donating substituents[9] but is significantly smaller than those observed for hydrolysis of ordinary benzaldehyde acetals,[9] the acid-catalyzed hydrolysis of purine nucleosides,[16] and the pH-independent decomposition of nicotinamide nucleosides.[17] On the basis of large isotope effects for the reverse reactions, the transition states for loss of cyanide from benzaldehyde cyanohydrins[18] and hydroxide ion and water from carbinolamines[19] also appear to occur quite early along the reaction coordinate. At any event, the isotope effect for the acid-catalyzed hydrolysis of the *O,S*-acetal is much less than the limiting value and clearly indicates only partial cleavage of the C–S bond in the transition state.

The situation is notably different for the pH-independent hydrolysis of the same substrate. In this case, the isotope effect is relatively large and requires either substantial or *complete* cleavage of the C–S bond in the transition state. The observed isotope effect is entirely consistent with the suggestion of Jensen and Jencks that the rate-determining step for this reaction is diffusion apart of the ion pair formed by unimolecular substrate decomposition with C–S bond cleavage.[4]

References and Notes

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(2) On leave from the Universidade de São Paulo, Ribeirão Preto, São Paulo, Brazil. Supported by a Fellowship from the Fundacão de Amparo a Pesquisas de Estado de São Paulo.
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Aliphatic Semidiones. 38. Conversion of Polymeric Peroxides and Hydroperoxides to 1,2- and 1,4-Semidiones in Basic Solution[1]

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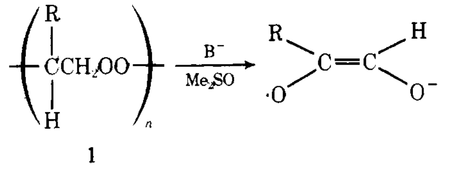
Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50011. *Received September 27, 1978*

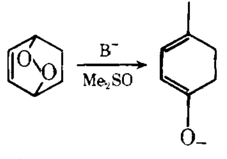
Abstract: Polymeric peroxides of substituted olefins or of cyclic 1,3-dienes are converted by potassium *tert*-butoxide in Me_2SO to 1,2-semidiones ($RC(O^-){=}C(O\cdot)H$) and 1,4-semidiones ($RC(O\cdot){=}CHCH{=}C(O^-)R$), respectively. The methylsulfinylmethide ion will convert $RC({=}O)C({=}O)X$, where $X = H$ or CO_2^-, to the methylated semidione $RC(O\cdot){=}C(O^-)CH_3$. However, in a flow system semidiones with the structure $RC(O\cdot){=}C(O^-)X$, where $X = H$, OR, or CO_2^-, can be observed before the methylation occurs. Secondary hydroperoxides containing an α-methylene group are converted in basic Me_2SO to 1,2-semidiones.

Treatment of polymeric peroxides prepared from a polymerizable olefin or a cyclic 1,3-diene with potassium *tert*-butoxide in Me_2SO leads to the formation of the 1,2- and 1,4-semidiones, respectively (eq 1 and 2). The process involves the known decomposition of a peroxide with α-hydrogen atoms by base (Scheme I)[2,3] followed by the recognized comproportionation reactions of α-hydroxy ketones (Scheme Ib).[4]



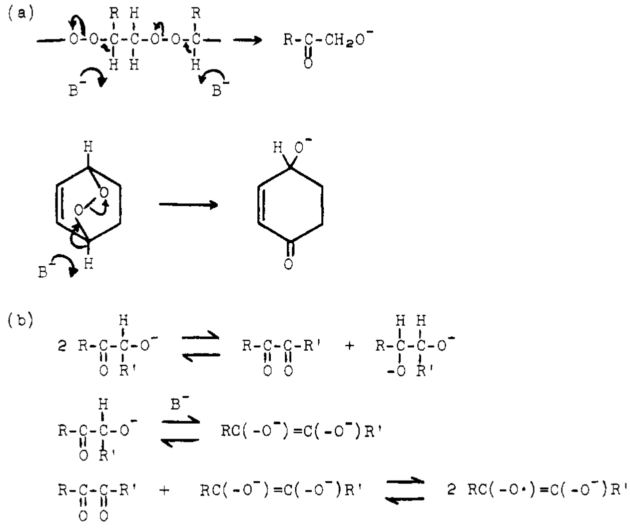
(1)

1



(2)

Scheme I



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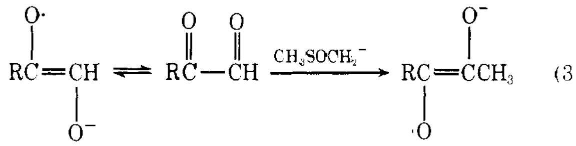
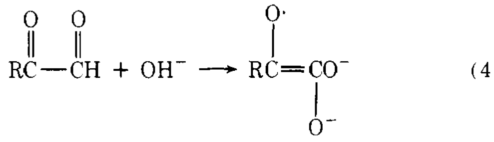
When R′ is H in Scheme Ib some additional reactions occur. The methylsulfinylmethide ion can alkylate the semidione or its precursor to form the semidione with R′ = CH_3 (eq 3).[5,6]

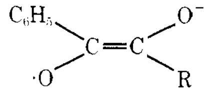


$$\mathrm{RC(O\cdot)=CH(O^-)} \rightleftharpoons \mathrm{RC(=O)-CH(=O)} \xrightarrow{CH_3SOCH_2^-} \mathrm{RC(\cdot O)=C(O^-)CH_3} \quad (3)$$



$$\mathrm{RC(=O)-CH(=O)} + \mathrm{OH^-} \longrightarrow \mathrm{RC(O\cdot)=CO^-(O^-)} \quad (4)$$

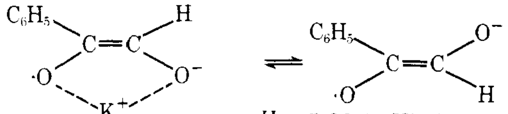
In some cases the aldehyde group has been observed to undergo the Cannizzaro reaction to give the semidione of an α-keto acid which has a low persistency (eq 4).[6] Thus, treatment of polymeric styrene peroxide (**1**, R = C_6H_5) with potassium *tert*-butoxide in Me_2SO or Me_2SO-d_6 in a static system gave a clean ESR signal of the previously reported **2**.[2]



2a, R = CH_3; a^H = 3.36 (3 H), 1.80 (2 H), 1.56 (2 H), 0.52 (2 H) G

2b, R = CD_3; a^H = 1.80 (1 H), 1.50 (2 H), 0.50 (2 H), a^D = 0.50 (3 D) G

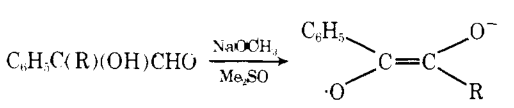
When polymeric styrene peroxide (0.07 equiv/L) in Me_2SO was mixed with an equal volume of potassium *tert*-butoxide in Me_2SO (0.14 M) and the ESR signal recorded 0.25 s after mixing, only the *cis*-phenylglyoxal radical anion **3** was detected (a^H = 6.70 (1 H), 1.70 (1 H), 1.50 (2 H), 0.50 (2 H) G). Semidione **3** exists as the cis ion pair in the presence of excess K^+, but as the trans ion in the presence of Cs^+ or K^+ plus 2.2.2 cryptand.[5,7] Similarly, polymeric indene peroxide[3] with basic Me_2SO gave indan-1,2-semidione,[8] a^H_{arom} = 2.90, 2.80, 0.75, 0.58, $a^H_{CH_2}$ = 0.58 G.



3

a^H = 5.99 (1 H), 1.52 (1 H), 1.34 (2 H), 0.45 (2 H)

Polymeric peroxides from 1-phenyl-1-alkyl olefins were not investigated. However, the formation of rearranged 1,2-semidiones by treatment with sodium methoxide in Me_2SO can be predicted with confidence, since we have previously demonstrated the rearrangement process of eq 5.[5]

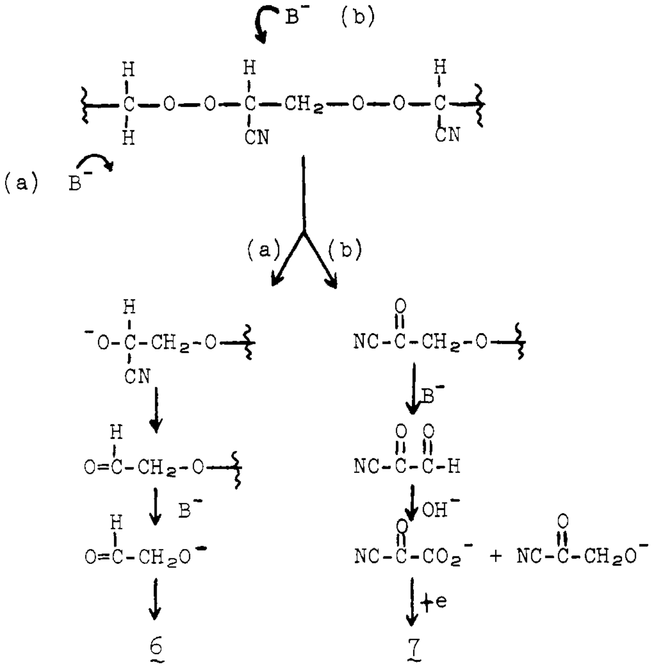


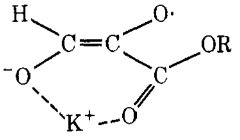
$$\mathrm{C_6H_5C(R)(OH)CHO} \xrightarrow[Me_2SO]{NaOCH_3} \mathrm{C_6H_5(\cdot O)C=C(O^-)R} \quad (5)$$

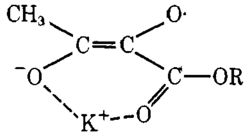
R = CH_3, C_2H_5

The polymeric peroxides from acrylate esters, acrylonitrile, and methyl vinyl ketone were examined because the expected semidiones are not readily available from other routes. In a flow system, semidiones **4** were produced from the corresponding polymeric peroxides of the acrylate esters. Only a single isomer was detected and the chelate structure shown seems reasonable. The hfsc assigned to **4** are realistic in view of the previously described **5**.[9,10]

Scheme II



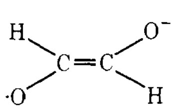




4a, R = CH_3; a^H = 4.63 (1 H), 0.56 (3 H) G
b, R = C_2H_5; a^H = 4.67 (1 H), 0.54 (2 H) G

5a, R = CH_3; a^H = 3.2 (3 H), 0.5 (3 H) G
b, R = C_2H_5; a^H = 3.2 (3 H), 0.5 (2 H) G

Polymeric acrylonitrile peroxide gave *trans*-glyoxal radical anion (**6**)[11] when treated with potassium *tert*-butoxide in a static system, a^H = 7.72 (2 H) G. In a flow system (1-30 s between mixing and detection) the glyoxal radical anion (g = 2.00515) and another major species with a^N = 1.62 (1 N) G, g = 2.002 00, were detected. The experiments gave the strongest glyoxal radical anion signals that we have ever observed.[11] The semidione of low persistency is undoubtedly **7**.



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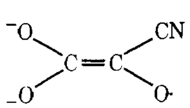
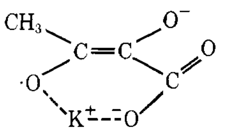


7

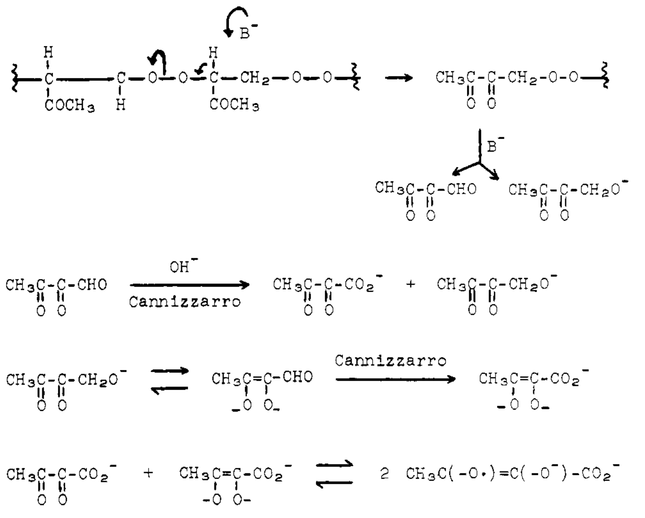
The formation of semidiones **6** and **7** can be reasonably formulated as shown in Scheme II, where process a is the predominant mode of decomposition.

The polymeric peroxide of methyl vinyl ketone (0.07 M) in a static system with 0.4 M potassium *tert*-butoxide in Me_2SO gave biacetyl radical anion. At lower base concentrations (0.15 M) another ESR signal was observed, a^H = 5.37 (3 H), a^K = 0.45 G (Figure 1). This species is the only semidione we have ever observed which has a potassium hfs and one of the few examples of potassium hfs ever observed in Me_2SO. Extremely strong ion pairing with a low rate of gegenion exchange must be involved. The structure **8** is suggested. The ion pairing is



8

Scheme III

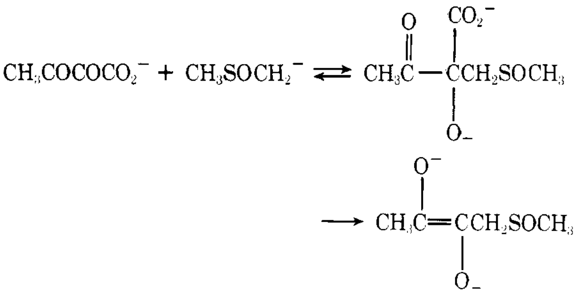


accentuated by the two negative charges and by the possibility of forming a six-membered chelate ring (resolved hfs by K^+ has not been observed for $CH_3C(O\cdot)=CO_2^{2-}$, a^H = 5.7-6.6 G).[6] In a flow system (0.05 equiv of peroxide, 0.1 M potassium *tert*-butoxide) only **8** was observed 30 s after mixing. At faster flows the spectrum of **8** was quite weak and another radical was present whose spectrum was not well resolved.

The formation of **8** can be rationalized as shown in Scheme III. The formation of biacetyl semidione at high base concentrations must involve a methylation reaction by the methylsulfinyl carbanion. This has been previously observed for phenyl-[4] or methylglyoxal[11] giving the overall reaction 6.

$$RC(=O)C(=O)H + CH_3SOCH_2^- \rightarrow [RCOCH(O^-)CH_2SOCH_3] \rightarrow\rightarrow CH_3COCOCH_3 + CH_3SO^- \quad (6)$$

Methyl lactate[9] or lactide when treated with potassium *tert*-butoxide in Me_2SO also forms the cis-trans mixture of biacetyl radical anions which can be easily rationalized as in Scheme IV. Analogously, the diketocarboxylate postulated in Scheme III can undergo addition of the methylsulfinylmethide ion followed by decarboxylation to give the dianions postulated in Scheme IV (reaction 7).



$$CH_3COCOCO_2^- + CH_3SOCH_2^- \rightleftarrows CH_3\overset{O}{\overset{\|}{C}}-\underset{O^-}{\overset{CO_2^-}{C}}CH_2SOCH_3 \rightarrow CH_3\overset{O^-}{C}=\underset{O^-}{C}CH_2SOCH_3 \quad (7)$$

Semidiones Derived from Polymeric Peroxides of 1,3-Dienes

1,3-Cyclohexadiene, 1,3-cycloheptadiene, bicyclo[4.2.2]deca-2,4,7,9-tetraene,[12] and bicyclo[4.1.0]nona-2,4,7-trien-9-one[13] were converted to polymeric peroxides by AIBN-catalyzed oxygenation at 50 °C in chlorobenzene. Removal of the solvent and unreacted starting material by vacuum (0.1 Torr, 50 °C) gave products containing 90-95% of the oxygen expected for a 1:1 copolymer. Treatment of the copolymers with potassium *tert*-butoxide in Me_2SO gave strong ESR signals for **9-11** in a static system and for **12** in a flow system wherein the ESR signal was detected 10 s after mixing. Semidione **12** was extremely sensitive to UV photolysis (in silica). The semidione disappeared rapidly without indication of the formation of 1,4-cyclooctatetraene semidione or its bicyclic valence isomer.[16]

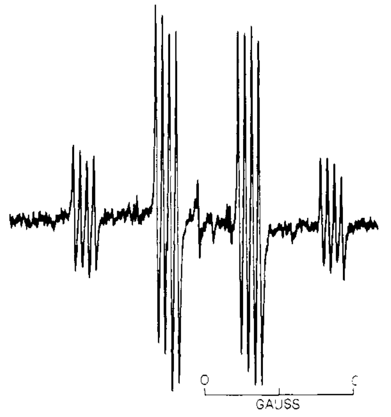
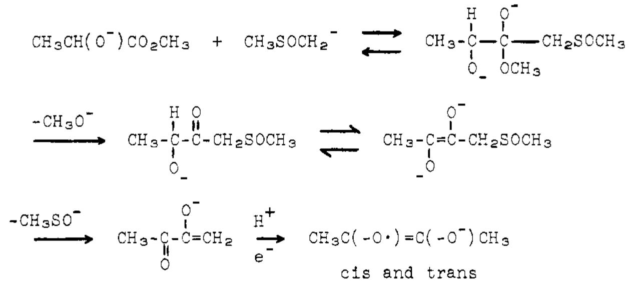
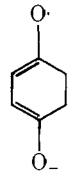


Figure 1. ESR spectra of **8** showing hfs by K^+ ($I = 3/2$).

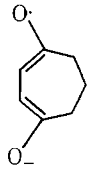
Scheme IV





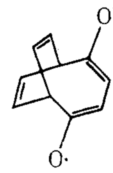
9[14]

a^H = 5.76 (2 H), 2.36 (4 H)



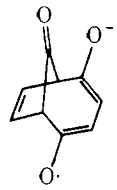
10[15]

a^H = 5.00 (2 H), 2.55 (4 H)



11

a^H = 4.60 (2 H), 0.25 (4 H), 0.12 (2 H)

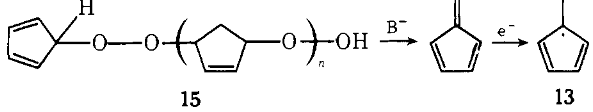


12

a^H = 5.03 (2 H), 0.69 (2 H), 0.20 (2 H)

The assignment of hfs in **11** is straightforward ($a_{3,4}^H$ = 4.60, $a_{1,6}^H$ = 0.12, a_{7-10}^H = 0.25 G). The most logical assignment in **12** is $a_{3,4}^H$ = 5.03, $a_{1,6}^H$ = 0.69, $a_{7,8}^H$ = 0.20. In **11** the bridgehead hydrogen atoms are near the nodal plane of the π-spin system, whereas in **12** the bridgehead atoms are removed from the nodal surface.[17]

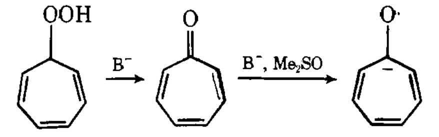
The conversion of a conjugated diene into a polymeric peroxide followed by treatment with base to form the 1,4-semidione represents a potential structure proof for the diene. In the case of bicyclo[4.2.2]deca-2,4,7,9-tetraene the experiment was performed using only 0.2 g of the tetraene. When this technique was applied to cyclopentadiene or cycloheptatriene, the only ESR signals that could be detected (flow) were from cyclopentadienone ketyl **13** (a^H = 5.25 (2 H), 2.95 (2 H))[18] and tropone ketyl **14** (a^H = 8.66 (2 H), 5.00 (2 H), 0.12 (2 H)).[19] It is known that cyclopentadiene-1,4-semidione without alkyl groups at the 5 position has little or no stability[15] and that γ-tropolone cannot be reduced to give a cycloheptatriene-1,4-semidione.[19] The ketyls observed apparently come from the cycloalkenylperoxy end groups of the polymeric peroxide, e.g., **15**.



15 **13**

Formation of Ketyls or 1,2-Semidiones from Secondary Hydroperoxides

Photosensitized oxygenations of cycloheptatriene at 0 °C with hematoporphyrin give the hydroperoxide as one of the major products (tropone can be isolated upon treatment of the oxidate with triethylamine). Treatment of the oxidate with potassium *tert*-butoxide in Me_2SO in a flow system or statically gives an excellent spectrum of tropone ketyl, **14**, via reduction of tropone.[20]

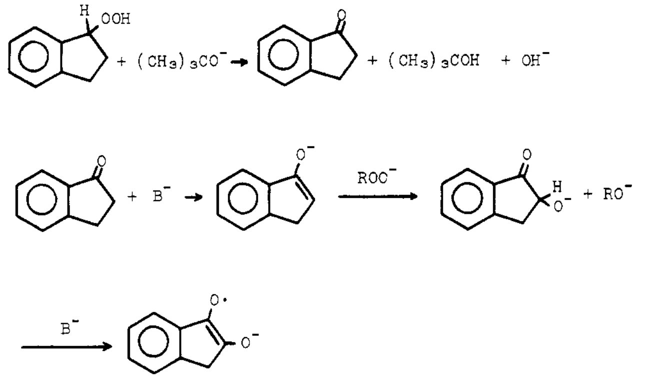


14

(8)

Secondary hydroperoxides having an α-methylene group can be converted in basic Me_2SO to 1,2-semidiones. Thus, 1-indanyl hydroperoxide gave the ESR signal of indan-1,2-semidione. Apparently the initially formed 1-indanone is converted to the enolate anion, which is oxidized by the hydroperoxide to give the α-hydroxy ketone, Scheme V. Hydroperoxides are readily reduced by Me_2SO in basic solution (eq 9),[21] but the reactions of Scheme V are sufficiently rapid to compete with this process.

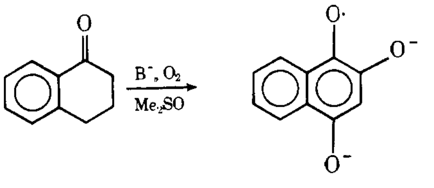
Scheme V



$$ROO^- + Me_2SO \rightarrow RO^- + Me_2SO_2 \quad (9)$$

1-Indanone and *tert*-butyl hydroperoxide reacted in basic Me_2SO to produce indan-1,2-semidione. This technique allows a ketone to be converted in situ to the semidione without use of molecular oxygen.

Treatment of α-tetralone with air in basic Me_2SO leads to the formation of naphthalene-1,2,4-semiquinone (**16**).[22]



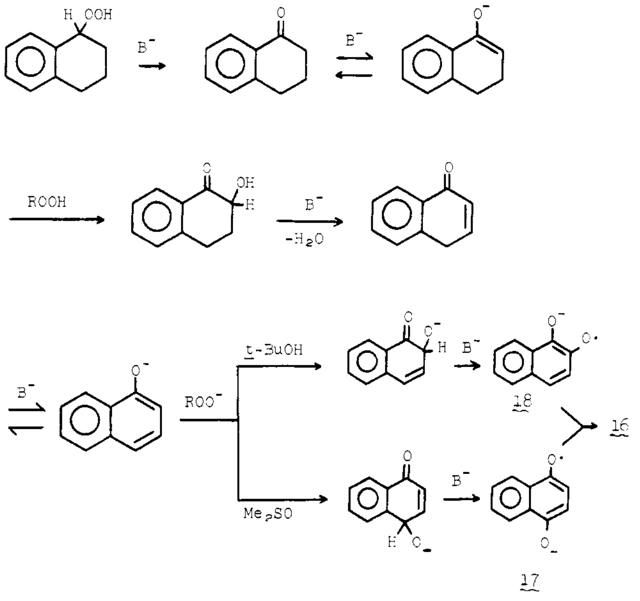
(10)

16

$a^H = 2.5, 1.5, 0.5, 0.1$ G

In a static system, 1-tetralyl hydroperoxide or α-tetralone plus *tert*-butyl hydroperoxide reacted with potassium *tert*-butoxide to form **16.** In a flow system with potassium *tert*-butoxide, 1-tetralyl hydroperoxide yielded the radical anion of naphthalene-1,4-semiquinone (**17**)[23] in Me_2SO, or the radical anion of naphthalene-1,2-semiquinone (**18**)[22] in *tert*-butyl alcohol when the time between mixing and detection was shorter than 30 s. The formation of naphthalene-1,2-semiquinone was also observed in flow experiments involving α-tetralone and *tert*-butyl hydroperoxide in *tert*-butyl alcohol. Scheme VI presents a rationalization of the observed results. Apparently hydrogen bonding between the peroxy anion, the enolate anion, and *tert*-butyl alcohol leads to hydroxylation at the C-2 in *tert*-butyl alcohol solution, whereas the peroxy anion in Me_2SO prefers to attack at C-4.

Scheme VI



Experimental Section

ESR spectra were recorded with a Varian Associates E-3 spectrometer. ESR spectral simulation was carried out with a Japan Electron Optic Laboratory Co. JNM-RA-1 spectrum accumulator. Flow experiments used a Varian Associates V-4549A flow cell (0.09 mL between the point of mixing and detection) and 50-mL polyethylene syringes driven by a Harvard Apparatus Co. compact infusion pump. The syringes were loaded in a nitrogen drybox and the solutions were deaerated by prepurified nitrogen for 30 min before the syringes were sealed. The syringes were connected to the flow cell by polyethylene tubing. Static experiments used an inverted H-cell[24] wherein the reagents could be deaerated by prepurified nitrogen before mixing. The mixing chamber was attached to a fused silica aqueous sample cell similar to Varian Associates V-4548.

The Me_2SO was distilled from calcium hydride under reduced pressure and stored over molecular sieves. Potassium *tert*-butoxide (Alfa Inorganic) was sublimed before use.

Styrene, indene, methyl acrylate, ethyl acrylate, acrylonitrile, methyl vinyl ketone, indan, tetralin, 1,3-cyclohexadiene, 1,3-cycloheptadiene, and cycloheptatriene from Aldrich Chemical Co. were distilled and stored under nitrogen.

Bicyclo[4.2.1]nona-2,4,7-trien-9-one was prepared according to the literature procedure[13] from cyclooctatetraene in 39% yield: bp 101-101.5 °C (15 Torr); ^1H NMR ($CDCl_3$) δ 2.9-3.1 (m, 2), 5.8-5.9 (m, 6); IR (neat) 3040, 2960, 1770, 1155, 870 cm^{-1}.

Bicyclo[4.2.2]deca-2,4,7,9-tetraene was prepared from bicyclo[4.2.1]-nona-2,4,7-trien-9-one by reaction with diazomethane to give bicyclo[4.2.2]deca-2,4,7-trien-9-one,[13] which was converted to the tosylhydrazone in 18% yield and to bicyclo[4.2.2]deca-2,4,7,9-tetraene in 16% yield by treatment of the tosylhydrazone with methyllithium:[14] ^1H NMR (CCl_4) δ 2.9-3.3 (m, 2 H), 5.3-5.6 (m, 4), 5.6-6.3 (m, 4); IR (neat) 3030, 3010, 2910, 1405, 985, 955, 850, 820, 755, 740 cm^{-1}.

Synthesis of Polymeric Peroxides. Olefins or dienes were stirred in an oxygen atmosphere at 50 °C in the presence of 0.3 mol % of 2,2′-azobis(2-methylpropionitrile) and the oxygen consumption was monitored. The peroxidic products soluble in benzene were isolated either by precipitation with methanol (styrene polyperoxide) or by vacuum distillation of the solvent. The percent peroxidic oxygen present was calculated from C and H analyses. The following polyperoxides were used in this work (olefin, weight, reaction time, reaction temperature if other than 50 °C, percent peroxidic oxygen, weight of polyperoxide): styrene, 5 g, 24 h, 20.5%, 1.45 g; indene, 29 g, 10 h, 20.2%, 9.8 g; methyl acrylate, 49 g, 24 h, 26.0%, 1.0 g; ethyl acrylate, 30 g, 20 h, 70 °C, 22.8%, 2.0 g; acrylonitrile, 54 g, 12 h, 21.0%, 1.7 g; methyl vinyl ketone, 30 g, 12 h, 42 °C, 15.5%, 0.7 g; cyclopentadiene, 41 g, 48 h, 30 °C, 32.3%, 11.2 g; 1,3-cyclohexadiene, 4 g in 5 mL of C_6H_5Cl, 7 days, 31.5%, 3.5 g; 1,3-cycloheptatriene, 0.9 g in 2 mL of C_6H_5Cl, 7 days, 25.4%, 1.2 g; bicyclo[4.2.1]nona-2,4,7-trien-9-one, 1.3 g in 2 mL of C_6H_5Cl, 7 days, 17.9%, 2.0 g; bicyclo[4.2.2]deca-2,4,7,9-tetraene, 0.2 g in 2 mL of C_6H_5Cl, 7 days, 0.2 g; cycloheptatriene, 2.6 g, 7 days, 33.7%, 1.1 g.

Synthesis of Hydroperoxides. Indan was autoxidized without initiator for 12 h at 110 °C. Iodometry showed a hydroperoxide content of 13.4% by weight. The solution was used without concentration. Tetralin was autoxidized without initiator for 12 h at 80 °C. Iodometry showed a hydroperoxide content of 14.5% by weight. The solution was used without concentration. Cycloheptatriene (9.2 g) and 0.2 g of hematoporphyrin were stirred in an oxygen atmosphere for 5 h at 0 °C in Pyrex while illuminated with a 370-W sunlamp. The product had a broad absorption band at 1650–1700 cm^{-1} (tropone). This crude oxidate was used directly in the ESR experiments.

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Competition between Reactive Sites in the Reactions of Oxygen Atoms and Hydroxyl Radicals with Phenylacetylene and Styrene

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Abstract: The products of the reactions of oxygen atoms and hydroxyl radicals with phenylacetylene and styrene were identified under single-collision conditions to determine whether these electrophiles prefer to react with either the ring or the unsaturated side chain. Previous work in another laboratory found that at 0.4 kPa oxygen atoms react exclusively with the C_2H group of phenylacetylene. The results obtained here under single-collision conditions show that the reactions of OH with phenylacetylene and of O and OH with styrene yield products which are typical of attack on both the ring and the side chain. The results for O + phenylacetylene are consistent with this trend. Qualitative arguments based on frontier electron theory support these findings.

Introduction

A recent publication by Blumenberg et al.[1] indicated that, given a choice between an alkynyl group and an aryl group in the same molecule, an oxygen atom reacts exclusively with the alkynyl group. At 0.4 kPa in a flow reactor, they found that the reaction of an oxygen atom with phenylacetylene gave only products characteristic of attack on the terminal alkynyl carbon atom. Since it is well-known that O(^{3}P) and OH react rapidly with alkenes,[2-5] alkynes,[4,6] and arenes,[7-10] the present investigation was undertaken to verify the O(^{3}P) + phenylacetylene results under single-collision conditions. The reactions of O(^{3}P) with styrene and OH with phenylacetylene and styrene were also studied to find out if a similar degree of selectivity was exhibited in these reactions.

One possible reason for the apparent selectivity observed by Blumenberg et al. is that C_2H may deactivate the ring for electrophilic radical addition. Another possibility is that the reaction of O(^{3}P) with the triple bond of phenylacetylene, a spin-allowed reaction, may be favored over reaction with the ring because of the spin-forbidden nature of the O(^{3}P) + arene reaction.[11] In the work reported here, deactivation of the aryl ring by unsaturated substituents might affect the selectivity of both the O(^{3}P) and OH reactions, whereas competition between spin-forbidden and spin-allowed paths would occur only for the oxygen atom reactions. It should be possible to distinguish between the two possibilities by identifying the products of these reactions. We expect that other information concerning the detailed mechanism of these reactions might also be obtained from this investigation.

Experimental Section

The apparatus used in this work has been described previously.[11] The two reactants collide in one chamber of a two-chamber vacuum system, and products are collimated before they enter the second

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