((*E*)-methylene). These assignments are in agreement with the signals expected for **1** on the basis of the spectrum of **2**. These signals clearly result from a reactive intermediate because they decrease as the flow rate is reduced.

Theoretical[2] and experimental[3] work has postulated that **1** exists as a singlet ground state. Our observation of **1** by flow ^{1}H NMR confirms this.

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Oxygen Isotope Exchange between Water and Semiquinones

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The no-spin oxygen atoms in the anion radicals of carbonyl systems are readily replaced by ^{17}O with its 5/2 nuclear spin by the simple addition of ^{17}O labeled water to the anion radical solutions in hexamethylphosphoramide (HMPA) or liquid ammonia. This reaction can be utilized to readily produce ^{17}O labeled anion radicals that yield strong well resolved ESR signals exhibiting splitting from the ^{17}O nucleus. This very simple procedure makes ^{17}O substituted carbonyl anion radicals for spin density,[1] ion association,[2] hydrogen bonding,[3] etc. studies readily available without necessitating the synthesis of the isotopically substituted precursors.

When water is added to a solution of the indane-1,2,3-trione (ninhydrin) anion radical in HMPA the formation of the hydrogen bonding between the water and the anion radical results in a decrease in the proton coupling constants (A_H = 0.93 G, 2 H's and A_H = 1.18 G, 2 H's), which is well documented.[4] However, when 5 μL (0.30 mmol) of 20% $H_2{}^{17}O$ is added to 1.0 mL of a ca. 10^{-3} M solution of the ninhydrin anion radical in HMPA,[4] the expected changes in the coupling constants are accompanied by the nine line spectrum being slowly replaced with that of the ^{17}O substituted (A_O = 3.99 G) anion radical. The intensity of the ^{17}O substituted anion radical continues to grow for a period of about 30 h, and the two spectra can be observed simultaneously without apparent loss of total anion radical concentration, Figure 1. When the same reaction is carried out with a solution containing 0.1 M neutral triketone, the reaction is complete within 10 min. The anion radical solutions generated in the presence of excess neutral ninhydrin exhibit large line widths due to rapid electron exchange. This together with the coupling constant changes due to hydrogen bonding reduces the nine line pattern to five resolvable ESR lines. After several hours, ESR analyses of these solutions clearly show the presence of the anion radical containing two ^{17}O atoms.

Scheme I

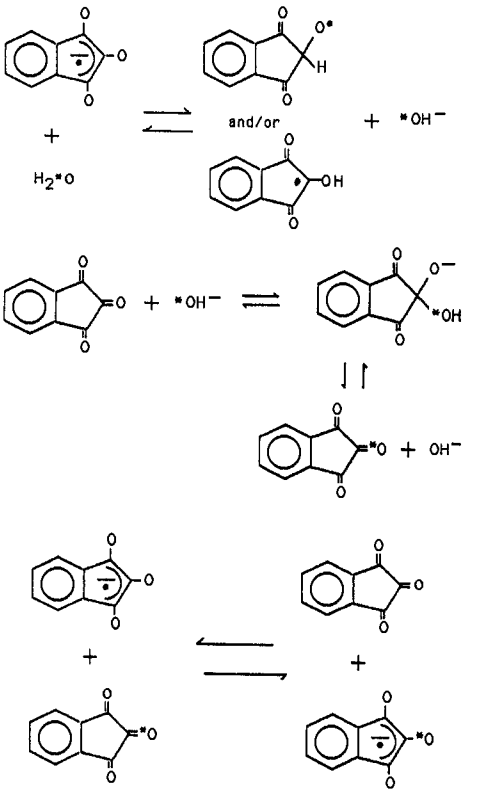

Table I. Oxygen-17 Hyperfine Splitting Constants in Gauss in DMF at 294 K[a]

anion radical	A_0 (DMF)	A_0 (solv, temp (K))
ninhydrin	unknown	3.99 (HMPA, 298)
benzoquinone	9.53	9.42 (NH_3, 205)
anthraquinone	7.53	7.32 (NH_3, 205)
		7.47 (HMPA, 298)
fluorenone	9.21	9.54 (HMPA, 298)

[a] Taken from ref 1 and those measured in this work.

It is interesting that only one ^{17}O coupling constant for $C_9H_4O_2{}^{17}O^{\bullet-}$ is observed despite the fact that there are two possible sites of substitution. This is, however, the expected result since the rates of isotopic substitution are probably not the same at the two different sites. Even if they were, LCAO calculations predict nearly the same spin and charge densities on all three oxygen atoms.[5]

The fact that the hydroxide ion will react with anthraquinone ($C_{14}H_8O_2$) to form the hydroxide addition complex[6] ($C_{14}H_8O_2$-OH^-) coupled with the strong dependence of the rate of ^{17}O substitution into the ninhydrin anion radical upon the neutral molecule concentration provides strong evidence that the reaction proceeds via the initial formation of the hydroxide ion followed by the formation of the hydroxide addition complex, Scheme I. That is, the anion radical acts as a base strong enough to deprotonate water, and the hydroxide addition must be followed by electron exchange.

The reaction appears to be quite general in nature; a strong well resolved ESR spectrum of benzoquinone-$^{17}O^{\bullet-}$ and anthraquinone-$^{17}O^{\bullet-}$ can be obtained in the absence of excess neutral molecule several hours after the addition of 5 μL of $H_2{}^{17}O$ to 1 mL of the anion radical solutions in HMPA or liquid ammonia. In HMPA, these anion radicals are free of ion association.[7] Thus, the ^{17}O coupling constants are unperturbed by interaction of the

(1) Oxygen-17 hyperfine coupling constants are a sensitive function of the σ-π interaction, see: Broz, M.; Luz, Z. *J. Chem. Phys.* **1969**, *51*, 738.

(2) The carbonyl oxygen atoms represent the site of anion radical–gegenion interaction in ion pairs involving ketyls, semidiones, and semiquinones, see for example: (a) Nakamura, K. *J. Am. Chem. Soc.* **1080**, *102*, 7847. (b) Felix, C. C.; Sealy, R. C. *J. Am. Chem.* Soc. **1982**, *104*, 1555. (c) Stevenson, G. R.; Alegria, A. E.; McB. Block, A. *J. Am. Chem. Soc.* **1975**, *97*, 4859.

(3) Hydrogen bonds with ketyls involve the carbonyl oxygen, see: Ichikawa, T.; Ichikawa, Y.; Yoshida, H. *J. Phys. Chem.* **1988**, *92*, 508.

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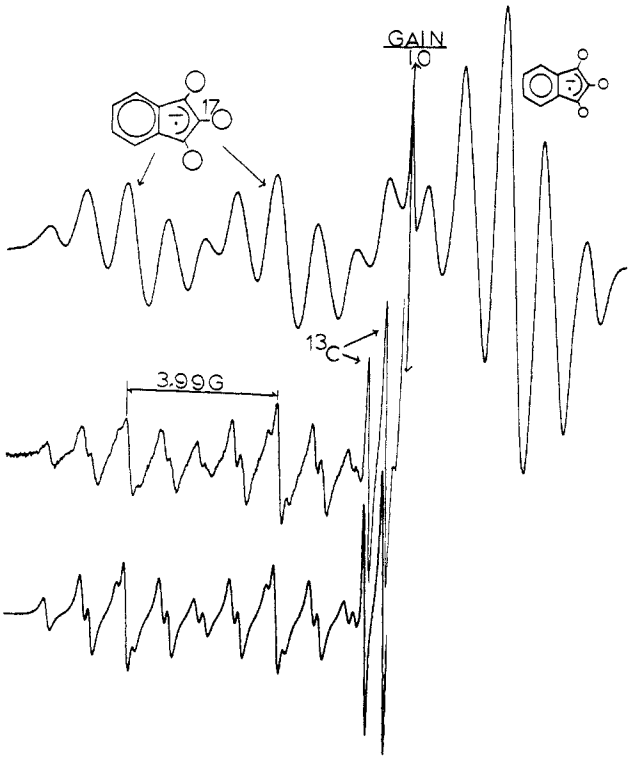

Figure 1. ESR spectra of an HMPA solution of the ninhydrin anion radical with 0.2 M added $H_2{}^{17}O$ recorded at 298 °C. Both spectra were recorded from the same anion radical solution. The top spectrum was recorded from a portion of the solution 4 min after the simultaneous addition of the $H_2{}^{17}O$ and 0.2 M neutral ninhydrin, and it shows the low field portion of the spectrum of the ^{17}O labeled anion radical and the unlabeled species. The gain was reduced by a factor of 10 at the vertical arrow. Computer simulation of this spectrum shows that the ^{17}O labeled anion radical represents 25% of the total anion radical. Line broadening is due to the rapid electron exchange between the neutral molecule and anion radical. The center spectrum was recorded 11 h after the addition of the $H_2{}^{17}O$. Neutral ninhydrin was not added to this portion of the solution, and no ^{17}O labeled anion radical could be observed within 1 h of the water addition. After 11 h, the ^{17}O labeled species only represents 3.5% of the total anion radical, and it yields ESR line heights that are comparable to those for the ^{13}C labeled materials that are present in natural abundance. The unlabeled anion radical is not shown and is off scale by more than a factor of 100. The spectrum shown on the bottom is a computer simulation and was generated by combining three spectra: (1) $C_9H_4O_2{}^{17}O$, A_H = 1.16 G, 2 H's, A_H = 0.93, 2 H's, A_o = 3.99 (anisotropic effects in the oxygen splitting not accounted for). (2) $C_8{}^{13}CH_4O_3$ (^{13}C on one of two equivalent positions), A_c = 3.15 G. (3) $C_8{}^{13}CH_4O_3$ (^{13}C on one of two equivalent positions), A_c = 2.20 G.

counter ion with the oxygen atom. The lack of ion association and hydrogen bonding generally results in smaller charge densities and higher spin densities on the oxygen atoms with correspondingly larger A_O's, Table I.

The reaction is functional even for ketyls, which are not stable in water. The ^{17}O labeled ketyl anion radicals can be prepared by simply adding a molar deficient amount of the $H_2{}^{17}O$ to the anion radical solution. The water probably first protonates the ketyl producing ^{17}O labeled hydroxide ion. This hydroxide ion can then add to the neutral ketone and follow a path that is analogous to that shown in Scheme I.

A number of side reactions can be envisioned that would lower the overall efficiency of the production of labeled anion radical, such as electron transfer from the hydroxide addition complex to neutral ketone followed by dimerization of the remaining radical.[6] Despite this, strong well resolved ESR spectra of ^{17}O labeled semiquinones, ketyls, and presumably semidiones can be recorded by use of this technique.

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Chemistry of Singlet Oxygen. 50. Hydroperoxide Intermediates in the Photooxygenation of Ascorbic Acid

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Ascorbic acid (vitamin C)[1] is an important aqueous antioxidant.[2] Tocopherol (a lipid-soluble antioxidant) is a powerful quencher for singlet oxygen,[3,4] and this is also true of ascorbic acid.[5] It is known that the double bond in ascorbic acid is cleaved on photooxygenation to give oxalate.[6] Careful studies of the mechanism of photooxygenation have not yet been carried out nor have initial products been determined. In this paper, we report the formation of unstable hydroperoxide intermediates and their decomposition to give oxalate esters. Spectral data for all compounds are summarized in Table I.

Rose bengal-sensitized photooxygenation of ascorbic acid (**1**[7,8]) in CD_3OD at −85 °C gave a reaction mixture which was kept in liquid N_2 until analysis by ^{13}C NMR (−80 °C). Two isomeric hydroperoxy ketones, **2** and **3**, are formed in 65% and 35% yield, respectively.[9]

When the reaction mixture stood at −78 °C for 5 h, the carbonyl peaks of **2** and **3** decreased, and new peaks at 105.91 and 99.08 ppm appeared, corresponding to hydroperoxydehydroascorbic acid **5**.[10] On further standing for 30 h at −78 °C, the reaction mixture showed only peaks for **5**. Hydroperoxy ketone **3**, which lacks a C-3 carbonyl group, apparently also rearranges to hydroperoxide **5**. Scheme I below provides a reasonable working model for these reactions.

Addition of the hydroperoxide in **3** to the C-2 carbonyl group may produce intermediate dioxetane **4**[11] which opens to **2**. We did not detect dioxetane **4**, which is likely to be very unstable.

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(8) Typical procedure: 1 mmol of ascorbic acid in CD_3OD (4 mL) containing rose bengal was photolyzed at −85 °C with a Varian-Eimac 300 W Xenon lamp and a 0.1 M K_2CrO_4 filter solution (in NH_4OH–NH_4Cl at pH 10, cutoff <460 nm) until **1** was gone (TLC). The reaction mixture was monitored by ^{13}C NMR (−80 °C). Upon warming to room temperature, over 80% of oxalate **11A** and less than 20% of the autoxidation product, dehydroascorbic acid **6**, were formed.

(9) The product ratio was approximately determined by comparing the peak height of carbonyl groups in the ^{13}C NMR; peaks of **2** and **3** were assigned by comparison of their chemical shifts with similar compounds from oxidation of L-ascorbic acid (Matusch, R. *Z. Naturforsch.* **1977**, *32B*, 562).

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