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MICELLAR CATALYSIS IN THE BASE—CATALYZED AUTOXIDATION OF DIOSPHENOL

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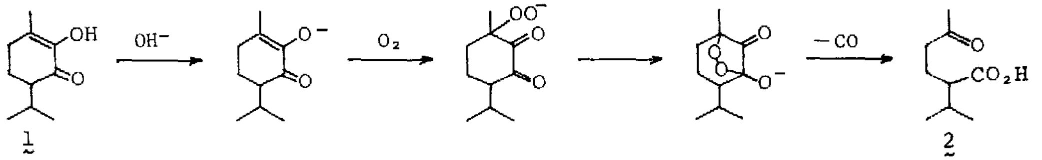
Abstract: The base-catalyzed autoxidation of diosphenol was catalyzed by cationic micelles with a remarkable selectivity to give an 1,5-keto acid by a mechanism analogous to the oxygenation of quercetin or 3-hydroxyflavones.

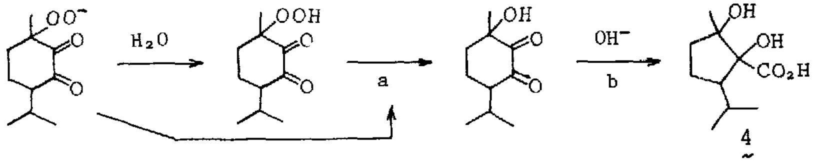
Here we report that the base-catalyzed autoxidation of diosphenol (**1**) to 2-isopropyl-5-oxohexanoic acid (**2**) can be accelerated with a remarkable selectivity by cationic micelles[1] by a mechanism analogous to the biological oxygenation of quercetin or 3-hydroxyflavones.[2] The autoxidation (eq 1) was carried out by vigorous stirring of aqueous 2 M NaOH solution (15 ml) containing 1 (0.32 g) and dedecyltrimethylammonium chloride (LTMAC) (0.31 g, 0.08 M)[3] at 25—30 °C under an oxygen atmosphere. The oxygen absorbed and carbon monoxide evolved, as shown in Figure 1, were determined by GC (molecular sieves, He).

In the presence of LTMAC, the absorption and evolution of the gases ceased virtually after 7 h (49 ml for O_2 and 44 ml for CO; the volume equimolar with 0.32 g of **1** is 47 ml). After usual extraction with ether,[4] **2** was obtained in 76% yield together with 2,6-dimethyl-5-oxoheptanoic acid (**3**) in 11%, being only accompanied by traces of by-products (HPLC, silica gel, n-hexane—ether).[5] The acid **3** can be taken as a similar oxidation product from isodiosphenol which was isomerized from **1** in the basic solution. The gas and product analyses suggest that one mole of the anion of **1** absorbed one mole of oxygen to give **2** and carbon monoxide each one mole. The mechanism of eq 1 has an analogy.[2]

In the absence of LTMAC, oxygen was absorbed up to 75 ml, the volume being 1.6 times as large as that equimolar with **1**, while carbon monoxide was evolved only half as small as the volume equimolar with **1** (Figure 1). The products were **2** (47%), **3** (9%), and several acidic by-products (—35%).[6] Interestingly the total



(1)



(2)

yield (56%) of **2** and **3** corresponded well to the volume (23 ml) of carbon monoxide evolved. This fact suggests that the acidic by-products were formed without decarbonylation. At least four components were found to exist and main two of them were isolated by HPLC, being tentatively identified as two stereoisomers of **4** by IR, ^{1}H and ^{13}C NMR, and high-resolution mass spectra.[7] The formation of **4** is possibly indicated by eq 2, where the step a is disproportionation[8] and the step b is benzilic acid-type rearrangement in the basic solution.

Such catalysis by micelles (eq 1 vs. eq 2) may be understood in terms of a hydrophobic environment in the micelle which enhances the activity of the peroxy anion to cyclize intramolecularly but prevents the formation of the hydroperoxide by repelling water molecules. The rate acceleration can be attributable to both the enhanced reactivity of the carbanion and the enhanced solubility[9] of oxygen gas in the micellar phase.

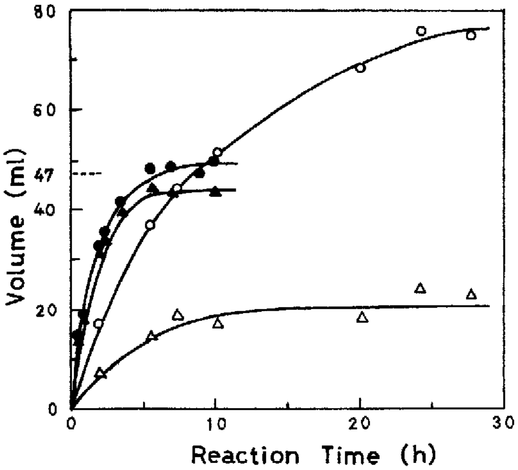


Figure 1. Plots of volumes of oxygen absorbed and carbon monoxide evolved vs reaction time. ●, O_2 absorbed and ▲, CO evolved in the presence of LTMAC. ○, O_2 absorbed and △, CO evolved in the absence of LTMAC.

References and Notes

1. Hitherto, autoxidations in micellar systems have rather been limited to the oxidation of aldehydes or linoleic acid using nonionic surfactants. See F. H. Fendler, E. J. Fendler, "Catalysis in Micellar and Macromolecular Systems", Academic press, New York, N. Y., L975, Chapter 8.
2. T. Matsuura, H. Matsushima, H. Sakamoto, *J. Am. Chem. Soc.*, **89**, 6370 (1967); A. Nishinaga, T. Tojo, T. Matsuura, *J. Chem. Soc. Perkin I*, 1979, 2511.
3. The cmc of LTMAC was reported to be 0.0095 M in the presence of 0.05 M NaCl by M. F. Emerson, A. Holtzer, *J. Phys. Chem.*, **71**, 1898 (1967).
4. When hexadecyltrimethylammonium bromide (CTMAB) was used as surfactant, separation of the aqueous and the organic layers became practically difficult.
5. The acids **2** and **3** were identified by IR, ^{1}H and ^{13}C NMR, and mass spectra after isolation. Similar results were obtained by using CTMAB. When the reaction was carried out under a nitrogen atmosphere in the presence of LTMAC, yields of **2** and **3** were negligibly small.
6. The yield (—35%) of by-products was calculated by assuming their average molecular weight being equal to that of **2**.
7. The authors are indebted to Dr. K. Kawazu of the Department of Agricultural Chemistry for recording of high-resolution mass spectra.
8. Y. Sprinzak, *J. Am. Chem. Soc.*, **80**, 5449 (1958).
9. F. M. Menger, *J. Phys. Chem.*, **83**, 893 (1979).

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