contact shifts have been observed for neodymium(III) and praseodymium(III) complexes of some substituted pyridines.[26] However, there the Ln-N distance of closest approach is much shorter. A more detailed computer analysis, by continuous variation of parameters until best fit to the experimental results is obtained, is of course possible and has been performed for the $Pr(DPM)_3$–borneol system[27] and more recently for lanthanide complexes of some mononucleotides.[28]

Conclusions

The study of the effects of paramagnetic lanthanide shift reagents on the proton magnetic resonance spectra of quinoline and pyridine led to the following conclusions.

(a) The induced isotropic chemical shifts are to a great extent stereospecific and therefore of dipolar pseudocontact origin.

(b) The enhancement of the transverse relaxation rates is mainly a result of chemical shift differences between the complexed and free states of the substrate.

(c) The longitudinal relaxation rate is enhanced due to the electron–nuclear dipolar interaction in the complexed state.

(d) Enhancement of the longitudinal relaxation rate of a nucleus leads to chemical-exchange spin-decoupling in the resonance of other nuceli coupled to it, and as a result broadening and collapse of multiplet structures are observed.

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Radical Attack on Propylene as Studied by Electron Spin Resonance

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Abstract: The reactions of propylene with hydroxyl, phenyl, and *tert*-butoxyl radicals have been studied in liquid propylene or mixtures of propylene with ethyl ether. Hydroxyl radicals add to either side of the olefinic linkage, phenyl radicals add predominantly to the terminal carbon atom to give alkyl radicals, and *tert*-butoxyl radicals abstract hydrogen to form allyl radicals. The different behavior of these and other radicals reported in the literature toward propylene is discussed in terms of their electron affinities, and some consequences regarding the formation of aerosols in polluted air are presented.

Propylene, released into the air in auto exhaust, plays an important role in the formation of photochemical smog, and is typical of many of the reactive hydrocarbons present in polluted air.[1] While the initial products of the bimolecular reactions between oxygen atoms (produced by the photodissociation of NO_2 in sunlight) and olefins have been determined,[2] the reactions between hydroxyl and other free radicals present in polluted atmospheres are still far from being understood in complete detail. Three routes for the radical–propylene reactions appear possible: addition to either side of the olefinic linkage or abstraction of a hydrogen atom, leading to alkyl radicals in the first two cases or to allyl radicals in the third case. Recently,

$$\mathrm{R\cdot + CH_2{=}CH{-}CH_3 \longrightarrow R{-}CH_2{-}\dot{C}H{-}CH_3} \qquad (1)$$

$$\mathrm{R\cdot + CH_2{=}CH{-}CH_3 \longrightarrow \cdot CH_2{-}CH(R){-}CH_3} \qquad (2)$$

$$\mathrm{R\cdot + CH_2{=}CH{-}CH_3 \longrightarrow RH + CH_2{\overset{\cdots}{-}}\dot{C}H{\overset{\cdots}{-}}CH_2} \qquad (3)$$

it was reported that triethylsilyl radicals, methylthiyl radicals, and *tert*-butylthiyl radicals add to propylene according to reaction 1 in the liquid phase at low temperatures.[3] Under the same conditions, however, *tert*-butoxyl radicals abstract hydrogen from propylene according to reaction 3[4] while no reactions with alkyl radicals were observed.[3] Of particular importance for the formation of smog products are reactions with hydroxyl radicals, whose most likely sources in the atmosphere are hydrogen abstraction from hydrocarbons by oxygen atoms

$$\mathrm{O + RH \longrightarrow R\cdot + \cdot OH} \qquad (4)$$

photolysis of nitrous acid

$$\begin{gathered}\mathrm{NO + NO_2 + H_2O \longrightarrow 2HONO} \\ \mathrm{HONO \xrightarrow{h\nu} \cdot OH + NO\cdot}\end{gathered} \qquad (5)$$

and reactions between hydroperoxy radicals and nitrous oxide

$$\mathrm{HO_2\cdot + NO\cdot \longrightarrow \cdot OH + NO_2} \qquad (6)$$

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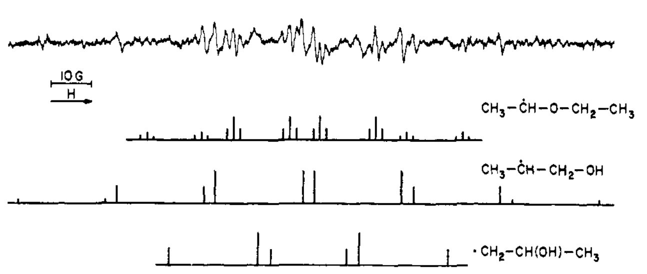

Figure 1. Esr spectra of radicals produced by photolysis of H_2O_2 in ethyl ether–propylene at −80°.

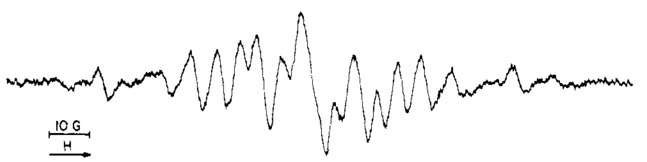

Figure 2. Esr spectra of radicals produced by photolysis of H_2O_2 in ethyl ether–propylene after 40 min of irradiation at −80°.

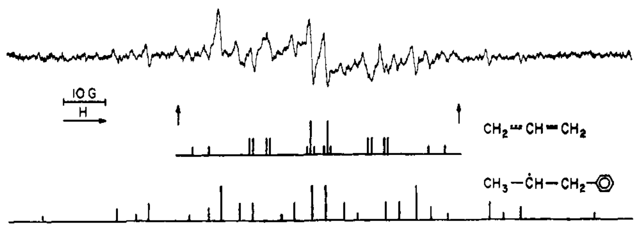

Figure 3. Esr spectra of radicals produced by photolysis of *tert*-butyl perbenzoate in propylene at −90°.

In a mass spectrometric study of OH–propylene reactions in a discharge flow system, Morris, *et al.*,[5] found mass peaks corresponding to OH adducts suggesting that addition might be the preferred route. They encountered difficulties in the product analysis, however, because of the transient nature of the products. Griffiths, *et al.*,[6] studied the reactions of amino and hydroxyl radicals with propylene in acidified aqueous solutions at room temperature by esr using a rapid flow–mix technique and reported the addition of these radicals to the olefin according to reaction 1.

In our study we have reexamined the reactions of hydroxyl radicals with propylene to determine whether addition occurs exclusively to the terminal carbon atom (eq 1). Furthermore, the reactions with *tert*-butoxyl, phenyl, and α-ethoxyethyl radicals were studied in degassed and oxygen-saturated solutions of pure propylene or mixtures of propylene and ethyl ether at low temperatures, and the short-lived intermediates were identified by esr.

Experimental Section

The esr experiments were carried out at temperatures between −60 and −90° with static samples which were irradiated with uv light in the cavity of an esr spectrometer. The light source and other details of the apparatus have been described previously.[7]

The primary radicals were produced by photolysis of *tert*-butyl peroxide (Matheson Coleman and Bell), *tert*-butyl perbenzoate (Ram Chemicals), and *tert*-butyl hydroperoxide (MCB) in liquid propylene, and 80% aqueous hydrogen peroxide (Food Machinery Corp., Becco Division) in a mixture of equal amounts of ethyl ether and propylene. The samples were free of oxygen, if not stated otherwise, and those containing ether and hydrogen peroxide were dried over sodium sulfate for at least 24 hr before use to remove water.

Products were identified by comparison of their glpc retention times with those of authentic samples.

Results

Irradiation of propylene without added peroxide gave no esr signals. Hydroxyl radicals were produced from hydrogen peroxide and *tert*-butyl hydroperoxide, *tert*-butoxyl radicals from *tert*-butyl peroxide, *tert*-butyl hydroperoxide, and *tert*-butyl perbenzoate, and phenyl radicals were generated from *tert*-butyl perbenzoate. As in earlier studies these initially formed radicals were not observed by esr.[8]

Hydrogen Peroxide. Since hydrogen peroxide is insufficiently soluble in liquid propylene, mixtures of approximately equal amounts of ethyl ether and propylene were used as solvent. Hydroxyl radicals produced by photolysis of hydrogen peroxide can attack both the ether and the propylene. Figure 1 shows the esr spectrum of a solution of 0.2 M H_2O_2 in ether–propylene at −80°. The center of the spectrum was recorded after 7 min of irradiation. Under continuous irradiation (40 min) the spectrum shown in Figure 1 was converted rapidly into the broad line spectrum of Figure 2. Some of the lines in Figure 1 can be assigned to radical **1** which is derived from ether by abstraction

$$CH_3\dot{C}HOCH_2CH_3$$

1

of an α-hydrogen atom by a hydroxyl radical. In the absence of propylene only **1** was observed. Its hyperfine splitting parameters, $a_H^{CH} = (13.75 \pm 0.1)$ G, $a_H^{CH_3} = (21.50 \pm 0.1)$ G, and $a_H^{CH_2} = (1.58 \pm 0.05)$ G agree well with those obtained in acetone[9] and water[10] at higher temperatures. The other lines in Figure 1 are presumably due to short-lived radicals derived from propylene. In contrast, the radicals of Figure 2 were relatively stable; their half-life at −80° was about 30 min. Ice crystals were visible in the system after prolonged irradiation.

***tert*-Butyl Peroxide.** *tert*-Butyl peroxide decomposes into two *tert*-butoxyl radicals which attack the solvent or fragment into acetone and methyl radicals.[11] In pure propylene at −80° we observed only allyl radicals (**2**) resulting from hydrogen abstraction by *tert*-

$$CH_2\!\cdots\!\dot{C}H\!\cdots\!CH_2$$

2

butoxyl radicals from propylene as reported previously by Kochi and Krusic.[4] No additional lines were observed in the spectra when the irradiation was continued for 1 hr. Comparison with Figure 1 showed that no allyl radicals were present in the spectra obtained by photolysis of hydrogen peroxide. When *tert*-butyl peroxide was photolyzed in a mixture of equal amounts of ether and propylene at −80° only radicals

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[5] E. D. Morris, Jr., D. H. Stedman, and H. Niki, *J. Amer. Chem. Soc.*, **93**, 3570 (1971).

[6] W. E. Griffiths, G. F. Longster, J. Myatt, and P. F. Todd, *J. Chem. Soc. B*, 530 (1967).

[7] E. J. Hamilton, Jr., D. E. Wood, and G. S. Hammond, *Rev. Sci. Instrum.*, **41**, 452 (1970).

[8] H. Hefter and H. Fischer, *Ber. Bunsenges. Phys. Chem.*, **74**, 493 (1970), and other references quoted therein.

[9] H. Zeldes and R. Livingston, *J. Chem. Phys.*, **45**, 1946 (1966).

[10] W. T. Dixon, R. O. C. Norman, and A. L. Buley, *J. Chem. Soc.*, 3625 (1964).

[11] Solutions of 1–3 M *tert*-butyl peroxide in benzene at 10° showed only methyl radicals during the first few minutes of irradiation.

1 were observed. This indicates that these radicals are too stable to attack propylene rapidly.

The additional lines in Figure 1, therefore, are expected to be due to radicals **3** and **4**, generated in reactions 1 and 2.

$$\underset{\mathbf{3}}{CH_3\dot{C}HCH_2OH} \qquad \underset{\mathbf{4}}{\cdot CH_2CH(OH)CH_3}$$

For comparison, radical **4** was produced by photolysis of hydrogen peroxide in a mixture of isopropyl alcohol and propylene at −80°, which yielded also acetone ketyl radicals derived from α-hydrogen abstraction from the alcohol. Its spectrum exhibited a doublet of triplets of relatively broad lines with 1.2-G line width and the coupling constants a_H^{CH} = (26.2 ± 0.1) G and $a_H^{CH_2}$ = (21.85 ± 0.1) G, which differ slightly from those obtained earlier by Livingston and Zeldes[12] in a mixture of water and isopropyl alcohol at −5° (a_H^{CH} = 24.38 G, $a_H^{CH_2}$ = 22.06 G). The broad lines in Figure 1 can be assigned to radical **4** and the remaining sharp lines to radical **3** with the coupling constants a_H^{CH} = (21.8 ± 0.1) G and $a_H^{CH_3} = a_H^{CH_2}$ = (24.7 ± 0.1) G as indicated by the computed spectra. The equivalence of the methyl and methylene protons in radical **3** indicates that rotation of the methylene group around the C_α–C_β bond axis is not hindered by the hydroxyl group. Little or no hindrance was also found in earlier studies on a series of radicals of the type $X\dot{C}HCH_2OH$ (X = CO_2H, CO_2CH_3, $CO_2C_2H_5$, and CN).[13] However, in water the coupling constant of the methylene protons was found to be only 19.8 G[6] indicating that in this solvent rotation might be hindered by interaction with the polar water molecules.

tert-**Butyl Hydroperoxide.** Since it was found that *tert*-butoxyl radicals exclusively abstract hydrogen from propylene while hydroxyl radicals add to the double bond it was expected that the photolysis of *tert*-butyl hydroperoxide in propylene would result in the superposition of the spectra of allyl radicals and radicals **3** and **4**. However, photolysis of 0.2 *M* *tert*-butyl hydroperoxide in propylene produced only the *tert*-butylperoxy radical, probably formed by hydrogen abstraction from *tert*-butyl hydroperoxide by the initially generated hydroxyl and *tert*-butoxyl radicals[14] (eq 7–9).

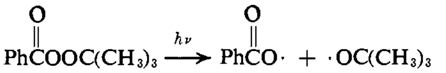
$$(CH_3)_3COOH \xrightarrow{h\nu} (CH_3)_3CO\cdot + \cdot OH \qquad (7)$$

$$(CH_3)_3COOH + \cdot OH \longrightarrow H_2O + (CH_3)_3COO\cdot \qquad (8)$$

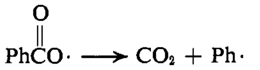
$$(CH_3)_3COOH + \cdot OC(CH_3)_3 \longrightarrow (CH_3)_3COH + (CH_3)_3COO\cdot \qquad (9)$$

After prolonged irradiation at −65° the peroxy radicals gradually disappeared with decreasing peroxide concentration and a broad line spectrum, as in Figure 2, emerged.

tert-**Butyl Perbenzoate.** *tert*-Butyl perbenzoate is photolyzed to give *tert*-butoxyl and benzoyloxy radicals.[8] In our samples with 0.2–0.5 *M* *tert*-butyl perbenzoate in propylene, a strong evolution of gas indicated that the benzoyloxy radicals probably decarboxylated into CO_2 and phenyl radicals which were not observed because of their short lifetime.[8] Figure 3 shows the spectrum obtained at −90°.



$$Ph\overset{O}{\overset{\|}{C}}OOC(CH_3)_3 \xrightarrow{h\nu} Ph\overset{O}{\overset{\|}{C}}O\cdot + \cdot OC(CH_3)_3 \qquad (10)$$



$$Ph\overset{O}{\overset{\|}{C}}O\cdot \longrightarrow CO_2 + Ph\cdot \qquad (11)$$

It is assigned to allyl radicals (**2**) and radical **5** whose coupling constants

$$\underset{\mathbf{5}}{CH_3\dot{C}HCH_2Ph}$$

are a_H^{CH} = (22.0 ± 0.1) G, $a_H^{CH_3}$ = (25.4 ± 0.1) G, and $a_H^{CH_2}$ = (17.8 ± 0.1) G. Two additional broad lines, indicated by arrows, are tentatively assigned to radicals **6**. The lines of the allyl radical in Figure 3 are

$$\underset{\mathbf{6}}{\cdot CH_2CH(Ph)CH_3}$$

strongly distorted because of the high modulation which was required to obtain a reasonable signal-to-noise ratio for radical **5**. They appeared more clearly when the modulation amplitude was below 100 mG. From the relative line intensities it is estimated that allyl radicals and radicals **5** are present in approximately equal concentrations.

The coupling constants of radical **5** for the α proton and the methyl protons agree well with those of radical **3**. The methylene protons of radical **5**, however, have coupling constants of only 17.8 G compared to 24.7 G in radical **3**. This shows that in radical **5** rotation of the methylene group around the C_α–C_β bond axis is hindered by the bulky phenyl group.

The structure of the spectra did not change under continuous irradiation for 1 hr.

Products. In order to confirm the results obtained by the esr experiments and to reveal the nature of the species causing the broad line spectrum of Figure 2, a qualitative product analysis of irradiated samples of hydrogen peroxide in ether–propylene was carried out by glpc. In addition to water and a large number of mostly unidentified products already obtained in samples of hydrogen peroxide in ether alone, the major products were *n*-propyl, isopropyl, and allyl alcohols, and acetone. These four products are expected from bimolecular reactions among the radicals **1**, **3**, and **4**. 1,5-Hexadiene, which is expected to be formed by dimerization of allyl radicals, could not be detected, probably indicating that no allyl radicals were present in this system. No polymeric products were found.

Because no polymerization was observed at the low temperatures employed, the broad line spectrum of Figure 2 was interpreted as predominantly due to radicals **3** and **4** trapped in ice crystals. This is in agreement with the high stability of the radicals, their large line widths, and the fact that the broad line spectra developed faster when the solutions of hydrogen peroxide in ether–propylene were not dried before use but initially contained small amounts of water. The water in the originally dry solutions is due to hydrogen abstraction by OH radicals from ether in the case of ether–propylene solutions or from *tert*-butyl hydroperoxide in the case of solutions of *tert*-BuOOH in propylene.

A product analysis of an irradiated sample of *tert*-butyl perbenzoate in propylene showed *tert*-butyl alcohol, 1,5-hexadiene, *n*-propylbenzene, allylbenzene,

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[12] R. Livingston and H. Zeldes, *J. Amer. Chem. Soc.*, **88**, 4333 (1966).

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benzene, and small amounts of cumene among the products. *tert*-Butyl alcohol is the expected product of hydrogen abstraction from propylene by *tert*-butyoxyl radicals, while 1,5-hexadiene, *n*-propylbenzene, allylbenzene, and cumene are formed in bimolecular reactions of the radicals **2**, **5**, and **6**. The formation of benzene indicates that phenyl radicals might also abstract hydrogen from propylene; however, benzene could also be formed as a secondary product by hydrogen abstraction from the *tert*-butyl alcohol already present.

Oxygen-Saturated Samples. Samples saturated with oxygen are expected to give the esr spectra of peroxy radicals resulting from the reaction

$$R\cdot + O_2 \longrightarrow ROO\cdot \qquad (12)$$

where $R\cdot$ = **1**–**6**. The g values of alkyl peroxy radicals are known to fall in the range from 2.014 to 2.019.[14–16]

Solutions of hydrogen peroxide in ether–propylene exhibited one line with 8-G line width and g = 2.0152 ± 0.0003. The line appeared to be split into a doublet with a spacing of 3.7 G which could be due to interaction with an α proton. The signal should be due to the peroxy radicals formed by addition of oxygen to **1**, **3**, and **4**. The peroxy radical from **1**, which was produced in oxygen-saturated solutions of hydrogen peroxide or *tert*-butyl peroxide in ether, gave a line width of only 3.5 G and a g value of 2.0151 ± 0.0003. In these systems radical **1** was also observed.

In solutions of *tert*-butyl perbenzoate in propylene, two broad esr lines were found. One, with a line width of 3.5 G and g = 2.0159 ± 0.0005, is clearly due to alkylperoxy radicals, probably the peroxy derivatives of the radicals **5** and **6**. The other line had a line width of 10 G and a g value of 2.0038 ± 0.0003. In solutions of *tert*-butyl peroxide in propylene only one broad line with a line width of 10 G and a g value of 2.0037 ± 0.0003 was found which should be due to the same species.[17]

Weiner and Hammond[18] observed the broad line of a short-lived radical with similar line width and g value in pure *tert*-butyl peroxide and attributed the signal to *tert*-butoxyl radicals. However, Symons[19] suggested that this signal might be due to the "ozonide" radical **7** whose g value is expected to be close to 2.004.

$$(CH_3)_3COOO\cdot$$

7

Since in our experiments the signal was found only in oxygen-saturated solutions, we believe that it is due to the "ozonide" radical **7**. The signal was not found in oxygen-saturated solutions of *tert*-butyl peroxide in ether, which shows that *tert*-butoxyl radicals react more rapidly with ether to form radicals **1** and *tert*-butyl alcohol than with oxygen to form radical **7**. Thus, it seems that no allyl radicals are formed during photolysis of *tert*-butyl peroxide in propylene in the presence of oxygen, and it is not known whether allyl radicals react with oxygen to form alkenylperoxy radicals.

Discussion

Our experiments have shown that hydroxyl radicals not only add to the terminal carbon atom of the double bond of propylene (eq 1) but also to the central carbon atom (eq 2). Phenyl radicals react preferably by addition rather than abstraction with propylene, while *tert*-butoxyl radicals exclusively abstract hydrogen from its methyl group. The behavior of the three radicals in reaction with propylene is interesting and somewhat surprising. We learn that even a very simple molecule can react predominantly in one way with one radical and show entirely different preference with another. Almost surely there can be no single reactivity variable which will account for the fact that both phenyl and hydroxyl radicals add whereas the *tert*-butoxyl radical abstracts hydrogen from propylene. As a broad generalization, there seems to be an increasing preference for hydrogen abstraction in preference to addition to a carbon–carbon double bond as the electron affinity of the attacking radical is increased. Thus, on the average, π-electronic carbon radicals, whose electron affinities in the gas phase are around 1 eV or less,[20,21] have a tendency to add, as in vinyl polymerization. Amino and methylthiyl radicals, whose electron affinities are reported to be 1.1 and 1.3 eV, respectively,[22] also add to propylene[3,6] and so does the triethylsilyl radical,[3] which is expected to have an even lower electron affinity. Chlorine atoms, however, usually abstract hydrogen as in photochlorination in accordance with their high electron affinity of 3.62 eV.[23–26] Between these two extremes we find hydroxyl, alkoxy, and probably phenyl radicals. The electron affinity of the hydroxyl radical was determined by several different methods to be between 1.8 and 1.9 eV.[20,27–30] In an electron impact study in a mass spectrometer the electron affinities of alkoxy radicals were recently found to fall in the range 1.7–1.9 eV,[29] although an earlier study using the magnetron method resulted in values between only 0.4 and 0.7 eV.[22,31] Finally, the electron affinity of the phenyl radical was determined by Gaines and Page with the magnetron method to be 2.2 eV.[32] This method uses the formation of negative ions by the surface ionization of gases on hot metallic filaments; in this study benzene, benzil, and diphenylmercury were used to produce phenyl ions. However, in a mass spectrometric study under similar conditions the dissociative ionization of benzene was not found to result in the formation of phenyl ions but the fragments C_2H^-, C_2^-, and CN^-,[33] the electron

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(15) M. Bersohn and J. R. Thomas, *J. Amer. Chem. Soc.*, **86**, 959 (1964).

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(31) C. J. Baldwin, Diploma Technical Thesis, College of Advanced Technology, Birmingham, 1964.

(32) A. F. Gaines and F. M. Page, *Trans. Faraday Soc.*, **59**, 1266 (1963).

affinities of the corresponding radicals being 2.1, 3.3,[34] and 3.2 eV,[35] respectively. Thus the high value reported for the phenyl radical might be somewhat uncertain.

Our results indicate that hydroxyl and alkoxy radicals as a class may be fairly delicately balanced in a borderline region of relative reactivity. If so, there are any number of reasons (steric hindrance, differences in polarizability, etc.) which could be cited as sources of the interesting difference between the reactivity of hydroxyl and *tert*-butoxyl radicals. Based on this discussion we would expect acyloxy radicals to abstract hydrogen from propylene rather than add to the double bond.[36]

The allyl **2** and alkyl radicals **1** and **3–6** do not add to the double bond of the olefin at the low temperatures employed; thus, no polymerization was observed. The alkyl radicals react rapidly with oxygen to form relatively stable alkylperoxy radicals, whereas the fate of the allyl radicals in the presence of oxygen remains unknown. Although in our experiments allyl radicals were probably not formed in the presence of oxygen, this should be the case at high temperatures where the highly unstable "ozonide" radical **7** is expected to be in equilibrium with the alkoxy radical. Similar behavior should hold for other alkoxy radicals.

$$(CH_3)_3CO\cdot + O_2 \rightleftharpoons (CH_3)_3COOO\cdot \qquad (13)$$

Finally, it was shown in this study that the bimolecular termination reactions of the radicals formed with propylene lead partially to unsaturated compounds such as allyl alcohol, allylbenzene, and 1,5-hexadiene.

Although this work was carried out at low temperatures and, consequently, was a study only of reactions with very low activation energies, some interesting possibilities for the formation of photochemical smog are presented. We have seen that there are two distinct types of radical species, those which add to the double bond leading to an alkylperoxy radical in air, and those which abstract a hydrogen atom leading to the formation of an allyl or an alkenylperoxy radical in air. The latter two species are particularly significant because they (as the alkenyloxy counterpart) can enter into reactions with other olefins, aromatics, or free radicals in polluted air resulting in larger products but still retaining a reactive double bond. It has been found that monoolefins of six carbon chains or more lead to organic aerosol formation in smog chambers.[38] In polluted air, however, in which hundreds of free-radical species are present, the chance of abstraction *vs.* addition to olefins increases substantially, and with it the possibility that unsaturated free radicals are formed which can serve as the nuclei for organic aerosol formation in polluted air.

A rather important, and disconcerting, conclusion of the work reported here relates to atmospheric chemical modeling studies. Reduction in the number of steps included in a mechanism is required to produce manageable computer programs. The task would be greatly simplified if one could assume that all radicals react predominantly in a single way with a molecule as simple as propylene. However, our study shows that such a simplification is not possible.[39]

Acknowledgment. We are very grateful to Mr. M. Wrighton who carried out the glpc product analyses and to Professor J. Seinfeld and Dr. D. MacGregor for helpful discussion. This work was supported by grants from the John A. McCarthy Foundation and the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Grant No. AFOSR-7-1958.

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