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Mechanistic study of the oxidation of isonicotinate ion by diperiodatocuprate(III) in aqueous alkaline medium

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The kinetics of oxidation of isonicotinate ion by diperiodatocuprate(III) (DPC) in aqueous alkaline medium at a constant ionic strength of 0.60 mol dm^{-3} was studied spectrophotometrically. A mechanism involving the formation of an intermediate complex between the diperiodatocuprate(III) as the oxidant species and isonicotinate ion is proposed. The reaction constants involved in the different steps of mechanism have been calculated. The activation parameters with respect to the slow step of the mechanism have been computed and discussed and thermodynamic quantities were also determined.

Keywords: kinetics, isonicotinate, diperiodatocuprate (III), oxidation

The periodate and tellurate complexes of copper in its trivalent state have been used extensively in the analysis of organic compounds.[1] The kinetics of self decomposition of these complexes was studied in detail.[2] Movius[3] reported the reactivity of some alcohols with diperiodatocuprate(III) (DPC). DPC is a versatile one-electron oxidant for various organic compounds in alkaline medium and its use as an analytical reagent is now well recognised,[4] as in the estimation of amino acids.[4] Cu(III) is shown to be an intermediate in the Cu(II)-catalysed oxidation of amino acids by peroxydisulphate.[5] The use of diperiodatocuprate(III) as an oxidant in alkaline medium is new and restricted to a few cases[6] due to the fact of its limited solubility and stability in aqueous medium. Moreover, when the Cu(III) periodate complex is oxidant, since multiple equilibria between the different copper(III) species are involved, it needs to be known which of the species is the active oxidant.

Nicotinic acid or niacin is a vitamin. It is the 3-isomer of pyridine carboxylic acid. There are no reports on the oxidation of isonicotinate ion by DPC. Because of its potential pharmaceutical importance, we have investigated the oxidative behaviour of isonicotinate ion towards DPC. In view of the multiple equilibria embracing the different copper(III)periodate species and the complexity of the title reaction, a detailed study of the reaction was undertaken.

Experimental

Materials and reagents

All chemicals used were of reagent grade. Double-distilled water was used throughout the work. A stock solution of pure isonicotinate ion (Fluka) was prepared by dissolving the appropriate amount in water. The copper(III) periodate complex was prepared by a standard procedure.[7] The purity of the complex was checked by its UV-Vis spectrum, which showed a broad absorption band at 415 nm. The aqueous solution of DPC was standardised by a back titration[7] method. The Cu(II) solution was made by dissolving a known amount of copper sulphate (BDH) in distilled water. The periodate solution was prepared by weighing out the required amount of sample in hot water and it was used after keeping 24 hours. Its concentration was ascertained iodometrically[8] at a neutral pH by phosphate buffer. Since periodate is present in excess in DPC, the possibility of oxidation of isonicotinate ion by periodate in alkaline medium at 25°C was tested. The progress of the reaction was followed iodometrically. However, it was found that there was no significant reaction under the experimental conditions employed compared to the DPC oxidation of isonicotinate ion. KOH and KNO_3 (BDH, AR) were employed to maintain the required alkalinity and ionic strength respectively, in reaction solutions.

Kinetic measurements

The oxidation of isonicotinate ion by DPC was followed under pseudo-first order conditions where [isonicotinate ion] was excess over [DPC] at 25 ± 0.1°C, unless otherwise stated. The reaction was initiated by mixing the required quantities of a previously-thermostatted solution of isonicotinate ion and DPC, which also contained definite quantities of KOH, KNO_3 and IO_4^- to maintain the required alkalinity, ionic strength and periodate concentration. Here the total concentration of hydroxide ion was calculated by considering the KOH in DPC as well as the KOH added additionally. Similarly, the total metaperiodate concentration was calculated by considering the metaperiodate present in the solution of DPC and that added additionally. The course of reaction was followed by measuring the absorbance of unreacted DPC in the reaction mixture in a 1cm quartz cell located in the thermostatted compartment of a Peltier Accessory (temperature control) attached to a Varian CARY 50 Bio UV–VIS spectrophotometer at its maximum absorption wavelength of 415 nm as a function of time. Earlier it was verified that there is negligible interference from other species present in the reaction mixture at this wavelength. The obedience of Beer's law by DPC at 415 nm was verified earlier and the molar absorbance coefficient, 'ε' was found to be 6231 ± 300 dm^3 mol^{-1} cm^{-1} at this wavelength. The first order rate constants, k_{obs}, were obtained from the plots of log $(a - x)$ *vs* time, where 'a' and 'x' are the initial concentration and change in concentration of diperiodatocuprate(III) at time 't' respectively. The plots were linear up to about 85% completion of the reaction and the rate constants were reproducible within ±5 %.

The effect of dissolved oxygen on the rate of reaction was studied by preparing the reaction mixture and following the reaction in an atmosphere of N_2. No significant difference between the results was observed. In view of the ubiquitous contamination of basic solutions by carbonate, the effect of carbonate on the reaction was also studied. Added carbonate had no effect on the reaction rate. However, fresh solutions were used during the experiments.

In view of the modest concentration of alkali used in the reaction medium, attention was also given to the effect of the surface of the reaction vessel on the kinetics. The use of polythene or acrylic ware and quartz or polyacrylate cells gave the same results, indicating that the surface does not have any significant effect on the rate.

Regression analysis of experimental data to obtain the "regression coefficient", r and "standard deviation", S of points from the regression line was performed using a Pentium-IV personal computer.

Results

Stoichiometry and product analysis

Different sets of reaction mixtures containing different concentrations of isonicotinate ion and DPC at constant ionic strength and alkali were kept for *ca* 6 h. at 25 ± 0.1°C in an inert atmosphere and in a closed vessel. When [DPC] was higher than [isonicotinate ion], the unreacted DPC was found by measuring its absorbance at 415 nm spectrophotometri-

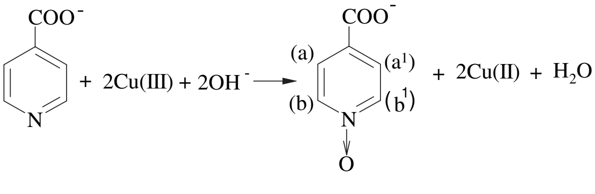

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Table 1 Effect of variation of [DPC], [ISNA], [OH$^-$], and [IO$_4^-$] on oxidation of isonicotinate ion by DPC at 25°C, I = 0.60 mol dm^{-3}

[DPC] x10^4 /mol dm^{-3}	*[ISNA] x 10^3 /mol dm^{-3}	[OH$^-$] /mol dm^{-3}	[IO$_4^-$] x10^5 /mol dm^{-3}	k_{obs} x 10^3 s^{-1} Found	Calc.
0.2	1.0	0.4	1.0	3.79	3.85
0.5	1.0	0.4	1.0	3.62	3.85
1.0	1.0	0.4	1.0	3.74	3.85
1.5	1.0	0.4	1.0	3.77	3.85
2.0	1.0	0.4	1.0	3.64	3.85
1.0	0.2	0.4	1.0	1.61	1.60
1.0	0.5	0.4	1.0	2.85	2.85
1.0	1.0	0.4	1.0	3.74	3.85
1.0	1.5	0.4	1.0	4.45	4.36
1.0	2.0	0.4	1.0	4.75	4.67
1.0	1.0	0.05	1.0	4.90	4.94
1.0	1.0	0.1	1.0	4.70	4.74
1.0	1.0	0.2	1.0	4.35	4.40
1.0	1.0	0.4	1.0	3.74	3.85
1.0	1.0	0.5	1.0	3.51	3.62
1.0	1.0	0.4	1.0	3.74	3.85
1.0	1.0	0.4	3.0	3.89	3.85
1.0	1.0	0.4	5.0	3.79	3.85
1.0	1.0	0.4	8.0	3.81	3.85
1.0	1.0	0.4	10	3.82	3.85

*ISNA- Isonicotinate ion.

cally. The results indicated that two moles of DPC consumed one mole of isonicotinate ion as in Eqn (1).

The reaction products were extracted with ether and Cu(II) was identified by UV-Vis spectra. The N–O bond attached to isonicotinate ion was identified by its spot test[9] (Libermann test). The presence of the nitroso group was also confirmed by I.R. spectroscopy which showed a band at 1225 cm^{-1} due to N→O stretching[10] and by NMR spectra (DMSO) (doublet at 8.7 ppm due to aromatic protons (a,a^1) and doublet at 7.8 ppm due to aromatic protons (b,b^1).

Reaction order

The order with respect to [isonicotinate ion] and [alkali] were found from log k_{obs} *vs* log (concentration) plots and the obtained orders were also confirmed by the plot log ($-dc/dt$) *vs* log (concentration) using the equation log($\pm dc/dt$) = log$k$ + n log$c$; these orders were obtained by varying the concentration of isonicotinate ion and alkali in turn while keeping others constant.

The concentration of diperiodatocuprate(III) was varied in the range 2.0 × 10^{-5} to 2.0 × 10^{-4} mol dm^{-3} at fixed [isonicotinate ion], [OH$^-$], [IO$_4^-$] and ionic strength. The non-variation in the pseudo-first order rate constants at various concentrations of DPC indicates the order in [DPC] as unity (Table 1). This was also confirmed from the linearity of plots of log absorbance *vs* time (r>0.9994, S≤0.021) up to 85% completion of the reaction (Fig.1). The substrate, isonicotinate ion, was varied in the range 2.0 × 10^{-4} – 2.0 × 10^{-3} mol dm^{-3} at 25°C keeping all other reactants concentrations constant (Table 1). The k_{obs} values increased with increase in concentration of isonicotinate ion indicating an apparent less than unit order dependence on [isonicotinate ion] (Table 1). The effect of [alkali] on the rate of reaction was studied. A rate decrease with increase in concentrations of alkali indicates negative fractional order (Table 1).

Effect of periodate

The effect of [IO$_4^-$] was observed by varying the concentration from 1.0 × 10^{-5} to 1.0 × 10^{-4} mol dm^{-3} at constant concentrations of diperiodatocuprate(III), isonicotinate ion, alkali and constant ionic strength (Table 1). It was found that the added periodate did not show any significant effect on the rate of reaction.

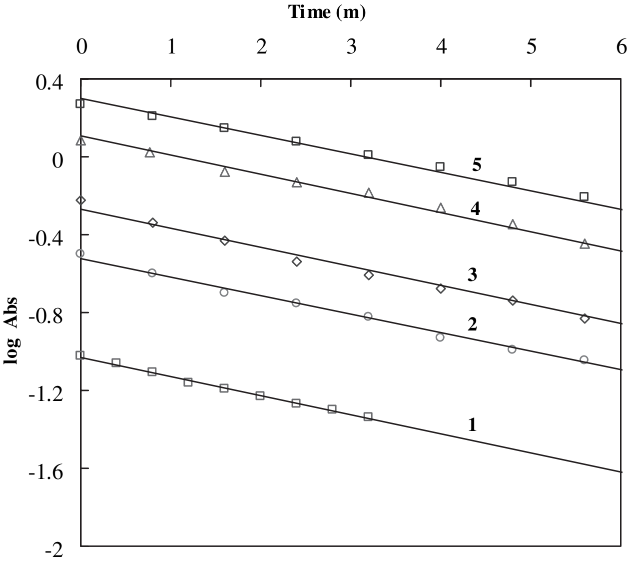


Fig. 1 First order plots of oxidation of isonicotinate ion by diperiodatocuprate(III) in aqueous alkaline medium at 25°C [DPC] x 10^4 mol dm^{-3}; (1) 0.2 (2) 0.5 (3) 1.0 (4) 1.5 (5) 2.0.

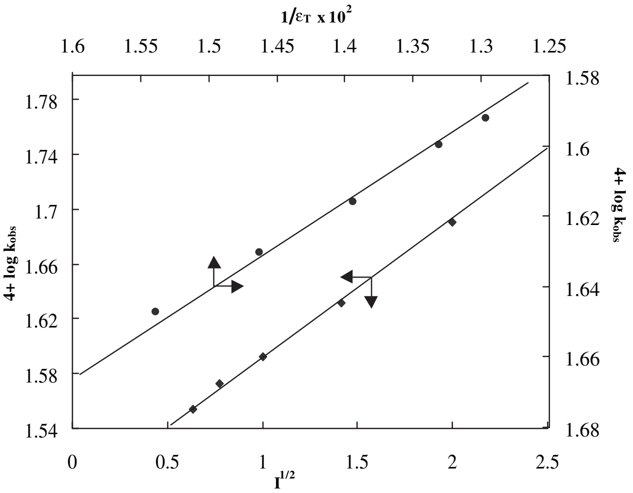


Fig. 2 Plot of (a) log k_{obs} *vs* I$^{1/2}$ and (b) log k_{obs} *vs* 1/ε$_T$ (a)[DPC]= 1.0 x10^{-4}, [ISNA]= 1.0 x 10^{-3}, [OH$^-$]= 0.40 and [IO$_4^-$] = 1.0x 10^{-5} mol dm^{-3}. (b)[DPC]= 1.0 x10^{-4}, [ISNA]= 1.0 x 10^{-3}, [OH$^-$]= 0.40 and [IO$_4^-$]= 1.0x 10^{-5} I=0.60 mol dm^{-3}.

Effect of ionic strength and solvent polarity

The effect of ionic strength was studied by varying the potassium nitrate concentration in the reaction medium. The ionic strength of the reaction medium was varied from 0.4 to 4.0 mol dm^{-3} at constant [DPC], [isonicotinate ion], [IO$_4^-$] and [alkali]. It was found that the rate constant increases with increase in the concentration of potassium nitrate and plot of log k_{obs} *vs* $I^{1/2}$ was linear(r>0.9993, S≤0.0150) with positive slope as shown in Fig. 2.

The relative permittivity (ε$_T$) effect was studied by varying the *t*-butyl alcohol–water content in the reaction mixture with all other conditions being constant. Attempts to measure the relative permittivities of the mixture of *t*-butyl alcohol-water were not successful. However, they were computed from the values of pure liquids.[11] It was also found that there was no reaction of the solvent with the oxidant under the experimental conditions used. The k_{obs} values increase with the decrease in the dielectric constant of the medium. The plot of log k_{obs} *vs* $1/\varepsilon_T$ was linear (r>0.9994, $S\leq0.0155$) (Fig. 2) with positive slope.

Effect of initially added products

The externally added products such as copper(II) did not have any significant effect on the rate of reaction.

Polymerisation study

To test the intervention of free radicals, the reaction mixture was mixed with acrylonitrile monomer and kept for 24 hours under an N_2 atmosphere. On dilution with methanol, a white precipitate of polymer was formed, indicating the intervention of free radicals in the reaction. The blank experiment of either DPC or isonicotinate ion in with acrylonitrile alone did not induce polymerisation. Initially added acrylonitrile decreases the rate of reaction indicating the free radical intervention, which was the case in earlier work.[12]

Effect of temperature

The rate of reaction was measured at different temperatures under varying isonicotinate ion concentration. The rate of reaction increased with the increase of temperature. The rate constants, k of the slow step of Scheme 1 were obtained from intercepts of the plots of $1/k_{obs}$ *vs* 1/ [isonicotinate ion] (r>0.9995, $S\leq0.0160$) (Fig. 3) at different temperatures and used to calculate the activation parameters. The values of k (s^{-1}) are given in Table 2. The activation parameters corresponding to these constants were evaluated from the plot of log k *vs* $1/T$ (r>0.9988, $S\leq0.0135$) and are tabulated in Table 2.

Discussion

The water soluble Cu(III) periodate complex is reported[6,13] to be $[Cu(IO_6)_2]^{7-}$. However, in an aqueous alkaline medium and at a high pH range as employed in the study, periodate is unlikely to exist as IO_6^{5-} (as present in the complex) as is evident from its involvement in the multiple equilibria[14](2) to (4) depending on the pH of the solution.

$$H_5IO_6 \xrightleftharpoons{K_1} H_4IO_6^- + H^+ \qquad K_1 = 5 \times 10^{-4} \qquad (2)$$

$$H_4IO_6^- \xrightleftharpoons{K_2} H_3IO_6^{2-} + H^+ \qquad K_2 = 4.9 \times 10^{-9} \qquad (3)$$

$$H_3IO_6^{2-} \xrightleftharpoons{K_3} H_2IO_6^{3-} + H^+ \qquad K_3 = 2.5 \times 10^{-12} \qquad (4)$$

Periodic acid (H_5IO_6) exists in acid medium and also as $H_4IO^-_6$ at pH 7. Thus, under alkaline conditions, the main species are expected to be $H_3IO_6^{2-}$and $H_2IO_6^{3-}$. At higher concentrations, periodate also tends to dimerise.[15] Hence, at the pH employed in this study, the soluble copper(III) periodate complex exists as diperiodatocuprate(III), $[Cu(H_3IO_6)_2]^-$, in aqueous alkaline medium, a conclusion also supported by earlier work.[6] The same can be written as $[Cu(HL)_2]^-$, where HL is a protonated periodate,$H_3IO_6^{2-}$ and L is the deprotonated form, $H_2IO_6^{3-}$.

The reaction between diperiodatocuprate(III) complex and isonicotinate ion in alkaline medium has a 1:2 stoichiometry of reductant to oxidant with first order dependence on [DPC], apparent less than unit order in [isonicotinate ion], negative fractional order in $[OH^-]$ and negligible effect on $[IO_4^-]$. The less than unit order in [isonicotinate ion] presumably results from formation of a complex, (C), between the oxidant and substrate prior to the formation of the products. Then (C) decomposes in a slow step to form an intermediate, free radical species of isonicotinate ion. This intermediate species further reacts with another molecule of DPC species in a fast step to yield the products. All the results indicate a mechanism as given in Scheme 1.

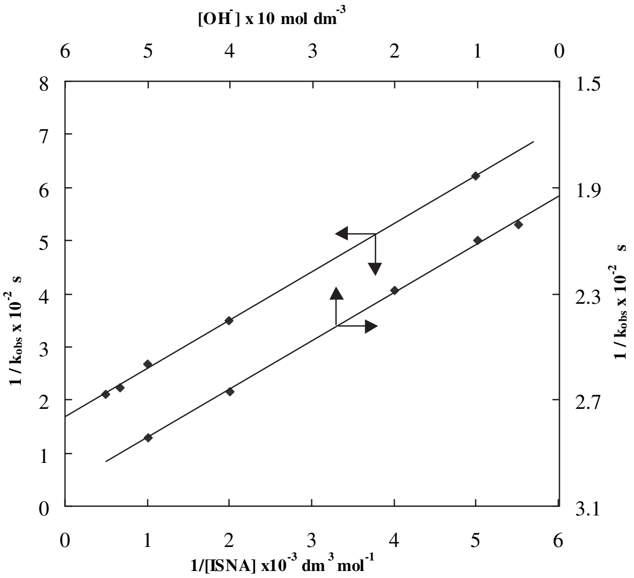


Fig. 3 Verification of rate law (6) in the form of (7) (conditions as in Table 1).

Table 2 Thermodynamic activation parameters for the oxidation of Isonicotinate ion by diperiodatocuprate(III) in alkaline medium with respect to the slow step of Scheme 1

(a) Effect of temperature

Temp. (K)	k x 10^3 s^{-1}
298	5.9
303	8.0
308	10
313	13

(b) Activation parameters for the slow step of Scheme 1

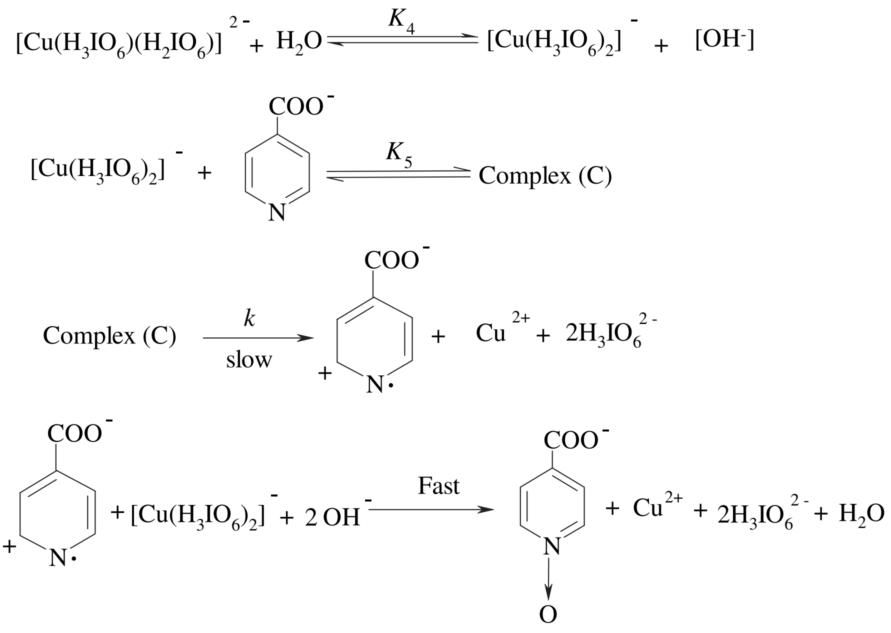
Parameters	Values
E_a / kJ mol^{-1}	40 ±2
log$A$	4.8±0.3
$\Delta H^{\#}$ / kJ mol^{-1}	37 ±1
$\Delta S^{\#}$ / JK^{-1} mol^{-1}	−161±10
$\Delta G^{\#}$ / kJ mol^{-1}	86 ±7

(c) Effect of temperature to calculate $K4$ and $K5$ for the oxidation of isonicotinate ion by DPC in alkaline medium

Temp. /K	K_4 mol dm^{-3}	K_5 $x10^{-3}$ /dm^3mol^{-1}
298	0.157	6.58
303	0.182	4.91
308	0.213	3.20
313	0.243	1.61

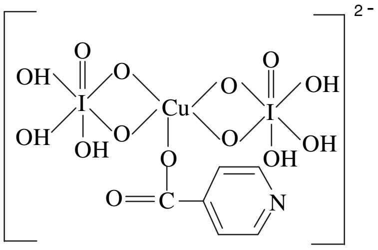
(d) Thermodynamic quantities using K_4 values

Thermodynamic quantities	Values
ΔH /kJ mol^{-1}	23±2
ΔS /JK^{-1} mol^{-1}	61±4
ΔG /kJ mol^{-1}	4.3±0.1



Scheme 1

The structure of the complex (C) is tentatively suggested to be:



Spectroscopic evidence for the complex formation between oxidant and substrate was obtained from the UV-Vis spectra of the DPC and mixture of isonicotinate ion and DPC. A bathochromic shift of about 6 nm from 263 nm to 269 nm was observed and hyperchromicity was also observed at 269 nm. Indeed, it is to be noted that a plot of $1/k_{obs}$ *vs* 1/[isonicotinate ion] ($r > 0.9995$, $s \leq 0.0160$) shows a straight line with non-zero intercept (Fig.3). Such complex formation between substrate and oxidant has been observed earlier.[16] The observed modest enthalpy of activation and a relatively low value of the entropy of activation as well as a higher rate constant of the slow step indicate that the oxidation presumably occurs *via* an inner-sphere mechanism. This conclusion is supported by earlier observation.[17] Since Scheme 1 is in accordance with the generally well-accepted principle of non-complementary oxidations taking place in a sequence of one-electron steps, the reaction between the substrate and oxidant would afford a radical intermediate. A free radical scavenging experiment revealed such a possibility. This type of radical intermediate has also been observed in earlier work.[18]

Scheme 1 leads to the rate law equation (6),

In view of the low concentration of DPC used, the term $[OH^-] + K_4 K_5 [DPC] \approx [OH^-]$

$$\text{Rate} = \frac{-d[\text{DPC}]}{dt} = \frac{k K_4 K_5 [\text{ISNA}][\text{DPC}][\text{OH}^-]}{([\text{OH}^-]+K_4 K_5[\text{DPC}])([\text{OH}^-]+K_4+K_4K_5[\text{ISNA}])} \quad \textbf{(5)}$$

Hence

$$\frac{\text{Rate}}{[\text{DPC}]} = k_{obs} = \frac{k K_4 K_5 [\text{ISNA}]}{[\text{OH}^-] + K_4 + K_4K_5[\text{ISNA}]} \quad \textbf{(6)}$$

Equation (6) can be rearranged to equation (7) which is suitable for verification.

$$\frac{1}{k_{obs}} = \frac{[\text{OH}^-]}{k K_4 K_5 [\text{ISNA}]} + \frac{1}{k K_5 [\text{ISNA}]} + \frac{1}{k} \quad \textbf{(7)}$$

According to Eqn (7), the plots of $1/k_{obs}$ *vs.* 1/[ISNA] (r>0.9995, $S \leq 0.0160$) and $1/k_{obs}$ *vs* $[OH^-]$ (r>0.9998, $S \leq 0.0210$) should be linear as shown in Figure 3. From the slopes and intercepts, the values of K_4, K_5 and k could be derived as 0.157 ± 0.006 mol dm^{-3}, (6.58 ± 0.30) × 10^3 dm^3 mol^{-1} and (5.93 ± 0.22) × 10^{-3} s^{-1} respectively. The value of K_4 is in agreement with a literature value.[19] Using these constants, the rate constants were calculated over different experimental conditions and there is a reasonable agreement between the calculated and experimental values (Table 1), which supplements the proposed mechanism.

The effect of increasing ionic strength on the rate qualitatively explains the reaction between two negatively charged ions as shown in Scheme 1. The effect of solvent on the reaction rate has been described elsewhere.[20] Increasing the content of *t*-butyl alcohol in the reaction medium leads to increase in the rate of the reaction, contrary to the expected slower reaction between like ions in media of lower relative permitivity. Perhaps this effect is countered substantially by the formation of active reactive species to a greater extent in low relative permitivity media leading to the net increase in the reaction rate.[21]

The thermodynamic quantities for the first step in Scheme 1 can be evaluated as follows. The [ISNA] and hydroxide ion concentration (as in Table 1) was varied at four different temperatures. The plots of $1/k_{obs}$ *vs* 1/[ISNA] (r>0.9995, $S \leq 0.0160$) and $1/k_{obs}$ *vs* $[OH^-]$ (r>0.9998, $S \leq 0.0210$) should be linear as shown in Fig. 3. From the slopes and intercepts, the values of K_4 and K_5 were calculated at different temperatures and these values are given in Table 2. A van't Hoff plot was made for the variation of K_4 with temperature [*i.e.*, log K_4 *vs* $1/T$ ($r > 0.9994$, $S \leq 0.0101$)] and the values of the enthalpy of reaction ΔH, entropy of reaction ΔS, and free energy of reaction ΔG, were calculated for the first equilibrium. These values are given in Table 2. A comparison of the latter values with those obtained for the slow step of the reaction shows that these values mainly refer to the rate limiting step, supporting the fact that the reaction before the rate determining step is fairly fast and involves low activation energy.[22]

The moderate values of $\Delta H^{\#}$ and $\Delta S^{\#}$ were both favourable for electron transfer processes. The negative value of $\Delta S^{\#}$ indicates that the complex (C) is more ordered than the reactants.[23]

Conclusion

Among various species of DPC in alkaline medium, diperiodatocuprate(III) (DPC) is considered as active species. It becomes apparent that in carrying out this reaction, the role of pH in the reaction medium is crucial. The rate constant of the slow step and other equilibrium constants involved in the mechanism have been evaluated and activation parameters with respect to the slow step of the reaction were computed. The overall mechanistic sequence described here is consistent with product studies, mechanistic studies and kinetic studies.

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