Inorg. Chem. **1984**, *23*, 2133–2138

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Kinetics and Mechanism of Oxidation of Methyl Ethyl Ketone and Cyclohexanone by Potassium Bis(tellurato)cuprate(III)

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Received October 13, 1982

Potassium bis(tellurato)cuprate(III) oxidizes methyl ethyl ketone and cyclohexane in aqueous alkaline medium. The kinetics of the process shows complex dependence in both ketone and alkali concentration. The inverse dependence on tellurate ion suggests that a hydroxo mono(tellurato) species of the oxidant is involved in the reaction with the substrate. The rate-limiting step has been proposed to be the collapse of a complex of (tellurato)cuprate(III) ion to a radical and Cu(II).

Introduction

Evidence for the existence of Cu(III) was provided by the work of Brauner and Kutzma.[1] Malaprade[2] succeeded in isolating sodium cupriperiodate. Some of these complexes of Cu(III) were found to be efficient analytical reagents for the determination of several organic substrates[3] in which the reagent was basically shown to act through its oxidizing property. Many biological systems involve electron-transfer processes wherein copper plays an important role.[4]

Bour and Steggerda[5] isolated Cu(III) complexes with biuret and oxamide, providing first evidence that Cu^{3+} could be stabilized by deprotonated amide groups. Subsequently two important groups of workers were engaged in synthesis and elucidation of Cu(III) chemistry. Meyerstein[6] and co-workers isolated Cu(III) compounds in pulse radiolysis of Cu(III) in acetate buffer medium saturated with N_2O. Similarly $Cu^{III}G_3CH_2C(CH_3)_2OH^-$ was obtained from $Cu_2G_3^-$.[7] In aqueous medium Cu(III) was reported to exist as $Cu(OH)^{2+}$(aq) or $Cu(OH)_2^+$(aq), which apparently oxidized slowly if at all, reductants not participating as ligands in the inner sphere of the copper(III).[8] Margerum and co-workers[9–11] synthesized several stable Cu(III)–peptide complexes in acidic medium either by chemical or by electrochemical methods; these complexes possessed properties characteristic of low-spin d^8 square-planar complexes. Mechanisms of electron-transfer reactions involving Cu(III) systems were extensively studied by these workers. The electron-transfer reaction between a Cu(III)–peptide complex and $IrCl_6^{3-}$ was recently elucidated.[12] The Cu(III) peptide complexes were shown to affect decarboxylation of glyoxylate ion[13] in basic medium. Similarly iodide ion was efficiently oxidized and the kinetic expression included both first-order and second-order terms in iodide.[14]

Mechanistic pictures of oxidation of several primary alcohols[15,16] and aldehydes[17] by potassium bis(tellurato)cuprate(III) and potassium bis(periodato)cuprate(III) are available in literature. The complexes were originally assigned the formulas $Na_xH_yCu(TeO_6)\cdot nH_2O$ and $Na_x\cdot H_y\cdot Cu(IO_6)_2\cdot nH_2O$, respectively, by Malatesta.[18] This has been questioned by Kirschenbaum et al.[19] The correct formulas of these Cu(III) complexes have been recently established by Balikungeri et al.[20] as $[Cu(H_2TeO_6)_2]^{5-}$ and $[Cu(HIO_6)_2]^{5-}$, respectively. In view of the enormous potentiality shown by these complexes, due to the presence of a metal atom in an unusually high oxidation state, we chose to study the kinetics of oxidation of ketones which have great biological importance. This paper incorporates results of a kinetic study of oxidation of methyl ethyl ketone and cyclohexanone by potassium bis(tellurato)cuprate(III) in aqueous medium.

Experimental Section

All the chemicals used were of either AR or pro Analysi grade. The organic substances were purified by standard procedures. A stock solution of potassium bis(tellurato)cuprate(III), $[Cu(H_2TeO_6)_2]^{5-}$, was prepared by the procedure of Chandra and Yadava[21] and was preserved in a refrigerator. An appropriate amount of this stock solution was used to prepare the oxidant for the kinetic study.[22] The other reactant was prepared by weighing out an appropriate quantity of the ketone into a second volumetric flask. To this an amount of KOH equivalent to that in the oxidant flask, potassium tellurate, and other salts if necessary were also added. The ionic strength was maintained by adding K_2SO_4. Both the reactants were thermostated at least for 1 h in a thermostatic water bath maintained at the desired temperature (±0.2 °C) before the kinetics was monitored. The reaction was followed by transferring 5-mL aliquots of the reaction mixture at different intervals into conical flasks that contained a definite volume of standard sodium arsenite solution. The unreacted sodium arsenite was estimated after acidifying with H_2SO_4 and titrating against standard iodine solution to a starch blue end point. For oxidant variation studies the kinetics was followed at 415 nm in a UV–visible spectrophotometer (Zeiss VSU 2p) fitted with a temperature cell holder and maintained at the desired temperature by

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(22) For oxidant variation and salt-effect studies, the sodium salt of potassium bis(tellurato)cuprate(III) was precipitated by addition of sodium hydroxide. The product was filtered on a G4 crucible and washed until the precipitates just began to redissolve. It was then sucked dry and finally dried under vacuum.

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Table I. Average Pseudo-First-Order Rate Constants for the Oxidation of Methyl Ethyl Ketone by Potassium Bis(tellurato)cuprate(III) in Aqueous Alkaline Medium at 30 °C

(a) [oxidant] = 3.5×10^{-3} M, $\mu = 0.25$ M

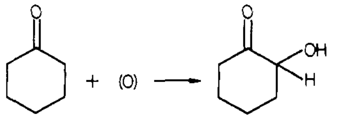
$10^2 \times$ [OH$^-$], M	$10^2 \times$ [substrate], M	$10^4 k_{\text{obsd}}$, s^{-1}	$10^4 k_{\text{calcd}}$, s^{-1}
5.6	1.2	3.4	4.10
5.6	3.5	9.8	10.6
5.6	5.2	16.3	14.52
5.6	7.0	13.7	18.04
5.6	8.6	18.3	20.75
5.6	10.8	24.8	23.97
6.3	1.8	5.2	6.05
6.3	2.7	7.6	8.64
6.3	3.6	9.8	11.00
6.3	4.5	10.2	13.15
10.5	1.8	8.4	6.42
10.5	3.5	14.4	11.25
10.5	4.5	18.1	13.86
6.6	1.8	7.4	6.08
9.2	1.8	8.6	6.37
12.7	1.8	12.7	6.56
20.5	1.8	16.7	6.87
31.5	1.8	17.9	

(b) [OH$^-$] = 8.5×10^{-2} M, $\mu = 0.25$ M, [substrate] = 5.5×10^{-3} M, [Tel] = 1.00×10^{-3} M

$10^5 \times$ [oxidant], M	$10^3 k_{\text{obsd}}$, s^{-1}	$10^5 \times$ [oxidant], M	$10^3 k_{\text{obsd}}$, s^{-1}
5.5	5.3	11.0	4.5
9.9	4.6	13.75	4.87

circulation of water from a thermostat. Quartz cells of 10-mm thickness were used to hold the solution. The hydroxide ion concentration in the reaction mixtures was determined by acidimetry before and after completion of the reaction. Hydroxide ion concentration remained constant during the period of the reaction. The self-decomposition of Cu(III) was routinely checked and was found to be negligible. The rate constants reported here are averages of at least three independent runs.

Product Study and Stoichiometry. The stoichiometry of the reaction with cyclohexanone under kinetic conditions was determined as follows. The reaction mixture containing cyclohexanone (0.0178 M), Cu(III) (0.0034 M), and KOH (0.05 M) was allowed to stand at 35 °C for several hours. Completion of the reaction was marked by the complete discharge of Cu(III) color. The reaction mixture was neutralized by acid and extracted into ether. The ether was then expelled, and the residue gave two spots on a TLC plate; one spot corresponded to unreacted cyclohexanone, and the second spot corresponded to the product of the reaction. The entire extract was then resolved into two zones on a large TLC plate. The zone corresponding to the reaction product was cut and extracted with alcohol and filtered. The filtrate also gave a precipitate with phenylhydrazine. The melting point of the phenylhydrazone derivative (120 °C against the literature value of 121 °C) established that the reaction product is 2-hydroxycyclohexanone. A subsequent experiment carried out quantitatively followed by the determination of weight of the phenylhydrazone derivative provided that 1 mol of cyclohexanone was oxidised by 2 mol of Cu(III) according to the equation



It has been established that cyclohexanone is oxidized to 2-hydroxycyclohexanone by several transition-metal ions. Subsequent oxidation of 2-hydroxycyclohexanone results in adipic acid. In fact, 2-hydroxycyclohexanone has been isolated in the Mn(III) oxidation of cyclohexanone,[23] and in the oxidation by Ce(IV), appearance of a pink coloration has been attributed to a complex[24] of Ce(IV) with 2-hydroxycyclohexanone.

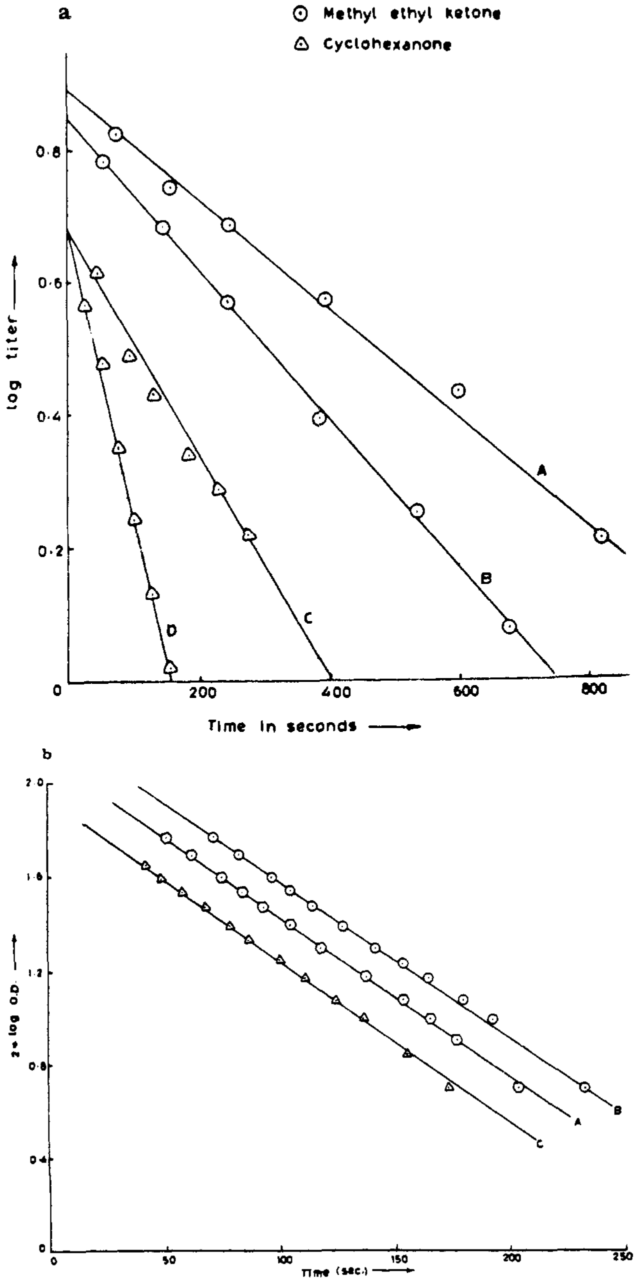


Figure 1. (a) Plot of log titer vs. time ([Cu^{3+}] = 3.5×10^{-3} M, temperature 30 °C): (A) [OH$^-$] = 0.205 M; (B) [OH$^-$] = 0.056 M; (C) [OH$^-$] = 0.230 M; (D) [OH$^-$] = 0.043 M. (b) Plot of log [OD] vs. time at different oxidant concentrations ([OH$^-$] = 0.087 M, [tellurate] = 0.001 M, [cyclohexanone] = 0.005 11 M, temperature 30 °C).

Results

Methyl ethyl ketone and cyclohexanone were oxidized with use of potassium bis(tellurato)cuprate(III) in aqueous alkaline media at 30 and 35 °C. For the kinetic study, the reactions were carried out under pseudo-first-order conditions with at least a 10-fold excess of reductant unless otherwise stated. The experimental data were used to calculate pseudo-first-order rate constants (k_{obsd}) by using the integrated form of the first-order rate expression, which fits up to 70% of the reaction, and confirmed by the least-squares slope of the plot of log titer

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Table II. Average Pseudo-First-Order Rate Constants for the Oxidation of Cyclohexanone by Potassium Bis(tellurato)cuprate(III) in Aqueous Alkaline Medium at 30 °C

(a) [oxidant] = 3.5×10^{-3} M, $\mu = 0.25$ M

$10^2 \times$ [OH$^-$], M	$10^2 \times$ [substrate], M	$10^3 k_{\text{obsd}}$, s^{-1}	$10^3 k_{\text{calcd}}$, s^{-1}
4.3	1.1	2.5	2.78
4.3	1.4	2.8	2.55
4.3	2.6	4.2	4.49
4.3	3.7	7.0	6.09
4.3	5.6	9.0	8.53
5.9	1.8	3.2	3.38
5.9	2.6	4.4	4.67
5.9	3.5	5.4	6.04
5.9	4.4	6.8	7.31
10.2	1.8	4.4	3.605
10.2	2.6	5.5	4.99
10.2	3.5	8.7	6.44
10.2	4.4	10.1	7.76
4.4	1.4	2.8	2.56
6.2	1.4	3.5	2.68
9.0	1.4	5.2	
13.6	1.4	8.8	
18.5	1.4	9.2	

(b) [OH$^-$] = 8.7×10^{-2} M, $\mu = 0.25$ M, [substrate] = 5.1×10^{-3} M, [Tel] = 1.00×10^{-3} M

$10^4 \times$ [oxidant], M	$10^3 k_{\text{obsd}}$, s^{-1}	$10^4 \times$ [oxidant], M	$10^3 k_{\text{obsd}}$, s^{-1}
0.825	16.12	1.3	16.12
1.1	16.12	2.6	16.15

vs. time (Figure 1). Incidentally the first-order constants were independent of the initial oxidant concentrations in the presence of a constant excess of tellurate and hydroxide as seen from parallel linear log OD vs. time plots (Figure 1b, Tables Ib and IIb).

To fix the order of the reaction with respect to the substrate at constant [OH$^-$] the rate of decrease of a constant bis(tellurato)cuprate(III) concentration in the presence of varying concentrations of the substrate was measured. No doubt, the rate of decrease of bis(tellurato)cuprate(III) increased with the increase of ketone concentration but the value of k_{obsd}/[ketone] decreased. Further, the plot of k_{obsd} vs. [ketone] was a smooth curve passing through the origin and the double-reciprocal plot of $1/k_{\text{obsd}}$ vs. 1/[ketone] exhibits excellent linearity (Figure 2) with an intercept. The kinetic data fit well into a Michaelis–Menten plot, indicating reversible formation of a complex between the oxidant and the substrate molecule preceding the rate-limiting step. Complexation of the substrate with Cu(III) has not been observed hitherto in other Cu(III) oxidations.[15-17]

Dependence on [OH$^-$]. The oxidation rate also increased with increase in [OH$^-$], but again the increase was nonlinear with a tendency for k_{obsd} to reach a maximum limiting value after a certain [OH$^-$] was reached. When $1/k_{\text{obsd}}$ values, obtained under constant oxidant and substrate concentrations, were plotted with 1/[OH$^-$], a linear plot (Figure 3) resulted with an intercept on the $1/k_{\text{obsd}}$ axis showing complex dependence on [OH$^-$]. The rate constants in the presence of varying substrate and varying hydroxide concentrations are also presented in Tables I and II.

Dependence on Tellurate Ion Concentration. The disappearance rate of bis(tellurato)cuprate(III) ion decreased with the addition of increasing concentrations of tellurate ion (Table III), indicating that tellurate ion is produced in an equilibrium step preceding the slow step. A plot of $1/k_{\text{obsd}}$ vs. [tellurate] yields a straight line with an intercept and is a indicator of removal of a tellurate ion from the bis(tellurato)cuprate(III) ion.

Table III. Average Pseudo-First-Order Rate Constants for the Oxidation of Methyl Ethyl Ketone and Cyclohexanone by Potassium Bis(tellurato)cuprate(III) by Addition of Different Salts in Aqueous Alkaline Medium at 35 °C ([oxidant] = 3.5×10^{-3} M)

$10^2 \times$ [substrate], M	$10^2 \times$ [OH$^-$], M	$10^2 \times$ [salt], M	μ, M	$10^4 k_{\text{obsd}}$, s^{-1}
Substrate = Methyl Ethyl Ketone, Salt = Potassium Tellurate				
3.5	6.5	0.00	0.25	17.2
3.5	6.5	1.0	0.25	11.5
3.5	6.5	2.0	0.25	10.7
3.5	6.5	2.5	0.25	7.8
3.5	6.5	4.50	0.25	5.15
3.5	6.5	5.50	0.25	4.54
Substrate = Methyl Ethyl Ketone, Salt = Sodium Acetate				
3.5	6.4	0.1	0.251	18.8
3.5	6.4	0.2	0.252	18.5
Substrate = Methyl Ethyl Ketone, Salt = Disodium Hydrogen Phosphate				
3.6	6.2	0.1	0.256	18.1
3.6	6.2	0.2	0.262	18.6
Substrate = Cyclohexanone, Salt = Potassium Tellurate				
3.1	6.6	0.00	0.25	100.9
3.1	6.6	1.0	0.25	81.8
3.1	6.6	2.0	0.25	58.3
3.1	6.6	4.0	0.25	35.0

Table IV. Average Pseudo-First-Order Rate Constants for the Oxidation of Cyclohexanone by Potassium Bis(tellurato)cuprate(III) in the Presence of KNO_3 in Aqueous Alkaline Medium at 30 °C ([oxidant] = 5.1×10^{-3} M, [OH$^-$] = 11.3×10^{-2} M, [cyclohexanone] = 3.5×10^{-2} M)

[KNO_3], M	μ, M	$10^4 k$, s^{-1}	[KNO_3], M	μ, M	$10^4 k$, s^{-1}
0.0145	0.027	81.2	0.0785	0.33	76.0
0.0588	0.31	75.0	0.0981	0.35	75.2

Effect of Added Salt. Added salts like sodium acetate, Na_2HPO_4, and KNO_3 in the presence of constant [OH$^-$], [Cu(III)], and [substrate] did not produce any appreciable effect (Tables III and IV). Similarly, our attempts to trap radicals, if formed, by adding acrylamide or acrylonitrile did not succeed. These reagents themselves appeared to consume copper(III) in the course of the reaction.

Discussion

Potassium (dihydrogen tellurato)cuprate(III) has recently been shown to possess the formula[20] $[Cu(H_2TeO_6)_2]^{5-}$ instead of $[Cu(OH)_2(H_4TeO_6)]^{3-}$ as proposed by Rozovskii et al.[25] or $[H_yM^{III}(TeO_6)_2]^{7-y}$ suggested by Malatesta.[18] The inverse order in [tellurate] indicates a dissociation preequilibrium in which the Cu(III) moiety loses a tellurate ligand to form the (tellurato)cuprate(III) ion, which also appears to be the reactive species. The alkali dependence shows that OH$^-$ is used up either in reversible formation of the enolate ion or in abstraction of a proton from the bis(tellurato)cuprate(III) ion as suggested by Movious.[15] If both steps occurred, an [OH$^-$] dependence more than unity but less than 2 would have been observed. The present [OH$^-$] dependence, less than unity but more than zero, confirms that OH$^-$ is involved in one of the steps. However, it is not reasonable to consider involvement of the enolate ion and consequent association of OH$^-$ with the enolization step since pK_{enol} of values of these ketones[26] are >16. The OH$^-$ ion therefore can be considered to be involved

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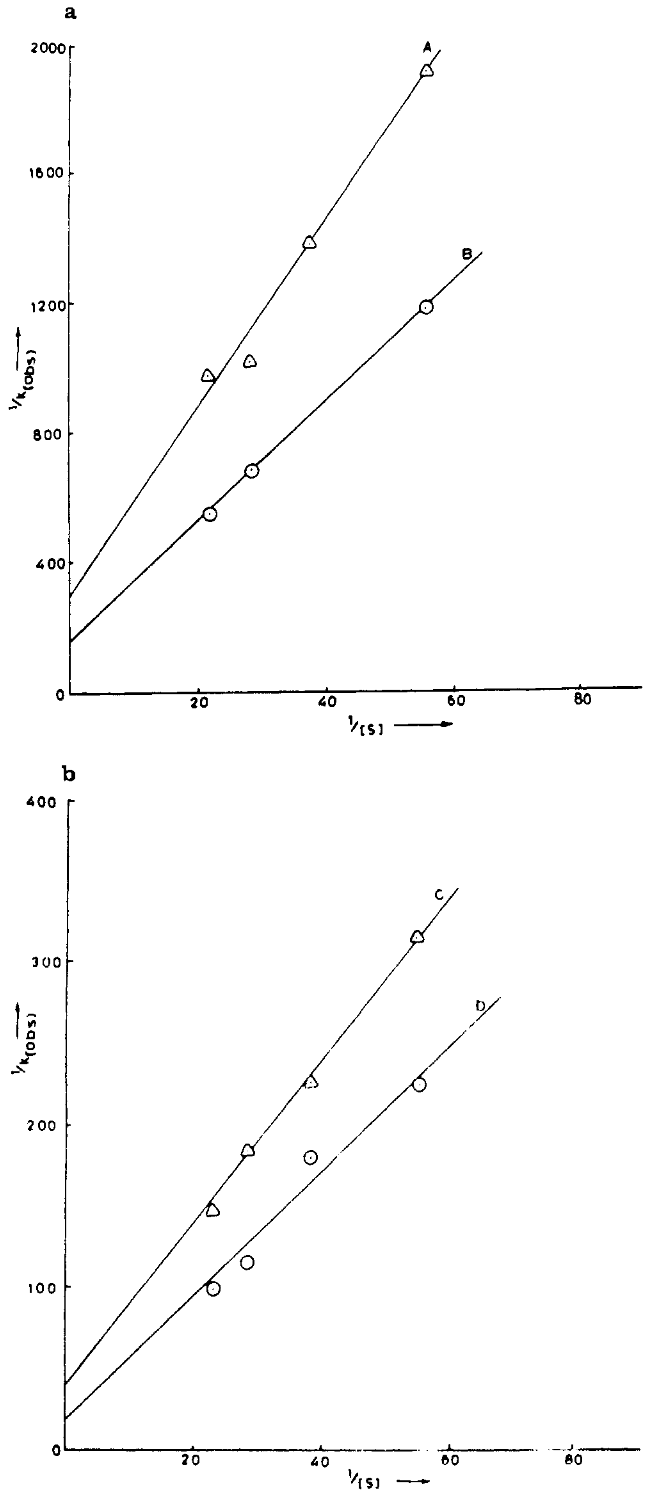

Figure 2. (a) Plot of $1/k_{\text{obsd}}$ vs. 1/[ketone] at 30 °C for the reaction of methyl ethyl ketone with Cu(III) at (A) $[\text{OH}^-] = 0.063$ M and (B) $[\text{OH}^-] = 0.105$ M ($[\text{Cu}^{3+}] = 3.5 \times 10^{-3}$ M). (b) Plot of $1/k_{\text{obsd}}$ vs. 1/[ketone] at 30 °C for the reaction of cyclohexanone with Cu(III) at (C) $[\text{OH}^-] = 0.06$ M and (D) $[\text{OH}^-] = 0.102$ M ($[\text{Cu}^{3+}] = 3.5 \times 10^{-3}$ M).

in reversible formation of the hydroxo(tellurato)cuprate ion from potassium bis(tellurato)cuprate(III) as shown in eq 1.

$$[\text{Cu}(\text{H}_2\text{TeO}_6)_2]^{5-} + \text{OH}^- \underset{}{\overset{K_1}{\rightleftharpoons}} [\text{CuOH}(\text{H}_2\text{TeO}_6)]^{2-} + \text{H}_2\text{TeO}_6{}^{4-} \quad (1)$$

The Michaelis–Menten kinetics with respect to ketone do suggest that ketone too is involved in the reversible formation of a complex that collapses in a rate-determining step to the products. It is reasonable that a hydroxo(tellurato)cuprate(III) species is the active species as OH^- dependence predicts. The steps consequently are as shown in eq 2–4.

$$[\text{CuOH}(\text{H}_2\text{TeO}_6)]^{2-} + \text{ketone} \overset{K_2}{\rightleftharpoons} \text{complex} \quad (2)$$

$$\text{complex} \xrightarrow{k} \text{radical} + \text{Cu(II)} \quad (3)$$

$$\text{radical} + \text{Cu(III)} \xrightarrow{\text{fast}} \text{products} + \text{Cu(II)} \quad (4)$$

Equations 1–3 are consistent with the observed salt effect, although several other equilibria can be written to describe the dissociation of the bis(tellurato)cuprate(III) ion, which cannot be rationalized in light of the observations.

The complex is presumed to yield in the rate-determining step a radical, which rapidly reacts with a second Cu(III) moiety to form the product. Although the radical could not be detected by the conventional polymerization tests presumably due to rapid oxidation of the radical formed, it is still possible to postulate formulation of a radical since Cu(III) is more likely to undergo one-electron transfer rather than two-electron transfer as postulated by Meyerstein.[6,7] If two-electron transfer occurred, a turbidity due to $\text{Cu}^{\text{I}}\text{OH}$ would appear during the reaction, which can be suppressed by adding a small amount of fumarate ion since fumarate ion is known to complex with Cu(I), thus stabilizing Cu(I).[27] Although we too observed faint turbidity toward the end of the reaction, it could not be suppressed by addition of fumarate ion, thus ruling out mediation of Cu(I) in these oxidation processes. Equations 1–4 result in the rate expression given by eq 5, where $[\text{Cu(III)}]_{\text{T}}$ = total copper(III) concentration and [Tel] = $[[\text{H}_2\text{TeO}_6]^{4-}]$.

$$-\frac{\text{d}[\text{Cu(III)}]_{\text{T}}}{\text{d}t} = \frac{kK_1K_2[\text{OH}^-][\text{ketone}][\text{Cu(III)}]_{\text{T}}}{[\text{Tel}] + K_1[\text{OH}^-] + K_1K_2[\text{OH}^-][\text{ketone}]} \quad (5)$$

At low $[\text{OH}^-]$ and moderate substrate concentrations, the term $K_1K_2[\text{OH}^-]$[ketone] in the denominator can be considered small compared to the other terms and hence can be negeleted. Thus eq 5 is reduced to

$$-\frac{\text{d}[\text{Cu(III)}]_{\text{T}}}{\text{d}t} = \frac{kK_1K_2[\text{OH}^-][\text{ketone}][\text{Cu(III)}]_{\text{T}}}{[\text{Tel}] + K_1[\text{OH}^-]} \quad (6)$$

or

$$k_{\text{obsd}} = \frac{kK_1K_2[\text{OH}^-][\text{ketone}]}{[\text{Tel}] + K_1[\text{OH}^-]} \quad (7)$$

or

$$\frac{1}{k_{\text{obsd}}} = \frac{[\text{Tel}]}{kK_1K_2[\text{OH}^-][\text{ketone}]} + \frac{1}{kK_2[\text{ketone}]} \quad (8)$$

Equation 8 suggests a plot of $1/k_{\text{obsd}}$ vs. [Tel] at constant $[\text{OH}^-]$ and [ketone] should be linear, which in fact has been observed. From the intercept and slope of the plot, K_1 values have been obtained, which are respectively 0.3296 and 0.3271 with use of the kinetic data of methyl ethyl ketone and cyclohexanone oxidations. The excellent agreement between the two values obtained independently of each other from two different sets of kinetic data confirms step 1. Further, the K_1 value was used to compute a value of 4×10^{-9} for the formation constant of bis(tellurato)cuprate(III). The computed value at 30 °C, though different from the value of Lister[28] at

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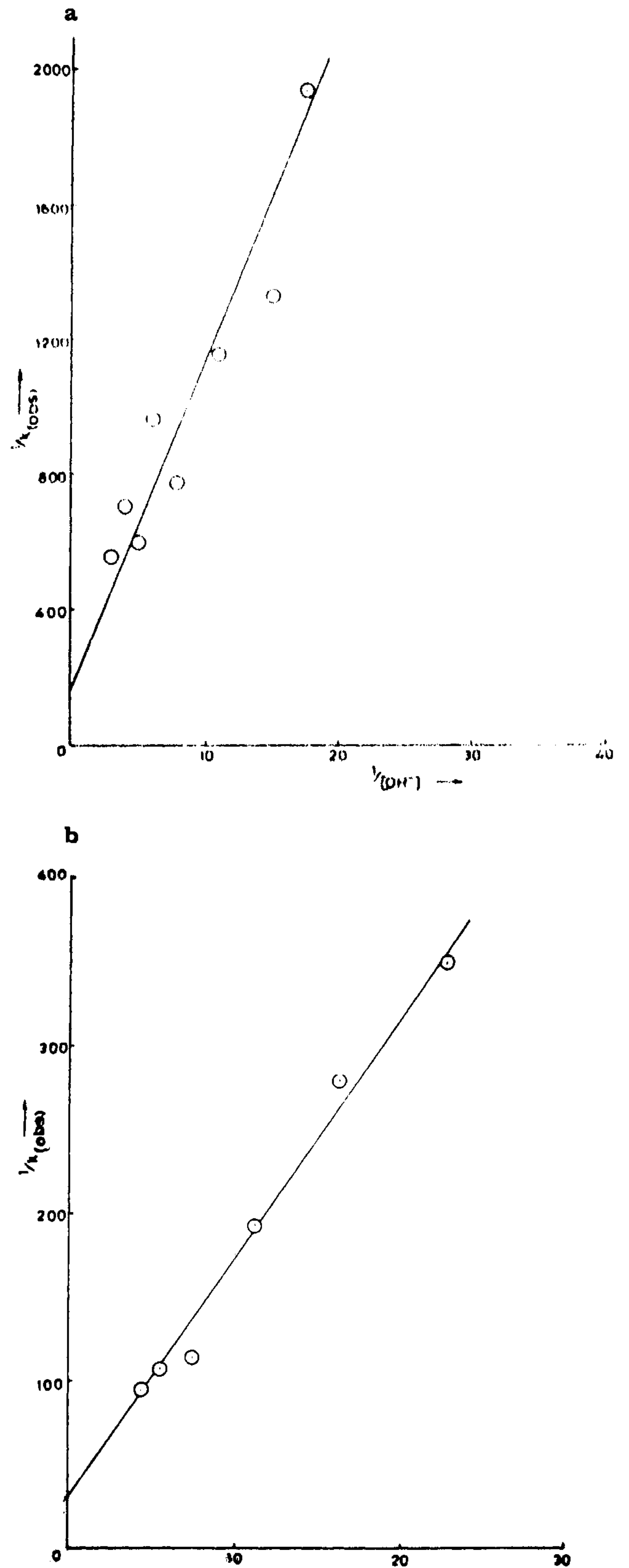

Figure 3. (a) Plot of $1/k_{obsd}$ vs. $1/[OH^-]$ at 30 °C for the reaction of (a) methyl ethyl ketone and (b) cyclohexanone with Cu(III).

40 °C by 3 orders of magnitude, is quite reasonable.

In order to evaluate K_2, rate data obtained by varying [ketone] at high constant $[OH^-]$ were employed. In the absence of added tellurate ion rate equation 5 reduces to eq 9.

$$k_{obsd} = \frac{kK_2[\text{ketone}]}{1 + K_2[\text{ketone}]} \tag{9}$$

The rate expression becomes independent of $[OH^-]$, which in fact is observed at high $[OH^-]$ (eq 10).

$$\frac{1}{k_{obsd}} = \frac{1}{k} + \frac{1}{kK_2[\text{ketone}]} \tag{10}$$

Plots of $1/k_{obsd}$ vs. 1/[ketone] are linear. From the slope and intercept of the plot k and K_2 values were computed. The K_2 values are 8.68 and 7.5 L mol^{-1} for methyl ethyl ketone and cyclohexanone, respectively. Corresponding k values are 6.06×10^{-3} and 3.33×10^{-2} mol L^{-1} s^{-1}. The K_2 values obtrained here, when substituted for the intercept and slope of the $1/k_{obsd}$ vs. [Tel] plot, result in k values for methyl ethyl ketone and cyclohexanone of 5.5×10^{-3} and 4.4×10^{-2} L mol^{-1} s^{-1}, in fair agreement with k values obtained from an entirely different plot involving a different set of conditions.

The higher k value for cyclohexanone over that of methyl ethyl ketone is consistent with the observed rate data.

The rate and the equilibrium constants computed as described above were substituted in the rate equation (eq 5) and calculated rate constants obtained. Comparison of k_1(obsd) and k_1(calcd) shows fair agreement (SD = 0.240 ± 0.037) between them.

The kinetic picture is consistent with the rate-limiting breakdown of an inner-sphere complex to yield a radical that in subsequent fast steps gives the final products. The formation of an inner-sphere complex between a hydroxo(tellurato)-cuprate(III) ion and a molecule of ketone through an electrophilic attack of Cu(III) on the reaction center in the ketone molecule may be envisaged. This is consistent with the observation that neither ionic strength effect nor any salt effect is observed except the effect due to added tellurate ion, which essentially behaves as a stabilizing ligand.

For all reactions between an ion and a neutral molecule or a reaction where there is no change of ionic charge on going from the reactant molecule to the transition state,[29] no change of ionic strength effect will be observed.

The one-electron transfer from the substrate to the oxidant is considered with the observation of Raycheba and Margerum, who have earlier noted a one-electron transfer in oxidation of iodide ions by copper(III)–deprotonated peptide complexes.[14] Additional justification as to Cu(III) behaving like a one-electron oxidant can also be sought from the following aspects in the ketone oxidations. The most interesting point in elucidation of the mechanism of oxidation of ketones by transition-metal ions pertains to the species of ketone involved in the rate-limiting step. Best, Littler and Waters[30] have conclusively established from solvent isotope effect studies that enolization of the ketone constitutes the rate-limiting step in oxidations by a two-electron oxidant like Cr(VI). This has been further established by using other two-electron oxidants[31] like I_2, Br_2, Hg(II), Tl(III), and Mn(VII) in acid medium.

In oxidations of ketones by one-electron oxidants[32,33] like V(V), Co(III), Mn(III), and Ce(IV) solvent isotope effect measurements provide confirmatory evidence of direct attack on the ketonic form and in all such oxidations the salient feature is rapid formation of a keto–oxidant complex breaking down in a slow step as opposed to a concerted mechanism in oxidations by two-electron oxidants.

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The experimental evidence leads to the conclusion that a one-electron redox step is involved in the oxidation of methyl ethyl ketone and cyclohexanone with Cu(III) and that in the rate-limiting step Cu(III) is reduced to Cu(II) only.

Acknowledgment. Thanks are due to Dr. S. N. Mahapatro and Dr. R. K. Panda of this department for their helpful discussions. A.C.P. thanks the Government of Orissa for sanction of study leave.

Registry No. $K_5[Cu(H_2TeO_6)_2]$, 74606-82-9; methyl ethyl ketone, 78-93-3; cyclohexanone, 108-94-1.

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Anisotropic Exchange in Transition-Metal Dinuclear Complexes. 3. Bis(μ-1,3-azido)bis(1,1,4,7,7-pentamethyldiethylenetriamine)dicopper(II) Bis(tetraphenylborate)

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Received August 9, 1983

The single-crystal EPR spectra of bis(μ-1,3-azido)bis(1,1,4,7,7-pentamethyldiethylenetriamine)dicopper(II) bis(tetraphenylborate), $Cu_2(Me_5dien)_2(N_3)_2(BPh_4)_2$, have been recorded in the range 5–140 K at both X- and Q-band frequencies. The **g** and **D** tensors have been found to be temperature dependent and not parallel to each other. The spectra at 5 K yield $g_{xx} = 2.056$, $g_{yy} = 2.038$, $g_{zz} = 2.211$, $D_{x'x'} = -136 \times 10^{-4}$ cm^{-1}, $D_{y'y'} = -432 \times 10^{-4}$ cm^{-1}, and $D_{z'z'} = 569 \times 10^{-4}$ cm^{-1}. The x and x' axes are practically parallel, while y and y' and z and z' make an angle of ~20°. The experimental zero-field splitting has been found to exceed the value expected for point dipoles centered on the metal ions. The deviation is attributed to a substantial exchange contribution, which is discussed in terms of the interaction between the ground state of one ion with an excited state of the other ion.

Introduction

The study of the terms of the exchange spin Hamiltonian

$$H = J\mathbf{S}_1\cdot\mathbf{S}_2 + \mathbf{S}_1\cdot\mathbf{D}\cdot\mathbf{S}_2 + \mathbf{d}\cdot\mathbf{S}_1\times\mathbf{S}_2 \tag{1}$$

has been mainly limited to the isotropic term,[1-6] for which now many useful correlations exist with the structural parameters of the complexes.[7] Much less information is available on the parameters of the anisotropic exchange, **D**, and of the antisymmetric exchange interactions, **d**, although in principle they can yield precious information on the interaction between the ground and excited states of the dinuclear units.[8,9] Recently we have reported that a very large zero-field splitting is operative in the triplet state of bis(μ-hydroxo)copper(II) complexes, much larger than would be expected on the basis of magnetic dipolar interactions between the two copper ions.[10] We interpreted the experimental data to show that a ferromagnetic coupling is operative between $x^2 - y^2$ and xy magnetic orbitals centered on the two metal ions.

Recently, Hendrickson[11] reported the magnetic susceptibility data and the crystal structure of bis(μ-1,3-azido)bis(1,1,4,7,7-pentamethyldiethylenetriamine)dicopper(II) bis(tetraphenylborate), $Cu_2(Me_5dien)_2(N_3)_2(BPh_4)_2$. The temperature dependence of the magnetic susceptibility yielded $J = 13$ cm^{-1}, and the zero-field splitting of the triplet state was found to be fairly large. On the basis of polycrystalline powder spectra, and of an analysis according to which the **g** and **D** tensors were considered as parallel to each other, the spin Hamiltonian parameters were assumed as $D = 870 \times 10^{-4}$ cm^{-1}, $E = 162 \times 10^{-4}$ cm^{-1}. These data clearly show that exchange contributions are operative in the anisotropic term, since the reported parameters largely exceed the values expected for a dominant dipolar mechanism,[11] but single-crystal data are required in order to obtain information on the relative orientation of **g** and **D** within the dinuclear units. We wish to report here the results of such a study with the aim of understanding the mechanism of exchange involving the ground and excited orbitals.

Experimental Section

The compound was prepared as previously described.[11] Single crystals were grown by slow evaporation of acetone solutions and found to conform to the reported crystal structure[11] with use of a Philips PW1100 automatic diffractometer. The unit cell is monoclinic, space group $P2_1/n$, with $a = 12.798$ Å, $b = 19.538$ Å, $c = 13.072$ Å, $\beta = 93.64°$, and $Z = 4$.

Single-crystal EPR spectra were recorded with a Varian E-9 spectrometer equipped with both X- and Q-band frequency (9 and 35 GHz). Spectra at liquid-helium temperature were measured with use of Oxford Instrument ESR 9 and ESR 35 continuous-flow cryostats.

Results

Single-crystal EPR spectra of $Cu_2(Me_5dien)_2(N_3)_2(BPh_4)_2$ were recorded at X-band frequency in the range of temperature 5–140 K. The static magnetic field was rotated around the three orthogonal directions a, b, c^*. The spectra are temperature dependent as shown in Figure 1. At low temperature the spectra comprise four septets of lines, for a general orientation in the static magnetic field, in agreement with the presence of two magnetically nonequivalent pairs of copper(II) ions. The spectra in Figure 1 are recorded in the bc^* plane with the static magnetic field parallel to c^*. When the temperature is increased, the signals broaden until eventually the hyperfine splitting at 77 K is completely washed out. Also, the resonance fields are found to be affected by the temperature. Complete rotation data were collected at 5 and 140 K, respectively. The angular dependences of the transition

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