Electron Spin Resonance Studies of Free-radical Reactions in Photolysed Solutions of Chloronitrobenzenes

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The e.s.r. signals detected during u.v. photolysis of chloronitrobenzenes in ethers are due to phenyl alkoxy nitroxide radicals and not to monohydronitrobenzene radicals as formerly supposed. The e.s.r. hyperfine splitting parameters of the radicals from eleven chlorine-substituted mononitrobenzenes are given. The alkoxy nitroxide radicals arise from the addition of solvent radicals, formed after hydrogen abstraction from the solvent by triplet-state nitrobenzene, to the parent nitrobenzene. The decay of alkoxy nitroxide radical derived from 2,3,5,6-tetrachloronitrobenzene in ethers involves a unimolecular non-ionic decomposition to yield the nitrosobenzene and an alkoxy-radical. β-Fission of the alkoxy-radical so formed can give an alkyl fragment which is then trapped by the nitrosobenzene to yield a characteristic alkyl nitroxide radical. Evidence is presented for the kinetic behaviour of alkyl aryl nitroxides in aqueous and aprotic systems which indicates that such radicals react with the monohydronitrobenzene radical during photolysis to yield a diamagnetic intermediate. In low-dielectric aprotic media this intermediate dissociates, to reform the original alkyl nitroxide radical after photolysis has ceased.

THE photoreduction of nitro-compounds in alcohols,^{1,2} ethers,³ and amines ^{4,5} has been investigated by several workers, and free radicals have been detected in the solutions during and after u.v. irradiation ^{3,6} by e.s.r. spectroscopic techniques.

U.v. spectral studies on chloronitrobenzenes in solution ⁷ indicate that a $\pi^* - n$ absorption band exists at ca. 330 nm.; excitation of the nitroaromatic compound by light in this spectral region leads to hydrogen abstraction from suitable solvents by a triplet state of the nitrobenzene.⁸ Testa⁹ has found that hydrogen abstraction reactions of the (n,π^*) triplet of nitrobenzene compete unfavourably with the exceptionally rapid deactivation processes ¹⁰ removing the triplet state.

From studies on u.v.-irradiated solutions of nitrobenzene in tetrahydrofuran (deuteriated and undeuteriated) Ward concluded that an electrically neutral radical is formed. This is formulated as $ArNO_2H$ (I) where the

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additional hydrogen atom has come from the solvent, and resides on the oxygen atom in (I) giving rise to a hyperfine doublet splitting of 0.038 millitesla (mT) in the e.s.r. spectrum. Other workers 1,9,11-13 have assumed this view but more recently 14 we have concluded that the species has the structure (II), where R is the solvent radical (III) formed by hydrogen abstraction from the solvent RH. The crucial observation is the absence of the small doublet-splitting in the e.s.r. spectrum of the radical obtained on photolysis of nitrobenzene in diisopropyl ether and 2,5-dimethyltetrahydrofuran solutions. Since the line width was 0.020 mT there is little possibility of the doublet being obscured. Similar results are obtained for other chloronitrobenzenes. The small hyperfine splittings (h.f.s.), additional to those given by the aromatic ring hydrogen atoms, are due to hydrogen atoms attached to the carbon atom situated in a γ -position with respect to the nitrogen atom, and are in good agreement with the known magnitudes of such h.f.s. Radical (II) is an adduct of the nitrobenzene and the

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Anion radicals

solvent radical (III) obtained in the following reaction sequence:

$$\operatorname{ArNO}_2 \xrightarrow{\mu} \operatorname{ArNO}_2^*(\operatorname{singlet})$$
 (1)

$$\operatorname{ArNO}_2^*(\operatorname{singlet}) \longrightarrow \operatorname{ArNO}_2^*(\operatorname{triplet})$$
 (2)
 $\operatorname{ArNO}_2^*(\operatorname{singlet}) \longrightarrow$

electronic and chemical deactivation (3)

$$\operatorname{ArNO}_2^*(\operatorname{triplet}) \longrightarrow$$

electronic deactivation (4) $\operatorname{ArNO}_2^*(\operatorname{triplet}) + \operatorname{RH} \longrightarrow$

$$ArNO_{2}H (I) + R \cdot (III) \quad (5)$$
$$ArNO_{2} + R \cdot \longrightarrow$$

$$[\operatorname{ArNO}_{2} \cdot \mathbb{R}^{+}] \xrightarrow{\operatorname{diffusion}} \operatorname{ArNO}_{2} \cdot (\operatorname{IV}) + \mathbb{R}^{+}$$
(7)

$$Ar-N(O)-OR$$
 (II) adduct formation (8)

The adduct radical (II), or in some circumstances the nitro-anion radical (IV), is observed only if the solvent radical \mathbf{R} possesses a group exerting a positive (electron-releasing) mesomeric effect adjacent to the site of unpaired spin density.

Free Radicals present during U.v. Photolysis.—(a) Aryl alkoxy nitroxides (II) ArN(O·)OR. A stationary concentration (ca. 10^{-4} M) of a phenyl alkoxy nitroxide radical (II) is established rapidly on u.v. photolysis of nitrobenzenes in various solvents (see Table 3) which had been de-oxygenated previously by vigorous passage of nitrogen gas. In the presence of oxygen in a closed system the radical (II) slowly appeared on prolonged irradiation, as the oxygen was consumed.

The hyperfine splittings measured in this work for radicals of structure (II) in tetrahydrofuran (THF) as solvent are listed in Table 1.

The nitrogen h.f.s. (a_N) in the aryl alkoxy nitroxide radicals varies little with solvent dielectric constant; for example, for (II) derived from 2,3,5,6-tetrachloronitrobenzene, a_N changed by 0.05 mT in the dielectric constant range 3-35 in aqueous tetrahydrofuran and other solutions. This a_N value may be contrasted with the nitrogen h.f.s. of the corresponding nitro-anion radicals (Table 1). The latter a_N values are much lower in magnitude and vary widely with the nature of the solvent, thus indirectly confirming the electrically neutral character of species (II) and discounting the alternative ion-pair formulation ¹⁵ of (II), namely

 TABLE 1

 E.s.r. hyperfine splittings (mT) of radical (II) and nitro-radical anions (IV)

Nitrobenzene substituents	Radical (II) in tetrahydrofuran							Methanol	Methyl	
	a_{N}	a_2	a_3	a_4	a_5	a_{6}	Others	$\Delta H^{\dot{a}}$	$a_{ m N}$	a _N
None	1.506	0.312	0.106	0.312	0.106	0.312	0.039 a	0.012	1.37	1.020
2-Chloro ^b	1.75		0.09	0.20	0.09	0.20				0.972
3-Chloro	1.415	0.304		0.304	0.106	0.304		0.052		0.943
4-Chloro	1.451	0.314	0.112	0.028 c	0.112	0.314	0.035 a	0.020	1.33	0.962
2,4-Dichloro	1.76		0.110		0.110	0.245		0.06	1.31	0.899
2,5-Dichloro	1.75			0.23		0.23		0.13	1.27	0.869
3,4-Dichloro	1.40	0.29				0.29		0.17	1.22	0.884
3,5-Dichloro	1.400	0.308		0.308		0.308		0.06	1.17	0.845
2,3,4-Trichloro	1.827				0.112	0.20		0.06		
2,4,6-Trichloro	$2 \cdot 430$		0.045		0.045		0.060 a	0.05	2.05	1.41
2,3,5,6-Tetrachloro	2.50							0.10	2.07	1.35

^{*a*} Doublet hyperfine splitting. ^{*b*} Recorded at -20° C. ^{*c*} Chlorine quartet hyperfine splitting. ^{*d*} Peak-to-peak line width of first-derivative spectrum.

We report here the detection and identity of free radicals present during and after u.v. photolysis of chloronitrobenzenes in ethers, alcohols, and hydrocarbons, and kinetic studies of some thermal reactions of the nitroxide free radicals present in these systems.

RESULTS AND DISCUSSION

The observations presented refer mainly to the u.v. photolysis of di-ortho-substituted chloronitrobenzenes in solution for which the spectral interpretation of the e.s.r. signals observed is straightforward. Despite some reactions in common, significant differences were observed in the modes of reaction of free radicals derived photochemically from unhindered nitrobenzenes and sterically hindered nitrobenzenes, which contained chlorine atoms in the ortho-positions. The differences are noted in the results and tentative explanations have been attempted.

 $ArNO_2^{-}R^+$. Table 2 gives the reported nitrogen h.f.s. of several nitroxide radicals and shows that the introduction of an alkoxy-group on the nitrogen in place of an

TABLE 2 Nitrogen h.f.s. in nitroxide radicals

$a_{\rm N}$	
(mT)	Ref.
$1 \cdot 4 - 1 \cdot 5$	a
1.18	a
0.96 - 1.09	a
2.8	16
2.5	b
1.5	b
	$\begin{array}{c} a_{\rm N} \\ (m{\rm T}) \\ 1\cdot4-1\cdot5 \\ 1\cdot18 \\ 0\cdot96-1\cdot09 \\ 2\cdot8 \\ 2\cdot5 \\ 1\cdot5 \end{array}$

R = Alkyl, Ar = 2,3,5,6-tetrachlorophenyl.

^a Landolt-Bornstein, New Series, Group II, vol. 1, 'Magnetic Properties of Free Radicals' by H. Fischer, Springer-Verlag, Berlin, 1965. ^b This work.

¹⁵ W. E. Griffiths, G. F. Longster, J. Myatt, and P. F. Todd, *J. Chem. Soc.* (B), 1966, 1130.

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alkyl group markedly increases a_N , probably via a π -electron donation (from oxygen lone-pair electrons). The 2,3,5,6-tetrachlorophenyl alkoxy nitroxide radical has an a_N value very close to that of alkyl alkoxy nitroxides 16,17 and may be considered as a sterically protected tertiary-alkyl alkoxy nitroxide radical. This is apparent also from the kinetic studies.

The stationary concentrations of radical (IIa) (where 'a' refers to 2,3,5,6-tetrachloro-substitution of the phenyl group hereafter) obtained on continuous photolysis of fresh equimolar solutions of 2,3,5,6-tetrachloronitrobenzene in various solvents under nitrogen are classified in Table 3. Since:

Rate of formation of (II) = Rate of decay of (II) =
$$k_{1 \text{ obs}} [(II)]_{u.v. \text{ on}}$$

allowance has been made for the variation of the firstorder rate constant $(0.15-0.80 \text{ sec.}^{-1})$ of the decay of the species (IIa) in the various media. The decay of species (IIa) in the dark follows first-order kinetics in almost every instance, and is assumed to be unchanged under illumination.

TABLE 3

Radical yields of (IIa) from 2,3,5,6-tetrachloronitrobenzene

Tetrahydrofuran, diethyl ether, di-n-butyl ether, dioxan, 2-methyltetrahydrofuran, and High yields 2,5-dimethyltetrahydrofuran Medium to low Di-isopropyl ether, s-trioxan in benzene, benzyl methyl ether, dimethylformamide, methanol, yields ethanol, benzyl alcohol, and bis-(2-chloroethvl) ether Zero yield Benzene, methylene dichloride, acetone, ethyl acetate, cyclohexane, toluene, cumene, and propan-2-ol

There is abundant evidence that organic free radicals having the tervalent carbon atom bonded to a hydroxyor an alkoxy-group reduce aromatic ¹⁵ and aliphatic ^{18,19} nitro-compounds by rapid one-electron transfer reactions. Recently, radicals of analogous structure to (II) have been observed in a flow system in both neutral and acidic media.¹⁹ In this instance the radicals were generated from alcohol or ether radicals reacting with nitroalkanes. On the basis of the solvent carbonium ion R⁺ stability, McMillan and Norman¹⁸ proposed that the reaction proceeds via electron transfer from the solvent radical \mathbf{R} to the nitro-compound [equation (6)] followed by rapid combination of the oppositely charged ions [equation (8)]. Reaction (6) can only proceed if the radical R. possesses suitable donor character and the nitro-compound suitable acceptor character.²⁰ Our data for the photochemical yields of the adduct radical (IIa) in various solvents are in close agreement with these ideas. The adduct radicals were detected in

ethers, alcohols, and dimethylformamide but were not observed in acetone and ethyl acetate. While it was deduced that photochemical hydrogen abstraction from hydrocarbon solvents such as cyclohexane, toluene, and cumene to yield alkyl radicals had taken place, no adduct radicals were detected in these solvents. This indicates that alkyl radicals are weak electron donors and do not attack nitrobenzenes appreciably 19 (but will attack nitrosobenzenes, which are more powerful electron acceptors).

(b) Solvent radical (III). We were unable to detect any e.s.r. signals attributable to the radicals formed in the initial hydrogen abstraction step although these have been detected by Zeldes and Livingston²¹ during intense u.v. photolysis of many of the solvents used in this study in the presence of hydrogen peroxide. Indirect evidence for the existence of R. in the present systems is provided by (i) the detection of the adduct radical (II) and (ii) the detection of nitroxide radicals having the structure Ph-N(O)-R which can only have arisen from the trapping of R. radicals by intermediate nitrosobenzene. The tetrahydrofuranyl radical has been trapped in this system using phenyl t-butyl nitrone.20

(c) Monohydronitrobenzene radical (I).²² As reported elsewhere ²³ we were able to record an e.s.r. spectrum consisting of six lines of equal intensity of a short-lived radical present in low concentration (ca. 5×10^{-6} M) during the u.v. photolysis of 2,3,5,6-tetrachloronitrobenzene. The same spectrum was obtained from 2,4,6-trichloronitrobenzene in a number of solvents but it was not possible to detect (I) formed from other nitrocompounds because of overlapping spectra of high intensity. The measured h.f.s. are given in Table 4.

TABLE 4
Hyperfine splittings (mT) of the monohydro-radical of
2,3,5,6-tetrachloronitrobenzene (Ia)

Solvent	<i>Ax</i>	a ^{OH}
	2.00	~н
Tetrahydrofuran	2.39	0.38
Benzyl ethyl ether	2.39	0.39
Benzyl alcohol	2.33	0.50
Isopropyl alcohol	2.32	0.47
Ethanol	$2 \cdot 32$	0.48

1 mT = 10 gauss.

ArNO₂H· was detected also in dioxan, benzyl methyl ether, and diethyl ether.

The nitrogen h.f.s. is $2 \cdot 4$ mT, indicating a close similarity with species (IIa), and the only other splitting is a solvent-dependent doublet of 0.38-0.50 mT which we attribute to the hydrocyclic hydrogen atom in a radical of structure ArNO₂H·.

Free Radicals present in the Dark after Photolysis of

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^{590.}

2,3,5,6-Tetrachloronitrobenzene (and 2,4,6-Trichloronitro-
benzene).—When the u.v. illumination is cut off abruptly
from the e.s.r. sample cell the concentration of the aryl
alkoxy nitroxide radical (IIa) falls rapidly to zero (half-
life ca. 4 sec.) as does that of the monohydronitro-
radical (Ia) also (half-life ca. 0.5 sec.). At the same
time other radical species, observed normally in low
concentration during u.v. illumination, build up to
concentrations of the same order as the earlier photo-
stationary concentration of species (IIa) over a period
of several seconds. We designate these radicals 'second-
ary' in that they appear to arise from decay reactions
of primary radical species (I)—(III).¹⁶ Photolysis of
nitrobenzenes in ethers at temperatures of about
$$-15^{\circ}$$
C
yields only species (II), whose decay in the dark is
negligible and the secondary radicals are not observed
in the dark. With increasing temperature the concentra-
tions of the secondary radicals during illumination in-
crease as also do the concentrations attained after
cessation of illumination until at about 40° C the
'secondary radicals predominate at all times. The
secondary radicals observed when both 2,4,6-trichloro-
nitrobenzene and 2,3,5,6-tetrachloronitrobenzene are
photolysed in ethers, alcohols, and hydrocarbons, are
easily characterised. Their e.s.r. hyperfine coupling
constants show that two types of radicals can be formed.
Both are nitroxides, ArN(O·)R.

(a) Radical (V) ArN(O·)R, (where RH is ether or cumene). This species appears to arise from the reaction:

$$PhNO + R \cdot \longrightarrow PhN(O \cdot)R \tag{9}$$

which is reasonable since nitrosobenzene is expected to be present in the system as an intermediate in the decay of species (I). The yields of (V) were variable and the e.s.r. signal was often overlaid by those of other species in ethers. The e.s.r. parameters of species (V) obtained from several solvents are recorded in Table 5. In

TABLE 5

E.s.r. hyperfine splitting (mT) of alkyl nitroxide radicals (V), PhN(O)R

Solvent	$a_{ m N}$	$a_{\rm H}$ Doublet h.f.s.	Chlorine substitution in parent nitrobenzene
THF	1.215	0.68	2,3,5,6
THFbenzene	1.21	0.66	2,3,5,6
Di-isopropyl ether	1.36		2,4,6
1,3,5-Trioxan	1.13	0.66	2,3,5,6
1,4-Dioxan *	1.15	0.47	2,3,5,6
Benzyl ethyl ether	1.28	0.78	2,3,5,6
Cumene	1.05		3,4
Cumene	1.25		2,5
Cumene	1.27		2,3,5,6

Alternating line width effects noticeable.

cumene, nitrobenzene and the chlorine-substituted nitrobenzenes yielded detectable concentrations of (V) after photolysis ceased, showing that photochemical hydrogen abstraction occurs and that nitrosobenzenes are able to trap alkyl radicals.

This type of radical was observed solely in the photolysis of 2,4,6-trichloro- and 2,3,5,6-tetrachloro-nitrobenzenes in ethers and ethanol, and was characterised by the presence in the nitroxide radical of an alkyl group adjacent to the nitrogen atom, which had previously occupied the β -position in the original solvent ether as shown in Table 6. The mechanism of formation of (VI) constitutes a major part of the later discussion.

TABLE 6
E.s.r. hyperfine splittings (mT) of alkyl nitroxide
radicals (VI)

sub	stitution parent
	parent
in	-
Solvent $a_N a_H a_H a_H b_{a_H c}$ nitr	obenzene
THF 1.24 1.02 ² 0.08 ¹ 0.04 ²	2,3,5,6
THF—benzene 1.24 1.02^2 0.08^1 0.04^2	2,3,5,6
THF-cyclohexane 1.20 0.992 0.081 0.042	2,3,5,6
Diethyl ether $1.28 1.15^3 0.06^2$	2,4,6
Di-isopropyl ether 1.28 1.15^3 0.06^2	2,4,6
Di-n-butyl ether $1.26 0.98^2 0.07^2 0.06^2$	2,4,6
Ethanol 1.29 1.15 ³ Not resolved	2,3,5,6

Superscripts 1, 2, and 3 refer to 1, 2, and 3 equivalent protons respectively.

"." H.f.s. from protons in the aliphatic group. b H.f.s. from the aromatic protons.

Secondary radicals were not detected, or were present in too low a concentration for proper e.s.r. spectral analysis with the following solvents: methanol, toluene, ethylbenzene, benzyl methyl ether, and dimethylformamide.

KINETIC AND MECHANISTIC STUDIES

Decay of the 2,3,5,6-Tetrachlorophenyl Alkoxy Nitroxide Radical (IIa).-In almost every instance the decay of the adduct radical (IIa) derived from 2,3,5,6-tetrachloronitrobenzene in tetrahydrofuran (THF) (or diethyl ether within the range of the available data) obeys good firstorder kinetics for over 80% reaction. Typical firstorder plots of the kinetic data are given in Figure 1. Computer analysis of the decay curves revealed that zero- and second-order contributions to the rate law were negligible except in the few cases indicated by an asterisk in Table 10. Tables 7-12 give the first-order

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First-order decay constants of alkoxy nitroxide radical (IIa). Variation of concentration of the radical in tetrahydrofuran

10 ⁵ [(IIa)] м k _{1, obs} (sec. ⁻¹)	$34.8 \\ 0.155$	9·6 0·146	$7.8 \\ 0.177$	3∙6 0•138	3∙0 0∙144
		-	•		

TABLE 8

First-order decay constants of radical (IIa). Variation % v/v of water in tetrahydrofuran

/0				-		
% v/v water	0	4 ·8	9.1	13.8	20	33
$k_{1, obs} (sec.^{-1})$	0.15	0.13	0.16	0.18	0.16	0.17
Concentrati	on of 2,	3,5,6,-te	trachlor	onitrobe	nzene =	0.09м

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rate constants obtained in various solvent mixtures. The first-order rate constant does not change markedly on varying such parameters as the concentration of the



FIGURE 1 First-order plots for the decay of alkoxy nitroxide radical (IIa) in A, tetrahydrofuran; B, 40% v/v tetrahydro-furan in cyclohexane; and C, 20% v/v tetrahydrofuran in water at pH 3.9. Concentration units are arbitrary and plots are positioned arbitrarily along the vertical scale

TABLE 9

2,3,5,6-Tetrachloronitrobenzene (0.115м) in tetrahydrofuran-benzene

0/ ++/++	ь. /TT)	Molar conce	ntrations of r	adicals $\times 10^4$
THF	$\binom{\pi_{1, \text{ obs}}}{(\text{sec.}^{-1})}$	u.v. on [(II)]	Final [(VI)]	u.v. off [(V)]
100	0.13	3.50	1.34	2.03
80	0.12	3.02	1.48	1.72
50	0.13	2.62	2.00	1.33
33	0.13	$2 \cdot 12$	2.02	1.20
20	0.14	1.60	1.97	0.99
10	0.13	0.95	0.84	0.24
4.7	0.14	0.62	0.43	0.12
$2 \cdot 4$	0.14	0.50	0.38	0.14
0		< 0.02	0	0

TABLE 10

2,3,5,6-Tetrachloronitrobenzene (0.10m) in tetrahydrofuran-cyclohexane

Molar concentrations of radicals $\times 10^4$

% v/v	k, che	kr (VI)		u.v. on		u.v. of	f, final
ŤHF	(II)	sec1	[(II)]	[(VI)]	[(V)]	[(VI)]	[(V)]
100	0.12	0.11	3.50	0.35	0.22	1.96	0.47
80	0.12	0.14	3.01	0.45	0.31	1.46	0.69
60	0.12	0.12	1.72	0.20	0.30	1.09	0.60
40	0.18	0.17	1.14	0.10	0.14	0.42	0.78
20	0.18 *	0.19	0.60	0.06	0.15	0.14	0.64
10	0.18 *		0.44	(0)	0.27	0.04	0.79
5	0.14 *		0.12	(0)	0.21	(0)	0.60

* Zero-order contribution of 5×10^{-7} M sec.⁻¹ present.

nitro-compounds, the acidity, the composition, or the dielectric constant of the media when mixed solvents are used. The relative invariance of $k_{1,obs}$ over the wide range of experimental parameters confirms the electrically neutral character of the radical species (IIa). This

TABLE 11

2,3,5,6-Tetrachloronitrobenzene (0.082M) in 20% v/v aqueous tetrahydrofuran containing hydrochloric acid Molar concentrations

				of radicals	
[HCl] (M) 0·07	\log_{10} [HCl] -1.16	$H_0 + 1 \cdot 10$	k _{1, obs} (II) 0·162	u.v. on 10 ⁴ [(II)] 2·20	u.v. off 10 ⁵ [(VI)] 10·0
0·139 0·279 0·371	-0.86 -0.55 -0.43	0·84 0·50 0·37	0·186 0·206 0·183	$2.35 \\ 2.03 \\ 1.74$	$12 \cdot 2 \\ 11 \cdot 2 \\ 8 \cdot 3$
0.556 0.763 1.11	-0.25 -0.12 0.047	0.15 - 0.04 - 0.26	0·188 0·227 0·322	$1.44 \\ 0.89 \\ 0.72$	$7 \cdot 3$ $5 \cdot 0$ $3 \cdot 1$
$1.54 \\ 2.28$	0·188 0·358	-0.48 - 0.82	$0.48 \\ 1.12$	0·56 0·27	1.9 1.0

 $[(VI)]_{u,v.\ on}$ was negligible in all cases. Radical (V) was not observed with light on or off.

TABLE 12

2,3,5,6-Tetrachloronitrobenzene (0.081m) in buffered * 20% v/v aqueous tetrahydrofuran

Mea: soluti	sured on pH		Molar concentrations of radicals $\times 10^4$ u.v. on		
Aqueous	Ag THE	$k_{1, obs}$ (II)	ίπη.		r(V))
Aqueous	Aq. 1111 0.00 ±	0.15	0.6	0.5	1(•)]
1.10	1.29 +	0.10	2.0	0.8	0
2.20	1.62 +	0.90	2.0	0.5	ő
2.10	3.70 +	0.17	2.0	1.4	0.6
2.35	3.90	0.15	1.8	1.9	1.5
2 00	4.53 +	0.19	1.9	1.8	1.7
2.85	5.05	0.10	3.7	$\overline{2 \cdot 1}$	0.8
4.08	5.85	0.11	2.7	1.4	0.6
5.09	6.23	0.12	2.7	1.2	0.4
6.03	6.84	0.13	2.6	1.1	0.4
6.97	7.84	0.14	2.3	1.4	0.6
7.90	8.72	0.16	1.5	1.6	1.3
10.8	11·5 ‡	0.12	1.1	$2 \cdot 1$	$2 \cdot 4$

* Buffer citrate-disodium phosphate except † hydrochloric acid addition; ‡ saturated sodium hydrogen carbonate.

leads us to conclude that the decay of the aryl alkoxy nitroxide radical (IIa) is a non-ionic unimolecular decomposition (10):

$$\operatorname{ArN} \underbrace{\operatorname{Or}}_{\operatorname{OR}} \xrightarrow{k_1} \operatorname{ArN} \cdot \operatorname{OR} + \cdot \operatorname{OR}$$
(10)

which is not expected to involve a high activation energy.* The reverse reaction of (10), namely the addition of alkoxy-radicals to nitroso-compounds ¹⁶ has been reported to occur at $ca. -60^{\circ}C$ but at higher temperatures the alkoxy nitroxides thus formed were found to decompose. The radicals (IIa) do not appear to abstract hydrogen from the solvent ethers at any appreciable rate (Tables 9 and 13).

It is interesting to note that the reduction of the nitrobenzene to the nitrosobenzene by ether radical R. involves the transfer of oxygen from the nitrobenzene.

In 20% v/v aqueous tetrahydrofuran the rate of decay of the alkoxy nitroxide radical while remaining strictly

^{*} Authors' unpublished results indicate an activation energy of about 42 kJ mole⁻¹ [10 kcal. mole⁻¹ for reaction (10)] for 2,3,5,6-tetrachloronitrobenzene in tetrahydrofuran.

2,3,5,6-Tetrachloronitrobenzene (0·12_M) in diethyl ether-benzene

		Molar concentrations of radicals		
% v/v ether	$k_{1, obs}$ (II)	u.v. on 104[(II)]	u.v. off, final 104[(VI)]	
100	0.20	1.56	0.42	
75	0.19	1.41	1.19	
50	0.21	1.07	1.05	
22	0.25	0.63	1.52	
10	0.21	0.44	1.43	
3	0.19	0.19	0	

Radical (V) was not present, and $\left[(\rm VI)\right]$ during u.v. irradiation was undetectable.

first-order increases on increasing the acidity by addition of hydrochloric acid (Table 11). The rate constant k_{obs} shows a peculiar variation at concentrations of hydrochloric acid between 0.1M and 0.4M but k_{obs} then increases smoothly towards the higher acidities. The aciddependent part of the observed rate constant was taken to be $k_{acid} = k_{obs} -0.15$ (since 0.15 sec.⁻¹ is the interpolated value of k_{obs} at very low acidities in the media,



FIGURE 2 The acid-catalysed decay of alkoxy nitroxide radical (IIa); (A) is the acidity function (H_0) plot and (B) is the \log_{10} [HCl] plot-shifted 0.6 units to give a common scale. See text for the definition of k_{acid}

i.e. non-acid-catalysed rate constant). The logarithm of this function was plotted with respect to both \log_{10^-} [HCl]_{molar} and the Hammett acidity function H_0 (see Experimental section for estimation of H_0 values) as shown in Figure 2. The latter plot gives a straight line of gradient -1.2; and in view of the problems associated with the determination of acidity in aqueous organic solvents, this result suggests that the acid-catalysed decay of (IIa) involves the equilibria

(IIa) + H₃O⁺
$$\stackrel{+}{\longrightarrow}$$
 ArN $\stackrel{+}{\longrightarrow}$ O-R + H₂O (11)

followed by the rate-determining decomposition step (r.d.s.)



Appreciable protonation of alkyl nitroxide radicals 24 is known to occur at acid concentrations of *ca*. IM. Protonation of the nitrogen atom (or alternatively of the nitroxide oxygen) would be expected to facilitate the movement of electrons required for the radical fission. The ionic strength of the solution was not kept constant and therefore the proposed mechanism of the acidcatalysed reaction is subject to some reservation.

General Kinetic Behaviour of Nitroxide Radicals in the System.—Alkyl nitroxide radicals, such as species (V) and (VI), are relatively stable (as dilute solutions) in aprotic media in the dark. Thus the low concentrations of such nitroxide radicals observed during photolysis in our case (see Tables 7-13) must result from a decay reaction involving the radicals occurring only during illumination. For the ethers used in our experiments the stable concentration of alkyl nitroxide radicals existing in the dark, after previous u.v. photolysis, was destroyed very rapidly (half-life ca. 0.5 sec.) when photolysis again commenced. We suggest that the decay reaction in the light involves the monohydronitrobenzene radical (Ia), which has the light-dark kinetic properties desired of the reactant which removes radicals (V) and (VI) during photolysis.

$$Ar(R)NO + ArNO_2H \xrightarrow{(13)} D \xrightarrow{(14)}$$

In some binary mixtures involving ethers and also in the hydrocarbon cumene, in which solvent no radicals were detected during photolysis, the increase in the concentration of nitroxide radicals of type (V) or (VI) after illumination ceased was far in excess of any concentration of radicals observed during u.v. photolysis. Thus the existence of a diamagnetic intermediate (D) which can reform the appropriate nitroxide radical is indicated. We have noted that the rate of formation of the nitroxide radicals (V) and (VI) in the dark decreases as the dielectric constant of the media decreases using mixtures of THF and cyclohexane; reaction occurs for periods of half an hour or more in some cases. Chachaty and Forchioni ⁶ have reported the above phenomena in similar systems but their suggestion, that a diamagnetic

intermediate $Ph\dot{N}^+R$ splits to yield a hydroxy-radical

and an alkyl nitroxide radical, seems energetically unfavourable. The complexity of the kinetic behaviour of the nitroxide radicals in these systems must be kept in mind in the subsequent discussion.

²⁴ A. L. Buchachenko, 'Stable Radicals,' Consultants Bureau, New York, 1965.

Formation of Alkyl Nitroxide Radical (VI).—(a) Aprotic and acidic aqueous media. Tables 7—12 give the observed concentrations of species (VI), where Ar =2,3,5,6-tetrachlorophenyl, both under illumination and in the dark when the solvent ether is tetrahydrofuran. The increase in the concentration of species (VI) after photolysis ceases appears to be a relatively constant fraction (ca. 0·4) of the concentration of the alkoxy nitroxide radical (IIa) observed during photolysis in both acidic aqueous tetrahydrofuran and tetrahydrofurancyclohexane mixtures. This suggests that radical (VI) is derived closely from radical (IIa) by a non-ionic process.



FIGURE 3 Formation of the alkyl nitroxide radical (VI) after the u.v. radiation is cut off, in A, tetrahydrofuran; B, 60% v/v tetrahydrofuran in cyclohexane; C, 40% v/v tetrahydrofuran in cyclohexane; and D, 20% v/v tetrahydrofuran in cyclohexane. Concentration units of (VI) are arbitrary and curves are displaced arbitrarily along the vertical scale for clarity

The formation of radical (VI) was found to obey the first-order law where t is the time after illumination

$$[(VI)]_t = [(VI)]_{\infty} \{1 - \exp(-k_{\rm F}t)\}$$

in tetrahydrofuran-cyclohexane mixtures. ceases Figure 3 shows that the appropriate plots of log $([(VI)]_{\infty})$ $- [(VI)]_t$ versus time t are linear in these cases. The rate constant $k_{\rm F}$ (Table 10) agrees closely with the firstorder decay constant of the alkoxy nitroxide radical (IIa) for mixtures containing greater than 20% v/v tetrahydrofuran. In these solvent mixtures of moderate dielectric constant, the effect of the dissociation of the diamagnetic intermediate (D) to yield (VI) must be negligible and this may be the result of the rapid removal of (D) in step 14. In media of low dielectric constant the 'efficiency of conversion' of species (IIa) into species (VI) apparently increases but the rate of formation of (VI) in the dark decreases, as noted earlier, indicating the importance of step (13) in such media. The data obtained for diethyl ether-benzene and tetrahydrofuran-benzene as solvent mixtures (Tables 9 and 13) illustrate this behaviour.

We consider that the *structure* and kinetic behaviour of the alkyl nitroxide radical (VI) are satisfactorily accounted for by the following scheme:

Ar-N(O·)-O-C
$$R^{1}$$
 R^{2} (IIa) $\xrightarrow{R^{1}}$
ArNO $+ \cdot O$ -C-R² (VII) (10)
O-R³

$$ArNO + R^{1} \longrightarrow PhN(O)R^{1} \quad (VI)$$
 (16)

(VII)
$$\longrightarrow$$
 Products (17);
 $R^{1} \longrightarrow$ products (18)

The β -fission of alkoxy-radicals (15) is energetically favourable and is known to be an important pathway in the reactions of such radicals.²⁵ The constant efficiency of the conversion of (II) into (VI) indicates that reactions (10), (15), and (16) are in some way concerted or involve cage-effects, *i.e.* the radical R¹ is captured within the solvent cage with constant efficiency by the nitrosoentity. Nitroso-compounds are known to be efficient scavengers of a variety of free radicals.²⁶ The process does not occur for R¹ = H.

(b) Neutral aqueous tetrahydrofuran. In 20% v./v. aqueous tetrahydrofuran a changeover in the kinetic behaviour of radical (VI) occurs around pH 4. Whereas in more acidic media the concentration of the radical is very low under photolysis and builds up in the dark, in more neutral to alkaline solution the radical (VI) is seen in good yield (but less than [(IIa)]_{u.v. on}) during photolysis. In the dark the concentration of the radical (VI) falls appreciably for a period corresponding to the decay of the alkoxy nitroxide species (IIa) and then assumes a more stable, lower level. The decay rate is almost independent of the acidity of the solution in the range pH 4-9 (Figure 4). Thus the alkyl nitroxide (VI) must be reacting in the dark with an intermediate whose concentration becomes exhausted, leaving some residual concentration of nitroxide radical. The pH at which the kinetic behaviour shows a dramatic change corresponds closely to the pK_a value of the monohydro-2,3,5,6-tetrachloronitrobenzene radical (Ia).²³

$$ArNO_2H \cdot + H_2O \Longrightarrow ArNO_2 \cdot + H_3O^+$$
 (19)

Thus, retaining reactions (13) and (14), we expect the intermediate reacting with the nitroxide (VI) to be solely the nitro-anion radical $ArNO_2$ in solutions of pH > ca. 4. Since the photostationary concentration of the nitro-anion radical is undetectable it must be produced in some measure from the alkoxy nitroxide

²⁵ C. Walling and J. C. Azar, J. Org. Chem., 1968, **33**, 3895, and references cited therein.

²⁶ (a) A. MacKor, T. A. J. W. Wajer, and T. J. de Boer, *Tetrahedron*, 1967, 1623; (b) C. Lagercrantz and S. Forschult, *Nature*, 1968, **218**, 1247.

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radical (IIa) in the dark in order that appreciably quantities of radical (VI) be consumed. A likely reaction is the displacement

$$ArN(O\cdot)OR + H_2O \xrightarrow{slow} ArN(O\cdot)OH + ROH$$
 (20)

followed by the rapid equilibria (19). We have found that the decay of the monohydronitro-radical (Ia) in acidic aqueous propan-2-ol is more rapid than the decay of the nitro-anion radical (IVa) at pH greater than 4. This is consistent with the corollary to the earlier postulate that the nitro-anion radical is sufficiently long-lived intrinsically to be able to react with radical (VI) in the dark after the anion radical is formed from species (II). The rapid natural decay of $ArNO_2H$ · under all conditions precludes the above event. The non-appearance of

 $\begin{bmatrix} u_{0}^{-0.4} \\ -12 \\$

FIGURE 4 Decay of the alkyl nitroxide radical (VI) in 20% v/v water in tetrahydrofuran: u.v. radiation is off. pH values are A, 6.23; B, 5.05; C, 6.84; D, 3.90; and E, 8.72. The plots are displaced arbitrarily along the vertical scale for clarity but when t = 0, \log_{10} ([VI]_t/[VI]_{u.v. on}) = 0 in all cases

 $ArNO_2^{-}$ in the solutions of neutral pH under photolysis and the expected increased level of $[(VI)]_{u.v. on}$ observed in such solutions must be due to the removal of $ArNO_2^{-}$ *during* photolysis by a rapid reaction. The reaction

$$ArNO_2H + ArNO_2 - ArNO_2H + ArNO_2$$
 (21)

is a possibility, which is known to be very rapid when $Ar = Ph.^{22}$ (N.B. $ArNO_2H^{\bullet}$ is formed first in all systems under photolysis).

Formation of Alkyl Nitroxide Radical (V).—As postulated earlier the formation of (V) is considered to arise by the trapping of solvent radicals by nitrosobenzene (present in low concentration as an intermediate). The kinetic behaviour of the alkyl nitroxide radical (V) is identical to that of radical (VI), which is structurally similar, and the same explanation involving reaction scheme (9), (17), (14) suffices for aprotic organic media.

In aqueous tetrahydrofuran, for which most data have been collected, the same phenomena as reported for species (VI) was found when the pH of the solution was greater than 4, and again the explanation given earlier suffices. At any pH < ca. 4, the alkyl nitroxide radical (V) could not be detected either during or after photolysis. This general type of radical is reasonably stable in aprotic and acidic aqueous organic media.²⁴ The solvent radicals and nitrosobenzene must still exist in the system, as adduced by the unchanged formation and decay rates of the alkoxy nitroxide species (IIa) and the qualitatively unchanged situation compared with aprotic media involving ArNO₂H· etc.

By analogy with the formation of the adduct radical (II) from nitrobenzenes, the formation of (V) is written

$$ArNO + R \cdot \longrightarrow [ArNO \overline{\cdot} R^+] \longrightarrow (V) \quad (22)$$

Thus it may be that at acid concentrations of higher than about 10^{-4} M, the nitroso-anion radical ArNO⁻ is effectively removed in a rapid protonation equilibrium to give ArNHO· before combination with the solvent cation can occur. Then ArNHO· is removed by reaction (23)²²

$$ArNO_2H + ArNHO \rightarrow ArNO_2 + ArNHOH$$
 (23)

Such considerations apply also to the formation of adduct radical (II) from nitrobenzene but in view of the wide difference in the pK_a values of PhNHO^{• 27} (>10) and PhNO₂H• (3·2) (for unhindered phenyl substituent) this effect on the formation of radical (II) would be observed only in highly acidic media.

Differences between Di-o-chloronitrobenzenes and Unhindered Nitrobenzenes.—Although the first-order decay constants of the adduct radicals (II) derived from nitrobenzene and 2,3,5,6-tetrachloro- (or 2,4,6-trichloro-) nitrobenzene are similar, the secondary alkyl nitroxide radicals (V) and (VI) were not detected when nitrobenzene was used.

The known phenyl nitroxide radical,27 characterised by a nitrogen h.f.s. of ca. 0.9 mT and a large hydrogen doublet h.f.s. of ca. 1.1 mT was observed as the major secondary' radical after photolysis of nitrobenzene or 3,5-dichloronitrobenzene in tetrahydrofuran, tetrahydrofuran-benzene, aqueous tetrahydrofuran, diethyl ether, and benzyl alcohol. We suggest that the difference lies in the properties of the nitroso-analogues. Nitrosobenzene is known to react readily to give azo- and azoxyderivatives but di-ortho-substituted nitrosobenzenes are very stable and are difficult to couple chemically ^{5,28} (to give an azoxy-compound etc.) on account of the steric protection of the nitroso-group. Thus the sterically protected nitroso-compound will persist in the photolytic system to a greater extent than nitrosobenzene itself, the bimolecular reaction being retarded on steric grounds. This reaction may be the source of PhNHO. in the case of unhindered nitrobenzene. In addition,

$$ArNO + ArNO_{2}H \rightarrow ArNHO + ArNO_{2}$$
 (24)

2,3,5,6-tetrachloronitrosobenzene will be a far stronger electron acceptor than nitrosobenzene by analogy with the corresponding nitrobenzenes * because of the



^{*} Nitrobenzene anion radical will transfer an electron to 2,3,5,6-tetrachloronitrobenzene in methyl cyanide solution.

²⁷ P. B. Ayscough, F. P. Sargent, and R. Wilson, J. Chem. Soc. (B), 1966, 903.

²⁸ E. Bamberger and A. Rising, Annalen, 1901, 316, 257.

electron-withdrawing effects of the chlorine atoms in the aromatic ring. This will facilitate reaction (22) and hence the ability to trap alkyl radicals.

From molecular models of the alkoxy nitroxide radicals (II) it appears that in the case of the 2,6-chlorine substitution of the phenyl group, the steric constraint thus imposed brings the nitroxide group into close proximity to the β -carbon atom of the ether grouping in the radical. This constraint would enhance the rate of trapping of the β-carbon alkyl radical by the nitroso-entity.

The photolysis of chloronitrobenzenes in solution is thus seen to be complex and the effects of the numerous factors involved provide a wide field for further study. The results of variable temperature studies on the photolysis of many substituted nitrobenzenes are to be published shortly.

EXPERIMENTAL

Materials.-2,3,4-Trichloronitrobenzene was prepared 29,30 by nitration of 1,2,3-trichlorobenzene (B.D.H. Ltd.), and was then recrystallised from ethanol. The other chloronitrobenzenes were 'pure' grade (Koch-Light Ltd.) chemicals; they were recrystallised from aqueous ethanol. For the kinetic studies, 2,3,5,6-tetrachloronitrobenzene was recrystallised three times from warm aqueous ethanol; m.p. 99-100°, (lit.,³¹ 99°). Solvents were freshly distilled before use from an appropriate drying agent.

Preparation of Radicals.-Dry 'white-spot' nitrogen was bubbled for at least 15 min. before photolysis through freshly prepared solutions ca. 0.2M in a nitrobenzene. The solutions were contained in Varian aqueous sample cells and irradiated in the e.s.r. spectrometer cavity with u.v. radiation from the arc element of an Osram 125w MB w/u mercury lamp. The light beam was focussed by means of two quartz lenses and passed through a Pyrex glass filter which cut off radiation at wavelengths shorter than about 300 nm.

Chloronitro-radical anions were prepared by u.v. photolysis of the parent compound in aqueous methanolic sodium hydroxide² and also by electron transfer from the nitrobenzene radical anion to the parent compound dissolved in dry methyl cyanide.³¹ The nitrobenzene radical anion in methyl cyanide was prepared according to the method of Maki and Geski,³² with tetra-n-butylammonium perchlorate as the supporting electrolyte.

E.s.r. Measurements.-E.s.r. spectra were recorded with a Varian V4500 spectrometer having a 6 in. electromagnet. The field sweep was calibrated with alkaline aqueous solutions of potassium nitrosodisulphonate (a_N 1.30 mT). Errors in hyperfine splitting constants were estimated to be ± 0.005 mT, except for complex spectra or for signals from low radical concentrations when the error increased to ± 0.01 mT. The instrumental line-width was less than 0.015 mT.

Relative radical concentrations were determined from the average signal heights of a suitable band in the e.s.r. spectrum of a given radical. With spectrometer operating conditions, sample cell, and its position as constant as

29 E. H. Huntress, 'Organic Chlorine Compounds,' Wiley, New York, 1948, 3:099a.

 F. Bailstein and Ap. Kirbatow, Annalen, 1878, 192, 236.
 A. R. Metcalfe and W. A. Waters, J. Chem. Soc. (B), 1969, 918.

possible, relative radical yields were reproducible to $\pm 10\%$. A measure of absolute radical concentration was obtained by comparison of samples with a standard solution of diphenylpicrylhydrazyl in benzene examined under similar instrumental conditions and allowing for small differences in line widths.

Kinetics.—All experiments were carried out at $22 \pm 2^{\circ}$ C. The decay or rise in concentration of the radicals was obtained by monitoring the maximum peak height of a suitable line (*i.e.* one that is not overlapped by e.s.r. lines of other radicals) in the first-derivative e.s.r. spectrum. The time variation of the peak height was measured with a Varian G10 chart recorder, time scale $1 \text{ mm} \equiv 0.597 \text{ sec. or}$ 2.37 sec. as required. The response time of the recorder was 0.3 sec. and the u.v. light could be cut off manually or by means of a rotating sector plate in a time of less than 0.2 sec.

First-order rate constants were obtained in the normal way from the decay or rise curves. The data were also analysed on a computer by use of an iterative procedure ³³ to determine any contributions to the decay from zero- or second-order terms. The second-order decay rate constants thus obtained were always less than 200 M⁻¹ sec.⁻¹ and could be neglected. A small zero-order contribution to the decay was found for cyclohexane solutions containing less than 20% v./v. of tetrahydrofuran.

Acidity in Aqueous Tetrahydrofuran.-The determination of acidity in aqueous organic media is a problem beset with many difficulties. Hammett acidity function (H_0) data are available for hydrochloric acid in some mixed solvents 34 and the data reveal a complex variation with solvent composition. However, for hydrochloric acid concentrations greater than 0.1M in diverse solvent mixtures, the difference in the H_0 values for two given acid concentrations is approximately constant. In determining kinetic acidity dependences the H_0 differences are the important quantities and we have, therefore, applied for this purpose the literature values ³⁵ of H_0 in aqueous solution to the hydrochloric acid solutions in 20% v./v. water in tetrahydrofuran (0.1 —2м) (see Table 11).

The acidity of solutions less than 0.1M in acid were measured with a Beckmann model 72 pH Meter fitted with a Combination glass electrode. Aqueous buffer solutions were made from $0{\cdot}02{\mbox{\scriptsize M}}$ citric acid in water and $0{\cdot}04{\mbox{\scriptsize M}}$ disodium hydrogen phosphate in water,36 and these were then added to tetrahydrofuran. The low molarity of the buffer concentration was unavoidable because of solubility problems. The measured pH values of the aqueous and the aqueous tetrahydrofuran solutions of the buffer are given in Table 11. The difference between any pair of solutions is in the range 0.8-2.2 pH units and thus the pH values of such solutions quoted for the kinetic experiments must be considered to be semi-quantitative,

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- ³³ D. Margerison, personal communication.
- ³⁴ E. A. Braude and E. Stern, J. Chem. Soc., 1948, 1971, 1976.
- ³⁵ M. A. Paul and F. A. Long, *Chem. Rev.*, 1957, 1.
 ³⁶ A. I. Vogel, 'Macro and Semimicro Qualitative Inorganic Analysis,' Longmans, London, 4th edn., 644.