One-Electron Reduction of 3,3,6,6-Tetramethyl-3,4,6,7,9,10-hexahydro-(1,8)-(2*H*,5*H*)-acridinedione: A Pulse Radiolysis Study

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The radical anion formed on reaction of e_{aq}^- with acridinedione dye (ADH) exhibits transient optical absorption bands at $\lambda_{max} = 315$, 460, and >780 nm. The bimolecular rate constant for the reaction of e_{aq}^- with the dye was determined to be 2.7×10^{10} dm^3 mol^{-1} s^{-1}. It is converted to ($ADH_2^\bullet$) on protonation and showed an absorption band at 310 nm. At pH = 1, acetone ketyl radicals are observed to react with the dye with a bimolecular rate constant of 2.3×10^8 dm^3 mol^{-1} s^{-1}, and the transient optical absorption bands ($\lambda_{max} = 315$, 540 nm) are assigned to $(ADH_3)^{\bullet+}$. The radical anion ($ADH^{\bullet-}$) is a strong reducing agent, with reduction potential = −1.37 V vs NHE, and is able to undergo electron-transfer reactions with methyl viologen (MV^{2+}) and *p*-nitroacetophenone (*p*-NAP) with bimolecular rate constants of 4.9×10^9 and 6.1×10^9 dm^3 mol^{-1} s^{-1}, respectively.

1. Introduction

The acridinediones have found applications as efficient laser dyes.[1,2] The bichromophoric structure of the dyes allows them to act as both an electron donor and acceptor.[3−7] They are similar in structure to the 1,4-dihydropyridines and the biologically important β-dihydro nicotinamide adenine dinucleotide (NADH) and its analogues. In fact the acridinediones have been shown to mimic NADH to a greater extent than the 1,4-dihydropyridines because of the tricyclic structure, which is capable of protecting the enamine moiety.[8] There have been extensive studies on the photochemistry and electrochemistry of the 1,4-dihydropyridines.[9−24] We have previously carried out the electrochemical studies on various substituted acridinedione dyes.[25] The studies reveal that these compounds undergo stepwise two-electron oxidation to form the products. The nature of the products formed depends on the substitution on the nitrogen and in the 9-position in the case of acridinediones.[25] It has been reported for the 1,4-dihydropyridines that the presence of at least one hydrogen in the 4-position is extremely necessary for the oxidation to proceed.[26] The photochemical studies on the 1,4-dihydropyridines and acridinediones also lead to the formation of oxidized compounds.[27] The products of oxidation of acridinediones have been isolated and shown to be the same as that of the electrochemically oxidized products. Generally the N−H substituted compounds undergo oxidation to form the amortized central ring, whereas *N*-alkyl-substituted compounds form the acridinium salts.

While all the above-mentioned studies have concentrated on the oxidation of the acridinediones dyes, we have tried to carry out the electrochemical reduction of the dyes in the spectrophotometer cuvette at a platinum electrode and recorded the absorption spectrum of the radical formed, which has a maximum around 480 nm. Laser flash photolysis experiments have shown the decay of the anion radical having a transient maximum around 480 nm. In continuation to our earlier studies on the one-electron reduction of the *N*-methyl-substituted acridinedione dye,[7] we report the one-electron reduction of the N−H acridinedione dye using the pulse radiolysis technique. We have carried out the reduction using e_{aq}^- and specific one-electron reducing agents generated on reaction of e_{aq}^- with acetophenone, *p*-nitroacetophenone, and methyl viologen and determined the reduction potential of the dye.

2. Experimental Section

The dye was prepared following the procedure reported in the literature.[25] The absorption spectra were recorded with 10^{-5} mol dm^{-3} dye solutions using a Hewlett-Packard 8452A diode array spectrophotometer.

Pulse radiolysis experiments were carried out with high-energy electron pulses (7 MeV, 50 ns) obtained from a linear electron accelerator whose details are given elsewhere.[28,29] The dose delivered per pulse was determined with aerated aqueous solution of KSCN (1×10^{-2} mol dm^{-3}) with $G\epsilon = 21\,520$ dm^3 mol^{-1} cm^{-1} per 100 eV at 500 nm for the transient $(SCN)_2^{\bullet-}$ species, and it was close to 15 Gy per pulse. The *G* denotes the number of species per 100 eV of absorbed energy, and ϵ is the molar absorptivity of $(SCN)_2^{\bullet-}$ at 500 nm. Methyl viologen (MV^{2+}), *p*-nitroacetophenone (*p*-NAP), and acetophenone (AcP) were of high purity and used without further purification. The freshly prepared solutions in deionized Nanopure water were used for pulse radiolysis experiments. The pH of the solution was adjusted with NaOH/$HClO_4$ in phosphate buffer. The other details about the sample preparation are reported elsewhere.[6,7]

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The reaction of e_{aq}^- was carried out in N_2-saturated solutions in the presence of *tert*-butyl alcohol to scavenge $^•OH$ radicals [$(CH_3)_3COH + {}^•OH \rightarrow {}^•CH_2(CH_3)_2COH + H_2O$]. The reaction of α-hydroxy alcohol radicals ($^•CH_2OH$, $CH_3{}^•CHOH$) was studied in N_2O-saturated solutions, to convert e_{aq}^- to $^•OH$ radicals ($e_{aq}^- + N_2O \rightarrow N_2 + {}^•OH + OH^-$), containing 1 mol dm^{-3} methanol, ethanol, respectively. The reaction of $(CH_3)_2{}^•$-COH radicals was studied in N_2-saturated mixed solvent solution (2-propanol = 1 mol dm^{-3}, acetone = 0.1 mol dm^{-3}) in the pH range of 0.1−12.[30]

The transient species formed on pulse radiolysis were monitored using a 450 W xenon arc lamp, and a Hamamatsu R-955 photomulitiplier was used as the detector.[31] The photomultiplier output was digitized using a 100 MHz storage oscilloscope interfaced to a computer for kinetic analysis.[31] The first-order rate constant (k_{obs}) values were determined from the plot of ln(OD) vs time. The points back-calculated from the slope and intercept of the plots were found to fit the actual formation curve quite well. The bimolecular rate constant values were determined from the slope of the linear plot of k_{obs} vs solute concentration. The rate constant values were the average of at least three experiments, and the variation was within ±10%.

3. Results and Discussion

The ground-state optical absorption spectrum of ADH in neutral aqueous solution shows absorption band with λ_{max} = 402 nm ($\epsilon = 8.2 \times 10^3$ dm^3 mol^{-1} cm^{-1}) and 252 nm ($\epsilon = 17.8 \times 10^3$ dm^3 mol^{-1} cm^{-1}). The spectrum remained unchanged in the pH range of 1−12. In highly alkaline solutions, the optical absorption shifted to 478 nm with a pK value of 13.35. In highly acidic solutions ($HClO_4 \geq 1$ mol dm^{-3}), the longer wavelength (402 nm) absorption maxima shifted to 440 nm.

Pulse Radiolysis Study. *Reaction with* e_{aq}^-. The decay of e_{aq}^-, formed on pulse radiolysis of a N_2-saturated neutral aqueous solution (*tert*-butyl alcohol = 0.3 mol dm^{-3}, λ = 700 nm), was found to become faster on addition of very low concentration (0−2.5) × 10^{-4} mol dm^{-3} of ADH, suggesting high reactivity of e_{aq}^- with ADH. The bimolecular rate constant, determined from the linear plot of pseudo-first-order rate (k_{obs}) vs solute concentration (0−2.5) × 10^{-4} mol dm^{-3}, was (2.7 ± 0.7) × 10^{10} dm^3 mol^{-1} s^{-1}. The differential absorption spectrum (2 μs after the pulse) showed absorption bands with λ_{max} = 315, 460 and $\lambda > 780$ nm (Figure 1). The ground-state absorption spectrum of the dye has practically no absorption at $\lambda > 450$ nm, and, therefore, ground-state absorption is not expected to change the position of the 460 nm band (Figure 1). However, at 315 nm, the molar absorptivity of the dye is 0.3 × 10^3 dm^3 mol^{-1} cm^{-1} and may slightly affect the nature of the transient absorption spectrum. Since e_{aq}^- has completly decayed during this time, this spectrum should be due to the product of e_{aq}^- reaction with ADH. The bimolecular rate constant, determined from the formation kinetic studies at 315 nm, also gave same value.

The rate of the reaction (rate constant × concentration) of e_{aq}^- with ADH (6.7 × 10^6 s^{-1}) is much higher than with itself (2.5 × 10^4 s^{-1}). Therefore, almost all the electrons must have reacted with ADH to form the transient species. Under these conditions, the concentration of the transient species could be taken equal to that of e_{aq}^-. The molar absorptivity at 315 and 460 nm was determined to be 10.4 × 10^3 and 6.4 × 10^3 dm^3 mol^{-1} cm^{-1}, respectively. The entire spectrum decayed by first-order kinetics, with k = (6.3 ± 1.5) × 10^3 s^{-1}. The decay also remained independent of solute concentration (1−3) × 10^{-4} mol dm^{-3} and dose rate (16−48 Gy per pulse).

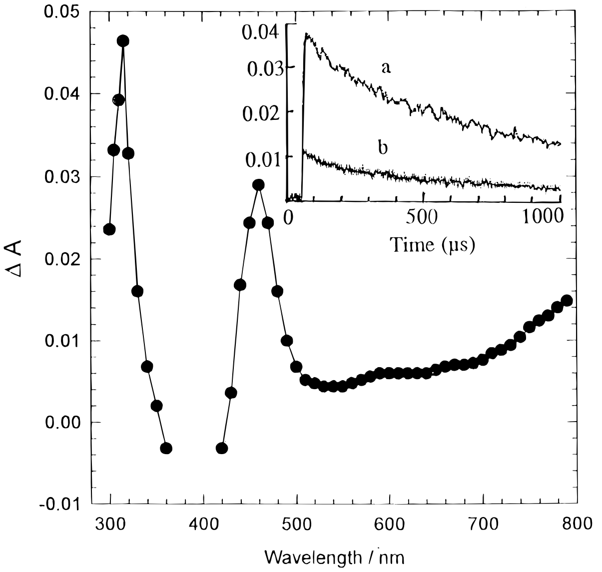
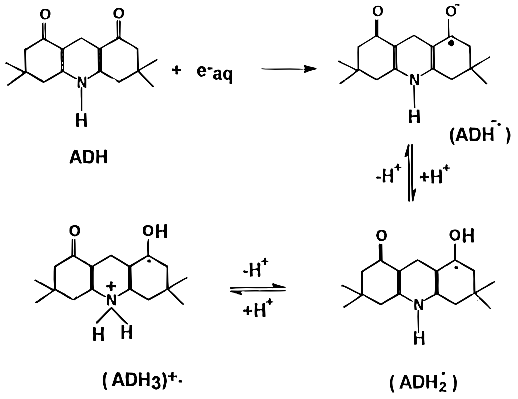


Figure 1. Transient optical absorption spectrum obtained on pulse radiolysis of N_2-saturated aqueous solution of ADH (2.5 × 10^{-4} mol dm^{-3}, pH = 6, *tert*-butyl alcohol = 0.3 mol dm^{-3}), 2 μs after the pulse. Inset show absorption−time signal at (a) 315 and (b) 780 nm.

SCHEME 1



The attack of e_{aq}^- is likely to occur at any one of the electron affinic heteroatoms [O(1), O(8)] of ADH leading to the formation of radical anion $ADH^{•-}$ (Scheme 1). It is also possible that the charge and the radical site may be spread over several sites including both oxygen and the nitrogen atom. The absorption bands (Figure 1) must be decaying to a stable or nonabsorbing (300−800 nm) species as the time-resolved studies do not show the formation of any new transient absorption band with the decay. At a slightly higher pH, the transient absorption at 315 nm started showing growth with the decay of transient absorption bands at 460 and >780 nm. Figure 2 shows the absorption time signal obtained on pulse radiolysis of N_2-saturated solution of the dye (2.5 × 10^{-4} mol dm^{-3}, pH = 11, *tert*-butyl alcohol = 0.3 mol dm^{-3}). The absorption at 315 nm showed buildup with k = 5.1 × 10^4 s^{-1}. Simultaneously, the absorption at 460 nm and $\lambda > 780$ nm showed decay with k = 5 × 10^4 s^{-1}. The differential transient optical absorption spectrum, 2.5 μs after the pulse, showed absorption bands at 315, 460 and $\lambda > 780$ nm (Figure 3a), similar to those observed at pH = 6. The bands in the differential absorption spectrum, 45 μs after the pulse, where the transformation is almost complete, showed a band with λ_{max} = 310 nm and with very little absorption in 450−780 nm region (Figure 3b). This

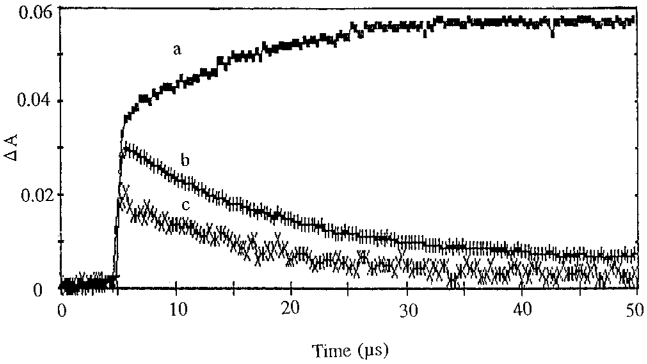


Figure 2. Absorption−time signal obtained on pulse radiolysis of N_2-saturated aqueous solution (pH = 11) of ADH (2.5×10^{-4} mol dm^{-3}) + *tert*-butyl alcohol (0.3 mol dm^{-3}) at (a) 315, (b) 460, and (c) 780 nm.

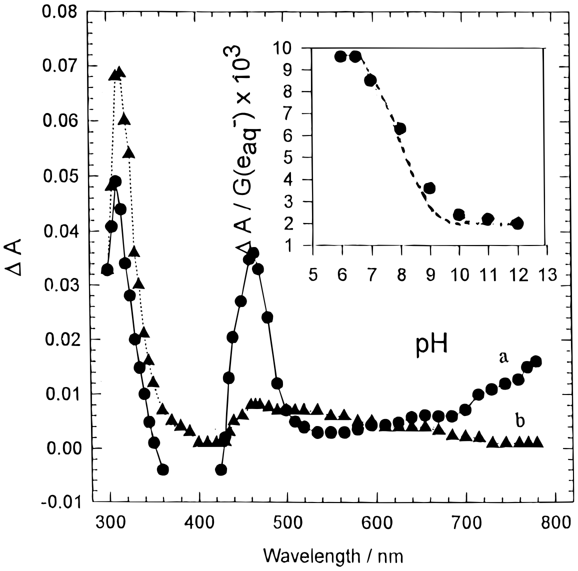


Figure 3. Transient optical absorption spectrum obtained on pulse radiolysis of N_2-saturated solution of ADH (2.5×10^{-4} mol dm^{-3}) + *tert*-butyl alcohol (0.3 mol dm^{-3}) at pH = 11, (a) 2.5 and (b) 45 μs after the pulse. Inset shows the variation of absorption (460 nm) as a function of pH, and - - - is the computed curve.

transient absorption spectrum should be due to $ADH_2^{\bullet}$ (Scheme 1). The bimolecular rate constant for the reaction of e_{aq}^- with the dye, determined from the decay of e_{aq}^- at 700 nm, was 1.8×10^{10} dm^3 mol^{-1} s^{-1}, close to the value determined at pH = 6. The molar absorptivity at 310 nm was determined to be 14.8×10^3 dm^3 mol^{-1} cm^{-1}. It decayed by second-order kinetics with $2k = 3.3 \times 10^8$ dm^3 mol^{-1} s^{-1}. *tert*-Butyl alcohol radicals, [$^{\bullet}CH_2(CH_3)_2COH$], formed on $^{\bullet}H$ atom abstraction by $^{\bullet}H/^{\bullet}OH$ radicals, are observed to be unreactive toward the dye. However, these radicals may interfere with the bimolecular decay of the radical species generated from the radiolysis of the dye. Therefore the actual bimolecular rate constant value in the absence of *tert*-butyl alcohol radicals may be slightly lower than the value reported here.

The transient absorption (λ = 460 nm) at pH = 6 showed very little decay during 45 μs after the pulse, whereas at pH = 11 it had almost completely decayed. The absorption values (ΔA_{obs}) as a function of pH were fitted to the modified Hendersen equation (eq 1)[32]

$$\Delta A_{obs} = \frac{\Delta A_1}{1 + 10^{pH-pK}} + \frac{\Delta A_2}{1 + 10^{pK-pH}} \qquad (1)$$

where ΔA_1 and ΔA_2 are the observed difference in the absorbance at pH values well before and well beyond the p*K*. The inflection point at pH = 8 (inset of Figure 3) should be due to the protonation of the radical anion as the dye in the ground state does not show any spectral changes in this pH range of 6−11.

The kinetic and spectral parameters of the transient species formed on reaction of e_{aq}^- with N−H and N−CH_3 acridinedione dyes were similar. The radical anion of N−CH_3 acridinedione dye showed protonation with a pK_a value of 4.7, whereas with N−H acridinedione dye the pK_a value was observed at 8. The kinetic and spectral parameters of the transient species formed on protonation, in both the cases, were also similar.

At pH > 12, the dye undergoes deprotonation with a pK_a = 13.35, and even at pH = 14, the dye may not be completely present in the deprotonated form. Moreover, the deprotonated form has high ground-state absorption with λ_{max} = 480 nm. Considering these difficulties, the reaction of e_{aq}^- with the deprotonated form could not be carried out.

In acidic solutions the transient bands in the differential absorption spectrum formed on reaction of e_{aq}^- with ADH showed slow growth at 315 nm with decay at 460 nm (pH ≤ 4). Simultaneously, a new absorption band appeared in the region of 540 nm. This transformation was not observed at pH ≥ 4. But the reaction of e_{aq}^- with ADH could not be carried out at pH < 3.5 owing to its conversion to $^{\bullet}H$ atoms ($e_{aq}^- + H^+ \rightarrow {}^{\bullet}H + H_2O$). However, it was possible to study one-electron reduction of the dye in this pH range (see text) with specific reducing agents.

Reaction with Specific Reducing Agents. One-electron reduction of organic compounds in the pH range of 0.1−12 could be conveniently studied with a relatively strong reducing agent, $(CH_3)_2{}^{\bullet}COH$ radical (redox couple = $(CH_3)_2{}^{\bullet}COH/(CH_3)_2CO$, H^+), which has a reduction potential of −1.1 V at pH = 7. A matrix containing 2-propanol (1 mol dm^{-3}) and acetone (0.1 mol dm^{-3}) would produce $(CH_3)_2{}^{\bullet}COH$ radicals with a *G* value of 6 in the pH range of 0.1−12 according to following reactions.

$$(CH_3)_2CO + e_{aq}^- \rightarrow (CH_3)_2CO^{\bullet -} \qquad (2)$$

$$(CH_3)_2CO^{\bullet -} + H_2O \rightarrow (CH_3)_2{}^{\bullet}COH + OH^- \qquad (3)$$

$$(CH_3)_2CHOH + {}^{\bullet}H/{}^{\bullet}OH \rightarrow (CH_3)_2{}^{\bullet}COH + H_2/H_2O \qquad (4)$$

Under these experimental conditions, e_{aq}^-, $^{\bullet}H$, and $^{\bullet}OH$ radicals would react with the matrix and $(CH_3)_2{}^{\bullet}COH$ radicals would be available for reaction with the dye. Pulse radiolysis of N_2-saturated neutral aqueous solution of ADH (2.5×10^{-4} mol dm^{-3}) in 2-propanol (1 mol dm^{-3}) + acetone (0.1 mol dm^{-3}) did not produce any transient absorption in 300−750 nm region, suggesting that the reduction potential for the $ADH/ADH^{\bullet -}$ couple is more negative than that of $(CH_3)_2{}^{\bullet}COH/(CH_3)_2CO$, H^+ couple (−1.1 V). These studies are in contrast to N−CH_3-substituted acridinedione dye where α-hydroxy alcohol radicals [$^{\bullet}CH_2OH$, $CH_3{}^{\bullet}CHOH$, $(CH_3)_2{}^{\bullet}COH$] were able to undergo one-electron reduction. Since the reduction potential value of $(CH_3)_2{}^{\bullet}COH/(CH_3)_2CO$, H^+ couple becomes more negative at lower pH, pulse radiolysis studies were carried out at pH = 1. At pH = 1, the pulse radiolysis of N_2-saturated solution [$(CH_3)_2CHOH$ = 1 mol dm^{-3}, $(CH_3)_2CO$ = 0.1 mol dm^{-3}, ADH = 2.5×10^{-4} mol dm^{-3}] showed transient bands in the differential absorption spectrum with λ_{max} = 315 and 540 nm (Figure 4), suggesting the reduction of ADH. The bimolecular rate

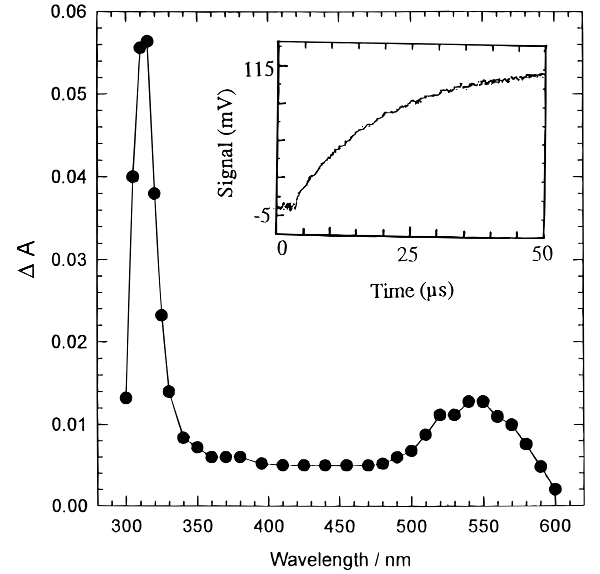


Figure 4. Transient optical absorption spectrum obtained on pulse radiolysis of N_2-saturated aqueous solution of 2-propanol (1 mol dm^{-3}), acetone (0.1 mol dm^{-3}), and ADH (2.5×10^{-4} mol dm^{-3}, pH = 1) 45 μs after the pulse. Inset shows absorption time signal at 315 nm.

constant, determined from the growth of transient absorption at 315 nm for various concentrations of ADH $(0.6-2.5) \times 10^{-4}$ mol dm^{-3} was 2.3×10^8 dm^3 mol^{-1} s^{-1}. Both the bands decayed by first-order kinetics with $k = 1.1 \times 10^3$ s^{-1}. Since the nature of the transient spectrum, its decay, and formation kinetics were different from those of $ADH^{\bullet-}$ and $ADH_2^{\bullet}$ species (Figure 4), it could not be assigned either to $ADH^{\bullet-}$ or to $ADH_2^{\bullet}$ species. It is possible that the radical anion formed on reduction of the dye gets protonated to $ADH_2^{\bullet}$ species and finally to $(ADH_3)^{\bullet+}$. The transient optical absorption spectrum is therefore assigned to $(ADH_3)^{\bullet+}$ species (Scheme 1). The observed absorbance at 540 nm as a function of pH was fitted according to eq 1, and the inflection point was observed at pH = 2.2 (Figure 5). This should be due to the protonation of the radical anion as the dye in the ground state has no pK in this region. Since $(CH_3)_2{}^{\bullet}COH$ radicals were unable to reduce ADH at pH = 6, the transient absorption bands due to $ADH_2^{\bullet}/ADH_3^{\bullet+}$ were not seen. At lower pH, $ADH^{\bullet-}$ after its formation is converted to $(ADH_3)^{\bullet+}$. The kinetic and spectral parameters of the transient species formed on one-electron reduction of N−H and $N-CH_3$ acridinedione dyes in acidic solutions were similar. N−H acridinedione dye showed pK_a value of 2.2, whereas $N-CH_3$ dye showed pK_a value of 2.6.

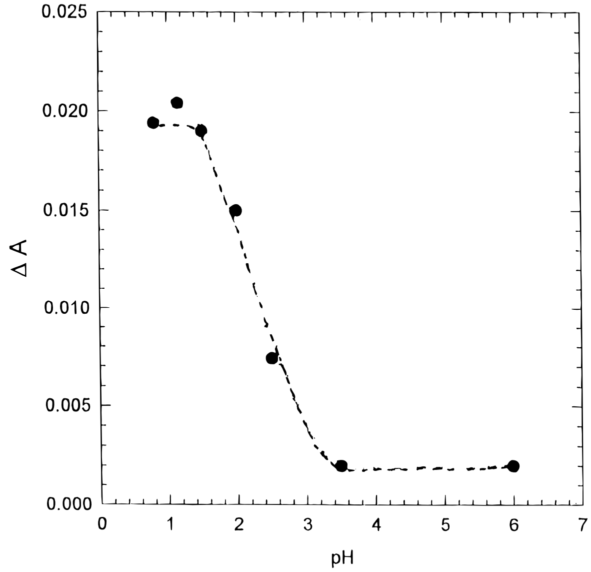


Figure 5. Variation of absorbance at 315 nm (45 μs after the pulse) as a function of pH. - - - is the computed curve.

α-Hydroxy alcohol radicals generated from ethanol and methanol were also able to reduce ADH at pH = 1 and formed a transient optical absorption spectrum similar to that shown in Figure 4. The bimolecular rate constant values are shown in Table 1. $CO_2^{\bullet-}$ is a strong reducing agent with reduction potential value of −1.9 V vs NHE. But it could not be used for such studies as the dye was not stable in this medium ($HCOO^- = 2 \times 10^{-2}$ mol dm^{-3}).

From these studies, it appears that the radical anion of ADH has high reduction potential value. Therefore, it should be able to undergo electron-transfer reaction with solute having lower reduction potential value. $MV^{2+}/MV^{\bullet+}$ and p-NAP/p-$NAP^{\bullet-}$ are such couples whose reduction potential values are low (−0.458 and −0.358 V, respectively), and the transient optical absorption bands of the reduced species have high molar absorptivity ($\epsilon_{605} = 12\,800$ and $\epsilon_{550} = 2900$ dm^3 mol^{-1} cm^{-1}, respectively). The pulse radiolysis of N_2-saturated solution of ADH (3×10^{-4} mol dm^{-3}) + (*tert*-butyl alcohol = 0.3 mol dm^{-3}) in the presence of low concentration of MV^{2+} (1×10^{-5} mol dm^{-3}) showed buildup at 605 nm, and the bimolecular rate constant was determined to be 4×10^9 dm^3 mol^{-1} s^{-1}. Similarly, with p-NAP, the buildup kinetics at 550 nm gave a bimolecular rate constant value of 6×10^9 dm^3 mol^{-1} s^{-1}, suggesting electron transfer from $ADH^{\bullet-}$ to MV^{2+} and p-NAP (reaction 5).

TABLE 1: Kinetic and Spectral Parameters for the Transient Species Formed on a Reaction of e_{aq}^- and Specific One-Electron Reductants with ADH

reaction	pH	λ_{max}/nm	bimolecular rate constant/ dm^3 mol^{-1} s^{-1}	ϵ/dm^3 mol^{-1} cm^{-1}	decay/s^{-1}
ADH + e_{aq}^-	6	315	2.7×10^{10}	10.4×10^3	6.3×10^3
		460		6.4×10^3	
		>780			
ADH + e_{aq}^-	11	310	1.8×10^{10}	14.8×10^3	3.3×10^{8}[a]
ADH + $(CH_3)_2{}^{\bullet}COH$	1	315	2.3×10^8	5.6×10^3	1.1×10^3
		540			
ADH + $CH_3{}^{\bullet}CHOH$	1	315	2.1×10^8		
		540			
ADH + ${}^{\bullet}CH_2OH$	1	315	1.5×10^8		
		540			
$ADH^{\bullet-}$ + MV^{2+}	6	395	4.9×10^9		
		605			
$ADH^{\bullet-}$ + p-NAP	6	550	6.1×10^9		

[a] Decay by second-order kinetics (dm^3 mol^{-1} s^{-1}).

$$\mathrm{ADH}^{\bullet-} + \mathrm{MV}^{2+}/p\text{-NAP} \rightarrow \mathrm{ADH} + \mathrm{MV}^{\bullet+}/p\text{-NAP}^{\bullet-} \quad (5)$$

The time-resolved studies showed the formation of characteristic absorption bands of $\mathrm{MV}^{\bullet+}$ and p-$\mathrm{NAP}^{\bullet-}$. These experiments were carried out at low dose rate (8 Gy per pulse) to avoid radical radical reactions. The G value of the reduced products, $\mathrm{MV}^{\bullet+}/p\text{-NAP}^{\bullet-}$, was close to 2.6, showing complete electron transfer from $\mathrm{ADH}^{\bullet-}$. These studies support the results that the reduction potential value of $\mathrm{ADH/ADH}^{\bullet-}$ couple is much higher than that of $\mathrm{MV}^{2+}/\mathrm{MV}^{\bullet+}$ and $p\text{-NAP}/p\text{-NAP}^{\bullet-}$ couples.

Reduction Potential of ADH/ADH$^{\bullet-}$ *Couple.* The decay of the transient band formed on pulse radiolysis of N_2-saturated aqueous solution of ADH (2.5×10^{-4} mol dm^{-3}, *tert*-butyl alcohol = 0.3 mol dm^{-3}) was affected on addition of low concentration of acetophenone [AcP, $(0.5-1) \times 10^{-4}$ mol dm^{-3}]. The transient absorption band of the radical anion of AcP also showed accelerated decay on addition of low concentration of ADH. The decay of $\mathrm{ADH}^{\bullet-}$, in the presence of low concentration of AcP, was also accelerated on increasing the concentration of ADH. These studies suggest the existence of the following equilibrium:

$$\mathrm{ADH}^{\bullet-} + \mathrm{AcP} \rightleftharpoons \mathrm{AcP}^{\bullet-} + \mathrm{ADH} \quad (6)$$

The pseudo-first-order rate (k_{obs}) for this equilibrium reaction could be written as follows

$$k_{\mathrm{obs}} = k_{\mathrm{f}}\,[\mathrm{AcP}] + k_{\mathrm{r}}\,[\mathrm{ADH}] \quad (7)$$

$$\frac{k_{\mathrm{obs}}}{[\mathrm{ADH}]} = k_{\mathrm{f}}\frac{[\mathrm{AcP}]}{[\mathrm{ADH}]} + k_{\mathrm{r}} \quad (8)$$

where k_{f} and k_{r} are the rate constant for the forward and reverse reactions, respectively. The pseudo-first-order rate (k_{obs}) was determined on monitoring the decay of the transient band of $\mathrm{ADH}^{\bullet-}$ ($\lambda = 315$ nm) for various concentrations of ADH $(1-4) \times 10^{-4}$ mol dm^{-3} and AcP $(3-10) \times 10^{-5}$ mol dm^{-3} under conditions such that the initial attack of e_{aq}^{-} is with ADH and $\mathrm{ADH}^{\bullet-}$ would then react with AcP. The plot of k_{obs}/[ADH] vs [AcP]/[ADH] was linear (Figure 6) with slope = $k_{\mathrm{f}} = 5.0 \times 10^{8}$ dm^3 mol^{-1} s^{-1} and intercept = $k_{\mathrm{r}} = 0.2 \times 10^{8}$ dm^3 mol^{-1} s^{-1}. The equilibrium constant $K = k_{\mathrm{f}}/k_{\mathrm{r}}$, was determined to be 25. This is related to the difference in the reduction potential value of two couples.

$$\Delta E^\circ = E^\circ_{\mathrm{ADH/ADH}^{\bullet-}} - E^\circ_{\mathrm{AcP/AcP}^{\bullet-}} \quad (9)$$

$$= 0.059 \log K = 0.082 \quad (10)$$

Taking the reduction potential value for the $\mathrm{AcP/AcP}^{\bullet-}$ couple = −1.29 V vs NHE,[33] the reduction potential value of the $\mathrm{ADH/ADH}^{\bullet-}$ couple was determined to be −1.37 V vs NHE. Owing to the solubility limitations, the k_{obs} values were determined over a narrow range of concentration of AcP and ADH. These limited studies resulted in scattered data, and the uncertainty in the redox potential value was high (± 0.03). The radical anion of N−H acridinedione dye is a strong reducing agent with reduction potential value of −1.37 V, whereas the reduction potential value of $\mathrm{N-CH_3}$ dye has a lower value of −0.586 V.

Conclusions

The hydrated electron showed high reactivity ($k = 2 \times 10^{10}$ dm^3 mol^{-1} s^{-1}) with N−H acridinedione dye (ADH). α-Hydroxy alcohol radicals were observed to react at a much lower rate (≈2×10^{8} dm^3 mol^{-1} s^{-1}). The radical anion has high reduction potential (−1.37 V vs NHE) and showed transformation to heteroatom (O) protonated species, $\mathrm{ADH_2}^{\bullet}$. In acidic solutions, it is converted to protonated species ($\mathrm{ADH_3}^{\bullet+}$) with a p$K$ value of 2.2.

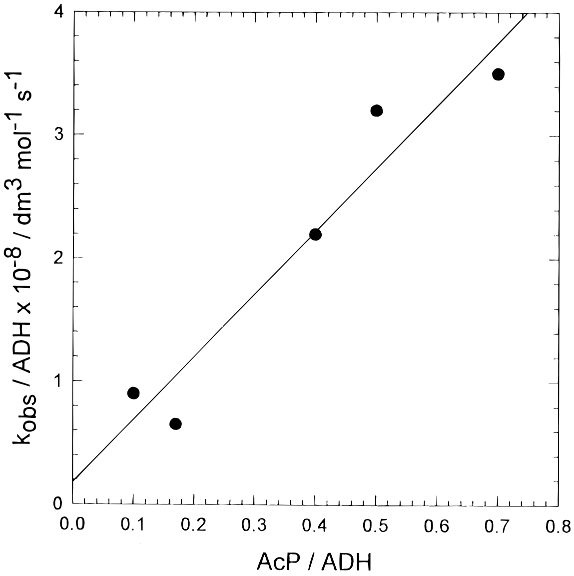


Figure 6. Plot of k_{obs}/[ADH] vs [AcP]/[ADH].

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