoxidation to a physical property of the attacking peroxyl radical. Therefore an investigation is made of the correlation of epoxidation activation energies with three parameters: the charge transfer that occurs during the formation of the peroxyalkyl adduct, the corresponding energy decrease due to the charge transfer, and the difference between the ionization energy of the alkene and the electron affinity of the peroxyl radical. These correlations are used to estimate epoxidation rate constants of relevance to the modeling of propene autoxidation.

Summary of Gas-Phase Epoxidation Rate Constants

Experimental rate parameters for 36 reactions between 17 alkenes and five peroxyl radicals are compiled in Table 1 (the quoted error bounds are standard errors). All rate parameters except that of Arsentiev and Mantashyan[17] have been determined by a competitive technique, using a previously determined rate constant for the reference reaction. The epoxidation rate constants for methylperoxyl and *tert*-butylperoxyl radicals have been reevaluated to take into account more recent critical evaluations of their reference reactions, the self-reactions of the peroxyl radicals.[21]

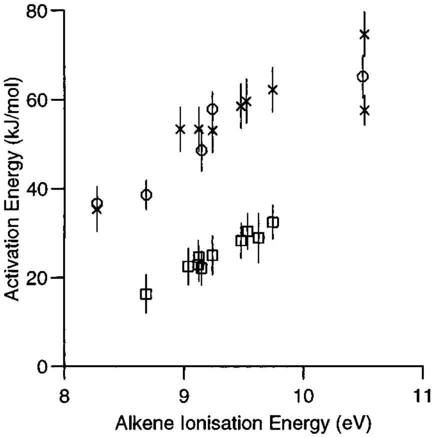


Figure 1. Relationship between alkene ionization energy and the activation energy for the epoxidation of the alkenes by acetylperoxyl (squares), methyperoxyl (circles), and hydroperoxyl radicals (diagonal crosses).

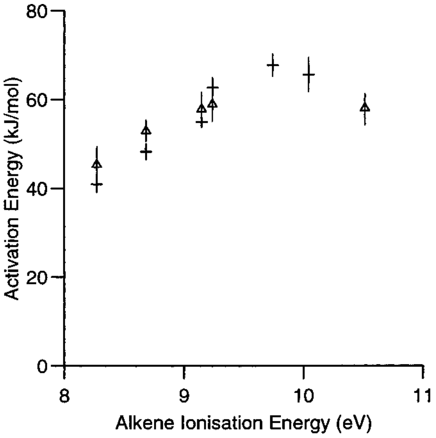


Figure 2. Relationship between alkene ionization energy and the activation energy for the epoxidation of the alkenes by isopropylperoxyl (horizontal lines) and *tert*-butylperoxyl radicals (triangles).

There have been no further evaluations of the reference reaction for epoxidation by acetylperoxyl radicals, the abstraction of hydrogen from acetaldehyde by acetylperoxyl radicals, since that of McDowell and Sharples.[22] However, the standard errors originally quoted for the epoxidation by acetylperoxyl represent the error in the ratio $k_{\text{epoxidation}}/k_{\text{reference}}$.[6,8,9] The values given here include the significant errors for the reference

---

[†] E-mail: mss1@york.ac.uk

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1997.

S1089-5639(97)02054-9 CCC: $14.00

TABLE 1: Summary of Rate Constants for the Epoxidation of Alkenes by Peroxyl Radicals in the Gas Phase

reaction	temp (K)	$\log_{10}(A/\mathrm{dm^3\,mol^{-1}\,s^{-1}})$	E (kJ/mol)	ref	ΔE_c (kJ/mol)[a]	ΔN_c[a]	$I_{alkene} - A_{peroxyl}$ (eV)[a]
$CH_3C(O)O_2$ + 2-methyl-2-butene	357−410	8.08 ± 0.76	16.3 ± 4.3	6	38.0	0.200	5.94
$CH_3C(O)O_2$ + *trans*-2-pentene[b]	373	8.10 ± 0.50	22.5 ± 4.1	6	32.9	0.185	6.29
$CH_3C(O)O_2$ + *cis*-2-pentene[b]	373	8.10 ± 0.50	22.5 ± 4.1	6	32.9	0.185	6.29
$CH_3C(O)O_2$ + *trans*-2-butene[b]	373	8.10 ± 0.50	24.6 ± 3.8	8	32.1	0.182	6.38
$CH_3C(O)O_2$ + *cis*-2-butene[b]	373	8.10 ± 0.50	22.9 ± 3.8	8	32.9	0.184	6.38
$CH_3C(O)O_2$ + 2-methyl-1-butene[b]	373	8.10 ± 0.50	22.1 ± 3.8	6	31.7	0.181	6.40
$CH_3C(O)O_2$ + 2-methylpropene	370−410	8.29 ± 0.77	25.0 ± 4.4	9	31.5	0.180	6.49
$CH_3C(O)O_2$ + 1-hexene[b]	373	8.10 ± 0.50	28.3 ± 3.9	6	27.4	0.167	6.73
$CH_3C(O)O_2$ + 3-methyl-1-butene[b]	373	8.10 ± 0.50	30.4 ± 4.0	6	26.9	0.166	6.78
$CH_3C(O)O_2$ + 1-butene	357−410	7.94 ± 0.89	28.9 ± 5.5	9	25.8	0.162	6.88
$CH_3C(O)O_2$ + propene[b]	373	8.10 ± 0.50	32.5 ± 3.8	6	25.3	0.160	7.00
CH_3O_2 + 2,3-dimethyl-2-butene	373−403	7.95 ± 0.45	36.6 ± 3.4	10	24.0	0.156	7.06
CH_3O_2 + 2-methyl-2-butene	373−403	7.43 ± 0.44	38.6 ± 3.3	10	20.4	0.142	7.47
CH_3O_2 + 2-methyl-1-butene	373−403	7.83 ± 0.63	48.6 ± 4.7	10	16.1	0.126	7.94
CH_3O_2 + 2-methylpropene[b]	410	8.10 ± 0.50	57.9 ± 3.9	11	16.1	0.125	8.03
CH_3O_2 + ethene[b]	410	9.00 ± 0.50	65.2 ± 4.8	11	7.2	0.082	9.30
HO_2 + 2,3-dimethyl-2-butene	653−773	8.58 ± 0.35	35.4 ± 5.0	7	23.8	0.152	7.46
HO_2 + *trans*-2-hexene	673−773	8.41 ± 0.35	53.4 ± 5.0	12	17.3	0.128	8.16
HO_2 + *cis*-2-hexene	673−773	8.41 ± 0.35	53.4 ± 5.0	12	17.3	0.128	8.16
HO_2 + *cis*-2-butene	673−793	8.61 ± 0.30	53.4 ± 5.0	13	16.4	0.124	8.31
HO_2 + 2-methylpropene	673−793	8.80 ± 0.35	53.1 ± 5.0	14	16.1	0.122	8.43
HO_2 + 1-hexene	673−773	8.91 ± 0.34	58.6 ± 5.0	12	13.3	0.111	8.67
HO_2 + 1-pentene	673−793	8.88 ± 0.34	59.7 ± 5.0	12	13.0	0.110	8.71
HO_2 + propene	673−773	9.01 ± 0.30	62.3 ± 5.0	15	12.0	0.105	8.93
HO_2 + ethene	653−773	9.58 ± 0.35	71.6 ± 5.0	16	7.4	0.081	9.70
HO_2 + ethene	673−773	9.58 ± 0.35	74.7 ± 5.0	14	7.4	0.081	9.70
HO_2 + ethene	637−688	9.10 ± 0.27	56.6 ± 3.4	17	7.4	0.081	9.70
i-$C_3H_7O_2$ + 2,3-dimethyl-2-butene	303−363	7.96 ± 0.50	40.9 ± 1.8	18	24.6	0.159	6.87
i-$C_3H_7O_2$ + 2-methyl-2-butene	303−408	8.03 ± 0.35	48.2 ± 1.8	19	20.9	0.145	7.28
i-$C_3H_7O_2$ + 2-methyl-1-butene	363−408	8.30 ± 0.08	54.9 ± 0.9	19	16.5	0.128	7.74
i-$C_3H_7O_2$ + 2-methylpropene	373−408	8.59 ± 0.19	62.7 ± 2.2	19	16.5	0.127	7.84
i-$C_3H_7O_2$ + propene	373−408	8.92 ± 0.36	67.7 ± 2.5	19	12.2	0.109	8.34
i-$C_3H_7O_2$ + 3-fluoropropene[b]	393	8.10 ± 0.50	65.6 ± 3.8	19	12.9	0.110	8.64
t-$C_4H_9O_2$ + 2,3-dimethyl-2-butene	313−393	7.96 ± 0.62	45.3 ± 4.1	20	24.7	0.160	6.80
t-$C_4H_9O_2$ + 2-methyl-2-butene	313−393	7.54 ± 0.39	52.9 ± 2.4	20	21.0	0.146	7.21
t-$C_4H_9O_2$ + 2-methyl-1-butene[b]	393	8.10 ± 0.50	57.8 ± 3.8	20	16.6	0.129	7.67
t-$C_4H_9O_2$ + 2-methylpropene[b]	393	8.10 ± 0.50	58.9 ± 3.8	20	16.5	0.128	7.76
t-$C_4H_9O_2$ + ethene[b]	393	9.00 ± 0.50	58.0 ± 3.8	20	7.4	0.083	9.04

[a] ΔN_c, ΔE_c, and ($I_{alkene} - A_{peroxyl}$) were determined using ionization energies and electron affinities from Table 2. [b] For rate constants determined at only one temperature, activation energies have been calculated assuming an A factor of 1.28×10^8 dm^3 mol^{-1} s^{-1}.

reaction, giving noticeably larger errors for the Arrhenius parameters for epoxidation than previously quoted.

Baldwin et al.[14] have reevaluated their rates for epoxidation by hydroperoxyl radicals using a recent recommendation for the reference reaction, the self-reaction of the radical.[23] These rates are quoted here. Of their two measurements of the activation energy for the epoxidation of ethene,[14,16] only the more recent is used in the analysis in this paper.

Rate constants for 14 epoxidation reactions by acetyl and alkyl peroxyl radicals were determined at only one temperature. To allow these results to be included in Figures 1−5, activation energies were calculated using an assumed A factor of $\log(A/\mathrm{dm^3\,mol^{-1}\,s^{-1}}) = 8.1 \pm 0.5$, which is the average of the 13 A factors that have been determined (the quoted error is the standard deviation of the measured A factors and is also equal to the average of the measured A factor standard errors).

The A factors for epoxidation by hydroperoxyl radicals are statistically significantly higher than for epoxidation by alkyl or acylperoxyl radicals, with an average of $\log(A/\mathrm{dm^3\,mol^{-1}\,s^{-1}}) = 8.83 \pm 0.36$ (the average of the measured standard errors of the A factors is ±0.34). Stothard and Walker have noted that the A factors for epoxidation by hydroperoxyl radicals tend to increase with increasing alkene ionization energy,[13] with a recent evaluation giving $\log(A/\mathrm{dm^3\,mol^{-1}\,s^{-1}}) = 0.763 I_{alkene}(\mathrm{eV}) + 1.290$.[24] However, the variation is due predominantly to the relatively high value for ethene of $\log(A/\mathrm{dm^3\,mol^{-1}\,s^{-1}}) = 9.35 \pm 0.35$, which is ×8 higher than the average for the other hydroperoxyl epoxidation reactions.

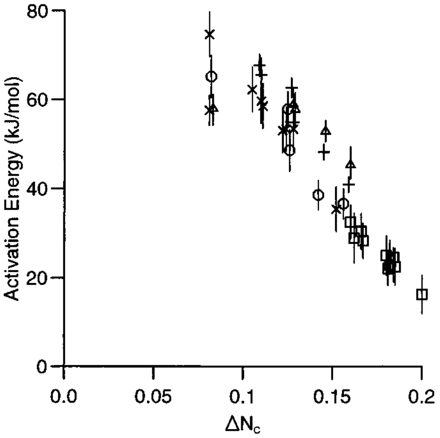


Figure 3. Relationship between activation energy for the epoxidation of alkenes by peroxyl radicals and the charge transfer in forming the adduct, ΔN_c: acetylperoxyl (squares), methyperoxyl (circles), hydroperoxyl (diagonal crosses), isopropylperoxyl (horizontal lines), and *tert*-butylperoxyl radicals (triangles).

The rate constants for the addition of hydroperoxyl radicals to ethene and 2-methylpropene from the discharge flow experiments of Avramenko et al.[25] have not been included in Table 1. In their experiments, HO_2 was produced via H atom (from

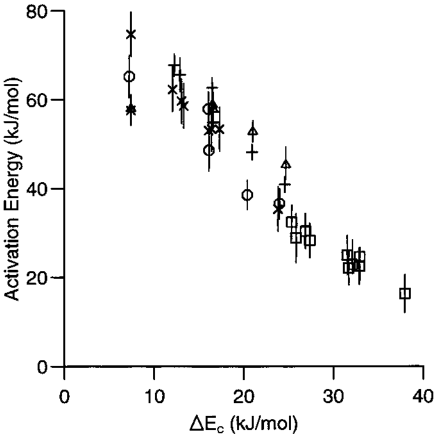


Figure 4. Relationship between activation energy for the epoxidation of alkenes by peroxyl radicals and the energy decrease due to the charge transfer in forming the adduct, ΔE_c: acetylperoxyl (squares), methyperoxyl (circles), hydroperoxyl (diagonal crosses), isopropylperoxyl (horizontal lines), and *tert*-butylperoxyl radicals (triangles).

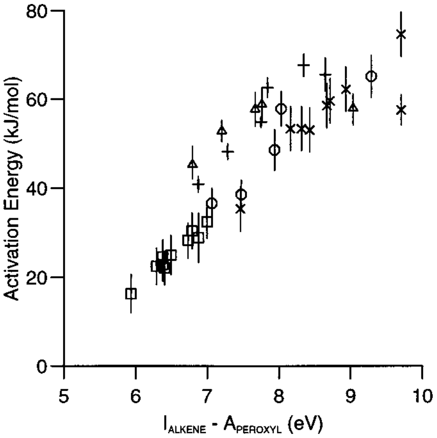


Figure 5. Relationship between activation energy for the epoxidation of alkenes by peroxyl radicals and the difference between the ionization energy of the alkene and the electron affinity of the peroxyl radical ($I_{\mathrm{alkene}} - A_{\mathrm{peroxyl}}$): acetylperoxyl (squares), methyperoxyl (circles), hydroperoxyl (diagonal crosses), isopropylperoxyl (horizontal lines), and *tert*-butylperoxyl radicals (triangles).

discharged H_2) addition to oxygen, and the review of Lloyd[26] suggests that there was significant contamination by oxygen atoms and hydroxyl radicals, both of which would react with the alkenes to give the main observed product, formaldehyde. Lloyd's review also discounts other early work on hydroperoxyl addition to ethene as unreliable due to the rate data being derived from a poorly understood, complex reaction mechanism describing the co-oxidation of methane and ethene.[27]

Arsentiev et al.[17,28] monitored the total peroxyl radical concentration in the gas phase by ESR during the autoxidation of ethene and propene. The rates of production of the epoxides (determined by GC analysis) were found to correlate well with the product of the peroxyl radical and alkene concentrations and were used to derive (effectively, species averaged) rate constants for the epoxidation of the alkene by the peroxyl radicals present. For ethene autoxidation at the temperatures used (637−688 K), the dominant peroxyl radical present is likely to be the hydroperoxyl radical, so the rate constant of Arsentiev et al.[17] is included in Table 1 as a value for epoxidation of ethene by hydroperoxyl radicals. The epoxide formed during the autoxidation of propene at 633 K[28] is likely to be due to a variety of radicals (e.g. methylperoxyl, 1-hydroxy-2-propylperoxyl, hydroxymethylperoxyl, and allylperoxyl[3]), so this value is not included.

Structure−Activity Relationships for the Addition of Peroxyl Radicals to Alkenes

Previous work, particularly on the hydroperoxyl and acetylperoxyl radicals, has established that the rate of addition of peroxyl radicals to alkenes is correlated to the ionization energy of the alkene (Figures 1 and 2), indicating a degree of charge transfer from the radical and to the alkene at the transition state for the initial addition forming the peroxyalkyl adduct, reaction 1.[6] It would also be of practical use to be able to relate the rate of epoxidation to a physical property of the attacking radical, as this would allow the estimation of rates of epoxidation for reactions that have not yet been examined experimentally.

One possible rationalization for the reactivity of electrophilic addition of radicals to alkenes is that during the reaction of two species to form an adduct, electron density flows between the two until an energy minimum is obtained.[29−31] The degree of charge transfer (ΔN_c) in forming the adduct and the corresponding energy decrease (ΔE_c) can be estimated from the absolute electronegativity (χ) and absolute hardness (η) of the two species (a and b) forming the adduct, which are in turn are related to their ionization energy (I) and electron affinity (A):[29]

$$\Delta N_c = (\chi_a - \chi_b)/2(\eta_a + \eta_b) \quad (1)$$

$$\Delta E_c = -(\chi_a - \chi_b)^2/4(\eta_a + \eta_b) \quad (2)$$

$$\chi = (I + A)/2 \quad (3)$$

$$\eta = (I - A)/2 \quad (4)$$

A fast rate of reaction for a reactive species attacking a substrate has been associated with a large charge transfer or corresponding energy decrease.[29−31]

An alternative explanation for electrophilic addition reactions is that the rate will be faster the smaller the energy gap between the highest occupied molecular orbital (HOMO) of the alkene and the lowest unoccupied molecular orbital (LUMO) of the radical, which can be approximated by the difference between the ionization energy of the alkene and the electron affinity of the radical ($I_{\mathrm{alkene}} - A_{\mathrm{peroxyl}}$).[32]

Typically, correlations have only been examined for an individual species attacking a number of substrates, e.g. ref 30. However, the assumption is tested here that for peroxyl radical addition to alkenes in the gas phase all 36 reactions that have been investigated between 17 alkenes and 5 peroxyl species share a common behavior, and correlations are examined between the activation energies of the reactions (E) and the charge transfer in forming the adduct, ΔN_c (Figure 3), the energy decrease due to the charge transfer, ΔE_c (Figure 4), and the difference between the alkene ionization energy and the peroxyl radical electron affinity, ($I_{\mathrm{alkene}} - A_{\mathrm{peroxyl}}$) (Figure 5). Calculations of ΔN_c, ΔE_c, and ($I_{\mathrm{alkene}} - A_{\mathrm{peroxyl}}$) are given in Table 1 using values of I, A, χ, and η given in Table 2. Linear regressions of Figures 3, 4, and 5 are given by eqs 5, 6, and 7 (r is the correlation coefficient, and δE is the standard error of the estimated activation energies, as calculated by eqs 5−7).

$$E\ (\mathrm{kJ/mol}) = 109\ \mathrm{kJ/mol} - (456 \pm 31\ \mathrm{kJ/mol})\Delta N_c \quad (r = 0.93,\ \delta E = 6.2\ \mathrm{kJ/mol}) \quad (5)$$

$$E\ (\mathrm{kJ/mol}) = 83.0\ \mathrm{kJ/mol} - (1.82 \pm 0.10)\Delta E_c\ (\mathrm{kJ/mol}) \quad (r = 0.95,\ \delta E = 5.3\ \mathrm{kJ/mol}) \quad (6)$$

$$E\ (\mathrm{kJ/mol}) = -61.0\ \mathrm{kJ/mol} + (14.0 \pm 1.2)(I_{\mathrm{alkene}} - A_{\mathrm{peroxyl}})\ (\mathrm{eV}) \quad (r = 0.89,\ \delta E = 7.4\ \mathrm{kJ/mol}) \quad (7)$$

TABLE 2: Values of Ionization Energy (*I*), Electron Affinity (*A*), Absolute Electronegativity (χ), and Absolute Hardness (η) Used in the Calculations of ΔN_c and ΔE_c

	I (eV)[a]	*A* (eV)	χ (eV)	η (eV)
2,3-dimethyl-2-butene	8.271	−2.27[b]	3.00	5.27
2-methyl-2-butene	8.682	−2.24[b]	3.22	5.46
trans-2-hexene	8.969	−2.07[c]	3.45	5.52
cis-2-hexene	8.969	−2.07[c]	3.45	5.52
trans-2-pentene	9.036	−2.09[c]	3.48	5.56
cis-2-pentene	9.036	−2.08[c]	3.47	5.56
trans-2-butene	9.122	−2.22[b]	3.45	5.67
cis-2-butene	9.124	−2.10[b]	3.51	5.61
2-methyl-1-butene	9.148	−2.08[b]	3.53	5.62
2-methylpropene	9.239	−2.19[c]	3.52	5.71
1-hexene	9.478	−1.93[c]	3.78	5.70
1-pentene	9.524	−1.93[c]	3.80	5.73
3-methyl-1-butene	9.533	−1.93[c]	3.80	5.73
1-butene	9.625	−1.90[b]	3.86	5.76
propene	9.744	−1.99[b]	3.88	5.87
ethene	10.515	−2.50[b]	4.37	6.15
3-fluoropropene	10.045	−1.78[c]	3.77	6.27
$CH_3C(O)O_2$	11.58[d]	2.75[d]	7.16	4.42
CH_3O_2	11.18[d]	1.21[d]	6.19	4.98
HO_2	11.69[d]	0.81[d]	6.25	5.44
i-$C_3H_7O_2$	11.00[d]	1.40[d]	6.20	4.80
t-$C_4H_9O_2$	10.92[d]	1.48[d]	6.20	4.72
$C_2H_3C(O)O_2$	11.49[d]	2.90[d]	7.19	4.30
$HOC_3H_6O_2$	10.86[d]	2.02[d]	6.44	4.42
$HOCH_2O_2$	11.43[d]	1.96[d]	6.70	4.73
$C_3H_5O_2$	11.14[d]	1.60[d]	6.37	4.77

[a] The alkene ionization energies are from Masclet et al.[33] apart from 3-fluoropropene, which was estimated by adding the calculated difference in ionization energy between it and propene (using Mopac 6.0, using the AM1 Hamiltonian[34]), to the experimental value for propene. [b] Experimental values from Jordan and Burrow[35] (except for 1-butene[36]). [c] For the alkenes, a reasonable correlation was obtained between the energy of the lowest unoccupied molecular orbital (from Mopac 6.0, AM1 Hamiltonian[34]) and experimentally determined electron affinities:[35,36] A (eV) = 1.77 × LUMO_{AM1}(eV) − 4.39(eV) (r = 0.93, standard error of the estimated affinities = 0.74 eV), which was used to estimate the unmeasured electron affinities via LUMO values calculated using Mopac 6.0. [d] The ionization energies and electron affinities were calculated by Jonsson[37] using Mopac 6.0 at the RHF level with the AM1 Hamiltonian (with configuration interaction (C. I.) = 1),[34] except for the values for *i*-$C_3H_7O_2$, $C_2H_3C(O)O_2$, $HOC_3H_6O_2$, $HOCH_2O_2$, and $C_3H_5O_2$, which were calculated by the same technique for this work. The electron affinities for the radicals were taken as the ionization energy for the corresponding anions.

Discussion

The correlations in Figures 3, 4, and 5 appear reasonable; for example, 21 of the 37 measured activation energies have error bounds that overlap the line of best fit when plotted against the energy decrease due to the charge transfer, ΔE_c (Figure 4); also, the standard error of the activation energies estimated by eq 6 (5.3 kJ/mol) is not significantly greater than the mean of the measured standard errors (3.9 kJ/mol). There is however noticeably more scatter for the reactions of ethene. The values of Baldwin et al.[14,16] and of Arsentiev et al.[17] for the activation energy for epoxidation of ethene by hydroperoxyl radicals differ by a margin considerably bigger than the measured standard errors. That of Arsentiev is noticeably below the line of best fit for the correlation of activation energy with alkene ionization energy (Figure 1) as well as those of Figures 3−5, although this is no reason per se to accept the value of Baldwin et al. over Arsentiev's. Indeed the suggested activation energy for the epoxidation of ethene by *tert*-butylperoxyl radicals also appears to be anomalously low with respect to its other epoxidation reactions (although this value should be viewed with caution as it is based on an assumed *A* factor: if, for instance, the *A* factor for epoxidation of ethene by alkylperoxyl radicals was ×8 larger than for other alkenes, as is the case with HO_2, then the recommended activation energy would be ca. 7 kJ/mol higher).

The activation energy for the reaction of hydroperoxyl radicals with ethene is of particular interest, as it has been suggested on the basis of experiments on the $O_2 + C_2H_5$ system that the barrier for $HO_2 + C_2H_4$ must be lower than the heat of formation of $O_2 + C_2H_5$.[38] More recent experiments on the temperature dependence of the yield of C_2H_4 from the reaction of $O_2 + C_2H_5$ gave a small positive activation energy of 4.6 ± 1.0 kJ/mol,[39] implying an activation energy for the addition of HO_2 to C_2H_4 of less than 58.9 ± 1.0 kJ/mol, which is consistent with the value determined by Arsentiev et al. of 56.6 ± 3.4 kJ/mol (ΔH_r(298 K) = 54.3 kJ/mol for $O_2 + C_2H_5 \rightarrow HO_2 + C_2H_4$[40]). The experiments of Arsentiev et al. are also of importance because it has been suggested[41] that side reactions involving oxygen atoms were forming the epoxide in the experiments of Baldwin et al. However, the good correlation between the rate of epoxide formation and the product of the peroxyl radical and alkene concentrations in the experiments of Arsentiev et al. provides direct evidence that epoxidation is by peroxyl radicals.

In the absence of experimental data, values for ionization energies and electron affinities of the peroxyl radicals have been calculated using Mopac 6.0 with the AM1 Hamiltonian.[34] Jonsson has noted the possible problems of this, pointing out that there is not a good correlation between the measured aqueous phase one electron reduction potentials of peroxyl radicals and their calculated gas-phase electron affinities, with in particular the calculated electron affinity for *t*-$C_4H_9O_2$ appearing to be too high.[37] However, a lower value for the electron affinity of *t*-$C_4H_9O_2$ would give lower values for ΔE_c, and ΔN_c and a higher value for ($I_{\text{alkene}} - A_{\text{peroxyl}}$) for this species, which could actually improve the correlations given in Figures 3−5. These correlations should be reinvestigated when experimental data or higher level calculations become available for the properties in question.

For correlations between a number of different peroxyl radicals and different alkenes, there is not a one to one relationship between ΔN_c, ΔE_c, or ($I_{\text{alkene}} - A_{\text{peroxyl}}$). Therefore, in principle, Figures 3−5 could be used to determine which of the explanations of reactivity was more appropriate, i.e. which has the best correlation. However, considering the uncertainties in the measured and estimated values used in Figures 3−5, the correlation coefficients do not differ by significant enough margins to answer this question.

Epoxidation Rate Constants for Propene Autoxidation

There has been interest recently in constructing reaction schemes to allow the simulation of propene autoxidation.[3,42,43] However, of the seven peroxyl radicals that have been identified as contributing to the epoxidation of the alkene, rate constants for only two have been measured, with the rest being estimated on the basis of ad hoc assumptions. Consequently, the relationship with the highest correlation coefficient, that between ΔE_c, the charge-transfer energy decrease, and the activation energy for the reaction, has been used to estimate activation energies for the unstudied reactions (epoxidation of propene by methylperoxyl (CH_3O_2), acrylperoxyl ($C_2H_3C(O)O_2$), 1-hydroxy-2propylperoxyl ($HOC_3H_6O_2$), hydroxymethylperoxyl ($HOCH_2O_2$), and allylperoxyl ($C_3H_5O_2$)). Electron affinities and ionization energies were estimated using Mopac 6.0 and are given in Table 2, while the charge-transfer energy decrease, ΔE_c, and the activation energies calculated using eq 6 are given in Table 3. These values, along with the average *A* factor of 1.28

TABLE 3: Calculated Values of Charge-Transfer Energy Decrease (ΔE_c) and Activation Energy (E) for the Reaction of Various Peroxyl Radicals and Propene. ΔE_c Values Are Calculated Using χ and η Values from Table 2, while the Activation Energies Are Determined Using Eq 6

	ΔE_c (kJ/mol)	E (kJ/mol)	
$CH_3C(O)O_2$	25.3	37.0 ± 5.3[a]	(32.5 ± 3.8)[b]
CH_3O_2	11.9	61.3 ± 5.3	(57.1 ± 5.2)[c]
HO_2	12.0	69.5 ± 5.3	(62.3 ± 5.0)[b]
$C_2H_3C(O)O_2$	26.1	35.5 ± 5.3	
$HOC_3H_6O_2$	15.4	55.0 ± 5.3	
$HOCH_2O_2$	18.1	50.1 ± 5.3	
$C_3H_5O_2$	14.1	57.4 ± 5.3	

[a] The error bound quoted is the standard error in the calculated activation energies. [b] Experimental values: $CH_3C(O)O_2$,[6] HO_2.[15] [c] For comparison, an activation energy for methylperoxyl was evaluated using the correlation between activation energy for epoxidation by methylperoxyl radicals and the alkene ionization energy (Figure 1).

$\times 10^8$ dm^3 mol^{-1} s^{-1}, can be used in subsequent computer models of propene oxidation.

An activation energy for methylperoxyl of 57.1 ± 5.2 kJ/mol was also calculated using only data for the correlation between activation energy for epoxidation by methylperoxyl radicals and the alkene ionization energy (Figure 1). This value is within one standard error of that calculated using eq 6 (61.3 ± 5.3 kJ/mol). Experimental values for epoxidation by acetylperoxyl and hydroperoxyl radicals are also given in Table 3 for comparison; the calculated values are higher by 4.5 and 7.2 kJ/mol, respectively, and fall within the combined standard errors of 6.5 and 7.2 kJ/mol.

The correlations of epoxidation activation energy with both ΔN_c and $(I_{alkene} - A_{peroxyl})$ (eqs 5 and 7) were also used to calculate activation energies for the epoxidation of propene; however, they are not significantly different from values calculated using eq 6. Those determined using eq 5 were lower by an average of 0.9 kJ/mol (with a standard deviation of 1.6 kJ/mol), whereas values found using eq 7 were lower by an average of 1.8 kJ/mol (standard deviation of 3.7 kJ/mol), within the estimated standard errors of the calculated values of 5−7 kJ/mol.

As described in the previous section, using MOPAC 6.0 with the AM1 Hamiltonian probably overestimates the electron affinities of the more branched radicals t-$C_4H_9O_2$ and i-$C_3H_7O_2$, so to examine the effect of these values on predicted activation energies, the correlation between $(I_{alkene} - A_{peroxyl})$ and epoxidation activation energy was recalculated without data for t-$C_4H_9O_2$ and i-$C_3H_7O_2$. The resulting predicted activation energies for the species given in Table 3 were lower than values found with eq 7 by 3.6 kJ/mol (with a standard deviation of 0.3 kJ/mol), which is less than the standard error on the estimated values found using eq 7 of 7.4 kJ/mol.

Of the five previously unmeasured activation energies for the epoxidation of propene, four are within one standard error (±5.3 kJ/mol) of the previous estimates, giving credence to the ad hoc assumptions used (that $C_2H_3C(O)O_2$ can be assumed analogous to $CH_3C(O)O_2$, $HOC_3H_6O_2$ behaves like i-$C_3H_7O_2$, etc.).[3] However, the activation energy for epoxidation by $HOCH_2O_2$ calculated here is significantly higher, by 15 kJ/mol, than the previous estimate used in computer simulation of propene autoxidation.[3] Preliminary modeling studies suggest that the higher activation energy gives a rate constant low enough for epoxidation by $HOCH_2O_2$ to be insignificant under all conditions. Previously, in the modeling of fuel-rich propene autoxidation at 500−550 K and relatively high pressures (4−50 bar), this route was the main source of formic acid (formed by the oxidation of the $HOCH_2O$ radical resulting from epoxidation by $HOCH_2O_2$).[4] Formic acid can be a significant product, particularly at the higher pressures; the mechanism of formic acid formation will therefore need to be reexamined.

Conclusion

Reasonable correlations have been demonstrated between the activation energies for epoxidation of alkenes by peroxyl radicals in the gas phase and the charge transfer that occurs during the formation of the peroxyalkyl adduct, or the corresponding energy decrease due to the charge transfer, or the difference between the ionization energy of the alkene and the electron affinity of the peroxyl radical. This demonstrates a high degree of coherence among previously published works on gas-phase epoxidation by peroxyl radicals and provides a useful method for the estimation of epoxidation rate constants that have not yet been measured.

Acknowledgment. The author would like to thank Prof. B. T. Sutcliffe and especially Prof. D. J. Waddington for much helpful discussion and for reviewing the manuscript.

References and Notes

(1) Pilling, M. J.; Robertson, S. H.; Seakins, P. W. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 4179.

(2) Pennington, B. T. A process for the direct oxidation of propylene to propylene oxide, U.S. Patent, 5, 142, 070, 1992.

(3) Stark, M. S.; Waddington, D. J. *Int. J. Chem. Kinet.* **1995**, *27*, 123.

(4) Pennington, B. T.; Stark, M. S.; Waddington, D. J. *Combust. Sci Technol.* **1995**, *106*, 297.

(5) Hayashi, T.; Han, L.-B.; Tsubota, S.; Haruta, M. *Ind. Eng. Chem. Res.* **1995**, *34*, 2298.

(6) Ruiz Diaz, R.; Selby, K.; Waddington, D. J. *J. Chem. Soc., Perkin Trans. 2* **1977**, 360.

(7) Baldwin, R. R.; Stout, D. R.; Walker, R. W. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 3481.

(8) Ruiz Diaz, R.; Selby, K.; Waddington, D. J. *J. Chem. Soc., Perkin Trans. 2* **1975**, 758.

(9) Selby, K.; Waddington, D. J. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1715.

(10) Osborne, D. A.; Waddington, D. J. *J. Chem. Soc., Perkin Trans. 2* **1980**, 925.

(11) Selby, K.; Waddington, D. J. *J. Chem. Soc., Perkin Trans. 2* **1980**, 65.

(12) Gulati, S. K.; Mather, S.; Walker, R. W. *J. Chem. Soc., Faraday Trans. 2* **1987**, *83*, 2171.

(13) Stothard, N. D.; Walker, R. W. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 2115.

(14) Baldwin, R. R.; Stout, D. R.; Walker, R. W. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2147.

(15) Baldwin, R. R.; Hisham, M. W. M.; Walker, R. W. *Symp. (Int.) Combust. [Proc.]* **1985**, *20*, 743.

(16) Baldwin, R. R.; Dean, C. E.; Walker, R. W. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 1445.

(17) (a) Arsentiev, S. D.; Mantashyan, A. A. *React. Kinet. Catal. Lett.* **1980**, *13*, 125. (b) Mantashyan, A. A.; Khachatryan, L. A.; Niazyan, O. M.; Arsentyev, S. D. *Combust. Flame* **1981**, *43*, 221.

(18) Sway, M. I.; Waddington, D. J. *J. Chem. Soc., Perkin Trans. 2* **1982**, 999.

(19) Sway, M. I.; Waddington, D. J. *J. Chem. Soc., Perkin Trans. 2* **1983**, 139.

(20) Morgan, M. E.; Osborne, D. A.; Waddington, D. J. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1869.

(21) Wallington, T. J.; Dagaut, P.; Kurylo, M. J. *Chem. Rev. (Washington, D.C.)* **1992**, *92*, 667.

(22) McDowell, C. A.; Sharples, L. K. *Can. J. Chem.* **1958**, *36*, 251.

(23) Baulch, D. L.; Cobos, C. J.; Cox, R. A.; Esser C.; Frank, P.; Just, T.; Kerr, J. A.; Pilling, M. J.; Troe, J.; Walker, R. W.; Warnatz, J. *J. Phys. Chem. Ref. Data* **1992**, *21*, 411.

(24) Stocker, D. W.; Pilling, M. J. *Estimating the Kinetics and Thermodynamics for the Oxidation of Alkyl Radicals*, XIVth International Symposium on Gas Kinetics, Leeds University, 7−12th Sept, 1996.

(25) Avramenko, L. I.; Evlashkina, L. M.; Kolesnikova, R. V. *Izv. Akad. Nauk, Ser. Khim.* **1967,** 252.

(26) Lloyd, A. C. *Int. J. Chem. Kinet.* **1974**, *6*, 169.

(27) Hoare, D. E.; Patel, M. *Trans. Faraday Soc.* **1969**, *65*, 1325.

(28) Grigoryan, R. R.; Arsentiev, S. D.; Mantashyan, A. A. *React. Kinet. Catal. Lett.* **1982**, *21*, 347.

(29) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc*. **1983**, *105*, 7512.

(30) Pearson, R. G. *J. Org. Chem*. **1989**, *54*, 1423.

(31) Pearson, R. G. *Coord. Chem. Rev*. **1990**, *100*, 403.

(32) Aird, R. W. S.; Canosa-Mas, C. E.; Cook, D. J.; Marston, G.; Monks, P. S.; Wayne, R. P.; Ljungstrom, E. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 1093.

(33) Masclet, P.; Grosjean, D.; Mouvier, G.; Dubois J. *J. Electron Spectrosc. Relat. Phenom.* **1973**, *2*, 225.

(34) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc*. **1985**, *107*, 3902.

(35) Jordan, K. D.; Burrow, P. D. *Acc. Chem. Res*. **1978**, *11*, 341.

(36) Giordan, J. C. *J. Am. Chem. Soc*. **1983**, *105*, 6544.

(37) Jonsson, M. *J. Phys. Chem*. **1996**, *100*, 6814.

(38) (a) Slagle, I. R.; Feng, Q.; Gutman D. *J. Phys. Chem*. **1984**, *88*, 3648. (b) Wagner, A. F.; Slagle, I. R.; Sarzynski, D.; Gutman, D. *J. Phys. Chem*. **1990**, *94*, 1853.

(39) Kaiser, E. W. *J. Phys. Chem*. **1995**, *99*, 707.

(40) Kee, R. J.; Rupley, F. M.; Miller, J. A. *The Chemkin Thermodynamic Data Base*, Sandia National Laboratories, Report SAND87-8215B, 1994.

(41) Bozzelli, J. W.; Dean, A. M. *J. Phys. Chem*. **1990**, *94*, 3313.

(42) Wilk, R. D.; Cernansky, N. P.; Pitz, W. J.; Westbrook, C. K. *Combust. Flame* **1989**, *77*, 145.

(43) Dagaut, P.; Cathonnet, M.; Boettner, J. C. *Combust. Sci. Technol.* **1992**, *83*, 167.