Photoreduction of 4-Cyano-1-nitrobenzene in Propan-2-ol

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The photoreduction of 4-cyano-1-nitrobenzene (CNB) in propan-2-ol (IP) proceeds *via* hydrogen abstraction by triplet nitro-compound from the solvent. The components of the resulting radical pair retransfer the hydrogen giving nuclear polarized reactants, diffuse apart, or undergo a second hydrogen transfer step which yields acetone and 4-cyanophenylhydroxylamine. This last material apparently leads to the nitroso-derivative, which yields 4-$\dot{N}CC_6H_4NHO$ in a second photochemical step. This radical with either 4-$NCC_6H_4\dot{N}O_2H$ or further 4-NCC_6H_4-$\dot{N}HO$ forms re-encounter pairs, and these lead to the arylhydroxylamine and to regeneration of the nitro- and nitroso-compounds.

MANY features of the photochemistry of nitrobenzene in propan-2-ol (IP) have previously been established.[1] Thus, the products have been identified,[2-5] Hurley and Testa have shown [6,7] that the reactive excited state is ^3n-π^*, and the main outlines of the reaction sequence seem to have been established.[8] Nevertheless, there are a number of unanswered questions. For example, it has not been established whether the primary dark reaction is an electron or hydrogen transfer from solvent, which would lead, respectively, to the radical anion of the nitro-compound or its conjugate acid. It is not clear why the rate of disappearance of the nitro-compound is low despite the high yield of triplet [6] and the high rate of hydrogen transfer.[1] Finally, the possibility does not appear to have been considered that the overall reaction involves consecutive photochemical steps.

In the case of the substituted nitrobenzenes the situation is less satisfactory. Thus Hashimoto and Kano report [2,3] that, on passing from nitrobenzene itself to its derivatives substituted by electron-withdrawing substituents in the *para*-position, the principal product becomes the amine rather than the hydroxylamine. This suggests that introduction of the substituent might lead to a change in the nature of the photolabile excited state.

In order to attempt to answer some of these questions we selected as reactant 4-cyano-1-nitrobenzene (CNB) as representative of the class of nitrobenzenes with electron-withdrawing substituents, with the expectation that the CNB + IP system would show photo-CIDNP effects and thus provide valuable information on some of the reaction steps. Complimentary to studies of these effects were studies of e.s.r. spectra of radicals produced on irradiation and of the visible-absorption spectra of species formed on flash photolysis and electrolysis.

EXPERIMENTAL

Instrumentation.—E.s.r. spectra were taken on Varian E-3 or E-12 spectrometers in the X-band using a flat water cell (thickness 0.04 ± 0.01 cm) and irradiating in the cavity. Radical *g* values were determined by comparison with diphenylpicrylhydrazyl in a double cavity measurement. In continuous flow experiments rates of flow were 0.6—1.0 ml min^{-1}. Spectra were simulated using Lorentzian line shapes.

The flash photolysis set-up [9] gives a pulse of width *ca.* 5 μs. A different sample, freshly deaerated by purging with argon for 1 min, was used for measurement at each wavelength.

N.m.r. spectra in the continuous wave mode were recorded on a 90 MHz spectrometer (Bruker HFX-10) and u.v. spectra on a Cary 14 spectrophotometer.

Electrolyses were performed at current densities of *ca.* 0.1 amp cm^{-2} using a mercury pool cathode and a platinum gauze anode in cells of cross-section 0.05 × 1 cm^2 for e.s.r. and 1 × 1 cm^2 for u.v. Measurements were made after electrolysis was allowed to proceed for a few minutes to give steady-state conditions. For u.v. measurements the cell position was such that the solution near the cathode lay in the centre of the measuring beam.

The photo-CIDNP set-up has been described.[10]

Irradiations were with high pressure mercury lamps, the light being filtered by Pyrex, Pyrex with Corning Glass Filter, No. 9863, and a Co–Ni solution (313 nm radiation). Apart from changes in the intensities of the resulting signals, no wavelength effect was found. Because of the marked overlap of the absorption spectra of the nitro- and nitroso-derivatives it was not possible specifically to excite one of these materials in the presence of the other, but absorption by the hydroxylamine and aniline could be avoided.

Materials and Solutions.—Propan-2-ol (IP) and 4-cyano-1-nitrobenzene (CNB) were commercial samples. The latter was recrystallized from ethanol as plates, m.p. 149 °C. 4-Cyanoaniline was obtained [11,12] as needles, m.p. 86—87 °C. 4-Cyano-1-nitrosobenzene was obtained [13] from ethanol as yellow needles, m.p. 136—137 °C, $\lambda_{max.}$ 283 (ε 11 500), 305sh, and 218 nm (4 300).

E.s.r. and flash photolysis experiments were carried out for solutions containing CNB (1 mg) in IP (1 ml) (0.006 7M) or in IP (1 ml) containing HCl (0.067M). For CIDNP the IP solution was saturated in CNB: the acidic solutions were 0.067 or 0.67M in HCl, 0.5M in H_2SO_4, or 0.067M in trifluoroacetic acid. Solutions in IP for electrolysis were 0.006 7 or 0.067M (e.s.r.) in CNB and 0.1M in tetrabutylammonium perchlorate.

Identification of Products.—The products were identified as follows: 4-cyanonitrosobenzene, 4-cyanoaniline, and 4-cyanophenylhydroxylamine by peak enhancement with authentic samples in g.l.c., and by n.m.r.; 4,4′-dicyanoazobenzene by m.p. and i.r. after crystallization from the product mixture; acetone by n.m.r. The n.m.r. spectrum of the hydroxylamine was obtained from that of a mixture of this material with CNB which was analysed by g.l.c. and mass spectrometry.

RESULTS AND DISCUSSION

The parameters of the simulated e.s.r. spectra are given in Table 1 and the CIDNP polarizations observed upon irradiation of CNB in [$^2H_8$]IP are summarized in Table 2.

TABLE 1

Spectral parameters at 25 °C for radicals observed during irradiation of 4-cyano-1-nitrobenzene in propan-2-ol

Radical	g^{H}	a^{N}/G	a^{H}_{ortho}†/G	a^{H}_{meta}†/G	a^{H}/G	$a^{\mathrm{N}}_{\mathrm{CN}}$/G
$\mathrm{CNC_6H_4NO_2^{-\cdot}}$	2.004 79	9.45	3.25	0.95		0.65
$\mathrm{CNC_6H_4NO_2H}$	2.004 59	12.15	3.15	1.10	$a^{\mathrm{H}}_{\mathrm{\dot{N}O_2H}}$ 3.15	0.55
$\mathrm{CNC_6H_4NHO}$	2.006 20	8.20	a_6 2.70 a_2 3.05	1.05	$a^{\mathrm{H}}_{\mathrm{\dot{N}H}}$ 11.30	0.40

† The sign of a^{H}_{ortho} is negative and that of a^{H}_{meta} positive.[24]

From these and the other results, given below, we infer the overall sequence of reaction steps shown in the Scheme, in which asterisks indicate nuclearly polarized species, superscripts S and T represent, respectively, excited singlet and triplet states, Ar is the 4-cyanophenyl group, F represents an encounter pair, and c and e are, respectively, collapse and escape processes.

TABLE 2

CIDNP observed upon irradiation of CNB in IP

Product	Type	Chemical shift δ *	Precursor	Sign of *a*
$\mathrm{ArNO_2}$	A	8.40 (*ortho*)	$\mathrm{ArNO_2H}$	–
	E	8.04 (*meta*)		+
ArNHOH	E,E + A/E	6.95 (*ortho*)	ArNHO	–
	A,A + A/E	7.37 (*meta*)		+
ArNO	E,E + E/A	8.08 (*ortho*)	ArNHO	–
PhOH	E	6.85 (*ortho*)	$\mathrm{Ph\dot{O}}$ [b]	–
	A	7.30 (*meta*)		+
$\mathrm{CH_3C_6H_4OH}$	A/E	6.63 (*ortho*)	$\mathrm{CH_3C_6H_4\dot{O}}$ [c]	–
	A/E	6.92 (*meta*)		+
		2.09 (Me)		+
DTBC [a]	E	2.16 (Me)	(DTBC–H˙) [d]	+
		6.90 (Ph)		

* From tetramethylsilane.

[a] Di-t-butyl-*p*-cresol. Radical *g* values not given in the text are: [b] 2.005 09; [c] as for $\mathrm{Ar\dot{N}O_2H}$; [d] 2.004 40.

This Scheme is in accord with the observed product distribution. We find the main products to be acetone and 4-cyanophenylhydroxylamine, and not 4-cyanoaniline as reported by Hashimoto and Kano.[2,3] This aniline is indeed formed, but appears, together with 4,4'-dicyanoazobenzene, only after other products are already present in appreciable concentrations. Thus these products, together with another of dimeric character which was not characterized, are not considered in the Scheme. Also formed is 4-cyano-1-nitrosobenzene.

$$\mathrm{ArNO_2 \xrightarrow{h\nu} ArNO_2{}^{S} \longrightarrow ArNO_3{}^{T}} \tag{1}$$

$$\mathrm{ArNO_2{}^{T} + (CH_3)_2CHOH \longrightarrow \overline{Ar\dot{N}O_2H + (CH_3)_2\dot{C}OH}^{\,T,F}} \tag{2}$$

$$\begin{array}{l} \mathrm{\overline{Ar\dot{N}O_2H + (CH_3)_2\dot{C}OH}^{\,T,F}} \\ \quad \mathrm{(a)} \longrightarrow {}^{\mathrm{c}}\,\mathrm{ArNO_2H_2 + (CH_3)_2CO} \\ \quad \mathrm{(b)} \longrightarrow {}^{\mathrm{e}}\,\mathrm{Ar\dot{N}O_2H + (CH_3)_2\dot{C}OH} \\ \quad \mathrm{(c)} \longrightarrow {}^{\mathrm{c}}\,\mathrm{ArNO_2{}^{*} + (CH_3)_2CHOH^{*}} \end{array} \tag{3}$$

$$\mathrm{Ar\dot{N}O_2H \rightleftharpoons ArNO_2^{-\cdot} + H^{+}} \tag{4}$$

$$\mathrm{(CH_3)_2\dot{C}OH + ArNO_2 \longrightarrow (CH_3)_2CO^{*} + Ar\dot{N}O_2H} \tag{5}$$

$$\mathrm{ArNO_2H_2 \longrightarrow ArNO + H_2O} \tag{6}$$

$$\mathrm{ArNO + (CH_3)_2CHOH \xrightarrow{h\nu} Ar\dot{N}HO + (CH_3)_2\dot{C}OH} \tag{7}$$

$$\mathrm{Ar\dot{N}O_2H + Ar\dot{N}HO \longrightarrow \overline{Ar\dot{N}O_2H + Ar\dot{N}HO}^{\,F}} \tag{8}$$

$$\begin{array}{l} \mathrm{\overline{Ar\dot{N}O_2H + Ar\dot{N}HO}^{\,F}} \\ \quad \mathrm{(a)} \xrightarrow{\text{neutral pH}} \mathrm{ArNO_2{}^{*} + ArNHOH^{*}} \\ \quad \mathrm{(b)} \xrightarrow{\text{acid pH}} \mathrm{ArNO_2H_2 + ArNO^{*}} \end{array} \tag{9}$$

SCHEME

The overall Scheme is in agreement with that of Ayscough and his co-workers [14] except that we argue that the 4-cyano-1-nitrosobenzene has to be formed photochemically and not through a short lived adduct such as $\mathrm{ArNOC(CH_3)_2OH}$.

The expectation that the photolabile state of CNB is the triplet comes by extrapolation from Testa's conclusions concerning nitrobenzene, and from the knowledge that in most nitrobenzenes intersystem crossing is very rapid. This expectation is supported by our photo-CIDNP studies of the reactions of CNB with various phenols.[15]

The evidence for steps (2) and (3) derives from flash photolysis and e.s.r. irradiation experiments on CNB in IP, and from the polarizations of CNB and IP observed on irradiation of this system in the n.m.r. cavity.

Irradiation of neutral solutions gives a species detectable by its strong e.s.r. absorption, and stable on the time scale of the measurements (minutes). Taking into account the solvent dependence of the nitrogen hyperfine coupling constant we take this species to be the radical anion of CNB. The spectrum consists of two 1 : 1 : 1 triplets, $a^{\mathrm{N}}_{\mathrm{NO_2^{-\cdot}}}$ 9.45 and $a^{\mathrm{N}}_{\mathrm{CN}}$ 0.65 G, and two 1 : 2 : 1 triplets, a^{H}_{ortho} 3.25 and a^{H}_{meta} 0.95 G (*ortho* and *meta* are relative to the nitro-group: *cf.* values in acetonitrile given by Maki and Geske [16]).

The assignment to the radical anion is confirmed by the identity of the e.s.r. spectrum produced on electrolysis: $a^{\mathrm{N}}_{\mathrm{NO_2^{-\cdot}}}$ changes from 9.45 to 9.15 G on addition of the electrolyte. Furthermore, the absorption spectrum in the visible of the electrolysed solution is similar to that of a transient formed on flash photolysis (Figure 1), which decays by a first-order process with a half-life of 44 ms at room temperature.

Irradiation of acid solutions gives another radical, observable in e.s.r. only in continuous flow experiments. We interpret the spectrum as due to the protonated radical anion, $\mathrm{Ar\dot{N}O_2H}$, with an accidental degeneracy of the hyperfine constants of the *ortho* and $\mathrm{\dot{N}O_2H}$ protons: $a^{\mathrm{H}}_{ortho} = a^{\mathrm{H}}_{\mathrm{NO_2H}} = 3.15$ G, 1 : 3 : 3 : 1 quartet; a^{H}_{meta} 1.15 G, 1 : 2 : 1 triplet; $a^{\mathrm{N}}_{\mathrm{NO_2H}}$ 12.15 and $a^{\mathrm{N}}_{\mathrm{CN}}$ 0.55 G, 1 : 1 : 1 triplet (computer simulation).

Flash photolysis of acid solutions gives apparently the same species. Such photolysis leads to a transient absorption which is blue-shifted with respect to that of the radical anion (Figure 1). This shift parallels that observed in 4-nitropyridine [8] and is associated with protonation of the radical anion. We conclude that here, as in the e.s.r. experiment, the absorption is due to the conjugate acid of the radical anion. (The possibility that the absorbing species is formed from intermediate 4-cyano-1-nitrosobenzene was tested by flashing an IP solution of this material; no transient absorption at $\lambda > 300$ nm developed). This transient decays by a first-order process with a half-life of 13 ms at room temperature.*

Additional support for our assignments for the two radical species and information regarding the chronology of their formations are obtained from CIDNP studies. On irradiation of CNB in neutral [$^2H_8$]IP in the cavity of the n.m.r. spectrometer at temperatures below −10 °C, we observe in the first scan enhanced absorption (A) for the CNB protons *ortho* to nitro, decreased absorption (*i.e.* net emission) for the *meta* protons, polarized [$^2H_6$]-acetone (A), and a decrease in the absorption by IP (E) (Figure 2). In addition we see emissions for the protons *ortho* to the hydroxylamine group and enhanced absorption for the protons *meta* to this group; these weak net polarizations are superposed on a multiplet effect A/E.

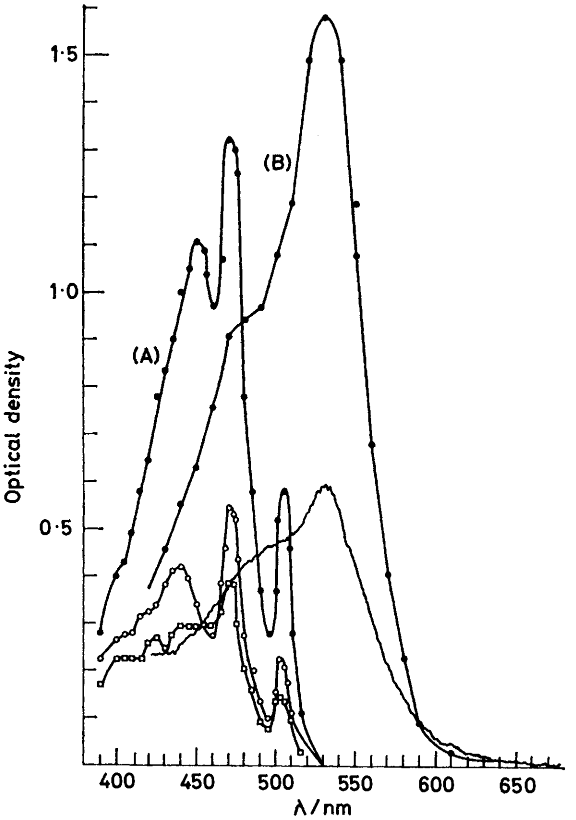

FIGURE 1 Electronic absorption spectra of transients obtained by irradiation of CNB in IP (0.0067M). Neutral solutions: (B), after flashing; unsmoothed spectrum, during electrolysis in spectrophotometer. Acidic solutions after flashing: (A), solution 0.67M in HCl; ○, solution 0.067M in HCl; □, solution 0.5M in H_2SO_4

Repetitive scanning enables us to determine the temporal behaviour of the polarizations. In the second scan we find broadening of the CNB signals, which obscures any possible polarizations. Upon prolonged irradiation we again see polarization of these signals, with A for *ortho*-protons and E for *meta*-protons, superposed on the broadened background. Similarly the polarizations associated with the hydroxylamine reach maximum intensities in the second or third scan, and gradually vanish on prolonged irradiation. By contrast, the CIDNP shown by acetone and IP decrease monotonically with continued irradiation.

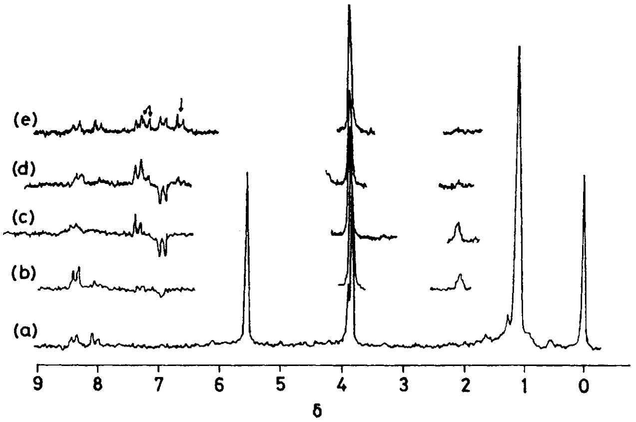

FIGURE 2 N.m.r. spectra of neutral solution of CNB in IP at < −10 °C. Before irradiation (a); during irradiation, first scan (b), second scan (c), sixth scan (d); (e) following (d), light off. Scan time 100 s. The signals near δ 8.0—8.4 are from CNB, 6.6—7.2 from the hydroxylamine, 3.9 from IP, and 2.0 from acetone. The signals marked with arrows are from 4-cyanoaniline

At room temperature the broadening of the CNB signals and the maximal polarization of the hydroxylamine are already established during the first scan.

In acid solution (Figure 3) we observe for CNB, at all temperatures in the range 213—283 K, the same polarizations as in neutral solution at low temperature, but with no broadening. We find no polarized acetone but

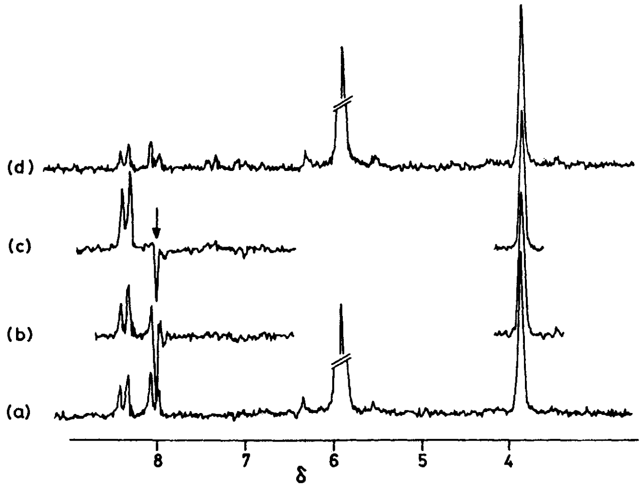

FIGURE 3 N.m.r. spectra of acidic (*ca.* 6 × 10^{-2}M-DCl) solution of CNB in IP at room temperature. (a) Before irradiation; during irradiation, first (b) and third (c) scans; (d) following (c), light off. The arrow indicates emission due to ArNO·

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* An estimate of the rate constant of decay of $C_6H_5NO_2H$ in aqueous acidic solution is 6×10^8 l mol^{-1} s^{-1}.[17] Ayscough [14] estimated the reaction to be slower in isopropyl alcohol. Apparently the rate constant is even further reduced through the introduction of the 4-cyano group: we measured $\tau_{\frac{1}{2}}$ 13 ms.

see again reduced absorption by IP and a weak polarization of the hydroxylamine. Unlike in neutral solution we observe the formation of polarized 4-cyanonitrosobenzene (E for protons *ortho* to nitroso).

No polarizations and no acetone formation is observed upon irradiation of 4-cyano-1-nitrosobenzene in neutral or acidic isopropyl alcohol in the n.m.s. cavity.

The broadening observed in Figure 2 must be due to the presence of a paramagnetic species undergoing an electron exchange reaction with $\mathrm{ArNO_2}$ [18] which could be $\mathrm{ArN\dot{O}_2H}$, $\mathrm{ArNO_2^{-\cdot}}$, or $\mathrm{Ar\dot{N}O_2H}$. The temporal behaviour of the CIDNP, its temperature dependence, and the influence of pH all suggest that the radical anion dominates the broadening [mechanism (10)].

$$\mathrm{ArNO_2^{*}} + \mathrm{ArNO_2^{-\cdot}} \longrightarrow \mathrm{ArNO_2^{*-\cdot}} + \mathrm{ArNO_2} \quad (10)$$

Thus the polarized CNB is formed more rapidly than its anion, and the former cannot be produced from the latter but rather from the protonated anion. The reaction sequence therefore involves initially the transfer of hydrogen and not of an electron.

The same is true of the system CNB–phenol in IP which we studied [15] in the e.s.r. spectrometer cavity. In the first scan we see only the spectrum of the phenoxyl radical (g 2.005 09), but in the second scan there is superposed the spectrum of the CNB radical anion. Therefore the CNB initially abstracts hydrogen to form the protonated radical anion (not observed) and phenoxyl radical and the former then dissociates to the radical anion.

The width of the broadened line of Figure 2 increases with increasing temperature so that the system must be near the slow exchange limit,[18] where we expect enhanced broadening of the signals of *ortho*-protons. The observation that the broadening is greater for the *meta*-protons ($a^{\mathrm{H}}_{ortho} > a^{\mathrm{H}}_{meta}$) is explained by the superposition of the enhanced absorption for the *ortho*-protons according to reaction (9a) in the Scheme.

We now investigate whether the observed polarizations are in keeping [19] with steps (1)—(5) of the Scheme. For acetone we have [20,*] $a^{\mathrm{H}}_{\mathrm{CH_3}}$ +19.20 G and we would expect $\Gamma_{\mathrm{NE}}^{\mathrm{(CH_3)_2CO}} = + - + - = + = \mathrm{A}$, which is in fact observed. For IP we have $\Delta g = g_{\mathrm{ArNO_2H_H}} - g_{\mathrm{(CH_3)_2COH}} = 2.004\,79 - 2.003\,1$ [20] > 0, and $\mu = +$, $\varepsilon = +$; as to a_{α}^{H} its sign is determined by the sign in $\mathrm{Ar\dot{N}O_2H}$ (*i.e.* 'frozen orbital' conformation [21,22]) and therefore is most likely negative. Then $\Gamma^{\mathrm{(CH_3)_2CHOH}} = - = \mathrm{E}$, as observed in first scan of Figure 2. The intensity of this effect, is, however, low compared to that of acetone polarization, which is reasonable in view of competing processes for depopulation of the 1-hydroxy-1-methylethyl radical, particularly enolization.[23] Also we do not see this radical in the e.s.r.[24,25] either in neutral or in weakly acid solution. Finally, for CNB we observe A for *ortho*-protons, E for *meta*-protons. We have $\mu = +$, $\varepsilon = +$, $\Delta g > 0$, a^{H}_{ortho} −3.15 G, a^{H}_{meta} 1.1 G (this work and ref. 26). This would give opposite polarizations. Further, the effect is weaker than expected, and we conclude that it is dominated by the polarization resulting from reaction (9a).

Thus, while not proving the sequence of reactions (1)—(5), the observed polarizations are compatible with them. We note that on a time scale (*ca.* 2 scans) in which there is a marked drop in the polarization of CNB, those of acetone and IP remain essentially unchanged. This relates to the fact that if the polarized species is part of the time present as paramagnetic species, spin–lattice relaxation is expected to be much faster.[27]

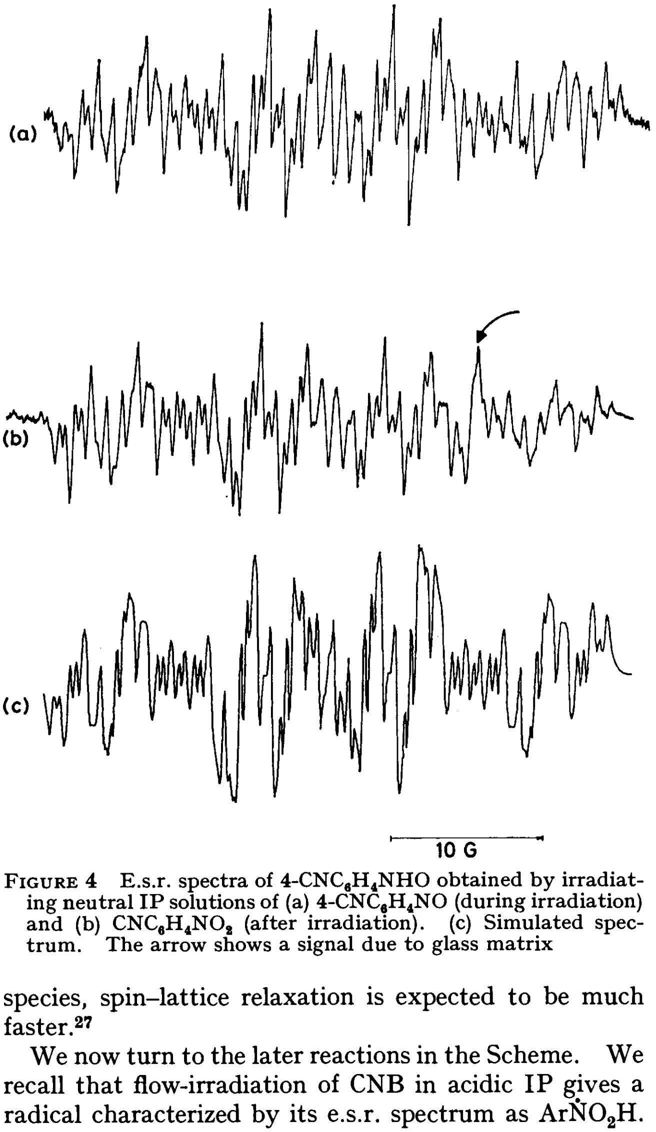

FIGURE 4 E.s.r. spectra of $4\text{-}\mathrm{CNC_6H_4NHO}$ obtained by irradiating neutral IP solutions of (a) $4\text{-}\mathrm{CNC_6H_4NO}$ (during irradiation) and (b) $\mathrm{CNC_6H_4NO_2}$ (after irradiation). (c) Simulated spectrum. The arrow shows a signal due to glass matrix

We now turn to the later reactions in the Scheme. We recall that flow-irradiation of CNB in acidic IP gives a radical characterized by its e.s.r. spectrum as $\mathrm{Ar\dot{N}O_2H}$. Irradiation of this solution in the cavity of the e.s.r. spectrometer gives the same spectrum in a rapid first scan. In subsequent scans, however, the spectrum [Figure 4(a)] is modified by the appearance of an additional component (computer analysis) which is due to $\mathrm{Ar\dot{N}HO}$. The spectrum of the latter [Figure 4(b)] persists even when irradiation is stopped. Computer simulation matches for the parameters (Table 1) $a_{\mathrm{NH}}^{\mathrm{N}}$ 8.20 and $a_{\mathrm{CN}}^{\mathrm{N}}$ 0.40 G, 1 : 1 : 1 triplet; $a_{\mathrm{NH}}^{\mathrm{H}}$ 11.30 G, 1 : 1 doublet; $a_2^{\mathrm{H}} = 3.05$ and a_6^{H} 2.70 G, two 1 : 1

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[*] It is accepted that the sign of the β-proton hyperfine coupling constant is positive.

doublets; $a_{3.5}^{\mathrm{H}}$ 1.05 G, 1 : 2 : 1 triplet. We assign this spectrum to the radical $\mathrm{Ar\dot{N}HO}$ on the basis of its high g value, its large proton hyperfine splitting, and the small nitrogen hyperfine splitting.[14,28] On continued irradiation the concentration of $\mathrm{Ar\dot{N}HO}$ increases while that of $\mathrm{Ar\dot{N}O_2H}$ decreases, but remains measurable even after irradiation of several hours.

Irradiation of neutral or acid solutions of 4-cyano-1-nitrosobenzene in IP gives a strong e.s.r. signal of $\mathrm{Ar\dot{N}HO}$, identical to that observed on photolysis of CNB in the same solvent (Figure 4a) and 4-cyanophenylhydroxylamine is formed (g.l.c.). These results parallel Ayscough and his co-workers' observation [14] of identical e.s.r. spectra for irradiated solutions of nitro- and nitrosobenzene in IP. These authors argued [14] for nitrosobenzene being an intermediate in the photoreduction of nitrobenzene in IP; we consider the possibility that in CNB the nitroso-intermediate is photochemically activated, then abstracting hydrogen to form $\mathrm{Ar\dot{N}HO}$ [step (7) in the Scheme].

CIDNP results indicate that both $\mathrm{Ar\dot{N}HO}$ and $\mathrm{Ar\dot{N}O_2H}$ are indeed intermediates in the formation of 4-cyanophenylhydroxylamine. The observed polarizations of this compound and of $\mathrm{ArNO_2}$ and ArNO can be accounted for only by reaction (9), which requires a prior encounter [reaction (8)] of uncorrelated radicals of the above two species. That this could be so is shown by the observation of both radicals by e.s.r.

The interpretation of the polarizations follows from $g_{\mathrm{Ar\dot{N}HO}}$ 2.006 20 and $g_{\mathrm{Ar\dot{N}O_2H}}$ 2.004 59 (Table 2); further, for the hydroxylamine $a^{\mathrm{H}}{}_{ortho} = -$, $a^{\mathrm{H}}{}_{meta} = +$, $\Delta g > 0$; for CNB $a^{\mathrm{H}}{}_{ortho} = -$, $\Delta g < 0$; for ArNO $a^{\mathrm{H}}{}_{ortho} = -$, $\Delta g > 0$; and $\mu = +$, $\varepsilon = +$.

From the intensity of the net polarization as opposed to the multiplet effect (see below) we conclude that the main reaction depopulating $\mathrm{Ar\dot{N}HO}$ is (9), which also depopulates $\mathrm{Ar\dot{N}O_2H}$. However, the latter radical is also consumed by the hydrogen transfer reactions (3a and c). This explains why on irradiation of acidic solutions of CNB in IP the ratio of the concentration of $\mathrm{Ar\dot{N}O_2H}$ to that of $\mathrm{Ar\dot{N}HO}$ continuously decreases. On the other hand the concentration of $\mathrm{Ar\dot{N}O_2H}$ remains finite even on prolonged irradiation since its precursor, CNB, is regenerated during reaction. Our observations with respect to the depopulation of $\mathrm{Ar\dot{N}HO}$ and $\mathrm{Ar\dot{N}O_2H}$ thus parallel Ayscough's.[14]

However, since during the irradiation of 4-cyano-1-nitrobenzene we do not observe 4-cyanobenzene or acetone formation, as required by Ayscough's mechanism, yet observe $\mathrm{Ar\dot{N}HO}$ in the e.s.r., we have to conclude that in the absence of other radical species photochemically excited 4-cyano-1-nitrosobenzene abstracts hydrogen from propan-2-ol. In the absence of CIDNP or other evidence we cannot speculate on the nature of the excited state of this molecule.

Of interest is an experiment we conducted [15] on CNB with 2,6-di-t-butyl-*p*-cresol in deuteriated methanol. On irradiation we observed 4-cyanophenylhydroxylamine (E for *ortho*-H) and CNB (A for *ortho*-H), in addition to emission associated with the methyl protons of the cresol. This implies that hydrogen donors other than IP can also give $\mathrm{Ar\dot{N}O_2H}$ and $\mathrm{Ar\dot{N}HO}$ radicals, which yield products *via* steps (8) and (9).

We presume that $\mathrm{ArNO_2H_2}$ decomposes [reaction (6)] too rapidly to be observed. The absence of polarization in ArNO in neutral solutions we interpret as due to the rapidity of the conversion of this species into $\mathrm{Ar\dot{N}HO}$ in such a solution; support for this comes from the observation that the concentration of this radical, produced by irradiation of CNB in IP, is appreciably less in acidic than in neutral solution.

Finally, for the hydroxylamine in neutral solution we see a very weak multiplet effect superposed on the net effect; this might be due to the additional reaction (11)

$$2\mathrm{Ar\dot{N}HO} \longrightarrow \mathrm{ArNO}^{(*?)} + \mathrm{ArNHOH}^{*} \qquad (11)$$

(for the hydroxylamine $J > 0$, $\sigma_{ij} = +$, $a^{\mathrm{H}}{}_{ortho} = -$, $a^{\mathrm{H}}{}_{meta} = +$; $\Gamma_{\mathrm{ME}} = - = \mathrm{A/E}$).

Conclusions.—The Scheme gives our analysis of the reaction. It explains the observed delay in the formation of $\mathrm{Ar\dot{N}HO}$ (e.s.r.) and of the product hydroxylamine (low-temperature CIDNP), and is compatible with the observed polarizations and with their temporal variations. On prolonged irradiation, when the concentration of CNB has appreciably decreased, there is a slow-down in those processes proceeding from this material; there result decreases in the polarizations of acetone and of IP, and of the paramagnetic broadening overlapping the CNB spectrum.

Acidification causes disappearance of the radical anion of CNB and the appearance of polarized nitroso-compound. While the former effect seems to be the result of a normal acid–base equilibrium, the nature of the process leading to polarized nitroso-compound is not clear. The absence of acetone polarization in acid solution we believe to be caused by tautomerization involving the methyl protons [29-31] and giving rise to spin–lattice relaxation.

Under acid conditions we may ignore the dissociation of $\mathrm{Ar\dot{N}O_2H}$ to give its anion. Then $\mathrm{Ar\dot{N}O_2H}$ is depopulated by reactions (3a), (3c), and (8) + (9b). The measured half-life of this depopulation is long compared to singlet–triplet mixing times, so that the particular processes involved cannot lead to polarized products. The slow process cannot be (3a) because it would have to be much slower than is the competitive reaction (3c). Step (9) must also be rapid. It is then probable that the measured rate is that of the re-encounter step (8).

We thank Dr. R. Poupko, Drs. K. A. Muszkat and M. Weinstein, and Professor E. Fischer for making available to us, respectively, the computer program for simulating the e.s.r. spectra, the photo-CIDNP equipment, and the flash-photolysis equipment. We also thank Professor H. Fischer, Zurich, for helpful comments.

[8/408 *Received, 6th March*, 1978]

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