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Kinetics and Mechanism of Oxidative Deoximation of Benzaldoxime by Diperiodatocuprate(III) in *tert.*-Butanol – Water Medium

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Summary. The kinetics of oxidation of benzaldoxime by diperiodatocuprate(III) (*DPC*) was studied spectrocolorimetrically at 414 nm in *tert.*-butanol – water medium. The order in [*DPC*] and that in [benzaldoxime] was unity. The rate increased with increasing [OH^-] and decreasing [IO_4^-]. A suitable mechanism is proposed based on the kinetic data.

Keywords. Oxidation; Benzaldoxime; Copper(III).

Kinetik und Mechanismus der oxidativen Deoximierung von Benzaldoxim mit Diperjodatocuprat(III) in *tert.*-Butanol/Wasser

Zusammenfassung. Es wurde die Kinetik der Oxidation von Benzaldoxim mit Diperjodatocuprat(III) (*DPC*) in *tert.*-Butanol/Wasser colorimetrisch bei 414 nm untersucht. Die Reaktionsordnung bezüglich [*DPC*] und [Benzaldoxim] war gleich 1. Die Reaktionsgeschwindigkeit erhöhte sich mit Zunahme der Konzentration von [OH^-] und Verminderung von [IO_4^-]. Basierend auf den kinetischen Daten wird ein passender Mechanismus vorgeschlagen.

Introduction

It is well known that copper in its trivalent form acts as a one electron oxidant in aqueous alkaline medium. Periodate and tellurate complexes of Cu(III) were also used as oxidants in oxidimetric determination of some organic compounds [1–3]. Earlier we have reported the kinetic study of oxidation of some organic compounds like alcohols, ketones, amino acids, and benzaldehydes by diperiodatocuprate(III) (*DPC*) [4–7]. Deoximation of oximes is known to occur either by hydrolytic methods or oxidative methods. The hydrolytic methods employed for the conversion of oximes into the corresponding carbonyl compounds are very slow and subject to side reactions. Hence the oxidative methods have been used as alternative methods. The oxidation of oximes with metal ions like Ce(IV), Pb(IV), Tl(III) are of interest to many workers in preparing carbonyl compounds [8–10]. The oxidative deoximation by metal ions is known to occur via the formation of intermediate iminoxy

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radicals or a complex between the substrate and the oxidant. Preliminary studies revealed that *DPC* reacts with benzaldoxime. In view of this it was thought worthwhile to find out which of the above two mechanisms operates during the oxidation of benzaldoxime by *DPC*, a one electron oxidant. Since benzaldoxime is insoluble in water, the kinetic study was made in *tert.*-butanol–water mixtures, because *tert.*-butanol does not undergo oxidation under the experimental conditions.

Experimental

All chemicals used were of highest purity. Benzaldoxime was prepared and purified by standard methods. *DPC* was prepared and standardized as reported elsewhere [3]. The progress of the reaction was followed by measuring the absorbance of *DPC* at various time intervals using a Carl Zeiss spectrocolorimeter at 414 nm. All the reactions were carried out in 30% (*v*/*v*) *tert.*-butanol–water mixtures. The product of oxidation has been identified as benzaldehyde and estimated gravimetrically as 2,4-dinitrophenyl hydrazone derivative. It was found that for every 2 mol of *DPC* consumed 1 mol of benzaldehyde was formed.

Results and Discussion

Under the conditions of [*DPC*] $\ll$ [oxime] the plots of log (absorbance) vs. time were linear ($r = 0.990$), indicating first order dependance of rate on [*DPC*]. From the slopes of such plots the pseudo first order rate constants (k') were evaluated. The k' was found to be independant of initial [*DPC*], which also confirms the order in *DPC* to be unity (Table 1). The k' was found to be increased with increasing [oxime] and the order in [oxime] was found to be unity (Table 1). The rate of oxidation was increased with increasing [OH^-] and decreased with increasing [IO_4^-] at constant [*DPC*], [oxime], and temperature (Table 2). The rate was uneffected by the addition of salts like KNO_3, $NaClO_4$. Induced polymerization of acrylamide was observed under nitrogen atmosphere.

The diperiodatocuprate(III) has been demonstrated to be an aquo or hydroxoperiodatocuprate(III) [11] which is denoted as Cu(H*L*)$_2$ in the discussion. The nature of dependance of rate on [OH^-] and [KIO_4] indicates that monoperiodatocuprate(III), Cu(H*L*) is the active species of *DPC* under the experimental con-

Table 1. Effect of [*DPC*] and [benzaldoxime] on k' in the *DPC*-benzaldoxime reaction; [KOH] = 0.010 mol dm^{-3}, [KIO_4] = 0.00068 mol dm^{-3}, *tert.*-butanol = 30% (*v*/*v*), temp. = 291 K

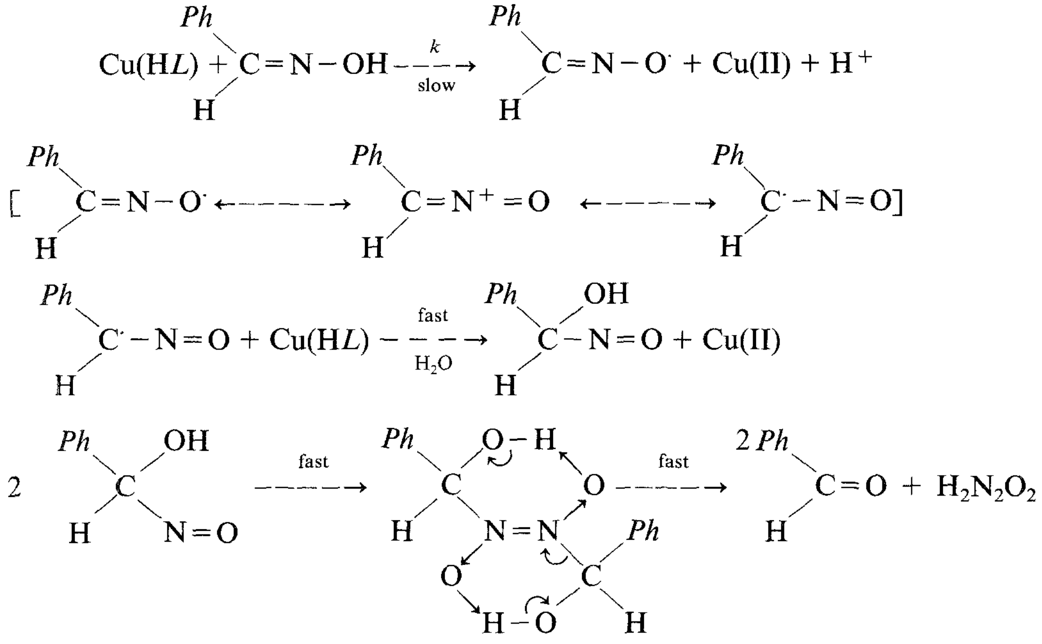
[*DPC*] · 10^5 mol dm^{-3}	[oxime] · 10^2 mol dm^{-3}	$k' \cdot 10^4\,s^{-1}$	k'/[oxime] = $k'' \cdot 10^3\,mol^{-1}\,dm^{-3}\,s^{-1}$
6.90	1.60	3.13	–
3.00	1.60	3.05	–
4.50	1.60	3.10	–
8.00	1.60	3.20	–
6.90	0.900	1.80	20.0
6.90	2.50	5.25	21.0
6.90	3.20	6.43	20.1
6.90	4.20	8.61	20.5
6.90	5.00	10.2	20.4

ditions as discussed earlier [6]. The absence of a salt effect indicates the reaction to be of ion-dipole type. A strict unit order dependance of each in [oxime] and [*DPC*] indicates the absence of any stable complex formation between the oxidant and substrate prior to oxidation. The iminoxy radical is known to be the first stage product of oxidation of oxime by metal ions such as Ce(IV), Pb(IV), Tl(III), Mn(III), etc. [8 – 10, 12]. This, together with the observation of a positive test for free radicals, indicates also a reaction path involving iminoxy radicals. In view of the above information the following meachnism is proposed for the oxidation of benzaldoxime by *DPC*:

$$\mathrm{Cu(H}L)_2 + \mathrm{OH}^- \overset{K_1}{\rightleftharpoons} \mathrm{Cu}L(\mathrm{H}L) + \mathrm{H_2O}$$

$$\mathrm{Cu}L(\mathrm{H}L) \overset{K_2}{\rightleftharpoons} \mathrm{Cu(H}L) + L$$

$$L + \mathrm{H_2O} \overset{K_3}{\rightleftharpoons} \mathrm{H}L + \mathrm{OH}^-$$



L stands for a periodate ligand of undetermined protonation and Cu(H*L*) is the monoperiodatocuprate(III) species. From the above mechanism the rate law comes out to be

$$-\,[DPC]/\mathrm{d}t = k K_1 K_2 [\mathrm{Cu(H}L)_2]\,[\mathrm{oxime}] \cdot \{K_3(1 + [\mathrm{H}L] + [\mathrm{OH}^-])\}/[\mathrm{H}L]\{1 + K_1[\mathrm{OH}]\}.$$

The rate law explains well the experimental observations.

The formulation of such canonical structures for the iminoxy radical formed in the slow step by 1 mol of oxidant has been demonstrated earlier by several workers. The role of iminoxy radicals as intermediates in some oxime oxidations has been recognized from ESR studies [13]. The dimerization and decomposition

Table 2. Effect of $[OH^-]$ and $[KIO_4]$ on k' in the *DPC*-benzaldoxime reaction; $[DPC] = 6.90 \cdot 10^{-5}\,\text{mol dm}^{-3}$, [benzaldoxime] $= 0.0162\,\text{mol dm}^{-3}$, *tert.*-butanol = 30% (*v*/*v*), temp. = 291 K

$[OH^-] \cdot 10^2\,\text{mol dm}^{-3}$	$[KIO_4] \cdot 10^4\,\text{mol dm}^{-3}$	$k' \cdot 10^4\,\text{s}^{-1}$
1.00	6.80	3.13
1.00	4.50	4.00
1.00	3.00	5.20
1.00	2.00	6.00
1.00	10.0	2.80
0.500	6.80	2.70
0.225	6.80	2.00
1.50	6.80	4.00
2.00	6.80	4.80
3.00	6.80	6.00

of hydroxy nitroso compounds is also well known as shown by Gowenlock [14] and has been postulated in the oxidation of oximes by Ce(IV) [8], Tl(III) [10], Mn(III) [12], periodic acid [13], etc. All the steps proposed in the reaction scheme are well in accordance with earlier observations thus supporting the mechanism proposed for the oxidation of benzaldoxime by *DPC*.

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