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Oxidation of Alcohols by Diperiodatocuprate(III)

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In aqueous base, diperiodatocuprate(III) oxidized primary and secondary alcohols by the following rate law: $-\mathrm{d}[\mathrm{Cu(III)}]/\mathrm{d}t = k[\mathrm{Cu(III)}][\mathrm{ROH}]/[\mathrm{H_3IO_6}^{2-}](1 + a/[\mathrm{OH}^-])$. Alcohols studied were methanol, ethanol, 2-propanol, benzyl alcohol, and allyl alcohol. The rate law indicates that the copper-containing reactive intermediate is a deprotonated monoperiodatocuprate(III) ion.

Several reagents for the oxidation of alcohols have been studied,[1,2] a wide range of oxidants being of interest for specificity or reactivity of other functional groups in the molecule. An interesting oxidant little before considered[3] is the diperiodatocuprate(III) ion, $\mathrm{Cu(IO_6)_2}^{7-}$, which homogeneously oxidizes alcohols in aqueous base. Reactions involving diperiodatocuprate(III), a diamagnetic square-planar d^8 complex, are of interest in themselves because the ion contains a metal in an unusually high oxidation state. Copper is involved in many biological electron-transfer reactions,[4] and although Cu(III) is usually not suggested as an intermediate because of its high oxidizing power, it should not be completely rejected until the redox reactions of Cu(III) have been fully investigated. We wish to report here the kinetics of the oxidation of several simple alcohols by diperiodatocuprate(III).

Experimental Section

Preparation of Sodium Diperiodatocuprate Dodecahydrate, $\mathrm{Na_7[Cu(IO_6)_2]\cdot 12H_2O}$. A solution of potassium diperiodatocuprate(III) was prepared by literature methods.[3,5] The sodium salt was precipitated by addition of sodium hydroxide.[6] The salt was redissolved in dilute aqueous KOH and again precipitated with NaOH. The product was filtered and sucked dry on the frit. Iodometric analysis[6] gave an equivalent weight of 49.0, theoretical weight 49.2 (18 equiv/mol).

Kinetic runs were made on a Cary 14 spectrophotometer. The rate of reaction was monitored by observing the disappearance of diperiodatocuprate(III) at λ 414 nm, ϵ 1.2×10^4 M^{-1} cm^{-1}.[7,8] Ionic strength was held constant at 0.1 *M* with $\mathrm{KNO_3}$. Hydroxide ion concentration was varied between 0.02 and 0.1 *M*. Methanol, ethanol, and 2-propanol concentrations varied between 0.2 and 0.7 *M*, while allyl alcohol concentrations varied between 0.1 and 0.3 *M* and benzyl alcohol concentrations varied between 0.02 and 0.2 *M*. Copper(III) concentration varied between 3 and 15×10^{-5} *M*. The temperature was 25°. Only freshly prepared solutions of Cu(III) were used. Alcohols were distilled before use.

The kinetic data were evaluated by the following procedure. The reaction followed the general scheme

$$\mathrm{A} \rightarrow 2\mathrm{B}$$

where

$$\frac{-\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \frac{k_{\mathrm{obsd}}[\mathrm{A}][\mathrm{C}]}{[\mathrm{B}]}$$

$$[\mathrm{B}] = [\mathrm{B}]_0 + 2[\mathrm{A}]_0 - 2[\mathrm{A}]$$

where A = Cu(III), B = periodate, and C = alcohol. Under pseudo-first-order concentrations of alcohol, substitution and integration yield

$$([\mathrm{B}]_0 + 2[\mathrm{A}]_0) \ln \frac{[\mathrm{A}]}{[\mathrm{A}]_0} - 2[\mathrm{A}] + 2[\mathrm{A}]_0 = -k_{\mathrm{obsd}}[\mathrm{C}]t$$

Setting $[\mathrm{B}]_0 = 0$ and rearranging yield

$$\frac{[\mathrm{A}]}{[\mathrm{A}]_0} - \ln \frac{[\mathrm{A}]}{[\mathrm{A}]_0} - 1 = \frac{k_{\mathrm{obsd}}[\mathrm{C}]}{2[\mathrm{A}]_0} t$$

Plotting the function on the left-hand side of the equation *vs.* time yielded plots linear for at least 2 half-lives, from whose slope could be evaluated k_{obsd}.

Results

Diperiodatocuprate(III) was found to oxidize a wide variety of organic compounds in basic solution, including primary and secondary alcohols, aldehydes, and ketones. Tertiary alcohols and carboxylate ions do not react appreciably under the conditions used. The aldehyde and ketone oxidations were found to be quite rapid; thus the oxidation of alcohols was chosen as the most tractable system for the study of reactions of Cu(III).

In the presence of a large excess of alcohol and at a pH of 13, the disappearance of Cu(III) did not follow simple kinetics. The rate decreased more slowly than given by second-order kinetics but faster than given by first-order kinetics. First-order kinetics were approached at long times. In addition the rate depended on the initial concentration of Cu(III). Addition of periodate ion, a product of the reaction, as $\mathrm{KIO_4}$ reduced the rate of reaction dramatically, suggesting an autoinhibitory mechanism. The appropriate kinetic plots (see Experimental Section) were also in accord with this interpretation, the slopes of which were combined with the initial concentrations to give consistent values of k_{obsd}. This indicates the reaction is first order in Cu(III), first order in alcohol, and inverse first order in periodate ion.[9]

The rate was found to be pH dependent, increasing with the hydroxide ion concentration. Plots of $1/k_{\mathrm{obsd}}$ *vs.* $1/[\mathrm{OH}^-]$ proved to be linear (see Figure 1). Thus the total overall rate law is

$$\frac{-\mathrm{d}[\mathrm{Cu(III)}]}{\mathrm{d}t} = \frac{k[\mathrm{Cu(III)}][\mathrm{ROH}]}{[\mathrm{H_3IO_6}^{2-}](1 + a/[\mathrm{OH}^-])} \tag{1}$$

Kinetic parameters for the oxidation of five simple alcohols are given in Table I.

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[1] K. B. Wiberg, Ed., "Oxidation in Organic Chemistry," Academic Press, New York, N. Y., 1965.

[2] L. J. Chinn, "Selection of Oxidants in Synthesis. Oxidation at the Carbon Atoms," Marcel Dekker, New York, N. Y., 1971.

[3] A. Berka, J. Vulterin, and J. Zyka, "Newer Redox Titrants," Translated by H. Weisz, Pergamon Press, New York, N. Y., 1965, pp 14-17.

[4] J. Peisach, P. Aisen, and W. E. Blumberg, Ed., "The Biochemistry of Copper," Academic Press, New York, N. Y., 1966.

[5] L. Jensovsky, *Chem. Listy*, **50**, 1103 (1956).

[6] L. Malatesta, *Gazz. Chim. Ital.*, **71**, 580 (1941).

[7] G. I. Roxovskii and R. Jankauskas, *Leit. TSR Mokslu Akad. Darb., Ser. B*, 73 (1967); *Chem. Abstr.*, **69**, 23360 (1968).

[8] L. Jensovsky, *Collect. Czech. Chem. Commun.*, **32**, 1996 (1967).

[9] The predominant form of periodate in the pH and concentration ranges used is probably $\mathrm{H_3IO_6}^{2-}$, although the dimerization of periodate has not been studied in this pH region. See K. Kustin and E. C. Liberman, *J. Phys. Chem.*, **68**, 3869 (1964); G. J. Buist and J. O. Lewis, *Chem. Commun.*, **66**, (1965).

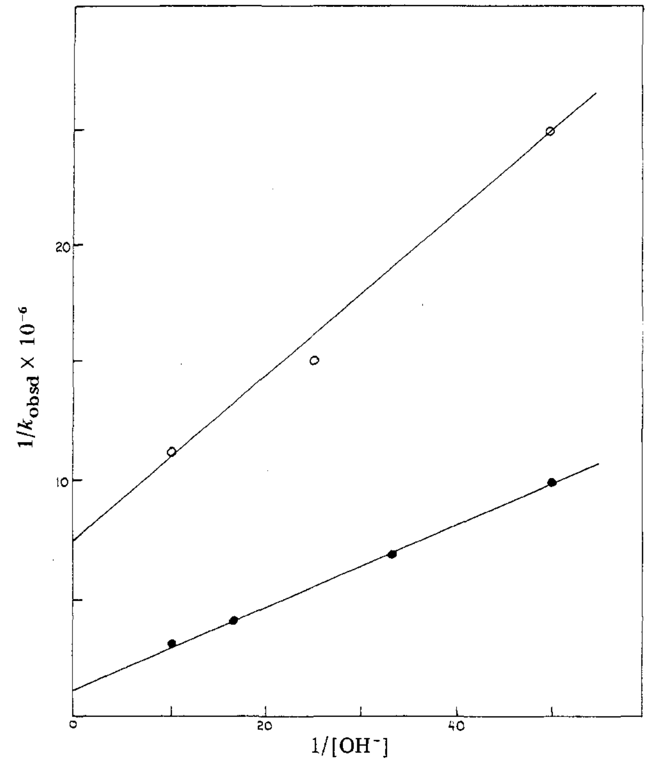

Figure 1. The pH dependence of the rate of oxidation of two alcohols by diperiodatocuprate(III): ○, 2-propanol; ●, ethanol. Each point represents the average of at least two experiments.

Discussion

The inorganic products of the reaction are Cu(II) and periodate ion, for at high concentrations, a copper(II) periodate precipitates. The organic product was not determined, because at the concentrations used (10^{-5} *M*) this would prove difficult. The supposed initial products of the oxidation of the alcohols are aldehydes or ketones, which are oxidized by Cu(III) even faster than are alcohols. Thus the final products will depend on relative concentrations of alcohol and aldehyde or ketone at all times and the relative rates of oxidation. At concentrations different than those used in the kinetic study, different organic products could be obtained. The problem could be settled by the determination of the rates of oxidation of the aldehydes and ketones, but these reactions are fast and would require more sophisticated methods than used here for their evaluation.

The inverse first order in periodate concentration indicates a dissociation preequilibrium in which the Cu(III) moiety loses a periodate ligand, the monoperiodatocuprate(III) being the reactive species but having a concentration much less than that of diperiodatocuprate(III). The pH dependence indicates an equilibrium between a deprotonated reactive species in equilibrium with a protonated unreactive species, both of whose concentrations are comparable to the total Cu(III) concentration. The simplest mechanism which fits the rate law is shown by eq 2-4 where L stands for a periodate ligand of undetermined protonation. If K_3 is

$$Cu(HL)_2 \rightleftharpoons CuL(HL) + H^+ \quad K_2 \qquad (2)$$

$$CuL(HL) \rightleftharpoons CuL + HL \quad K_3 \qquad (3)$$

$$CuL + ROH \rightarrow products \quad k_4 \qquad (4)$$

small, this yields the observed rate law where $k = k_4K_3$ and $a = K_w/K_2$. An alternative mechanism is reactions 2 and 4 in conjunction with reactions 5 and 6.

Table I. Kinetic Parameters for the Oxidation of Alcohols by Diperiodatocuprate(III)[a]

Alcohol	10^7k, sec^{-1}	a, M^{-1}	pK_2	10^7k_{obsd} (at [OH⁻] = 0.02 *M*), sec^{-1}
Methanol	5.9	0.091	12.96	1.03
Ethanol	6.4	0.104	13.02	1.02
2-Propanol	2.4	0.096	12.98	0.42
Benzyl alcohol	60	0.094	12.97	10.5
Allyl alcohol	74	0.111	13.05	11.2

[a] See Discussion for error limits on the values of the rate constants.

$$Cu(HL)_2 \rightleftharpoons CuHL + HL \quad K_5 \qquad (5)$$

$$CuHL \rightleftharpoons CuL + H^+ \quad K_6 \qquad (6)$$

This also gives the rate law where $k = k_4K_5K_6/K_2$ and $a = K_w/K_2$. The first mechanism seems preferable, since the loss of periodate ion occurs from a species of higher negative charge. From the value of a, K_2 can be determined. Values of pK_2 are listed in Table I. The deprotonation of the Cu(III) species is not observed spectrophotometrically in this pH range; changes in other pH ranges are noted however.[7]

The observed rate law also fits a mechanism in which monoperiodatocuprate(III) reacts with alkoxide ion. If so, the measured p*K* of 13 would apply to the alcohol. This is far from that measured in aqueous solution for some of these alcohols.[10] In any case one would not expect all these alcohols to have the same p*K*.[11]

When comparing kinetic parameters for the several alcohols, it is important to note that the values of k are susceptible to a large error (estimated ±20%) because they are the reciprocal of a small extrapolated intercept. Much more reliable in comparing relative rates are the values of k_{obsd} at $[OH^-] = 0.02\ M$ (estimated ±5%) listed in Table I. Note that the relative rates of two alcohols will be the same at any pH, for $k_{obsd} = k/(1 + a/[OH^-])$.

The simple primary alcohols methanol and ethanol are oxidized at the same rate within experimental error; the secondary alcohol 2-propanol is oxidized at just less than half as fast. Inductive effects do not seem important in this series. Why 2-propanol reacts more slowly is not clear. The effect may be steric. A more plausible explanation arises from the possible stoichiometry of the reactions. If under experimental conditions methanol and ethanol were oxidized all the way to carboxylate ions but 2-propanol were oxidized only to acetone and the first step of each reaction was of the same rate, the observed relative rates of the disappearance of Cu(III) would be observed. As stated before these secondary reactions are fast, and the rates are difficult to measure.

The rates of oxidation of benzyl and allyl alcohols are over 10 times faster than those of the saturated primary alcohols. If the transition state contains appreciable free-radical character at the α carbon, the unpaired electron can be delocalized over the allyl or benzyl moiety, giving resonance stabilization to the transition state and increasing the reaction rate. In the case of allyl alcohol, there is the possibility of oxidation at the double bond; Cu(III) does oxi-

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[10] P. Ballinger and F. A. Long, *J. Amer. Chem. Soc.*, **82**, 795 (1960).

[11] The pH dependence of the rate might also be due to dimerization, and hence deactivation, of periodate ion,[9] a reaction which has been shown to be pH dependent. However as no data for this reaction are available in the pH range of interest, it will not be further considered.

dize maleate ion, but not acetate or benzoate.

Diperiodatocuprate(III) does not appear to be an attractive oxidant for alcohols from a synthetic point of view since the products inhibit further reaction. This kinetic study does shed significant light upon the chemistry of Cu(III). Since monoperiodatocuprate(III) is a much more active oxidant than diperiodatocuprate(III), the periodate ligand must have some stabilizing effect upon the Cu(III). Since the copper complexes are diamagnetic and square planar, it is not a steric effect but electronic.

Registry No. Methanol, 67-56-1; ethanol, 64-17-5; 2-propanol, 67-63-0; benzyl alcohol, 100-51-6; allyl alcohol, 107-18-6; $Cu(IO_6)_2{}^{7-}$, 36202-28-5.

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Contribution from the Clippinger Laboratories, Department of Chemistry, Ohio University, Athens, Ohio 45701

Complexes of 1,8-Naphthyridines. VII. Eight-Coordinate Transition Metal Perchlorate Complexes of 1,8-Naphthyridine[1]

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The syntheses of a number of transition metal complexes of the type $M(napy)_4(ClO_4)_2$ where M = Mn, Fe, Co, Ni, Cu, Zn, Pd, and Cd and napy = 1,8-naphthyridine are described. Elemental analyses, molar conductances, magnetic moments, molecular weights, and powder X-ray, infrared, electronic, and pmr spectral data have been applied to the characterization of the compounds. The arrangement of the eight nitrogen atoms around the metal in the Fe(II) complex is best described as a dodecahedron. The geometry of the other complexes in the solid state is discussed in terms of a dodecahedron with the shape parameters r_a and r_b becoming more divergent as the metal is changed from Mn to Cu. Solution spectral data for several complexes indicate a different geometry than is found in the solid state. A comparison with other eight-coordinate transition metal complexes where the metal has more than two d electrons is made.

Introduction

Although eight-coordination is common for the lanthanides, transition metal complexes of this type are extremely rare unless the electronic configuration of the metal ion is d^0, d^1, or d^2.[3] Bergman and Cotton have shown that $[As(C_6H_5)_4]_2[Co(NO_3)_4]$ contains eight-coordinate cobalt(II) in which the nitrate groups are bidentate and located in a dodecahedral geometry distorted relative to the cobalt atom.[4] Drummond and Wood[5] have shown that the nitrate groups are also bidentate in the tetraphenylarsonium salt of the dodecahedral $Mn(NO_3)_4{}^{2-}$ ion while preliminary data suggest that $Zn(NO_3)_4{}^{2-}$ is also eight-coordinate. Recently, King, *et al.*, have shown that $Fe(NO_3)_4{}^-$ also contains four bidentate nitrate groups yielding an eight-coordinate Fe(III).[6] Eight-coordination has been found for both Cd(II) and Cu(II) in the compound $Ca[M(O_2CCH_3)_4]\cdot 6H_2O$, where M = Cd or Cu.[7] Other possible eight-coordinate transition metal complexes in which the metal ion contains more than two d electrons are discussed by Lippard.[3]

Recently we reported the first known example of an eight-coordinate iron(II) complex.[8] The compound, tetrakis(1,8-naphthyridine)iron(II) perchlorate, has been shown to possess a distorted dodecahedral geometry.[9,10] We have also reported partial synthetic and physical data for the other transition metal complexes of stoichiometry $M(napy)_4(ClO_4)_2$ where M = Mn, Co, Ni, Cu, Zn, Pd, and Cd and napy = 1,8-naphthyridine.[11] It is the purpose of this paper to present and examine in detail the syntheses and physical and chemical data of the transition metal complexes of stoichiometry $M(napy)_4(ClO_4)_2$.

Experimental Section

Materials. Metal perchlorates were purchased from G. F. Smith Chemical Co. and used without further purification. Potassium tetrachloropalladate(II) was prepared according to the method of Grube.[12] Commercially available ethyl acetate, dried before use,[13] and absolute methanol and ethanol were used in the preparation of the metal complexes. Practical grade 2,2-dimethoxypropane (dmp) and spectral grade acetonitrile and nitromethane were obtained from Eastman Chemicals. Purity of the ligand 1,8-naphthyridine, prepared by the method of Paudler and Kress,[14] was verified by pmr spectroscopy.

Instrumentation. The infrared (4000–200 cm^{-1}) and solution (CH_3CN) electronic absorption spectra, conductivities, and carbon, hydrogen, and nitrogen contents were obtained as previously described.[15] Diffuse reflectance spectra were measured on finely ground pure solids with a Beckman DU spectrophotometer fitted with a Beckman Model 2500 reflectance attachment using magnesium carbonate as the reference. Solid electronic absorption spectra were recorded using a Cary Model 14 recording spectrophotometer with the samples mulled with Nujol or hexachlorobutadiene and supported on

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(1) Abstracted in part from the Ph. D. dissertation of R. L. Bodner, Ohio University, 1970. Presented in part at Metrochem 70, Hoboken, N. J., March 25, 1970; see Abstracts, No. 43.

(2) To whom correspondence should be addressed.

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