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Kinetic and mechanistic study of oxidative degradation of paracetamol by diperiodatonickelate (IV) in aqueous alkaline medium

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A mechanism involving the monoperiodatonickelate (IV) (MPN) as the reactive species of the oxidant has been proposed. The reaction constants involved in the different steps of the mechanism are calculated. The activation parameters with respect to the slow step of the mechanism are computed and discussed.

Keywords: paracetamol, diperiodatonickelate (IV)

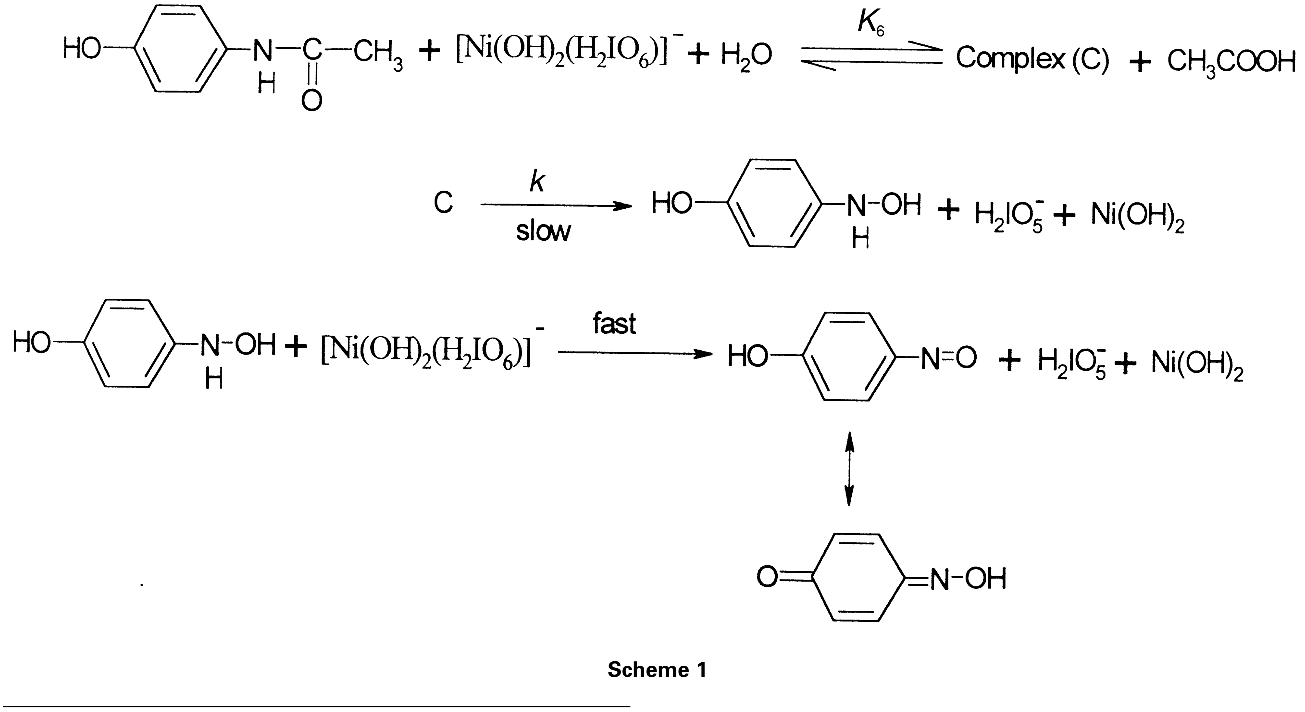
The kinetics of oxidation of paracetamol by diperiodatonickelate (IV) (DPN) in aqueous alkaline medium at a constant ionic strength of 1.0 mol/dm^3 was studied spectrophotometrically. The reaction is of first order in DPN and of less than unit order in both paracetamol and alkali under the experimental conditions. However the order in paracetamol and alkali changes from first order to zero order as the concentration change from lower to higher concentrations respectively. Addition of periodate has a retarding effect on the reaction. It was found that the ionic strength has negligible effect on the rate of the reaction. The rate constants, k_{obs}, increased with the decrease in dielectric constant of the medium. The initially-added products such as Ni (II) and quinone oxime did not show any significant effect on the rate of the reaction.

The results of rate increase with increase in alkalinity and the rate decrease with increase in periodate suggest that equilibria of different Ni(IV) periodate complexes as in equations (5) and (6) are possible. Such types of equilibria have been well recorded in the literature.[14] It may be expected that monoperiodatonickelate (IV) (MPN) is more important in the reaction than the diperiodatonickelate (IV) (DPN). The inverse fractional order in [IO$_4^-$] may also be due to this reason. Added acrylonitrile monomer did not undergo polymerisation under inert atmosphere indicating the absence of free radical formation in the mixture.

$$[Ni(OH)_2\,(H_3IO_6)_2]^{2-} + OH^- \xrightleftharpoons{K_4} [Ni(OH)_2\,(H_3IO_6)\,(H_2IO_6)]^{3-} + H_2O \qquad (5)$$

$$[Ni(OH)_2\,(H_3IO_6)\,(H_2IO_6)]^{3-} \xrightleftharpoons{K_5} [Ni(OH)_2\,(H_2IO_6)]^{-} + H_3IO_6^{2-} \qquad (6)$$

The reaction between DPN and paracetamol shows a first order dependence on [DPN] and fractional order dependence on both paracetamol and OH$^-$. The fractional order in paracetamol presumably results from a complex formation between the oxidant and substrate prior to the formation of the products. Spectroscopic evidence for the complex formation between oxidant and substrate obtained from UV–VIS spectra of the paracetamol, DPN and mixture of both. A bathochromic shift of about 7 nm from 285 to 292 nm of paracetamol was observed and a new band appeared at 268 nm. Indeed, it is to be noted that a plot of $1/k_{obs}$ versus 1/[paracetamol] ($r \geq 0.9999$, $S \leq 0.0124$) shows a straight line with non-zero intercept. Such a complex formation between the oxidant and substrate has been observed in other studies.[5,15,16,19] K_6 is the composite



Scheme 1

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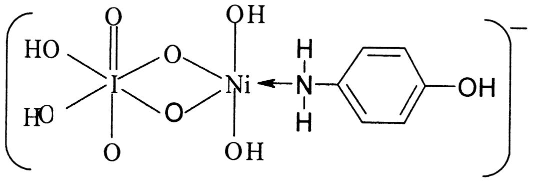
equilibrium constant comprising the equilibrium to bind paracetamol to Ni as well as hydrolysis of paracetamol. When there is strong donor group (-NH_2), CH_3COOH may not be involved in the formation of the complex. All experimental results indicate a mechanism of the type as given below in Scheme 1.

$$[Ni(OH)_2\,(H_3IO_6)_2]^{2-} + OH^- \overset{K_4}{\rightleftharpoons} [Ni(OH)_2\,(H_3IO_6)\,(H_2IO_6)]^{3-} + H_2O$$

$$[Ni(OH)_2\,(H_3IO_6)\,(H_2IO_6)]^{3-} \overset{K_5}{\rightleftharpoons} [Ni(OH)_2\,(H_2IO_6)]^{-} + H_3IO_6^{2-}$$

The probable structure of complex (C) is



Scheme 1 leads to the rate law equation (7),

$$\text{Rate} = -\frac{d[Ni(IV)]}{dt}$$

$$= \frac{kK_4K_5K_6[Ni(IV)]\,[\text{paracetamol}]\,[OH^-]}{[H_3IO_6^{2-}] + K_4\{OH^-\}\,[H_3IO_6^{2-}] + K_4K_5[OH\text{-}] + K_4K_5K_6[\text{paracetamol}]\,[OH^-]} \quad (7)$$

Therefore,

$$k_{obs} = \frac{\text{Rate}}{\text{Ni (IV)}} = \frac{kK_4K_5K_6[\text{paracetamol}]\,[OH^-]}{[H_3IO_6^{2-}] + K_4[OH^-]\,[H_3IO_6^{2-}] + K_4K_5[OH^-] + K_4K_5K_6[\text{paracetamol}]\,[OH^-]} \quad (8)$$

Equation (8) can be arranged to (9), which can be used for verification

$$\frac{1}{k_{obs}} = \frac{[H_3IO_6^{2-}]}{kK_4K_5K_6[\text{paracetamol}]\,[OH^-]} + \frac{[H_3IO_6^{2-}]}{kK_5K_6[\text{paracetamol}]} + \frac{1}{kK_6[\text{paracetamol}]} + \frac{1}{k} \quad (9)$$

According to equation (9), other conditions being constant, the plots of $1/k_{obs}$ versus 1/[OH-]($r \geq 0.9933$, $S \leq 0.0216$), 1/[paracetamol] ($r \geq 0.9999$, $S \leq 0.0124$) and $[H_3IO_6^{2-}]$ ($r \geq 0.9998$, $S \leq 0.0157$) should be linear. From the slopes and intercepts the values of K_4, K_5, K_6 and k could be derived as 1.23±0.05 dm^3/mol, 2.51±0.10 × 10^{-4} mol/dm^3, 284±14 dm^3/mol^1 and 3.5±0.1 × 10^{-3} s^{-1} respectively. The values of K_4 and K_5 are in agreement with earlier values[6] (1.16 dm^3/mol and 6.0 × 10^{-4} mol/dm^3 respectively). Using these constants, the k_{obs} values were regenerated. The negligibly small effect of ionic strength on the reaction is presumably due to the fact that the reaction takes place between a neutral and charged species (Scheme 1). The effect of solvent on reaction rate is described elsewhere.[20] The plot of log k_{obs} versus $1/D$ ($r \geq 0.9939$, $S \leq 0.0223$) gives a straight line with positive slope which is contrary to the expected slower reaction between ions of the same polarity in media of lower relative permittivity. Perhaps the effect is opposed substantially by an increased formation of active reaction species in low-permittivity media, thus leading to the observed net increase in the rate.[21]

A high negative value of $\Delta S^{\#}$ suggests that the intermediate complex is more ordered than the reactants.[22]

Techniques used: Spectrophotometry, IR and ^{1}H NMR.

References: 26

Tables: 1

Figure 1: Plot of log k_{obs} versus $1/D$

Figure 2: Verification of rate law (8) in the form of (9) (conditions as in Table 1)

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