# ARTICLES

## One-Electron Reduction of Acridine-1,8-dione in Aqueous Solution: A Pulse Radiolysis Study

**H. Mohan,[†] N. Srividya,[‡] P. Ramamurthy,[‡] and J. P. Mittal*,[†,§]**

*Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India, and Department of Inorganic Chemistry, University of Madras, Madras 600 025, India*

In a neutral aqueous solution of acridine-1,8-dione (AD) the $e_{aq}^-$ was observed to react with a bimolecular rate constant of $1.5 \times 10^{10}$ dm$^3$ mol$^{-1}$ s$^{-1}$ and form transient optical absorption bands with $\lambda_{max} = 305$, 475 nm, a shoulder at 680 nm, and increasing absorption with $\lambda > 800$ nm. The entire spectrum from $\lambda > 450$ nm decayed by first-order kinetics with $k = 1.5 \times 10^5$ s$^{-1}$, whereas the absorption at 315 nm showed growth with $k = 1.6 \times 10^5$ s$^{-1}$. It decayed by second-order kinetics with $2k/\epsilon l = 1 \times 10^4$ s$^{-1}$. The transient optical absorption bands at 305, 475, 680, and >800 nm are assigned to the electron adduct, AD$^{\bullet-}$, which on protonation forms H adduct (ADH$^\bullet$) with $\lambda_{max} = 315$ nm and a p$K$ value of 4.7. In basic solutions (pH = 13), AD$^{\bullet-}$ does not show slow transformation to ADH$^\bullet$ while in acidic solutions (pH = 3), only ADH$^\bullet$ was observed ($\lambda_{max} = 315$ nm). ADH$^\bullet$ in highly acidic solutions (pH < 3) protonates to form (ADH$_2$)$^{\bullet+}$ ($\lambda_{max} = 315$, 560 nm) with a p$K$ value of 2.6. AD/AD$^{\bullet-}$ established an equilibrium with MV$^{2+}$/MV$^{\bullet+}$ and the reduction potential for AD/AD$^{\bullet-}$ couple was determined to be $-0.586 \pm 0.03$ V. α-Hydroxyalklly radicals ((CH$_3$)$_2$C$^\bullet$OH, CH$_3$C$^\bullet$HOH, and $^\bullet$CH$_2$OH) were able to reduce AD with bimolecular rate constant values of $3.2 \times 10^8$, $2.3 \times 10^8$, and $1.2 \times 10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$, respectively. The radical anion AD$^{\bullet-}$ was able to transfer electron to *p*-nitroacetophenone with a bimolecular rate constant of $6 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$.

## Introduction

The early studies on the dyes, which could act as both electron donors and acceptors, focused attention on the efficiency of these dyes to act as a class of good laser dyes, having stimulated emission in the blue region with lasing yields comparable to that of coumarin-102.[1−3] The photophysical and photochemical characteristics of these dyes were studied briefly by Timpe et al.[4] These dyes have also been used as photosensitizers for onium salt decomposition[5] in the polymerization of acrylates and methacrylates.[6] These dyes are important because of the similarity in structure to the 1,4-dihydropyridines which are analogs of the biologically important coenzymes, NADH (β-dihydronicotinamide adenine dinucleotide) and NADPH [β-dihydronicotinamide adenine dinucleotide (3′-phosphate)].[7−10] The photochemical reactions of 1,4-dihydropyridines, NADH, and NADPH have been studied in great detail.[11−20] In fact, the acridinedione dyes have been shown to mimic NADH to a greater extent than the 1,4-dihydropyridines due to the tricyclic structure which is capable of protecting the enamine moiety.[21] Recently, the electrochemical characteristics of the acridinedione dyes have been reported.[22] The electrochemical oxidation leads to the formation of products which have been isolated and characterized. As a continuation to the one-electron oxidation of acridinedione using pulse radiolysis,[23] the present study is carried out to understand the one-electron reduction of these dyes. We report the one-electron reduction of acridinedione dye with $e_{aq}^-$ and other reducing agents (CO$_2^{\bullet-}$, α-hydroxyalkyl radicals).

## Experimental Section

3,3,6,6,10-Pentamethyl-3,4,6,7,9,10-hexahydro-1,8-(2*H*,5*H*)-acridinedione (AD), shown in Scheme 1), was prepared following the procedure reported in the literature.[2,22]

Radiolysis of N$_2$-saturated neutral aqueous solution leads to the formation of three highly reactive species (H$^\bullet$, $^\bullet$OH, and $e_{aq}^-$) in addition to the formation of other less reactive molecular products (H$_2$, H$_2$O$_2$).[24]

$$H_2O \rightsquigarrow {}^\bullet H, {}^\bullet OH, e_{aq}^-, H_3O^+, H_2O_2, H_2 \qquad (1)$$
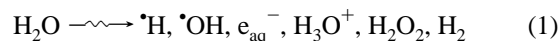
The reaction of $e_{aq}^-$ was carried out in an N$_2$-saturated solutions containing *tert*-butyl alcohol (0.3 mol dm$^{-3}$) to scavenge $^\bullet$OH radicals

$$(CH_3)_3COH + {}^\bullet OH \rightarrow {}^\bullet CH_2(CH_3)_2COH + H_2O \qquad (2)$$
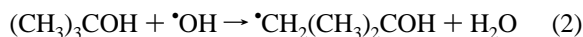
The pH of the solution was adjusted with NaOH/HClO$_4$ in phosphate buffers. The solutions were prepared in deionized Nanopure water and freshly prepared solutions were used in each case.

Pulse radiolysis experiments were carried out with high-energy (7 MeV) electron pulses (50 ns) generated from a linear electron accelerator.[25] An aerated aqueous solution of KSCN (10 mmol dm$^{-3}$) was used for measuring the dose delivered per pulse.[26] The dose delivered per pulse was ca. 15 J kg$^{-1}$. The reactions induced by α-hydroxyalkyl radicals were inves-

---

[†] Bhabha Atomic Research Centre.
[‡] University of Madras.
[§] Also affiliated as Honorary Professor with the Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India.
[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1997.

**SCHEME 1**
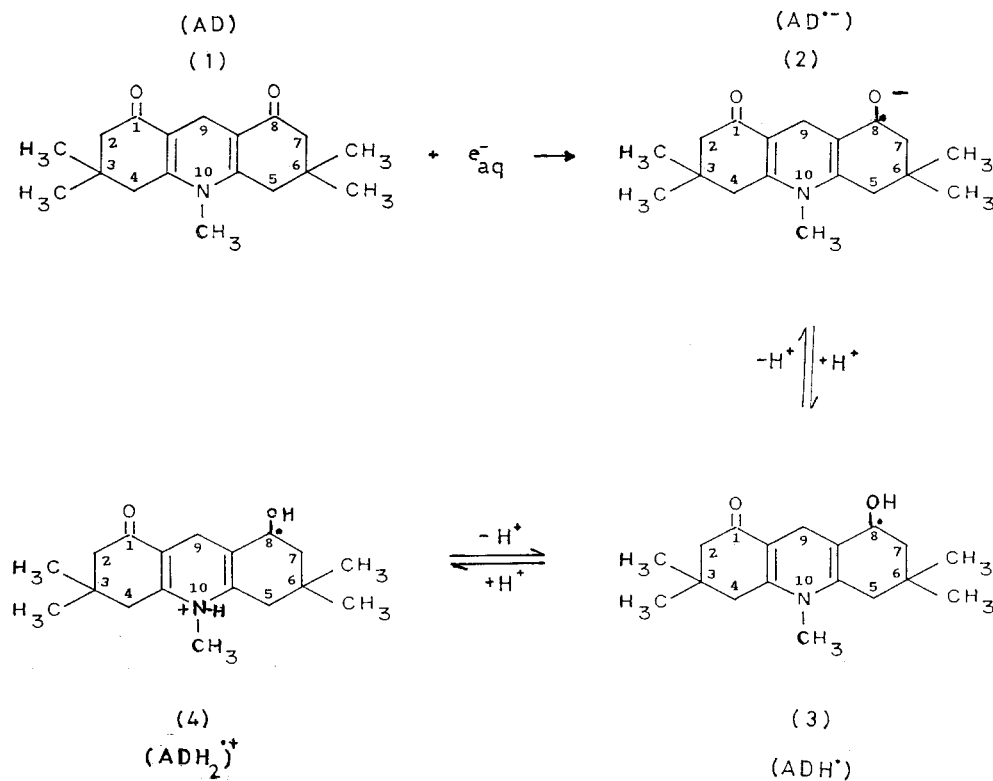


tigated using $N_2O$-saturated solutions of AD $(0.5-3) \times 10^{-4}$ mol $dm^{-3}$ in the presence of high concentration (1 mol $dm^{-3}$) of methanol, ethanol, and 2-propanol.[25b] All other experimental details have been described elsewhere.[23]

**Results and Discussion**

**Optical Absorption Studies.** The ground state optical absorption spectrum of AD in aqueous solution shows absorption bands with $\lambda_{max} = 410$ nm ($\epsilon = 5.6 \times 10^3$ $dm^3$ $mol^{-1}$ $cm^{-1}$), 275 nm ($\epsilon = 5.5 \times 10^3$ $dm^3$ $mol^{-1}$ $cm^{-1}$), and 255 nm ($11.3 \times 10^3$ $dm^3$ $mol^{-1}$ $cm^{-1}$). The spectrum remained independent of pH in the range 1−13, indicating that it has no p$K$ in this pH range.

**Reaction with $e_{aq}^-$.** *In Neutral Solutions.* The rate constant for the reaction of $e_{aq}^-$ with AD was studied by monitoring the decay of $e_{aq}^-$, formed on pulse radiolysis of $N_2$-saturated aqueous solution (*tert*-butyl alcohol = 0.3 mol $dm^{-3}$, pH = 6) containing different concentrations of AD ($(0-2.5) \times 10^{-4}$ mol $dm^{-3}$). The decay (700 nm) was observed to become faster and of first order. The pseudo-first-order rate ($k_{obs}$) was found to increase with AD concentration. The bimolecular rate constant, determined from the slope of linear plot of $k_{obs}$ with solute concentration, was $1.5 \times 10^{10}$ $dm^3$ $mol^{-1}$ $s^{-1}$. Time-resolved studies showed the formation of transient bands with $\lambda_{max} = 305$ and 475 nm, a shoulder at 680 nm, and increasing absorption at $\lambda > 800$ nm (Figure 1a). Since $e_{aq}^-$ has completely decayed during this time (2 $\mu$s after the pulse), the observed spectrum should be due to the product of the reaction of $e_{aq}^-$ with AD. The bimolecular rate constant, determined from the growth of the 305 nm band, was $9.6 \times 10^9$ $dm^3$ $mol^{-1}$ $s^{-1}$, close to the value obtained from the decay of $e_{aq}^-$. The absorption at 475 and 800 nm was observed to decay by first-order kinetics with $k = (1.5 \pm 0.2) \times 10^5$ $s^{-1}$ (inset of Figure 1). Since the decay at these wavelengths was similar, it should be due to the same species. Simultaneous to the decay, the absorption at 315 nm was observed to grow by first-order
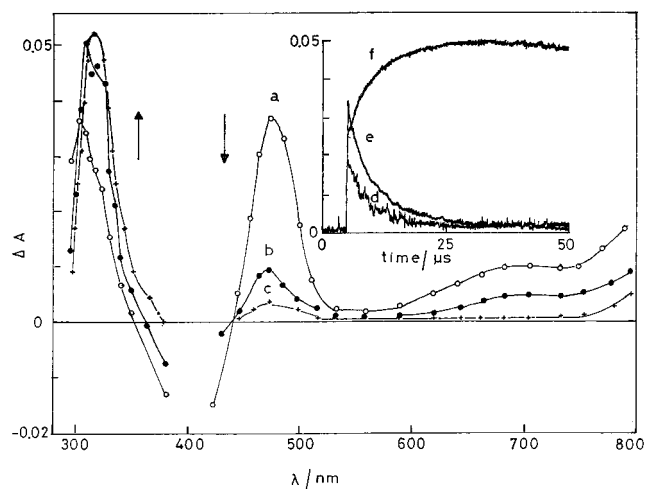


**Figure 1.** Transient optical absorption spectrum obtained on pulse radiolysis of $N_2$-saturated aqueous solution of AD ($2.5 \times 10^{-4}$ mol $dm^{-3}$, *tert*-butyl alcohol = 0.3 mol $dm^{-3}$, pH = 6): (a) 2; (b) 10; and (c) 45 $\mu$s after the pulse. Inset shows absorption-time signal at (d) 800, (e) 475, and (f) 315 nm.

kinetics with $k = 1.6 \times 10^5$ $s^{-1}$ (inset of Figure 1), reaching saturation in 30 $\mu$s. Since the decay matched with the formation at 315 nm, the transient species absorbing at 475 and >800 nm might have been converted into another transient species absorbing at 315 nm. The decay of the transient band at 315 nm as determined from the plot of 1/OD vs time followed second-order kinetics with $2k/\epsilon l = 1 \times 10^4$ $s^{-1}$.

The rate of reaction (rate constant × concentration) of $e_{aq}^-$ with AD is ($2.5 \times 10^6$ $s^{-1}$), much higher than with itself ($2.5 \times 10^4$ $s^{-1}$). Almost all the electrons must have reacted with AD to form the transient species. Under these conditions, the molar absorptivity at 475 and 315 nm was determined to be $8.2 \times 10^3$ and $11.4 \times 10^3$ $dm^3$ $mol^{-1}$ $cm^{-1}$, respectively.

The initial attack of $e_{aq}^-$ is likely to occur at any one of the electron-affinic heteroatoms [O(1), O(8)] of the AD leading to

One-Electron Reduction of Acridine-1,8-dione

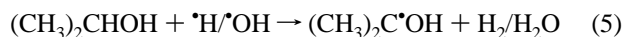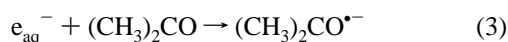*J. Phys. Chem. A, Vol. 101, No. 16, 1997* **2933**

the formation of radical anion, $AD^{\bullet-}$, (**2**, Scheme 1). It is also possible that the charge and radical site may be spread over several sites including both oxygens and the nitrogen. The radical anion may then protonate giving rise to H adduct, $ADH^{\bullet}$, (**3**, Scheme 1). The transient absorption bands (305, 475, >800 nm), 2 $\mu$s after the pulse, are assigned to $AD^{\bullet-}$ (Figure 1a) and the transient band (315 nm) 45 $\mu$s after the pulse (Figure 1c) is assigned to $ADH^{\bullet}$ (Scheme 1).

If the observed spectral changes are due to the protonation of the radical anion, then the transformation reaction would be affected by the pH of the solution. The radical anion ($AD^{\bullet-}$) should be observed immediately after the pulse in basic solutions with only slow if any transformation to $ADH^{\bullet}$. Similarly, $ADH^{\bullet}$ should be observed in acidic solutions immediately after the pulse as the slow transformation of $AD^{\bullet-}$ to $ADH^{\bullet}$ (pH = 6) would be fast in acidic solutions.

In basic solutions (pH = 13), the bimolecular rate constant for the reaction of $e_{aq}^-$ with AD was determined to be $1.1 \times 10^{10}$ dm$^3$ mol$^{-1}$ s$^{-1}$. Time-resolved studies showed the formation of transient optical absorption band with $\lambda_{max}$ = 300 and 475 nm and at $\lambda$ > 800 nm (similar to Figure 1a). Since the entire spectrum decayed by the same kinetics ($2k/\epsilon l = 4.5 \times 10^5$ s$^{-1}$), it should be due to one species and is assigned to the radical anion, $AD^{\bullet-}$. The growth at 315 nm was not observed, suggesting that the transformation of $AD^{\bullet-}$ to $ADH^{\bullet}$ is not taking place at pH = 13, thus supporting the earlier conclusion. The decay of the transient optical absorption bands (pH = 13) was different from that at pH = 6 which might be due to the stabilization of the radical anion at pH = 13. The molar absorptivity at 300 nm was determined to be $9.6 \times 10^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$.

In acidic solutions (pH < 6), the absorbance at 475 nm, immediately after the pulse, started decreasing with decrease in the pH of the solution. Even the decay became faster showing the reaction of $AD^{\bullet-}$ with H$^+$. The growth at 315 nm was also observed to decrease at lower pH. This, and the fact that more and more of the 315 nm absorption was present immediately after the pulse, support the formation of $ADH^{\bullet}$ immediately after the pulse in acidic solutions. Since $G$ ($e_{aq}^-$) would decrease with pH of the solution, the absorbance at 475 nm has been normalized and plotted as a function of pH (Figure 2). It showed the existence of an equilibrium (Scheme 1) with a p$K$ value of 4.7.

*pK of ADH$^{\bullet}$.* The reaction of $e_{aq}^-$ with AD at pH < 3 could not be carried out in N$_2$-saturated aqueous solutions as $e_{aq}^-$ is quantitatively converted to $^{\bullet}$H ($e_{aq}^- + H^+ \rightarrow H^{\bullet} + H_2O$). Even in the pH range of 3−4, the yield of H$^{\bullet}$ atom is quite high and the reaction of H$^{\bullet}$ atom with AD forms transient bands which interfere with the absorption bands formed on the reaction of $e_{aq}^-$ with AD.[23] A matrix containing 2-propanol (1 mol dm$^{-3}$) and acetone (0.1 mol dm$^{-3}$) can be used in the pH range of $\sim$0.1−13.[25b,27] In basic solutions, $e_{aq}^-$ reacts with acetone to produce $(CH_3)_2C^{\bullet}OH$ radicals and the same radical species is produced even in the acidic solutions (reactions 3−5). $(CH_3)_2C^{\bullet}OH$ radical, with

$$e_{aq}^- + (CH_3)_2CO \rightarrow (CH_3)_2CO^{\bullet-} \quad (3)$$

$$(CH_3)_2CO^{\bullet-} + H_2O \rightarrow (CH_3)_2C^{\bullet}OH + OH^- \quad (4)$$

$$(CH_3)_2CHOH + {}^{\bullet}H/{}^{\bullet}OH \rightarrow (CH_3)_2C^{\bullet}OH + H_2/H_2O \quad (5)$$

almost the same yield, is the only reactive species produced in the pH range of $\sim$0.1−13. As $(CH_3)_2C^{\bullet}OH$ radical has been shown to react with AD in a manner similar to that of $e_{aq}^-$ (see
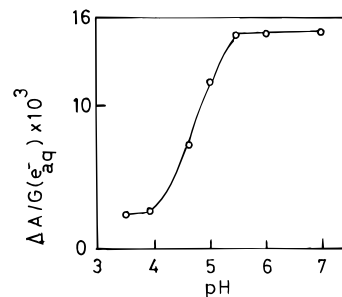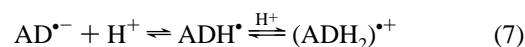


**Figure 2.** Variation of normalized absorbance [$\Delta A/G(e_{aq}^-)$] at 475 nm as a function of pH.
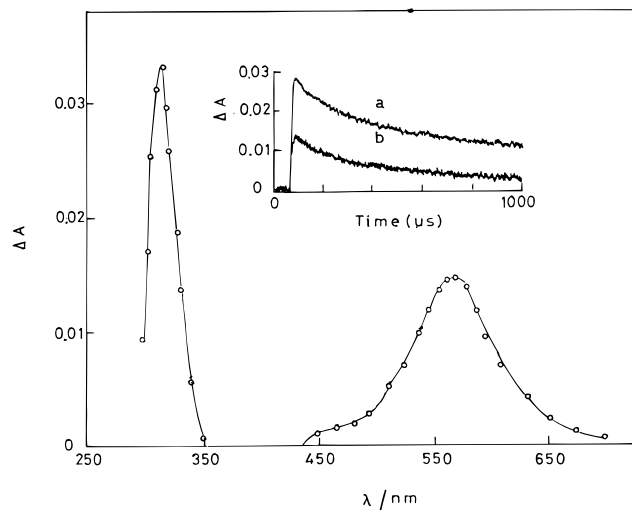


**Figure 3.** Transient optical absorption spectrum of pulse radiolysis of N$_2$-saturated acidic (pH = 1) aqueous solution (AD = $2.5 \times 10^{-4}$ mol dm$^{-3}$, isopropyl alcohol = 1 mol dm$^{-3}$, acetone = 0.1 mol dm$^{-3}$) 25 $\mu$s after pulse. Inset shows absorption-time signal at (a) 315 and (b) 560 nm.

text), this matrix was used in this pH range to determine the p$K$ value of the transient species $ADH^{\bullet}$ and the reduction of AD in acidic pH region.

Figure 3 shows the transient optical absorption spectrum on pulse radiolysis of N$_2$-saturated acidic (pH = 1) aqueous solution (2-propanol = 1 mol dm$^{-3}$, acetone = 0.1 mol dm$^{-3}$, AD = $2.5 \times 10^{-4}$ mol dm$^{-3}$), 25 $\mu$s after the pulse. It exhibits absorption bands at 315 and 560 nm. The rate constant for the reaction of isopropyl alcohol radical with AD was determined by formation kinetics at 315 and 560 nm and the value was same at both the wavelengths ($7.5 \times 10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$). The entire spectrum decayed by second-order kinetics with $2k/\epsilon_l = 5 \times 10^4$ s$^{-1}$ (inset Figure 3), suggesting it to be due to one species. The spectrum could not be assigned to $ADH^{\bullet}/AD^{\bullet-}$ as it (Figure 3) was not matching with that of $AD^{\bullet-}/ADH^{\bullet}$ (Figure 1). The absorption at 560 nm was monitored as a function of pH (Figure 4), which suggests the existance of an equilibrium (Scheme 1). The transient species (Figure 3) is assigned to protonated $ADH^{\bullet}$ [$(ADH_2)^{\bullet+}$] with a p$K$ value of 2.6 and formed according to reactions 6 and 7.

$$(CH_3)_2C^{\bullet}OH + AD \rightarrow AD^{\bullet-} + (CH_3)_2CO + H^+ \quad (6)$$

$$AD^{\bullet-} + H^+ \rightleftharpoons ADH^{\bullet} \overset{H^+}{\rightleftharpoons} (ADH_2)^{\bullet+} \quad (7)$$

In this case also, the charge and radical site may be spread over several sites. The reaction of isopropyl alcohol radical with AD was also carried out at pH 6 and 11. At pH = 6, a transient optical absorption band with $\lambda_{max}$ = 315 nm was observed. The

**2934** *J. Phys. Chem. A, Vol. 101, No. 16, 1997*

Mohan et al.
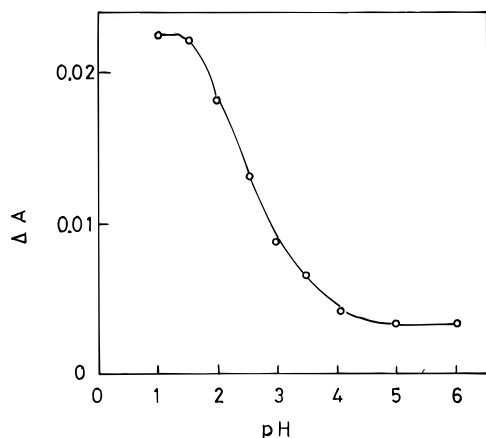


**Figure 4.** Variation of absorbance (560 nm) as a function of pH.

**TABLE 1: Spectral and Kinetics of the Transient Species Formed from AD**

| reaction | pH | $\epsilon$ (dm$^3$ mol$^{-1}$ cm$^{-1}$) | bimolecular rate const (dm$^3$ mol$^{-1}$ s$^{-1}$) | $\lambda$ (nm) | transient species |
|---|---|---|---|---|---|
| AD + e$_{aq}^-$ | 6 | $8.2 \times 10^{3a}$ | $1.0 \times 10^{10}$ | 305, 475, >800 | AD$^{\bullet-}$ |
| AD + e$_{aq}^-$ | 6 | $11.4 \times 10^{3b}$ | | 315 | ADH$^{\bullet}$ |
| AD + e$_{aq}^-$ | 13 | $9.6 \times 10^{3c}$ | $1.1 \times 10^{10}$ | 300, 475, >800 | AD$^{\bullet-}$ |

$^a$ 475 nm. $^b$ 315 nm. $^c$ 300 nm.

**TABLE 2: Kinetic Parameters for the Reaction of Various Reducing Species with AD**

| reducing agents | pH | $E°$ (V) | $\lambda_{max}$ (nm) | bimolecular rate const (dm$^3$ mol$^{-1}$ s$^{-1}$) | transient species |
|---|---|---|---|---|---|
| CO$_2^{\bullet-}$ | 6 | −1.9 | 315 | $3.4 \times 10^8$ | ADH$^{\bullet}$ |
| (CH$_3$)$_2$C$^{\bullet}$OH | 1 | | 315, 560 | $7.5 \times 10^8$ | (ADH$_2$)$^{\bullet+}$ |
| (CH$_3$)$_2$C$^{\bullet}$OH | 6 | −1.1 | 315 | $3.2 \times 10^8$ | ADH$^{\bullet}$ |
| (CH$_3$)$_2$C$^{\bullet}$OH | 11 | | 305, 475 | $2.0 \times 10^9$ | AD$^{\bullet-}$ |
| CH$_3$C$^{\bullet}$HOH | 6 | −0.95 | 315 | $2.3 \times 10^8$ | ADH$^{\bullet}$ |
| $^{\bullet}$CH$_2$OH | 6 | −0.73 | 315 | $1.2 \times 10^8$ | ADH$^{\bullet}$ |

absorption in the region of 450−650 nm was very small. The bimolecular rate constant, determined from the growth of the transient band at 315 nm, was $3.2 \times 10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$. The spectrum was similar to that of ADH$^{\bullet}$. The AD$^{\bullet-}$ formed (reaction 6) is slowly converted to ADH$^{\bullet}$ even at pH = 6. At pH = 11, transient optical absorption bands with $\lambda_{max} = 305$ and 475 nm were observed. The spectrum was similar to that of AD$^{\bullet-}$. At this pH, slow transformation of AD$^{\bullet-}$ to ADH$^{\bullet}$ is not taking place. The bimolecular rate constant for the reaction of isopropyl alcohol radical with AD at pH = 11, determined from the growth of bands at 315 and 475 nm, was the same ($2 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$). These studies support that earlier conclusion that AD$^{\bullet-}$ is slowly converted to ADH$^{\bullet}$ at pH = 6. In basic solutions, its transformation to ADH$^{\bullet}$ is not taking place. In acidic solutions, it is converted to ADH$^{\bullet}$/(ADH$_2$)$^{\bullet+}$.

**Reaction with Reducing Species.** The reducing species such as CO$_2^{\bullet-}$ ($E° = -1.9$ V)[28] and α-hydroxyalkyl radicals (Table 2) were able to react with AD and showed the formation of transient optical absorption band at 315 nm. The bimolecular rate constant for the reaction of these reducing species with AD was determined from the growth of 315 nm band as a function of AD concentration $(0.4−1.8) \times 10^{-4}$ mol dm$^{-3}$ and the values are shown in Table 2. The tetrahydrofuran radical failed to react with AD, suggesting that the redox potential value for AD/AD$^{\bullet-}$ couple is more negative than that of tetrahydrofuran radical. (The $E°$ for this reducing species is estimated to be −0.55 V.)[25b]

*With p-NAP$^{\bullet-}$.* The decay of the radical anion p-NAP$^{\bullet-}$ ($\lambda_{max}$ = 350, 550 nm) formed on pulse radiolysis of N$_2$-saturated
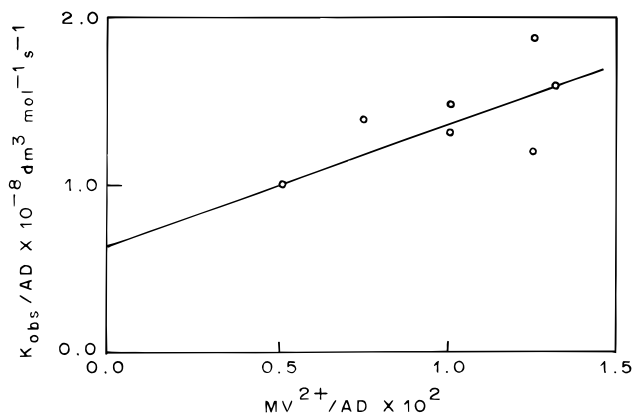


**Figure 5.** Plot of $k_{obs}$/AD vs MV$^{2+}$/AD.

aqueous solution of *p*-nitroacetophenone, *p*-NAP, $(1 \times 10^{-3}$ mol dm$^{-3}$, *tert*-butyl alcohol = 0.3 mol dm$^{-3}$), remained unaffected on addition of AD $(2.5 \times 10^{-4}$ mol dm$^{-3}$), showing that the reduction potential of AD/AD$^{\bullet-}$ couple is more negative than that of *p*-NAP/*p*-NAP$^{\bullet-}$ (−0.358 V).[29] On the other hand, pulse radiolysis of N$_2$-saturated aqueous solution of AD $(3 \times 10^{-4}$ mol dm$^{-3}$, *tert*-butyl alcohol = 0.3 mol dm$^{-3}$) containing low concentration of *p*-NAP $(0−1) \times 10^{-5}$ mol dm$^{-3}$ showed buildup at both 350 and 550 nm and the transient spectrum was similar to that of *p*-NAP$^{\bullet-}$. Under these conditions, more than 90% of electrons would react with AD to form AD$^{\bullet-}$, which would then react with *p*-NAP to form *p*-NAP$^{\bullet-}$. The bimolecular rate constant, determined from the build up at 350 nm, for the reaction of AD$^{\bullet-}$ with *p*-NAP (reaction 8) was $6 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$.

$$AD^{\bullet-} + p\text{-NAP} \rightarrow p\text{-NAP}^{\bullet-} + AD \qquad (8)$$

*With MV$^{2+}$.* MV$^{\bullet+}$, formed on pulse radiolysis of N$_2$-saturated aqueous solution of methyl viologen, MV$^{2+}$ $(1 \times 10^{-3}$ mol dm$^{-3}$, *tert*-butyl alcohol = 0.3 mol dm$^{-3}$), is a reducing agent with reduction potential for the couple MV$^{2+}$/MV$^{\bullet+}$ = −0.465 V.[29] Its decay was slightly affected by low concentrations of AD. Pulse radiolysis of N$_2$-saturated aqueous solution of AD $(4 \times 10^{-4}$ mol dm$^{-3}$, *tert*-butyl alcohol = 0.3 mol dm$^{-3}$) containing low concentration of MV$^{2+}$ $(0−8) \times 10^{-6}$ mol dm$^{-3}$ showed build up at 605 nm, suggesting electron transfer from AD$^{\bullet-}$ to MV$^{2+}$. The first-order rate for the growth of 605 nm band of MV$^{\bullet+}$ was found to depend on AD concentration. These results suggest the existence of following equilibrium:

$$AD^{\bullet-} + MV^{2+} \rightleftharpoons AD + MV^{\bullet+} \qquad (9)$$
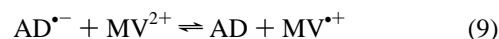
The first-order rate ($k_{obs}$) for this equilibrium reaction could be written as follows:

$$k_{obs} = k_f[MV^{2+}] + k_r[AD] \qquad (10)$$

$$\frac{k_{obs}}{[AD]} = k_f \frac{[MV^{2+}]}{[AD]} + k_r \qquad (11)$$

$k_f$ and $k_r$ are the rate constant for the forward and reverse reactions, respectively. The equilibrium constant $K = k_f/k_r$ can be determined from the first-order rate ($k_{obs}$). The growth of the transient absorption band at 605 nm of MV$^{\bullet+}$ was determined for various concentrations of AD $(1−4) \times 10^{-4}$ mol dm$^{-3}$ and MV$^{2+}$ $(1−6) \times 10^{-6}$ mol dm$^{-3}$. Under these conditions, the initial reaction of e$_{aq}^-$ would mainly be with AD and AD$^{\bullet-}$ would then react with MV$^{2+}$. The plot of $k_{obs}$/AD vs MV$^{2+}$/AD was linear (Figure 5) with slope $k_f = 0.73 \times 10^{10}$ dm$^3$ mol$^{-1}$

$s^{-1}$ and intercept $k_r = 0.64 \times 10^{-2}$. The equilibrium constant was determined to be $1.13 \times 10^2$. It is related to the difference in the redox potential value of two couples.

$$E^\circ = E^\circ_{AD/AD^{\bullet-}} - E^\circ_{MV^{\bullet+}/MV^{2+}} \qquad (12)$$

$$= 0.059 \log K \qquad (13)$$

From the value of $K = 1.13 \times 10^2$ and $E^\circ_{MV^{\bullet+}/MV^{2+}} = -0.465$ V, the redox potential value for the couple $AD/AD^{\bullet-}$ is determined to be $= -0.586 \pm 0.03$ V vs NHE.

## Conclusions

The radical anion ($AD^{\bullet-}$), formed on reaction of $e_{aq}^-$ with AD showed slow transformation to heteroatom (O) protonated species, $ADH^\bullet$ at neutral pH. In acidic solutions, $ADH^\bullet/(ADH_2)^{\bullet+}$, depending on the pH, is formed immediately after the pulse. The reduction potential for $AD/AD^{\bullet-}$ couple was determined to be $-0.586 \pm 0.03$ V.

## References and Notes

(1) Joseph Prabahar, K.; Ramakrishnan, V. T.; Sastikumar, D.; Selladurai, S.; Masilamani, V. *Indian J. Pure Appl. Phys.* **1991**, *29*, 382.

(2) Shanmugasundaram, P.; Joseph Prabahar, K.; Ramakrishnan, V. T. *J. Heterocycl. Chem.* **1993**, *30*, 1003.

(3) Shanmugasundaram, P.; Murugan, P.; Ramakrishnan, V. T.; Srividya, N.; Ramamurthy, P. *Heteroatom Chem.* **1996**, *6*, 17.

(4) Timpe, H. J.; Ulrich, S.; Fouassier, J. P. *J. Photochem. Photobiol., A: Chem.* **1993**, *73*, 139.

(5) Ulrich, S.; Timpe, H. J.; Fouassier, J. P.; Morelet Savary, F. *J. Photochem. Photobiol., A: Chem.* **1993**, *74*, 165.

(6) Timpe, H. J.; Ulrich, S.; Decker, C.; Fouassier, J. P. *Macromolecules* **1993**, *26*, 4560.

(7) Fuzukimi, S.; Tanaka, T. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M. Elsevier: Amsterdam, 1988; p 578.

(8) Fuzukimi, S.; Komitsu, S.; Hironaka, K.; Tanaka, T. *J. Am. Chem. Soc.* **1987**, *109*, 305.

(9) Stout, D. M.; Meyers, A. *Chem. Rev.* **1982**, *82*, 223.

(10) Martens, F. M.; Verhoeven, J. W.; Varma, C. A. G.; Bergwerf, P. *J. Photochem.* **1983**, *22*, 99.

(11) Lindqvist, L.; Czochralska, V.; Kawaczynski, W. *J. Photochem. Photobiol., B: Biol.* **1994**, *23*, 207.

(12) Meijer, L. H.; Van Neil, C. G.; Pandit, U. K. *Tetrahedron* **1984**, *40*, 5185.

(13) Chipman, D. M.; Yaniv, R.; Van Eikeren, P. *J. Am. Chem. Soc.* **1980**, *102*, 3244.

(14) Verhoevan, H. W.; Van Gerresheim, W.; Martens, F. M.; Van Der Kerk, S. M. *Tetrahedron* **1986**, *42*, 975.

(15) Sammes, J. D.; Widdowson, D. A. *J. Chem. Soc., Chem. Commun.* **1972**, 1023.

(16) Powell, M. F.; Wu, J. C.; Bruice, T. C. *J. Am. Chem. Soc.* **1984**, *106*, 3850.

(17) Taraban, M. B.; Kruppa, A. I.; Polyakov, N. E.; Leshina, T. V.; Lusis, V.; Mucieniece, D.; Duburs, G. *J. Photochem. Photobiol., A: Chem.* **1993**, *73*, 151.

(18) Kruppa, A. I.; Taraban, M. B.; Polyakov, N. E.; Leshina, T. V.; Lusis, V.; Mucieniece, D.; Duburs, G. *J. Photochem. Photobiol., A: Chem.* **1993**, *73*, 159.

(19) Polyakov, N. E.; Taraban, M. B.; Kruppa, A. I.; Avdievich, N. I.; Mokurshin, V. V.; Schastnev, P. V.; Leshina, T. V.; Lusis, V.; Mucieniece, D.; Duburs, G. *J. Photochem. Photobiol., A: Chem.* **1993**, *74*, 74.

(20) Meijer, L. H. P.; Pandit, U. K. *Tetrahedron* **1985**, *41*, 472.

(21) Singh, S.; Chhina, S.; Sharma, V. K. *J. Chem. Soc., Chem. Commun.* **1982**, 453.

(22) Srividya, N.; Ramamurthy, P.; Shanmugasundaram, P.; Ramakrishnan, V. T. *J. Org. Chem.* **1996**, *61*, 5083.

(23) Mohan, H.; Srividya, N.; Ramamurthy, P.; Mittal, J. P. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 2353.

(24) Spinks, J. W. T.; Woods, R. J. In *An Introduction to Radiation Chemistry*; Wiley: New York, 1990; p 243.

(25) (a) Priyadarsini, K. I.; Naik, D. B.; Moorthy, P. N.; Mittal, J. P. *Proc. 7th Tihany Symp. Radiat. Chem., Hungarian Chem. Soc.* **1991**, 205. (b) Guha, S. N.; Moorthy, P. N.; Kishore, K.; Naik, D. B.; Rao, K. N. *Proc. Indian Acad. Sci. (Chem. Sci.)* **1987**, 261.

(26) Fielden, E. M. In *The Study of Fast Process and Transient Species by Electron Pulse Radiolysis*; Baxendale, J. H., Busi, F., Eds.; Reidel: Boston, **1984**; p 59.

(27) Pal, H.; Mukherjee, T.; Mittal, J. P. *Radiat. Phys. Chem.* **1994**, *44*, 603.

(28) Surdhar, P. S.; Mezyk, S. P.; Armstrong, D. A. *J. Phys. Chem.* **1989**, *93*, 3360.

(29) (a) Meisel, D.; Neta, P. *J. Am. Chem. Soc.* **1975**, *97*, 5198. (b) Wardman, P. *J. Phys. Chem. Ref. Data* **1989**, *11*, 1637.