Kinetics and mechanism of oxidation of allyl, crotyl and propargyl alcohols by diperiodato cuprate(III) in alkaline medium

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The kinetics and mechanism of oxidation of α, β-unsaturated alcohols (UA) such as allyl, crotyl and propargyl alcohols by periodate complex of trivalent copper in aqueous alkaline medium has been studied spectrophotometrically at 416 nm. The order in [oxidant] and [substrate] is found to be unity each. The rate decreases with increase in [periodate] and increases with increase in [OH$^-$]. There is no effect of addition of salts like Na$_2$SO$_4$ and KNO$_3$. The primary kinetic isotopic effect k_H/k_D is 3.87 at 313 K. The solvent isotopic effect k_{H_2O}/k_{D_2O} is 0.912 at 313 K. The product of oxidation has been identified as the corresponding aldehyde. Participation of double bond in the oxidation reaction has not been observed. Under the experimental conditions monoperiodato cuprate(III) species has been assumed to be the active species. The results are discussed in terms of + I effect of methyl group and resonance stabilisation of free radical. The observed results are explained in terms of an outersphere electron transfer mechanism.

Diperiodato cuprate(III) (DPC) is a powerful one electron oxidant towards nearly all organic functional groups and is well known in analytical chemistry in the estimation of sugars, trihydric alcohols, aminoacids, proteins[1], carboxylic acids[2], carbonyl compounds[3] and alcohols[4]. The presence of copper (III) as intermediate was also reported in some Cu(II)-catalysed oxidation reactions by peroxydisulphate and vanadium (V)[5]. The kinetics of decomposition and formation of Cu(III)-diperiodate and tellurate complexes were studied by Rozovskii and coworkers[6]. Fairly large amount of work has been reported on the oxidation of alcohols, amines, diols, aldehydes and cyclic alcohols[7-8] by DPC in alkaline medium and different mechanisms involving either O—H, C—H, N—H or C—C bond fission in the rate determining step has been put forth. Kinetics of oxidation of unsaturated alcohols has been extensively studied by several workers using different metal ions and their complexes as oxidants[9-12]. In the oxidation of unsaturated alcohols (UA) there exists a possibility of attack on double bond or the α-C—H bond or the hydroxyl group. This has received some support from the identification of unsaturated carbonyl compounds and double bond cleavage products during the oxidation of unsaturated alcohols by oxidants such as Ce(IV)[11] and Os(VIII)[13].

However, there is no systematic report on the reactivity of Cu(III) towards $\rangle$C = C$\langle$ when other functional groups are attached to it. We have therefore studied the oxidation of α, β-unsaturated alcohols using DPC in order to establish the selectivity of Cu(III) towards carbon-carbon double bonds, to get an insight into the mechanism of oxidation of the substrates and to study the characteristic behaviour of Cu(III) in these oxidations.

Materials and Methods

DPC solution was always prepared a fresh and estimated according to the standard procedure[2]. The water used for the reactions was doubly distilled. The unsaturated alcohols used were of either Fluka or BDH grade. α, α'-dideutero allyl alcohol was prepared by the standard method[14] and its purity checked by PMR spectra. Deuterium oxide was obtained from BARC, Bombay, India. UV-vis absorption spectra of DPC were recorded on a Hitachi U-3410 spectrophotometer. The solutions containing substrate along with required amounts of base and ligand were taken in the reaction flask and DPC in another flask and thermally equilibrated at the desired temperature before mixing. The kinetics was monitored by observing the change in absorbance of DPC using U-1000 Hitachi digital spectrophotometer at 416 nm. The molar absorption coefficient of DPC under the experimental conditions was 1.00×10^4 dm^3 mol^{-1} cm^{-1}. For all sets blank reactions

were carried out for checking any self decomposition of DPC during the course of reaction. The reactions were generally followed upto 50% of the reaction.

Stoichiometry and product analysis

Stoichiometric runs with an excess of [DPC] over [α, β-unsaturated alcohol] revealed that one mole of unsaturated alcohol requires two moles of DPC in the presence of [OH⁻] and [periodate]. Copper(III)-allyl alcohol mixture induced polymerisation of acrylamide in nitrogen atmosphere suggesting that free radicals are formed as intermediates.

The products of oxidation of unsaturated alcohols were the corresponding aldehydes. All the aldehydes were detected by preparing their 2,4-DNP derivatives and comparing melting points with the literature values. This was confirmed by characteristic absorption of unsaturated aldehydes in UV-absorption spectrum, which was around 250 nm. Further confirmation was obtained by comparing the peaks of authentic sample as well as the product obtained in the experiment by GC analysis (using Datacat instrument—carbowax column at 100°C—detector-TCD—carrier gas N_2, pressure—2.5 kg cm² —flow rate 40 cc min⁻¹).

Results and Discussion

Under the conditions [DPC] ≪ [UA], plots of log (a/a-x) versus time were linear indicating first order dependence of rate on [oxidant]. From the slopes of such plots pseudo-first order rate constants k' were evaluated at different concentrations of DPC and found to be same (Table 1), a representative plot for allyl alcohol is given in Fig. 1A. The order in [UA] was one (Table 2) as observed from the slopes of linear plots of log k' versus log [UA], (Fig. 1B). Added salts such as KNO_3 and Na_2SO_4 had negligible effect on the rate.

At constant [DPC], [UA], [periodate] and temperature the order in [OH⁻] was found to be fractional (Table 1). At constant [DPC], [UA], [OH⁻] and temperature the rate decreased with increase in [IO₄⁻], (Table 1). The rate constant for the oxidation of deuterated and undeuterated allyl alcohol at 313 K were 1.35×10^{-4} and 5.26×10^{-4} s⁻¹ respectively. This gives the kinetic isotopic effect k_H/k_D as 3.87. The solvent isotopic effect was observed to be 0.912.

The periodate complex of trivalent copper was found to exist mainly in three forms in alkaline medium viz., diperiodatocuprate(III), monoperiodatocuprate(III) and tetrahydroxocuprate(III)

Table 1—Effect of varying [DPC], [OH⁻], [IO₄⁻] on the reaction rate

[AA] = 7.5×10^{-3} mol dm⁻³; temp. = 313 K.

10^5 [DPC] (mol dm⁻³)	10^2 [OH⁻] (mol dm⁻³)	10^4 [IO₄⁻] (mol dm⁻³)	10^4 k' (s⁻¹)
5.70	1.00	5.80	5.26
11.4	1.00	5.80	5.47
17.1	1.00	5.80	5.26
22.8	1.00	5.80	5.26
5.70	1.20	5.80	5.76
5.70	1.55	5.80	6.23
5.70	1.90	5.80	7.16
5.70	2.20	5.80	8.00
5.70	1.00	2.90	13.4
5.70	1.00	8.70	4.98
5.70	1.00	11.6	4.31
5.70	1.00	14.5	3.66
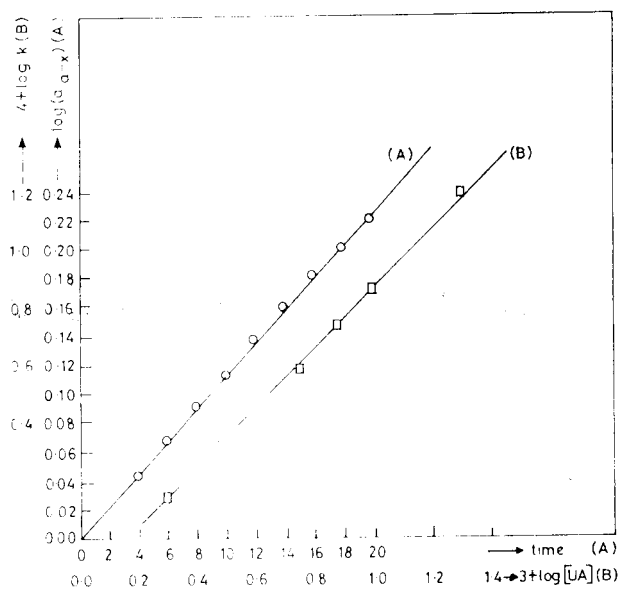
Fig. 1—(A) Plot of log (a/a-x) versus time ([UA] = 7.50×10^{-3} mol dm⁻³; [DPC] = 5.70×10^{-5} mol dm⁻³; [OH⁻] = 1.00×10^{-2} mol dm⁻³; [IO₄⁻] = 5.80×10^{-4} mol dm⁻³; temp. = 313 K); (B) Plot of (4 + log k') versus (3 + log [UA]) (Conditions same as in A).

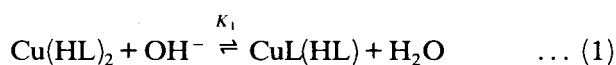which were characterised by Lister[15], by the following equilibria:

$$Cu(Per)_2 \overset{OH^-}{\rightleftharpoons} Cu(OH)_4^- + 2Per$$
$$K = 8.0 \times 10^{-11}$$

$$Cu(Per) \overset{OH^-}{\rightleftharpoons} Cu(OH)_4^- + Per$$
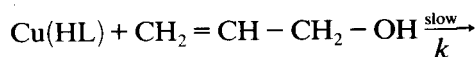$$K = 3.4 \times 10^{-5}$$
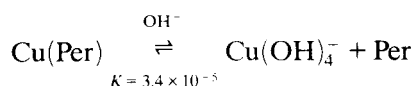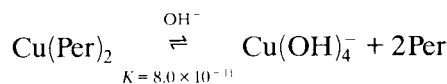
Diperiodato Cuprate (III) has been given the general formula $M_{7-n}H_n[Cu(IO_6)_2] \times H_2O$, where M is Na or K. But it was demonstrated by Rozovskii and coworkers[6] to be actually an aquo or hydroxyhydro diperiodato cuprate (III) complex. Due to lack of information regarding the exact nature of diperiodato cuprate(III) under the experimental conditions employed ($[OH^-] = 0.010$ mol dm^{-3}: $[IO_4^-] = 5.8 \times 10^{-4}$ mol dm^{-3}) Bal Reddy *et al.*[7] expressed the complex as $Cu(HL)_2$, where HL is the protonated form of periodate molecule.

The inhibitory effect of $[IO_4^-]$ and increase in rate with increase in $[OH^-]$ suggest monoperiodato cuprate (III) i.e. $Cu(HL)$ to be the reactive species as discussed earlier[7].

This is expressed by equilibria (1) and (2)

$$Cu(HL)_2 + OH^- \overset{K_1}{\rightleftharpoons} CuL(HL) + H_2O \qquad \ldots (1)$$

$$CuL(HL) \overset{K_2}{\rightleftharpoons} Cu(HL) + L \qquad \ldots (2)$$

A strict unit order dependence of rate on [DPC] and [UA] each and the linear plot of $1/k'$ versus $1/[UA]$ passing through the origin indicate that the substrate is not involved in any complex formation with the oxidant. Prior to oxidation induced polymerisation was observed when acrylamide was added to the reaction mixture under nitrogen atmosphere, indicating that free radicals are formed during the course of reaction. The absence of salt effect suggests that it is probably an ion-dipole type of reaction. The most probable mechanism that explains all the above observations could be written by taking allyl alcohol as a typical example as follows.

$$Cu(HL) + CH_2 = CH - CH_2 - OH \xrightarrow[k]{slow}$$

$$CH_2 = CH - CHOH + Cu(II) + H^+$$

$$CH_2 = CH - \dot{C}HOH + Cu(HL) \xrightarrow{fast}$$

$$CH_2 = CH - CHO + Cu(II) + H^+$$

The rate law for the above mechanism is given by Eq. (3)

$$Rate = \frac{-d[DPC]}{dt} = \frac{kK_1K_2[Cu(HL)_2][UA][OH^-]}{[L]\{1 + K_1[OH^-]\}}$$

$$\ldots (3)$$

which substantiates the rate data obtained. The K_1 and K_2 values were found to be 14.02 and 1.00×10^{-2} mol dm^{-3} respectively.

The slow step in the mechanism envisages an α-C—H bond fission. If a O—H bond fission is assumed in the slow step, then the effect of substituents at α-carbon on the rate of oxidation would not be that significant compared to the case of α-C—H bond fission. Since there is a marked difference in the rates of oxidation (Table 2) of allyl, crotyl and propargyl alcohols an α-C—H bond fission is proposed in the slow step. This also receives support from the non-reactivity of *tert*-butyl alcohol and primary kinetic isotopic effect of 3.87 (k_H/k_D) observed. It is unlikely that the cleavage of O—H bond is synchronous with the cleavage of α-C—H bond in view of the absence of solvent isotopic effect. The radical thus formed in the slow step is resonance stabilised and this then reacts with another Cu(III) ion to give the final product. This accounts for the stoichiometry of 2 moles of Cu(III) to 1 mole of unsaturated alcohol observed in the present work.

The order of reactivity of unsaturated alcohols is propargyl > crotyl > allyl alcohol. The higher rate of oxidation of crotyl compared to allyl alcohol is attributed to the + I effect of the methyl group present in the crotyl alcohol. The highest reactivity of propargyl is probably due to the greater stabilisation of the α-C—H radical

Table 2—Effect of varying substrate on the reaction rate

$[DPC] = 5.70 \times 10^{-5}$ mol dm^{-3}; $[OH^-] = 1.00 \times 10^{-2}$ mol dm^{-3}; $[IO_4^-] = 5.80 \times 10^{-4}$ mol dm^{-3}; temp. = 313 K)

Substrate	10^3 [UA] (mol dm^{-3})	10^4 k' (s^{-1})
Allyl alcohol	2.00	1.66
	5.60	3.83
	7.50	5.26
	10.0	6.71
	20.0	16.0
Crotyl alcohol	2.00	1.99
	5.60	4.80
	7.50	6.95
	10.0	9.11
	20.0	18.3
Propargyl alcohol	5.60	8.83
	7.50	14.0
	10.0	19.0
	20.0	38.0
	25.0	43.5

Table 3—Comparison of rate constants of saturated and unsaturated alcohols, aldehydes and acids

$[ROH] = 7.50 \times 10^{-3}$ mol dm^{-3}; $[DPC] = 5.70 \times 10^{-5}$ mol dm^{-3}; $[OH^-] = 1.00 \times 10^{-2}$ mol dm^{-3}; $[IO_4^-] = 5.80 \times 10^{-4}$ mol dm^{-3}; temp. $= 313$ K

Unsaturated compound	$10^5 k'$ s^{-1}	Saturated compound	$10^5 k'$ s^{-1}
Allyl	52.6	n-Propyl	0.054
Crotyl	69.5	n-Butyl	0.194
Propargyl	140	—	—
Acrolein	0.600	Propionaldehyde	16.0
Crotonaldehyde	1.00	n-Butyraldehyde	75.0
*Acrylic acid	0.005	Propionic acid	26.0
*Crotonic acid	0.072	n-Butyric acid	40.0

*These rate constants were computed by extrapolating the Arrhenius plot for comparison purposes (actual E_a were calculated in the temperature range 328-348 for these acids).

formed. In all these cases the presence of double/triple bond appears to be enhancing the rate of formation of the product although the double/triple bond itself is not attacked. This contention receives confirmation from a study of the oxidation of saturated alcohols such as 1-propanol and 1-butanol by DPC under similar experimental conditions. The rate constants (Table 3) obtained for the oxidation of saturated alcohols are very much less compared to the corresponding unsaturated alcohols. The mechanism of oxidation of saturated alcohols appears to be same as seen from the similar rate law obtained[16]. The higher reactivity of 1-butanol compared to 1-propanol indicates that inductive effect is predominant. This view further supports α-C—H bond fission in the rate determining step.

The rate of oxidation of unsaturated aldehydes (acrolein) by DPC under similar experimental conditions is very low suggesting that acrolein, the first stage oxidation product of allyl alcohol is quite stable. Under similar conditions the rate of oxidation of unsaturated acids (acrylic acid and crotonic acid) was found to be negligible compared to the corresponding unsaturated alcohols or unsaturated aldehydes discounting formation of unsaturated acids as the products during the oxidation of unsaturated alcohols.

Kinetics of oxidation of saturated aldehydes like propionaldehyde and n-butyraldehyde and saturated acids like propionic and butyric acids were also studied for comparison purposes and the rate constants are recorded in Table 3. Aldehydes are known to get oxidised via enolisation[10] process and since this is more likely with saturated aldehydes compared to unsaturated aldehydes, the rates of oxidation of saturated aldehydes are expected to be higher. This indeed was the trend observed with propionaldehyde and acrolein. In the case of saturated acids abstraction of an electron from the carboxylate group in the rate determining step giving rise to carboxylate radical has been suggested by earlier workers[8] as the possible route for oxidation. Such a process is difficult when unsaturated acids are the substrates due to the presence of adjacent double/triple bond. The higher rates of oxidation of saturated acids compared to unsaturated acids support this contention.

The activation energies E_a, calculated using the observed k' values at different temperatures for allyl, crotyl and propargyl alcohols are 124, 95.7 and 83.8 kJ mol^{-1} respectively.

Acknowledgement

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