Does Superoxide Ion Oxidize Catechol, α-Tocopherol, and Ascorbic Acid by Direct Electron Transfer?

Edward J. Nanni, Jr., Martin D. Stallings, and Donald T. Sawyer*

Contribution from the Department of Chemistry, University of California, Riverside, California 92521. *Received December 3, 1979*

Abstract: Combination of superoxide ion ($O_2^{-}\cdot$) with reducing substrates such as 3,5-di-*tert*-butylcatechol, α-tocopherol, and ascorbic acid in dimethylformamide yields substrate oxidation products and H_2O_2 in each case. However, the results of cyclic voltammetric measurements indicate that these substrates are not oxidized by a direct one-electron transfer to $O_2^{-}\cdot$. Rather, the reaction mechanism involves abstraction of a proton from the substrate by $O_2^{-}\cdot$ to give substrate anion and the dismutation products of superoxide, H_2O_2 and O_2. In turn, the substrate anion is oxidized by O_2 in a multistep process to yield oxidation products and H_2O_2.

The reactivity of the superoxide ion, $O_2^{-}\cdot$, with organic substrates has enjoyed increasing interest because of its ubiquitous generation in aerobic organisms and the belief that it is a potent cytogenic agent.[1] This has prompted a number of efforts to identify $O_2^{-}\cdot$–substrate reactions that are toxic or yield such products; the studies to date indicate that $O_2^{-}\cdot$ is fairly innocuous.[2-5]

The ability to electrochemically generate $O_2^{-}\cdot$ solutions in aprotic media has been known since 1965.[6-11] While the development of the crown ether solubilization of KO_2 in organic solvents has aided in the study of the reactivity of $O_2^{-}\cdot$,[12] controlled-potential electrolysis provides the most stable pure solutions of $O_2^{-}\cdot$ available.[7,13]

In addition to the well-documented nucleophilicity, Brønsted basicity, and one-electron reducing capacity of $O_2^{-}\cdot$,[12] there are numerous reports that $O_2^{-}\cdot$ results in a net oxidation of reducing substrates.[14-26] However, for solution conditions where $O_2^{-}\cdot$ is stable, i.e., aprotic media, direct electron transfer to $O_2^{-}\cdot$ is an unreasonable characteristic.[27] Under rigorously aprotic conditions the oxidative inertness of $O_2^{-}\cdot$ is confirmed by its nonreactivity with a wide variety of functional groups, including benzaldehyde.[28] Addition of $O_2^{-}\cdot$ to substrate molecules with acidic protons, e.g., catechols,[14-17] α-tocopherol,[22] ascorbic acid,[23,24] and related model compounds,[25,26] results in a net oxidation. In the presence of proton sources $O_2^{-}\cdot$ dismutates rapidly to H_2O_2 and O_2 and the latter may be the direct oxidant.

The present paper summarizes the results of a detailed study of the reactivity of $O_2^{-}\cdot$ with the reducing substrates 3,5-di-*tert*-butylcatechol, α-tocopherol, and ascorbic acid, and outlines several mechanistic schemes to account for the net overall oxidation of the substrates.

Experimental Section

Instrumentation. The cyclic voltammetric experiments were accomplished either with a three-electrode potentiostat-amperiostat constructed with operational amplifiers[29] or with a Princeton Applied Research Model 173/179 potentiostat-galvanostat. The voltammograms were recorded with a Houston Instruments Omnigraph 2000 X-Y recorder. A Princeton Applied Research Model 179 digital coulometer was utilized for the controlled potential electrolysis experiments. All air-sensitive electrochemical experiments were conducted inside a Vacuum Atmosphere Corp. Dri-Train HE 193 Dry-Lab glovebox in the presence of purified nitrogen.

The working electrode for the cyclic voltammetric experiments was a Beckman platinum inlay electrode (no. 39273) which had a surface area of 0.23 cm^2. The auxiliary electrode was a platinum flag electrode which was isolated from the bulk solution by a medium-porosity glass frit which contained solvent. The reference electrode was a Ag/AgCl (aqueous tetramethylammonium chloride) cracked glass-bead electrode which was adjusted to 0.000 V vs. SCE.[30] The reference electrode was located inside a Luggin capillary in the cell assembly. A cylindrical platinum mesh electrode was used as the working electrode for the controlled potential electrolysis experiments.

The UV-visible spectra were recorded with either a Cary 17D or a Cary 219 spectrophotometer. In all experiments the concentration of the supporting electrolyte in the matched reference and sample cells was the same as in the electrochemical experiments (0.1 M tetraethylammonium perchlorate). ESR spectra were recorded with a Varian Model 4502 spectrometer equipped with standard quartz cells. Low-temperature ESR measurements were made by use of liquid nitrogen in a Wilmad quartz Dewar flask. The field was standardized with 1,1-diphenyl-2-picrylhydrazyl (Eastman Kodak Co.) (g = 2.0037).

Chemicals and Reagents. Burdick and Jackson "distilled in glass" dimethylformamide (DMF) was obtained in quartz bottles to minimize contamination by water. The water content as specified by the manufacturer was 0.008%. Tetraethylammonium perchlorate (TEAP) (G. Frederick Smith Chemical Co.) was used as the supporting electrolyte (0.1 M TEAP) in the electrochemical experiments. High-purity argon and oxygen were obtained from the Chemetron Corp.

Superoxide ion was generated by electrochemically reducing a solution through which oxygen was continuously bubbled. Upon completion of the electrolysis the $O_2^{-}\cdot$ solution was degassed with argon to remove any residual oxygen. The concentration of $O_2^{-}\cdot$ was monitored by cyclic voltammetry with the anodic peak current measured at −0.7 V vs. SCE. Standardization of the current relative to the concentration of $O_2^{-}\cdot$ was accomplished by controlled-potential coulometric analysis. Tetraethylammonium hydroxide (TEAOH) was obtained from Eastman Kodak Co. as a 25% solution in ethanol. 3,5-Di-*tert*-butylcatechol (DTBC) was purchased from the Aldrich Chemical Co., L(+)-ascorbic acid from Matheson Coleman and Bell, and α-tocopherol from Calbiochem. The remaining chemicals were reagent grade and were used without further purification.

Results

Estimates of pK_a' Values and Anion Redox Potentials. The effective pK_a' values for ten acidic substrates in dimethylformamide are summarized in Table I. These have been evaluated by determining the reduction potential, $E_{50\mu A}$, from the cyclic voltammogram for a 5 mM solution of the substrate. The pK_a' values are calculated from the $E_{50\mu A}$ values by assuming that this represents a condition of unit activity for the species in the redox couples at the electrode surface; i.e., $E_{50\mu A} \approx E°$. In other words, the half-reaction $HA + e^- \rightarrow {}^1/_2H_2 + A^-$ with the Nernst expression

$$E = E° - \frac{0.059}{1} \log \frac{(a_{H_2})^{1/2}(a_{A^-})}{a_{HA}} \qquad (1)$$

represents the addition of the half-reaction $H^+ + e^- \rightleftarrows {}^1/_2H_2$

$$E = 0.00 - \frac{0.059}{1} \log \frac{(a_{H_2})^{1/2}}{a_{H^+}} \qquad (2)$$

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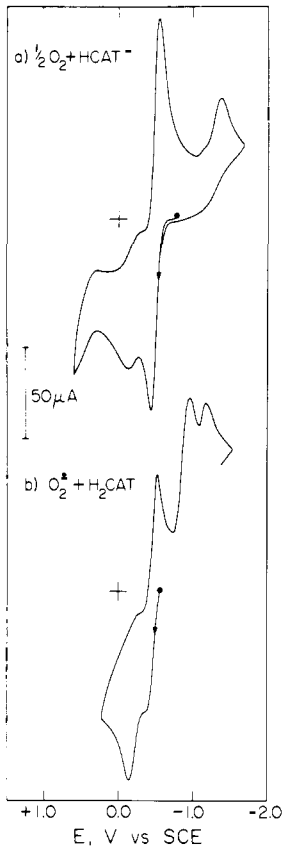

Figure 1. Cyclic voltammograms of (a) 1.05 mM O_2 plus 2.10 mM 3,5-di-*tert*-butylcatechol monoanion; (b) 2.10 mM $O_2^{-\cdot}$ plus 2.10 mM 3,5-di-*tert*-butylcatechol, all in DMF that contains 0.1 M TEAP and at a Pt electrode (surface area 0.23 cm^2). Scan rate was 0.1 V s^{-1}.

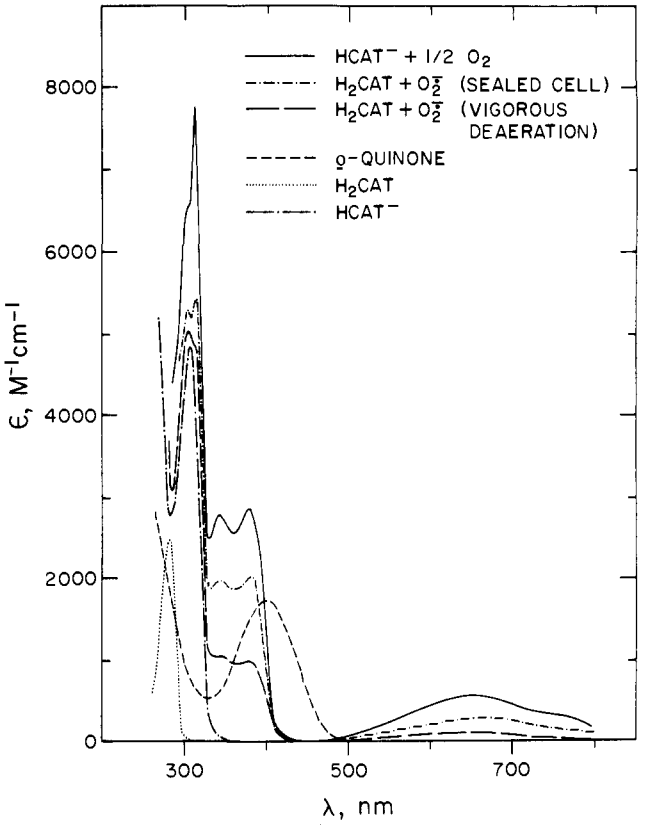

Figure 2. Absorption spectra for 2.10 mM solutions of 3,5-di-*tert*-butylcatechol (H_2cat), 3,5-di-*tert*-*o*-quinone, 3,5-di-*tert*-butylcatechol anion ($Hcat^-$), 1:1 combinations of H_2cat plus $O_2^{-\cdot}$ (sealed cell and with vigorous argon deaeration), and 1:1/2 combination of $Hcat^-$ plus O_2, all in DMF that contains 0.1 M TEAP.

Table I. Effective pK_a' Values for Acidic Substrates in Dimethylformamide[a]

substrate (HA), 5 mM	$(E_{50\mu A})$, V vs. NHE[b]	pK_a'
$HClO_4$ (H_2O)	0.00	0.0
$HClO_4$	−0.05	0.8
HCl	−0.07	1.2
NH_4ClO_4	−0.50	8.5
ascorbic acid	−0.62	10.5
H_2O_2[c]	−0.63	10.7
phenol	−1.17	19.8
di-*tert*-butylcatechol	−1.18	19.9
di-*tert*-butylcatechol monoanion	−1.67	28.2
α-tocopherol	−1.68	28.4
ascorbic acid monoanion	−1.79	30.3
H_2O	−1.93	32.6
n-butyl alcohol	−1.97	33.3
blank	−2.25	38.0

[a] For HA + $e^- \rightarrow$ ½H_2 + A^-; $pK_a' = -E_{50\mu A}/0.059$ V. The potentials at a current of 50 μA are estimated to represent a condition of equal activities for HA and H_2 at the electrode surface. The acidity of the substrates, pK_a, is indicated by the reduction potentials, $E_{50\mu A}$, at a cathodic current of 50 μA and is standardized for a proton activity of unity in H_2O vs. NHE (scan rate 0.1 V s^{-1}). [b] Measured by cyclic voltammetry (scan rate = 0.1 V s^{-1}). [c] Measured at half-peak height.

to the equilibrium reaction HA ⇄ H^+ + A^-

$$K_a = a_{H^+}a_{A^-}/a_{HA} \quad (3)$$

Thus, substituting for $a_{H^+} = K_a a_{HA}/a_{A^-}$ into eq 2 yields

$$E = -0.059 \log K_a - 0.059 \log (a_{HA}/a_{A^-}) \quad (4)$$

and if $a_{HA} = a_{A^-}$ then $E = E^\circ$ (which is assumed to be true for $E_{50\mu A}$), and eq 4 reduces to

$$pK_a = -E_{50\mu A}/0.059 \quad (5)$$

Table II. Standard Redox Potentials (E°_{red}) for the Oxidation of Substrate Anions to Radical Species ($A^\cdot + e^- = A^-$)

substrate	(E°_{red}), V vs. NHE[a]
ascorbic acid monoanion	+0.33
di-*tert*-butylcatechol monoanion	+0.11
α-tocopherol anion	−0.25

[a] The E°_{red} values are estimated to be equal to the half-peak potential ($E_{p/2}$) for the oxidation of 5 mM substrate anion by cyclic voltammetry at a scan rate of 0.1 V s^{-1}.

Table II summarizes the estimated standard redox potentials (E°_{red}) for the oxidation of the three substrate anions. These represent the half-peak potential, $E_{p/2}$, of the cyclic voltammograms for the oxidation of deaerated solutions of the tetraethylammonium salts of the anions.

3,5-Di-*tert*-butylcatechol. Figure 1 illustrates the cyclic voltammograms for (a) the combination of one-half O_2 per 3,5-di-*tert*-butylcatechol anion, and (b) the combination of one O_2 per 3,5-di-*tert*-butylcatechol (H_2Cat), all in DMF. The voltammogram for the former indicates that most of the O_2 has been consumed and that 1 equiv of the semiquinone anion radical of 3,5-di-*tert*-butylcatechol is formed (E_{pa} = −0.44 V vs. SCE). ESR spectra confirm this conclusion.[27,31] The UV-visible spectrum of this solution is shown in Figure 2 and is identical with the spectrum obtained for the one-electron reduction of 3,5-di-*tert*-butyl-*o*-quinone. The voltammogram for $O_2^{-\cdot}$ plus 3,5-di-*tert*-butylcatechol (Figure 1b) indicates that three major products are present in solution; the semiquinone anion radical (E_{pc} = −1.34 V vs. SCE), 3,5-di-*tert*-

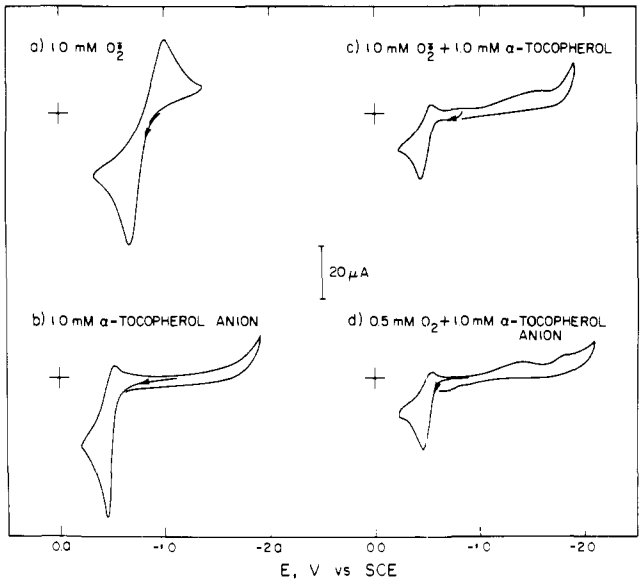

Figure 3. Cyclic voltammograms of (a) 1.0 mM $O_2^{-}\cdot$; (b) 1.0 mM α-tocopherol anion; (c) 1.0 mM $O_2^{-}\cdot$ plus 1.0 mM α-tocopherol; (d) 0.5 mM O_2 plus 1.0 mM α-tocopherol anion, all in DMF that contains 0.1 M TEAP and at a Pt electrode (surface area 0.23 cm^2). Scan rate was 0.1 $V\ s^{-1}$.

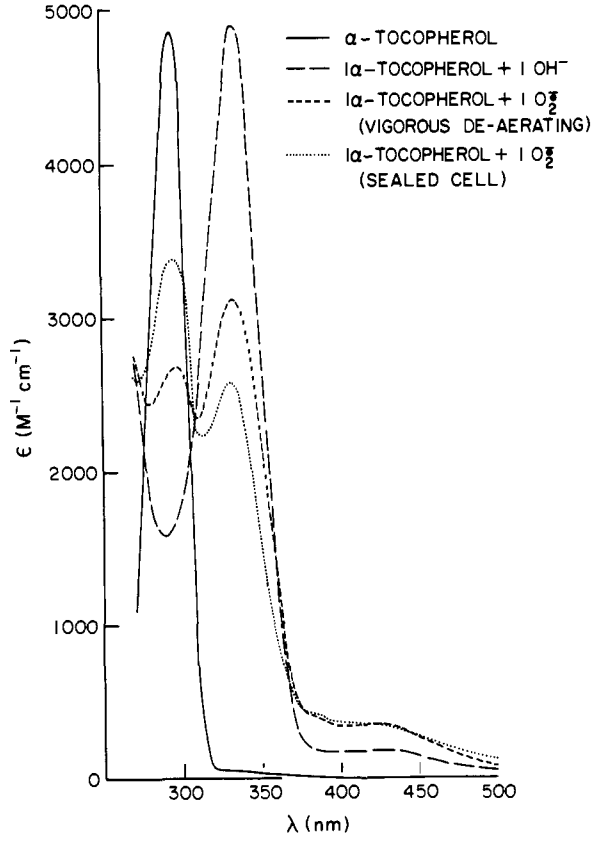

Figure 4. Absorption spectra for 1 mM solutions of α-tocopherol, α-tocopherol anion, and 1:1 combinations of α-tocopherol plus $O_2^{-}\cdot$ in DMF (0.1 M TEAP).

butylcatechol monoanion (E_{pa} = −0.14 V vs. SCE), and O_2 (E_{pc} = −1.03 V vs. SCE). When this solution is purged with argon, the O_2 is removed from the solution and the concentration of the monoanion is increased at the expense of semiquinone anion radical (see Figure 2). Addition of O_2 after purging with argon restores the solution to its original blue color and the concentration of the semiquinone anion radical increases at the expense of the monoanion.

α-Tocopherol. Figure 3 illustrates a series of cyclic voltammograms for (a) $O_2^{-}\cdot$, (b) α-tocopherol anion, (c) $O_2^{-}\cdot$ plus α-tocopherol, and (d) $^1/_2O_2$ plus α-tocopherol anion, all in DMF. The almost identical voltammograms for the latter two solutions are convincing evidence that the reaction products and pathways are closely related. Moreover, comparison of the spectra (Figure 4) and voltammograms for argon-purged and sealed-cell solutions of $O_2^{-}\cdot$ plus α-tocopherol provide clear evidence that O_2 is an intermediate of the reaction with a higher yield of the monoanion for the deaerated solution. In addition, voltammetric and spectroscopic measurements confirm that neither the 3,5-di-*tert*-butylcatechol monoanion[12,27] nor the α-tocopherol monoanion reacts with $O_2^{-}\cdot$, and that neither 3,5-di-*tert*-butylcatechol nor α-tocopherol reacts with H_2O_2.

L(+)-Ascorbic Acid. Voltammetric studies of the reaction of $O_2^{-}\cdot$ with ascorbic acid do not indicate the presence of O_2 in the orange product solution. However, as with α-tocopherol and 3,5-di-*tert*-butylcatechol, continuously purging with Ar during the addition of $O_2^{-}\cdot$ results in an increased yield of the monoanion (E_{pa} = +0.12 V vs. SCE). Superoxide also reacts with the monoanion of ascorbic acid to give a pale yellow-orange solution (λ_{max} 285 nm (ϵ 1000 M^{-1} cm^{-1}) and 350 (1100 M^{-1} cm^{-1}) in DMF and oxidation peaks at E_{pa} = +0.40 and +0.87 V vs. SCE). Almost identical results are obtained with (a) the addition of 2 equiv of $O_2^{-}\cdot$ to ascorbic acid and (b) the addition of 1 equiv of O_2 to the ascorbate monoanion. The yellow-orange product has spectroscopic properties that are similar to those of the anion of L(+)-2,3-diketogulonic acid,[32] which is formed when dehydroascorbate reacts with base.

Discussion and Conclusions

To answer the question whether acidic substrates undergo oxidation by electron transfer to $O_2^{-}\cdot$, two mechanistic schemes need to be considered. The first involves direct electron transfer of one electron from the acidic substrate (ROH) to $O_2^{-}\cdot$:

$$O_2^{-}\cdot + ROH \rightarrow HO_2^{-} + RO\cdot \quad E^\circ_{rxn} \qquad (6)$$

This may be envisaged either as a concerted H-atom abstraction

$$O_2^{-}\cdot + ROH \rightarrow [RO\text{-}H\text{-}O_2^{-}\cdot]^{\ddagger} \rightarrow RO\cdot + HO_2^{-} \qquad (7a)$$

or as a proton abstraction followed by hydroperoxyl oxidation:

$$O_2^{-}\cdot + ROH \rightarrow HO_2\cdot + RO^{-} \qquad (7b)$$

$$HO_2\cdot + RO^{-} \rightarrow HO_2^{-} + RO\cdot \qquad (7c)$$

Reaction 6 and its thermodynamics (E°_{rxn}) result from the subtraction of the half-reaction of eq 9 from that of eq 8:

$$O_2^{-}\cdot + ROH + e^{-} \rightarrow HO_2^{-} + RO^{-} \quad E^\circ_8 \qquad (8)$$

$$RO\cdot + e^{-} \rightarrow RO^{-} \quad E^\circ_9 \qquad (9)$$

For 3,5-di-*tert*-butylcatechol we estimate that E°_8 = −0.15 V vs. NHE[33] and E°_9 = +0.11 V vs. NHE (see Table II). These values yield E°_{rxn} = −0.26 V, which indicates that the direct one-electron oxidation of 3,5-di-*tert*-butylcatechol by $O_2^{-}\cdot$ is not feasible. For α-tocopherol and ascorbic acid the values for E°_{rxn} are −0.43 and +0.05 V vs. NHE, respectively. Thus, the direct one-electron oxidation of α-tocopherol by $O_2^{-}\cdot$ is not favored thermodynamically, and it is only marginally favored for ascorbic acid.

In the second scheme (eq 10-12) $O_2^{-}\cdot$ acts as a Brønsted base and is dismutated by the acidic reductant to yield HO_2^{-} and O_2 as well as the anion of the substrate. The latter is oxi-

dized by the O_2 from the dismutation process:

$$O_2^{-}\cdot + ROH \rightarrow HO_2\cdot + RO^- \quad (10)$$

$$HO_2\cdot + O_2^{-}\cdot \rightarrow HO_2^- + O_2 \quad (11)$$

$$O_2 + RO^- \rightarrow RO\cdot + O_2^{-}\cdot \quad (12)$$

The overall reaction is the sum of reactions 10–12, and is the same as the primary step of the first scheme (eq 7). However, the second scheme does not have $O_2^{-}\cdot$ acting as a direct acceptor of an electron from the substrate. Also, the transient formation of O_2 is a unique feature of the second scheme.

3,5-Di-*tert*-butylcatechol and α-Tocopherol. Recent work in our laboratory has established that the dismutation rate of $O_2^{-}\cdot$ in DMF in the presence of acidic substrates is first order with respect to $O_2^{-}\cdot$ and acidic substrate and is directly related to the substrate's acidity, not its ease of oxidation.[35] The second-order rate constants [which range from 1.6×10^3 (phenol) to 1.5×10^{-3} M^{-1} s^{-1} (1-butanol)] for 3,5-di-*tert*-butylcatechol, α-tocopherol, and ascorbic acid are 1.5×10^3, 7.8×10^1, and $>2.0 \times 10^3$ M^{-1} s^{-1}, respectively. For example, the potential for the oxidation of α-tocopherol is 0.5 V more negative than that for the phenoxide ion, but the rate of $O_2^{-}\cdot$ disappearance is an order of magnitude faster with phenol. This is consistent with the higher acidity of phenol relative to α-tocopherol (Table I). The alkyl substituents enhance the electron density in the aromatic ring to lower its acidity and enhance the ease of free-radical formation. For these reasons, O_2 oxidizes α-tocopherol anion, but not phenoxide ion in DMF.

The net oxidation of 3,5-di-*tert*-butylcatechol and α-tocopherol by $O_2^{-}\cdot$ follows similar reaction pathways. Both substrates yield a nearly stoichiometric amount of O_2 when combined with one $O_2^{-}\cdot$ per substrate molecule. Neither the monoanion of 3,5-di-*tert*-butylcatechol nor the α-tocopherol anion reacts with $O_2^{-}\cdot$. Argon-purged and sealed-cell experiments confirm the equilibrium between O_2, $O_2^{-}\cdot$, substrate anion, and its redox products. For 3,5-di-*tert*-butylcatechol (H_2cat), a reasonable mechanism is represented by

$$O_2^{-}\cdot + H_2cat \rightarrow Hcat^- + HO_2\cdot \quad (13)$$

$$O_2^{-}\cdot + HO_2\cdot \rightarrow O_2 + HO_2^- \quad (14)$$

$$H_2cat + HO_2^- \rightarrow H_2O_2 + Hcat^- \quad (15)$$

$$2Hcat^- + O_2 \rightleftarrows H_2O_2 + 2cat^{-}\cdot \quad (16)$$

For α-tocopherol (Ht) a related mechanism is proposed:

$$O_2^{-}\cdot + Ht \rightarrow t^- + HO_2\cdot \quad (17)$$

$$O_2^{-}\cdot + HO_2\cdot \rightarrow HO_2^- + O_2 \quad (18)$$

$$O_2 + t^- \rightleftarrows O_2^{-}\cdot + t\cdot \quad (19)$$

$$2t\cdot \rightarrow \text{dimeric and dismutation products} \quad (20)$$

The second step in both of these mechanisms (eq 14 and 18), on the basis of pulse radiolysis studies in water, is almost diffusion controlled, $k_{14} = 10^8$ M^{-1} s^{-1}.[36] For the reaction of cysteine (RSH) with $HO_2\cdot$

$$HO_2\cdot + RSH \rightarrow RS\cdot + H_2O_2 \quad (21)$$

recent work has shown that $k_{21} \simeq 10^3$ M^{-1} s^{-1}.[37] Hence, the lifetime of $HO_2\cdot$ is limited by reactions 14 and 18, which precludes significant reaction via eq 21. Also, the experimental results confirm the transient formation of O_2 and the equilibria represented by eq 16 and 19. Hence, the second scheme appears to be the dominant pathway and $O_2^{-}\cdot$ does not act as a direct one-electron oxidant for α-tocopherol and 3,5-di-*tert*-butylcatechol. Rather, it undergoes a proton-induced dismutation to give peroxide and O_2. The latter oxidizes the substrate anion.

L(+)-Ascorbic Acid. The net oxidation of L(+)-ascorbic acid (H_2asc) by $O_2^{-}\cdot$ is different from that of 3,5-di-*tert*-butylcatechol and α-tocopherol because (a) the primary oxidation product (dehydroascorbic acid (deasc)) reacts in basic media to form 2,3-deketogulonic acid[32] and (b) the transient formation of O_2 in a reversible equilibrium is not observed. Continuous purging with argon during the addition of $O_2^{-}\cdot$ results in an increased yield of the monoanion, which implies a similar mechanism to that for catechol, with the O_2 from the proton-induced dismutation acting as the oxidizing agent of the ascorbate monoanion.

$$O_2^{-}\cdot + H_2asc \rightarrow Hasc^- + HO_2\cdot \quad (22)$$

$$HO_2\cdot + O_2^{-}\cdot \rightarrow O_2 + HO_2^- \quad (23)$$

$$O_2 + Hasc^- \rightarrow deasc + HO_2^- \quad (24)$$

$$deasc \xrightarrow{OH^-} 2,3\text{-diketogulonic acid} \quad (25)$$

Reaction 24 does not appear to be reversible, but transient amounts of O_2 for the sealed-cell experiments should have been observed if this is the controlling mechanism. Because O_2 is not detected, the direct reduction of $O_2^{-}\cdot$, i.e., the first scheme, may be competitive and equally viable.

However, the thermodynamics for the oxidation of ascorbic acid via the first scheme are only slightly favorable ($E°_{rxn}$ = +0.05 V). This prompts us to suggest a third mechanism to account for the rapid and complete oxidation of ascorbic acid when it is combined with $O_2^{-}\cdot$. If $O_2^{-}\cdot$ reacts by a concerted two-electron transfer (or concerted two-hydrogen atom transfer) from ascorbic acid

$$O_2^{-}\cdot + H_2asc \rightarrow deasc + OH^- + \cdot OH \quad (26)$$

the absence of transient O_2 is accounted for and the thermodynamics are strongly favorable ($E°_{rxn}$ = +0.55 V). Equation 26 results from the subtraction of eq 28[39] from eq 27:[40]

$$O_2^{-}\cdot + 3H^+ + 2e^- \rightarrow H_2O + \cdot OH \quad E°_{27} = +0.63 \text{ V} \quad (27)$$

$$deasc + H^+ + 2e^- \rightarrow Hasc^- \quad E°_{28} = +0.08 \text{ V} \quad (28)$$

and illustrates that the two-electron reduction of $O_2^{-}\cdot$ is thermodynamically feasible. Indeed, the two-electron reduction of $O_2^{-}\cdot$ by substrates such as ascorbic acid may represent a serious biological hazard because the reduction product, ·OH, is a potent cytogenic oxidant. With acidic reducing substrates, such as ascorbic acid, it is difficult to determine whether $O_2^{-}\cdot$ functions only to deprotonate the substrate (the second scheme) or to, in fact, oxidize it by two electrons (the third scheme). Preliminary studies indicate that $O_2^{-}\cdot$ oxidizes two-electron reductants which *do not contain acidic protons*.[41] Further work in this area is in progress.

In summary, the oxidation of acidic substrates by superoxide ion involves an initial rate-determining proton transfer from the substrate to $O_2^{-}\cdot$. This is followed by rapid dismutation to give peroxide and O_2; the latter oxidizes the substrate anion by a one- or two-electron process. The reported oxidation of thiols,[15,21] alcohols,[15] and hydrazines[20,22,38] by $O_2^{-}\cdot$ presumably occurs also by the same initial proton-induced dismutation step. That the oxidation of hydrazines is catalyzed by protons or metal ions is further support for this conclusion.

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$$O_2^{-}\cdot + e^- + 2H^+ \rightarrow H_2O_2 \quad E^\circ_{27a} = 0.87\text{ V}$$

$$H_2O_2 + e^- + H^+ \rightarrow H_2O + \cdot OH \quad E^\circ_{27b} = 0.38\text{ V}$$

as follows:

$$E^\circ_{27} = (E^\circ_{27a} + E^\circ_{27b})/2 = +0.63\text{ V}$$

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^1H and ^{13}C NMR Spectroscopic Study of 9-Fluorenyl Cations[1a]

George A. Olah,* [1b] G. K. Surya Prakash,[1b] Gao Liang,[1c] Philip W. Westerman,[1d] Klaus Kunde,[1e] Jayaraman Chandrasekhar,[1f] and Paul v. R. Schleyer* [1f]

Contribution from the Hydrocarbon Research Institute, Department of Chemistry, University of Southern California, Los Angeles, California 90007, and Insitute fur Organische Chemie, Friedrich-Alexander Universitat, Erlangen-Nurnberg, 8520 Erlangen, West Germany.

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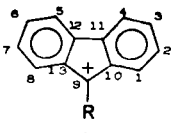
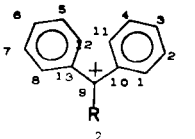
Abstract: A series of 9-substituted 9-fluorenyl cations were prepared and characterized by ^1H and ^{13}C NMR spectroscopy. Unsuccessful attempts were made to observe intramolecular interconversion of 9-methyl-9-fluorenyl cation via capped pyramidal ions with ring deuterated and methylated analogues. MINDO/3 calculations on isomeric structures of cyclopentadienyl, indenyl, and fluorenyl cations indicated strongly decreasing relative stabilities of the pyramidal forms due to benzoannulation. In deuterated fluorosulfonic acid solution, the 9-methyl-9-fluorenyl (**1**-CH_3) and 3,9-dimethyl-9-fluorenyl cations (**14**) underwent hydrogen–deuterium exchange consistent with a protonation–deprotonation mechanism.

Introduction

Diphenylmethyl and the related but "antiaromatic" fluorenyl cations have been compared previously.[2-6] Although the reported preparation of the parent 9-fluorenyl cation (**1**-H) in sulfuric acid now appears to be in doubt[3] (in fact, rapid polymerization to unidentifiable products occurs), the 9-phenyl-9-fluorenyl cation[2] (**1**-C_6H_5) was sufficiently stable in aqueous sulfuric acid to permit cryoscopic and ^1H NMR spectroscopic measurements. The low pK_R^+ value of **1**-C_6H_5 (−10.8) relative to that of more stable triphenylmethyl cation **2**-C_6H_5 ($pK_R^+ = -6.6$) provides direct evidence for antiaromatic destabilization of cyclopentadienyl-type cations.[7] Similarly, the solvolysis rates of a variety of 9-fluorenyl chlorides are significantly slower than those of their benzhydryl analogues.[6]



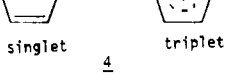
1



2

The square pyramidal $C_5H_5^+$ cation **3** was first predicted theoretically.[8,9] Molecular orbital calculations indicated that conversion into more stable forms such as **4** (singlet or triplet) should require high activation energies.[9,10]


3



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