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Study of radiation chemical reactions of oxidising and reducing radicals with furazan derivatives

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Abstract

Reactions of ${}^{\bullet}OH$, $O^{\bullet -}$, $N_3^{\bullet}$ and $SO_4^{\bullet -}$ and e_{aq}^- radicals with furazan and its dimethyl and diamino derivatives were studied by radiation chemical methods. The ${}^{\bullet}OH$ radical reaction is selective with the rates following the order furazan < 3,4-dimethylfurazan (3,4-DMF) < 3,4-diaminofurazan (3,4-DAF), the k values being $<10^7$, 3.5×10^8, $3.9 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$, respectively. The transient absorption spectra measured in the ${}^{\bullet}OH$ radical reaction with 3,4-DMF and 3,4-DAF exhibited maxima at 270 and 290 nm, respectively, which are assigned to the benzylic and anilino type radicals. The same intermediates are also formed in the $O^{\bullet -}$ reaction by H abstraction. All three derivatives showed lack of reactivity with $N_3^{\bullet}$ radical and was only 3,4-diaminofurazan found reactive with $SO_4^{\bullet -}$ ($k = 3.6 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$). The rates of e_{aq}^- with all the three derivatives are diffusion controlled $k = (0.8\text{–}1.9) \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}$ and its reaction mechanism involves very fast protonation of the initially formed radical anions by water ($k \geq 10^7\ s^{-1}$) followed by tautomerisation of the N-atom protonated C-centred radical to the C-atom protonated N-centred radical. The transformation is catalysed by OH^- and the rates for the spontaneous transformation in neutral solution are 5.4×10^4 and $1.5 \times 10^5\ s^{-1}$ with furazan and 3,4-diaminofurazan, respectively. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Pulse radiolysis; Transient absorption spectra; Furazan derivatives; Oxidising and reducing radicals

1. Introduction

Radiation chemical methods form an excellent tool [1–17] for studying the reactions of oxidising (e.g. ${}^{\bullet}OH$, $N_3^{\bullet}$, $SO_4^{\bullet -}$) and reducing (e.g. e_{aq}^- and alcohol radicals) radicals with organic and biologically important molecules in aqueous solution because of several advantages. Radiation chemical studies are generally aimed [4] at the evaluation of kinetics and measurement of transient absorption spectra with a view to understand the underlying reaction mechanism. In the recent past, we have carried out detailed studies on the reactions of oxidising and reducing radicals with substituted benzenes [18–27] of the type $C_6H_{5-n}X_nY$ where X = halogen, and Y = –Cl, –Br, $-CH_3$, $-CH_2Cl$, $-CHCl_2$, $-CF_3$ or $-OCH_3$ and purine bases [28–35] using pulse radiolysis combined with product analysis to gain further insight into the reaction mechanism, especially with regard to the radiation chemical oxidation of these compounds. The reaction mechanism of e_{aq}^- with purine bases involves [2,5,28,29] the tautomerisation of initially formed N-protonated C-centred radicals to thermodynamically more favourable C-protonated N-centred radicals and the rates of this reaction are catalysed by OH^- and have been found to be structure dependent. It is, therefore, interesting to examine whether such tautomerisation occurs with other heterocyclic compounds.

One important class of heterocyclic compounds for radiation chemical studies is furazan and its derivatives which, to our knowledge, have not been well explored. Furazan (structure 1), the unsubstituted oxadiazole, a five membered ring, is expected to be susceptible to the nucleophilic attack (e_{aq}^-) whereas its substitution by $-CH_3$ and $-NH_2$ groups should facilitate the electrophilic attack by the ${}^{\bullet}OH$ radical. We have, therefore, undertaken the study of reactions of ${}^{\bullet}OH$, $O^{\bullet -}$, $N_3^{\bullet}$, $SO_4^{\bullet -}$ and e_{aq}^- with furazan, 3,4-dimethylfurazan (3,4-DMF) and 3,4-diaminofurazan (3,4-DAF) with a view to examine the differences in the rates, and transient absorption spectra between furazan and the $-CH_3$ and $-NH_2$

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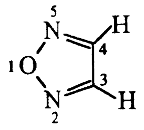
substituted derivatives.



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2. Experimental

2.1. Chemicals

Furazan and 3,4-DMF were synthesised according to the method published [36,37] in literature. Their purity was checked by HPLC and the UV and NMR spectra recorded in $CDCl_3$ showed only one peak indicating >98% purity. 3,4-DAF — synthesised as reported in literature [38] — was a gift from the High Energy Materials Research Laboratory, Pune, which also showed a single HPLC peak and was used as received. Other chemicals used were commercially available analytical grade reagents of high purity. All solutions were freshly prepared using deionised water purified by the Millipore Milli-Q water system having a resistivity of $18\,\mathrm{M\Omega\,cm^{-1}}$. All experiments were carried out at ~25°C.

2.2. Irradiations

The oxdising and reducing radicals were generated by pulse radiolysis using appropriate conditions.

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

The reaction of the ${}^{\bullet}OH$ radical was studied in N_2O saturated solutions containing $1 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ solute at pH 6.2 (natural solutions) where e^-_{aq} is quantitatively converted into ${}^{\bullet}OH$ (reaction (2); $k = 9.1 \times 10^9\,\mathrm{dm^3\,mol^{-1}\,s^{-1}})^4$.

$$e_{aq} + N_2O \xrightarrow{H_2O} N_2 + OH^- + {}^{\bullet}OH \qquad (2)$$

The reaction of $O^{\bullet-}$ was studied in N_2O-saturated basic solutions (pH ~ 13). At this pH, almost all OH radicals are converted into $O^{\bullet-}$ as pK_a (${}^{\bullet}OH$) = 11.9 (reaction (3), $k = 1.3 \times 10^{10}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}})^4$.

$$\text{–}OH + OH^- \rightleftharpoons O^{\bullet-} + H_2O \qquad (3)$$

N_2O saturated solutions of the substrate containing NaN_3 were radiolysed to produce $N_3{}^{\bullet}$ radical (reactions (2) and (4), $k = 1.2 \times 10^{10}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}})^4$.

$$N_3{}^- + {}^{\bullet}OH \rightarrow N_3{}^{\bullet} + OH^- \qquad (4)$$

$SO_4{}^{\bullet-}$ radicals were produced by the reaction of e^-_{aq} and $H^{\bullet}$ with persulphate in N_2 saturated solutions of the solute containing $1.5 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$ $K_2S_2O_8$ and $2 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$ *tert*-butyl alcohol (reaction (5), $k(e^-_{eq}) = 1.2 \times 10^{10}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$, $k(H^{\bullet}) = 2.5 \times 10^7\,\mathrm{s^{-1}})^4$.

$$S_2O_8{}^{2-} + e^-_{aq}(H^{\bullet}) \rightarrow SO_4{}^{\bullet-1} + SO_4{}^{2-}(HSO_4^-) \qquad (5)$$

2-Propanol scavenges ${}^{\bullet}OH$ and $H^{\bullet}$ effectively and, hence, the reaction of e^-_{aq} can be studied.

$$\begin{aligned} &{}^{\bullet}OH(H^{\bullet}) + CH_3\text{–}CH(OH)\text{–}CH_3 \\ &\quad \rightarrow H_2O(H_2) + CH_3\text{–}C^{\bullet}(OH)\text{–}CH_3 \qquad (6) \end{aligned}$$

Pulse radiolysis experiments were carried out using high energy 7 MeV electron pulses from the linear accelerator facility at the Radiation Chemistry and Chemical Dynamic Division, Bhabha Atomic Research Centre, (BARC), Mumbai. Thiocyanate dosimetry was used to determine the dose rate using $10^{-2}\,\mathrm{mol\,dm^{-3}}$ KSCN. The absorbance of $(SCN)_2{}^{\bullet-}$ was monitored at 500 nm ($G\varepsilon_{500} = 21522\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}/100\,eV}$). In all experiments, a pulse width of 50 ns was usually used and the dose per pulse was kept in the range 15–17 Gy. The transient absorption spectra were recorded as a function of time on a storage oscilloscope interfaced to a computer for kinetics analysis using cell of 1 cm pathlength. The details of this facility were described elsewhere [39].

3. Results and discussion

3.1. Kinetics

3.1.1. Reactions of ${}^{\bullet}OH$, $O^{\bullet-}$, $N_3{}^{\bullet}$ and $SO_4{}^{\bullet-}$

The rates of the reaction of the ${}^{\bullet}OH$ radical with furazan, 3,4-DMF and 3,4-DAF were studied from the build-up of the transient species at the absorption maxima in the solute concentration range $(0.2\text{–}1) \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$. No absorption build-up was seen in the wavelength range 270–550 nm in the reaction of the ${}^{\bullet}OH$ radical with furazan ($1 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$) on the time scale of 50 μs and its rate must be $k < 10^7\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$. The rate of the OH radical reaction with 3,4-DMF was monitored at $\lambda_{max} = 270\,\mathrm{nm}$ and the trace depicting the absorption build-up when $1 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ N_2O saturated solution of 3,4-DMF was pulse radiolysed is given in inset of Fig. 1a. As can be seen, the rate of this build-up was found to $3.5 \times 10^5\,\mathrm{s^{-1}}$ and the second-order rate constant was, thus, estimated to be $3.5 \times 10^8\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$. The rates at lower concentrations of the substrate were not determined due to the poor signal-to-noise ratio.

The rate of the ${}^{\bullet}OH$ radical reaction with 3,4-DAF monitored at the absorption maximum 290 nm was found to be pseudo first-order and the second-order rate constant was estimated to be $3.9 \times 10^9\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$. The rates of the ${}^{\bullet}OH$ radical reaction with 3,4-DMF and 3,4-DAF differ by an order of magnitude which can be clearly seen from the absorption traces given as inset of Figs. 1 and 2, respectively. The order of measured k values for the ${}^{\bullet}OH$ radical reaction is 3,4-DAF > 3,4-DMF > furazan. This is in accord with the activation effects of NH_2 and CH_3 groups for the electrophilic ${}^{\bullet}OH$ radical attack.

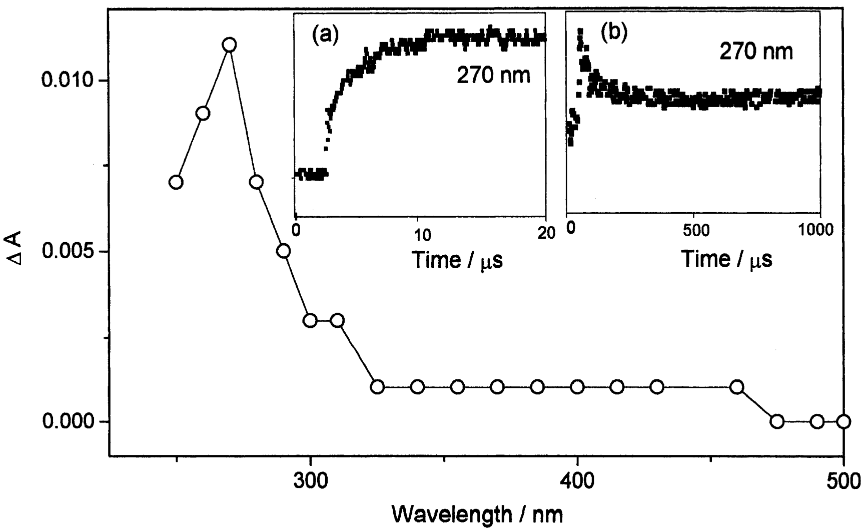


Fig. 1. Transient absorption spectrum measured at 15 μs after the pulse in the reaction of $^{\bullet}$OH with 3,4-dimethylfurazan (1×10^{-3} mol dm^{-3}) at neutral pH. Inset: (a) build-up and (b) decay traces at 270 nm; dose: 15 Gy.

The rates for the $O^{\bullet -}$ reaction with furazan and its methyl and amino derivatives were also determined in basic medium (pH $\sim$ 13) where >90% of the reacting species exists as $O^{\bullet -}$. No growth in absorption was observed in the reaction of $O^{\bullet -}$ with 1×10^{-3} mol dm^{-3} furazan on the time scale of 50 μs. However, the rate constants obtained for the $O^{\bullet -}$ reaction with 3,4-DMF ($\lambda_{\max} = 270$ nm) and 3,4-DAF ($\lambda_{\max} = 290$ nm) from the plots of k_{obs} versus concentration are 5.0×10^8 and 2.0×10^9 dm^3 mol^{-1} s^{-1}. The relevant absorption traces of the build-up are shown in Figs. 3 and 4.

Experiments were also carried out to study the reaction of the $N_3^{\bullet}$ with furazan and its derivatives, but they were found to be comparatively slower ($k < 10^7$ dm^3 mol^{-1} s^{-1}). Similarly, both furazan and 3,4-DMF did not show any reactivity toward the $SO_4^{\bullet -}$. However, the kinetics for the $SO_4^{\bullet -}$ reaction with 3,4-DAF could be determined from the rate of formation of the intermediate absorbing at 290 nm for various concentrations of the solute $(0.2–1) \times 10^{-3}$ mol dm^{-3} and k_{obs} values were found to increase linearly with the [solute]. The second-order rate constant was determined to be 3.6×10^9 dm^3 mol^{-1} s^{-1} at neutral pH. In contrast, the lack of reactivity with the $N_3^{\bullet}$ radical must be due to the lower E^0 value of $N_3^{\bullet}/N_3^-$ couple (1.33 V)[10] compared to the $SO_4^{\bullet -}$ ($E^0 = 2.5$ V)[10] indicating that the reduction

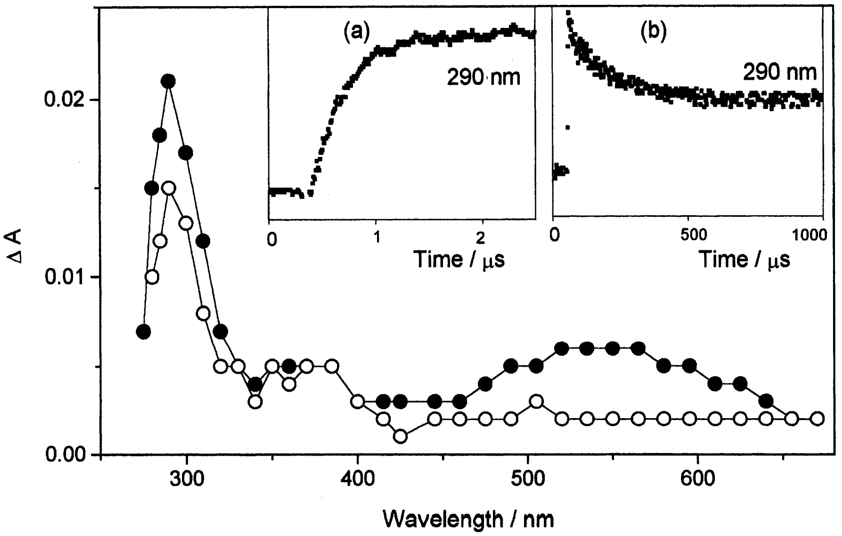


Fig. 2. Transient absorption spectra measured in the reactions of $^{\bullet}$OH (●) and $SO_4^{\bullet -}$ (○) (normalised) at 2 μs after the pulse with 3,4-diaminofurazan (1×10^{-3} mol dm^{-3}) at neutral pH. Inset (a) build-up trace with $^{\bullet}$OH radical at 290 nm with 3,4-DAF and (b) decay trace at 290 nm with 3,4-DAF; dose: 17 Gy.

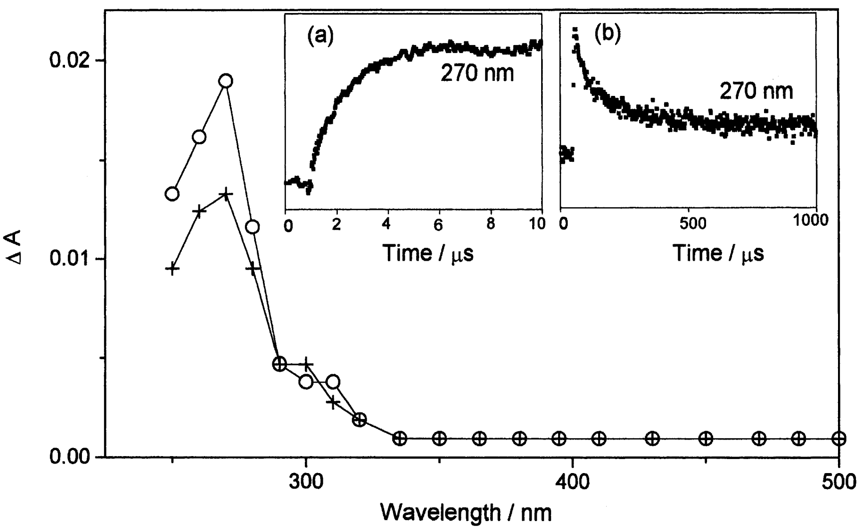
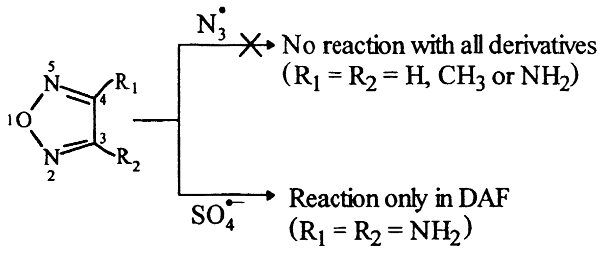


Fig. 3. Time resolved transient absorption spectra measured at (○) 2 and (+) 40 μs after the pulse in the reaction of $O^{\bullet -}$ with 3,4-dimethylfurazan (1×10^{-3} mol dm^{-3}) at pH ~ 13. Inset: (a) build-up and (b) decay traces at 270 nm; dose: 15 Gy.

potential of 3,4-DAF must be >1.33 V, but <2.5 V whereas it must be still higher in the case of furazan and 3,4-DMF (reaction (7)). This is not surprising considering the high electron donating nature of the NH_2 group.



(7)

3.1.2. Reaction of e_{aq}^-

The rate constants for the reaction of e_{aq}^- with furazan, 3,4-DMF and 3,4-DAF were measured following the decay of e_{aq}^- at 700 nm. The decay was found to be very fast and the trace showing the decay in the case of furazan is given as an inset in Fig. 5. This decay corresponded to the build-up at 270 nm. The second-order rate constants obtained from the plot of k_{obs} versus concentration for the reaction of e_{aq}^- with furazan, 3,4-DMF and 3,4-DAF are 1.9×10^{10}, 9.7×10^{9} and 8.4×10^{9} dm^3 mol^{-1} s^{-1}, respectively, at neutral pH. The second-order rate constant measured for the reaction of e_{aq}^- with 3,4-DAF at pH = 4 is nearly identical to that obtained at neutral pH. The k values obtained in this work

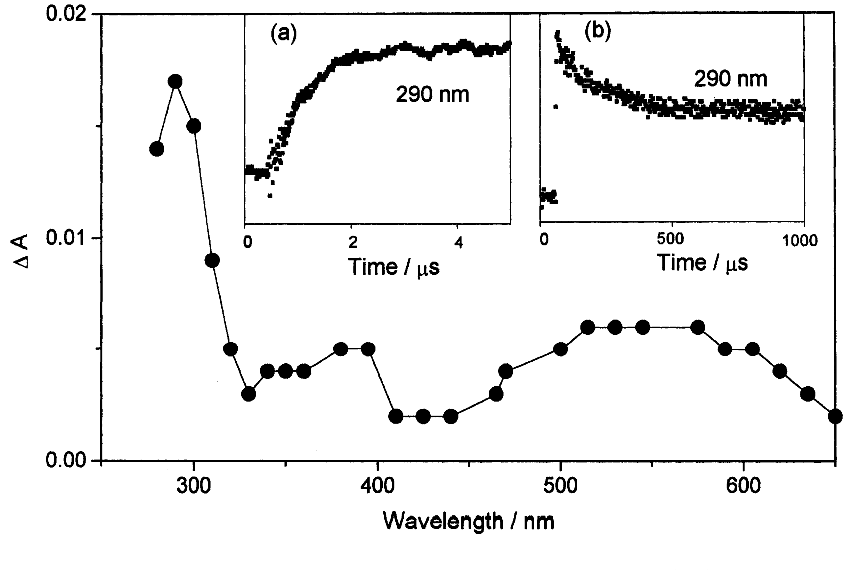


Fig. 4. Transient absorption spectrum measured at 2 μs after the pulse in the reaction of $O^{\bullet -}$ with 3,4-diaminofurazan (1×10^{-3} mol dm^{-3}) at pH ~ 13. Inset: (a) build-up and (b) decay traces at 290 nm; dose: 17 Gy.

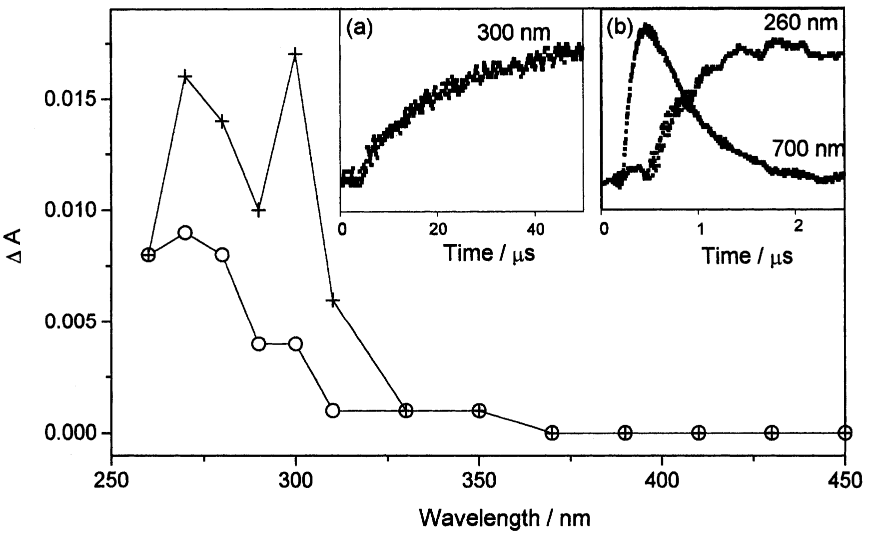


Fig. 5. Time resolved transient absorption spectra measured at (○) 2 and (+) 40 μs after the pulse in the reaction of e_{aq}^- with furazan (1×10^{-3} mol dm^{-3}) at neutral pH. Inset: (a) delayed build-up (300 nm) and (b) build-up (260 nm) and decay (700 nm) traces; [furazan] $= 1\times10^{-4}$ mol dm^{-3}; dose: 16 Gy.

are compiled in Table 1. Also shown in this table are the absorption maxima of the intermediates formed in different reactions.

3.2. Transient absorption spectra

3.2.1. Reactions of $^\bullet$OH, $O^{\bullet-}$ and $SO_4^{\bullet-}$

The spectra obtained with 3,4-DMF and 3,4-DAF exhibited a sharp peak around 270–290 nm, and a very weak absorption in the region 500–600 nm with 3,4-DAF. However, the absorption intensity of the peak in the case of 3,4-DMF is nearly half as compared to 3,4-DAF (Figs. 1 and 2). The time resolved transient absorption spectra measured at 40 μs after the pulse with both the derivatives have not shown any further spectral changes except the bimolecular decay since the first-order fit for this decay is not proper and the trace showing this decay at 270 nm in 3,4-DMF is given in Fig. 1.

In order to obtain further information on the redox nature of the intermediates formed in the $^\bullet$OH reaction, pulse radiolysis experiments were carried out in N_2O saturated 3,4-DAF solution (1×10^{-3} mol dm^{-3}) containing the oxidant methylviologen (MV^{2+}) (1×10^{-4} mol dm^{-3}). Under these conditions, e_{aq}^- is still scavenged by N_2O and $MV^{\bullet+}$, if at all formed, must be due to the reduction of MV^{2+} by the intermediates generated in the OH reaction. Only a marginal build-up of $MV^{\bullet+}$ at both the absorption maxima (390 and 605 nm) corresponding to ≤15% was seen indicating that the intermediates formed in the OH reaction are not reducing in nature. This is further supported by product analysis study under steady state conditions. The HPLC chromatograms after γ-radiolysis are given in Fig. 6. When N_2O saturated solutions of 1×10^{-3} mol dm^{-3} (dose = 260 Gy) 3,4-DAF were radiolysed with and without $K_3Fe(CN)_6$ (1×10^{-4} mol dm^{-3}), only one major product (peak 2) was formed and it is clearly seen that the yield of this product formed under both conditions is nearly the same. In the presence of $Fe(CN_6)^{3-}$, the OH adduct is oxidised to the hydroxylated product resulting in an increase in its yield compared to that produced in its absence. Since the yield of the radiation product formed in our study with and without the oxidant are the same, it is suggested that the intermediate generated is non-reducing in nature.

The spectra after the completion of the $O^{\bullet-}$ reaction with 3,4-DMF ($\lambda_{max} = 270$ nm) and 3,4-DAF ($\lambda_{max} = 290$ nm, Figs. 3 and 4) are more or less similar to that measured in the $^\bullet$OH reaction (Figs. 2 and 3). The spectrum recorded

Table 1

Second-order rate constants (k (10^9 dm^3 mol^{-1} s^{-1})) and the absorption maxima (λ_{max} (nm)) obtained in the reaction of $^\bullet$OH, $O^{\bullet-}$, $N_3^\bullet$, $SO_4^{\bullet-}$ and e_{aq}^- with furazan, 3,4-dimethylfurazan and 3,4-diaminofurazan. The accuracy of the measured rate constants is within ±10%

Compound	$^\bullet$OH		$O^{\bullet-}$		$N_3^\bullet$		$SO_4^{\bullet-}$		e_{aq}^-	
	k	λ_{max}	k	λ_{max}	k	λ_{max}	k	λ_{max}	k	λ_{max}
Furazan	< 0.01	–	<0.01	–	<0.01	–	<0.01	–	19	270, 300
3,4-Dimethylfurazan	0.35[a]	270	0.5	270	<0.01	–	<0.01	–	9.7	270
3,4-Diaminofurazan	3.9	290, 550	2.0	290, 550	<0.01	–	3.6	290	8.4	290

[a] Determined from measurement at 1×10^{-3} mol dm^{-3}.

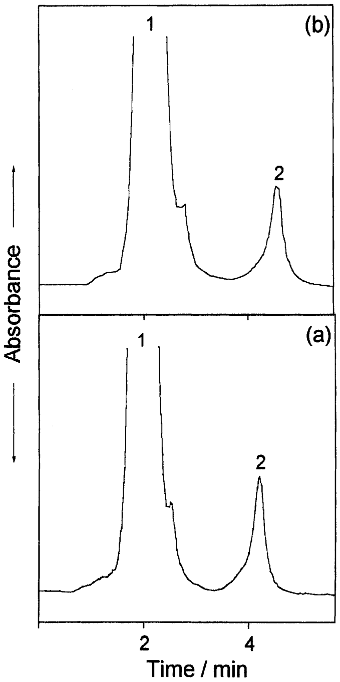


Fig. 6. HPLC chromatograms obtained in the γ-radiolysis of N_2O saturated solutions of 3,4-DAF (1×10^{-3} mol dm^{-3}) (a) without and (b) with ferricyanide (1×10^{-4} mol dm^{-3}); eluent: 10% acetonitrile in water; dose: 260 Gy; peak 1: 3,4-DAF, peak 2: radiation product.

at 40 μs after the pulse in the case of 3,4-DMF (Fig. 3) has revealed only the second-order decay. It is interesting to note that the decay rates of the intermediate radicals formed in the $^\bullet$OH and $O^{\bullet-}$ reactions with 3,4-DMF (inset of Figs. 1 and 3) as well as 3,4-DAF (Figs. 2 and 4) are nearly equal.

The spectrum recorded in the $SO_4^{\bullet-}$ reaction with 3,4-DAF (1×10^{-3} mol dm^{-3}) measured in the wavelength region 280–500 nm has an absorption maximum at 290 nm which is similar to that obtained in the $^\bullet$OH radical reaction. However, the spectral intensity at 290 nm measured with $SO_4^{\bullet-}$ reaction was reduced by about 50% and the spectrum was normalised by multiplying its absorbance values by 1.7, i.e. the ratio of ($G_{OH}/G_{SO_4^{\bullet-}}$). The normalised spectrum is depicted in Fig. 2. Even though the intensity of the absorption maximum in the spectrum measured in the $SO_4^{\bullet-}$ reaction with 3,4-DAF is lower by about 25% than that obtained in the $^\bullet$OH radical reaction, the overall spectral features are similar in both cases. It is, therefore, proposed that the same intermediate species is formed in both $^\bullet$OH and $SO_4^{\bullet-}$ radical reactions.

3.2.2. Reaction of e_{aq}^-

The transients absorption spectra measured in the reactions of e_{aq}^- with furazan, 3,4-DMF and 3,4-DAF were monitored in the range 260–550 nm. The spectra recorded at 2 and 40 μs after the pulse in the e_{aq}^- reaction with furazan (1×10^{-3} mol dm^{-3}) are given in Fig. 5. The initial spectrum measured after the completion of the reaction (2 μs) has shown two broad maxima at 260 and 300 nm. A subsequent increase in absorption at the two wavelengths was noticed in the spectrum recorded at 40 μs after the pulse. The rate of this growth (300 nm) was found to be 5.1×10^4 s^{-1} as can be seen from the inset of Fig. 5. The absorption spectrum of the intermediates formed in the e_{aq}^- reaction with 3,4-DAF (1×10^{-3} mol dm^{-3}) at 2 μs after the pulse has shown a single peak at 290 nm (Fig. 7). This spectrum transformed within 50 μs in neutral solution with a shift in absorption maximum to 320 nm. The traces showing the decay at 290 and build-up at 320 nm are shown in inset of Fig. 7. The rate for this transformation was measured to be 1.5×10^5 s^{-1}, which is nearly three times more than that found with furazan. Furthermore, this transformation was catalysed by OH^- as can be seen from the spectrum measured at pH = 11 (Fig. 7) where it was complete within 2 μs.

The dependence of the rate of build-up at 320 nm on pH was studied to examine if the transformation follows a pK_a type behaviour. The first-order rate constants for the transformation (k_t) are ploted as a function of the pH (inset in Fig. 7). As can be seen, no significant change in (k_t) was observed in the pH range 6.2–8.0; but it was accompanied by a slow increase up to pH 9.0. The transformation became much faster thereafter and reached a plateau value at pH 12 with a k_t value of 2.3×10^6 s^{-1}. The spectral change at 40 μs after the pulse at pH = 7 is attributed to the tautomerisation of initially formed intermediate species. The pK_a value for the transformation was estimated to be 10.0.

3.3. Reaction mechanism

3.3.1. Reactions of $^\bullet$OH, $O^{\bullet-}$ and $SO_4^{\bullet-}$

The OH radical, being electrophilic in nature, is expected to add equally to C_3/C_4 positions of the furazan ring. Considering 3,4-DAF and C-4 position, as an example, this is shown in reaction (1), Scheme 1. Since two electronegative atoms are attached to the same carbon, the dehydration reaction leading to the formation of the anilino type radical **2** (reaction (2)) must occur very fast. The intermediate species responsible for the spectrum measured in the $^\bullet$OH radical reaction at 2 μs after the pulse (Fig. 2) is attributed to the radical **2**. The initial radical **1** formed from addition of $^\bullet$OH radical is not likely to absorb in the UV region due to the loss of conjugation. The rate of dehydration reaction in the case of methyl derivative resulting in benzylic type radical is expected to be relatively slower. The direct H abstraction from the NH_2 group by the $^\bullet$OH radical (reaction (3)) is considered less likely. The assignment for the formation of the anilino type radical in the $^\bullet$OH radical reaction is based on the observed lack of oxidation by $K_3Fe(CN)_6$ under steady-state γ-radiolysis. It is known [28,29] that the N-centred radical of purine bases is not easily oxidised because it is relatively more stable than the C-centred radical. Secondly, the similarity of the spectra of the transients and the decay rates measured in the $^\bullet$OH and $O^{\bullet-}$ reactions

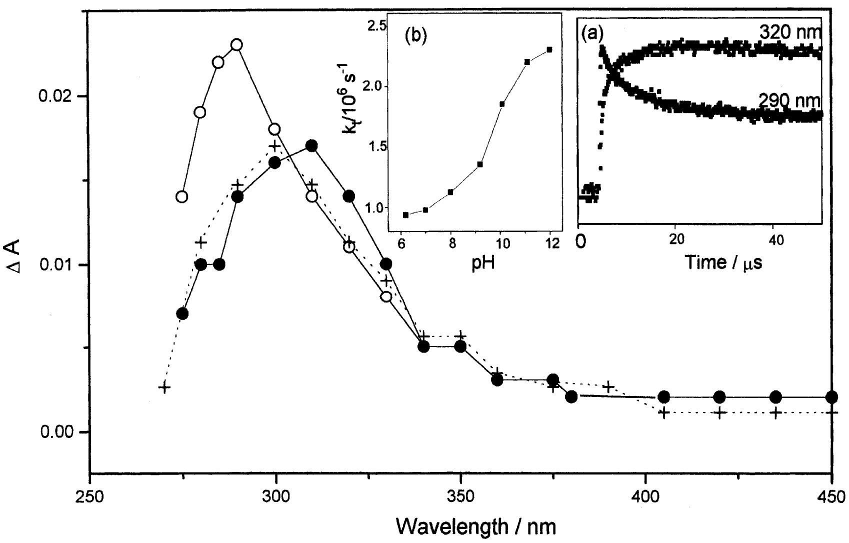


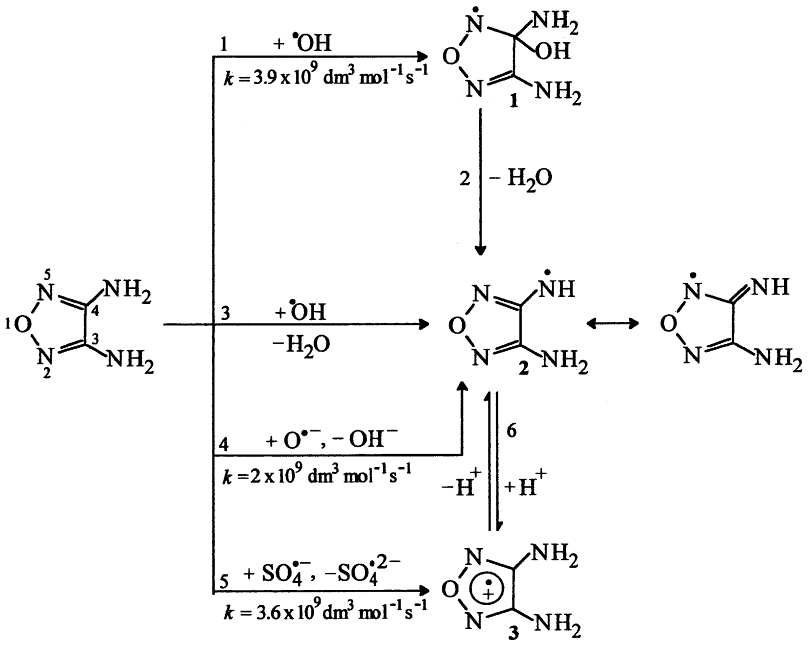
Fig. 7. Time resolved transient absorption spectra measured at (○) 2 and (●) 15 μs after the pulse pH = 7 and (+) 2 μs, pH = 11 in the reaction of e_{aq}^- with 3,4-DAF (1×10^{-3} mol dm^{-3}). Inset: (a) build-up (320 nm) and decay (290 nm) traces; (b) plot of k_t vs. pH; dose: 17 Gy.

clearly suggest the formation of anilino type of radical in the former reaction.

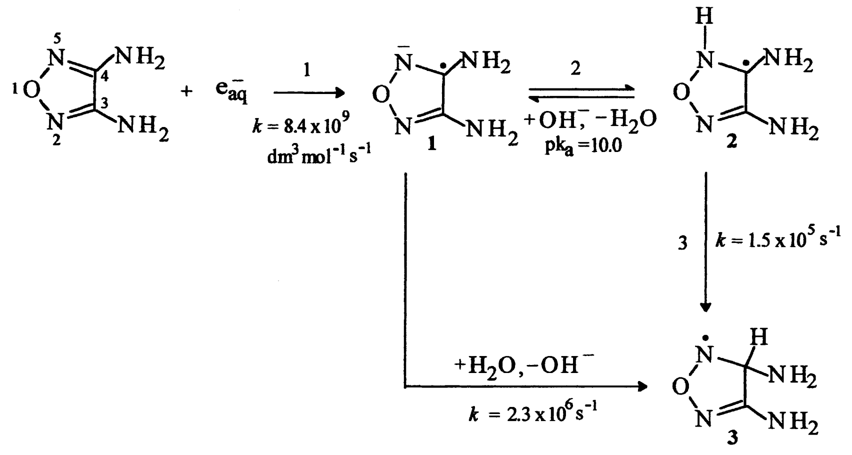
The main reaction pathway for the $O^{\bullet -}$ reaction is hydrogen abstraction (reaction (4)) generating the anilino type radical as its addition to the ring is unlikely. This is evident from the lack of $O^{\bullet -}$ reactivity with furazan. Assuming that the $^{\bullet}OH$ radical reaction of the radical entirely leads to the formation of the radical **2**, its molar absorptivity at 290 nm was estimated to be 2440 dm^3 mol^{-1} cm^{-1}. The anilino type radical is also formed in the $SO_4^{\bullet -}$ reaction with 3,4-DAF. In this case, the electron transfer process (reaction (5)) is followed by deprotonation (reaction (6)) generating the radical **2**.

3.3.2. Reaction of e_{aq}^-

The e_{aq}^- is expected to attack the electron affinic N atom (N_2/N_5) of the furazan ring resulting in the formation of the corresponding radicals anion. This reaction is shown



Scheme 1. Mechanism of the $^{\bullet}OH$, $O^{\bullet -}$ and $SO_4^{\bullet -}$ reaction with 3,4-DAF.



Scheme 2. Mechanism of the reaction of e_{aq}^- with 3,4-DAF.

considering 3,4-DAF and addition of e_{aq}^- to N-5 as an example (reaction (1), Scheme 2). The electron adducts, thus, formed are likely to be highly proton affinic in nature and it is proposed that the radical anion **1** is rapidly protonated by water. The rate of protonation of the radical anion in neutral solution by water is as fast as the reaction of e_{aq}^- with the furazan derivatives to yield the neutral N-atom protonated radical **2**. Such fast protonation by water was reported [2,5,28,29] in electron adducts of adenine, guanine and hypoxanthine nucleosides. The initial spectra recorded after the completion of the reaction of e_{aq}^- with furazan and 3,4-DAF (Figs. 5 and 7) are attributed to the neutral N-atom protonated adducts. Further changes in the spectra (i.e. delayed increase in absorption) must be due to the transformation of these neutral adducts to the more stable C-atom protonated N-centered radical **3** The spontaneous transformation is facilitated by water in neutral solution and its rates were determined to be 5.4×10^4 and $1.5 \times 10^5\,s^{-1}$ for furazan and 3,4-DAF, respectively. Moreover, the conversion from N-atom protonated to C-protonated adducts (reaction (3)) is catalysed by OH^- in a reversible process and the pK_a value for this conversion is estimated to be 10.0 with 3,4-DAF. Such OH^- catalysed transformation has been reported [2,5] earlier in the case of purine nucleosides.

4. Conclusions

The rates of the $^{\bullet}OH$ radical reaction with furazan and its dimethyl and diamino derivatives differ by an order of magnitude with the k values in the range $<10^7$–$10^9\,dm^3\,mol^{-1}\,s^{-1}$. The same intermediates (benzylic, $\lambda = 270\,nm$ or anilino, $\lambda = 290\,nm$ types of radicals) are formed in the reactions of $^{\bullet}OH$, $O^{\bullet -}$ and $SO_4^{\bullet -}$. The tautomerisation of the electrons adducts of furazan and 3,4-DAF (N-protonated C-centred radical to C-protonated N-centred radical) occurs in neutral solution with $k = 5.4 \times 10^4$ and $1.5 \times 10^5\,s^{-1}$, respectively.

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