only one, sharp Si–CH_3 resonance line is observed for the labile isomer at -53.7°, which is the result predicted for the *cis* enol ether structure. The ability of the *cis* isomer to undergo a rapid rearrangement which leads to environmental averaging of nonequivalent acetylacetonate methyl groups is attributed to the facile formation of a five-coordinated silicon intermediate, as shown in Schemes I and II. A similar process for the *trans* isomer should be hindered by rotation about the C=C bond. Indeed, no broadening of the acetylacetonate methyl lines for the *trans* isomer was observed even at 120°.

Mean lifetimes for the methyl protons in the two, equally populated, nonequivalent sites of the *cis* isomer were estimated at five temperatures in the range 20–40° from the fast-exchange approximation of Piette and Anderson.[5] No change in mean lifetimes was observed on doubling the solute concentration in chlorobenzene. Also, a solution containing $(CH_3)_3Si(acac)$ and free acetylacetone in relative amounts 3:1 showed no broadening of the free ligand methyl line under conditions where rearrangement of the *cis* isomer is fast. These results, which indicate that the rearrangement is first order and that an intramolecular mechanism operates, are in agreement with the processes shown in Schemes I and II. Values of first-order rate constants for the five temperatures investigated gave an estimated Arrhenius activation energy of 15 ± 4 kcal/mole and a frequency factor of $\exp(14.3 \pm 3.0)$. A more detailed nmr line-shape analysis of the rearrangement kinetics is in progress.

Acknowledgment. We wish to acknowledge support of this research by the National Science Foundation, Grant GP-9503.

(5) L. H. Piette and W. A. Anderson, *J. Chem. Phys.*, 30, 899 (1959), eq 23.

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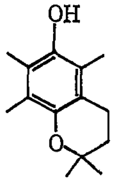
Anodic Alkyl Transfer from Hydroquinone Ethers. II.[1] Anodic Oxidation of an α-Tocopherol Model Compound

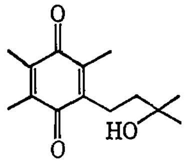
Sir:

We report the first case of a reversible two-electron oxidation of a phenol in aprotic media. The α-tocopherol model compound (I) undergoes quasi-reversible oxidation at a platinum electrode in acetonitrile. A 1.0 mM solution of I in acetonitrile exhibits an oxidation peak at +0.76 V[2] at a stationary platinum electrode. The peak current at a voltage sweep rate of 10 V/min is 170 μA. Two well-characterized one-electron oxidation systems, 9,10-diphenylanthracene[3a] and 4,4′-dimethoxystilbine,[3b] give peak currents of 90 and 93 μA, respectively, under the same conditions. Therefore, the oxidation of I involves the transfer of two electrons.[4] When the direction of the potential scan is switched in the cathodic direction after the initial anodic peak, a reduction peak is observed at +0.60 V. The ratio of cathodic to anodic peak currents, i_{pc}/i_{pa}, was determined to be equal to 0.78, indicating that the dication is fairly stable during the time scale of cyclic voltammetry.



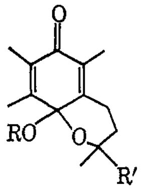
I

Controlled potential coulometry of I in either acetonitrile or acetonitrile–acetic acid (3:1) containing sodium acetate (0.25 M) resulted in the consumption of 2 Faradays per mole of substrate. A preparative electrolysis in the latter media resulted in the formation of the quinone II. The structure of II was established on the basis of ir, nmr, and mass spectra as well as from a voltammetric study.



II

Chemical oxidation of I with alkaline ferricyanide or benzoquinone results in the formation of a spiro dimer thought to form *via* the quinone methide.[5] α-Tocopherol oxidation in ethanol[6] or dry acetonitrile containing acetate ion[7] results in the formation of the corresponding dienone III. The latter observations have been cited as evidence that the cyclic hemiacetal IIIc is an intermediate in the chemical oxidation of α-tocopherol to α-tocopherylquinone. The direct formation of II, rather than IIIb, when the oxidation is carried out in the presence of high acetate concentration is indicative that the anodic generation of the quinone does not involve hemiacetal formation. However, it has been observed that the oxidation of α-tocopherol in the presence of a small amount of water in aprotic media containing a large excess of acetate ion results only in the formation of IIIc.[7] Further study is necessary to clarify this point.



IIIa, R = Et
b, R = Ac
c, R = H

The quinone II is reduced at −0.56 V (R_1) in acetonitrile containing lithium perchlorate. When the potential sweep is reversed after R_1, a corresponding oxida-

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[1] Part I: V. D. Parker, *Chem. Commun.*, 610 (1969).

[2] All potentials refer to the aqueous saturated calomel electrode.

[3] (a) M. E. Peover and B. S. White, *J. Electroanal. Chem.*, 13, 93 (1967); (b) V. D. Parker and L. Eberson, *Chem. Commun.*, 340 (1969).

[4] While the over-all result of the oxidation is the transfer of two electrons, the detailed mechanism may involve two closely spaced one-electron steps.

[5] J. L. G. Nilsson, *Acta Pharm. Suecica*, 5, 1 (1969).

[6] P. D. Boyer, *J. Amer. Chem. Soc.*, 73, 733 (1951).

[7] W. Durckheimer and L. A. Cohen, *ibid.*, 86, 4388 (1964).

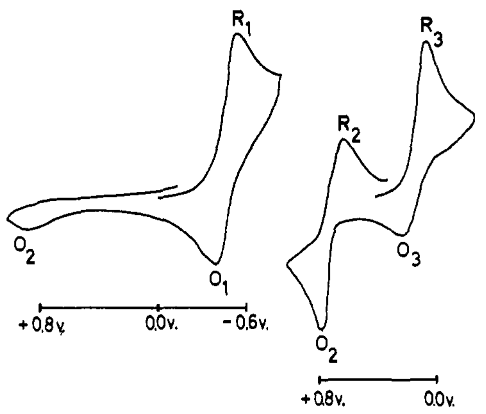


Figure 1: Cyclic voltammogram of α-tocopherylquinone model compound (II) in acetonitrile: (a) in the absence of acid; (b) with 2 equiv of perchloric acid. $LiClO_4$ = 0.1 *M*, voltage sweep rate = 10 V/min.

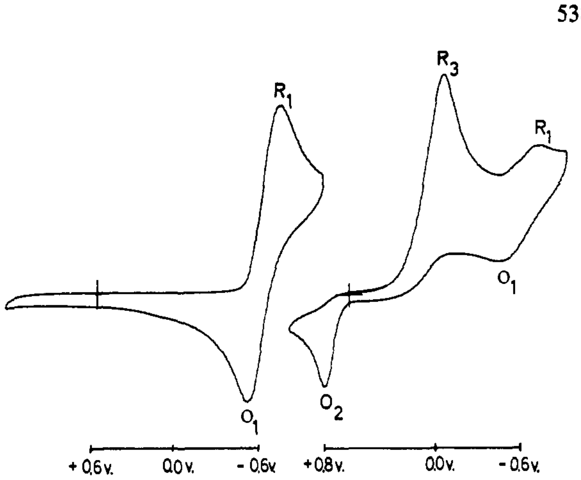
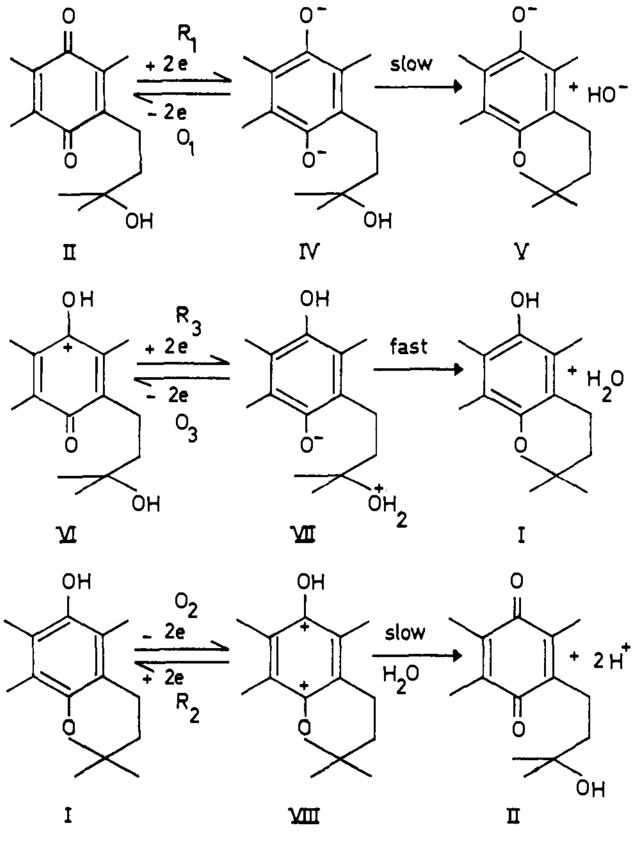


Figure 2. Cyclic voltammogram of tetramethyl-*p*-quinone in acetonitrile: (a) in the absence of acid; (b) with 2 equiv of perdhloric acid. $LiClO_4$ = 0.1 *M*, voltage sweep rate = 10 V/min.

tion peak, O_1, is observed at −0.36 V and a very small oxidation peak, O_2, is observed at +0.8 V (Figure 1). Addition of 2 equiv of perchloric acid results in the observation of a new cathodic peak, R_3, at +0.04 V and nearly eliminates the redox couple, R_1–O_1 (Figure 2).[8a] The oxidation peak, O_2, is greatly enhanced and a reduction peak, R_2, is observed. The redox couple, R_2–O_2, matches that observed during the oxidation of I. The cyclic voltammogram does not reveal the presence of the hydroquinone.[8b] We conclude that in the absence of acid, the quinone dianion IV[10a,b] cyclizes very slowly, if at all, and is stable during the time scale of cyclic voltammetry, while in the presence of acid, the monoanion resulting from two-electron reduction of the protonated quinone rapidly cyclizes to I. The processes occurring at each of the voltammetric peaks are summarized in Scheme I. Structure VI is written as a convenient representation of the protonated quinone, but is not meant to imply knowledge of the actual structure. Figure 2, showing the cyclic voltammogram of tetramethyl-*p*-benzoquinone, is included to show the behavior of a structurally similar quinone which cannot undergo the cyclization reaction.

Scheme I



The anodic oxidation of I is formally similar to the oxidation of α-tocopherol by a variety of metal ion oxidants in which an intermediate dienone cannot be detected by uv spectroscopy[7] and thus a dication may also be an intermediate in these chemical oxidations. Oxidations by tetrachloroquinone and N-bromosuccinimide, during which the intermediate dienone is detectable,[7] proceed by a different mechanism which could conceivably involve hydroxylation of the cation radical, an intermediate of a one-electron oxidation.

A detailed study of electrolytic oxidation and reduction of the tocopherol–tocopherylquinone system and related model compounds is under way. This approach is expected to produce valuable insight into the biological interconversion of these compounds.

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(8) (a) The reduction peak, R_3, most likely involves reduction of the protonated quinone;[9] both R_3 and O_2 have been shown to involve two-electron transfers in similar systems.[9] (b) The quinone–hydroquinone couple is irreversible in acetonitrile.[9]

(9) B. R. Eggins and J. Q. Chambers, *Chem. Commun.*, 232 (1969).

(10) (a) Previous studies[10b] have shown that quinones undergo one-electron reduction in acetonitrile; however since the peak current for the two-electron[9] reduction of the protonated quinone (R_3) is almost the same as that of R_1, it is conceivable that a two-electron reduction occurs in this case; (b) M. E. Peover, *J. Chem. Soc.*, 4540 (1962).