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MECHANISM OF SELECTIVE p-QUINOL FORMATION IN THE COBALT SCHIFF BASE COMPLEX-CATALYZED OXYGENATION OF 4-ALKYL-2,6-DI-t-BUTYLPHENOLS

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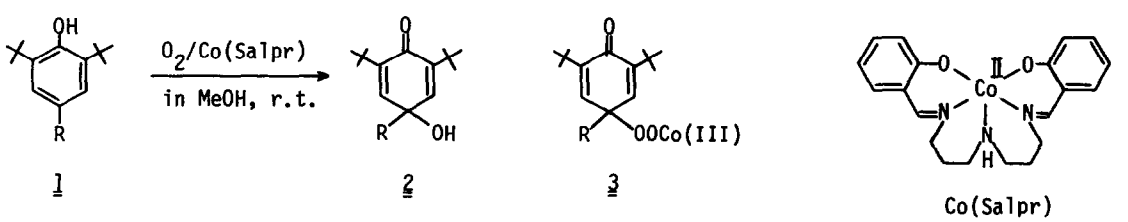
The selective formation of p-quinols in the Co(Salpr)-catalyzed oxygenation of 4-alkyl-2,6-di-t-butylphenols in MeOH has been found to involve the rate determining reduction of peroxy-p-quinolato Co(III) complex formed in the initial fast step. An ionic mechanism of the reduction of the O-O bond in the peroxy complex by MeOH has been discussed based on kinetic studies. The reactive species in the catalytic cycle is found to be [Co(III)(Salpr)(OH)].

The oxygenation of organic substances catalyzed by transition metal complexes which are able to interact reversibly with dioxygen is of particular interest in connection with organic synthesis and biological oxidations.[1] A pentadentate cobalt(II) Schiff base complex, Co(Salpr), has been found to catalyze the oxygenation of 4-alkyl-2,6-di-t-butylphenols (1) in MeOH leading to the selective formation of the corresponding p-quinols (2).[2] The peroxy-p-quinolato Co(III) complex (3) has been postulated to be the key intermediate in this reaction[2] and found to be stoichiometrically formed in quantitative yield when the oxygenation of 1 is carried out with Co(Salpr) derivatives in aprotic solvents.[3] In this communication, we report the mechanism of the inter-



1 2 3 Co(Salpr)

a; R = Me b; R = Et c; R = i-Pr d; R = t-Bu Co(III); Co(III)(Salpr)

esting catalytic p-quinol formation from 1

The time course of O_2-uptake and product analysis in the Co(Salpr)-catalyzed oxygenation of 1a in MeOH show that the reaction involves the rapid formation of the peroxy complex 3a in the initial step followed by the slow formation of 2a (Figure 1). The O_2-uptake corresponds to the formation of 3a and 2a which was isolated quantitatively from the final reaction mixture. When the catalysis is carried out with the peroxy complex 3a, the time dependent O_2-uptake gave a proportional straight line with nearly the same slope ($k = 1.8 \times 10^{-3}$ min^{-1}) as that observed for the slow step in the catalysis with Co(Salpr) ($k = 1.5 \times 10^{-3}$ min^{-1}) (Figure 1).[4] These facts clearly indicate that the peroxy complexe 3a is the intermediate in the Co(Salpr)-catalyzed p-quinol formation from 1a. The peroxy complexes 3 are fairly stable in aprotic solvents but found to be easily reduced in alcohols quantitatively to give 2 and Co(III)(Salpr)(OH), which is isolated and characterized by its analytical and spectral data. When the reduction of 3a was carried out with an excess of benzyl alcohol in CH_2Cl_2 at 10 °C for 20 h, benzaldehyde was obtained in 97% yield (based on the conversion of 3a (37%) as determined by GLC).

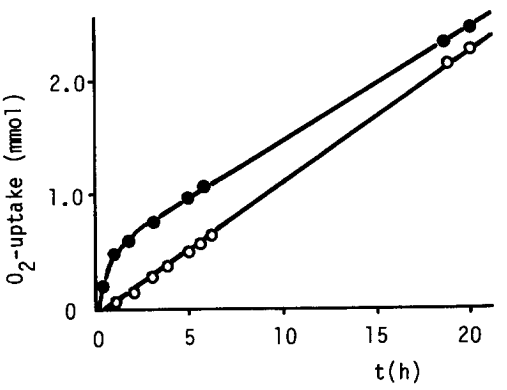


Figure 1. Time course of the O_2-uptake in the catalytic p-quinol formation from 1a with Co(Salpr) (-●-) and 3a (-○-). [1] = 0.1 M; [Co(Salpr)] = 0.02 M; [3a] = 0.02 M in MeOH (50 ml) at 20 ± 0.2 °C: P_{O_2} = 780 mmHg.

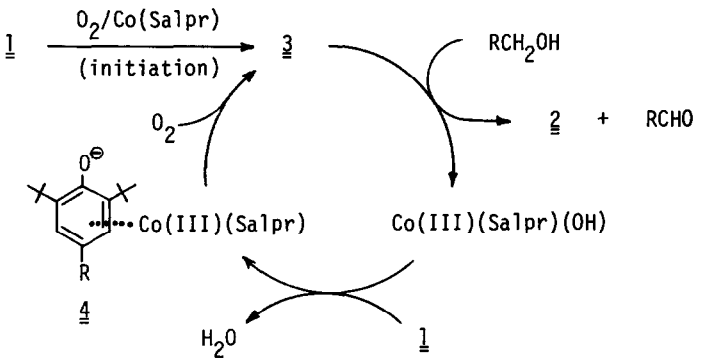
The rate of the reduction of 3a in MeOH is found to follow pseudo first order kinetics up to the 85% conversion with a rate constant, $k = 1.4 \times 10^{-3}$ min^{-1} at 20 °C,[5] which is practically the same as those described above. The peroxy complexes 3 are, therefore, reasonably considered to be reduced directly by alcohols but not by a bimolecular reaction between 3 and the corresponding hydroperoxide obtainable by an acid-base equilibrium,[3] although the latter mechanism has been argued for base-catalyzed decomposition of hydroperoxides to the corresponding alcohols.[6]

Thus, the following stoichiometry can be depicted for the reduction of 3 with alcohols.

$$3 + RCH_2OH \longrightarrow 2 + Co(III)(Salpr)(OH) + RCHO$$

Since Co(III)(Salpr)(OH) reacts with 1 rapidly to give the corresponding phenolato Co(III)

complex (4) into which O_2 is incorporated giving 3 [3] and shows the same catalytic activity as 3 itself, it should be the actual reactive species in the Co(Salpr)-catalyzed p-quinol formation from 1. From all these findings the following mechanism can reasonably be described.



The formation of 2 from 3 obviously involves a reductive cleavage of the O-O bond in 3. Among three possible mechanisms for the reductive cleavage, a concerted hydrogen transfer mechanism is the most probable.[7] This mechanism is supported by the isotopic effect of methanol on the reaction rate: pseudo first order rate constants in CH_3OH, CH_3OD, and CD_3OD were 1.8×10^{-4}, 9.7×10^{-5}, and 7.9×10^{-5} min^{-1} (10 °C), respectively (k_H/k_{D_1} = 1.8 and k_H/k_{D_4} = 2.3). The results indicate that both of the hydroxy and α-hydrogen groups participate in the rate determining step. The rate of the reduction of 3a also depends on the nature of the alcohol used (Table 1). As seen from Table 1, the reaction is affected by the acidity

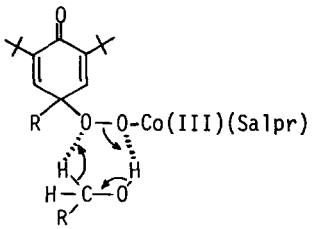


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Table 1. Pseudo First Order Constants for the Reduction of 3a with Various Alcohols.[a]

Alcohol	$k(X10^4)$ min^{-1}
CCl_3CH_2OH	5.8
MeOH	1.8
EtOH	1.1
i-PrOH	0.5
t-BuOH	~ 0
$PhCH_2OH$	3.5
Ph_2CHOH	0.8

[a] [3a]=0.01 M in ROH(4 ml) + CH_2Cl_2(6 ml), 10 °C.

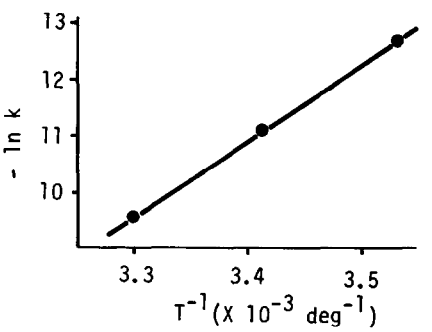


Figure 2. Arrhenius plot for the reduction of 3a with MeOH.

of hydroxy group, the transferability of α-hydrogen, and the steric nature of the alcohol used. These findings are also in accord with the mechanism 5. The Arrhenius plot gave the activation energy of the reduction of 3a with MeOH to be ca. 27 kcal/mol (Figure 2).

In contrast with 3, the corresponding peroxy-p-quinols are fairly stable in alcohols. The reactivity of 3 may result from an anionic nature of the peroxy group in 3. Thus, the hydrogen bonding between the coordinated peroxy anion and the hydroxy group in the alcohols accelerates the reaction as shown in 5. The present results provide a new finding in the organic peroxide reaction mechanism.

References and Notes

(1) Abstracts, First International Symposium on O_2 Activation and Selective Oxidations Catalyzed by Transition Metals, Bendor, France, May, 1979, p 1.

(2) A. Nishinaga, K. Watanabe, and T. Matsuura, Tetrahedron Lett., 1291 (1974).

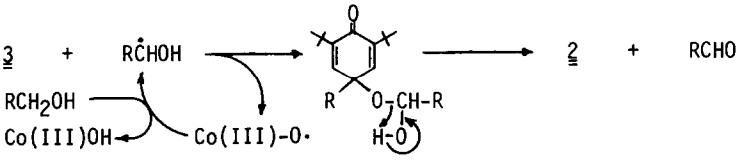
(3) A. Nishinaga, H. Tomita, and T. Matsuura, Tetrahedron Lett., 2893 (1979).

(4) The slight difference between the two slopes may result from errors in the reguration of reaction temperature.

(5) Determined by the iodometry of 3a in aliqotes during the course of the reaction.

(6) R. Hiatt,"Organic Peroxides," Vol. 2, D. Swern, Ed., Wiley-Interscience, New York, London, Sydney, Tronto, 1971, p 1.

(7) Other possible mechanisms include (i) homolysis of the O-O bond followed by the hydrogen abstraction by the resulting quinoxy radical from alcohols, which can, however, be ruled out because the quinoxy radical has been known to undergo ring expansion efficiently to give seven membered oxepinone derivatives[8] which are not detectable at all in the present reaction and (ii) a more attractive radical induced chain mechanism (the following scheme), which can



also be ruled out because the peroxy complexes 3 are quite stable in ethers including benzyl methyl ether favorable for the hydrogen abstraction. Furthermore, the reduction is not hindered by radical trapping agents.

(8) A. Nishinaga, K. Nakamura, and T. Matsuura, Tetrahedron Lett., 3557 (1978).

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