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Addition−Elimination in the Reaction of α-Hydroxyalkyl Radicals with 3,5-Pyridinedicarboxylic Acid and Nicotinic Acid: Example of Inner Sphere Organic Electron Transfer

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Reactions of α-hydroxyalkyl radicals with 3,5-pyridinedicarboxylic acid (3,5-PDCA) and nicotinic acid (NA) were studied at appropriate pHs in aqueous solutions by pulse radiolysis technique. At pH 1, $CH_3C^{\bullet}HOH$ and $^{\bullet}CH_2OH$ radicals were found to react with 3,5-PDCA by rate constants of 2.2×10^9 and 5.1×10^8 $dm^3\ mol^{-1}\ s^{-1}$, respectively, giving radical adduct species. The adduct species formed in the reaction of $CH_3C^{\bullet}HOH$ radicals with 3,5-PDCA underwent unimolecular decay ($k = 9.8 \times 10^4\ s^{-1}$) giving pyridinyl radicals. Reaction of $(CH_3)_2C^{\bullet}OH$, $CH_3C^{\bullet}HOH$, and $^{\bullet}CH_2OH$ radicals with NA at pH 3.3 gave the adduct species which subsequently decayed to the pyridinyl radicals. At pH 1, wherein NA is present in the protonated form, $(CH_3)_2C^{\bullet}OH$ radicals directly transfer electrons to NA, whereas $CH_3C^{\bullet}HOH$ and $^{\bullet}CH_2OH$ radicals react with higher rate constants compared with those at pH 3.3, initally giving the adduct species which subsequently undergo elimination reaction giving pyridinyl radicals. Reactions of α-hydroxyalkyl radicals with 3,5-pyridinedicarboxylic acid and nicotinic acid are found to proceed by an addition−elimination pathway that provides one of the few examples of organic inner sphere electron-transfer reactions. Rate constant for the addition reaction as well as rate of elimination varies with the reduction potential of α-hydroxyalkyl radicals.

1. Introduction

Free radicals of heterocyclic compounds are very important in biology and chemistry.[1,2] Pyridinyl radicals formed on one-electron reduction of pyridines are of considerable interest as these participate as intermediates in biochemical redox reactions of the enzyme couples $NADH/NAD^+$ (nicotinamide adenine dinucleotide).[2,3] Nicotinic acid (NA) as well as its amide are pellagra preventive factors and their derivatives are H-transferring coenzymes.[3,4] 3,5-pyridinedicarboxylic acid (3,5-PDCA) is the basic moiety of biologically important compounds such as Nifedipine and so forth which are calcium channel blockers.[5] One electron reduction of pyridines yields pyridinyl radicals. Possible participation of these radicals in biochemical processes have led to many studies using the pulse radiloysis technique.[3,4] Radiolysis of aqueous solutions containing organic compounds can be used to study the different types of radicals under appropriate experimental conditions. Normally reducing radicals generated in aqueous solutions, such as $CO_2^{\bullet-}$, $(CH_3)_2C{\bullet}OH$, $CH_3C{\bullet}HOH$, and ${\bullet}CH_2OH$ radicals of varying reduction potentials undergo electron tranfer reactions with many of the dye molecules giving semi-reduced species depending on the reduction potential of dyes.[6,7] In a few cases, it is reported that being nucleophilic radicals, these undergo addition reactions giving the adduct species.[8−10] Only in the case of nitroaromatics, it is reported in the literature that $(CH_3)_2C^{\bullet}OH$ and others react with nitro compounds giving the nitrosyl type of adducts which subsequently give radical anions of nitro compounds.[11] Compared to this, oxidizing hydroxyl radicals are well-known to undergo addition−elimination reactions with variety of organic compounds.[12] We have earlier carried out pulse radiolysis studies on a good number of nitrogen heterocyclics where organic radicals either transfer an electron giving pyridinyl type of radicals which are highly reducing in nature[13] or in a few cases radical−adduct species were formed.[10,14] We report here that the reaction of such reducing organic radicals (viz. α-hydroxyalkyl radicals) with 3,5-pyridinedicarboxylic acid and nicotinic acid at suitable pHs give the radical−adduct species which subsequently undergo an elimination reaction giving the pyridinyl radicals.

2. Experimental Methods

3,5-pyridinedicarboxylic acid was from Aldrich Chemical Co. and nicotinic acid was from BDH Laboratory Chemicals and were used as received. Pulse radiolysis experiments were carried out using 7 MeV energy electron pulses of 50 ns duration from linear accelerator (Viritech Technologies, U.K.). Details of the pulse radiolysis setup are discussed elsewhere.[15,16] Dose absorbed per pulse was determined using aerated 0.01 mol dm^{-3} potassium thiocynate solution, using a value of 21 520 $dm^3\ mol^{-1}\ cm^{-1}\ (100\ eV)^{-1}$ for $(G{\bullet}\epsilon)$ of $(SCN)_2^{\bullet-}$ at 500 nm[17] and was usually kept at 15 Gray per pulse. As such, $(SCN)_2^{\bullet-}$ species has absorption maximum at 472 nm with molar extinction coefficient of 7580 $dm^3\ mol^{-1}\ cm^{-1}$ which is about 11% higher compared with that at 500 nm.[18] For pulse radiolysis experiments, solutions were prepared in water from Millipore A-10 system. The solution pHs were adjusted using appropriate concentrations of AnalaR grade $HClO_4$, KH_2PO_4, and Na_2HPO_4. Irradiation of water with high-energy electrons gives highly reactive species such as e^-_{aq}, H atom, and $^{\bullet}OH$ radicals as given in reaction 1. In the acidic region, that is, below pH 3.0, hydrated electrons (e^-_{aq}) are converted into H atoms by reaction with H_3O^+ as shown in reaction 2. At pH 1, solutions were purged with IOLAR grade N_2 to remove dissolved oxygen, whereas at

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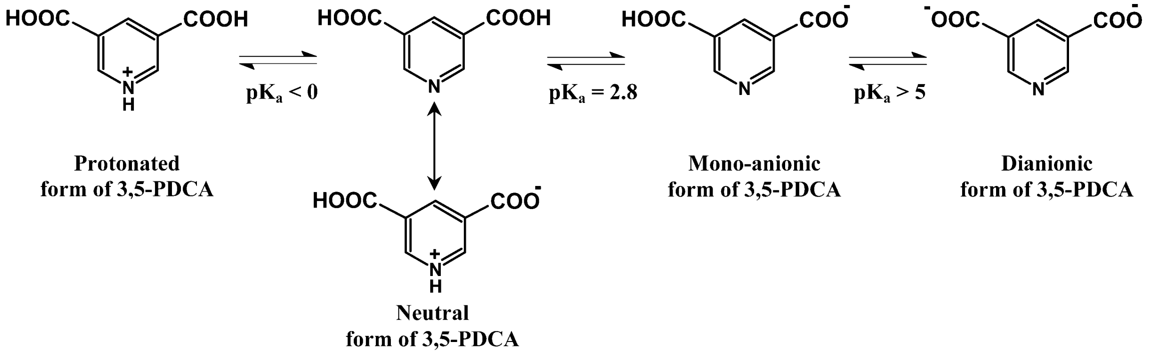
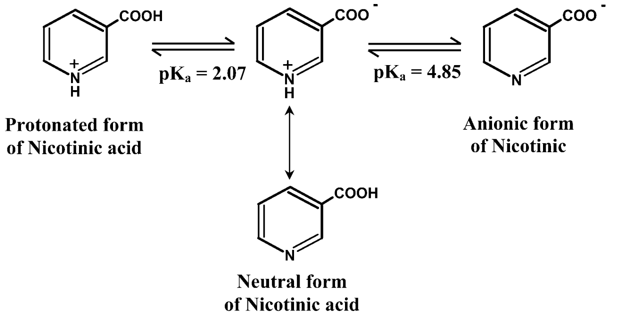
SCHEME 1: Protolytic Forms of 3,5-PDCA



SCHEME 2: Protolytic Forms of Nicotinic Acid



pHs above 3, the same were saturated with high purity N_2O wherein e^-_{aq} are converted into $^{\bullet}OH$ radicals as shown in reaction 3.

$$H_2O \rightsquigarrow e^-_{aq}, {}^{\bullet}H, {}^{\bullet}OH, H_2, H_2O_2, H_3O^+ \qquad (1)$$

$$\text{At pH} < 3, \qquad e^-_{aq} + H_3O^+ \rightarrow {}^{\bullet}H + H_2O \qquad (2)$$

$$\text{At pHs} > 3, \qquad e^-_{aq} + N_2O \rightarrow {}^{\bullet}OH + OH^- + N_2 \qquad (3)$$

Reaction of $^{\bullet}OH$ radicals and H atoms, generated in water radiolysis, with alcohol give mainly corresponding α-hydroxyalkyl radicals. Typically, alcohol such as ethanol reacts with H atoms and $^{\bullet}OH$ radicals giving α-hydroxyethyl radicals, as given below (reaction 4), with some proportion of *β*-hydroxy radicals which are rather unreactive.[19,20]

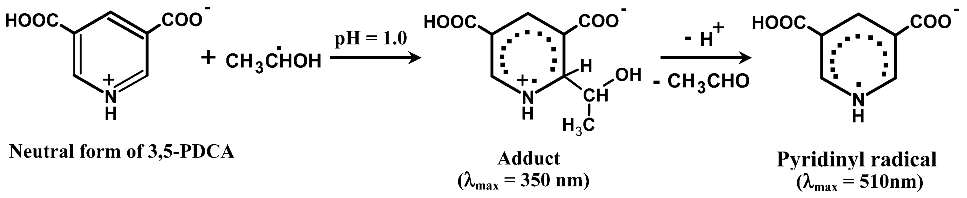
$$CH_3CH_2OH + {}^{\bullet}H\,({}^{\bullet}OH) \rightarrow CH_3C^{\bullet}HOH + H_2(H_2O) \quad (4)$$

Concentrations of alcohols (>1 mol dm^{-3}) were chosen so that H atoms and $^{\bullet}OH$ radicals do not react with the solutes directly.

3. Results and Discussion

3,5-pyridinedicarboxylic acid (3,5-PDCA) exists in different protolytic forms. Above pH 5, it is mainly present in the dianionic form. In the pH region 3.4, it is present as a monoanion, and at pH ~1, it is present in the neutral form as shown in Scheme 1. Nicotinic acid (NA) has pK_a's at 2.07 and 4.85[21] (Scheme 2). Electron transfer to these different charged states of 3,5-PDCA and NA is expected to be pH dependent. In Figure 1, we have given the time-resolved absorption spectra of the transient species formed by the reaction of $CH_3C^{\bullet}HOH$ radicals with 3,5-PDCA (1×10^{-3} mol dm^{-3}) at pH 1. It is interesting to observe that initially a transient species is formed with absorption maximum at 350 nm which decays to give another transient species of which absorption spectrum has maximum at 510 nm having an isosbestic point at 440 nm. Following the build-up of transient absorption at 350 nm at various concentrations of 3,5-PDCA, the rate constant for the reaction of $CH_3C^{\bullet}HOH$ radicals with 3,5-PDCA at pH 1 was determined to be 2.2×10^9 dm^3 mol^{-1} s^{-1}. This initially formed transient species decayed by first-order kinetics with $k = 9.8 \times 10^4$ s^{-1}. This rate constant was not dependent on concentration of 3,5-PDCA indicating that there is no reaction of the initially formed species with 3,5-PDCA. When concentration of 3,5-PDCA was varied from 1×10^{-3} mol dm^{-3} to 3×10^{-3} mol dm^{-3}, there was no change in the value of rate constant as can be seen from the decay traces at three concentrations of 3,5-PDCA given in Figure 2. At H^+ concentration in the region of 0.1 to 0.6 mol dm^{-3}, the rate constant did not change. The time profile for the formation of transient absorption at 510 nm follows the identical time profile as that of the initially formed species decay at 350 nm. This is given in the inset of Figure 1. The latter time window spectrum was found to match very well with the absorption spectrum of pyridinyl radicals of 3,5-PDCA formed in the reaction of $(CH_3)_2C^{\bullet}OH$ and $COOH/CO_2^{\bullet-}$ radicals species at this pH; the one which obtained in the reaction of $(CH_3)_2C^{\bullet}OH$ radicals is given in Figure 3. The rate constant for the reaction of $(CH_3)_2C^{\bullet}OH$ radicals with 3,5-PDCA was determined by following the buildup of absorption of pyridinyl radical at 510 nm and is given in Table 1. This shows that reaction of $CH_3C^{\bullet}HOH$ radicals with 3,5-PDCA initially gives an adduct species which decays to give pyridinyl radicals. Reduction potential of $(CH_3)_2C^{\bullet}OH$ radicals at pH 1 is −1.45 V versus NHE,[22] and the reduction potential of $CO_2^{\bullet-}$ radicals is −1.9 V versus NHE which has a pK_a at 1.4 below which it exists as $^{\bullet}COOH$.[23] This clearly showed that $CH_3C^{\bullet}HOH$ radicals undergo inner sphere electron-transfer reaction with 3,5-PDCA as given in Scheme 3.

SCHEME 3: Reaction of $CH_3C^{\cdot}HOH$ Radicals with 3,5-PDCA at pH 1



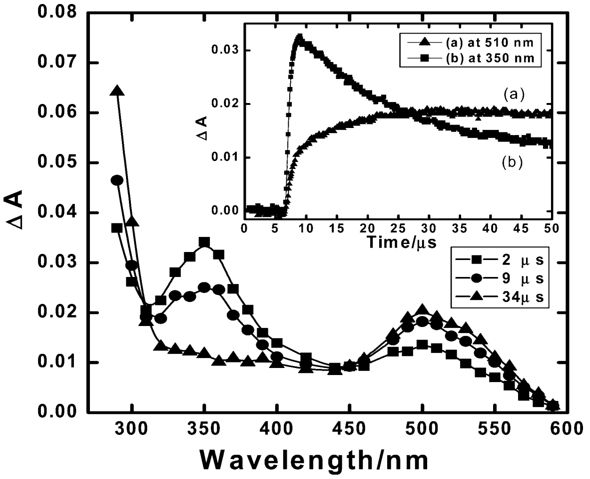


Figure 1. Time-resolved absorption spectra of the transients species formed in the reaction of $CH_3C{\cdot}HOH$ radicals with 3,5-PDCA (1×10^{-3} mol dm^{-3}) at pH 1. Inset: kinetic traces (a) at 510 nm and (b) at 350 nm.

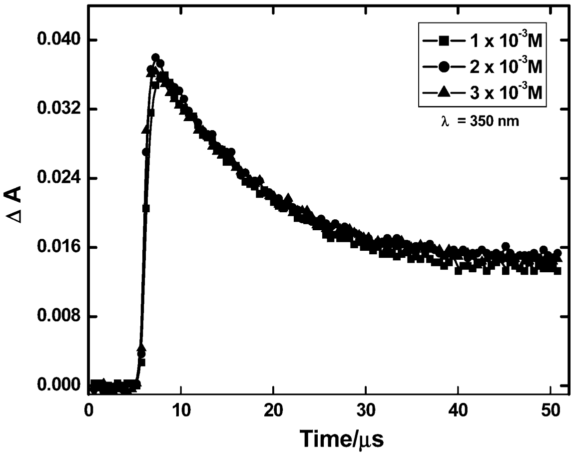


Figure 2. Kinetic traces at 350 nm for the decay of the adduct species formed in the reaction of $CH_3C{\cdot}HOH$ radicals with 3,5-PDCA at pH 1 at various 3,5-PDCA concentrations.

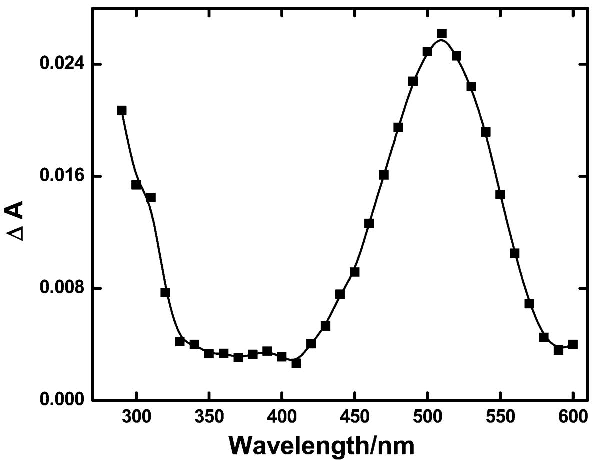


Figure 3. Absorption spectrum of the transient species fromed (at 2 μs after the electron pulse) in the reaction of $(CH_3)_2C^{\bullet}OH$ radicals with 3,5-PDCA (1×10^{-3} mol dm^{-3}) at pH 1.

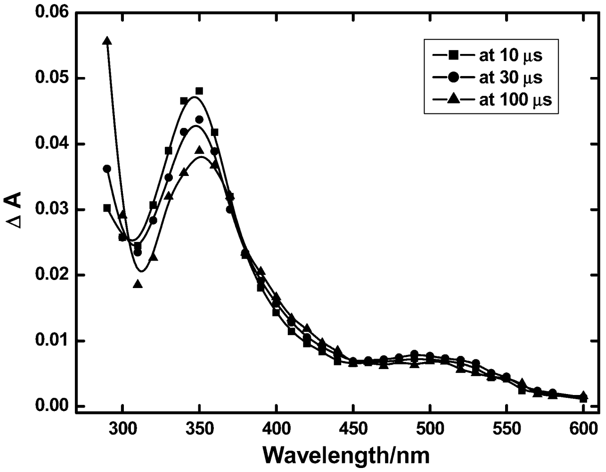


Figure 4. Time-resolved absorption spectra of the transient species formed in the reaction of $^{\bullet}CH_2OH$ radicals with 3,5-PDCA (1×10^{-3} mol dm^{-3}) at pH 1.

Reaction of $^{\bullet}CH_2OH$ radicals with 3,5-PDCA at pH 1 was also found to give the adduct species with absorption maximum at 350 nm spectrum which is given in Figure 4. Rate constant for the addition reaction of $^{\bullet}CH_2OH$ radicals with 3,5-PDCA at pH 1 ($k = 5.1 \times 10^8$ dm^3 mol^{-1} s^{-1}) was found to be lower than that for the reaction of $CH_3C^{\bullet}HOH$ radicals with 3,5-PDCA at this pH (see Table 1). Also, the adduct formed was found to decay with a slower rate, namely, $k = 9.1 \times 10^3$ s^{-1}. Molar extinction coefficients of the pyridinyl radicals as well as adduct formed in the reaction of $CH_3C^{\bullet}HOH$ and $^{\bullet}CH_2OH$ radicals with 3,5-PDCA are also given in Table 1. These were calculated considering the fact that only 85% of α-hydroxyalkyl radicals are formed in the case of 2-propanol and ethanol,[19] and in the case of methanol, 93% are $^{\bullet}CH_2OH$ radicals. In this calculation, radical−radical reactions taking place in competition with their reaction with 3,5-PDCA was also taken care of in addition to the decay of the adduct radical. In the reactions of all of the above α-hydroxyalkyl radicals with 3,5-PDCA, steady-state gamma radiolysis of 3,5-PDCA at pH 1 in the presence of respective alcohols in N_2-bubbled solutions gave identical absorption spectra for the product formed confirming that adducts undergo elimination reaction giving pyridinyl radicals in all of the cases which subsequently undergo decay to give the identical product. As mentioned in Scheme 3, on radiolysis of 3,5-PDCA in the presence of alcohols, acetone and respective aldehydes were detected as products by the 2,4-dinitrophenyl hydrazine reagent. At pH 3.4, where 3,5-PDCA is present in the monoanionic form, $(CH_3)_2C^{\bullet}OH$, $CH_3C^{\bullet}HOH$, and $CH_3C^{\bullet}$-HOH radicals did not react with 3,5-PDCA by any measurable

TABLE 1: Kinetic and Spectral Parameters of the Transients Species Formed by the Reaction of Various Reducing Radicals with 3,5-PDCA at pH 1.0

reducing radicals	λ_{max} (nm) adduct	pyridinyl radical	k_f (dm^3 mol^{-1} s^{-1})	ϵ (dm^3 mol^{-1} cm^{-1}at λ_{max})	decay rates of the adduct (s^{-1})	decay of the pyridinyl radicals, 2k (dm^3 $mol^{-1}s^{-1}$)
$(CH_3)_2C{\cdot}OH$		510	2.1×10^9	3400 (510 nm)		1.4×10^9
$CH_3{\cdot}CHOH$	350	510	2.2×10^9	4300 (350 nm)	9.8×10^4	1.4×10^9
$\cdot CH_2OH$	350	510	5.1×10^8	5600 (350 nm)	9.1×10^3	
$\cdot COOH$		510	2.5×10^9			1.4×10^9

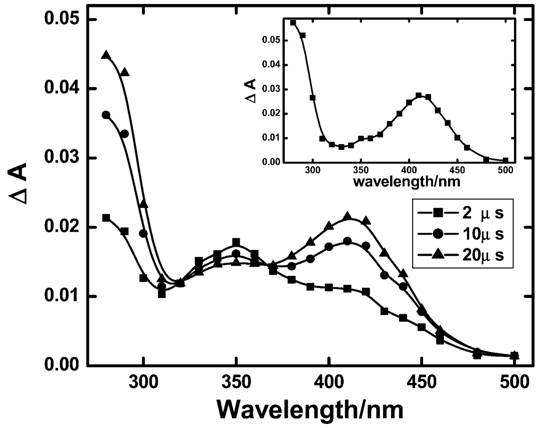


Figure 5. Time-resolved absorption spectra of the transient species formed in the reaction of $(CH_3)_2C^{\bullet}OH$ radicals with NA (2×10^{-3} mol dm^{-3}) at pH 3.3. Inset: absorption spectrum of transient species formed (at 5 μs after the electron pulse) in the reaction of $CO_2^{\cdot -}$ radicals with NA (1×10^{-3} mol dm^{-3}) at pH 3.3.

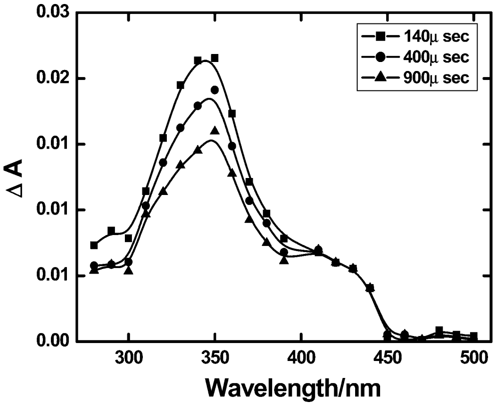


Figure 6. Time-resolved absorption spectra of the transient species formed in the reaction of $^{\bullet}CH_2OH$ radicals with NA (1×10^{-3} mol dm^{-3}) at pH 3.3.

rate as no absorption signal could be seen in the 300−500 nm region. This suggests that the reduction potential of the monoanionic form of 3,5-PDCA is more negative than that of neutral 3,5-PDCA. As is seen in the case of nicotinic acid (discussed in subsequent section), on protonation rate of the addition reaction also increases.

Having observed the formation of adduct species followed by elimination in 3,5-PDCA at pH 1, we were interested in finding whether similar reactions take place in the case of NA where only one carboxylic acid group is present in the third position in the pyridine ring. Pyridinyl radicals of NA generated by the reaction of hydrated electrons with NA were already characterized by pulse radiolysis technique earlier.[3,4,21] There were also detailed studies carried out on the transient formed during the reaction of H atom and $^{\bullet}OH$ radicals with nicotinic acid.[4,24] It is also reported that $(CH_3)_2C^{\bullet}OH$ radicals transfer electron to NA at pH 1 where NA is present in the protonated form.[4,24] We have carried out reactions of $(CH_3)_2C^{\bullet}OH$, $CH_3C^{\bullet}HOH$, and $^{\bullet}CH_2OH$ radicals with NA at appropriate pHs to investigate the formation of the adduct species. These α-hydroxyalkyl radicals do not react with anionic form of NA at pH 6.8 with any measurable rate as no buildup of transient absorption in the 300−600 nm region was seen. At pH 3.3, where nicotinic acid is present mainly in the neutral form, reaction of reducing radicals was found to follow a definite pattern. $CO_2^{\bullet -}$ radicals were found to react with NA giving pyridinyl radicals having absorption peak at 410 nm as shown in the insert of Figure 5, whereas reactions of $(CH_3)_2C^{\bullet}OH$, $CH_3C^{\bullet}HOH$, and $^{\bullet}CH_2OH$ radicals at pH 3.3 initially gave adduct species having an absorption peak at ∼350 nm. These adduct species were found to undergo unimolecular decay with varying rates giving the pyridinyl radicals of NA. Spectrum of

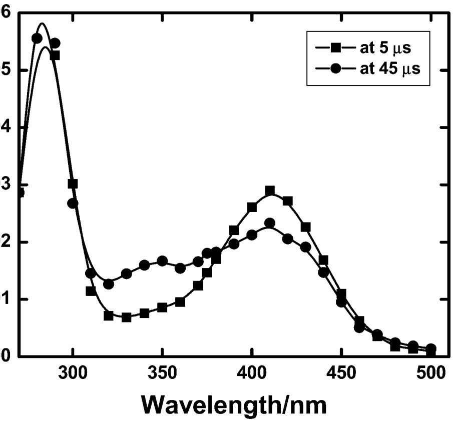


Figure 7. Time-resolved spectra of the transient species formed in the reaction of $(CH_3)_2C^{\bullet}OH$ radicals with NA (1×10^{-3} mol dm^{-3}) at pH 1.

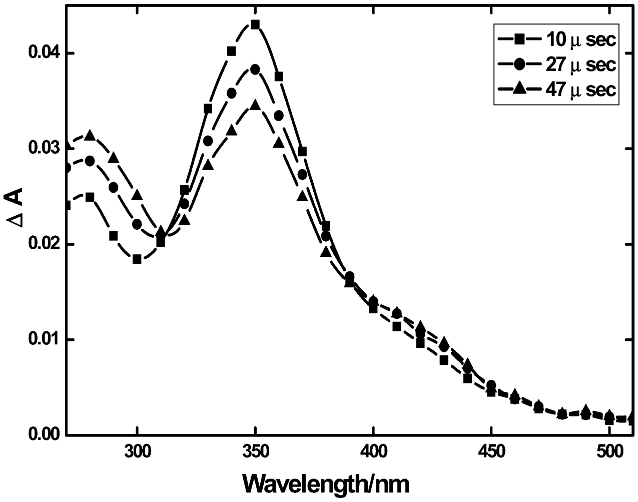


Figure 8. Time-resolved absorption spectra of the species formed in the reaction of $CH_3C^{\bullet}HOH$ radicals with NA (1×10^{-3} mol dm^{-3}) at pH 1.

TABLE 2: Kinetic and Spectral Parameters of the Transients Species Formed by the Reaction of Various Reducings Radicals with Nicotinic Acid at pH 3.3

	λ_{max} (nm)					
reducing radicals	adduct	pyridinyl radical	k_f (dm^3 mol^{-1} s^{-1})	ϵ (dm^3 mol^{-1} cm^{-1})	decay rates of the adduct (s^{-1})	decay of the pyridinyl radicals, 2k (dm^3 mol^{-1}s^{-1})
$(CH_3)_2C^{\cdot}OH$	350	280, 410	4.7×10^8		2.5×10^5	1.6×10^9
$CH_3{}^{\cdot}CHOH$	350	410	2.0×10^8	3900 (350 nm)	7.0×10^3	
$^{\cdot}CH_2OH$	350	410	3.3×10^7	5100 (350 nm)	2.6×10^3	
$CO_2^{\cdot -}$		280, 410	3.8×10^8	3200		1.6×10^9

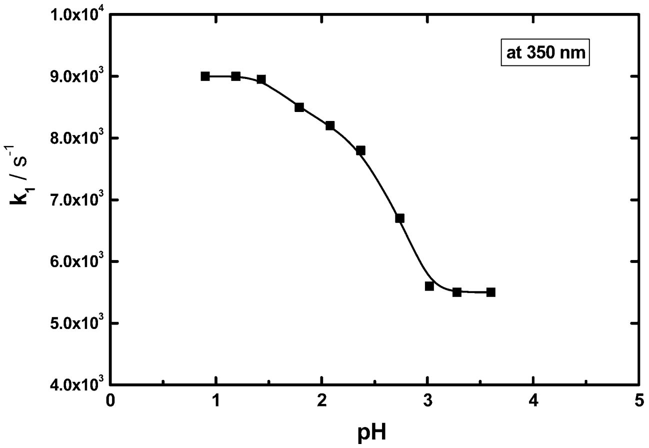


Figure 9. Plot of rate constants for the decay of adduct formed in the reaction of $CH_3C^{\bullet}HOH$ radicals with NA (1×10^{-3} mol dm^{-3}) versus the pH of the solution.

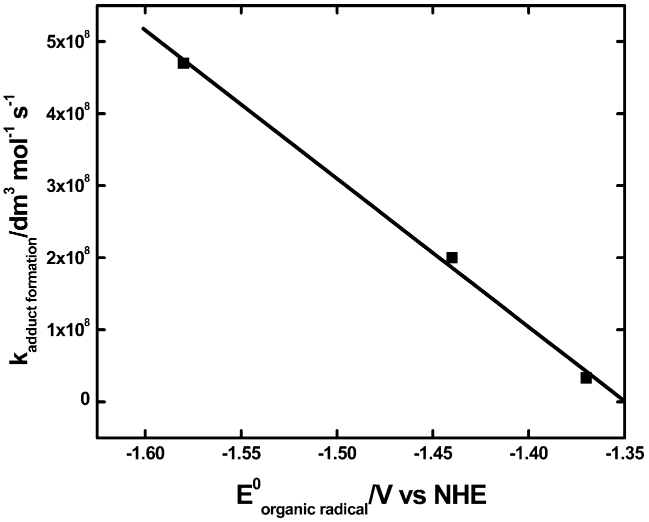


Figure 10. Plot of rate constant for the reaction of α-hydroxyalkyl radicals with NA (adduct formation) versus the reduction potential of corresponding α-hydroxyalkyl radical at pH 3.3.

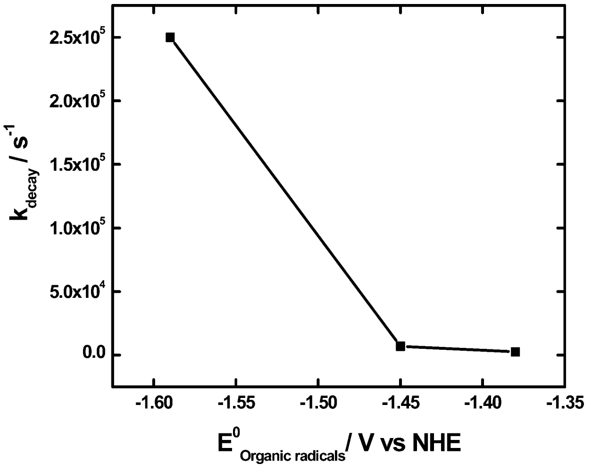


Figure 11. Plot of rate of decay of adducts formed with NA versus the reduction potential of corresponding α-hydroxyalkyl radical at pH 3.3.

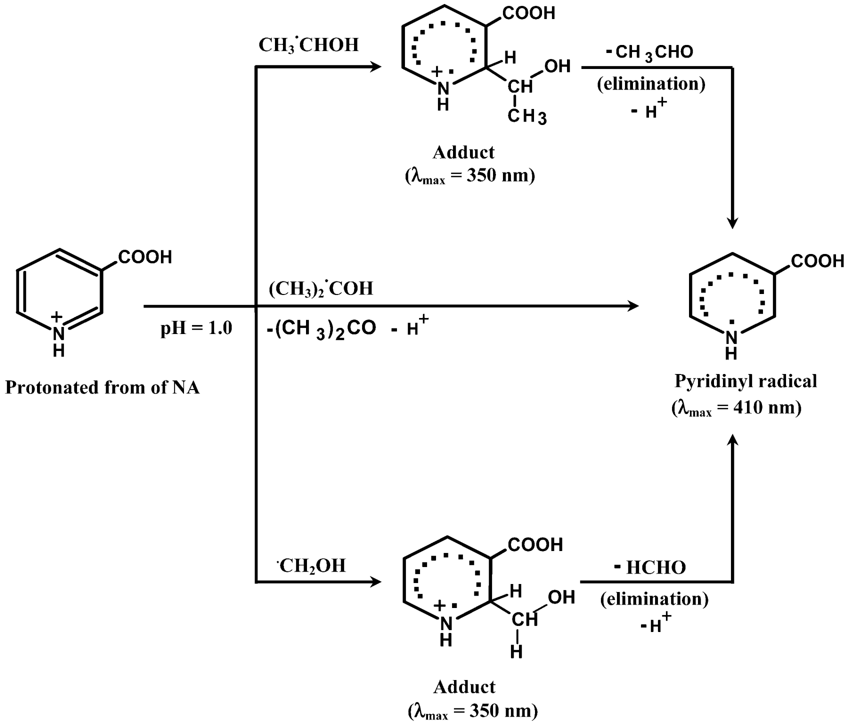
the transient species formed in the reaction of $(CH_3)_2C^{\bullet}OH$ radicals with NA at pH 3.3 is given in Figure 5. Adduct formed in the reaction of $(CH_3)_2C^{\bullet}OH$ radicals ($k = 4.7 \times 10^8$ dm^3 mol^{-1} s^{-1}) decays by a rate constant of 2.5×10^5 s^{-1}. In the reaction of $(CH_3)_2C^{\bullet}OH$ radicals with NA at pH 3.3, part of the absorption at 410 nm is formed within 2 μs time, which indicated that possibly there is electron-transfer reaction by outer-sphere electron-transfer mechanism taking place concurrently to some extent. Solar et al.[4] have observed both the pyridinyl radical and the ring adduct in the H-atom reaction with protonated NA at pH 1. This was explained in terms of a direct attack of the H atom on the protonated nitrogen as well as instantaneous conversion of some of the ring adducts into the pyridinyl radicals. Considering the rate constant for the reaction of $(CH_3)_2C^{\bullet}OH$ radicals ($k = 4.7 \times 10^8$ dm^3 mol^{-1} s^{-1}) and rate of decay of the adduct ($k = 2.5 \times 10^5$ s^{-1}), the absorption buildup in 2 μs cannot be assigned to direct electron transfer. Additionally, adduct species also will have contribution at 410 nm in the observed absorption signal. Reaction rate of NA with $CH_3C^{\bullet}HOH$ radicals ($k = 2 \times 10^8$ dm^3 mol^{-1} s^{-1}) and $^{\bullet}CH_2OH$ radicals ($k = 3.3 \times 10^7$ dm^3 mol^{-1} s^{-1}) at pH 3.3 were slower compared with that of $(CH_3)_2C^{\bullet}OH$ radicals. The radical adduct species formed in these reactions were also found to decay slowly compared with the decay of the adduct formed in the case of the $(CH_3)_2C^{\bullet}OH$ radicals reaction at the same pH. Time-resolved spectra of the species formed in the reaction of $^{\bullet}CH_2OH$ radicals with NA at pH 3.3 are given in Figure 6. Kinetic as well as spectral parameters for these reactions at pH 3.3 are given in Table 2.

At pH 1, where NA is mainly present in the protonated form, reaction of $(CH_3)_2C^{\bullet}OH$ radicals directly give pyridinyl radicals without any adduct formation. This was also reported earlier.[4] For the sake of comparison, absorption spectrum of the pyridinyl radicals formed in the reaction of $(CH_3)_2C^{\bullet}OH$ radicals with NA at pH 1 is given in Figure 7. These pyridinyl radicals decay by second-order kinetics giving a product having absorption maximum at around 350 nm. At the same time, reactions of $CH_3C^{\bullet}HOH$ and $^{\bullet}CH_2OH$ radicals with NA at pH 1 were found to give the adduct species. Time-resolved absorption spectra of the transient species formed in the reaction of $CH_3C^{\bullet}HOH$ radicals with NA at pH 1 are given in Figure 8. Rate constants for the reaction of $CH_3C^{\bullet}HOH$ and $^{\bullet}CH_2OH$ radicals with NA at pH 1, as determined by following the buildup of transient absorption at 350 nm, were found to be 5.0×10^8 dm^3 mol^{-1} s^{-1} and 2.6×10^8 dm^3 mol^{-1} s^{-1}, respectively (Table 3). These rate constants are appreciably higher than those observed at pH 3.3 even though reduction potentials of these α-hydroxyalkyl radicals are less negative at pH 1 than at pH 3.3. Unimolecular decay of the adduct species giving the pyridinyl radicals was also found to be faster at pH 1 compared with that at pH 3.3.

TABLE 3: Kinetic and Spectral Parameters of the Transients Species Formed by the Reaction of α-Hydroxyalkyl Radicals with Nicotinic Acid at pH 1.0

	λ_{max} (nm)					
reducing radicals	adduct	pyridinyl radical	k_f (dm^3 mol^{-1} s^{-1})	ϵ (dm^3 mol^{-1} cm^{-1})	decay rates of the adduct (s^{-1})	decay of the pyridinyl radicals, 2k (dm^3 mol^{-1}s^{-1})
$(CH_3)_2C^{\cdot}OH$		280, 410	6.3×10^8	3600 (410 nm)		1.4×10^9
$CH_3{\cdot}CHOH$	350	280, 410−420	5.0×10^8	5600 (350 nm)	1.1×10^4	
$^{\cdot}CH_2OH$	350	280, 410−420	2.6×10^8	4200 (350 nm)	4.2×10^3	

SCHEME 4: Reaction of Various α-hydroxyalkyl Radicals with NA at pH 1



We determined the decay constant of the adduct formed in the reaction of $CH_3C^{\bullet}HOH$ radicals with NA in the pH range 3.6−0.7. The plot of rate constants for the decay of adducts versus pH is given in Figure 9. It is clearly seen that in the pH range 3.6−3 there is no change in decay rate, and below pH 1.6, it is almost constant. The inflection point at ∼2.2 suggests that the decay of the adduct is not catalyzed by external protons in the solution but is the result of protonation of the parent molecule which has a $pK_a \sim 2.07$. Adduct formed in the reaction of $CH_3C^{\bullet}HOH$ radicals with NA at pH 1 decayed by a rate constant of 1.1×10^4 s^{-1}, and those formed in the reaction of $^{\bullet}CH_2OH$ radicals decayed by a rate constant of 4.2×10^3 s^{-1}. Kinetic and spectral parameters of α-hydroxyalkyl radical with NA at pH 1 are given in Table 3. Mechanisms for the reactions of $(CH_3)_2C^{\bullet}OH$, $CH_3C^{\bullet}HOH$, and $^{\bullet}CH_2OH$ radicals with NA at pH 1 are shown in Scheme 4.

It is most likely that the key factor controlling these reactions is the reduction potential of the α-hydroxyalkyl radical and/or the steric effect. Reduction potential of the α-hydroxyalkyl radical determines whether the transient species formed is a radical anion species or the adduct species. At pH 1, as can be seen, in the reaction of $(CH_3)_2C^{\bullet}OH$ radicals with NA, one gets directly pyridinyl radicals, and there was no evidence of an adduct species. At pH 3.3, we have plotted the observed rate constant for the formation of adduct of α-hydroxyalkyl radical with NA as a function of reduction potential of α-hydroxyalkyl radicals at this pH which is given in Figure 10. Reduction potentials of the above α-hydroxyalkyl radicals at this pH 3.3 are computed using E^0 values reported by Schwarz and Dodson.[22] As per the Marcus equation, the rate constant for electron transfer decreases as the difference of reduction potential of electron donor and acceptor decreases. It is interesting to note here that the rate constants for the adduct formation decrease linearly as the reduction potential of α-hydroxyalkyl radical becomes more positive. It has been pointed out earlier that the adducts formed decay by unimolecular rates. Rate constants for the decay of adducts are higher for the adducts formed with the α-hydroxyalkyl radical with more negative reduction potential. Decay rates of these adducts were plotted against the reduction potential of α-hydroxyalkyl radicals and are given in Figure 11. It is seen that the adduct formed with $(CH_3)_2C^{\bullet}OH$ radicals decays much faster compared with those formed in the reaction with $CH_3C^{\bullet}HOH$ and $^{\bullet}CH_2OH$ radicals, thus, showing that the adduct species formed with a lower difference in reduction potential are more stable compared with those where the difference is larger.

4. Conclusions

It is observed for the first time that the reaction of reducing α-hydroxyalkyl radicals with pyridine carboxylic acids such as 3,5-pyridine dicarboxylic acid and nicotinic acid at appropriate pHs takes place by an inner-sphere electron-transfer mechanism initially giving the radical adduct species. These adduct species subsequently undergo an elimination reaction giving the pyridinyl radicals. It is also observed that the rate constant for the adduct formation reaction as well as the rate of elimination reaction depends strongly on the reduction potential of the reducing α-hydroxyalkyl radical. The rate constant for adduct formation in the reaction of α-hydroxyalkyl radicals with NA at pH 3.3 is found to vary linearly as a function of the reduction potential of α-hydroxyalkyl radicals.

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References and Notes

(1) Carlson, B. W.; Miller, L. L. *J. Am. Chem. Soc.* **1983**, *105*, 7453.

(2) Grodkowski, J.; Neta, P.; Carlson, B. W.; Miller, L. *J. Phys. Chem.* **1983**, *87*, 3135.

(3) Neta, P.; Patterson, L. K. *J. Phys. Chem.* **1974**, *78*, 2211.

(4) Solar, S.; Solar, W.; Getoff, N.; Holcman, J.; Sehested, K. *Radiat. Phys. Chem.* **1988**, *32*, 585.

(5) Rosales, C.; Brown, E. J. *J. Biol. Chem.* **1992**, *267*, 1443.

(6) Hunt, P.; Worrall, D. R.; Wilkinson, F.; Batchelor, S. N. *Photochem. Photobiol. Sci.* **2003**, *2*, 518.

(7) Yadav, P.; Rao, B. S. M.; Batchelor, S. N.; O'Neill, P. *J. Phys. Chem.* **2005**, *109*, 2039.

(8) Swallow, A. J. In *The study of fast processes and transient species by electron pulse radiolysis*; Baxendale, J. H., Busi, F., Eds.; D. Riedel Publishing Co.: Dordrecht, Holland, 1982; pp 289−315.

(9) Batchelor, S. N.; Fischer, H. *J. Phys. Chem.* **1996**, *100*, 9794.

(10) Naik, D. B.; Moorthy, P. N. *J. Chem. Soc., Perkin Trans. 2* **1990**, 705.

(11) Jagannadham, V.; Steenken, S. *J. Am. Chem. Soc.* **1984**, *106*, 6542.

(12) Steenken, S. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 113.

(13) Naik, D. B.; Mukherjee, T. *Radiat. Phys. Chem.* **2006**, *75*, 42.

(14) Naik, D. B.; Dey, G. R.; Kishore, K.; Moorthy, P. N. *J. Phys. Chem. A* **1998**, *102*, 684.

(15) Guha, S. N.; Moorthy, P. N.; Kishore, K.; Naik, D. B.; Rao, K. N. *Proc. Indian Acad. Sci. (Chem. Sci.)* **1987**, *99*, 361.

(16) Mukherjee, T. In *Atomic, Molecular and Cluster Physics*; S.A. Ahmad(ed.) Narosa: New Delhi **1997**, p. 299.

(17) Fielden, E. M. In *The study of fast processes and transient species by electron pulse radiolysis*; Baxendale, J. H., Busi, F., Eds.; D. Riedel Publishing Co.: Dordrecht, Holland, 1982; pp 49−62.

(18) Schuler, R. H.; Patterson, L. K.; Janata, E. *J. Phys. Chem.* **1980**, *84*, 2088.

(19) Von Sonntag, C. *The Chemical Basis of Radiation Biology*; Taylor and Francis: London, 1987; pp 37−38.

(20) Asmus, K. D.; Mockel, H.; Henglein, A. *J. Phys. Chem.* **1973**, *77*, 1218.

(21) Simic, M.; Ebert, M. *Int. J. Radiat. Phys. Chem.* **1971**, *3*, 259.

(22) Schwarz, H. A.; Dodson, R. W. *J. Phys. Chem.* **1989**, *93*, 409.

(23) Buxton, G. V.; Sellers, R. M. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 55.

(24) Solar, S.; Getoff, N.; Sehested, K.; Holcman, J. *Radiat. Phys. Chem.* **1991**, *38*, 323.