Kinetics and Mechanism of the Reactions of Superoxide Ion in Solution. Part 5.† Kinetics and Mechanism of the Interaction of Superoxide Ion with Vitamin E and Ascorbic Acid

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The reactions of electrochemically generated $O_2^{-\bullet}$ with α-tocopherol and α-tocopheryl acetate have been studied in acetonitrile and with ascorbic acid in acetonitrile and mixed acetonitrile–water solvents. It was found that both α-tocopherol and ascorbic acid react with superoxide ion *via* a deprotonation mechanism to form the corresponding anions. On subsequent steps of the process these anions are oxidized by O_2 to form $O_2^{-\bullet}$ The mechanism of the oxidation of ascorbate anion depended on the solvent composition: in aqueous solution the reaction proceeded only in the presence of Fe^{3+} ion, but in acetonitrile a direct one-electron transfer from the ascorbate anion to dioxygen was observed. Both mechanisms were suppressed to a considerable extent in mixed solvents.

The mechanism of the interaction of superoxide ion and dioxygen with vitamins E (α-tocopherol and α-tocopheryl acetate) and C (ascorbic acid) is of considerable interest for understanding the role of these vitamins in living cells. At present, there are controversial data concerning the kinetics and mechanism of these processes in aqueous[1–6] and aprotic media.[7–10] For example it remains uncertain whether a proton or a hydrogen atom is abstracted by superoxide ion from α-tocopherol, and whether $O_2^{-\bullet}$ is formed in the oxidation of α-tocopherol and ascorbic acid by dioxygen.

There is also a significant difference in the kinetic data obtained by various authors for the interaction of superoxide ion with α-tocopherol and its analogues. Earlier, it was found[1,2] that the rate constants for the reaction of $O_2^{-\bullet}$ with the water-soluble analogues of α-tocopherol, 6-oxo-2,5,7,8-tetramethylchroman-2-carboxylic acid and 3-(6-oxo-2,5,7,8-tetramethylchroman-2-yl)propionic acid, are 1.7×10^4 and 5.9×10^5 l mol^{-1} s^{-1}, respectively. But recently, Arudi *et al.*[3] have shown that the rate constant for the reaction of $O_2^{-\bullet}$ with α-tocopherol in aqueous ethanol is $\leqslant 6$ l mol^{-1} s^{-1}. Sawyer and his co-workers[8,9] have found that this value is 70—800 and 600 l mol^{-1} s^{-1}, respectively, in dimethylformamide and acetonitrile.

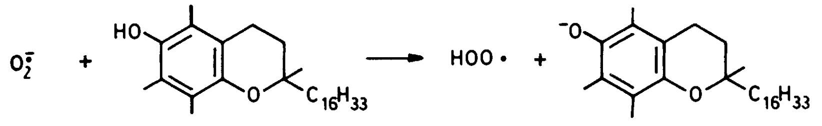
In this work we studied the interaction of electrochemically generated superoxide ion with α-tocopherol, α-tocopheryl acetate, and ascorbic acid as well as the mechanism of the oxidation of their anions by dioxygen.

Results

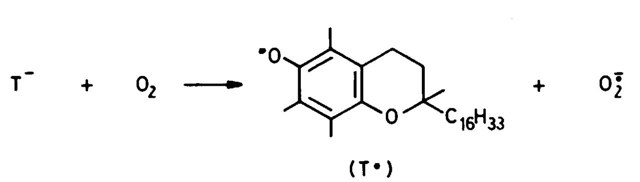
Reaction of Superoxide Ion with α-Tocopherol.—The tocopheryl anion (T^-) with a maximum at 323 nm was the main product of the reaction of $O_2^{-\bullet}$ with α-tocopherol. An identical spectrum was obtained in the reaction of α-tocopherol with tetrabutylammonium hydroxide. Under the conditions studied, the tocopheryl anion was unstable and was transformed into a compound with an absorption maximum at 400—420 nm (Figure 1) which on the basis of literature data[2,3] was identified as the neutral free radical of tocopherol ($T^\bullet$).‡

As seen from Figure 1, the absorption maxima of α-tocopherol at 294 nm and of the tocopheryl anion at 323 nm decreased simultaneously (that apparently indicates that $k_2 \gg k_1$), their decrease being accompanied by an increase in the maximum of the neutral radical. As might be expected, the oxidation of the tocopheryl anion was accelerated by saturation of reaction mixture with oxygen. The subsequent fate of the radical $T^\bullet$ was not studied. In accord with literature data, it appears to be converted into α-tocopherol[2] or tocopherylquinone.[3]

The rate of reaction (1) was determined by following spectrophotometrically the disappearance of both reactants: superoxide ion (at 249 nm) and α-tocopherol (at 294 nm). The reaction was studied for the initial parts of kinetic curves to avoid the interference of reaction products and superoxide


(T) (T⁻)

(1)


(T•)

(2)

$$O_2^{-\bullet} + HOO^\bullet \longrightarrow O_2 + HOO^- \qquad (3)$$

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† For Part 4, see ref. 16.

‡ Under these conditions the e.s.r. spectrum of $T^\bullet$ was also obtained.[7]

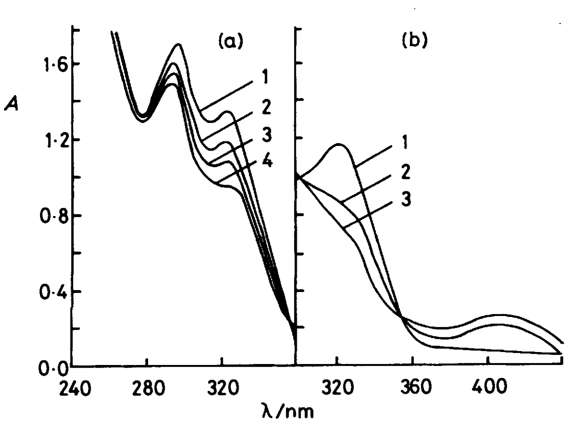


Figure 1. Reaction of $O_2^{-\bullet}$ with α-tocopherol: (a) $[O_2^{-\bullet}]_0$ 4.0 × 10^{-3}M, $[T]_0$ 3.8 × 10^{-3}M, 1—4 absorption spectrum 100, 265, 390, and 500 s after mixing the reactants; (b) $[O_2^{-\bullet}]_0$ 4.7 × 10^{-3}M, $[T]_0$ 2.2 × 10^{-3}M, 1—3 absorption spectrum 75, 160, and 250 s after mixing the reactants

ion repeatedly formed in reaction (2).* The k_1 values were calculated from equations (4) and (5). Here, A_{249} and A_{294} are

$$-dA_{249}/dt = 2k_1A_{249}[T] \quad (4)$$

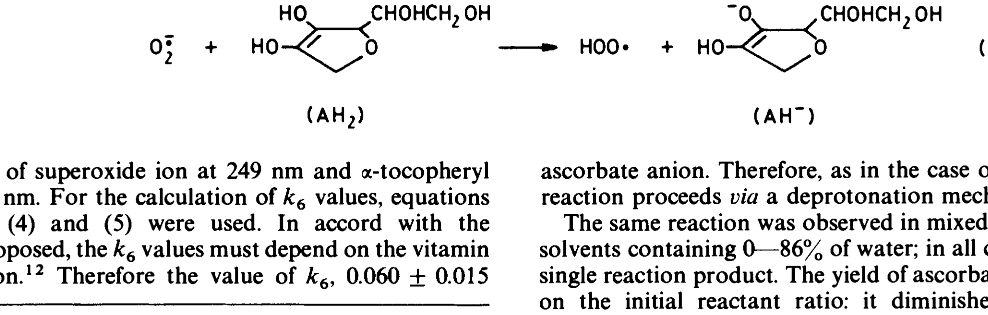
$$-dA_{294}/dt = 2k_1A_{294}[O_2^{-\bullet}] \quad (5)$$

the absorbances corresponding to the absorption maxima of $O_2^{-\bullet}$ and α-tocopherol. A factor of 2 takes into account reaction (3). (It is assumed that $k_3 \gg k_1$ as for reactions of $O_2^{-\bullet}$ with water and ethanol.[11])

It was found that the k_1 values calculated from equation (4) depend on the initial $[O_2^{-\bullet}]$:[T] ratio, whereas those calculated from equation (5) do not. From equation (5), k_1 = 0.59 ± 0.23 l mol^{-1} s^{-1}. The origin of this discrepancy will be discussed below.

Reaction of Superoxide Ion with α-Tocopheryl Acetate.—The interaction of superoxide ion with α-tocopheryl acetate was studied during the initial period when the maxima of reaction products were not yet observed. We suggested that as in reactions with other esters, $O_2^{-\bullet}$ splits off the ester group of vitamin E (such a two-step mechanism has been earlier proposed by us[12] for the reaction of $O_2^{-\bullet}$ with ethyl acetate).

The rate of reaction (6) was determined by following the disappearance of superoxide ion at 249 nm and α-tocopheryl acetate at 279 nm. For the calculation of k_6 values, equations analogous to (4) and (5) were used. In accord with the mechanism proposed, the k_6 values must depend on the vitamin E concentration.[12] Therefore the value of k_6, 0.060 ± 0.015 l mol^{-1} s^{-1}, can be used only for the studied interval of concentration of α-tocopheryl acetate (10^{-3}—10^{-4}M).



(6)

(7)

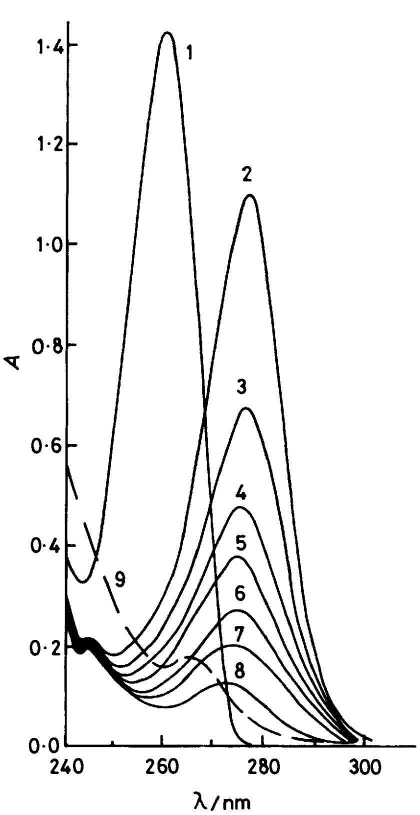


Figure 2. Reaction of $O_2^{-\bullet}$ with ascorbic acid: $[O_2^{-\bullet}]_0$ 6.3 × 10^{-4}M, $[AH_2]_0$ 8.9 × 10^{-4}M, 1 absorption spectrum of AH_2, 2—8 absorption spectrum 30, 100, 170, 220, 300, 370, and 480 s after mixing the reactants, 9 absorption spectrum after flushing the final solution with O_2

Reaction of Superoxide Ion with Ascorbic Acid.—Immediately after mixing of the acetonitrile solutions of $O_2^{-\bullet}$ and ascorbic acid (AH_2), the maxima of the reactants at 249 and 238.5 nm disappeared and a new maximum at 272 nm appeared (Figure 2). The same maximum was obtained in the reaction of ascorbic acid with NBu_4OH, so this compound can be identified as the ascorbate anion. Therefore, as in the case of α-tocopherol, the reaction proceeds *via* a deprotonation mechanism (7).

The same reaction was observed in mixed water–acetonitrile solvents containing 0—86% of water; in all cases AH^- was the single reaction product. The yield of ascorbate anion depended on the initial reactant ratio: it diminished with increasing $[O_2^{-\bullet}]_0$:$[AH_2]_0$. It was shown[6] that in aqueous solution $O_2^{-\bullet}$ reacts with AH^- with rate constant 5 × 10^4 l mol^{-1} s^{-1}. There-

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* The consumption of $O_2^{-\bullet}$ is 1—2% and that of α-tocopherol is 2—10%.

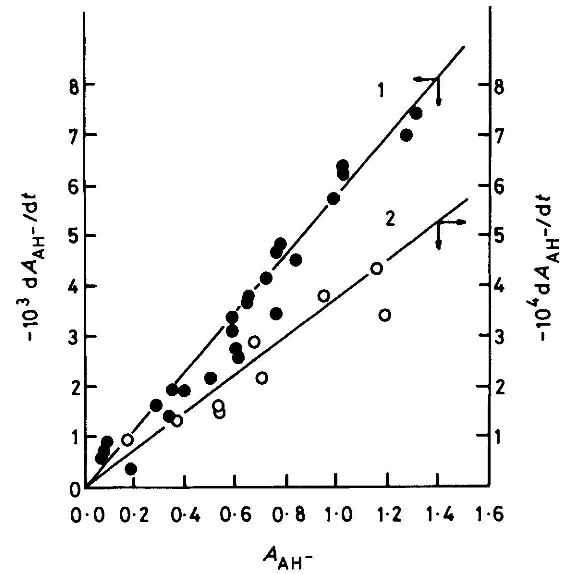

Figure 3. Oxidation of the ascorbate anion by dioxygen: 1 in acetonitrile, 2 in water

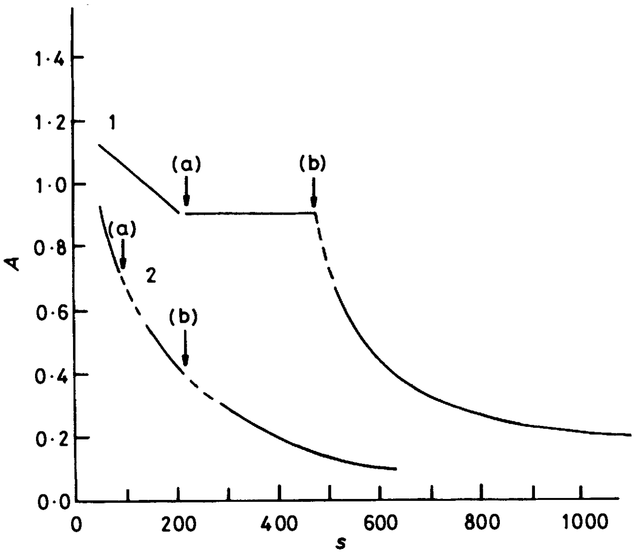

Figure 4. Kinetics of the AH$^-$ oxidation in water (1) and acetonitrile (2): (a) EDTA added; (b) FeCl$_3$ added

fore it may be suggested that the dependence of AH$^-$ yield on the $[O_2^{-\bullet}]_o$:$[AH_2]_o$ ratio is explained by the interaction of the AH$^-$ formed with excess of $O_2^{-\bullet}$. This suggestion was confirmed by the fact that AH$^-$ prepared from ascorbic acid and NBu$_4$OH reacted quantitatively with superoxide ion in acetonitrile.

Reaction of Ascorbate Anion with Dioxygen.—In acetonitrile the ascorbate anion is unstable under aerobic conditions (Figure 2). As the rate of AH$^-$ decay increased upon flushing the solution with dioxygen, one may assume that reaction (8)

$$AH^- + O_2 \longrightarrow AH\bullet + O_2^{\bar{\bullet}} \qquad (8)$$

was observed. We studied the autoxidation of the ascorbate anion in acetonitrile, water (at pH 6—10), and mixed water–acetonitrile solvents saturated with oxygen at room temperature. The reaction was studied by following spectrophotometrically the disappearance of AH$^-$. In all cases the disappearance of AH$^-$ was not accompanied by the appearance of any absorption bands. It was found that in both aqueous and acetonitrile solutions the initial rate of AH$^-$ decay depended linearly on [AH$^-$] (Figure 3). From equation (9) with [O$_2$] 1.15×10^{-3}M in water[13] and 8.5×10^{-3}M in acetonitrile,[14] we have $k_8 = 0.32 \pm 0.08$ l mol^{-1} s^{-1} for aqueous solution and $k_8 = 0.68 \pm 0.21$ l mol^{-1} s^{-1} for acetonitrile solution.

$$-dA_{AH^-}/dt = k_8 A_{AH^-}[O_2] \qquad (9)$$

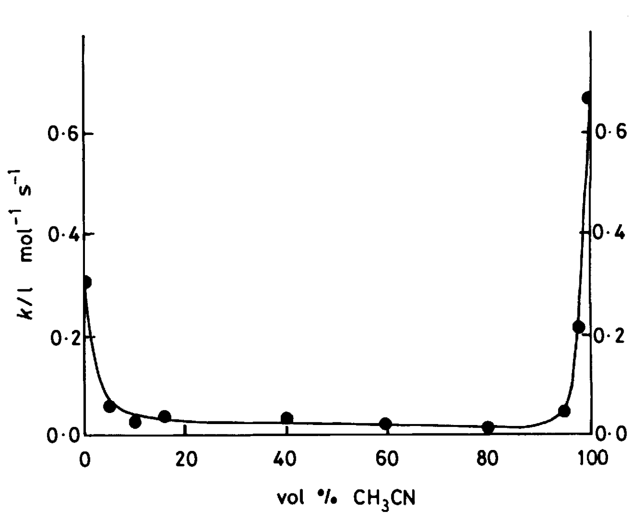

Figure 5. Dependence of the rate constant for AH$^-$ oxidation on the solvent composition

The oxidation rates of AH$^-$ in mixed water–acetonitrile solvents were considerably smaller than those in aqueous and acetonitrile solutions (Figure 5). (The oxygen concentrations in mixed solvents were calculated according with the additivity rule on the basis of the oxygen concentration in pure acetonitrile and water.) For elucidation of the mechanism of AH$^-$ oxidation we studied the effect of Fe^{3+} ion on oxidation rate. It was found that in aqueous solution the oxidation rate sharply increased in the presence of Fe^{3+} ion; on the other hand oxidation was completely inhibited by EDTA (Figure 4). Therefore one may suppose that the oxidation of the ascorbate anion in aqueous solution proceeds only with the participation of Fe^{3+} ion. Unlike the oxidation of AH$^-$ in aqueous solution, the rate of AH$^-$ decay in mixed solvents and acetonitrile solution was affected neither by Fe^{3+} ion nor by EDTA.

Discussion

Our results show that superoxide ion reacts with α-tocopherol and ascorbic acid *via* a deprotonation mechanism to form corresponding anions, *i.e.* in the same way as with other proton donors water and ethanol,[11] hydrogen peroxide,[15] and alkyl hydroperoxides.[15,16] Therefore we may conclude that although α-tocopherol and ascorbic acid are good radical scavengers, superoxide ion is not able to abstract a hydrogen atom from them.

In accord with our results and the data obtained by Nanni *et al.*,[8] the formation of a neutral radical in the reaction of $O_2^{-\bullet}$ with α-tocopherol is a two-step process. In the beginning the tocopheryl anion is formed *via* reaction (1), then it is oxidized by dioxygen into a neutral radical [reaction (2)]. There is no doubt that a fantastic mechanism such as the reduction of superoxide ion to O_2^{2-} by α-tocopherol[7] is impossible.

Nanni *et al.*[8] observed the formation of ascorbate anion in

$$O_2^{\cdot-} + AH_2 \longrightarrow HO\cdot + HO^- + A \tag{10}$$

$$O_2^{\cdot-} + AH_2 \longrightarrow A_2^{\cdot-} + H_2O_2 \tag{11}$$

$$AH_2 + O_2 \longrightarrow A + H_2O_2 \tag{12}$$

the reaction of $O_2^{-\cdot}$ with ascorbic acid, but in spite of this they concluded that a main direction of this process is the concerted two-hydrogen-atom transfer reaction (10). Later they gave preference to the more probable reaction (11) with the concerted transfer of a hydrogen atom and a proton.[10] This mechanism was proposed in order to explain the absence of dioxygen in the reaction mixture, as reaction (7) must be followed by reaction (3). It has been suggested[17] that reaction (11) occurs in both aprotic and aqueous media.

On the other hand we found that $O_2^{-\cdot}$ reacts with ascorbic acid to form ascorbate anion in 50—70% yield. As the quantitative yield of AH^- cannot apparently be achieved owing to the interaction of AH^- with $O_2^{-\cdot}$ and O_2, we believe that deprotonation [reaction (7)] is a main and perhaps the single pathway of the interaction of superoxide ion with ascorbic acid and that there is no need to consider the concerted processes (10) and (11).

Now we may discuss the kinetic data obtained. The k_1 value obtained in this work for the reaction of $O_2^{-\cdot}$ with α-tocopherol in acetonitrile (0.59 ± 0.29 l mol^{-1} s^{-1}) is in agreement with the estimate made by Arudi *et al.*[3] for this reaction in aqueous solution (<6 ± 3 l mol^{-1} s^{-1}). It is difficult to understand why k_1 values of 10^2—10^5 l mol^{-1} s^{-1} were obtained in refs. 1, 2, 8, and 9. We found that in acetonitrile the k_1 values calculated on the basis of $O_2^{-\cdot}$ consumption increased to 7 l mol^{-1} s^{-1} with an increase in the excess of $O_2^{-\cdot}$. This is apparently explained by the fact that in an excess of $O_2^{-\cdot}$ the interaction of superoxide ion with chromanoxyl radical and tocopherylquinone begins to play an important part.

However, in the work referred to, the reaction was studied with an excess of α-tocopherol; at any rate the difference between our and literature data is certainly too large to be accounted for by such effects. It should be noted that we used freshly prepared α-tocopherol. It is possible that tocopherylquinone can accumulate in samples of α-tocopherol during storage which will greatly increase the decay rate of superoxide ion.

With the experimental technique used, it was impossible to determine the rate constants for the reaction of superoxide ion with ascorbic acid. Sawyer *et al.*[10] found that this rate constant is equal to 2.8 ± 0.3 × 10^4 l mol^{-1} s^{-1} in DMF. Contrary to their conclusion, we believe that this value corresponds to reaction (7) and not (11).

Mechanism of the Oxidation of Ascorbic Acid by Dioxygen.— Yamazaki and Piette[18] did not find superoxide ion at the autoxidation of ascorbic acid in neutral and alkaline solutions. On these grounds they proposed a two-electron mechanism of autoxidation. However, using superoxide dismutase (an enzyme that catalyses the disproportionation of superoxide ion) it has later been shown[19,20] that $O_2^{-\cdot}$ does form in this process. Khan and Martell[21] have studied metal- and metal-chelate catalysed oxidation of ascorbic acid by dioxygen. They showed the following important features of the process: (1) the oxidation rate for the neutral non-dissociated form of ascorbic acid is close to zero; (2) catalytic oxidation proceeds to form the intermediate metal–ascorbate–dioxygen complex in the case of metal catalysis and the intermediate metal chelate–ascorbate complex in the case of metal chelate catalysis.

We found that the rate of AH^- oxidation in aqueous solution

In aprotic media

$$O_2^{\cdot-} + AH_2 \longrightarrow HO_2\cdot + AH^- \tag{7}$$

$$AH^- + O_2 \rightleftharpoons AH\cdot + O_2^{\cdot-} \tag{8}$$

$$O_2^{\cdot-} + AH^- \longrightarrow \text{transient product} \tag{13}$$

$$O_2^{\cdot-} + HO_2\cdot \longrightarrow O_2 + HO_2^- \tag{3}$$

$$HO_2\cdot + AH_2 \longrightarrow H_2O_2 + AH\cdot \tag{14}$$

$$HO_2\cdot + AH^- \longrightarrow H_2O_2 + A^{\cdot-} \tag{15}$$

$$HO_2\cdot + AH\cdot \longrightarrow H_2O_2 + A \tag{16}$$

$$HO_2\cdot + A^{\cdot-} \longrightarrow HO_2^- + A \tag{17}$$

In aqueous solution

$$O_2^{\cdot-} + AH_2 \longrightarrow HO_2\cdot + AH^- \tag{7}$$

$$\text{or } AH_2 \rightleftharpoons AH^- + H^+ \; * \tag{18}$$

$$O_2^{\cdot-} + H^+ \longrightarrow HO_2\cdot \tag{19}$$

$$AH^- + O_2 \xrightleftharpoons{Fe^{3+}} \text{complex } (A^{\cdot-} + HO_2\cdot\ ?) \tag{20}$$

$$O_2^{\cdot-} + AH^- \longrightarrow \text{transient product} \tag{13}$$

$$O_2^{\cdot-} + A^{\cdot-} \xrightarrow{H^+} A + HO_2^- \tag{21}$$

$$O_2^{\cdot-} + HO_2\cdot \longrightarrow O_2 + HO_2^- \tag{3}$$

$$HO_2\cdot + AH_2 \longrightarrow H_2O_2 + A^{\cdot-} + H^+ \tag{22}$$

$$HO_2\cdot + AH^- \longrightarrow H_2O_2 + A^{\cdot-} \tag{15}$$

$$HO_2\cdot + A^{\cdot-} \longrightarrow HO_2^- + A \tag{17}$$

Scheme.

was independent of pH (at pH 6—10). Our k_8 value for aqueous solution (0.32 ± 0.08 l mol^{-1} s^{-1}) is close to k_8 0.568 l mol^{-1} s^{-1} obtained in ref. 21 for uncatalysed oxidation (taking into account the different experimental techniques based on determining AH^- consumption and the rate of the formation of dehydroascorbic acid). But as the AH^- oxidation in aqueous solution is completely inhibited by EDTA (Figure 4), in accord with the data of Rigo *et al.*[20] only catalytic oxidation of ascorbic acid can occur under these conditions.

There is another disagreement between our and the Khan–Martell[21] data. These authors found that the catalytic activity of Fe^{3+}–EDTA complex in AH^- oxidation is close to that of free Fe^{3+} ion (the corresponding rate constants are 1.8 × 10^3 and 6.4 × 10^3 l mol^{-1} s^{-1}). But in this case it is difficult to understand why the addition of EDTA should inhibit the AH^- oxidation. Far more activity by Fe^{3+} ions (in comparison with Fe^{3+}–EDTA complexes) is evident from a sharp increase in oxidation rate after the addition of Fe^{3+} ion (Figure 4).

We found that the catalytic oxidation of ascorbate proceeds only in pure water; in all mixed solvents and pure acetonitrile neither EDTA nor Fe^{3+} ion affect the rate of autoxidation. The rate constants for ascorbate oxidation remain small almost up to 95% content of acetonitrile when they sharply increase. Therefore it may be supposed that in pure acetonitrile another mechanism for ascorbate oxidation is realized, namely direct one-electron transfer [reaction (8)].

We believe that transmission from the Fe^{3+}-catalysed reaction in pure water to the uncatalysed one-electron transfer

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* A referee commented that reactions (18) and (19) describe the deprotonation of ascorbic acid by $O_2^{-\cdot}$ (in aqueous solution) better than reaction (7).

in pure acetonitrile can be explained by a change in the solvation of the ascorbate anion. It might be expected that the ascorbate anion solvated by water molecules is not able to transfer an electron directly to dioxygen, and therefore this reaction can take place only in the absence of water. In contrast, acetonitrile apparently forms an unreactive complex with Fe^{3+} ion and this inhibits the catalytic process. Therefore both mechanisms of ascorbate oxidation are suppressed in all water–acetonitrile solvents (Figure 5).

Now all stages of the interaction of ascorbic acid with superoxide ion and dioxygen can be written (Scheme). As is seen, the mechanisms in aprotic media and aqueous solution mainly differ by stages (8) and (20) and by different structure of ascorbate radical ($AH^{\bullet}$ in aprotic media and $A^{-\bullet}$ in water). The mechanism in aqueous solution differs from the Cabelli and Bielski mechanism[6] only by excluding reaction (11) and including reactions (7) and (20). As the rate constants for radical disproportionation reactions (16), (17), (21), and (3) are much greater than those for stages (7), (8), and (20), AH^- and A are single products which can be readily observed.

Experimental

Materials.—α-Tocopherol of 97.3% purity was obtained by the condensation of 2,3,5-trimethylhydroquinone with isophytol.[22] α-Tocopheryl acetate (98.3% purity) and pharmaceutical ascorbic acid (99.6% purity) were used without purification. Acetonitrile was dried by refluxing over P_2O_5 and was distilled over anhydrous potassium carbonate.

Reactions of Superoxide Ion with α-Tocopherol, α-Tocopheryl Acetate, and Ascorbic Acid.—Solutions of superoxide ion in acetonitrile were prepared by the electrochemical reduction of oxygen, as described earlier.[23,24] The supporting electrolyte was tetrabutylammonium perchlorate, which was obtained from tetrabutylammonium hydroxide and perchloric acid. The cell had a mercury cathode and a platinum anode. The anode and cathode compartments were separated by a cock. Solutions of superoxide ion were freshly prepared prior to each experiment. After argon flushing the $O_2^{-\bullet}$ solutions were transported in a quartz cell under argon. The reactions were carried out in the 1 and 2 mm cells of a Cary 218 spectrophotometer at room temperature.

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