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CORRELATION OF CATALYTIC ACTIVITY OF METAL IONS IN AUTOXIDATION OF 1,2-DIHYDROXYNAPHTHALENE-4-SULFONATE AND STABILITY CONSTANT OF METAL COMPLEXES

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The catalytic activities of 9 metal ions in the autoxidation of potassium salt of 1,2-dihydroxynaphthalene-4-sulfonate in aqueous solution were measured. All the metal ions including the first transition metals were found to accelerate the autoxidation. The catalytic activities of the metal ions were correlated with the stability constants of the substrate-metal ion complexes.

It is well known that some metal ions catalyze the autoxidation of dihydroxy compounds, such as ascorbic acid (Vitamin C),[1-3] hydroquinones,[4,5] catechols,[6,7] and acetoin[8] in aqueous solution. Among these compounds, the oxidation of ascorbic acid catalyzed by cupric ion has been studied by many workers. As the results of the kinetic studies, two different mechanisms, free radical mechanism[1,3] and O_2-complex mechanism[2,9] have been proposed for the ascorbic acid oxidation.

However, the role of metal ions in the catalytic autoxidation of the dihydroxy compounds is still not completely elucidated. In other words, it is not clarified what kinds of properties of the metal ions are responsible for the catalytic activity. In the present study, the catalytic activities of 9 metal ions in autoxidation of 1,2-dihydroxynaphthalene-4-sulfonate in aqueous solution were measured and correlated with the stability constants of metal ion-substrate complex.

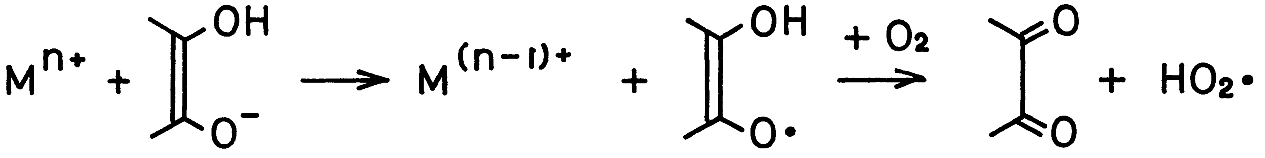
Experimental Potassium salt of 1,2-dihydroxynaphthalene-4-sulfonate [I] was synthesized according to the literature.[10] Elemental analysis: Found, K 14.11%; Calcd for $C_{10}H_7O_5SK$, K 14.04%. IR(KBr): $\nu_{\text{O-H}}$ 3070, 3250, $\nu_{\text{C-O}}$ 1155, $\delta_{\text{O-H}}$ 1340, $\nu_{s\text{SO}_2}$ 1040, $\nu_{\text{S=O}}$ 670cm^{1}.

The apparatus for measuring the rate of oxygen uptake is the same as that described elsewhere.[11] All reactions were carried out at 30.00±0.05°C in 100 ml of 0.1M acetate buffer solution (pH 4.45) containing 0.1M sodium perchlorate. The initial concentration of [I] and a metal ion were 0.01M. The metal salts used were acetates of Cu(II), Pb(II), Ni(II), Co(II), Zn(II), and Mn(II), sulfates of Cd(II) and Mg(II), and ammonium sulfate of Fe(II).

The reaction product of non-catalyzed and metal ion-catalyzed autoxidation of [I] was identified as the corresponding quinone by dropping mercury electrode polarography ($E_{\frac{1}{2}}$=0.11±0.03V vs SCE) and UV spectroscopy (λmax=251mμ). The yield of the 1,2-quinone were almost quantitative, except for Fe(II).

Since the time course of the oxygen uptake of [1] generally gave S-shaped curves, the maximum rate of the oxygen uptake (Rmax) was used as a measure of the catalytic activity of the metal ions.

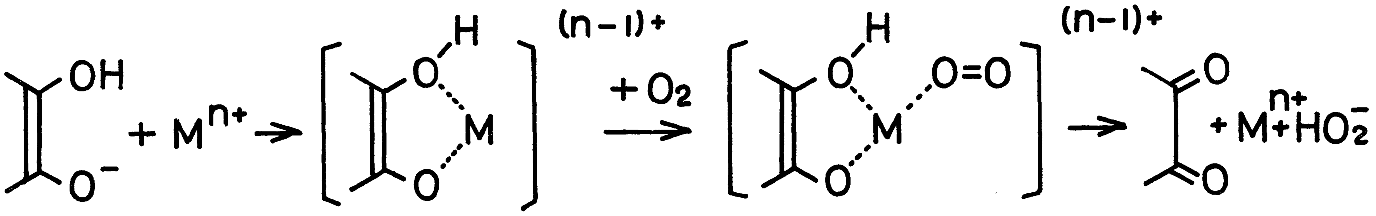
Results and Discussion All the metal ions used were found to accelerate the autoxidation of [1]. Rmax's for each metal ion were as follows (ml O_2/min): Cu(II), 3.10; Pb(II), 1.31; Zn(II), 0.14; Ni(II), 0.25; Co(II), 0.14; Cd(II), 0.08; Mn(II), 0.13; Mg(II), 0.04; Fe(II), 16.1; None, 0.028. It is noteworthy that the transition metal ions such as Fe(II), Pb(II), Co(II), Ni(II), Zn(II), Cd(II), and Mn(II) which can not be easily reduced to the lower oxidation state exhibit the definite catalytic effect. This result does not seem to be explicable by the free radical mechanism[1,3] which includes the direct oxidation of the substrate by the metal ion to form a free radical [II] and the metal ion of the lower oxidation state ($M^{(n-1)+}$).



[II]

In fact, it was confirmed that in the absence of molecular oxygen [I] did not measurably react even with Fe(II), Pb(II) or Cu(II).

The alternate mechanism, O_2-complex mechanism[2,9] which includes the formation of substrate-metal ion-O_2 complex [IV] can explain the catalytic activity of these metal ions.



[III] [IV]

By forming pi bonds with both ligands, the metal ion effectively extends the conjugation so that one pi-orbital overlaps both ligands, and electron transfer from the substrate to O_2 can occur very easily.[9] According to the O_2-complex mechanism, it follows that the catalytic activity of metal ions may be correlated with the stability constant of the substrate-metal ion complex [III]. In Fig. 1, the logarithm of Rmax's is plotted against the logarithm of stability constants (K_{ML}) of metal complexes. As the K_{ML} of [I]-metal ion complex is not yet measured, the K_{ML}'s of Tiron (1,2-dihydroxybenzene-3,5-disulfonate)-metal ion complexes are used in Fig. 1. The linear relationship shown in Fig. 1 may be somewhat doubtful because the K_{ML}'s for Tiron are used in place of K_{ML}'s for [I]. For the metal ion complexes with catechol homologs such as 4-carboxycatechol,[13] catechol-4-sulfonate[13] and catechol,[14] however, the K_{ML} is approximately related, as shown in Fig. 2, to the K_{ML} of Tiron complex by the formula,

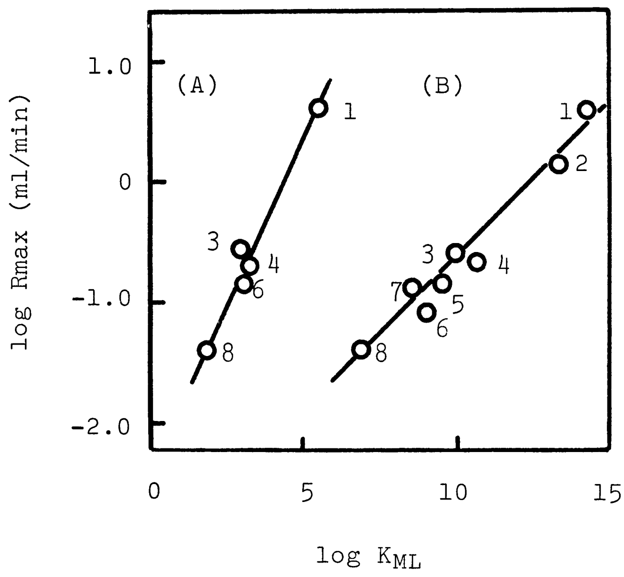


Fig. 1 Correlation of stability constant of (A) Tiron monoanion- and (B) Tiron dianion-metal ion complex with catalytic activity of metal ions in autoxidation of [I],

Metal ions: 1, Cu(II); 2, Pb(II); 3, Ni(II); 4, Zn(II); 5, Co(II); 6, Cd(II); 7, Mn(II); 8, Mg(II).

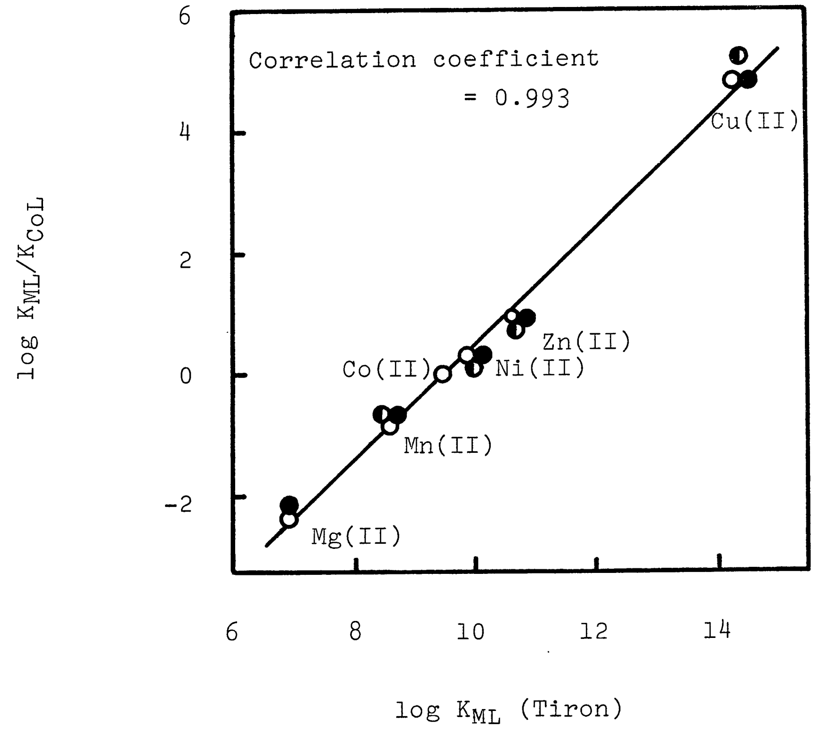


Fig. 2 Plots of stability constant of (A) 4-carboxycatechol-(○),13) (B) catechol-4-sulfonate-(●)13) and (C) catechol-(◐)14) metal ion complex against stability constant of Tiron-metal ion complex.

$$\log K_{ML} = \log K_{ML}\ (\text{Tiron}) + C$$

where C is constant and M is Cu(II), Zn(II), Ni(II), Co(II), Mn(II) and Mg(II). Taking into account this relationship, the use of K_{ML}'s of Tiron complex in Fig. 1 is not so unreasonable . It is sure that, at least qualitatively, the catalytic activity of the metal ions increases with the stability of the substrate-metal ion complexes. This correlation strongly indicates that the autoxidation of [I] proceeds through an intermediate complex between [I] and the metal ion.

The behavior of Fe(II) is peculiar in that its catalytic activity is much greater than expected from the K_{ML} of Fe(II)-complex15) and a blue intermediate is observed during the autoxidation of [I] catalyzed by Fe(II). A study of the blue intermediate is now being initiated in our laboratory.

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