Redox Reactions of Dopamine Transients in Aqueous Solution: a Pulse Radiolysis Study

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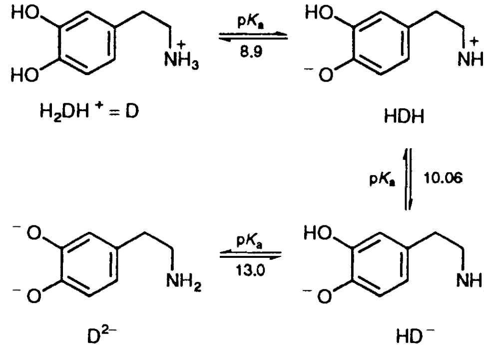
On reaction of e_{aq}^- with protonated dopamine (D) a transient optical absorption band [formed at $\lambda_{max} = 355$ nm ($\varepsilon = 5100$ dm^3 mol^{-1} cm^{-1})] has been assigned to an e_{aq}^- adduct of the dopamine ring ($D^{\bullet-}$) (the first site of attack of e_{aq}^-), which subsequently goes to the amine site to cleave the C–N bond. The bimolecular rate constant for the reaction of e_{aq}^- with protonated dopamine has been determined to be 2.5×10^8 dm^3 mol^{-1} s^{-1}. The transient optical absorption band ($\lambda_{max} = 355$ nm, $\varepsilon = 3760$ dm^3 mol^{-1} cm^{-1}) formed on reaction of H atoms with protonated dopamine has been assigned to a H-adduct of dopamine. The bimolecular rate constant for the reaction has been determined to be 4.2×10^9 dm^3 mol^{-1} s^{-1} from the build-up kinetics of the 355 nm band. The transient H-adduct decays with the formation of ammonia. The isopropanol radical is unable to undergo a one electron transfer reaction with dopamine, whereas an equilibrium is established between the benzamide radical anion and dopamine from which the redox potential for the $D/D^{\bullet-}$ couple has been determined to be -1.91 V. The dopamine radical anion ($D^{\bullet-}$) is a strong reducing agent and is able to reduce methyl viologen with a bimolecular rate constant of 3.3×10^{10} dm^3 mol^{-1} s^{-1}. Specific one electron oxidants are able to undergo one electron transfer reactions forming a dopamine semiquinone radical ($DSQ^{\bullet}$) ($\lambda_{max} = 290$ nm, $\varepsilon = 7750$ dm^3 mol^{-1} cm^{-1}).

Compounds containing both amines and phenolic groups form an important class of compounds which are used as radiosensitizers and radio-protective agents and are also found in biological systems.[1,2] Therefore, it is important to study the electron transfer reactions with such biologically important classes of compounds. Dopamine deficiency in the neuron system of the brain causes Parkinson's disease and psychotic disorders.[3,4] Free radical induced oxidation of 3,4-dihydroxyphenylalanine has been shown to form melanine, a characteristic compound found in the cancer of the pigment cells.[5,6] The pulse radiolysis technique has been employed for the study of transient species formed on reaction of primary radiolytic species of water with such compounds. Such studies have gained importance as they can be used to monitor the early steps involved in the electron transfer reactions.[7]

The reactions of OH radicals with dopamine are reported in the literature.[3] In the present paper, electron transfer reactions with dopamine and the redox properties of transient species formed on reaction with e_{aq}^-, H atoms and different oxidising and reducing species are reported.

Experimental

Preparation of Solutions.—Dopamine [4-(2-aminoethyl)-benzene-1,2-diol] obtained from Sigma Chemicals was used after repeated crystallisation from methanol and dried in a vacuum oven. The solvent was deionised 'nano' pure water and freshly prepared solutions were used for each experiment. Indian oxygen 'iolar' grade N_2, O_2 and N_2O gases were used for purging the solutions. The reaction with H atoms was studied in N_2 saturated solutions at pH = 1.0, where e_{aq}^- are converted to H atoms ($H^+ + e_{aq}^- \rightarrow H + H_2O$) with G(H) = 3.5 (species per 100 eV absorbed energy)[8] and OH radicals are scavenged by *tert*-butanol [$(CH_3)_3COH + OH \rightarrow {}^{\bullet}CH_2(CH_3)_2COH + H_2O$]. The reaction with e_{aq}^- was studied in N_2 saturated solutions at pH $\geqslant$ 7.0 in the presence of *tert*-butanol to scavenge OH radicals. The pK values of different deprotonated forms of dopamine are shown in Scheme 1.[9] The aqueous solutions of dopamine (pH $\geqslant$ 7) are highly sensitive to oxygen to give the characteristic red colour of quinone, hence the solutions were rigorously protected from oxygen by first flushing the cell containing dopamine with N_2 and then N_2 saturated solution was introduced into the cell through a rubber septum. In this way, aqueous solutions (pH $\geqslant$ 7) of dopamine did not give the characteristic red colour on prolonged storage. The ground state absorption spectra of an aqueous solution of dopamine indicated λ_{max} at 275 nm and the extinction coefficient was determined to be 2265 dm^3 mol^{-1} cm^{-1} from the linear plot of optical density (OD) *vs.* concentration in the lower concentration region.



Scheme 1

Irradiations.—The pulse radiolysis experimental set-up employing 50 ns pulses of 7 MeV electrons from a linear accelerator has been described elsewhere.[10] An aerated aqueous solution of KSCN (10 mmol dm^{-3}) was used for measuring the dose delivered per pulse taking $G\varepsilon$ = 20 490 dm^3 mol^{-1} cm^{-1} per 100 eV at 500 nm for the transient $(SCN)_2^-$ species.[11] The dose per pulse was ~16 Gy. Steady state γ-irradiations were carried out with a Cobalt-60 γ-source whose dose rate, measured by Fricke dosimeter, was 16.6 Gy min^{-1}. All the experiments were carried out at 25 °C and the error in the measurement of bimolecular rate constant was within ±10%.

Estimations.—Ammonia was identified as a stable end product formed on reaction of e_{aq}^- with dopamine at neutral pH

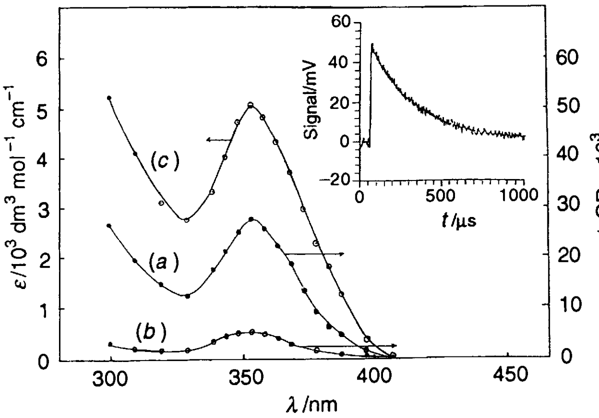


Fig. 1 Transient optical absorption spectrum obtained on pulse radiolysis of an aqueous solution of dopamine (1.0 × 10^{-2} mol dm^{-3}), phosphate buffer (pH = 7.0) and *tert*-butanol (1.0 mol dm^{-3}) at 1.6 µs after the pulse: (*a*) N_2 saturated; (*b*) N_2O saturated; (*c*) subtracting (*b*) from (*a*) and with correction for ground state absorption. Inset: decay trace of the transient at 355 nm. Dose = 16.0 Gy per pulse.

and was estimated by Nessler's reagent followed by colorimetry (λ_{max} = 420 nm)[12] using a Hitachi 330 model spectrophotometer. Since dopamine was interfering in NH_3 estimation by this method, we first separated NH_3 by distillation from the irradiated aqueous solution of dopamine using a Kjeldahl flask.[12] The flask was heated so that the contents boiled gently and the distillation was continued for 40 min. This time was suitable for complete removal of ammonia from the solution. Independent experiments with a standard solution of NH_4Cl were carried out and ammonia estimated directly (without distillation) and this modified method gave equal yields of ammonia. This method was fairly sensitive even up to 10^{-7} mol dm^{-3} NH_3 solution.

Results and Discussion

One Electron Reduction of Dopamine.—Reaction with e_{aq}^-. Fig. 1(*a*) shows the transient optical absorption spectrum obtained after 1.6 µs of the pulse in the pulse radiolysis of a N_2 saturated aqueous solution (pH = 7, phosphate buffer) containing dopamine (1 × 10^{-2} mol dm^{-3}) and *tert*-butanol (1.0 mol dm^{-3}). The transient band with λ_{max} = 355 nm was observed to decay by first order kinetics with $t_{\frac{1}{2}}$ = 200 µs. The decay pattern and the lifetime of the transient did not show any change with the solute concentration (10^{-3}–10^{-2} mol dm^{-3}) or dose (7.5–16.0 Gy per pulse).

The reaction of e_{aq}^- with dopamine (D) is studied by following the decay of transient absorption of e_{aq}^- produced on pulse radiolysis of a N_2 saturated aqueous solution (pH = 7.0, phosphate buffer, *tert*-butanol = 1.0 mol dm^{-3}, λ_{max} = 700 nm), containing different concentrations of dopamine (10^{-3}–10^{-2} mol dm^{-3}). The transient decay of e_{aq}^- becomes faster and of pseudo first order suggesting the reaction of e_{aq}^- with dopamine. The pseudo first order rate constant is observed to depend linearly with dopamine concentration. The bimolecular rate constant for the reaction of e_{aq}^- with dopamine as determined from the slope of linear plot of pseudo first order rate constant with dopamine concentration is 2.5 × 10^8 dm^3 mol^{-1} s^{-1}. The bimolecular rate constant for the reaction of e_{aq}^- with dopamine was also determined from the formation kinetics at 355 nm and the rate constant value was 1.8 × 10^8, close to that determined from the decay of e_{aq}^-.

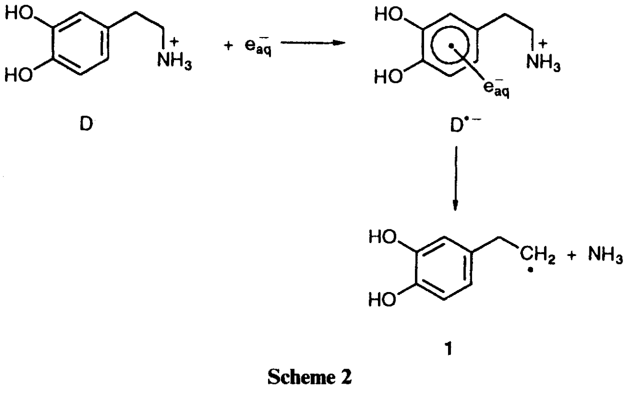
Under these conditions, the primary reactive species produced from the radiolysis of water would be e_{aq}^- and H atoms. The contribution from H atom reaction could be determined on pulse radiolysis of N_2O saturated aqueous dopamine containing *tert*-butanol, as *tert*-butanol is a strong OH radical and weak H atom scavenger. Fig. 1(*b*) indicates the transient optical absorption spectrum obtained on pulse radiolysis of a N_2O saturated aqueous solution of dopamine (1.0 × 10^{-2} mol dm^{-3}) containing *tert*-butanol (1.0 mol dm^3). This exhibits a small band at 355 nm as seen from Fig. 1(*b*). In order to obtain the true spectrum of the transient species formed on reaction of e_{aq}^-, correction has to be applied for H atom and ground state absorption of dopamine. The correction for the ground state absorption is applied to the observed ΔOD by using eqn. (1), where c_T is the concentration of the transient

$$\varepsilon^T = \varepsilon^G + \frac{\Delta OD}{c_T} \qquad (1)$$

produced (ε^T and ε^G are transient and ground state extinction coefficients at a given λ). Fig. 1(*c*) shows the corrected absorption spectra of transient species formed on reaction of e_{aq}^- with dopamine. The extinction coefficient of the transient species (ε^T) at 355 nm is thus determined to be 5100 dm^3 mol^{-1} cm^{-1}.

The bimolecular rate constant for the reaction of dopamine with e_{aq}^- at pH ~ 13.5 where dopamine is expected to be completely in deprotonated form (D^{2-}), is determined to be 2.3 × 10^7 dm^3 mol^{-1} s^{-1}. The rate constant for the reaction of e^-_{aq} has been reported for a number of amines both in the protonated and free amine form.[13] The amines in their free form react with e_{aq}^- with a rate constant value in the range 10^7–10^8 dm^3 mol^{-1} s^{-1} which is lower (~ 2–8 times) than that for the same in the protonated form. The present result of a low rate constant value for the free amine form of dopamine compared to that for the protonated form does support the earlier observation. The reaction of e_{aq}^- with other deprotonated forms could not be studied as the p*K* values are quite close and at a given pH, dopamine would not be present in one form alone.

Under steady state γ-radiolysis of dopamine (pH = 7.0, *tert*-butanol = 1.0 mol dm^{-3}, dopamine = 5.0 × 10^{-3} mol dm^{-3}, N_2 saturated), NH_3 was identified as the stable end product at different dose rates (1.8–16.6 Gy min^{-1}) and $G(NH_3)$ was determined to be 2.5 ± 0.3. The formation of NH_3 was also investigated in pulse irradiated aqueous solutions of dopamine under a different dose per pulse (9.1–16.0 Gy per pulse). $G(NH_3)$ was determined to 2.3 ± 0.3, close to the value obtained in steady state γ-radiolysis experiments. Hydrated electrons are known to lead to reductive deamination with aliphatic amino acids,[14] tyramine, tyrosine[13] and adrenalin.[1] The present experimental results show that almost all the hydrated electrons (taking *G* for e_{aq}^- as 2.7) take part in the reaction to split off ammonia from the side chain of protonated dopamine. Considering the reports in the literature on the reaction of e_{aq}^- with aromatic amines, it is suggested that the 355 nm band for the reaction of e_{aq}^- with dopamine is due to an e_{aq}^- adduct of dopamine ($D^{\bullet -}$, see Scheme 2). The transient band (355 nm)



Scheme 2

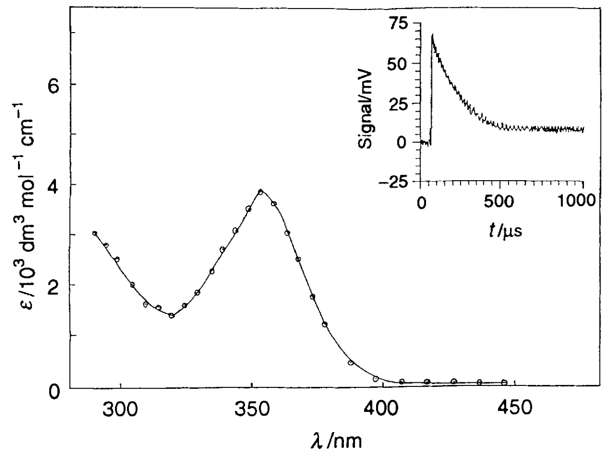


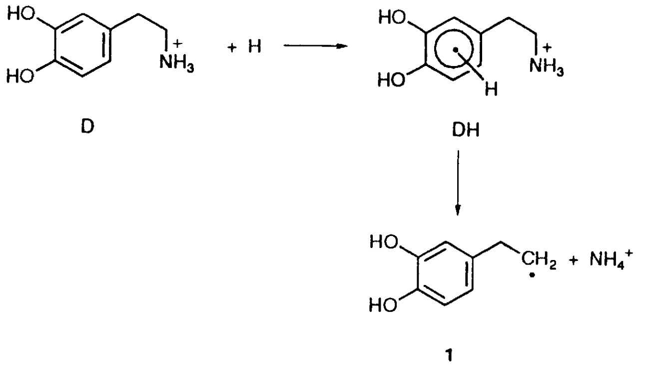
Fig. 2 Corrected transient optical absorption spectrum obtained on pulse radiolysis of aqueous solution of dopamine (1.0×10^{-2} mol dm^{-3}) (pH = 1.0) and *tert*-butanol (1.0 mol dm^{-3}) (N_2 saturated) immediately after the pulse. Inset: decay trace of the transient at 355 nm.

decay pattern (first order kinetics, see inset of Fig. 1) does support the assignment. The radical **1** which is expected to absorb at a wavelength of less than 270 nm may be formed after splitting off NH_3 from the electron adduct of dopamine ($D^{\bullet -}$). The decay modes of radical **1** are already described in the literature.[1] It can be concluded that the hydrated electron first adds to the phenyl ring of dopamine and successively goes to the C–N bond which breaks up to form ammonia. The exact mechanism for the formation of ammonia from the hydrated electron adduct of dopamine is difficult to determine at this stage. However, (i) first order decay of the transient band, (ii) its independent nature on solute concentration and dose rate and (iii) absence of dose rate and dose per pulse effect on $G(NH_3)$, suggest that the decay of the transient band and deamination processes are of unimolecular nature.

Reaction with H *atoms.* Pulse radiolysis of N_2 saturated aqueous dopamine (1.0×10^{-2} mol dm^{-3}, pH = 1.0, *tert*-butanol = 1.0 mol dm^{-3}) showed the formation of a transient band with $\lambda_{max} \sim 355$ nm. When the same experiment was repeated in the presence of isopropanol (H atom scavenger) the ΔOD value at 355 nm drastically reduced to 0.003 from 0.022. This essentially shows that the band with $\lambda_{max} = 355$ nm is due to the reaction of a H atom with dopamine. The possibility of the *tert*-butyl alcohol radical reacting with dopamine to give the 355 nm band was also examined (pH 6.0, N_2O saturation) and observed to be inert. Fig. 2 displays the corrected transient optical absorption spectrum for the transient formed by the reaction of H atoms and dopamine under the above mentioned pulse radiolytic condition. The band with $\lambda_{max} = 355$ nm was observed to decay by first order kinetics with $t_{\frac{1}{2}} = 150$ µs. The solute concentration (10^{-3}–10^{-2} mol dm^{-3}) and dose (7.5–16.0 Gy per pulse) did not show any effect on the decay kinetics of 355 nm band.

The rate constant, for the reaction of H atoms with dopamine was studied from build-up kinetics of the 355 nm band. The band was observed to grow by first order kinetics, the pseudo first order rate constant (k_{obs}) increases linearly with dopamine concentration. The bimolecular rate constant, determined from the slope of a linear plot of k_{obs} *vs.* dopamine concentration, was 4.2×10^9 dm^3 mol^{-1} s^{-1}. The high rate constant value excludes the possibility of this band being due to a H atom abstraction reaction. Under these experimental conditions, the reactivity (rate constant × concentration) of H atoms towards dopamine is 4.2×10^7 s^{-1} which is much higher than its reactivity towards *tert*-butanol (1.0×10^5 s^{-1}) and H atoms (5.6×10^4 s^{-1}). Therefore, all the H atoms are reacting with dopamine and the concentration of H atoms could be taken to be equal to the concentration of the transient species formed on reaction of H atoms with dopamine. This transient concentration (c_T) has been taken to correct the observed ΔOD and to give an extinction coefficient for the transient (ε^T) at a different wavelength. The extinction coefficient is thus determined to be 3760 dm^3 mol^{-1} cm^{-1} for the transient at 355 nm.

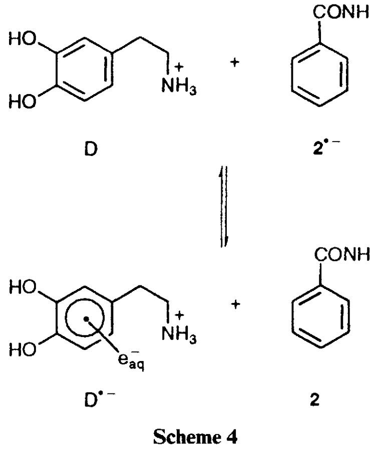
It is suggested that the 355 nm band is due to a H-adduct of dopamine (DH, see Scheme 3). It has been shown earlier that in acidic aqueous solutions of adrenalin (a catecholamine), the H atom reacts with solute to form the respective H-adduct ($\lambda_{max} = 360$ nm).[15] Tyramine and tyrosine are also known to form their respective H-adducts under appropriate pulse radiolytic conditions.[13] The absorption maxima, extinction coefficient and the decay kinetics matches nicely with those for the present case. It has also been shown that H atoms react with aryl alkyl amines and form a H atom adduct on the ring.[16]



Scheme 3

Ammonia was identified as the stable end product on γ-radiolysis of an aqueous solution of dopamine (pH = 1.0, *tert*-butanol = 1.0 mol dm^{-3}, N_2 saturated, dopamine = 5.0×10^{-3} mol dm^{-3}), with $G(NH_3) = 2.7$, which is lower than $G(H) = 3.5$. It suggests that the H-adduct of dopamine has more than one way to decay. In the absence of detailed product analysis, a complete decay scheme of H-adduct is difficult to determine at this stage. Time resolved studies did not show the formation of any new transient band (300–600 nm) with the decay of the 355 nm band. It is possible that a major part of the H-adduct may be decaying with the formation of radical **1** (see Scheme 3), which is expected to absorb at a wavelength of less than 270 nm. The fate of this type of radical is described elsewhere.[1]

Reaction with specific one electron reductants. Isopropyl alcohol radicals, formed on reaction of OH radicals with isopropanol, are a strong reducing agent with a reduction potential of −1.05 V with respect to NHE.[17] The pulse



Scheme 4

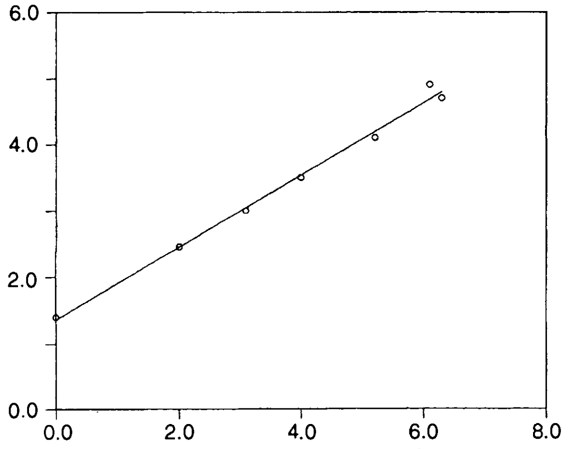


Fig. 3 Variation of k_{obs} with dopamine concentrations for the reactions of dopamine with benzamide radical anion

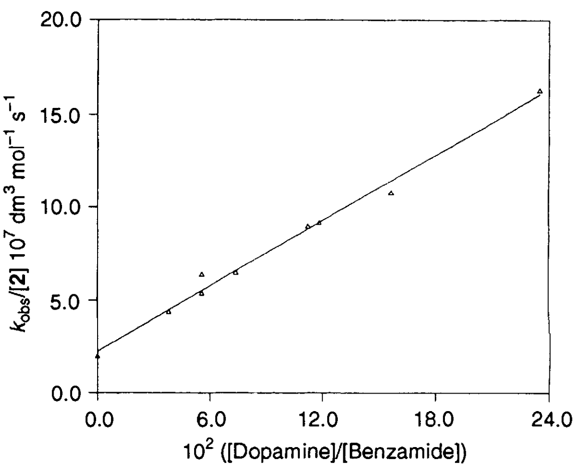


Fig. 4 Plot of k_{obs}/[**2**] *versus* [D]/[**2**] for various concentrations of dopamine (D) and benzamide (**2**) (Scheme 4)

radiolysis studies of N_2O saturated aqueous solutions (isopropanol = 1.0 mol dm^{-3}, pH = 6.0, dopamine = 4.0×10^{-3} mol dm^{-3}) showed the absence of the 355 nm band. Therefore, isopropyl alcohol radicals are unable to reduce dopamine and the reduction potential for the D/D$^{\bullet -}$ couple should be more negative than -1.05 V *versus* NHE.

The radical anion of benzamide is shown to be a strong reducing agent with redox potential $\simeq -2.0$ V *versus* NHE.[18] The reduction of dopamine by the radical anion of benzamide is studied by following the decay of the transient band of benzamide radical anion (430 nm) for various concentrations of dopamine (2.0×10^{-4}–1.0×10^{-3} mol dm^{-3}) (Scheme 4). The decay becomes faster and of first order showing the reduction of dopamine by radical anion of benzamide. Fig. 3 shows the variation of pseudo first order rate constant (k_{obs}) for the decay of the 430 nm band of benzamide radical anion formed on pulse radiolysis of N_2 saturated aqueous solutions (benzamide = 4.0×10^{-3} mol dm^{-3}, *tert*-butanol = 0.5 mol dm^{-3}) for various dopamine concentrations. The transient decay of the 430 nm band does not come to the base line for higher concentrations of dopamine and the decay was found to be affected by benzamide concentrations. In addition to these observations, the decay of the 355 nm band, formed on reaction of e_{aq}^- with dopamine was also observed to be affected in the presence of small concentrations of benzamide.

These results suggest that the reduction of dopamine by the radical anion of benzamide is a reversible process. The equilibrium constant $K = k_f/k_r$ could be evaluated by the use of eqn. (2), where k_f and k_r are forward and reverse reaction rate constants.

$$k_{obs} = k_f[\mathrm{D}] + k_r[\mathbf{2}] \qquad (2)$$

$$\frac{k_{obs}}{[\mathbf{2}]} = k_f([\mathrm{D}]/[\mathbf{2}]) + k_r \qquad (3)$$

A plot of k_{obs}/[**2**] *versus* [D]/[**2**] [eqn. (3)] (Fig. 4) gives a straight line with slope $k_f = 5.9 \times 10^8$ dm^3 mol^{-1} s^{-1} and intercept $k_r = 2.2 \times 10^7$ dm^3 mol^{-1} s^{-1}. The equilibrium constant is thus determined to be 27 at 25 °C. The difference in redox potential of **2**/**2**$^{\bullet -}$ and D$^{\bullet -}$/D couples equals RTF^{-1} ln$K$ = 0.059 log$K$. Taking the redox potential for the **2**/**2**$^{\bullet -}$ couple as -2.0 V,[18] the redox potential for the D/D$^{\bullet -}$ couple is determined to be -1.91 V *versus* NHE. These studies show that the radical (D$^{\bullet -}$) formed on reaction of e_{aq}^- with dopamine is also a strong reducing agent and is expected to reduce methyl viologen (MV^{2+}), whose redox potential is -0.45 V.[19] Semi-reduced methyl viologen (MV^+) is known to have transient optical absorption bands with λ_{max} = 395 and 605 nm. On pulse radiolysis of a N_2 saturated aqueous solution of dopamine (5.0×10^{-2} mol dm^{-3}, pH = 6.0, *tert*-butanol = 1.0 mol dm^{-3}), containing low concentrations (2.0–4.0×10^{-6} mol dm^{-3}) of methyl viologen, showed the formation of characteristic absorption bands of semi-reduced methyl viologen. This shows the reduction of methyl viologen by the dopamine radical anion. The bimolecular rate constant for this reaction, determined from the growth of the 395 and 605 nm bands, were 3.1×10^{10} and 3.5×10^{10} dm^3 mol^{-1} s^{-1} respectively.

One Electron Oxidation of Dopamine.—Reactions with specific one electron oxidants. $Cl_2^{\bullet -}$ is a strong oxidizing agent with an oxidation potential of 2.10 V. $Cl_2^{\bullet -}$ formed on pulse radiolysis of an O_2 saturated aqueous solution (Cl^- = 2.0×10^{-2} mol dm^{-3}, pH = 1.5, λ_{max} = 345 nm) was observed to decay faster in presence of low concentrations of dopamine (10^{-4} mol dm^{-3}). The decay is of first order and the pseudo first order rate constant was observed to depend linearly on dopamine concentration. The bimolecular rate constant, for the reaction of $Cl_2^{\bullet -}$ with dopamine as determined from the slope of a linear plot of first order rate constant with dopamine concentrations, is 1.6×10^9 dm^3 mol^{-1} s^{-1}. The time resolved studies showed the formation of a new band with λ_{max} = 290 nm. Fig. 5 displays the corrected spectra obtained after 5 μs of the pulse. The concentration of OH radicals under the experimental condition has been taken to be the transient concentration. The extinction coefficient for the transient at 290 nm is determined to be 7650 dm^3 mol^{-1} cm^{-1}. It is known that one electron oxidation of dihydroxybenzenes (*e.g.* dopamine, catechol) results in the formation of the radical cation[20] at pH < 1 and semiquinone radical[1] at pH > 1. Moreover, the spectra shown in Fig. 5 depicts the same features as that shown for dopamine semiquinone radical in the literature.[3] Thus, the 290 nm band is suggested to be due to semiquinone radical of dopamine (DSQ$^{\bullet}$, see Scheme 5).

The oxidation of dopamine is also studied by various other specific one electron oxidants having different redox potentials.[21–23] In all these cases (Table 1), the transient band with λ_{max} = 290 nm was observed. In the case of $I_2^{\bullet -}$, the reaction is very slow and even at high dopamine concentrations significant absorbance of $I_2^{\bullet -}$ is observed at 290 nm. Therefore, the formation of a transient band at 290 nm is difficult to observe. The bimolecular rate constant values for the oxidation of dopamine are determined from the decay/growth of the transient bands. These values are observed to decrease with systems of lower redox potential values. Although the redox

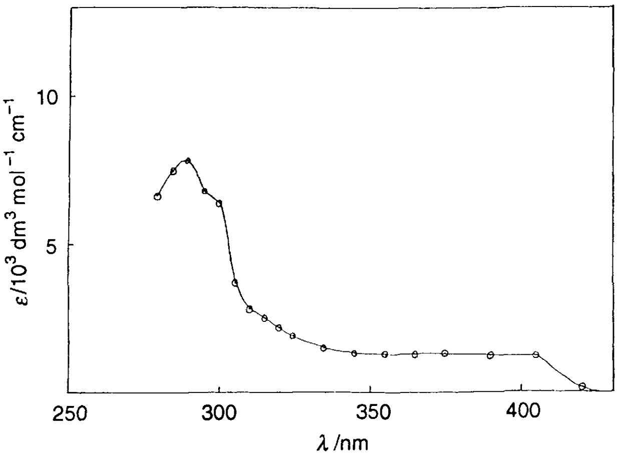
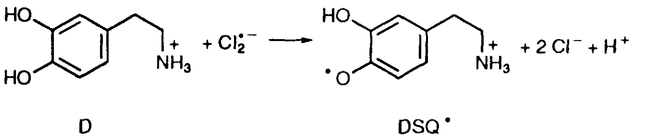


Fig. 5 Corrected transient optical absorption spectrum obtained on pulse radiolysis of aqueous solution of dopamine (1.5×10^{-3} mol dm^{-3}), Cl$^-$ (2.0×10^{-2} mol dm^{-3}), pH 1.5, O_2 saturated, at 5 μs after the pulse



Scheme 5

Table 1 Bimolecular rate constant (k) values for the oxidation of dopamine by various specific one electron oxidants

Redox reaction[a]	E°/V[b]	k/dm^3 mol^{-1} s^{-1}
$Cl_2^{\bullet -}$ + D	2.09	2.4×10^9
Tl^{+2} + D	1.98	1.3×10^9
$CH_3S^+SCH_3$ + D	1.39	1.3×10^9
$Br_2^{\bullet -}$ + D	1.63	1.1×10^8
$(SCN)_2^{\bullet -}$ + D	1.31	9.2×10^7
$N_3^{\bullet}$ + D	1.32	7.2×10^9
$[(CH_3)_2S]_2^{+}$ + D	—	5.1×10^7
$I_2^{\bullet -}$ + D	1.03	1.3×10^7

[a] D = Dopamine. [b] For oxidants.

potential for the couple $CH_3S^+SCH_3/CH_3SSCH_3$ is 1.39 V, the bimolecular rate constant value is observed to be quite high. One reason could possibly be due to the formation of thiyl radicals ($CH_3S^{\bullet}$) on reaction of OH radicals with CH_3SSCH_3 (ref. 24). The thiyl radicals are strong oxidising agents.[25] The oxidation of dopamine by thiyl radicals could contribute towards the higher rate constant value observed in the present case. The rate constant for the oxidation of dopamine by $N_3^{\bullet}$ radicals (pH = 6.0, N_2O-saturated) is also higher. The higher rate constant value by $N_3^{\bullet}$ radicals is reported in the literature and is explained as being due to a faster self-exchange rate for $N_3^{\bullet}/N_3^-$ (ref. 23).

Conclusions

Reductive deamination is observed in H-atom and hydrated electron induced reactions of dopamine. The hydrated electron form a radical anion of dopamine at the first site of attack. The radical anion of dopamine is observed to be a strong reducing agent with a redox potential of −1.91 V.

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