which polyhedron is likely to be the most stable for a particular value of n. The equation $U = d^{-2} - d^{-1}$, corresponding to a shallow potential energy minimum at $d = 2.0$ Å, in our opinion grossly overemphasizes the significance of the longer range interactions and is not directly transferable to smaller or larger polyhedra than those used for calibration purposes. A more satisfactory variation of the approach would, we suggest, be one that focused attention on the dominant bonding interactions, i.e. those between nearest neighbors, by use of a more realistic bond length–bond energy relationship, according much lesser significance to the internal cross-polyhedral interactions. Ideally, it would also make some allowance for the way the skeletal electron density of *closo*-borane-type clusters varies with the cluster size. We have elsewhere outlined an approach[15] by which the known structures of the borane anions $B_nH_n^{2-}$ ($n = 6, 8, 9, 10,$ or 12) can be used as guides to the strength of their skeletal bonding and are extending this approach to allow its use for structural predictions.

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Kinetics and Mechanism of the Copper(II)-Catalyzed Oxidation of Lactic Acid with Chloramine T (CAT) in Alkaline Solutions

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N-Chloro-*p*-toluenesulfonamide, better known as chloramine T or CAT, has long been used as an analytical reagent. There are excellent reviews covering its oxidizing action, by Ozerassi,[1] Filler,[2] Mathur and Narang,[3] Mukherji,[4] and Campbell and Johnson.[5] There are a number of publications on the mechanistic aspects of the redox reactions in acidic media in which one of the species, RNHCl (R = $CH_3C_6H_4SO_2$), HOCl, or H_2OCl^+, has been considered reactive. A recent report[6] describes the oxidation of iodide studied by a fast-mixing technique. Osmium(VIII)-catalyzed oxidations[7-11] have received greater attention in alkaline medium with an operation of the Os(VIII)/Os(VI) cycle and/or complex formation of Os(VIII) with the reducing substance. Since copper(II) is known to form[12,13] copper(III) if oxidized and stabilized by suitable ligands in alkaline solutions, we thought the mechanistic study involving copper(II) as a catalyst in oxidations with CAT might enable us to know more of the chemistry of copper(III). α-hydroxy acids seemed to us a suitable family of reducing substances for the study, and a beginning was

made with lactic acid (LA). There is one report[14] on copper(II) catalysis in the oxidation of arginine hydrochloride with CAT in alkaline solutions, and the catalysis has been ascribed to the complexation of Cu(II) and the reducing substance.

Experimental Section

Chloramine T of E. Merck quality was used as received, and its solution was prepared in doubly distilled water and stored in black-coated bottles to prevent its photochemical decomposition.[15] It was standardized iodometrically.[16] Solutions of lactic acid (Koch Light), sodium hydroxide (BDH AnalaR), and copper(II) sulfate (BDH AnalaR) were also prepared in doubly distilled water and standardized by the known methods. Other chemicals employed were either of BDH AnalaR or E. Merck quality. All glass vessels were of Corning make.

CAT and other constituents in required quantities were separately temperature equilibrated in a thermostat at 45 ± 0.1 °C unless mentioned otherwise. The reaction was initiated by adding a known volume of CAT to the other bottle. Aliquots of 5 or 10 mL were analyzed iodometrically after intervals of 10 or 15 min and acidification of the mixture. A blank for copper(II) was deducted from the volume of thiosulfate required for titration. The data were initially treated for initial rates[17] to make a plot of rate vs. [CAT] and to know the order in this respect. This was unity, and hence subsequently pseudo-first-order plots were made in all cases by plotting log [CAT] vs. time. The duplicate measurements were reproducible to ±10%. In most cases the extent of the reaction studied was 50–60%.

Spectrophotometric measurements were made on a Toshniwal spectrophotometer with a 1-cm cell to characterize the various species existing in the system and to detect the complex formation between copper(II) and CAT, copper(II) and lactic acid, and copper(II) and *p*-toluenesulfonamide, which is one of the products.

Results

Stoichiometry and Products. Reaction mixtures containing excess CAT along with 0.5 M NaOH and 5×10^{-5} M Cu(II) were left for more than 100 h at 80 °C for the completion of the reaction. One mole of lactic acid required 1.0 ± 0.1 mol of CAT for its oxidation to pyruvic acid, identified by sub-

Table I. Variation of OH⁻ and Cu(II) in the Oxidation of Lactic Acid with CAT and the Values of k_0 ([LA] = 0.05 M, [CAT] = 4.0×10^{-3} M, $I = 0.5$ M, 45 °C)

$10^5 \times$ [Cu(II)]/ M	$10^5 k_0/s^{-1}$				
	0.1 M [OH⁻]	0.2 M [OH⁻]	0.3 M [OH⁻]	0.4 M [OH⁻]	0.5 M [OH⁻]
1.0	3.2	3.7	4.0	4.6	5.0
2.0					5.5
3.0	3.7	4.2	4.8	5.5	6.0
4.0					6.6
5.0	4.1	4.9	5.3	6.4	7.0
6.0					8.0
7.0	4.4	5.3	6.3	7.3	
9.0	4.5	5.7	6.9	8.4	
10.0		6.35	7.4	8.8	10.0

Table II. First-Order Rate Constants of the Cu(II)-Catalyzed Reaction between CAT and Lactic Acid in the Presence of PTS ([CAT] = 2.5×10^{-3} M, [LA] = 5.0×10^{-2} M, [OH⁻] = 0.5 M, 45 °C)

$10^3 \times$ [PTS]/M	$10^5 k_0/s^{-1}$			
	1.0×10^{-5} M [Cu(II)]	3.0×10^{-5} M [Cu(II)]	5.0×10^{-5} M [Cu(II)]	7.0×10^{-5} M [Cu(II)]
1.0	3.2	4.4	5.4	
3.0		3.7	4.15	5.0
5.0	2.7	3.5	3.7	4.5
7.0	2.6	3.15	3.45	4.0
9.0	2.5	3.0	3.15	3.7

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jecting its hydrazone to TLC, IR spectrometry, and a determination of melting point. The following stoichiometry may be suggested:

$$CH_3C_6H_4SO_2N\cdot NaCl + CH_3CHOHCOO^- \rightarrow$$
$$CH_3C_6H_4SO_2NH_2 + CH_3COCOO^- + NaCl \quad (1)$$
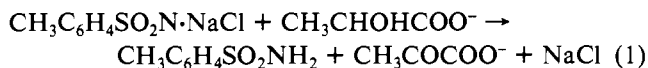
The same stoichiometry is reported in the Os(VIII)-catalyzed reaction. In the oxidation with N-chlorobenzenesulfonamide[18] (CAB) also, which is an oxidant similar to CAT, the product of the oxidation of lactic acid was pyruvic acid.

Rate Law. The concentrations of CAT in the range (1×10^{-4})–(5×10^{-3}) M and of lactic acid in the range (2×10^{-2})–(1×10^{-1}) M were varied at constant [OH$^-$] = 0.5 M. The order in CAT was found to be unity, but the rate was independent of the concentration of lactic acid. An average value of the pseudo-first-order rate constant from 40 experiments was found to be $(6.8 \pm 0.3) \times 10^{-5}$ s^{-1} at 45 °C. The variation of [OH$^-$] was made at different concentrations of copper(II), and the ionic strength was adjusted to 0.5 M with NaNO$_3$. The results are given in Table I. The concentration of copper(II) sulfate was varied in the range $(1.0–10.0) \times 10^{-5}$ M. Since autoinhibition was observed after about 50% reaction, a few reactions were carried out in the presence of p-toluenesulfonamide (PTS), a reduction product of CAT. The results at different concentrations of copper(II) are given in Table II. Pyruvic acid, which is the oxidation product of lactic acid, had no effect on the rate. The ionic strength was varied from 0.1 to 0.5 M with NaNO$_3$, but the reaction rate was unaffected. From the various types of concentration dependences, the following rate law seems to hold:

$$k_o = k_1 + k_2[OH^-] + \frac{(k_3 + k_4[OH^-])[Cu(II)]}{1 + K[PTS]} \quad (2)$$

where k_o is the observed first-order rate constant and K is the formation constant of the complex between Cu^{II} and PTS. The various rate constants, k_1, k_2, k_3, and k_4, have been defined later. The two terms $k_1 + k_2[OH^-]$ can be referred to the uncatalyzed reaction.

Rate Constants. A plot of k_o vs. [OH$^-$] (at fixed [Cu(II)] from Table I) yields a straight line with a nonzero intercept. The intercepts (s^{-1}) and slopes (M^{-1} s^{-1}) at 10^5[Cu(II)]/M = 1.0, 3.0, 5.0, 7.0, 9.0, and 10.0 were found to be 2.8×10^{-5}, 3.0×10^{-5}, 3.3×10^{-5}, 3.4×10^{-5}, 3.6×10^{-5}, and 3.7×10^{-5} and 4.5×10^{-5}, 6.5×10^{-5}, 7.5×10^{-5}, 9.5×10^{-5}, 11×10^{-5}, and 13×10^{-5}, respectively. The two separate plots of intercepts and slopes vs. [Cu(II)] again yield straight lines with nonzero intercepts. The intercepts 2.6×10^{-5} s^{-1} and 3.6×10^{-5} M^{-1} s^{-1} can be identified with k_1 and k_2, respectively. The slopes 0.12 M^{-1} s^{-1} and 0.94 M^{-2} s^{-1} can be identified with k_3 and k_4.

If a plot of k_o vs. [Cu(II)] (from Table I) at fixed [OH$^-$] is made, again a straight line with a nonzero intercept is obtained. At [OH$^-$] = 0.1, 0.2, 0.3, 0.4, and 0.5 M the intercepts (s^{-1}) and slopes (M^{-1} s^{-1}) were found to be 3.0×10^{-5}, 3.2×10^{-5}, 3.6×10^{-5}, 4.0×10^{-5}, and 4.4×10^{-5} and 0.19, 0.30, 0.37, 0.47, and 0.56, respectively. Plots of intercepts vs. [OH$^-$] and those of slopes vs. [OH$^-$] again yield straight lines with nonzero intercepts. These values of intercepts and slopes, 2.7×10^{-5} s^{-1}, 3.2×10^{-5} M^{-1} s^{-1} and 0.10 M^{-1} s^{-1}, 0.96 M^{-2} s^{-1} can again be identified with k_1, k_2, k_3, and k_4, respectively. The two sets of values are quite similar.

If now plots of k_o vs. [Cu(II)] at different concentrations of PTS (from Table II) are made, again straight lines with nonzero intercepts are obtained. The intercepts of these plots are almost the same because they refer to $k_1 + k_2[OH^-]$, and
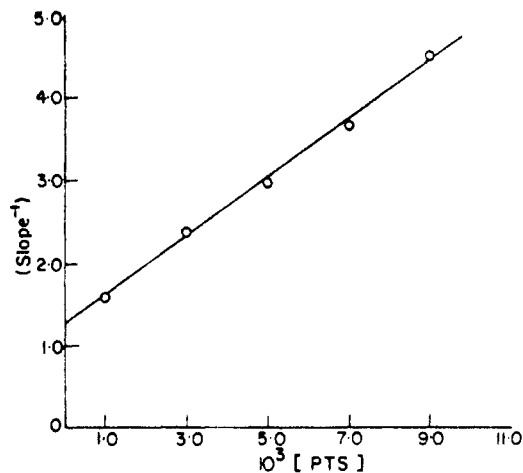

Figure 1. Plot of (slope)$^{-1}$ vs. [PTS]; [OH$^-$] = 0.5 M. Slopes have been obtained from a plot of k_o vs. [Cu(II)] at different [PTS].
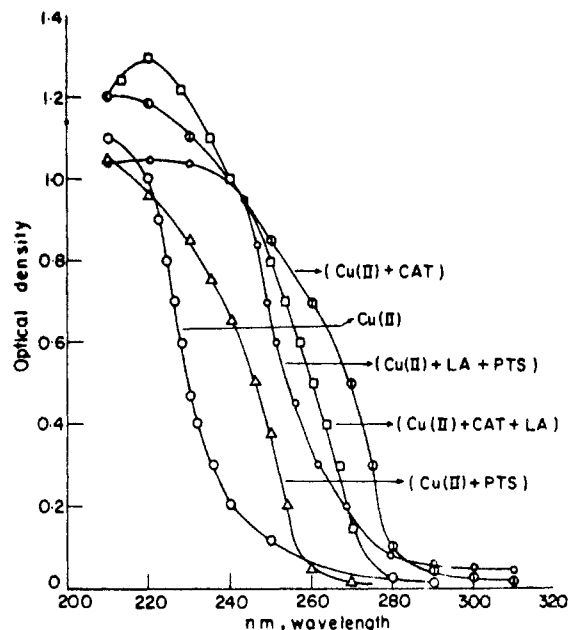
Figure 2. UV spectra of mixtures of Cu(II) and other reactants in 0.5 M [OH$^-$]: (○) 5×10^{-5} M [Cu(II)]; (o) 5×10^{-5} M [Cu(II)] + 5×10^{-4} M [CAT]; (□) 5×10^{-5} M [Cu(II)] + 5×10^{-4} M [CAT] + 0.05 M [LA]; (△) 5×10^{-5} M [Cu(II)] + 1×10^{-3} M [PTS]; (◊) 5×10^{-5} M [Cu(II)] + 1×10^{-3} M [PTS] + 0.05 M [LA].

[OH$^-$] is constant. The constant value found is 2.2×10^{-5} s^{-1} at 0.5 M [OH$^-$]. The slopes (M^{-1} s^{-1}) at 10^3[PTS] = 1.0, 3.0, 5.0, 7.0, and 9.0 M were found to be 0.63, 0.42, 0.33, 0.27, and 0.22, respectively. A plot of (slope)$^{-1}$ vs. [PTS] is given in Figure 1, and from the intercept and slope of the line obtained, one calculates the value of $K = 270 \pm 30$ M^{-1}.

Spectrophotometry. These results indicated that there is no change in the absorption of mixtures of Cu(II) and OH$^-$ and of Cu(II) and lactic acid by the variation of OH$^-$ and lactic acid in the concentration ranges employed in the investigation. Copper(II) seems to be present completely in the form of the lactate complex. There are a few papers[19] reporting the formation constant to be about 1000. A paper[20] on X-ray analysis also indicates a large formation constant. There is spectral evidence for a complex of Cu(II) and PTS. The formation constant was found to be 350 ± 50 M^{-1} determined

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by the Yatsimirskii method[21] by measuring the absorptions of the mixtures of Cu(II) (in solutions of OH⁻ and lactic acid) and PTS at 250 nm and 30 °C. There is evidence for a complex of Cu(II) and CAT too, but no such complexation is indicated kinetically. Some of the results are given in Figure 2.

Discussion

Various Species Participating in the System. There are three main reactants, CAT, lactic acid, and copper(II). The form of their species may depend on the concentration of OH⁻ and/or the interaction among themselves to form complexes. Lactic acid would be present as the acetate ion. CAT ionizes in solution into RNCl⁻ and Na⁺, and thus the predominant species of CAT in alkaline solutions would be RNCl⁻. The concentration of RNHCl would be insignificant in alkaline solutions since the protonation constant[7,22] is only 4.2×10^2 and hence subsequent hydrolytic and disproportionation reactions would also be insignificant. The hydroxide ion dependence should be connected with copper(II). Margerum and co-workers[23] have reported two species, $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$, in alkaline solutions of Cu(II), and the formation constant for the equilibrium (3) is reported to be about 16.

$$Cu(OH)_3^- + OH^- \xrightleftharpoons{K_3} Cu(OH)_4^{2-} \qquad (3)$$
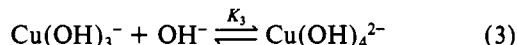
Our kinetic results indicate a lower value (<0.1) so that $[Cu(OH)_3^-] \gg [Cu(OH)_4^{2-}]$. Alternatively K_3 may be much larger than 16 and an equilibrium (eq 4) with a small value

$$Cu(OH)_4^{2-} + OH^- \xrightleftharpoons{K_4} Cu(OH)_5^{3-} \qquad (4)$$
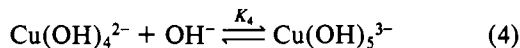
for K_4 may exist in the system. In any case the two copper(II) species in the present investigation are undefined, but they differ by one OH⁻ in an equilibrium of the type

$$Cu(OH)_n^{(n-2)-} + OH^- \rightleftharpoons Cu(OH)_{n+1}^{(n-1)-} \qquad (5)$$
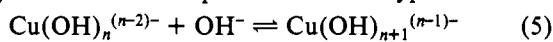
The hydroxy species of copper(II) form a complex with the lactate ion, and this further complexes with CAT at the nitrogen site as shown, yielding a ternary complex:
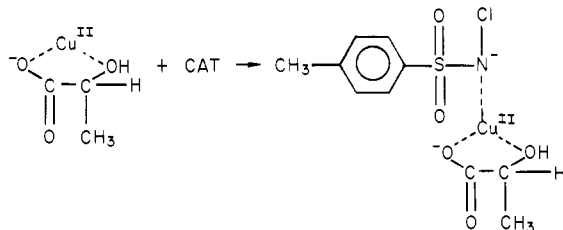
Such a configuration for the intermediate and then activated complex is facile for the electron transfer, and such ternary reactive complexes have been reported also in the oxidations with peroxydisulfate[24] and hydrogen peroxide.[25]

Visual observations on systems containing CAT, copper(II), and OH⁻ have indicated a transient yellow species, which is likely to be Cu^III. However, in the presence of lactic acid, it either is not formed or disappears quickly. Lister[26] and Margerum[27] have reported the formation of $Cu(OH)_4^-$ in the copper(II)-catalyzed decomposition of hypochlorite. There are other copper(II)-catalyzed reactions[28] in which copper(III)

is said to be formed. It is therefore very likely that Cu^III is formed in the present investigation too. In general, copper(II) catalysis in an acid medium operates through a more reactive coordination complex with oxidant or reductant, and in alkaline solutions, it operates through the Cu^II/Cu^III cycle. The latter is more probable if some coordinating oxidant ligand is present,[29] and since the oxidant CAT can serve as a ligand in the present case, the formation of transient Cu^III is possible.

Some calculations and comparisons may be worthwhile to make. The calculated value of $k_1 + k_2[OH^-]$ with an average value of $k_1 = 2.7 \times 10^{-5}$ s⁻¹ and that of $k_2 = 3.4 \times 10^{-5}$ M⁻¹ s⁻¹ is 4.4×10^{-5} s⁻¹ at $[OH^-] = 0.5$ M. The extrapolated value from the plot of k_o vs. [Cu(II)] was found to be 4.3×10^{-5} s⁻¹. Similarly the calculated value of $k_3 + k_4[OH^-]$ with an average value of $k_3 = 0.11$ M⁻¹ s⁻¹ and that of $k_4 = 0.95$ M⁻² s⁻¹ is 0.585 M⁻¹ s⁻¹ at $[OH^-] = 0.5$ M. The extrapolated value (Figure 1) from the plot of (slope)⁻¹ vs. [PTS] was found to be 0.77 M⁻¹ s⁻¹. The agreement in the calculated and extrapolated values should be considered satisfactory in view of the complexity of the system.

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An Easy Preparation with Full Characterization of Pd6Cl12: A Form of Palladium Chloride Soluble in Aromatic Solvents

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Palladium chloride is reported to exist in two forms called α and β.[1,2] An usual method of preparation involves the direct chlorination of metallic palladium or its reaction with HCl in the presence of an oxidant (e.g., HNO_3 or NO_2). When the preparation is carried out at temperatures below 550 °C, the resulting $PdCl_2$ is claimed to be the β-form.[1-3]

The structural nature of this form was investigated by Shäfer et al.[4] Its isomorphism with β-$PtCl_2$[5] together with the determination of the molecular mass by mass spectroscopy supported the conclusion that the β-form contains discrete molecular clusters of formula Pd_6Cl_{12}. This proposed structure is quite different from that of the α-form, which is known to be a polymeric chain of $PdCl_2$ units, bridged by chlorine atoms.[6]

Unfortunately Shäfer et al. did not report the experimental method of preparation of the β-form that they have investigated. Only later was it claimed[1-3] that the β-form corresponded to ordinary commercial $PdCl_2$.

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