Primary Processes in the Reduction of Azo Dyes in Alcohols Studied by Pulse Radiolysis

Lucia Flamigni* and Sandra Monti

Istituto di Fotochimica e Radiazioni d'Alta Energia del C.N.R., 40126 Bologna, Italy

(Received: January 17, 1985)

The transient species produced in the reactions of solvated electrons and alcohol radicals with azobenzene and 4-(diethylamino)azobenzene have been studied in methanol and 2-propanol by spectrophotometric pulse radiolysis. One-electron reduction of the -N=N- bond is observed in both solvents by reaction of electrons ($k \simeq 10^{10}$ M^{-1} s^{-1}). Only $(CH_3)_2\dot{C}OH$, between the two α-hydroxyalkyl radicals, can give reduction of the azo bond. Both alcohol radicals undergo a very fast addition reaction with diethylaminoazobenzene ($k \simeq (4-5) \times 10^9$ M^{-1} s^{-1}). Subsequent formation of the hydrazyl radical is observed only on dissociation of the adduct of $(CH_3)_2\dot{C}OH$. The time evolution of the primary species formed has been followed. Association of hydrazyl radicals with the starting azo compounds has been detected.

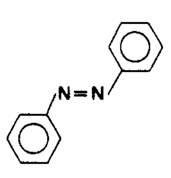
Introduction

The photoreduction of azo dyes is known to be an important fading process.[1] It is believed to occur when these dyes are adsorbed to protein substrates[2] or to synthetic polymers such as epoxy resins[3] or polypropylene[4] under conditions of limited supply of oxygen.

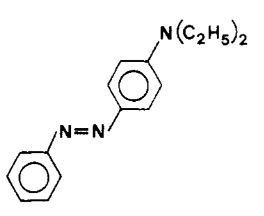
The present knowledge of this process mainly comes from studies on model systems such as azobenzene[5] and simple substituted azobenzenes in solution.[6-8] The final products have been generally identified to be the hydrazo derivative of the dye and/or the substituted anilines.[5-10] Hydrazyl radicals have been detected as intermediates.[9] They can be formed both via a direct process, i.e., hydrogen abstraction from the solvent by the photoexcited dye[7a,8] or by a sensitized process, i.e., reaction of the dye with radicals generated by photoexcitation of added reducing substrates.[7b,8-10]

When the reduction takes place in alcoholic solvents by H abstraction, either by the dye or by the sensitizer, α-hydroxyalkyl radicals ($R^1R^2\dot{C}OH$) are formed. These radicals contribute to the fading process of the dye by acting themselves as reducing agents.[10] The initial step of the reduction has been proposed to be an electron transfer from the radical to the dye followed by protonation which leads to the hydrazyl radical.[10] This mechanism has been found to be operative in the reduction of azobenzene by the isopropyl alcohol radical in a pulse radiolysis study.[11] No detailed studies have been so far reported concerning other alcohol radicals and/or other azobenzene derivatives.

The present study deals with a comparative investigation of the transient species formed in the reactions of solvated electrons and different alcohol radicals with azo dyes. The pulse radiolysis technique, which has been proved to be powerful and versatile,[11] was used, being very effective both to produce reducing species in alcohols (e_s^-, $R^1R^2\dot{C}OH$, H·)[12] and to detect their interaction with solutes. Two simple azo compounds have been examined, *trans*-azobenzene (A) and *trans*-4-(diethylamino)azobenzene (DA), the former as a parent molecule of the azo dyes family, the latter as the simplest azo dye. Two alcohols have been investigated: methanol and 2-propanol.



A



DA

By means of time-resolved absorption measurements, rate constants for reactions of solvated electrons and alcohol radicals have been determined. The primary species formed have been identified and their time evolution has been followed in the nanosecond to second time range. Significant differences have been found in the two alcohols. The role of the primary species in the fading of the -N=N- double bond has been examined.

Experimental Section

Methyl alcohol (MeOH) and isopropyl alcohol (*i*-PrOH) were fluorimetric grade products (RS Carlo Erba) and were used without further purification. The solvated electron (e_s^-) half-life was 1.3 μs in *i*-PrOH and 2.9 μs in MeOH. *trans*-Azobenzene (A) was an Aldrich Gold Label product and was used as purchased; *trans*-4-(diethylamino)azobenzene (DA) was synthesized by Aziende Colori Nazionali Affini (Italy) and purified by column chromatography.[8a] Solutions ($c \le 2 \times 10^{-4}$ M) were freshly prepared and protected from light before each experiment. This precaution prevents trans → cis isomerization of the compound. Solutions were deaerated by bubbling Ar or N_2O for 30 min.

The radiation source was the 12-MeV Vickers linear accelerator of the F.R.A.E.-C.N.R. Institute in Bologna.[13] Pulses of 20-100 ns were used and doses were measured by a charge collector, calibrated against the thiocyanate dosimeter, using a $G\epsilon_{500\mathrm{nm}} = 2.15 \times 10^4$ M^{-1} cm^{-1} for the $(SCN)_2^{-}\cdot$ radical. The absorbed doses were in the range 4.5-26 Gy.

---

(1) I. H. Leaver in "Photochemistry of Dyed and Pigmented Polymers", N. S. Allen and F. McKellar, Eds., Applied Science Publishers, London, 1980, pp 173-180.

(2) H. R. Chipalkatti, N. F. Desai, L. H. Giles, and N. McCaulay, *J. Soc. Dyers Colour.*, **70**, 487 (1954).

(3) N. S. Allen, J. P. Binkley, B. J. Parsons, G. O. Phillips, and N. H. Tennent, *Dyes Pigm.*, **5**, 209 (1984).

(4) V. N. Mallet and B. T. Newbold, *J. Soc. Dyers Colour.*, **90**, 4 (1974).

(5) S. Hashimoto and K. Kano, *Bull. Chem. Soc. Jpn.*, **45**, 852 (1972); J. Ronayette, B. Arnaud, and J. Lemaire, *Can. J. Chem.*, **52**, 1858 (1974).

(6) V. Rehak, F. Novak, and I. Cepciansky, *Collect. Czech. Chem. Commun.*, **38**, 697 (1973).

(7) (a) G. Irick and J. G. Pacifici, *Tetrahedron Lett.*, 1303 (1969); (b) J. G. Pacifici and G. Irick, *ibid.*, 2207 (1969).

(8) (a) A. Albini, E. Fasani, and S. Pietra, *J. Chem. Soc., Perkin Trans. 2*, 1393 (1982); (b) *ibid.*, 1021 (1983).

(9) H. C. A. van Beek, P. M. Heertjes, C. Houtepen, and D. Retzloff, *J. Soc. Dyers Colour.*, **87**, 87 (1971).

(10) H. C. A. van Beek, P. M. Heertjes, and K. Schaafsma, *J. Soc. Dyers Colour.*, **87**, 342 (1971).

(11) P. Neta and H. Levanon, *J. Phys. Chem.*, **81**, 2288 (1977).

(12) (a) D. W. Johnson and G. A. Salmon, *Can. J. Chem.*, **55**, 2030 (1977); (b) M. C. Sauer, Jr., S. Arai, and L. M. Dorfman, *J. Chem. Phys.*, **42**, 708 (1965); G. R. Freeman in "The Study of Fast Processes and Transient Species by Electron Pulse Radiolysis", J. H. Baxendale and F. Busi, Eds., Nato Advanced Study Institute Series, Reidel, Dordrecht, 1982, pp 399-416 and references cited therein.

(13) A. M. Hutton, G. Roffi, and A. Martelli, *Quad. Ric. Emilia Romagna*, **5**, 67 (1974).

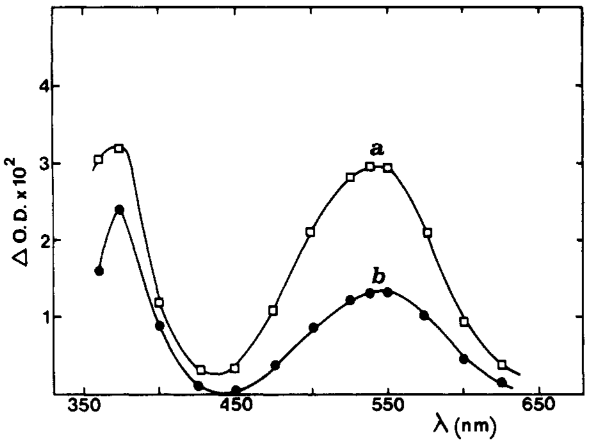


Figure 1. Difference spectra observed in the pulse radiolysis of a 1.5 × 10^{-4} M solution of A in MeOH, saturated with Ar: (a) □, 5 μs; (b) ●, 900 μs after the pulse. Dose = 22 Gy. Optical path = 2 cm.

Irradiations were carried out at room temperature; samples were contained in a cylindrical cell of 2-cm path length, filled through an automatically operated tap. Changes in absorbance following the electron pulse were monitored by using a xenon lamp (XBO 450 W, 2-ms pulse). The probe light was focussed into the slit of a 0.2-m monochromator (Bausch-Lomb, f = 2.8, bandwidth 5 nm). The light intensity at the exit slit was detected by a photomultiplier (Hamamatsu R955). The signal was recorded on a transient digitizer (Tektronix R7912AD) and processed by means of a PDP 11/23 computer (Digital).

The radiolytic behavior of liquid alcohols has been widely investigated.[12] Among the various products, the main reactive species which live long enough to react with solutes present in low concentration ($\leq 10^{-3}$ M) are e_s^- and $R^1R^2\dot{C}OH$. Only the reactions of these species were significant under our experimental conditions. In N_2O-saturated solutions e_s^- are rapidly converted to α-hydroxyalkyl radicals:[14]

$$N_2O + e_s^- \xrightarrow{R^1R^2CHOH_2^+} N_2 + H_2O + R^1R^2\dot{C}OH$$

Thus the alcohol radicals are the only reactive species under these conditions.

In the calculations of molar extinction coefficients of transients, G values for e_s^- were taken to be 1.2 and 1.0 in MeOH[12a] and i-PrOH,[12b] respectively.

The errors are estimated to be ≤20% on the extinction coefficients and ≤15% on the rate constants. In cases of mixed kinetics situations the rate constants are affected by larger errors and must be taken as approximate values (the symbol $\simeq$ is used).

The second-order rate constants for the R + R → products reaction are defined by the expression $-d[R]/dt = 2k[R]^2$.

Results and Discussion

1. Azobenzene. 1.1. Transient Spectra and Kinetics in MeOH. Azobenzene (A) reacts with e_s^- in MeOH with a rate constant $k_1 = 1.6 \times 10^{10}$ M^{-1} s^{-1}. The difference spectrum, obtained in argon-saturated solutions at the end of this reaction, is displayed in Figure 1, curve a. It shows a maximum at 540 nm and a UV band in a region of overlap with A absorption. The spectrum is similar to that observed in neutral aqueous solution and in neat i-PrOH[11] and is assigned to the hydrazyl radical $-\dot{N}-N(H)-$, ($\dot{A}H$) formed in the rapid protonation of the anion.[11]

$$A + e_s^- \xrightarrow[MeOH]{H^+} \dot{A}H \qquad (1)$$

$$k_1 = 1.6 \times 10^{10}\ M^{-1}\ s^{-1}$$

A molar extinction coefficient of ca. 5800 M^{-1} cm^{-1} can be evaluated at 540 nm. The calculated ϵ_{max} is in agreement with that given for aqueous solutions (ca. 6000 M^{-1} cm^{-1}).[11]

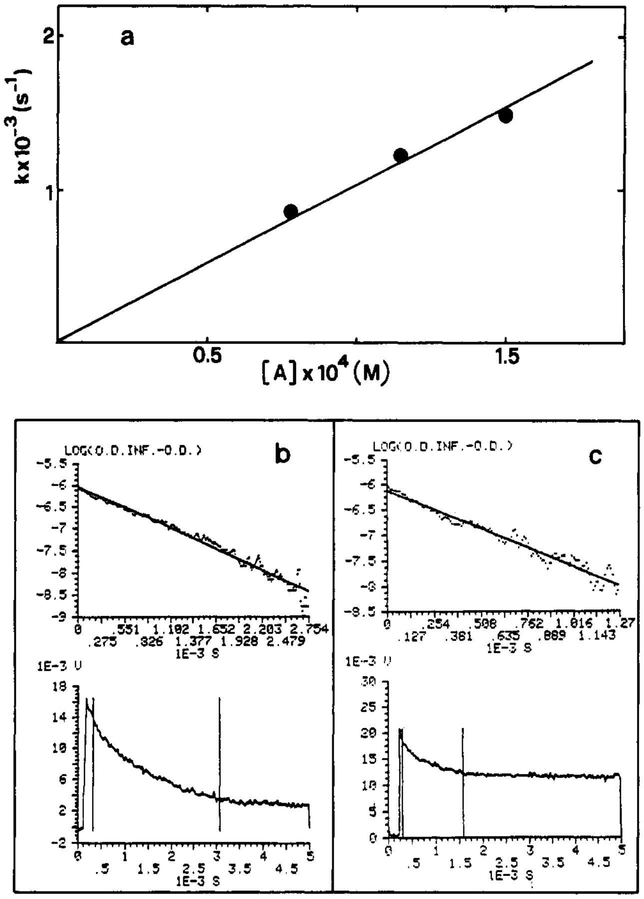


Figure 2. (a) Rate constants for the pseudo-first-order decay of the absorbance at λ = 540 nm as a function of [A] in MeOH, saturated with Ar. Oscillograms showing the variation in the optical transmission at 540 nm: (b) [A] = 7.8 × 10^{-5} M; I_0 = 2.04 V. (c) [A] = 1.5 × 10^{-4} M; I_0 = 1.27 V. Dose = 4.5 Gy. Optical path = 2 cm. Best fittings by the least-squares method are also shown.

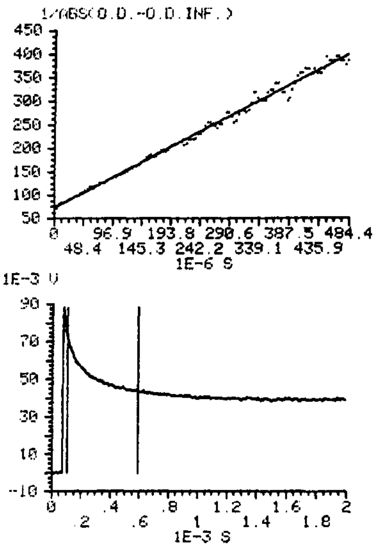


Figure 3. Oscillogram showing the variation in the optical transmission at λ = 540 nm of a 1.5 × 10^{-4} M solution of A in MeOH, saturated with Ar. I_0 = 1.18 V. Dose = 25 Gy. Optical path = 2 cm. The best fitting by the least-squares method is shown on the basis of second-order kinetics.

The decay of $\dot{A}H$ can be followed over the millisecond time scale. the kinetics shows mixed pseudo-first- and second-order character and is therefore highly dependent on dose. At low dose (4.5 Gy) the decay is pseudo-first order vs. A concentration (Figure 2), according to a bimolecular process with $k_2 \simeq 1 \times 10^7$ M^{-1} s^{-1}. At the end of this reaction, the difference spectrum exhibits a maximum at about 550 nm and a UV band in the region of A

---

[14] P. W. Johnson and G. A. Salmon, *J. Chem. Soc., Faraday Trans. 1*, **71**, 583 (1975).

absorption. At high dose (25 Gy) the decay of $\dot{A}H$, at least in the initial part, is better described by second-order kinetics (Figure 3) with $k_3/\epsilon_{540} \simeq 6 \times 10^5$ s^{-1}. A residual absorption is still left (Figure 1, curve b). The spectrum is the same as that formed at low dose, but the yield is lower.

From this experiment it can be inferred that the $\dot{A}H$ radical undergoes two competitive reactions: a second-order disproportionation clearly seen at high radical concentrations and a reaction involving one molecule of A, leading to a long-lived radical product with an absorption spectrum very similar to that of $\dot{A}H$ itself. This second path is clearly seen at low radical concentrations.

$$A + \dot{A}H \xrightarrow[\text{MeOH}]{} \dot{A}_2H \qquad (2)$$

$$k_2 \simeq 1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$$

$$\dot{A}H + \dot{A}H \xrightarrow[\text{MeOH}]{} AH_2 + A \qquad (3)$$

$$k_3 \simeq 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

The rate constants, given the mixed character of the kinetics, are to be considered an approximate evaluation. The formation of an association product (reaction 2) is proposed on the basis of both kinetic evidence and of spectral similarities with the species $\dot{A}H$. This reaction has never been reported for A or derived molecules, but the tendency of stilbene-like molecules to give radical dimers is known,[15] due probably to a more favorable conformation attained in the radical form. Evaluation of the molar extinction coefficient of the species $\dot{A}_2H$ is difficult because of the low precision of the reaction rates. A lower limit of $\epsilon_{550} = 4000$ M^{-1} cm^{-1} can be derived from Figure 2c. Reaction 3 represents the disproportionation of hydrazyl radicals which leads to hydrazobenzene, a species absorbing in the UV region,[5] and regenerates azobenzene.[9]

The disappearence of the species $\dot{A}_2H$ takes place over seconds and shows, similarly to $\dot{A}H$ decay, mixed first- and second-order kinetics. At low doses an exponential decay prevails with $\tau_{1/2} \simeq 0.4$ s, while at high doses the decay is second order with $k_4 \simeq 3.2 \times 10^6$ M^{-1} s^{-1} (lower limit).

$$\dot{A}_2H + \dot{A}_2H \xrightarrow[\text{MeOH}]{} AH_2 + 3A \qquad (4)$$

$$k_4/\epsilon_{550} \simeq 800 \text{ s}^{-1}$$

$$\dot{A}_2H \text{ (+ impurities) } \xrightarrow[\text{MeOH}]{} \text{products} \qquad (5)$$

$$\tau_{1/2} \simeq 0.4 \text{ s}$$

Reaction 4 is a disproportionation reaction which is proposed to occur for radical dimers, in analogy to the hydrazyl reaction 3, to account for the second-order decay. The exponential decay, observed at low doses, can be interpreted as a quenching by impurities or a decomposition[9] (reaction 5).

Saturation of the solution with N_2O completely eliminates the transient absorption, indicating that there is no reaction of $\dot{C}H_2OH$ with A. This result can be discussed on the basis of thermodynamic arguments. The half-wave potential for the reversible reduction of A (in aqueous medium vs. SCE) is -0.986 V[16] whereas the half-wave potential for the oxidation of $\dot{C}H_2OH$ under comparable conditions has been measured to be -0.98.[17,18] It has been shown that these potentials can be compared to predict whether a solute can be reduced by an α-alcohol radical. A few 0.1 V of difference are requested to make the reduction competitive with other radical reactions.[17] Therefore in this case the reduction does not take place.

1.2. Transient Spectra and Kinetics in i-PrOH. Azobenzene reacts with e_s^- in *i*-PrOH with a rate constant $k_6 = 9.0 \times 10^9$ M^{-1} s^{-1}. The difference spectrum obtained in argon-saturated solutions at the end of this reaction is shown in Figure 4, curve a. It has a visible band with maximum at 540 nm and a UV band overlapping with A absorption. The spectrum is almost identical with the one detected in aqueous[11] and MeOH solutions (see Figure 1) and therefore is assigned to the hydrazyl $\dot{A}H$ radical.

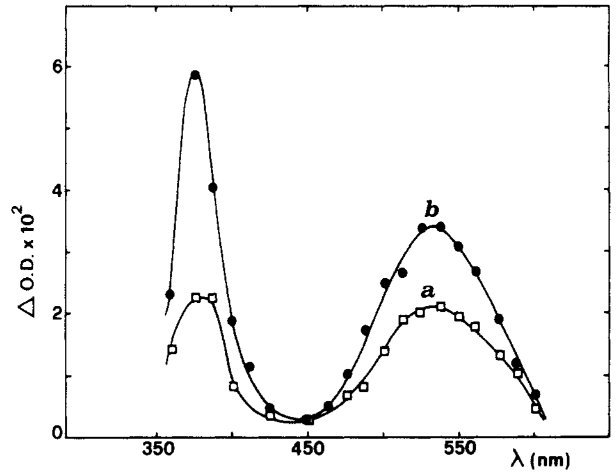


Figure 4. Difference spectra observed in the pulse radiolysis of a 1.5 × 10^{-4} M solution of A in *i*-PrOH, saturated with Ar: (a) □, 3.5 μs; (b) ●, 850 μs after the pulse. Dose = 26 Gy. Optical path = 2 cm.

$$A + e_s^- \xrightarrow[i\text{-PrOH}]{H^+} \dot{A}H \qquad (6)$$

$$k_6 = 9.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

A molar extinction coefficient of ca. 5200 M^{-1} cm^{-1} was calculated on the maximum of the visible band, in reasonable agreement with the ϵ_{max} in methanolic solutions and with the one reported previously[11] for $\dot{A}H$ in aqueous solution.

The time evolution of the signal shows that there is a further increase in transient absorption; the final spectrum is shown in Figure 4b. This increase has been ascribed to the reduction of A by the radical $(CH_3)_2\dot{C}OH$ to produce $\dot{A}H$ with a rate constant of 3×10^7 M^{-1} s^{-1} in aqueous solutions.[11] The same reaction should take place also in neat *i*-PrOH as expected from the redox potentials of A and the radical $(CH_3)_2\dot{C}OH$.

The formation kinetics were followed both on the visible and on the UV band and analyzed at different doses and A concentrations. A simple exponential treatment gives rate constants roughly independent of the A concentration, but increasing with dose. Similar results were obtained in N_2O-saturated solutions. These data can hardly be explained merely by a reduction of A by $(CH_3)_2\dot{C}OH$. In this case in fact a pseudo-first-order rate constant dependent only on the A concentration would be expected. The final spectrum at the completion of the reaction is shown in Figure 4b. The decay of the absorption is described both in N_2O and in Ar-saturated solutions by second-order kinetics with $k_{10}/\epsilon_{550} \simeq 700$ s^{-1} at high doses (26 Gy), while at lower doses (4.7 Gy) it is exponential with a half-life of $\tau_{1/2} \simeq 0.2$ s. These rate constants are quite different from those of $\dot{A}H$ in MeOH solution, but surprisingly similar to the ones assigned to the radical dimer $\dot{A}_2H$ in MeOH. Therefore the hypothesis is advanced that we are observing the radical $\dot{A}_2H$, probably formed very rapidly from $\dot{A}H$, the primary product of the reduction. The following scheme is proposed to account for the observed phenomena:

$$A + (CH_3)_2\dot{C}OH \xrightarrow[i\text{-PrOH}]{} \dot{A}H + (CH_3)_2CO \qquad (7)$$

$$A + \dot{A}H \xrightarrow[i\text{-PrOH}]{} \dot{A}_2H \qquad (8)$$

$$\dot{A}H + \dot{A}H \xrightarrow[i\text{-PrOH}]{} AH_2 + A \qquad (9)$$

$$\dot{A}_2H + \dot{A}_2H \xrightarrow[i\text{-PrOH}]{} AH_2 + 3A \qquad (10)$$

$$k_{10}/\epsilon_{550} \simeq 700 \text{ s}^{-1}$$

$$\dot{A}_2H \text{ (+ impurities) } \xrightarrow[i\text{-PrOH}]{} \text{products} \qquad (11)$$

$$\tau_{1/2} \simeq 0.2 \text{ s}$$

---

(15) E. A. Robinson and G. A. Salmon, *J. Phys. Chem.*, **82**, 382 (1978).

(16) G. Klopman and N. Doddapanemi, *J. Phys. Chem.*, **78**, 1825 (1974).

(17) J. Lilie, G. Beck, and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **75**, 458 (1971).

(18) Irreversible half-wave oxidation potentials. The system is assumed to be scarcely sensitive to changes in solvent, provided the medium is protic.[16]

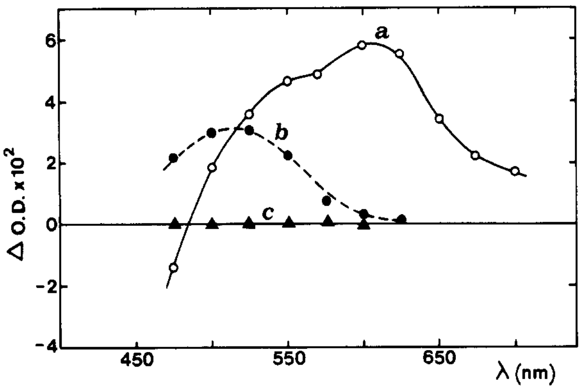


Figure 5. Difference spectra observed in the pulse radiolysis of a 7.1 × 10^{-5} M solution of DA in MeOH: (a) ○, 3 μs after the pulse, solution saturated with Ar; (b) ●, 2 μs and (c) ▲, 30 μs after the pulse, solution saturated with N_2O. Dose = 22 Gy. Optical path = 2 cm.

Reactions 7–9 take place on the same time scale and this fact results in a difficult evaluation of the single rate constants, given also the similar spectral features of $\dot{A}H$ and $\dot{A}_2H$. In fact, reaction 7 has in water a rate of 3 × 10^7 M^{-1} s^{-1},[11] reaction 8 has in MeOH a rate of 10^7 M^{-1} s^{-1}, and reaction 9 a rate of 4 × 10^9 M^{-1} s^{-1}, as reported in the previous section. An accurate treatment of the consecutive plus competitive kinetic scheme 7–9 is far too complex and also requires precise information on the molar extinction coefficient of $\dot{A}_2H$, for which only a lower limit in MeOH is available. Therefore the kinetic scheme proposed cannot be straightforwardly checked but it appears consistent with the observations and is supported by the knowledge of the system A–MeOH.

2. *4-(Diethylamino)azobenzene. 2.1. Transient Spectra and Kinetics in MeOH.* 4-(Diethylamino)azobenzene (DA) reacts with solvated electrons in methanol with a rate constant k_{12} = 1.6 × 10^{10} M^{-1} s^{-1}, identical with that of the reaction of A with e_s^- in the same solvent. The difference spectrum obtained in Ar-saturated solutions, at the end of the reaction, is shown in Figure 5, curve a. The broad absorption is characterized by a maximum at 600 nm and a shoulder in the 500–550-nm range, a region of overlap with DA absorption. In N_2O-saturated solution, only the absorption around 520 nm is left as can be seen in Figure 5, curve b. Therefore the band at 600 nm is assigned to the product of the reaction of e_s^- with DA. By comparison with the behavior of A in the same solvent, it is identified as $D\dot{A}H$, the hydrazyl radical derived from DA:

$$\mathrm{DA} + e_s^- \xrightarrow[\mathrm{MeOH}]{\mathrm{H^+}} \mathrm{D\dot{A}H} \qquad (12)$$

$$k_{12} = 1.6 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}$$

An approximate value of 15 000 M^{-1} cm^{-1} is calculated for ϵ_{max} at 600 nm for the species $D\dot{A}H$. The radical $\dot{C}H_2OH$ is not expected to reduce the –N=N– bond in DA, since the alkylamino-substituted azobenzenes have reduction potentials more negative than the unsubstituted compound.[16] Therefore the product of the fast reaction of the $\dot{C}H_2OH$ radical with DA, Figure 5, curve b, is identified as an adduct. The formation of the adduct is described by an exponential law. The rate constant is linear vs. the concentration of DA, with a slope of 5 × 10^9 M^{-1} s^{-1} and an intercept of 1 × 10^6 s^{-1}; no dose effect was found within the range 10–26 Gy. The intercept could arise from competing decay pathways. Nevertheless, the $\dot{C}H_2OH$ + $\dot{C}H_2OH$ reaction is excluded on the basis of the lack of dose effect and also a reaction with impurities is unlikely because of the too high concentration required to account for the intercept. Therefore the hypothesis is advanced of the existence of the reversible reaction

$$\mathrm{DA} + \dot{\mathrm{C}}\mathrm{H_2OH} \underset{\mathrm{MeOH}}{\overset{f}{\underset{b}{\rightleftharpoons}}} (\mathrm{DACH_2OH})\cdot \qquad (13)$$

$$k^{f}_{13} = 5 \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}} \qquad k^{b}_{13} = 1 \times 10^{6}\ \mathrm{s^{-1}}$$

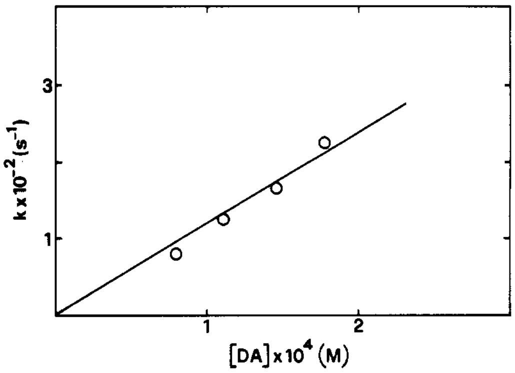


Figure 6. Rate constants for the pseudo-first-order decay of the absorbance at λ = 600 nm as a function of DA concentration in MeOH, saturated with Ar. Dose = 4.5 Gy.

This product, as can be clearly seen in N_2O-saturated solutions, decays via a first-order process, independent of both dose and DA concentration, with a rate constant of 1.5 × 10^5 s^{-1}, leaving neither residual absorption nor appreciable bleaching of the visible band of DA (Figure 5c). It is unlikely that the disappearance of the adduct is caused by the consumption of the reactant $\dot{C}H_2OH$ by reaction with impurities; in fact this would imply a slower process. Therefore we can propose the reaction:

$$(\mathrm{DACH_2OH})\cdot \xrightarrow[\mathrm{MeOH}]{} \overline{\mathrm{DA}} + \text{“radical”} \qquad (14)$$

$$k_{14} = 1.5 \times 10^{5}\ \mathrm{s^{-1}}$$

where $\overline{DA}$ is a molecule very similar to DA. No further variation of the optical transmission could be detected in the visible region, indicating the absence of reaction of the "radical" with DA.

In argon-saturated solutions, the decay of the hydrazyl radical $D\dot{A}H$, as already found for $\dot{A}H$ in the same solvent, can be described by competition of two processes, one of pseudo-first order and the other of second order. The second-order process dominates at high doses and a value of $k_{15}/\epsilon_{600} \simeq 2 \times 10^5$ s^{-1} was obtained. The exponential process was studied at low doses and the rate was found to depend linearly on the DA concentration, in agreement with a bimolecular rate constant $k_{16} \simeq 1 \times 10^6$ M^{-1} s^{-1}, as shown in Figure 6.

$$\mathrm{D\dot{A}H} + \mathrm{D\dot{A}H} \xrightarrow[\mathrm{MeOH}]{} \mathrm{DAH_2} + \mathrm{DA} \qquad (15)$$

$$k_{15} \simeq 3 \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}}$$

$$\mathrm{D\dot{A}H} + \mathrm{DA} \xrightarrow[\mathrm{MeOH}]{} \text{products} \qquad (16)$$

$$k_{16} \simeq 1 \times 10^{6}\ \mathrm{M^{-1}\ s^{-1}}$$

Reaction 16, at variance with the analogous reaction 2 of $\dot{A}H$ in MeOH, does not lead to an association product. Unfavorable steric factors and/or a scarce stabilization by the solvent can explain this result. The rate constant of the disproportionation reaction 15 appears to be very similar to that of the radical $\dot{A}H$ in the same solvent (reaction 3). On the contrary reaction 16 is considerably slower than the analogous reaction 2, confirming the presence of less-favorable conditions for the interaction of the hydrazyl with DA.

This system has been found to be extremely sensitive to incomplete change of irradiated solution in the millisecond range in argon-saturated medium, suggesting the reaction of a transient with a stable product of radiolysis.

2.2. *Transient Spectra and Kinetics in i-PrOH.* DA reacts with e_s^- in *i*-PrOH with a rate constant k_{17} = 7.0 × 10^9 M^{-1} s^{-1}, very similar to that of A in the same solvent. The difference spectra obtained in Ar-saturated solutions shortly after the electron pulse (Figure 7a,b) show a broad band with λ_{max} = 600 nm and a shoulder around 470 nm, a region of DA absorption. This spectrum is due to the contribution of two different products coming from the reactions of e_s^- and $(CH_3)_2\dot{C}OH$ with DA. This

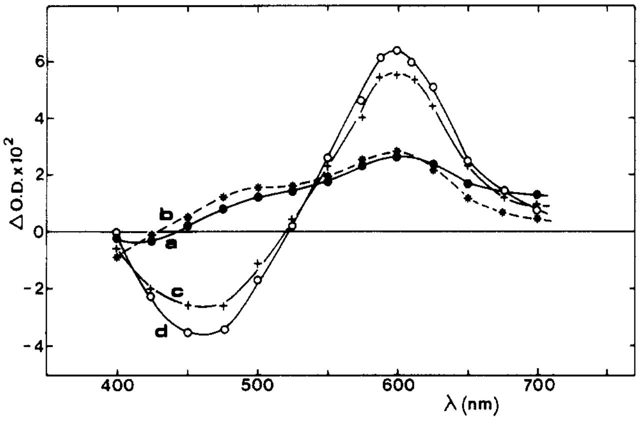


Figure 7. Difference spectra observed in the pulse radiolysis of a 4 × 10^{-5} M solution of DA in *i*-PrOH, saturated with Ar: (a) ●, 2.2 μs; (b) *, 13 μs; (c) +, 250 μs; (d) ○, 900 μs after the pulse. Dose = 22 Gy. Optical path = 2 cm.

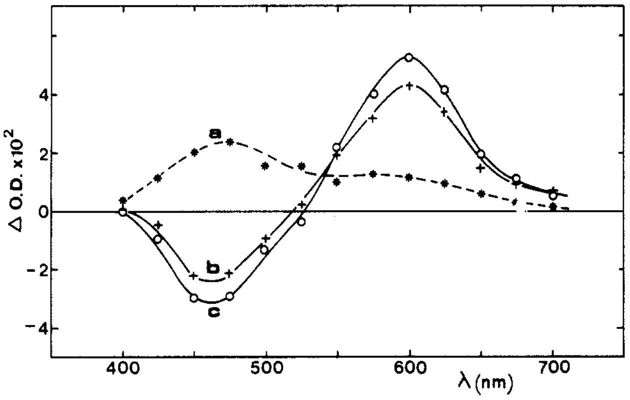


Figure 8. Difference spectra observed in the pulse radiolysis of a 4 × 10^{-5} M solution of DA in *i*-PrOH, saturated with N_2O: (a) *, 15 μs; (b) +, 250 μs; (c) ○, 900 μs after the pulse. Dose = 22 Gy. Optical path = 2 cm.

is clearly shown by the spectra in N_2O-saturated solutions in which only $(CH_3)_2\dot{C}OH$ reacts. In this case, Figure 8a, the broad absorption around 470 nm prevails. Therefore this band is assigned to the product of the reaction of the isopropyl radical with DA. A rate constant $k_{18} = 4 \times 10^9$ M^{-1} s^{-1} has been measured for this reaction, very similar to that of reaction 13 in MeOH, but much higher than the one characterizing the reduction of –N═N– bond in A by $(CH_3)_2\dot{C}OH$ itself (ca. 10^7 M^{-1} s^{-1}). Since reduction by the alcohol radical of the azo bond in DA would be expected to occur at rates similar to that found for A, we assign the 470-nm band to an adduct of the alcohol radical to the solute. The band at 600 nm, formed by the reaction of e_s^-, can be assigned by analogy with the findings in MeOH, to the hydrazyl radical.

$$DA + e_s^- \xrightarrow[i\text{-PrOH}]{H^+} D\dot{A}H \qquad (17)$$

$$k_{17} = 7.0 \times 10^9\ M^{-1}\ s^{-1}$$

$$DA + (CH_3)_2\dot{C}OH \xrightarrow[i\text{-PrOH}]{} (DA(CH_3)_2COH)\cdot \qquad (18)$$

$$k_{18} = 4.0 \times 10^9\ M^{-1}\ s^{-1}$$

Reaction 18, in contrast to the analogous reaction 13 in MeOH, is found to be irreversible. In fact the plot of the experimental rate constant vs. the concentration of DA is linear but with a zero intercept. The evolution at longer times of both the Ar- and the N_2O-saturated solutions is very similar as can be seen from Figure 7c,d and Figure 8b,c. In both cases the formation of a long-lived product absorbing at 600 nm is accompanied by the consumption of the starting product. The kinetics of this reaction, both at 470 and 600 nm, is pseudo-first order vs. DA concentration, according to a rate constant $k_{20} \simeq 8 \times 10^7$ M^{-1} s^{-1}, as shown in Figure 9. A dissociation of the adduct to produce the same species formed by e_s^- reduction, $D\dot{A}H$, followed by a reaction of the hydrazyl with DA, is proposed.

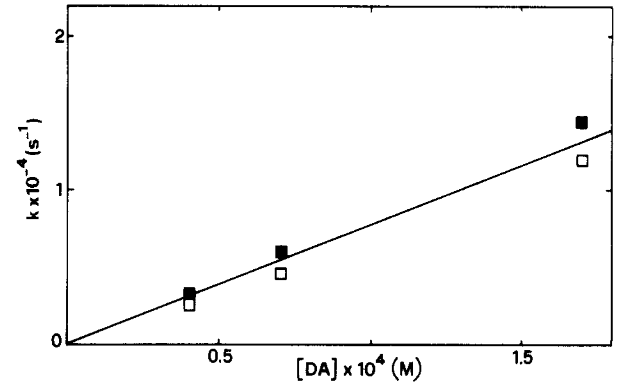


Figure 9. Rate constants for the pseudo-first-order absorbance variations at □, λ = 600 nm; ■, λ = 470 nm as a function of DA concentration in *i*-PrOH, saturated with Ar. The experimental values were unchanged in N_2O-saturated solutions. Dose = 4.5 Gy.

$$(DA(CH_3)_2COH)\cdot \xrightarrow[i\text{-PrOH}]{} D\dot{A}H + (CH_3)_2CO \qquad (19)$$

$$k_{19} \simeq 10^4\ s$$

$$D\dot{A}H + DA \xrightarrow[i\text{-PrOH}]{} (DA)_2\dot{}H \qquad (20)$$

$$k_{20} \simeq 8 \times 10^7\ M^{-1}\ s^{-1}$$

Reaction 19 should take place with a mechanism of intramolecular H transfer. The determination of its rate constant is made difficult by the superposition in time with reaction 20. However, an initial deviation even at low doses from the first-order kinetics of reaction 20 both at 470 and 600 nm allows us to evaluate an approximate rate $k_{19} \simeq 10^4$ s^{-1}.

Again, as already seen for $\dot{A}H$, a disproportionation reaction competes at high doses with reaction 20.

$$D\dot{A}H + D\dot{A}H \xrightarrow[i\text{-PrOH}]{} DAH_2 + DA \qquad (21)$$

$$k_{21} \geqslant 10^9\ M^{-1}\ s^{-1}$$

k_{21} cannot be measured because of the superposition of process 20, present even at high doses. It can be estimated to be of the order of 10^9 M^{-1} s^{-1}.

The decay of the species $(DA)_2H\cdot$ takes place over seconds. Similarly to what was found for the analogous radical $\dot{A}_2H$, the decay can be described by a competition scheme between a second-order dismutation and a first-order fragmentation (or reaction with impurities). The rate constants are very similar to those previously found for similar radical dimers.

$$(DA)_2H\cdot + (DA)_2H\cdot \xrightarrow[i\text{-PrOH}]{} DAH_2 + 3DA \qquad (22)$$

$$k_{22}/\epsilon_{600} \simeq 700\ s^{-1}$$

$$(DA)_2H\cdot\ (+\ \text{impurities}) \xrightarrow[i\text{-PrOH}]{} \text{products} \qquad (23)$$

$$\tau_{1/2} \simeq 0.1\ s$$

Comments and Conclusion

The rate constants of the reaction of A and DA with e_s^- are identical both in MeOH (1.6 × 10^{10} M^{-1} s^{-1}) and in *i*-PrOH ((8 ± 1)) × 10^9 M^{-1} s^{-1}), indicating a very high reactivity of the azo bond. The primary species detected with nanosecond time resolution are hydrazyl radicals formed from the rapid protonation of the anions. As regard to the reaction with e_s^-, it can be concluded that alkylamino substitution does not alter substantially the behavior of the azo bond.

α-Hydroxyalkyl radicals react, in general, with azo compounds to give reduction of the azo bond whenever energetically possible or/and addition in the case of diethylamino substitution. The $\dot{C}H_2OH$ radical neither has sufficient reducing power to reduce the azo bond nor does it have tendency to add to the unsubstituted

J. Phys. Chem. **1985**, *89*, 3707–3714

A, therefore it does not react in this case. On the contrary, it reacts with DA to give an adduct which subsequently dissociates to yield a product very similar to the starting dye.

The $(CH_3)_2\dot{C}OH$ radical can give both addition and reduction. With A the addition, as observed also in the case of the $\dot{C}H_2OH$ radical, is unfavored, so that only reduction of the azo bond takes place. With DA the addition reaction occurs at first, but formation of the hydrazyl radical is observed with the dissociation of the adduct.

Complete reduction of the azo bond occurs by second-order disproportionation of the semireduced radical intermediate, leading to the hydrazo derivative and to the original azo compound in a 1:1 ratio.[9] The rate constants for this process have been found to be of the order of $10^9\ M^{-1}\ s^{-1}$, similar to that found for the disproportionation of hydrazyl radicals in aqueous media, but 2–3 orders of magnitude higher than that attributed to this reaction in alcoholic solvents.[9] In competition with this second-order process, hydrazyl radicals have been found to undergo a pseudo-first-order reaction with the parent compound (rate constants 10^7–$10^8\ M^{-1}\ s^{-1}$), leading to a radical dimer with spectroscopic characteristics quite similar to the hydrazyl itself. These radical dimers undergo a second-order reaction themselves with a much slower rate compared to that of the hydrazyl radicals. Rates of 10^6–$10^7\ M^{-1}\ s^{-1}$ can be calculated for the disproportionation of radical dimer, assuming ϵ similar to that of the hydrazyl. This order of magnitude matches with that of the rate constants attributed to hydrazyl dismutation in alcohols.[9] Since the solvent dependence of the disproportionation rate constants of hydrazyl radicals has not been reasonably explained so far, we propose that association phenomena with negligible spectral consequences similar to those observed by us can be at the origin of the observed rate constant lowering in alcohols.[9]

Acknowledgment. This work was supported by the Progetto Finalizzato del Consiglio Nazionale delle Ricerche per la Chimica Fine e Secondaria. We thank Dr. S. Emmi for the set up of the computerized data acquisition system and Dr. A. Martelli for the maintenance of the LINAC. The interest of Dr. Mulazzani and Dr. S. Dellonte during the course of this work is also acknowledged.

Registry No. A, 17082-12-1; DA, 6860-63-5; MeOH, 67-56-1; *i*-PrOH, 67-63-0; $(CH_3)_2\dot{C}OH$, 5131-95-3; $\dot{C}H_2OH$, 2597-43-5.

Bromine-Hydrolysis Control in the Cerium Ion–Bromate Ion–Oxalic Acid–Acetone Belousov–Zhabotinskii Oscillator

Richard J. Field* and Patrick M. Boyd

Department of Chemistry, University of Montana, Missoula, Montana 59812 (Received: January 17, 1985)

Chemical oscillations in reacting systems containing BrO_3^- have been interpreted as a switching phenomenon in which control of the overall reaction is passed back and forth between a set of radical reactions and a set of nonradical reactions. Switching is assumed to be controlled by $[Br^-]$. When $[Br^-]$ is high, control is by the nonradical reactions, whose major effect is the removal of Br^-. Control switches to the radical reactions when $[Br^-]$ is driven low enough. Oscillation occurs because Br^- is an indirect product of the radical reactions, causing control to be returned to the nonradical reactions. Bromide ion control of BrO_3^--driven oscillations has been challenged on the basis that in some systems the usual source of Br^- from the radical reactions is absent. It has been suggested that the oscillations are in fact Br_2 controlled. It is shown here that one of these puzzling oscillators can be simulated as Br^- controlled. By implication the others also can be. Bromine is an important intermediate in these systems as the controlling Br^- comes from Br_2 hydrolysis and is in equilibrium with Br_2 and HOBr. We call such an oscillator Br_2-hydrolysis controlled. The simulation is based on 31 elementary reactions of which 9 are reversible. It was constructed on the basis of a large number of experiments on simpler, nonoscillatory reactions involving the same reactants and is much simpler than the mechanisms of other BrO_3^--driven oscillators because of the relative simplicity in it of the reactions of oxalic acid and acetone. The rate constants thus determined were used without modification to obtain an essentially quantitative simulation of the oscillatory system. It is thus the most complete and quantitatively accurate simulation of a BrO_3^--driven oscillator with an organic substrate yet carried out. The complete mechanism can be reduced to a simple five-variable Oregonator-like model that contains no expendable stoichiometric factor and whose rate parameters all can be related directly to the concentration of a principal reactant.

Introduction

In its classic form the Belousov–Zhabotinskii (BZ) reaction is the metal-ion-catalyzed oxidation of an easily brominated organic substrate by BrO_3^- in a strongly acid medium.[1,2] Oscillations may be readily measured in the ratio of the concentration of the oxidized form to the concentration of the reduced form of the metal-ion catalyst and in $[Br^-]$. In 1972 Field, Körös, and Noyes (FKN)[1] proposed a detailed mechanism for the BZ reaction with malonic acid as the organic substrate. The FKN mechanism is fundamentally dependent upon control of the oscillations by $[Br^-]$ and has been successful in rationalizing[2] essentially all observed behaviors of the BZ reaction and various bromate-ion-driven[3,15] oscillators derived from it. The FKN mechanism can be reduced to a much simpler model,[4] called the Oregonator, which has proved to be very useful for connecting the observed behavior of the BZ reaction to basic ideas from nonlinear dynamics.[5-7]

However, several modifications of the BZ reaction have been reported by Noszticzius[8-10] and others[11,12] that do not fit easily

---

[1] Field, R. J.; Körös, E.; Noyes, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 8649.

[2] Field, R. J. In "Oscillations and Traveling Waves in Chemical Systems", Field, R. J., Burger, M., Eds.; Wiley-Interscience: New York, 1985; Chapter 2. See also Kumpinsky, E.; Epstein, I. R. *J. Phys. Chem.* **1985**, *89*, 688.

[3] Noyes, R. M. *J. Am. Chem. Soc.* **1980**, *102*, 4644.

[4] Field, R. J.; Noyes, R. M. *J. Chem. Phys.* **1974**, *60*, 1877.

[5] Tyson, J. J. In "Oscillations and Traveling Waves in Chemical Systems", Field, R. J., Burger, M., Eds.; Wiley-Interscience: New York, 1985; Chapter 4.

[6] Troy, W. C. Reference 5, Chapter 5.

[7] De Kepper, P.; Boissonade, J. Reference 5, Chapter 7.

[8] Noszticzius, Z.; Bódiss, *J. Am. Chem. Soc.* **1979**, *101*, 3177.