

## Kinetics and spectral properties of electron and $\cdot\text{OH}$ adducts of dimethylpyridines: a pulse radiolysis study

R. GROVER<sup>1</sup>, M. MUDALIAR<sup>1</sup>, B. S. M. RAO<sup>1,\*</sup>, H. MOHAN<sup>2</sup>  
and J. P. MITTAL<sup>2,3</sup>

<sup>1</sup> Department of Chemistry, University of Pune, Pune 411 007, India

<sup>2</sup> Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

<sup>3</sup> Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur Campus,  
Bangalore 560 064, India

**Abstract**—The reactions of  $e_{\text{aq}}^-$ ,  $\cdot\text{OH}$ ,  $\text{O}^{\cdot-}$  and  $\text{SO}_4^{\cdot-}$  with 2,4-, 2,6- and 3,5-dimethylpyridines have been investigated in aqueous solution by pulse radiolysis with optical detection. Both  $e_{\text{aq}}^-$  and  $\cdot\text{OH}$  radicals have high reactivity toward these compounds with  $k = (4-8) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The rates of  $\text{O}^{\cdot-}$  and  $\text{SO}_4^{\cdot-}$  reactions ( $(1-3) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) were lower compared to the rate observed with the  $\cdot\text{OH}$  radical. The transient absorption spectra obtained in the reaction of  $e_{\text{aq}}^-$  with three isomers exhibited a weak broad band around 340–410 nm. The absorption maxima of the intermediates formed in the  $\cdot\text{OH}$  and  $\text{SO}_4^{\cdot-}$  reactions were centred around 320–330 nm ( $\epsilon = 2450-3500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) with an additional broad peak in the range 460–520 nm which are attributed to the corresponding  $\cdot\text{OH}$  adducts. The spectra in the  $\text{O}^{\cdot-}$  reaction have absorption maxima between 300 and 320 nm and it reacts both by addition and H-abstraction from the  $\text{CH}_3$  group. A reaction mechanism consistent with the observed results is proposed.

### INTRODUCTION

Studies on the reaction of the primary radicals of water radiolysis,  $\cdot\text{OH}$  and  $e_{\text{aq}}^-$ , and secondary radicals derived from them (e.g.  $\text{SO}_4^{\cdot-}$ ) with heterocyclic compounds have been of current interest due to their relevance to the free radical chemistry of the nucleic acid bases [1–5]. The reactions have been studied by both ESR [1–3] and pulse radiolysis methods. Pyridine is a six membered aromatic heterocyclic compound characterised by a built-in electron withdrawing group and is as highly

\*To whom correspondence should be addressed. E-mail: bsmr@chem.unipune.ernetin

stabilised as benzene, but unlike benzene, the orbitals will be deformed by being attracted towards the nitrogen atom because the latter is more electronegative than carbon. This is reflected in the dipole of pyridine which has the negative end on N and the positive end on the nucleus. Pyridine is therefore referred to as a deficient heterocycle and by analogy it is similar to benzene that carries an electron-withdrawing substituent.

The hydrated electron is found to be less reactive towards aromatic compounds such as benzene; but when an electron-withdrawing group is present on the aromatic ring, the reactivity increases considerably. For example, the reactivity of  $e_{aq}^-$  with benzene is very low, the rate constant is  $1.7 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , whereas it is  $1.9 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  with cyanobenzene [6]. In contrast, when an electron donating group is present on the ring, the rate constant decreases, e.g.  $e_{aq}^-$  reacts with toluene with a rate constant of  $1.4 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  [7]. Earlier studies [3, 8] have shown that pyridine has a very high reactivity ( $k = 1.0 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) towards  $e_{aq}^-$ . The rate constants for the reaction of the  $\cdot\text{OH}$  radical with benzene and pyridine derivatives, by the method of competing acceptors, have already been reported [9]. Due to the lower reactivity of the pyridine nucleus in comparison with the benzene nucleus toward the electrophilic  $\cdot\text{OH}$  radical, the rate constants for the benzene derivatives were found to be a factor of 2 higher than those for pyridine derivatives [9]. However, as in the case of benzene derivatives, the rates of the reactions of hydroxyl radicals with substituted pyridines were accelerated by electron donor and retarded by electron acceptor substituents [9]. Electron-donating substituents raise the electron density on the nitrogen atom and correspondingly enhance the rate at which it is attacked by the hydroxyl radicals.

Thus, the methyl derivatives of pyridine form an interesting class of compounds. Solar *et al.* [10] have earlier reported the results from the study of radiation chemical reactions of water radicals with 2,4-, 2,6- and 3,5-dimethylpyridines in acidic (pH 2–4.5) and basic (pH 10) solutions. Their results have shown that the transient absorption spectra are more or less similar in both media. We have now extended this study to include the reactions of  $\text{O}^{\cdot-}$  in basic solutions as well as  $e_{aq}^-$ ,  $\cdot\text{OH}$  and  $\text{SO}_4^{\cdot-}$  with 2,4-, 2,6- and 3,5-dimethylpyridines in neutral solution. A detailed investigation of the kinetic and spectral properties of their adducts has been made to elucidate the rate, probable site of attack and reaction pathways, in both neutral and basic media using pulse radiolysis.

## EXPERIMENTAL

All chemicals used were of high purity (98%). Commercially available 2,4-, 2,6- and 3,5-dimethylpyridines (Sisco Research Laboratories), *t*-butyl alcohol and 2-propanol (S.D. Fine Chemicals) were used without further purification.  $\text{N}_2$ , Ar and  $\text{N}_2\text{O}$  gases of Iolar grade (Indian Oxygen) were used.

All solutions were prepared using deionised water from a Millipore Milli-Q system. In the investigation of the reactions induced by oxidising or reducing

radicals with dimethylpyridines, the appropriate concentration of the solutes was chosen in order to ensure that the reaction of interest proceeded. All experiments were done at ambient temperature (25°C).

Pulse radiolysis studies of the  $e_{\text{aq}}^-$  reactions with isomers of dimethylpyridines were conducted in  $\text{N}_2$  saturated aqueous solutions containing either *t*-butanol or 2-propanol (0.2 M) as a scavenger for the  $\cdot\text{OH}$  radicals and  $\cdot\text{H}$  atoms. The 2-propanol radicals were found to be unreactive on the time scale employed in the pulse radiolysis. 2-Propanol was used to ensure complete scavenging of  $\cdot\text{H}$  and  $\cdot\text{OH}$  radicals and the radicals generated from 2-propanol were found to be non-reactive with the solute. The reaction of the  $\cdot\text{OH}$  radical with dimethylpyridines was carried out at neutral pH in  $\text{N}_2\text{O}$  saturated aqueous solutions. Reactions of  $\text{O}^{\cdot-}$  were studied using  $\text{N}_2\text{O}$  saturated aqueous solutions of dimethylpyridines at pH 13, where more than 90% of the  $\cdot\text{OH}$  radicals are quantitatively converted into  $\text{O}^{\cdot-}$  ( $\cdot\text{OH} + \text{OH}^- \rightarrow \text{O}^{\cdot-} + \text{H}_2\text{O}$ ) with a  $\text{p}K_{\text{a}}$  of 11.9.

The  $\text{SO}_4^{\cdot-}$  radical ion was produced from the reaction of  $e_{\text{aq}}^-$  and  $\text{H}\cdot$  atom with  $\text{S}_2\text{O}_8^{2-}$  ( $1.5 \times 10^2$  M) in  $\text{N}_2$ - or Ar-saturated solutions of the solute containing 0.2 M *t*-butyl alcohol. A high concentration of *t*-butyl alcohol ensures complete scavenging of the  $\cdot\text{OH}$  radicals.

High-energy electron pulses (7 MeV, 50 ns) generated from a linear electron accelerator were used for the pulse radiolysis experiments. The details of the pulse radiolysis set up have been described elsewhere [11]. The dose per pulse was monitored with an aerated aqueous solution KSCN (0.01 M) with  $G_{\varepsilon 500} = 21\,520 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  per 100 eV of absorbed energy, where  $\varepsilon$  is the molar absorptivity of  $(\text{SCN})_2^{\cdot-}$  at 500 nm. The dose was usually kept in the range 13–16 Gy per pulse.

## RESULTS AND DISCUSSION

### *Reactions of $e_{\text{aq}}^-$ with dimethylpyridines*

*Evaluation of rate constants.* The rate for the reaction of  $e_{\text{aq}}^-$  with 2,4-, 2,6- and 3,5-dimethylpyridines were determined by following the decay of hydrated electron absorption at 700 nm for various concentrations of the solute. In the presence of the solute, the life-time of  $e_{\text{aq}}^-$  decreased considerably due to which the decay of the hydrated electron follows the pseudo-first-order kinetics. The rate of decay of  $e_{\text{aq}}^-$  absorption at 700 nm was found to be linearly dependent on the concentration of the solute. The concentration of the solute was varied in the range  $10^{-4}$ – $10^{-3} \text{ mol dm}^{-3}$ . The second-order rate constants ( $k = (3.3\text{--}4.5) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) given in Table 1 indicate that the rates of the reactions of  $e_{\text{aq}}^-$  with 2,4-, 2,6- and 3,5-dimethylpyridines are close to diffusion-controlled and they are in accord with the rate constants reported for carboxy, carbamido and pyridyl derivatives of pyridine [3, 12], as well as with the other pyridine derivatives such as 2,4-bypyridine and pyridinol isomers.

The optical absorption spectrum of the aqueous solution of 2,6-dimethylpyridines showed an absorption band at  $\lambda_{\max} = 265$  nm with practically no absorption at wavelengths  $> 290$  nm. The optical absorption spectrum remained the same in the pH range of 1 to 13. The measured optical absorption spectra of other pyridine derivatives are similar to 2,6-dimethylpyridines. The transient absorption spectra were therefore measured only at wavelengths above 300 nm due to strong absorption of the solute molecules in the lower wavelength region.

*Absorption spectra of the transients.* The transient absorption monitored in the wave length region 300–600 nm showed a weak broad band around 340–410 nm for 2,4 dimethylpyridines. The transient absorbance at 370 nm remained independent of solute concentration ( $2 \times 10^{-4}$ – $1 \times 10^{-3}$  mol dm<sup>-3</sup>). Under these experimental conditions, the concentration of  $e_{\text{aq}}^-$ , the values of  $\lambda_{\max}$  and the molar absorptivities ( $\varepsilon$ ) obtained in the reaction of  $e_{\text{aq}}^-$  with isomers of dimethylpyridines are given in Table 1. The transient absorption spectrum obtained on reaction of  $e_{\text{aq}}^-$  with other solutes (Table 1) is similar to that found for 2,4-dimethylpyridine. The time-resolved studies did not show the formation of any new band with the decay of the transient absorption. Due to very small absorptions the decay kinetics could not be studied accurately.

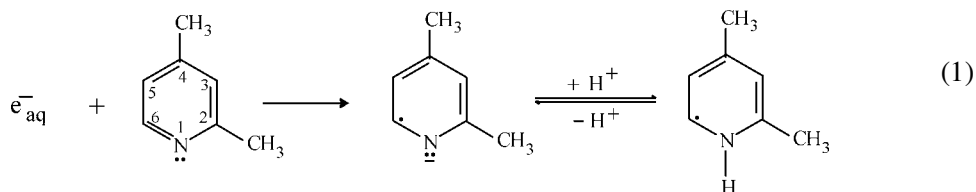
In the case of dimethylpyridines, the  $e_{\text{aq}}^-$  is expected to attack the electrophilic heteroatom. The radical anions thus, formed are highly proton affinic in nature, and it can be reasonably assumed that they are rapidly protonated by water to yield the natural heteroatom-protonated adducts. Hence, the spectra recorded at 2  $\mu$ s after the pulse are attributed to the natural heteroatom-protonated adducts. Since the electron density in the pyridine molecule is about 60% higher around the nitrogen atom [13], a similar distribution of the negative charge is expected in the

**Table 1.**

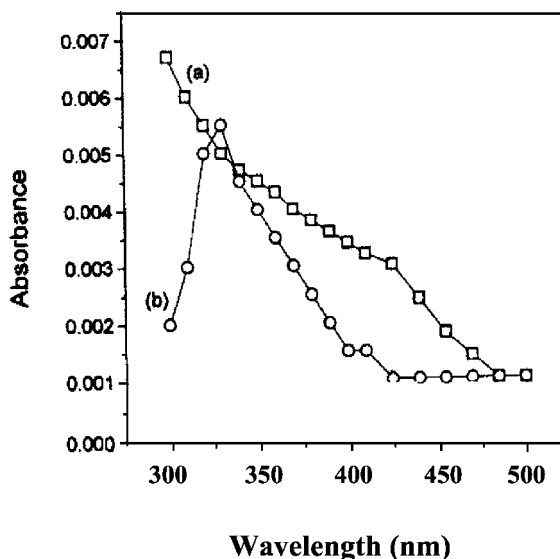
Second-order rate constants ( $k$ ,  $10^9$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>) of formation and decay, absorption maxima ( $\lambda_{\max}$ , nm) and molar absorptivities ( $\varepsilon$ , dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) obtained for the reaction of  $e_{\text{aq}}^-$ ,  $\cdot\text{OH}$ ,  $\text{O}\cdot^-$  and  $\text{SO}_4^{\cdot-}$  with isomers of dimethylpyridine

Reacting species	Parameter	2,4-Dimethylpyridine	2,6-Dimethylpyridine	3,5-Dimethylpyridine
$e_{\text{aq}}^-$	$k$	4.5	3.3	3.7
	$\lambda_{\max}$	370	370	375
	$\varepsilon$	770	850	1000
$\cdot\text{OH}$	$k$	7.8	8.2	5.6
	$\lambda_{\max}$	330	330	320
	$\varepsilon$	3250	2490	3450
$\text{O}\cdot^-$	$k$	1.3	2.0	1.4
	$k$	1.9	1.7	2.0
	$\lambda_{\max}$	320	320	300
$\text{SO}_4^{\cdot-}$	$k$	1.7	2.0	3.1
	$\lambda_{\max}$	330	330	330

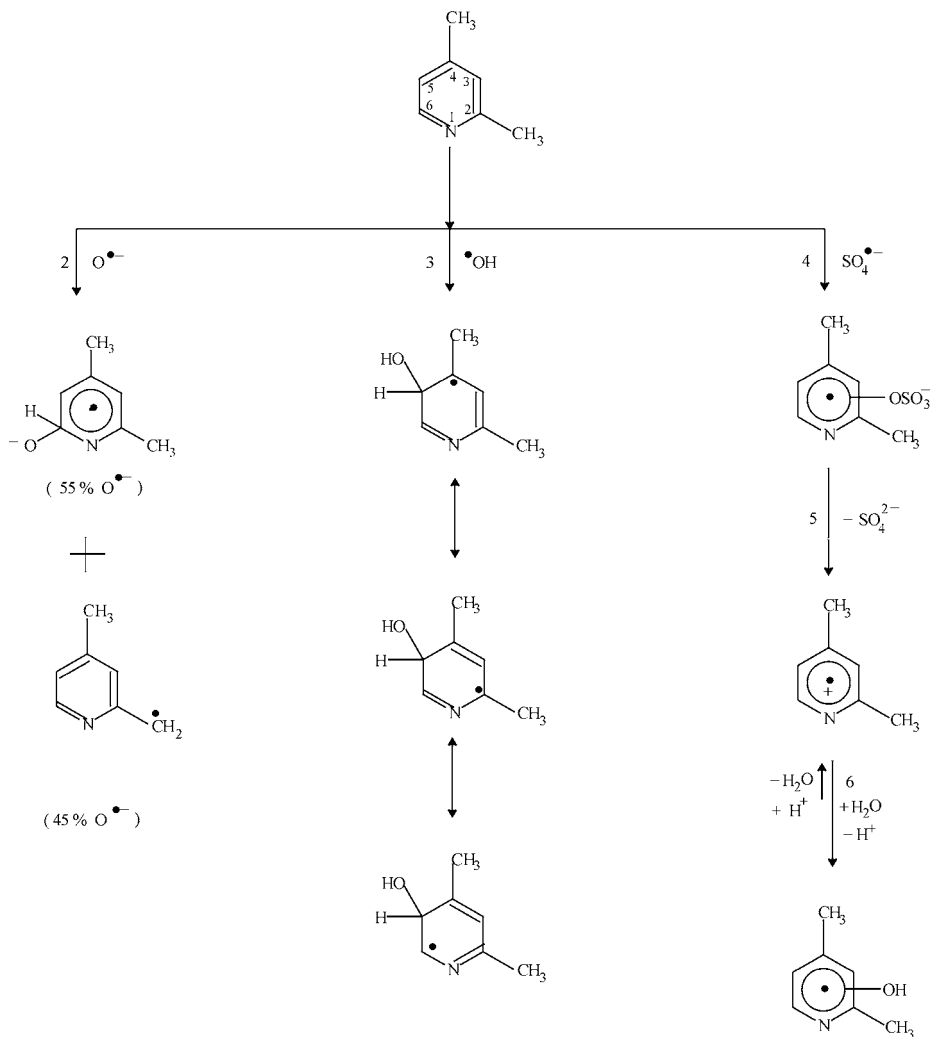
pyridine electron adducts, due to which the electrostatic forces in the adduct favour the protonation to occur at the nitrogen position of the pyridine ring. Therefore, the transient optical absorption has been ascribed to  $\text{PyNH}^-$ . Similar conclusions have been drawn about 2,2'-dipyridyl, where  $e_{\text{aq}}^-$  is known to add to the pyridine ring forming the heteroatom protonated adducts, leading to transients with the same structure. As an example, the most likely reaction pathway for the  $e_{\text{aq}}^-$  reaction with 2,4-dimethylpyridine is given below:



This reaction suggests that a H-adduct would be obtained at neutral/acidic solutions and electron adduct in basic solutions. Figure 1a shows the transient optical absorption spectrum obtained in the reaction of H-atoms with 2,6-dimethylpyridine at pH 1, which exhibits a weak broad band in the 340–410 nm range. It is similar to the transient absorption obtained on reaction of  $e_{\text{aq}}^-$  with 2,6-dimethylpyridine at neutral pH (not shown). The transient optical absorption obtained in the reaction of  $e_{\text{aq}}^-$  at pH 12 exhibits an absorption band with  $\lambda_{\text{max}} = 330$  nm (Fig. 1b) which is different from that of the H-adduct (radical 2). The former is attributed to the electron adduct (radical 1) and thus supports the reaction depicted in Scheme 1.



**Figure 1.** Transient absorption spectra obtained on pulse radiolysis of  $\text{N}_2$  saturated aqueous solution of 2,6-dimethylpyridine containing *t*-butyl alcohol. (a) pH = 1 and (b) pH = 12. Dose = 16 Gy.

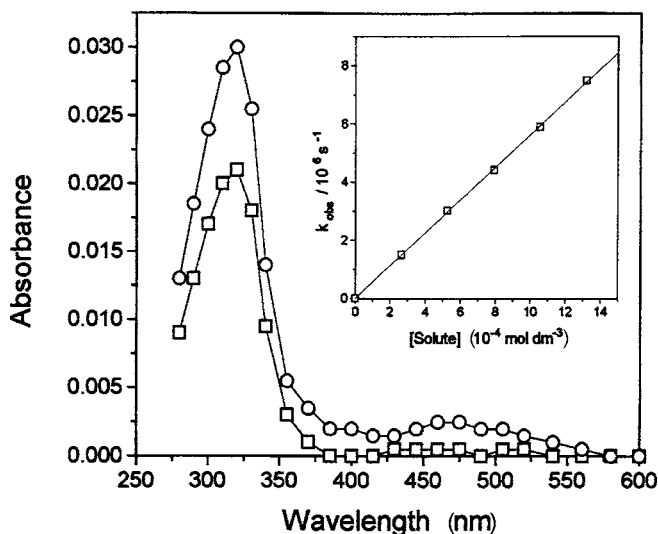


**Scheme 1.** Mechanism for radiation chemical reactions of  $\bullet\text{OH}$ ,  $\text{O}^{\bullet-}$  and  $\text{SO}_4^{\bullet-}$  with 2,4-dimethylpyridine.

Due to the small variation in the absorbance in this pH region, the  $\text{p}K_{\text{a}}$  value for the protonation reaction (reaction 1) could not be determined.

### Reactions of $\bullet\text{OH}$ with dimethyl pyridines

**Evaluation of rate constants.** The rate constants for the reaction of  $\bullet\text{OH}$  radicals with the solutes were determined by monitoring the growth of the transient band at the absorption maxima (320–330 nm) in the solute concentration range  $(0.2\text{--}1.3) \times 10^{-3}$  M. A good least-squares fit of the plots of  $k_{\text{obs}}$  versus [solute] for 2,4-, 2,6- and 3,5-dimethylpyridines was obtained. The inset of Fig. 2 shows



**Figure 2.** Transient optical absorption spectra obtained on pulse radiolysis of  $\text{N}_2\text{O}$  saturated neutral aqueous solution of 3,5-dimethylpyridine ( $1 \times 10^{-3} \text{ mol dm}^{-3}$ ) at 10 (○) and 80  $\mu\text{s}$  (□) after the pulse. Inset shows variation of  $k_{\text{obs}}$  as a function of solute concentration.

this plot for 3,5-dimethylpyridine. The bimolecular rate constants are given in Table 1. The rate constants ( $(5.6\text{--}8.2) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) are higher than those observed in the reaction of  $\text{e}_{\text{aq}}^-$  (Table 1). Electron-donating substituents raise the electron density on the nitrogen atom and correspondingly enhance the rate at which it is attacked by the hydroxyl radicals. This accounts for the lower reactivity of pyridine as compared to that of dimethylpyridines. The rate constant values differ considerably from the values determined by competition kinetics method ( $k_{2,4\text{DMP}} = 2.6 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $k_{2,6\text{DMP}} = 2.75 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) by Shevchuk *et al.* [9]. Since our values are based on the direct monitoring of the formation of the OH-adducts, it is likely to be more reliable than the value obtained by competition kinetics. The decay of transient absorption showed second order kinetics and the bimolecular rate constants are given in Table 1.

*Absorption spectra of the transients.* Optical absorption spectra of the intermediate transients formed in the reaction of  $\cdot\text{OH}$  radical with 2,4-, 2,6- and 3,5-dimethylpyridines exhibited maxima centred around 320–330 nm with an additional broad weak peak in the wavelength range 460–520 nm. A typical spectrum obtained with 3,5-dimethylpyridine as an example is shown in Fig. 2. A decrease in the intensity of absorption with time was observed for all the systems. In the case of pyridine [2], the OH-adduct showed an absorption maxima at 320 nm and by analogy, the transients absorbing at 320–330 nm would be consistent with the formation of the OH-adducts. The values of  $\lambda_{\text{max}}$  and molar absorptivities are presented in Table 1. The molar absorptivity values for the transients were determined

assuming a radiation chemical yield of  $5.6 \times 10^{-7} \text{ molJ}^{-1}$  for  $\text{G}(\cdot\text{OH})$  [14] and assuming that all the  $\cdot\text{OH}$  radicals have reacted with the dimethylpyridines

In its reaction with the substituted pyridines, the position of  $\cdot\text{OH}$  radical attack is generally directed by the substituents and their positions on the pyridine ring. From earlier studies [2, 3, 5, 9], it has been concluded that the  $\cdot\text{OH}$  radical adds to the heterocyclic ring preferentially at the least electron-deficient position of the pyridine ring. Thus, the positions of addition of the electrophilic  $\cdot\text{OH}$  radical depends on the electron density distribution at different sites of the compounds. Pyridine has four possible reaction sites, nitrogen and *ortho*-, *meta*- and *para*-carbons. Of the 4 positions, the order of electron density on the atoms is calculated to be in order of  $\text{N} > \textit{meta} \text{ C} > \textit{para} \text{ C} > \textit{ortho} \text{ C}$  [15]. Thus, based on electron density, it is expected that the  $\cdot\text{OH}$  radical adds to N-atom. Attempts were made to find out the actual position of attack by ESR studies and pulse radiolysis studies followed by final product analysis. These indicated [15] that approx. 80% of the  $\cdot\text{OH}$  radical addition takes place at the *meta*-carbon atom. There was no evidence for any addition at the nitrogen atom. This observation suggests that factors other than electron density must be contributing towards the site selectivity. *Ab initio* SCFMO (self-consistent field molecular orbital) calculations on the reactions of  $\cdot\text{OH}$  radical with pyridine and pyridine ions by Anthony *et al.* [16] have shown that the addition at different positions follows the order of  $\textit{meta} \text{ C} > \text{N} \gg \textit{para} \text{ C} > \textit{ortho} \text{ C}$ . The advantageous delocalisation of the odd electron in the *meta*-species appears to play a major role in the order of relative stability. In the case of dimethylpyridines, apart from the above mentioned factors, the presence of the two electron-donating  $\text{CH}_3$  groups on the ring will also influence the site of  $\cdot\text{OH}$  attack

In the reaction of  $\cdot\text{OH}$  radical with 2,4-dimethylpyridine (reaction 3 in Scheme 1), addition of  $\cdot\text{OH}$  radical at position 5 may be preferred over that of position 3 because of partial steric shielding of this position by the adjacent methyl groups, whereas in the case of 2,6-dimethylpyridine, addition at both *meta*-positions is likely. In 3,5-dimethylpyridine, the  $\cdot\text{OH}$  radical attack is expected at the nitrogen atom, since neither of the *meta*-positions 3 or 5 is available. Therefore, as can be seen in Table 1, not much difference is observed in the rate constants of 2,4- and 2,6-dimethylpyridine, whereas 3,5 dimethylpyridine shows a much lower rate constant value in its reaction with  $\cdot\text{OH}$  radical.

### *Reactions of $\text{O}\cdot^-$ with dimethylpyridines*

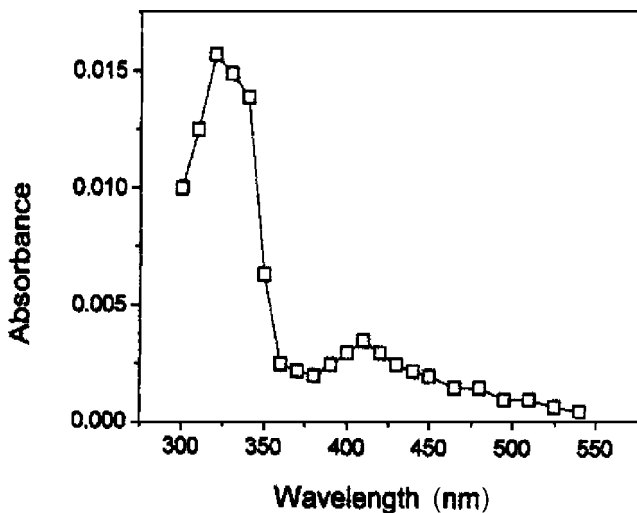
*Evaluation of rate constants.* The rate constants for the reaction of  $\text{O}\cdot^-$  with 2,4-, 2,6- and 3,5-dimethylpyridines were determined by following the build-up of the products transient absorption at the  $\lambda_{\text{max}}$  as a function of solute concentration. The second-order rate constants, obtained from the plots of  $k_{\text{obs}}$  versus solute concentration are given in Table 1.



### Absorption spectra of the transients

The transient absorption spectra obtained with 2,4-, 2,6- and 3,5-dimethylpyridines exhibit  $\lambda_{\text{max}}$  between 300 and 320 nm and a weak absorption band in the 380–440 nm region. Figure 3 shows the typical transient absorption spectrum obtained with 3,5-dimethylpyridine. The nature of the spectra is similar to that obtained in the  $\cdot\text{OH}$  reaction. The spectral properties of the intermediates are given in Table 1. Assuming molar absorptivities of the  $\text{O}\cdot^-$  adducts similar to those of the OH-adducts, the  $G$ -values of the  $\text{O}\cdot^-$  adducts of 2,4-, 2,6- and 3,5-dimethylpyridines are calculated to be 3.1, 4.3 and 4.1, respectively. Accordingly, the extent of H-abstraction from the methyl group is determined to be 45, 23 and 27% for 2,4-, 2,6- and 3,5-dimethylpyridines respectively. If an aromatic molecule carries an aliphatic side chain,  $\cdot\text{OH}$  radicals adds preferentially to the aromatic ring, whereas  $\text{O}\cdot^-$  is known to react with the side group by abstraction of an H atom [17]. The radicals from H-abstraction may absorb at lower wavelengths (270–275 nm). However, due to intense absorption of the parent compounds in this range, the spectra could not be measured below 300 nm.

In the reactions of the nucleophilic  $\text{O}\cdot^-$  with 2,4-dimethylpyridine (reaction 2 in Scheme 1), it is expected to abstract H preferentially from the  $\text{CH}_3$  group present in the ortho position of the pyridine ring because the electron-withdrawing inductive effect of N, due to its electronegative character, diminishes with increasing distance/chain length. In the case of 2,6- and 3,5-dimethylpyridines, H-abstraction from either of the methyl groups is equally possible.  $\text{O}\cdot^-$  is likely to add to the meta position with respect to the methyl groups, whereas with 3,5-dimethylpyridine, it is expected to add to the ortho position of the pyridine ring.



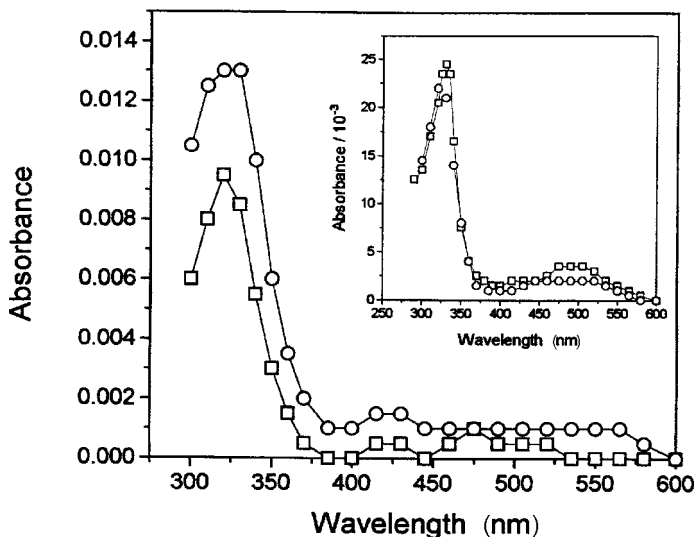
**Figure 3.** Transient optical absorption spectra obtained on pulse radiolysis of  $\text{N}_2\text{O}$ -saturated aqueous solution of 3,5-dimethylpyridine ( $1 \times 10^{-3}$  mol  $\text{dm}^{-3}$ , pH = 13) at 2  $\mu\text{s}$  after the pulse. Dose = 15 Gy.

### Reactions of $\text{SO}_4^{\cdot-}$ with dimethylpyridines

*Evaluation of rate constants.* The  $\text{SO}_4^{\cdot-}$  radical anion is known to be a strong one-electron oxidant ( $E^\circ = 2.5\text{--}3.1$  V versus NHE) [18] and behaves as an electrophile in its reactions. Aromatic compounds are reported [19] to be oxidised by  $\text{SO}_4^{\cdot-}$  radical anion. The high oxidising power of  $\text{SO}_4^{\cdot-}$  was demonstrated by the ESR spectra of radical zwitterions from methoxy benzoic acids [17] and of radical cations [20] from methoxy benzenes. The  $\text{SO}_4^{\cdot-}$  radical anion was found to have lower reactivity than the  $\cdot\text{OH}$  radicals, towards the dimethylpyridines. The pseudo-first-order rate constant ( $k_{\text{obs}}$ ) was plotted as a function of the solute concentration. The second-order rate constants ( $k$ ) for the reactions of  $\text{SO}_4^{\cdot-}$  with dimethylpyridines were found to be  $(1.7\text{--}3.1) \times 10^9$   $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$  (Table 1). The entire spectrum decayed by good second-order kinetics.

*Absorption spectra of the transients.* The maximum absorbance of the transients had reached within about  $2 \mu\text{s}$ . All three dimethylpyridines showed similar spectral characteristics, having the absorption maxima centred at 310–330 nm with an additional weak band at 430–475 nm. The transient absorption spectra obtained in the reaction of  $\text{SO}_4^{\cdot-}$  with 2,4-dimethylpyridine is shown in Fig. 4. The molar absorptivities of the adducts at 330 nm was determined considering  $G(\text{SO}_4^{\cdot-}) = 3.3$ . The spectral parameters are listed in Table 1. For direct comparison these transient absorption spectra are normalised to  $G(\text{SO}_4^{\cdot-}) = G(\cdot\text{OH}) = 5.6$ . It can be seen (inset of Fig. 4) that these spectra are similar. The  $\text{SO}_4^{\cdot-}$  radical anion is known [19] to react very rapidly with several aromatic compounds but with higher selectivity, which indicates that the  $\text{SO}_4^{\cdot-}$  radical anion do not react by addition to the aromatic ring, but most likely by an electron transfer mechanism to produce initially the radical cation [21, 22]. The reaction of  $\text{SO}_4^{\cdot-}$  with substituted benzenes in aqueous solution was explained to proceed by both an inner-sphere (addition/elimination) and an outer-sphere (electron transfer) process, where the former process involves the formation of  $\text{SO}_4^{\cdot-}$  adducts while the latter leads to the formation of the radical cation intermediate [21, 22]. However, a clear-cut distinction between the two processes has not been reported so far, except for substituents containing highly electron donating ( $\text{OCH}_3$ ) groups where the outer-sphere processes were observed to be significant due to the stabilisation of ensuing radical cation by the electron releasing groups [21, 22].

In the case of the pyrimidine bases, due to the depletion of the  $\pi$ -electron system, by the electron withdrawing nitrogen, the primary step in the reaction of  $\text{SO}_4^{\cdot-}$  was reported [23, 24] to be addition to the olefinic double bond to form the sulphate adduct rather than the direct radical cation formation by one electron oxidation. The resulting  $\text{SO}_4^{\cdot-}$  adduct will undergo  $\text{SO}_4^{2-}$  elimination producing the corresponding radical cation. This radical cation will then react with water resulting in the formation of OH-adducts. Similarly (Scheme 1, reactions 4, 5 and 6), the transients formed at 330 nm, in the reaction of  $\text{SO}_4^{\cdot-}$  with the isomers of dimethylpyridines is attributed to the corresponding OH-adducts.



**Figure 4.** Transient optical absorption spectra obtained on the reaction of  $\text{SO}_4^{\bullet-}$  with  $\text{N}_2$  saturated neutral solutions of 2,4-dimethylpyridine containing  $0.2 \text{ mol dm}^{-3}$  butanol and  $1.5 \times 10^{-2} \text{ mol dm}^{-3}$   $\text{K}_2\text{S}_2\text{O}_8$  at 2 ( $\circ$ ) and 40  $\mu\text{s}$  ( $\square$ ) after the pulse. Inset shows absorption spectra for the reaction of  $\bullet\text{OH}$  ( $\square$ ) radicals and  $\text{SO}_4^{\bullet-}$  ( $\circ$ ) with 2,4-dimethylpyridine. The  $G(\text{SO}_4^{\bullet-})$  is normalised to 5.6 for direct comparison with  $\bullet\text{OH}$  spectrum. Dose per pulse = 14 Gy.

## CONCLUSION

The pulse radiolysis study of the reactions of reducing ( $e_{\text{aq}}^-$ ), oxidising ( $\text{SO}_4^{\bullet-}$ ),  $\bullet\text{OH}$  and  $\text{O}^{\bullet-}$  radicals with 2,4-, 2,6- and 3,5-dimethylpyridines revealed that the rates of these reactions are nearly diffusion controlled ( $k = (1-9) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ). The transient absorption spectra of the intermediates formed in  $\text{O}^{\bullet-}$ ,  $\bullet\text{OH}$  and  $\text{SO}_4^{\bullet-}$  reactions with dimethylpyridines exhibited maxima in the range 300–330 nm. The hydrated electron attacks the heteroatom to give the radical anion which gets immediately protonated. The  $\bullet\text{OH}$  radical adds to the pyridine ring to form the OH-adducts. Same species were also obtained in the case of  $\text{SO}_4^{\bullet-}$  reactions.  $\text{O}^{\bullet-}$  reacts by addition, as well as H-abstraction in all the systems.

## Acknowledgements

The authors are thankful to Prof. M. S. Wadia of the University of Pune for useful discussions.

## REFERENCES

1. S. Steenken and P. O'Neill, *J. Phys. Chem.* **82**, 372 (1978).
2. B. Cercek and M. Ebert, *Trans. Faraday Soc.* **63**, 1687 (1967).
3. M. Simic and M. Ebert, *Int. J. Radiat. Phys. Chem.* **3**, 259 (1971).
4. S. Steenken and P. O'Neill, *J. Phys. Chem.* **83**, 2407 (1979).

5. T. Shiga, T. Kishimoto and E. Tomita, *J. Phys. Chem.* **77**, 330 (1973).
6. C. L. Greenstock, *Trans. Faraday Soc.* **66**, 2541 (1970).
7. D. Razem and W. H. Hamill, *J. Phys. Chem.* **81**, 5931 (1977).
8. E. J. Hart, S. Gordon and J. K. Thomas, *J. Phys. Chem.* **68**, 1271 (1964).
9. L. G. Shevchuk, V. S. Zhikarev and N. A. Vysotskaya, *J. Org. Chem. USSR* **5**, 1606 (1969).
10. S. Solar, N. Getoff, K. Sehested and J. Holoman, *Radiat. Phys. Chem.* **41**, 825 (1993).
11. S. N. Guha, P. N. Moorthy, K. Kishore, D. B. Naik and K. N. Rao, *Proc. Indian Acad. Sci. (Chem. Sci.)* **99**, 261 (1987).
12. D. B. Naik and P. N. Moorthy, *J. Chem. Soc., Perkin Trans. 2*, 705 (1990).
13. I. L. Finar, *Org. Chem.* **1**, 730 (1960).
14. R. H. Schuler, A. L. Hartzell and B. Behar, *J. Phys. Chem.* **85**, 192 (1981).
15. N. Selvarajan and N. V. Raghavan, *J. Phys. Chem.* **84**, 2548 (1980).
16. M. C. Anthony, W. L. Waltz and P. G. Mezcy, *Can. J. Chem.* **60**, 813 (1982).
17. H. C. Christensen, K. Sehested and E. J. Hart, *J. Phys. Chem.* **77**, 983 (1973).
18. S. Steenken, P. O'Neill and D. Schulte-Frohlinde, *J. Phys. Chem.* **81**, 26 (1977).
19. P. Neta, V. Madhavan, H. Zemel and R. W. Fessenden, *J. Am. Chem. Soc.* **99**, 163 (1977).
20. P. O'Neill, S. Steenken and D. Schulte-Frohlinde, *J. Phys. Chem.* **79**, 2773 (1975).
21. S. Steenken, *J. Chem. Soc., Faraday Trans.* **87**, 113 (1987).
22. S. Steenken, *Nato ASI Ser. C* **260**, 213 (1989).
23. J. Brown and S. F. Mason, *The Pyrimidines*. Wiley, New York, NY (1962).
24. G. Behrens, K. Hildenbrand, D. Schulte-Frohlinde and J. N. Herak, *J. Chem. Soc., Perkin Trans. 2*, 305 (1988).