

Redox reactions of 2-hydroxy pyridine: A pulse radiolysis study

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Abstract. Rate constants for reactions of 2-pyridinol with one electron reductants, such as e_{aq}^- and H atoms and one-electron oxidants, viz. OH, N_3 , Br_2^- , Cl_2^- and O^- have been determined at different pH values using the pulse radiolysis technique. From the corrected absorption spectra of the product transient species, the extinction coefficients of these species at their respective absorption maxima have been determined. The kinetics of decay of these transients have been investigated. The pK_a values of transients formed by e_{aq}^- and OH radical reactions have been estimated to be 7.6 and 3.5 respectively. Rate constants for electron transfer from semireduced 2-pyridinol to different electron acceptors have been determined.

Keywords. 2-Hydroxy pyridine; pulse radiolysis; rate constants; transient absorption spectra.

1. Introduction

In nonradical electrophilic substitution reactions pyridones show a reactivity similar to that of benzene and the distribution of electron density at the ring positions (Borisov 1975) is such that electrophilic reagents preferentially attack positions 3 and 5 (Albert 1959). Pyridones may be considered as model compounds for biologically important molecules such as uracil (Steenken and O'Neill 1987). Recently we have reported the results of our studies on reactions of 3-pyridinol with pulse radiolytically generated reducing and oxidizing radicals (Naik and Moorthy 1990, 1991). Whereas 3-pyridinol mainly exists in the enol form, the keto/enol ratios in the case of 2- and 4-pyridinols are 340:1 and 2200:1 respectively (Albert 1959). Theoretical studies on the non-dissociative proton transfer, 2-pyridone \leftrightarrow 2-hydroxy pyridine, in the gas phase and in aqueous solutions have been reported (Field and Hillier 1987). In the literature there are reports of only a few pulse radiolysis and ESR studies on reactions of OH radicals with 2-pyridinol (O'Neill and Steenken 1977). In the present paper we report the results of our detailed investigations on the reactions of 2-pyridinol with reducing and oxidizing radicals generated by pulse radiolysis of aqueous solutions. The results are compared with similar data reported earlier in the case of 3-pyridinol (Naik and Moorthy 1991).

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2. Experimental

The pulse radiolysis set-up employed, using 7 MeV electron pulses from linear accelerator (Viritech Ltd, UK), has been described in detail elsewhere (Guha *et al* 1987). For dosimetry, aqueous solutions of 0.05 mol dm^{-3} KCNS were used [$G \cdot \epsilon = 2.23 \times 10^{-4} \text{ m}^2 \text{ J}^{-1}$ at 500 nm (Fielden 1985) for the transient $(\text{CNS})_2^-$ species formed in this system]. 2-hydroxy pyridine (2-pyridinol) (Fluka, practical grade) was purified by recrystallization from ethanol. For pH adjustments H_2SO_4 , KH_2PO_4 , $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and NaOH were used in suitable combinations. Iolar grade N_2 , O_2 (IOL, India) and instrument grade N_2O (IOL, India) were used for saturating the solutions with the respective gases as required. Fresh solutions were used for each single pulse exposure in a suprasil quartz cell (light path 1 cm). For studying reactions of e_{aq}^- and H atoms *t*-butanol was used as OH radical scavenger. At pH 5, H atoms were obtained by reactions of e_{aq}^- with H_2PO_4^- (Ye and Schuler 1986). Solutions were purged with N_2O at pH 6.8 and 13.3 to convert e_{aq}^- to OH and O^- radicals respectively. One-electron oxidants such N_3 , Br_2^- and Cl_2^- were generated by reactions of OH or O^- with azide or the respective halide ions at appropriate pH values. SO_4^- radicals were generated by reaction of e_{aq}^- with persulphate ions in a matrix containing *t*-butanol as OH radical scavenger. At pH 6.8 Cl_2^- radicals were generated by reaction of SO_4^- radicals with chloride ions (Chawla and Fessenden 1975).

3. Results and discussion

3.1 Reactions with e_{aq}^-

Pulse radiolysis of deoxygenated solutions of 2-pyridinol containing *t*-butanol as OH radical scavenger results in the enhancement of e_{aq}^- decay rate monitored in the 600–750 nm wavelength region. Concomitantly, the formation of a long lived species is observed in the shorter wavelength region: 300–450 nm. The observed pseudo first order rate constant (k_{obs}) for e_{aq}^- decay was measured as a function of 2-pyridinol (2-pyl) concentration. At pH 6.8, the rate constant for the reaction,



obtained as the slope of the plot of k_{obs} versus 2-pyridinol concentration, is $1.4 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ which is of the same order as that of 3-pyridinol at the same pH (Naik and Moorthy 1990). At pH 13.3 where 2-pyridinol is in the deprotonated form, the rate constant for the e_{aq}^- reaction is $9.3 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ which is lower by more than an order of magnitude compared to the one at pH 6.8 and is also lower than the value obtained for the deprotonated form of 3-pyridinol. The absorption spectrum of the transient species formed at pH 5 is shown in figure 1. As the spectrum of the transient is in close proximity to that of the parent ground state, correction of the former for depletion of the latter was made, assuming the stoichiometry implied in (1). The corrected spectrum is shown in figure 2. From the experiments carried out at different pH values it was observed that the absorbance at 340 nm decreases with increasing pH. From the plot of absorbance versus pH, the pK_a of the transient

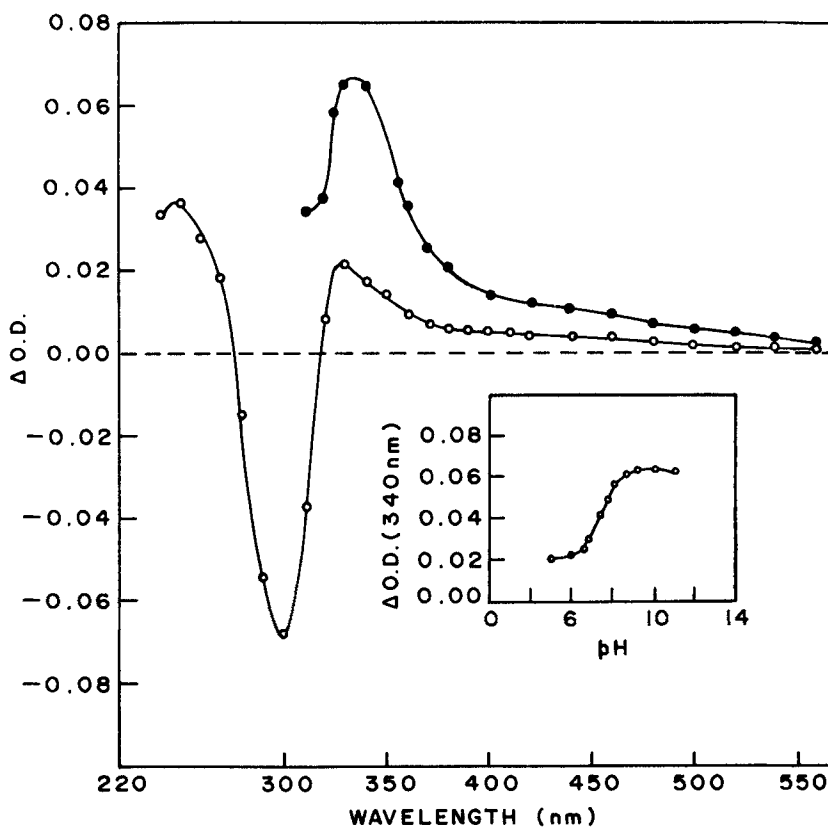


Figure 1. Absorption spectra of the transient species formed by reaction of e_{aq}^- with 2-pyridinol in deoxygenated solutions containing $2 \times 10^{-4} \text{ mol dm}^{-3}$ 2-pyridinol, 0.1 mol dm^{-3} *t*-butanol at pH 5 (○) and $1 \times 10^{-3} \text{ mol dm}^{-3}$ 2-pyridinol, 0.2 mol dm^{-3} *t*-butanol at pH 13.3 (●). Inset: Plot of OD at 340 nm versus pH.

species has been inferred to be 7.6. The spectrum of the e_{aq}^- reaction product observed at pH 13.3 is also shown in figure 1. At both these pH values (6.8 and 13.3) the transient species decays by second-order kinetics. At pH 6.8 experiments were carried out to see whether $(\text{CH}_3)_2\text{COH}$ ($E_0 = -1.39 \text{ V}$) and CO_2^- ($E_0 = -1.9 \text{ V}$) (Schwarz and Dodson 1989) radicals react with 2-pyridinol and were found to be unreactive, whereas they were found to react with 3-pyridinol by addition reaction (Naik and Moorthy 1990). The reason for this may be that in 3-pyridinol positions 2 and 4 are free where nucleophilic addition reaction is favourable on the basis of electron density distribution whereas in 2-pyridinol position 2 is not free and also it exists predominantly in the keto form. This suggests that the one-electron reduction potential of 2-pyridinol must be more negative than ($<$) -1.9 volts vs. NHE. Similarly at pH 13.3, $(\text{CH}_3)_2\text{CO}^-$ ($E_0 = -2.1 \text{ V}$) (Schwarz and Dodson 1989) was found to be unreactive towards the deprotonated form of 2-pyridinol.

3.2 Reactions with H atoms

At pH 2.5, the rate constant for the reaction of H atoms with 2-pyridinol was found to be $1.9 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ as determined by following the build-up of the transient

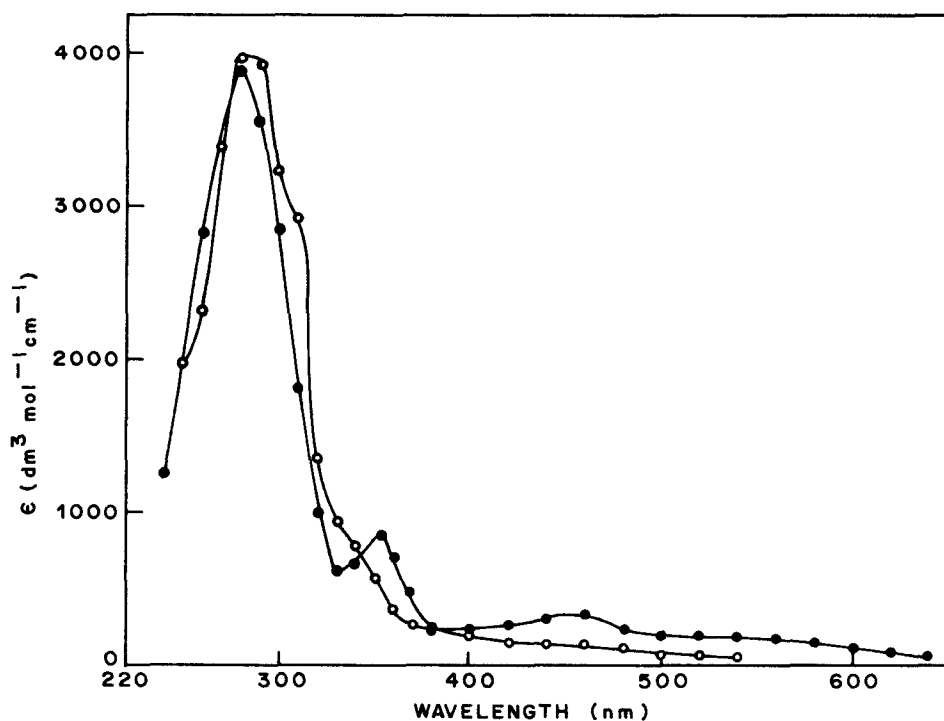


Figure 2. Absolute absorption spectra of the transient species formed by reaction of 2-pyridinol with e_{aq}^- (○) and OH radicals (●).

absorbance at 350 nm. The transient absorption spectrum exhibits λ_{max} at 350 nm and a broad hump in the region 420–500 nm (figure 3). The transient decays by second-order kinetics at 350 nm and also at 460 nm. The absorption spectrum of the transient species formed by reaction of H atoms with 2-pyridinol at pH 5 is given in figure 3. This is different from the one obtained by e_{aq}^- reaction at this pH implying that the H-atom does not bring about one-electron reduction of 2-pyridinol. Kinetic and spectral parameters for the reactions of the above reducing radicals with 2-pyridinol are given in table 1.

3.3 Reactions with OH radicals

At pH 6.8 the transient species formed by reaction of OH radicals with 2-pyridinol absorbs in the 320–640 nm region with λ_{max} at 355 nm and broad humps in the 420–480 nm and 240–270 nm regions. The observed spectrum of the transient (figure 4) is seen to merge with the ground state absorption spectrum and the transient absorption was corrected for parent ground state depletion as in the case of e_{aq}^- reaction product at pH 5. The corrected absorption spectrum of the OH reaction product is shown in figure 2. It decays by second-order kinetics with a $2k/\epsilon l$ value of $7.6 \times 10^5 \text{ s}^{-1}$ at 355 nm. Experiments carried out in the presence of high salt concentrations suggest that the transient is a neutral species. This is in agreement with the earlier conclusions reached by other workers (O'Neill and Steenken 1977). The rate constant for the reaction of OH radicals with 2-pyridinol was determined

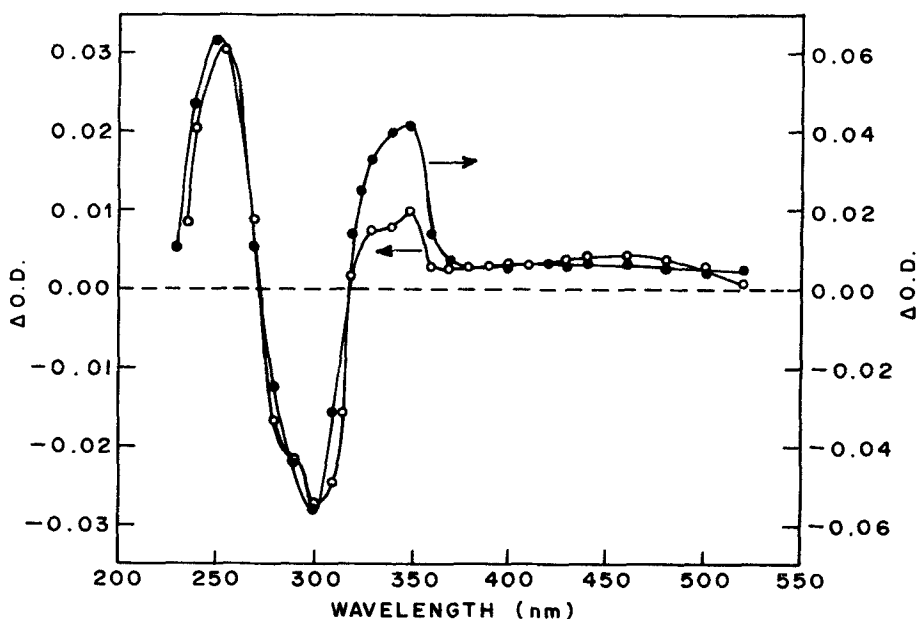


Figure 3. Absorption spectra of the transient species formed by H atom reaction with 2-pyridinol in deoxygenated solutions containing $4 \times 10^{-4} \text{ mol dm}^{-3}$ 2-pyridinol, 0.2 mol dm^{-3} at pH 2.5 (●) and $5 \times 10^{-5} \text{ mol dm}^{-3}$ 2-pyridinol, 0.2 mol dm^{-3} *t*-butanol, 1.0 mol dm^{-3} KH_2PO_4 and 0.02 mol dm^{-3} $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ (○).

by following the build-up of transient absorbance at 355 nm at various concentrations of the substrate molecule. The rate constant thus determined ($1.1 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) is higher than that of 3-pyridinol ($8.9 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). In 2-pyridinol, positions 3 and 5 in the pyridine ring which are favourable for electrophilic reactions are free and thus the reaction with OH radical is more favoured as compared to 3-pyridinol where position 3 is occupied by the hydroxy group. At pH 2.5 the absorption spectrum of the OH reaction product is entirely different as compared to the one at pH 6.8 and is given in figure 4b. Making use of the fact that ϵ at 355 nm changes as a function of pH, experiments were carried out to determine the pK_a of the OH reaction product which was found to be 3.6.

At pH 13.3, the deprotonated form of 2-pyridinol was found to react with O^- with a rate constant of $1.26 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ as determined by following the build-up of transient absorption at 360 nm. This rate value also is higher than the one for 3-pyridinol for the same reasons as for OH reactions. Observed spectrum of the transient species after $5 \mu\text{s}$ of the electron pulse is also shown in figure 4. The transient decays by second-order kinetics at 360 nm with a $2k/\epsilon l$ value of $6.0 \times 10^5 \text{ s}^{-1}$ whereas at 430 nm the decay is first-order, the rate constant being $9.6 \times 10^3 \text{ s}^{-1}$.

3.4 Reactions of N_3 and Br_2^- at pH 13.3

At pH 13.3 the reaction of 2-pyridinol with N_3 is fast with a rate constant of $5.89 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ as determined by following the build-up of the transient absorption at 390 nm. The transient absorbs in the 320–580 nm region with λ_{max} at 390 nm

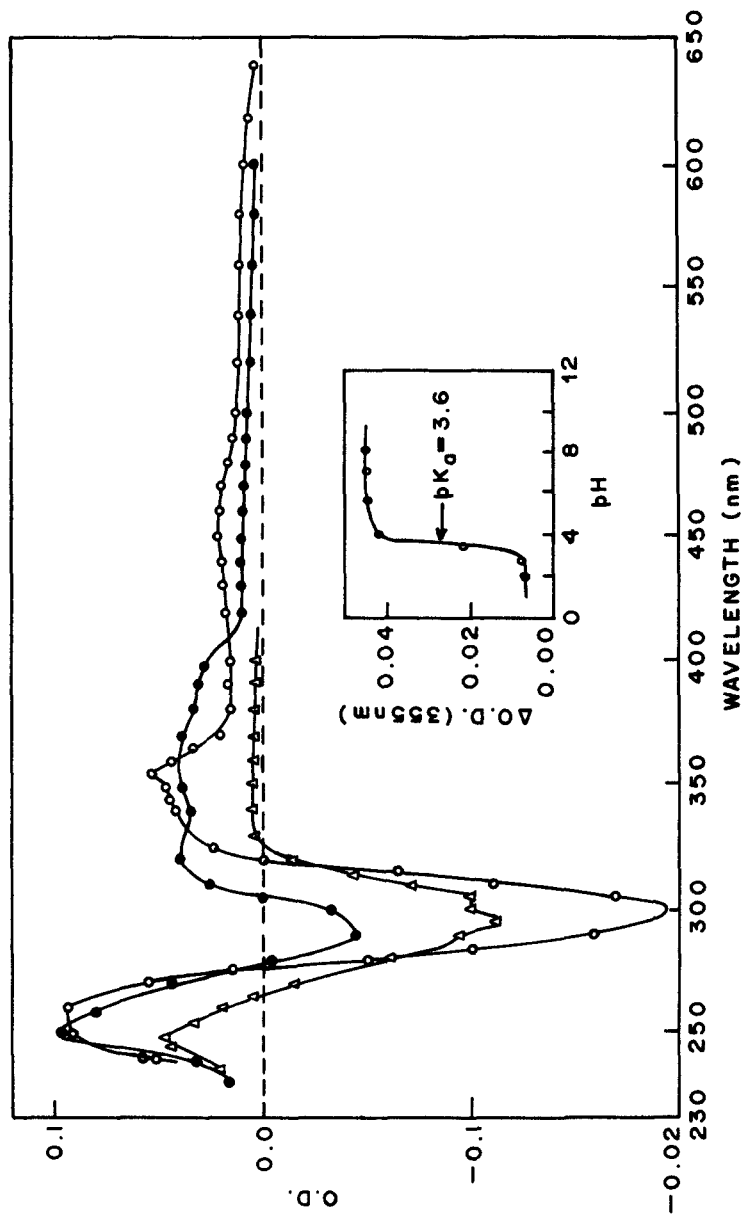


Figure 4. Absorption spectra of the transient species formed by OH^- reaction with 2-pyridinol in N_2O saturated solution containing $2 \times 10^{-4} \text{ mol dm}^{-3}$ 2-pyridinol at pH 6.8 (\circ), O_2 saturated solution containing $2 \times 10^{-4} \text{ mol dm}^{-3}$ 2-pyridinol at pH 13.3 (Δ) and by OH^- reaction with 2-pyridinol ($2 \times 10^{-4} \text{ mol dm}^{-3}$) at pH 13.3 (\bullet). Inset: Plot of OD at 355 nm versus pH.

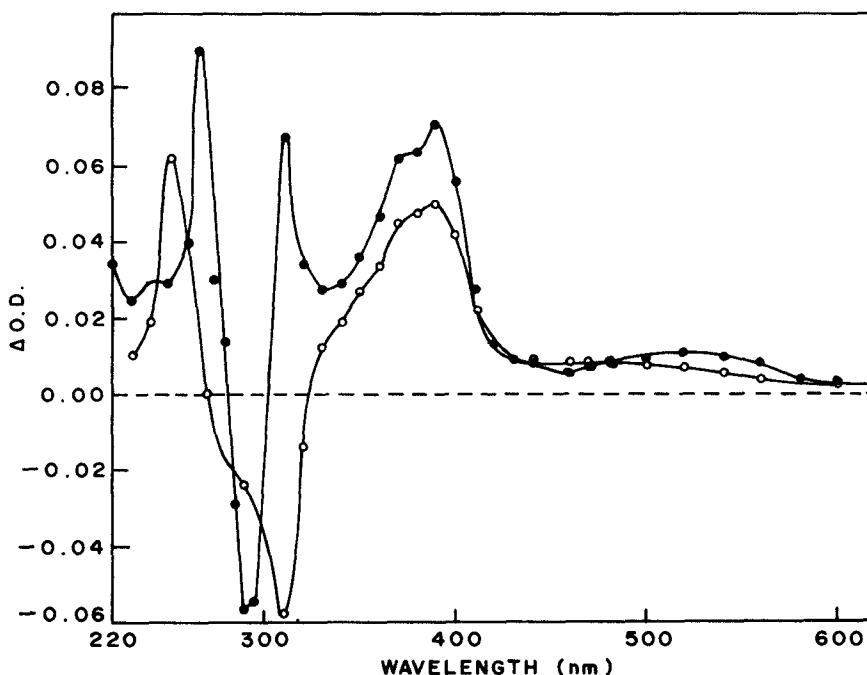


Figure 5. Absorption spectra of the transient species formed by reaction of N_3 with 2-pyridinol in N_2O saturated solution containing $2 \times 10^{-4} \text{ mol dm}^{-3}$ 2-pyridinol, 0.1 mol dm^{-3} NaN_3 , 0.2 mol dm^{-3} $NaOH$ (●) and SO_4^- with 2-pyridinol in deoxygenated solution containing $4 \times 10^{-4} \text{ mol dm}^{-3}$ 2-pyridinol, 0.4 mol dm^{-3} *t*-butanol, 0.03 mol dm^{-3} $K_2S_2O_8$ at pH 6.8 (○).

(figure 5). Decay profiles at all the wavelengths are not similar. At 390 nm, the initial fast decay is followed by a slower decay which does not follow either first or second-order kinetics. On the other hand, at 430 nm peak absorbance is observed at later time windows and the decay is second order with $2k/rl = 1.52 \times 10^5 \text{ s}^{-1}$. At the same pH Br_2^- reacts with 2-pyridinol (III) with a rate constant of $2.55 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ as determined by following the pseudo first-order decay of Br_2^- at 350 nm. Absorption spectrum of the transient obtained by Br_2^- reaction with 2-pyridinol is identical to the one obtained by the reaction of N_3 at this pH. The $2k/rl$ value for the decay of the transient at 430 nm ($1.53 \times 10^5 \text{ s}^{-1}$) agrees well with the one obtained for the species formed by reaction with N_3 . From this, we conclude that N_3 and Br_2^- both bring about one-electron oxidation of 2-pyridinol at pH 13.3. On comparing the absorption spectra obtained by N_3 , Br_2^- and O^- radical reactions with 2-pyridinol at pH 13.3 and also by comparing decay parameters it is concluded that the O^- radical does not bring about one-electron oxidation of this molecule at pH 13.3.

At pH 6.8, 2-pyridinol is found to be unreactive towards N_3 and Br_2^- as no change in the decay rates of these radical absorbance was observed in presence of appreciable concentrations of 2-pyridinol, whereas these radicals do react with the neutral form of 3-pyridinol suggesting that the one-electron oxidation potential of 2-pyridinol is higher than that of 3-pyridinol.

Table 1. Spectral and kinetic parameters for the reactions of reducing and oxidizing radicals with 2-pyridinol (2-pyl).

Reaction	pH	Rate constant ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	λ_{max} (nm)	ϵ ($\text{dm}^{-3} \text{mol}^{-1} \text{cm}^{-1}$) at λ_{max}	Decay rate $2k/\epsilon l$ (s^{-1})*
2-pyl + e_{aq}^-	5.0	1.4×10^{10}	280	3960	2.7×10^6 (340 nm)
2-pyl + e_{aq}^-	13.3	9.3×10^9	340	2760	6.6×10^5
2-pyl + H	2.5	1.9×10^9	350	1520	1.7×10^6
2-pyl + OH	6.8	1.1×10^{10}	280	3875	7.6×10^5 (355 nm)
2-pyl + O^-	13.3	1.26×10^9	355–365	1160	6.0×10^5 (360 nm) 9.6×10^3 (1st order at 430 nm)
2-pyl + N_3	13.3	5.89×10^9	390	1385	1.52×10^5 (430 nm)
2-pyl + Br_2^-	13.3	2.55×10^9	390	1385	1.53×10^5 (430 nm)
2-pyl + Cl_2^-	2.5	1.31×10^8	—	—	—
2-pyl + SO_4^-	6.8	—	390	—	7.6×10^5

Values in parentheses are wavelengths in nm.

3.5 Reactions of Cl_2^- and SO_4^-

At pH 2.5, Cl_2^- was found to react with 2-pyridinol with a rate constant of $1.3 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ as determined by following the decay of Cl_2^- absorbance at 340 nm. No fresh product absorbance could be seen in the 250–650 nm region.

At pH 6.8, SO_4^- was found to react with 2-pyridinol. The absorption spectrum of the transient species formed is shown in figure 5. It is seen that the initial transient formed having an absorption maximum at 390 nm decays to a product with the absorption maximum at 320 nm. Decay at 390 nm is second order with a $2k/\epsilon l$ value of $7.6 \times 10^5 \text{ s}^{-1}$. The kinetic and spectral parameters for reactions of oxidizing radicals with 2-pyridinol are given in table 1.

3.6 Electron transfer from semireduced 2-pyridinol at pH 6.8

At pH 6.8, the reaction product formed by the reaction of e_{aq}^- with 2-pyridinol was found to be reducing in nature. It transferred electrons to thionine, methylene blue, safranin, anthraquinone 2-sulphonate, paraquat and benzophenone with almost diffusion controlled rate constants ($1 - 6 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). The rate constants for the above reactions were measured by following the product absorption build up at their respective absorption maxima. Previously, similar electron transfer processes were observed with the 3-pyridinol anion (Naik and Moorthy 1990). It is observed that except for benzophenone in all cases the rate constants for the reaction of the 2-pyridinol anion with the above acceptors are higher than those observed in the case of 3-pyridinol. This indirectly suggests that the 2-pyridinol anion is a stronger reducing agent and hence the one-electron reduction potential of 2-pyridinol is more negative than that of 3-pyridinol.

4. Conclusions

Both in the case of reducing and oxidizing radicals, the reactivity of 2-pyridinol changes significantly with its state of protonation. Oxidizing radicals viz. N_3 and Br_2^- quite easily bring about one-electron oxidation at pH 13.3, whereas such oxidation is not observed at pH 6.8. Both $(CH_3)_2COH$ and CO_2^- radicals do not reduce 2-pyridinol at pH 6.8 suggesting that its one-electron reduction potential has a value < -1.9 V. Also the magnitudes of electron transfer reaction rate constants for the reaction of the 2-pyridinol anion with different acceptors suggest that the one-electron reduction potential of 2-pyridinol is more negative than that of 3-pyridinol.

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