which determines the axial mass transport of the reactant (i.e., U_A must be given by Eq. (3) which is independent of C_A). It is widely accepted, especially on heterogeneous surfaces, that it may be only a few sites having a rather narrow range of adsorption energies which are kinetically active. Thus, the adsorption coefficients deduced from the kinetic measurements could be quite different from the coefficients for the average adsorption site. It is this average adsorption site which influences axial transport and, thus, it is quite conceivable that the adsorptive retention characteristics of a catalyst might be consistent with a linear isotherm at conditions where the kinetically active sites are decidedly nonlinear. Furthermore, the general form of the LH rate equations is characteristic of many complex mechanisms and complexities in the surface chemistry could easily give rate equations similar to those based on LH mechanisms under conditions where the assumption of linear isotherms is quite valid.

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Correlation of Catalytic Oxidation Activity of Metal Macrocyclic Amine Complexes and Redox Potential

INTRODUCTION

A variety of metal salts are known to catalyze hydrocarbon autoxidation by inducing the catalytic decomposition of intermediate alkyl hydroperoxides to radicals. The commonly accepted mechanism for metal salt catalyzed hydroperoxide decomposition is the Haber-Weiss redox cycle (*1*, *2*).

$$\mathrm{ROOH} + \mathrm{M}^{n+} \rightarrow \mathrm{RO}\cdot + \mathrm{OH}^- + \mathrm{M}^{(n+1)+}$$
$$\mathrm{ROOH} + \mathrm{M}^{(n+1)+} \rightarrow \mathrm{RO_2}\cdot + \mathrm{H}^+ + \mathrm{M}^{n+}$$

Each step involves rapid complex formation between the hydroperoxide and the metal salt followed by decomposition of these complexes to free radical products. Several investigators have attempted to correlate the activity of metal complexes in catalyzing hydrocarbon oxidation with the standard redox potentials for the metal cations as measured in aqueous medium (*3*, *4*). In view of the sensitivity of redox potential to change in medium and to the nature of the ligands, it is not surprising that only qualitative correlations between oxidation activity and redox potential have been observed. A rigorous analysis of the role of redox potential requires that the redox potentials of the metal catalysts be known in the same solvent as used for the oxidations. Furthermore, the ligand must have a high stability constant so that it would not be displaced by other ligands during the course of the oxidation with the resultant change in redox potential of the metal cation. Recently the redox potentials of a series of macrocyclic tetradentate amine complexes which satisfy these two requirements have been measured (*5*). The redox potentials were measured in acetonitrile and the tetradentate ligand is extremely inert to displacement.

In the present study, the rates of cyclohexene oxidation catalyzed by Cu(II), Ni(II), Fe(II), and Co(II) complexes of the macrocyclic amine ligand, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, have been measured in acetonitrile and correlated with the oxidation potentials of the metal complexes in the same solvent. In addition, the rates of the decomposition of cyclohexenyl hydroperoxide, the key intermediate in cyclohexene oxidation, catalyzed by the same metal complexes have been determined.

EXPERIMENTAL METHODS

The preparation of the various metal macrocyclic amine complexes has been described previously (*5*). Cyclohexene (Phillips Research Grade) was purified by a standard procedure to remove trace peroxides and then distilled through 12 in. tantalum helices packed column. The purified material was stored under nitrogen until used. Acetonitrile (Mallinckrodt AR) was distilled from CaH_2 through the 12 in. tantalum helices packed column and stored under nitrogen. Cyclohexenyl hydroperoxide was prepared by a standard procedure for preparing alkenyl hydroperoxides described by Van Sickle *et al.* (*6*). Cyclohexenyl hydroperoxide, bp 42–45° (0.5 mm), with a purity of 80–90% was obtained. The impurities were cyclohexenol and cyclohexone (ratio 1.2:1).

Oxidation rates were determined in the following manner: The desired amount of metal macrocyclic amine complex (0.05 m*M*) and a small Teflon covered magnetic stirring bar were added to an oxidation vessel (a 25 ml Erlenmeyer flask fitted with a break-off joint and a side arm). Acetonitrile (10 ml) and 50 m*M* (5 ml) of cyclohexene (passed over aluminum oxide, Woelm neutral grade, just before using) were added. The reaction vessel was then degassed and sealed *in vacuo*. The reaction vessel was then attached to an oxidation apparatus, and oxygen was introduced through the break seal. The rate of oxygen uptake was measured automatically at constant pressure. When ca. 3.5 m*M* oxygen had reacted (about 7% conversion of cyclohexene) the oxidation was terminated. The oxidation apparatus was capable of detecting the uptake of as little as 0.5 ml of oxygen (0.04 m*M*). The products were analyzed in the following manner. An aliquot was analyzed by iodometric titration to determine the yield of hydroperoxide (*7*). Then an aliquot was reacted with sufficient triphenylphosphine in ethanol to reduce the hydroperoxide to alcohol (*8*). Toluene was added as an internal standard and the product was analyzed by glc using a 5 ft × ¼ in. XF1150/Chromosorb W column programmed from 50 to 160° at 6°/min with a helium flow rate of 80 ml/min. All glc analyses were performed in duplicate. This glc column was capable of fully resolving cyclohexene oxide, cyclohexenol, and cyclohexenone. The actual yield of cyclohexenol from oxidation was determined by subtracting the yield of cyclohexenyl hydroperoxide from the total yield of cyclohexenol.

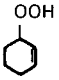
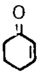
The rates of catalytic decomposition of cyclohexenyl hydroperoxide were determined by adding a solution of 10 m*M* (1.16 g) hydroperoxide in 25 ml of acetonitrile to a 100 ml glass Fisher Porter vessel containing the metal macrocyclic amine complex (0.1 m*M*). The reactants were agitated in a constant temperature bath at 60.0° in a nitrogen atmosphere. Periodically, small aliquots were withdrawn through a sampling port and analyzed by iodometric titration for cyclohexenyl hydroperoxide. The ratio of cyclohexenone to cyclohexenol in the final product was determined by the same procedure described for cyclohexene oxidation products.

RESULTS AND DISCUSSION

Our results from the study of the oxidation of cyclohexene in the presence of catalytic amounts of metal macrocyclic amine complexes are summarized in Table 1. The principal products are those expected for the free radical chain oxidation of cyclohexene: cyclohexenyl hydroperoxide, cyclohexenol, cyclohexenone, and small amounts of cyclohexene oxide. The Fe(II), Co(II), and Ni(II) macrocyclic amine complexes

TABLE 1

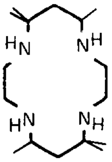
Catalytic Oxidation of Cyclohexene (3.3 M) in Acetonitrile with Oxygen (1 atm) at 40.0°

Catalyst[c] (3.3 × 10^{-3} M)	Rate $-(dO_2/dt)$ (moles/liter hr)	Conv (%)	Product distribution (mole %[a])			
						
None	0.011	5.2	72.0	18.7	4.5	0.7
$Fe(II)A(BF_4)_2$[b]	0.304	7.4	11.7	38.6	43.8	1.9
$Co(II)A(ClO_4)_2$	0.054	8.8	65.6	19.1	10.4	0.8
$Ni(II)A(ClO_4)_2$	0.015	3.5	88.5	4.9	2.4	0.4

[a] A 4% yield of dimeric hydroperoxide is assumed, based on Ref. (8).

[b] 2.3 × 10^{-3} M catalyst.

[c] A =



accelerated the rate of cyclohexene oxidation by factors of 1.5 to 30. The Cu(II) complex was inactive. The role of the active metal macrocyclic amine complexes is likely to induce the catalytic decomposition of cyclohexenyl hydroperoxide to yield free radicals. This induced decomposition of the hydroperoxide was directly verified by determining the rates of decomposition of cyclohexenyl hydroperoxide in the presence of catalytic amounts of the metal complexes. These results, summarized in Table 2, clearly demonstrate that Fe, Co, and Ni macrocyclic amine complexes induce the catalytic decomposition of cyclohexenyl hydroperoxide and that the rates parallel their activity as oxidation catalysts, i.e., Fe > Co > Ni > Cu. The standard oxidation potentials of the metal macrocyclic amine complexes determined in acetonitrile are also summarized in Table 2. The correlation of both the rates of cyclohexene oxidation and cyclohexenyl hydroperoxide decomposition with redox potential of the

TABLE 2

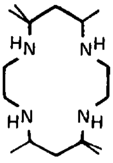
Catalytic Decomposition of Cyclohexenyl Hydroperoxide (0.4 M) in Acetonitrile at 60.0°C

Catalyst[c] (4 × 10^{-3} M)	$t_{1/2}$ (hr)	k_2 (liters/mole sec)	Ratio cyclohexenone: cyclohexenol	Oxidation[a] potential (V)
None	73		1.7	
$Fe(II)A(BF_4)_2$		Very fast at 0°	2.17	0.92
$Co(II)A(ClO_4)_2$	10	5 × 10^{-3}	1.37	0.67
$Ni(II)A(ClO_4)_2$	17	2.8 × 10^{-3}	1.60	1.47
$Cu(II)A(ClO_4)_2$[b]	34.4	1.44 × 10^{-3}	2.40	1.81

[a] Half wave potentials, $E_{1/2}$ for M(II) → M(III) + e (ref. is standard hydrogen electrode). For reversible electrode reactions the $E_{1/2}$ is essentially equal to standard redox potential E^0.

[b] 2.3 × 10^{-3} M catalyst.

[c] A =



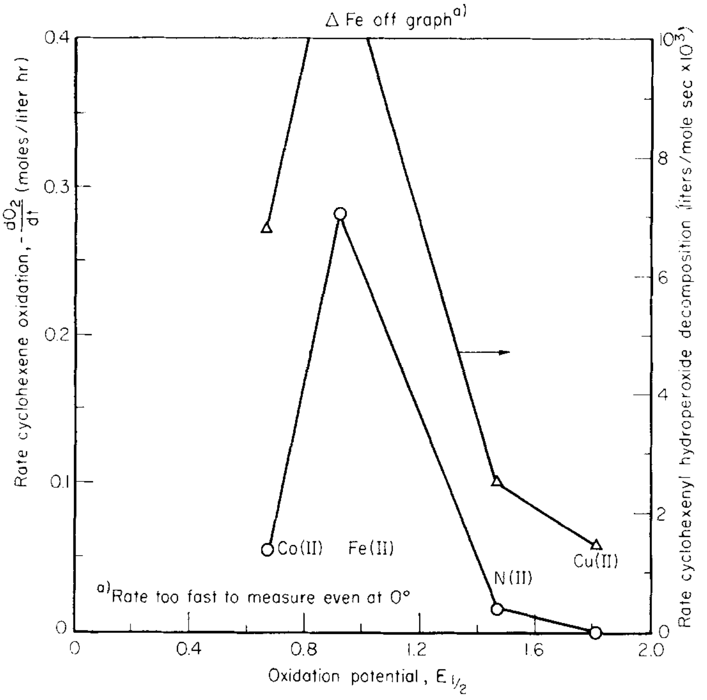


FIG. 1. Correlation of redox potential of $M(II)A(ClO_4)_2$, with rate of cyclohexene oxidation and cyclohexenyl hydroperoxide decomposition.

metal cation is shown in Fig. 1. Both rates reach a maximum with Fe which has an oxidation potential of 0.92 V.

The interpretation of these data on a purely kinetic basis is not well defined since E^0 is a thermodynamic and not a kinetic parameter. It does appear from these data that, with a given series of structurally identical metal complexes, there is an optimum redox potential for hydroperoxide decomposition. An optimum value for the redox potential of the metal cation is reasonable when one considers that the alkyl hydroperoxide must function both as an oxidizing and a reducing agent in the Haber-Weiss cycle. Thus the decrease in rate observed with Ni(II) and Cu(II) macrocyclic amine complexes could be due to the fact that these complexes are only slowly oxidized by the hydroperoxide relative to the Fe(II) complex. In the case of the Co(II) complex, the reverse would be true; Co(II) will be easily oxidized by the hydroperoxide; however, the subsequent reduction of Co(III) by the hydroperoxide must be slow relative to reduction of the Fe(III) complex.

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