

# Kinetic and mechanistic investigation of oxidative degradation and deamination of atenolol by diperiodatonickelate(IV) in aqueous alkaline medium

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

**Keywords:** atenolol, diperiodatonickelate(IV).

The use of diperiodatonickelate(IV) (DPN) as an oxidant in alkaline medium is new and restricted to a few cases due to its limited solubility and stability in aqueous medium. When nickel(IV) periodate is oxidant, it is necessary to know which species is the active form of the oxidant, since multiple equilibria between the different nickel(IV) species are involved. There are no reports on the oxidative mechanism of atenolol by any oxidant. The present study deals with the title reaction to investigate the redox chemistry of nickel(IV) in aqueous alkaline media and to arrive at a plausible mechanism of the reaction on the basis of kinetic and spectral results.

The water soluble Ni(IV) periodate complex is reported<sup>5, 15–18</sup> to be  $[\text{Ni}(\text{HIO}_6)_2(\text{OH})_2]^{6-}$ . Although periodate is involved in multiple equilibria which prevail to varying extents depending on the pH employed, under the conditions of high pH as maintained in this study, periodate is likely to exist<sup>5</sup> as  $[\text{H}_3\text{IO}_6^{2-}]$ . Hence, the species of Ni(IV) in alkali can be expected to be  $[\text{Ni}(\text{H}_3\text{IO}_6)_2(\text{OH})_2]^{2-}$  (DPN), a conclusion also supported by earlier work.<sup>15,16</sup> The reaction between DPN and atenolol in alkaline medium has 2:1 stoichiometry of oxidant to reductant, with first order dependence each in [DPN], the apparent order of less than unity in  $[\text{OH}^-]$ , and with zero order in [atenolol]. It is interesting to note the zero order in [atenolol] which is rarely observed. In most of the reports on DPN oxidation, periodate had a retarding effect, the order in  $[\text{OH}^-]$  was found to be less than unity, and monoperiodatonickelate(IV) (MPN), is considered to be the active species. However, in the present kinetic study, different kinetic observations have been obtained *i.e.*, periodate has totally no effect on the rate of reaction. Accordingly, deprotonated DPN is considered to be the active species of the oxidant. In view of the zero order in atenolol, it is concluded that the deprotonated form of DPN decomposes in a slow step to give Ni(III) species and hydroxyl radical. This type of hydroxyl radical ( $\text{OH}^\bullet$ ) is evidenced from literature.<sup>19</sup> The active hydroxyl free radical ( $\text{OH}^\bullet$ ) interacts with a molecule of atenolol in a fast step to form an intermediate, amino-free radical ( $\text{NH}_2^\bullet$ ). Such a type of free radical ( $\text{NH}_2^\bullet$ ) formation is in accordance with earlier work.<sup>20</sup> This intermediate reacts with nickel(III) species and free radical ( $\text{NH}_2^\bullet$ ) in further fast steps to give the products. A free radical scavenging experiment revealed the intervention of free radicals in the reaction (*infra*). Based on the observed kinetic results a mechanism involving free radical has been proposed which is shown in Scheme 1.

Scheme 1 leads to the rate law equation (2),

$$\text{Rate} = - \frac{d[\text{Ni(IV)}]}{dt} = \frac{kK[\text{Ni(IV)}][\text{OH}^-]}{(1 + K[\text{OH}^-])(1 + K[\text{Ni(IV)}])}$$

In view of the low concentration of Ni(IV) used, the term  $(1 + K[\text{Ni(IV)}])$  in the denominator is approximated to unity. Therefore,

$$k_{\text{obs}} = \frac{\text{Rate}}{[\text{Ni(IV)}]} = \frac{kK[\text{OH}^-]}{1 + K[\text{OH}^-]} \quad (3)$$

Equation (3) can be arranged to (4), which is suitable for verification

$$\frac{1}{k_{\text{obs}}} = \frac{1}{kK[\text{OH}^-]} + \frac{1}{k} \quad (4)$$

According to equation (4), other conditions being constant, the plot of  $1/k_{\text{obs}}$  versus  $1/[\text{OH}^-]$  ( $r \geq 0.9991$ ,  $S \leq 0.0213$ ), should be linear as shown in Fig. 2. From the slope and intercept the values of  $K$  and  $k$  could be derived as  $1.53 \pm 0.07 \text{ dm}^3/\text{mol}$ , and  $2.2 \pm 0.1 \times 10^{-2} \text{ s}^{-1}$  respectively. The value of  $K$  is in agreement with an earlier value.<sup>15</sup> 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 verifies the proposed mechanism. Since Scheme 1 is in accordance with the generally well-accepted principle of non-complimentary 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. The same type of radical intermediate has also been observed earlier in the context of alkaline nickel(IV) oxidation of various substrates.<sup>21, 22</sup>

The effect of ionic strength on the rate qualitatively explains the reaction between the charged ions of similar kind as shown in Scheme 1. The effect of solvent on the reaction rate has been described in detail in the literature.<sup>23, 24</sup> The negligible effect of dielectric constant on the rate indicates the involvement of a neutral molecule and an ion which supports the proposed mechanism.<sup>25</sup> The moderate values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were both favorable for electron transfer processes. The value of  $\Delta H^\ddagger$  was due to energy of solution changes in the transition state. The negative values of  $\Delta S^\ddagger$  within the range of radical reaction has been ascribed<sup>26</sup> to the nature of electron pairing and electron unpairing processes. Spectrofluorimetric studies reveal that the fluorescence intensity is quenched, which may be due to the electron transfer reaction.<sup>27</sup>

Techniques used: Spectrophotometry, IR, <sup>1</sup>H NMR and Mass spectra.

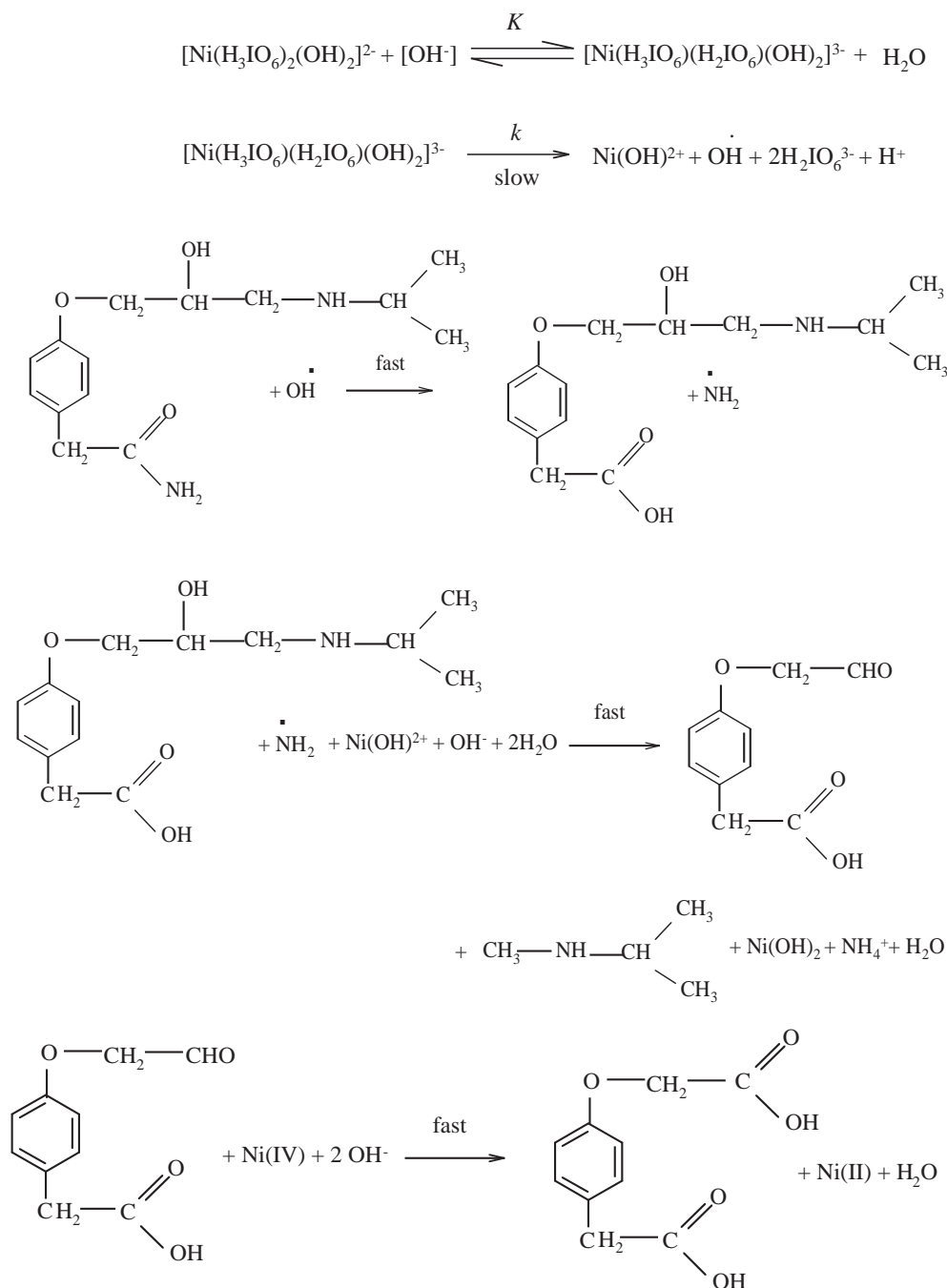
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Tables: 2

Figure 1: Plot of  $\log k_{\text{obs}}$  versus  $1/[\text{OH}^-]$ .

Figure 2: Verification of rate law (3) in the form of (4) (conditions as in Table 1).

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Scheme 1

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