

Figure 6. Transient spectrum in $[Ir((C^3, N'-Hbpy)(bpy)_2)]^{3+}$ -Fe(III): 5 × 10⁻⁵ M $[Ir((C^3, N'-Hbpy)(bpy)_2)]^{3+}$, 2 × 10⁻² M Fe(ClO₄)₃, pH 0.6 (HClO₄). Difference spectrum measured 20 μ s after a laser pulse, 1.7 × 10⁻⁵ einstein L⁻¹ pulse⁻¹.

pulsed laser experiments show that the quenching obeys the Stern-Volmer law, yielding $k_{11} = (1.7 \pm 0.2) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ compared with the previously published value of $^2 3.7 \times 10^7 \text{ M}^{-1}$ s⁻¹ which was reported for FeCl₃. The quenching is accompanied by a buildup of absorption, the spectrum of which is not identical with the spectrum of the oxidized iridium complex. The decay of this absorption obeys a first-order rate law. The transient spectrum obtained 20 μ s after the laser pulse in a solution containing $2 \times 10^{-2} \text{ M Fe(III)}$ is shown in Figure 6. Thus the product of reaction 11 is not the Fe(III) and the oxidized sensitizer as

$$[Ir((C^3, N'-Hbpy)(bpy)_2)]^{3+*} + Fe(III) \rightarrow product (11)$$

might be a priori expected, but probably a complex involving both Ir and Fe. Such a complex may be produced by the interaction of the excited state of the sensitizer and Fe³⁺ ions, perhaps followed by charge rearrangement so that Fe^{2+} and $[Ir((C^3, N-Hbp))$ -

 $(bpy)_2)$ ⁴⁺ are produced (hence some resemblance to the oxidized iridium complex spectrum in the range $\lambda = 390-450$ nm). A relatively slow first-order reaction to the ground-state starting materials takes place rather than charge separation of the electron-transfer products.

Conclusions

Several electron acceptors were found to quench the emission of the lowest excited state of the iridium sensitizer and to produce absorbance changes. The spectra and kinetics observed show that $[Ir((C^3, N'-Hbpy)(bpy)_2]^{4+}$ is produced in at least three of these systems. This oxidized species is a strong oxidant, capable of oxidizing Cl⁻ to Cl₂⁻. It is probably also capable of oxidizing water, even in acid pH, although our experiments indicate its kinetics stability at pH 1.5. Oxidation of the iridium complex in acetonitrile solutions has been investigated by cyclic voltammetry. The resulting product is reported to be a strong oxidant.^{16,17} A similar compound obtained by the oxidation of Ir(bpy)₃³⁺ was show to be a powerful oxidant. An irreversible oxidative wave was observed by cyclic voltammetry at 2.17 V.^{17,18} We do not known whether the iridium complex is oxidized at the metal or at a ligand site.

Acknowledgment. This research was supported by the Balfour and Schreiber Foundations, Israel.

Registry No. MV⁺, 25239-55-8; $[Ir((C^3, N'Hbpy)(bpy)_2)]^{3+}$, 99531-93-8; $[Ir((C^3, N'Hbpy)(bpy)_2)]^{4+}$, 99531-94-9; $[Co(NH_3)_5F]^{2+}$, 15392-06-0; $S_2O_8^{2-}$, 15092-81-6; $Fe(ClO_4)_3$, 13537-24-1; methylviologen nitrate, 72517-38-5.

(18) We thank the referee for the remark that the oxidation of $Ir(bpy)_3^{3+}$ is not reversible.

Primary Processes in the Reduction of 4-Nitroazobenzene. A Pulse Radiolysis Study in Alcoholic Solvents

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The transient species produced in the reactions of solvated electrons and α -hydroxyalkyl radicals with 4-nitroazobenzene have been studied by spectrophotometric pulse radiolysis in 2-propanol and methanol. Solvated electrons were found to react with rate constants of 1.6×10^{10} and 2.3×10^{10} M⁻¹ s⁻¹ in 2-propanol and methanol, respectively, giving the anion as primary product. The same species is produced by electron transfer from both alcohol radicals, with rate constants ca. 10^9 M⁻¹ s⁻¹ for (CH₃)₂COH and ca. 6×10^7 M⁻¹ s⁻¹ for CH₂OH. Protonation of the anion is observed in the microsecond time scale, leading to the hydrazyl radical. pK values for the protolytic dissociation of this species are evaluated to be 14.8 and 12.3 in 2-propanol and methanol, respectively. Association of the hydrazyl with the starting compound is observed in 2-propanol. Complete reduction of the azo bond occurs by very efficient second-order disproportionation of hydrazyl and/or dimer radicals.

Introduction

Reduction processes have been demonstrated to play an important role in the photofading of azo dyes adsorbed on H-donating substrates.¹ Nitro-substituted phenylazo dyes show anomalous photofading behavior; i.e., their light fastness is much lower than those of similar compounds in which other substituents are present (see ref 2 and bibliography therein). This effect has been investigated in detail in 1-(substituted) phenylazo-2-naphthols in alcoholic solvents.²

It has been suggested that photoreductive processes, induced by solvent radicals, involve both the nitro and the azo groups and, combined with the normal photooxidative reactions by singlet oxygen, cause a dramatic decrease in the light stability of the dye.² No information has been reported on the intermediates involved in the production of the final reduction products, which are known to be amines.

The primary processes in the reduction of azo dyes by solvated electrons (e_s^-) and α -hydroxyalkyl radicals $(R^1R^2\dot{C}OH)$ have been recently investigated by pulse radiolysis with the aid of spectro-

⁽¹⁶⁾ Brateman, P. S.; Heath, G. A.; MacKenzie, A. J.; Noble, B. C.;
Peacock, R. D.; Yellowlees, L. Y. Inorg. Chem. 1984, 23, 3425.
(17) Kahl, J. L.; Hanck, K. W.; DeArmond, K. J. Phys. Chem. 1978, 82,

⁽¹⁷⁾ Kain, S. E., Hanck, K. W., Dekrinold, K. S. 1 hys. Chem. 17(6, 62, 540).

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

⁽²⁾ Kuramoto, N.; Kitao, T. J. Soc. Dyers Colour. 1980, 96, 529.



photometric detection in alcoholic solvents.³ Two azo derivatives were studied as model systems: azobenzene (A) and 4-(diethylamino)azobenzene (DA). The technique used was found to be very effective in the production of the reducing species, in the identification of intermediates involved, and in the determination of their role in the fading of the -N=N- bond.

The purpose of the present work is to extend the study to the mechanism of reduction of nitrophenylazodyes induced by radical species. To this aim pulse radiolysis of the simple model, 4nitroazobenzene (NA), dissolved in methanol and 2-propanol, has been performed. The primary species, formed in the reactions of e_s^- and R^1R^2COH radicals with the dye, have been identified and their time evolution has been followed to the formation of stable reduction products. Rate constants for primary and secondary reactions have been determined. The distinct roles of the two reducible groups, $-NO_2$ and -N=N-, have been evidenced.

Experimental Section

Methyl alcohol (MeOH) and isopropyl alcohol (*i*-PrOH) were fluorimetric grade products (RS-Carlo Erba), and were used without further purification. The e_s^- half-life was 2.9 μ s in MeOH and 1.3 μ s in *i*-PrOH.

trans-4-Nitroazobenzene (NA) was synthesized by Aziende Colori Nazionali Affini (Italy). Solutions ($c < 3.2 \times 10^{-4}$ M) were freshly prepared and protected from light before each experiment to prevent trans \rightarrow cis isomerization of the compound. Basic solutions were prepared by first dissolving a known quantity of Na metal in *i*-PrOH and MeOH and then adding the solute. Acidic solutions were prepared by adding measured quantities of HClO₄ (Merck, Suprapur) to alcoholic solutions. Samples were deaerated by bubbling argon or N₂O for 30 min.

The radiation source (12 MeV, Vickers Linear Accelerator) and the spectrophotometric detection system have been described previously.³ Doses were measured by a charge collector calibrated against the thiocyanate dosimeter, using a $G\epsilon_{500 \text{ nm}} = 2.15 \times 10^4$ molecules $(100 \text{ eV})^{-1} \text{ M}^{-1} \text{ cm}^{-1}$ for the $(\text{SCN})_2^{-1}$ radical. Measurements were performed at 20 ± 2 °C.

In neutral alcohols only reactions of e_s⁻ and R¹R²COH radicals with the solute have been considered to be significant in our experimental conditions. In N2O-saturated solutions, es are rapidly converted to R¹R²COH radicals,⁴ so that α -hydroxyalkyl radicals are the only reactive species. In basic solutions $([R^{1}R^{2}CHO^{-}] \simeq 0.1 \text{ M})$, the alcohol radical is present in the dissociated form R¹R²CO⁻,⁴ which is known to be a stronger reductant than the neutral form.⁵

G values for e_s^- were taken to be 1.2 in MeOH⁶ and 1.0 in *i*-PrOH.⁷ G values for R^1R^2COH were taken to be 5.6 in Arsaturated MeOH⁸ and 4.9 in Ar-saturated *i*-PrOH.⁹

The second-order rate constants for the $2R \rightarrow$ products reaction are defined by the expression $-d[R]/dt = 2k[R]^2$. The final concentration of a product P (anion or neutral radical) deriving from the competition reaction scheme

$$R^1R^2\dot{C}OH \text{ (or } R^1R^2\dot{C}O^-) + NA \xrightarrow{k_{II}} P$$

 $2R^{1}R^{2}\dot{C}OH$ (or $2R^{1}R^{2}\dot{C}O^{-}$) \xrightarrow{n} products

where NA is in excess, was calculated with the expression

$$[\mathbf{P}]_{\text{final}} = \frac{k_{\text{I}}[\mathbf{NA}]_{0}}{2k_{\text{II}}} \ln \left(\frac{2k_{\text{II}}[\mathbf{R}^{1}\mathbf{R}^{2}\dot{\mathbf{C}}\mathbf{OH}]_{0}}{k_{\text{I}}[\mathbf{NA}]_{0}} + 1 \right)$$

 $[NA]_0$ and $[R^1R^2\dot{C}OH]_0$ being the initial concentrations of the dye and of the radical. This expression was derived from the treatment of competitive reactions involving a pseudo-first-order and a second-order component.¹⁰ $k_{\rm II}$ values for the 2R¹R²COH \rightarrow products reactions were assumed to be 1.4 \times 10⁹ M⁻¹ s⁻¹ for \dot{CH}_2OH^4 and ca. 10⁸ M⁻¹ s⁻¹ for $(CH_3)_2\dot{C}OH$ on the basis of a value of 3×10^8 M⁻¹ s⁻¹ reported for CH₃CHOH.⁴ k_{II} values for the $2R^1R^2\dot{C}O^- \rightarrow$ products were assumed to be of the order of 108 M⁻¹ s⁻¹ for both radicals.^{4,6}

 pK_a values for CH₃OH and (CH₃)₂CHOH in MeOH and *i*-PrOH respectively were taken to be 18.1¹¹ and 20,¹² respectively. From these pK values, the equilibrium $[H^+]$ in neat alcohols was calculated to be 3.6×10^{-10} M in *i*-PrOH and 4.4×10^{-9} M in MeOH; addition of a solute with acidic or basic properties changes the H^+ concentration. The calculation of $[H^+]$ in the presence of NA⁻ and/or NAH under the simultaneous equilibria

$$N\dot{A}H \rightleftharpoons N\dot{A}^- + H^+$$

 $R^1R^2CHOH \rightleftharpoons H^+ + R^1R^2CHO^-$

was done by assuming $[R^1R^2CHO^-] \simeq [NAH]$.

The errors are estimated to be $\leq 20\%$ on the extinction coefficients and ≤15% on the rate constants, unless mixed kinetics are involved. In these cases the symbol \simeq is used and the rates reported must be regarded as approximated values.

The corrections in the difference spectra due to the consumption of NA are not very important at $\lambda \ge 390$ nm, where $\epsilon_{NA} \le 10^3$ $M^{-1}~cm^{-1}.~At~\lambda$ <390 nm the ϵ_{NA} drastically increases (λ_{max} = 330 nm, $\pi\pi^*$ band, $\epsilon_{max} \simeq 2.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), corrections become very large, and no real meaning must be assigned to the maxima appearing in the difference spectra around 390 nm.

Results and Discussion

1. 2-Propanol as Solvent. NA reacts with e_s^- in *i*-PrOH with a rate constant $k_1 = 1.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, higher than those found for the reactions A and DA with e_s^- in the same solvent,³ as expected for a nitro derivative.¹³ The difference spectra, obtained in a 1.4×10^{-4} M NA, Ar-saturated solution, at 1 μ s (a), 12 μ s (b), 42 μ s (c), 650 μ s (d), and 9.5 ms (e) after a 22-Gy electron pulse, are shown in Figure 1. Saturation of the solution with N_2O produces very little changes in the spectra, as can be seen in Figure 2. By a closer inspection of Figures 1 and 2, it appears that the spectra at $t < 42 \ \mu s$ after the pulse in Ar are richer in the 470-nm component. It can be observed that also in N₂O-saturated solutions the initial spectrum 2a is richer with respect to 2b and 2c in the region around 470 nm.

In order to obtain more information for the attribution of the transient absorption, the following experiments were performed. A basic solution of 1.4×10^{-4} M NA, containing ca. 10^{-1} M *i*-PrO⁻ Na⁺, was irradiated by a 22-Gy electron pulse. The spectrum recorded is shown in Figure 3; it presents a maximum around 470 nm which is assigned to the radical anion NA⁻. Its formation

⁽³⁾ Flamigni, L.; Monti, S. J. Phys. Chem. 1985, 89, 3702.

⁽⁴⁾ Johnson, D. W.; Salmon, G. A. J. Chem. Soc., Faraday Trans. 1 1975, 71, 583.

⁽⁵⁾ Lilie, J.; Beck, G.; Henglein, A. Ber. Bunsenges. Phys. Chem. 1971, 75, 458.

⁽⁶⁾ Johnson, D. W.; Salmon, G. A. Can. J. Chem. 1977, 55, 2030.
(7) Sauer, Jr., M. C.; Arai, S.; Dorfman, L. M. J. Chem. Phys. 1965, 42, 708

⁽⁸⁾ Johnson, D. W.; Salmon, G. A. J. Chem. Soc., Faraday Trans. 1 1977, 73, 256.

⁽⁹⁾ Freeman, G. R. In "Action Chimiques et Biologiques des Radiations"; Haissinski, M., Ed.; Masson: Paris, 1970; Vol. 14, Chapter 2, p 103.

⁽¹⁰⁾ Emanuel, N.; Knorre, D. "Cinetique Chimique"; Editions Mir: Moscow, 1975; pp 217-222.

⁽¹¹⁾ Rochester, C. H. In "The Chemistry of the Hydroxyl Group", Part (11) Rotatel, G. H. H. H. Andra, 1972; Chapter 7, p. 373.
 (12) Neta, P.; Levanon, H. J. Phys. Chem. 1977, 81, 2288.
 (13) Greenstock, C. In "The Chemistry of Functional Groups", Supple-

ment F; Patai, S., Ed.; Interscience: New York, 1982; Chapter 7, p 291.



Figure 1. 1.4×10^{-4} M NA in Ar-saturated *i*-PrOH; dose = 22 Gy. Difference spectra recorded at (a) 0, 1 μ s; (b) \Box , 12 μ s; (c) Δ , 42 μ s; (d) \bullet , 650 μ s; (e) *, 9.6 ms after the electron pulse. Optical path = 2 cm.



Figure 2. 1.4×10^{-4} M NA in N₂O-saturated *i*-PrOH; dose = 22 Gy. Difference spectra recorded at (a) O, 1 μ s; (b) \Box , 12 μ s; (c) Δ , 42 μ s; (d) \oplus , 650 μ s; (e) *, 9.6 ms after the electron pulse. Optical path = 2 cm.

proceeds in two subsequent steps via reactions with e_s^- and $(CH_3)_2\dot{C}O^-$. This last reaction has a rate constant $k_2 = 2.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in agreement with the value reported for the reduction of A by the same radical.¹²

$$NA + e_s^- \rightarrow N\dot{A}^-$$
 (1)
 $k_1 = 1.9 \times 10^{10} M^{-1} s^{-1}$

NA + (CH₃)₂ĊO⁻ → NÅ⁻ + (CH₃)₂CO (2)

$$k_2 = 2.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$



Figure 3. 1.4×10^{-4} M NA in *i*-PrOH. Difference spectra after the electron pulse recorded at (a) *, 2.2 μ s; (b) O, 15 μ s, both in the presence of 0.1 M *i*-PrO⁻Na⁺, Ar-saturated solution; (c) Δ , 42 μ s in the presence of 5 $\times 10^{-5}$ M HClO₄, N₂O-saturated solution. Dose = 22 Gy. Optical path = 2 cm.

Reaction 2 is effective only in basic medium. Calculating a $G_{N\dot{A}^-}$ = 5.7 (see Experimental Section) an extinction coefficient of 18 500 M⁻¹ cm⁻¹ is derived, from spectrum b of Figure 3, for NÅ⁻ at 470 nm.

Acidic solutions of 1.4×10^{-4} M NA, in N₂O-saturated *i*-PrOH, containing different concentrations of HClO₄, were irradiated. The difference spectrum obtained for [HClO₄] = 5×10^{-5} M at 42 µs after the pulse in N₂O saturated solutions, is shown in Figure 3, curve c. Since the spectrum did not change on increasing the acid concentration by a factor of 10, it was assigned to the neutral radical NAH formed by rapid protonation of the anion NA⁻ produced in the reaction with (CH₃)₂COH. G = 5.5 was calculated for NAH (see Experimental Section) which gives an extinction coefficient of 3600 M⁻¹ cm⁻¹ for NAH at 470 nm.

Going back to the neutral solutions (Figures 1 and 2), we can therefore assign the spectra obtained both in N₂O and in Ar to mixtures of NÅ⁻ and NÅH. The spectra at $t < 42 \ \mu$ s in Ar are richer in the 470-nm component, with respect to those in N₂O, due to the initial higher concentration of the anion formed in the fast reaction 1. The spectrum at $t = 42 \ \mu$ s is almost the same in Ar- and N₂O-saturated solutions, because protonation of NÅ⁻ occurs in the time scale of the (CH₃)₂COH reaction. This spectrum is therefore assigned to the equilibrium mixture of the anion and the protonated radical.

$$NA + (CH_3)_2 \dot{C}OH \rightarrow N\dot{A}^- + (CH_3)_2 CO + H^+ \quad (3)$$

$$k_3 \simeq (1-2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

 $N\dot{A}^- + H^+ \frac{f}{5} N\dot{A}H$ (4)
 $k_4^{b}/k_4^{f} = 1.5 \times 10^{-15} \text{ M}$

The value of k_3 has been estimated with a simple exponential treatment of the oscillograms at 400, 500, and 600 nm in N₂O-saturated solution and is given as approximate value because of the time superposition of reaction 4. This last appears as a slight decrease of the optical density around 470–500 nm, particularly evident in Ar-saturated solution. k_3 is of the order of the rates found for the reduction of nitro aromatics by $(CH_3)_2\dot{C}OH$ in aqueous solution, in cases of strong coupling between the nitro substituted and the ring π system.¹⁴ The increase in the order of the unsubstituted A ($k \simeq 10^7 \text{ M}^{-1} \text{ s}^{-1}$) by the same radical must be ascribed to the decrease of reduction potential of the molecule by substitution with an electron-withdrawing group.^{15,16}

⁽¹⁴⁾ Neta, P.; Meisel, D. J. Phys. Chem. 1976, 80, 519.
(15) Millefiori, S.; Millefiori, A. J. Chem. Soc., Faraday Trans. 2 1981, 77, 245.



Figure 4. 1.5×10^{-4} M NA in Ar-saturated *i*-PrOH; dose = 4.5 Gy. Difference spectra recorded at: (a) \Box , 42 μ s; (b) O, 1.3 ms; (c) *, 50 ms after the electron pulse. Optical path = 2 cm. Curve b must be compared with curve d of Figure 1, taken at the time when maximum optical density was reached around 600 nm. In the inset are reported the rate constants for the pseudo-first-order growth of absorbance at 550 nm vs. NA concentration. The experimental values were unchanged in N2Osaturated solutions.

A calculation of the composition of the equilibrium mixture, based on the ϵ values derived for NÅ⁻ and NÅH and a G_{NA^-+NAH} = 5.6 in N_2 O-saturated solutions (see Experimental Section), gives a degree of dissociation of 12%. This, with $[H^+] = 1.1 \times 10^{-14}$ (see Experimental Section) leads to a $pK_{NAH} = 14.8$ for the protolytic dissociation of NAH, lower than that reported for the semireduced radical of A in the same solvent $(pK_{AH} = 17)$.¹² The increase of the acidic properties of the radical NAH with the introduction of the -NO2 group is a well-established phenomenon and is due to the stabilization of the anionic form by the contribution of the resonance structure $-NO_2^{-1}$.

On the nature of NAH the following considerations can be done. The reduction of the NA molecule could occur either at the -N=N- or at the $-NO_2$ site; a comparison of the reversible reduction potentials in comparable conditions of azobenzene¹⁶ and nitrobenzene¹⁷, taken as models of the two sites, indicates the last as more available to reduction. However, in a study of the electrochemical reduction of 4-nitroazoxybenzene,¹⁸ it has been shown that between the two groups, the first one to be reduced is the -N==N- bond. The hydrazo derivative formed is sufficiently stable to be isolated.¹⁸ We, therefore, identify NAH as the hydrazyl radical, $-\dot{N}-N(H)-$. This seems to indicate that the electron transfer occurs via the nitro group, but the additional electron is delocalized over the rest of the molecule included the -N=N- bond, where the protonation takes place. The role played by the whole π system in the reduction of nitroaromatics has been clearly pointed out by Neta and Meisel.¹⁴

The identification of NAH with the hydrazyl is further confirmed by the mechanism of disappearance of this species, which shows significant analogies with that of hydrazyl radicals derived from A and DA.³ The decay of NAH can be followed within a few milliseconds. At low dose (4.5 Gy) the simultaneous buildup of a very broad absorption in the 500-700-nm region can be detected (Figure 4, curve b). The rate constant for the formation

of this absorption increases linearly with NA concentration (Figure 4, inset) with a slope $k_5 = 5.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and an intercept of $2.0 \times 10^3 \ s^{-1}.$ On the basis of these kinetic evidences and by analogy with the behavior of other hydrazyl radicals,³ the formation of a radical dimer is proposed:

$$N\dot{A}H + NA \rightarrow (NA)_2 H$$
 (5)

$$k_5 = 5.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$$

The meaning of the intercept is doubtful. It could be due to the occurrence of a competitive disproportionation reaction of NAH leading to the hydrazo and the azo compounds. This could also explain the lower relative yield of radical dimer (NA), H, observed at higher dose (Figure 1, curve d). Unfortunately it is not possible to confirm this interpretation by measuring the expected dose dependence of the intercept. In fact, at higher doses, the absorption around 600 nm, which grows in due to the formation of (NA), H. is too small compared with the initial absorption to permit a reliable kinetic analysis. This fact can also be due to the second-order decay of (NA)₂H itself (see later). On the other hand, kinetic treatment of oscillograms in the 400-nm region is made difficult by the superposition of the absorptions of (NA)₂'H and of the final products to that of NAH. However, by analogy with the behavior of other hydrazyl radicals,³ the disproportionation reaction 6 is proposed where the rate constant k_6 can be only roughly estimated:

$$N\dot{A}H + N\dot{A}H \rightarrow NAH_2 + NA$$
 (6)

$$k_6 \simeq 10^7 - 10^8 \text{ M}^{-1} \text{ s}^{-1}$$

The decay of the radical dimer (NA)₂'H takes place in the millisecond range and is well described by second-order kinetics with $k_7/\epsilon_{550} = 1.2 \times 10^4$ cm s⁻¹. As already reported,³ a disproportionation process can be invoked and to the hydrazo derivative NAH₂ are tentatively attributed the final spectra of Figures 1, 2, and 4.

$$(NA)_2 H + (NA)_2 H \rightarrow NAH_2 + 3NA$$
 (7)
 $k_7/\epsilon_{550} = 1.2 \times 10^4 \text{ cm s}^{-1}$

No evidence of a competitive first-order reaction, reported for other hydrazyl dimers,³ is found in this case, probably because of the much higher efficiency of the dismutation reaction 7.

2. Methanol as Solvent. NA reacts with e_s in MeOH with a rate constant $k_8 = 2.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. As already observed in i-PrOH, this rate is higher than that found for other azo derivatives in MeOH³ and is in agreement with the rate of reaction of $e_s^$ with nitrobenzene in the same solvent.⁶ The difference spectra obtained in Ar-saturated 1.5×10^{-4} M NA solution are displayed in Figure 5 at 1 μ s (a), 170 μ s (b), and 45 ms (c), after a 22-Gy electron pulse. The spectrum a, recorded at the end of the e_s reaction, shows a band with $\lambda_{max} = 450$ nm. The same spectrum is obtained by irradiating a basic Ar-saturated solution, containing ca. 10⁻¹ M MeO⁻Na⁺ (Figure 6). It is therefore assigned to the radical anion NA⁻, which, in basic solution, is formed in two steps.

$$NA + e_s^- \rightarrow N\dot{A}^-$$
 (8)

$$k_8 = 2.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$$

$$NA + \dot{C}H_2O^- \rightarrow N\dot{A}^- + CH_2O \tag{9}$$

$$k_9 = 3.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

Reaction 9 is effective only in basic medium. The rate constant k_9 is of the same order of that found for the reduction of NA by $(CH_3)_2 \dot{C}O^-$, in agreement with the high reducing power of the α -hydroxyalkyl radical anions.⁵ By calculating a $G_{NA^-} = 6.7$ (see Experimental Section) an extinction coefficient of $21\,000$ M⁻¹ cm⁻¹ is derived at 450 nm for the NA⁻ radical in MeOH, in fairly good agreement with $\epsilon_{max} = 18500 \text{ M}^{-1} \text{ cm}^{-1}$, determined in *i*-PrOH for the corresponding band.

In Figure 6 is also reported the difference spectrum obtained in a 1.5×10^{-4} M NA, N₂O-saturated solution, containing HClO₄

⁽¹⁶⁾ Klopman, G.; Doddapanemi, N. J. Phys. Chem. 1974, 78, 1825.
(17) Meisel, D.; Neta, P. J. Am. Chem. Soc. 1975, 97, 5198.
(18) Hazard, R.; Tallec, A. Bull. Soc. Chim. Fr. 1971, 2917.



Figure 5. 1.5×10^{-4} M NA in Ar-saturated MeOH; dose = 22 Gy. Difference spectra recorded at (a) 0, 1 μ s; (b) \Box , 170 μ s; (c) *, 45 ms, after the electron pulse. Optical path = 2 cm.



Figure 6. 1.5×10^{-4} M NA in MeOH. Difference spectra after the electron pulse recorded at (a) \Box , 1 μ s; (b) O, 12 μ s, both in the presence of 1.3×10^{-1} M MeO-Na⁺, Ar-saturated solution; (c) Δ , 300 μ s, in the presence of 4.6 × 10⁻⁵ M HClO₄, N₂O-saturated solution. Dose = 22 Gy. Optical path = 2 cm.

4.6 × 10⁻⁵ M, at 300 μ s after the pulse (curve c). By increasing the acid concentration (by a factor of 10) no change was detected in the spectrum; therefore it was assigned to the radical NÅH, formed by protonation of the anion NÅ⁻, produced in the reduction of NA by the radical CH₂OH. By calculating a $G_{NÅH} = 2.4$ (see Experimental Section) an extinction coefficient of 2700 M⁻¹ cm⁻¹ is obtained for NÅH at 475 nm, in reasonable agreement, given the approximation involved, with that derived in *i*-PrOH.

In neutral, Ar-saturated solution, the $N\dot{A}^-$ initially formed protonates on the same time scale of the $\dot{C}H_2OH$ reaction and in Figure 5b a mixture of $N\dot{A}^-$ and $N\dot{A}H$ can be recognized. The equilibrium is not fully achieved since the second-order decay of



Figure 7. 1.5×10^{-4} M NA in N₂O-saturated MeOH. Difference spectra recorded at (a) \Box , 300 μ s; (b) *, 45 ms after the electron pulse. Dose = 22 Gy. Optical path = 2 cm.

the radical NÅH (see later) subtracts the product. In N_2O saturated solution, on the contrary, because of the lower transient yields, the second-order decay is slowed down and the equilibrium composition is attained (Figure 7, curve a).

$$NA + \dot{C}H_2OH \rightarrow N\dot{A}^- + CH_2O + H^+$$
(10)

$$k_{10} \simeq 6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$$

 $\text{N}\dot{\text{A}}^- + \text{H}^+ \stackrel{\text{f}}{\longleftrightarrow} \text{N}\dot{\text{A}}\text{H}$ (11)

$$k_{11}^{b}/k_{11}^{f} = 4.7 \times 10^{-13} \text{ M}$$

The rate constant k_{10} is given as an approximate value due to the time superposition with reaction 11 and is obtained by exponential treatment of oscillograms around 400 and 500 nm in N₂O-saturated solution, at low dose (4.5 Gy). Due to the initial higher concentration of NÅ⁻ deriving from reaction 8, the superposed reaction 11 is more evident in Ar-saturated solution.

The decrease in the reduction potential of NA compared to A, due to the substitution with the electron-withdrawing group, allows the reduction of NA by $\dot{C}H_2OH$ to be observed, in contrast with the findings for A and DA.³ From the order of magnitude of k_{10} , it can be inferred that the process is only slightly exoergonic. This low rate constant, compared to that for $(CH_3)_2\dot{C}OH$ and $e_s^$ reactions, can explain the lower transient yield both in MeOH with respect to *i*-PrOH and in N₂O-saturated with respect to Ar-saturated solutions. In fact competitive reactions (e.g., $2\dot{C}H_2OH \rightarrow$ products) play in this case a major role.

The evaluation of the equilibrium composition is made on spectrum a of Figure 7, using $G_{N\dot{A}H} + G_{N\dot{A}^-} = 2.4$ and the ϵ values derived for NÅ⁻ and NÅH. A degree of dissociation of 11% in agreement with that found in *i*-PrOH is calculated. This, [H⁺] = 4 × 10⁻¹² (see Experimental Section), leads to a $pK_{N\dot{A}H} = 12.3$. The difference in the $pK_{N\dot{A}H}$ in MeOH and *i*-PrOH is expected on the basis of the different pK_a of the alcohols.

The time evolution of the difference spectra in the millisecond range is consistent with the disappearance of the species NÅH by a second-order process, which is proposed to be the disproportionation reaction 12. A rate constant $k_{12}/\epsilon_{475} = 1.9 \times 10^4$ cm s⁻¹ is measured.

$$N\dot{A}H + N\dot{A}H \rightarrow NAH_2 + NA$$
 (12)

$$k_{12} = 5.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$$

As already proposed in *i*-PrOH, the final spectra of Figures 5 and 7 are attributed to the hydrazo derivative NAH_2 .

In contrast with the behavior of other azobenzene derivatives in the same solvent,³ no indications of a pseudo-first-order reaction of NAH with the starting compound were found. This is probably caused by the higher efficiency of the second-order dismutation, which consumes most of the radicals before reaction with the starting compound can occur (assuming a rate constant of ca. $10^6 \ M^{-1} \ s^{-1}$ as found for another para-substituted azobenzene³).

Conclusions

NA undergoes one-electron reduction by e_s^- and α -hydroxyalkyl radicals with reactivities which are strongly enhanced, with respect to other azobenzene derivatives, by the nitro substitution. In fact the rate constants of the reaction of NA with e_s^- , both in *i*-PrOH and in MeOH, are higher than those found for A and DA in the same solvents.³ (CH₃)₂COH gives electron transfer to NA with a rate constant $k \simeq 10^9 \text{ M}^{-1} \text{ s}^{-1}$, 2 orders of magnitude faster than that found for A;³ furthermore CH₂OH reduces NA ($k \simeq 6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$), whereas it was found not reducing A, in the same conditions.³ The above findings can be ultimately assigned to the increased stability of the anion NA⁻, due to the resonance structure $-NO_2^{--}$. To the same effect can also be ascribed the acid-base behavior of this radical. In fact NA⁻ is found to be a weaker base than the analogous A⁻ and DA⁻.

The site of protonation is, in spite of the presence of the $-NO_2$ reducible group, the central azo bond and the semireduced radical is therefore identified as the hydrazyl, $-\dot{N}-N(H)-$. It undergoes in *i*-PrOH a pseudo-first-order reaction with the starting com-

pound, leading to a dimer. This reaction seems to find unfavorable conditions in MeOH.

Disproportionation of the hydrazyl and/or dimer radicals produces the complete reduction of the azo bond. This reaction is found to be more efficient for NA than for other azobenzene derivatives. This fact must be ascribed to the higher concentration of NAH attained, which favors the second-order dismutation, leading to complete reduction without any loss.

It is concluded than the $-NO_2$ group plays the important role of antenna for the one-electron reduction, enhancing the reactivity of the molecule. It is proposed that this effect is at the origin of the anomalous photofading of nitro-substituted phenylazo dyes in alcoholic solvents.²

Acknowledgment. This work was supported by the Progetto Finalizzato del CNR per la Chimica Fine e Secondaria. We thank Dr. S. Emmi for the setup of the computerized data acquisition system, and Dr. A. Martelli and Mr. A. Monti for the maintenance of the LINAC accelerator. The interest of Dr. M. Venturi is also acknowledged.

Registry No. NA, 3646-57-9; NAH, 99798-28-4; *i*-PrOH, 67-63-0; (CH₃)₂COH, 5131-95-3; CH₂OH, 2597-43-5; MeOH, 67-56-1.

Kinetics of the Insertion of Singlet CH₂ into Methylfluorosilanes

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 ${}^{1}CH_{2}$ produced from the photolysis of ketene inserts into the C-H bond of methylfluorosilanes (Me_xSiF_{4-x}, x = 1-4), the relative rates being in the order Me₄Si > Me₃SiF > Me₂SiF₂ > MeSiF₃. In one case, that of Me₂SiF₂, the observed products are also consistent with insertion into the Si-F bond. ${}^{3}CH_{2}$ undergoes reactions leading to hydrocarbon products and a radical exchange process is proposed in its reaction with the silanes.

Introduction

The reactions of methylfluorosilanes with the CF_3 or CH_3 radical result in H abstraction, and such experiments have indicated¹ a significant polar character of the C-H bond, which varies with the degree of fluorine substitution. In studies of CCl with the Si-H bonds of silanes where insertion is presumed to occur,² the rates correlate well with the polarity of the Si-H bond and the electrophilic nature of CCl. In the case, however, of Me₃SiCl and Me₃SiF, the rates are too small to measure.³

It was of interest, therefore, to extend the studies of methylfluorosilanes to their reactions with ${}^{1}CH_{2}$ which is electrophilic in character, and to examine the relative rates for insertion as a function of fluorine substitution. During the course of this work, it was also opportune to study the reactions of ${}^{3}CH_{2}$, and these latter proved to be of considerable interest.

Experimental Section

The photolysis source was a P.E.K. 200-W high-pressure mercury arc, associated with a filter system to isolate 313-nm radiation. The reaction vessel was made of quartz, volume 215 mL, fitted with planar windows and maintained in a furnace assembly at 25 °C. Light transmitted through the cell was

monitored with a scanning monochromator/photomultiplier system.

Materials. Ketene was prepared by decomposing acetone vapor and purified by trap-to-trap distillation. It was stored in the dark at -196 °C. Ketene- d_2 was prepared^{4,5} from acetic- d_6 anhydride, purified,⁶ and stored at -196 °C.

The methylfluorosilanes were obtained from PCR Chemicals, Inc., and contained small quantities of CO_2 and Me_2SiF_2 as impurities. A combination of trap-to-trap distillation and preparative gas chromatography sufficed to produce these materials free from contamination.

Tetramethylsilane (Alfa Inorganics) was sufficiently pure that degassing at -196 °C was the only procedure necessary.

Nitric oxide (Matheson Co.) was purified by trap-to-trap distillation and trapped at -196 °C, while the system was continuously pumped.

Analytical Methods. Purity checks and product analysis was by use of gas chromatography, mass spectrometry, infrared, and 400-MHz NMR spectroscopy. Having ascertained that the main silicon-containing products of the reaction of ketene with the silanes were the ethyl derivatives resulting from the insertion of ¹CH₂ into the C-H bond, and in one case, (Me₂SiF₂), into the Si-F bond, these products were prepared in bulk, isolated by gas chromatography, and used for GC calibration purposes. This enabled

⁽¹⁾ Bell, T. N.; Platt, A. E. J. Phys. Chem. 1971, 75, 603.

⁽²⁾ James, F. C.; Choi, K. J.; Strausz, O. P.; Bell, T. N. Chem. Phys. Lett. 1979, 68, 131.

⁽³⁾ James, F. C.; Choi, K. J.; Strausz, O. P.; Bell, T. N. Chem. Phys. Lett. 1980, 73, 522.

⁽⁴⁾ Jenkins, A. D. J. Chem. Soc. 1982, 2563.

⁽⁵⁾ Hasek, R. H.; Gott, P. G.; Martin, J. C. J. Org. Chem. 1964, 29, 2510.
(6) Laufer, A. H. J. Chromatogr. Sci. 1970, 8, 677.