E.s.r. Investigation of Alkoxynitroxide Free Radicals from the Photolysis of Nitrobenzenes and of Heterocyclic Nitro Compounds

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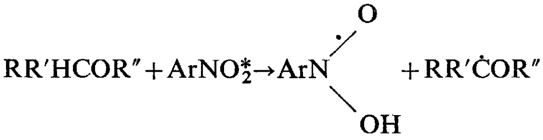
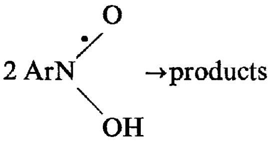
Electron-donating effects of substituents have been found to affect critically the formation of alkoxynitroxide radicals by u.-v. photolysis of aromatic and heterocyclic nitro compounds. This has been explained in terms of the relative hydrogen-abstracting abilities of (n,π^*) and (π,π^*) triplet states. The magnitudes of nitrogen coupling constants appear to be dependent upon inductive and resonance effects and, in some cases, upon steric hindrance from ortho substituents. Energetics of the decay reactions of some arylalkoxynitroxide radicals are reported.

The identity of the free radical species obtained by the ultra-violet photolysis of certain nitroaromatic compounds in ethereal solvents has been in doubt for some time.[1-4] The most satisfactory suggestion is that the observed e.s.r. spectra originate from arylalkoxynitroxide radicals produced by the following sequence of reactions,[5, 6]

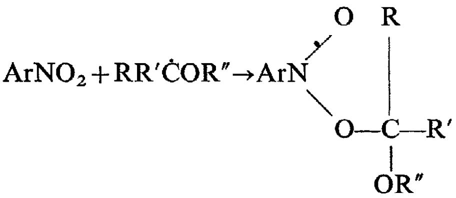
$$\mathrm{ArNO_2} \xrightarrow{h\nu} \mathrm{ArNO_2^*} \qquad (1)$$



$$\mathrm{RR'HCOR''} + \mathrm{ArNO_2^*} \rightarrow \mathrm{ArN}\begin{matrix}\diagup \dot{\mathrm{O}} \\ \diagdown \mathrm{OH}\end{matrix} + \mathrm{RR'\dot{C}OR''} \qquad (2)$$



$$2\,\mathrm{ArN}\begin{matrix}\diagup \dot{\mathrm{O}} \\ \diagdown \mathrm{OH}\end{matrix} \rightarrow \text{products} \qquad (3)$$



$$\mathrm{ArNO_2} + \mathrm{RR'\dot{C}OR''} \rightarrow \mathrm{ArN}\begin{matrix}\diagup \dot{\mathrm{O}} \\ \diagdown \mathrm{O{-}C(R)(R')(OR'')}\end{matrix} \qquad (4)$$

Further support for this scheme comes from spin-trapping experiments[7] and from the e.s.r. detection[8] of the short-lived monohydro-2,3,5,6-tetrachloronitrobenzene free radical.

The purpose of this paper is to describe the substituent effects observed in the e.s.r. spectra of radicals produced by reaction (4). Additionally, the decay rates of some of these radicals were measured.

EXPERIMENTAL

The compounds 2-nitrothiazole, 2-nitrothiophene and 2-nitrofuran were obtained from Dr. P. N. Preston of Heriot-Watt University, 2-nitropyrrole from Prof. K. J. Morgan, of Lancaster University, 2-bromo-5-nitrothiazole from Dr. P. J. Islip of Parke-Davis Company, and 3-nitro-4-fluorobenzoic acid from Dr. J. Chapman of I.C.I. Mond Division: the remaining nitro compounds were obtained commercially. The solvents tetrahydrofuran, 2,5-dimethyltetrahydrofuran and di-isopropyl ether were vacuum-distilled in the presence of B.D.H. type 4A molecular sieve, immediately before use.

Dissolved oxygen was removed from the solutions (normally 0.1-0.2 M in nitro compound) by purging with oxygen-free nitrogen for 15 min. The aqueous sample cells used were also flushed with nitrogen. Photolysis was carried out in the cavity of a Varian V-4500 e.s.r. spectrometer, radiation being provided from the internal element of a 125 W Osram MB/U lamp, enclosed in an evacuated silica jacket. Wavelengths shorter than 330 nm were removed with the aid of a 2.5 mm thick piece of plane soda glass. The magnetic field sweep was calibrated as described previously.[9]

The decay of arylalkoxynitroxide radicals was measured by monitoring a single e.s.r. peak after interruption of the u.-v. irradiation. First-order rate constants were obtained from least-squares plots of the logarithm of peak height against time. The sample temperature was varied using a Varian V-4343 control unit in conjunction with a specially-designed heater/sensor mounted in the transfer dewar of a Varian V-4547 variable temperature accessory. Sample temperatures were measured by means of a copper/constantan thermocouple inserted into the aqueous sample cell.

RESULTS

Table 1 lists the hyperfine splittings of the arylalkoxynitroxide radicals obtained when the parent nitroaromatic compounds were undergoing continuous ultra-violet photolysis (see fig. 1 for typical spectra). At room temperature, spectra disappeared within a few seconds of cutting-off the radiation, In some cases, new spectra developed in the dark period and these were assigned to substituted monophenyl nitroxide

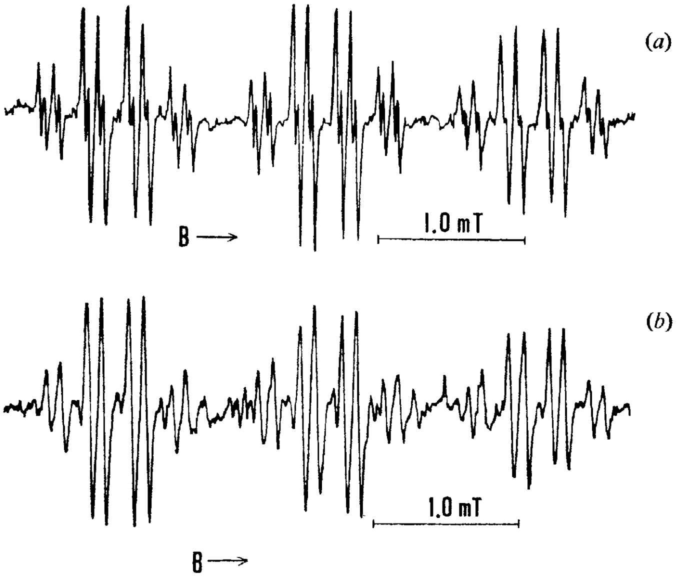


FIG. 1.—E.s.r. spectrum obtained *during* u.-v. photolysis of 3-nitrobenzoic acid dissolved in (*a*) tetrahydrofuran and (*b*) 2,5-dimethyltetrahydrofuran.

TABLE 1.—HYPERFINE SPLITTINGS (mT) OF ARYLALKOXYNITROXIDE RADICALS OBSERVED DURING U.-V. PHOTOLYSIS OF NITROBENZENES IN ETHERS

substituent	solvent	a_N	a_2	a_3	a_4	a_5	a_6	a solvent
2-COOH	THF	1.614	——	0.102	0.274	0.102	0.274	—
3-COOH	THF	1.466	0.292	—	0.292	0.098	0.292	0.029
	IPE	1.423	0.295	—	0.295	0.102	0.295	—
	MTHF	1.454	0.284	—	0.284	0.093	0.284	—
4-COOH	THF	1.342	0.300	0.103	—	0.103	0.300	0.021
2-CN	THF	1.346	—	0.103	0.306	0.103	0.306	—
	MTHF	1.332	0.041[f]	0.098	0.282	0.098	0.282	—
4-CN	THF	1.301	0.300	0.104	—	0.104	0.300	—
	MTHF	1.275	0.299	0.099	0.046[f]	0.099	0.299	—
4-CHO	THF	1.298	0.296	0.107	—	0.107	0.296	—
	MTHF	1.260	0.290	0.107	—	0.107	0.290	—
2-COCH$_3$	THF	1.558	—	0.107	0.294	0.107	0.294	—
3-CH=CH$_2$	THF[a]	1.497	0.306	0.036[b]	0.306	0.096	0.306	0.036[b]
	MTHF[a]	1.442	0.292	0.044[c]	0.292	0.103	0.292	—
2,3-di-COOH[d]	THF	1.565	—	—	0.273	0.099	0.273	—
2,3-CO—O—CO—	THF	1.322	—	—	0.290	0.105	0.290	—
3,4-di-COOH	THF	1.241	0.290	—	—	0.099	0.290	—
2,5-di-COOH	THF	1.508	—	0.079	0.272	—	0.272	—
2,6-di-COOH	THF	1.806	—	0.100	0.197	0.100	—	—
3,5-di-COOH	THF	1.454	0.304	—	0.304	—	0.304	0.027
	MTHF	1.410	0.283	—	0.283	—	0.283	—
2-F,5-COOH[d]	THF	1.644	0.549	0.073	0.285	—	0.295	0.034
2-Cl,5-COOH[e]	THF	1.743	—	—	0.228	—	0.228	—
3-COOH,4-Cl	THF	1.421	0.296	—	—	0.082	0.296	—
2-COOH,4-Cl	THF	1.556	—	0.105	—	0.105	0.291	—
2-COOH,5-Cl	THF	1.553	—	0.094	0.279	—	0.279	—

THF denotes tetrahydrofuran; MTHF denotes 2,5-dimethyltetrahydrofuran; IPE denotes di-isopropyl ether.

[a] sample temperature of 268 K; [b] 1 : 2 : 1 triplet; [c] 1 : 1 doublet; [d] sample temperature of 273 K; [e] sample temperature of 283 K; [f] refers to a_N^{CN}.

radicals (see table 2 and fig. 2). The spectrum of the arylalkoxynitroxide derived from 4-nitrophenol could only be obtained (see fig. 3) when 10 % v/v ditertiarybutyl peroxide was incorporated into the solvent. The t-butoxy radicals produced can abstract hydrogen atoms from the alpha position of tetrahydrofuran.[10] This method has not been applied yet to the other nitro compounds investigated.

TABLE 2.—HYPERFINE SPLITTINGS (mT) OF PHENYL NITROXIDE RADICALS OBSERVED AFTER U.-V. PHOTOLYSIS OF NITROBENZENES IN TETRAHYDROFURAN

substituent	a_N	a_H^{NH}	a_2	a_3	a_4	a_5	a_6	a_H^{NH}/a_N
2-COOH	0.813	1.191	—	0.101	0.307	0.101	0.307	1.47
3-COOH	0.869	1.211	0.293	—	0.293	0.097	0.293	1.39
4-COOH	0.816	1.148	0.279	0.099	—	0.099	0.279	1.41
3,4-di-COOH	0.797	1.148	0.268	—	—	0.094	0.268	1.44
2,3-CO—O—CO—	0.747	1.116	—	—	0.294	0.101	0.294	1.49
3,5-di-COOH	0.856	1.141	0.299	—	0.266	—	0.299	1.33
2,5-di-COOH	0.770	1.152	—	0.090	0.290	—	0.290	1.50

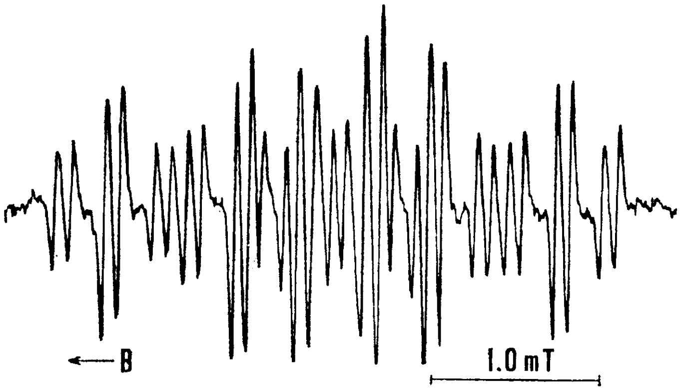


FIG. 2.—E.s.r. spectrum obtained *after* u.-v. photolysis of nitroterephthallic acid dissolved in tetrahydrofuran.

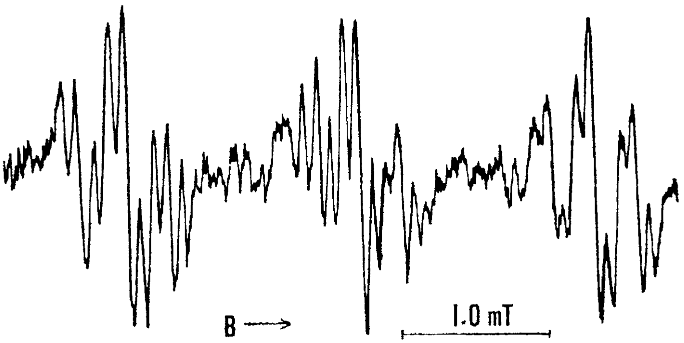


FIG. 3.—E.s.r. spectrum obtained *during* u.-v. photolysis at 278 K of 4-nitrophenol dissolved in 90 % v/v tetrahydrofuran+10 % v/v di-tertiarybutyl peroxide.

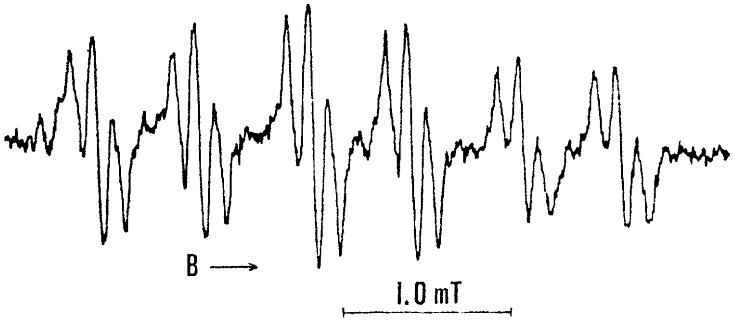


FIG. 4.—E.s.r. spectrum obtained *during* u.-v. photolysis at 233 K of 5-nitro-2-furaldehyde diacetate dissolved in tetrahydrofuran.

Some of the nitroaromatic compounds did not yield detectable amounts of alkoxynitroxide radicals when they were photolyzed in tetrahydrofuran; these were 4-nitrophenol, 2-nitrophenol, 1-nitronaphthalene, 2-nitrophenylhydrazine, 4-fluoro-2-nitrophenol, 2-nitrobenzyl bromide, 2-bromonitrobenzene and 2-nitroaniline. Previous work[11] has shown that 5-hydroxy-2-nitrotoluene, 4-hydroxy-2-trifluoromethylnitrobenzene, 4-amino-3-trifluoromethylnitrobenzene and 4-amino-2-trifluoromethylnitrobenzene behave similarly.

TABLE 3.—HYPERFINE SPLITTINGS (mT) OF ALKOXYNITROXIDE RADICALS OBSERVED DURING U.-V. PHOTOLYSIS OF HETEROCYCLIC NITRO COMPOUNDS IN ETHERS

compound	solvent	nucleus	hyperfine splitting
2-nitrothiophene	THF	N	1.375
		H	0.427
		H	0.525
		H	0.095
		H[a]	0.028
2-nitrofuran	MTHF[b]	N	1.339
		H	0.536
		H	0.426
		H	0.083
5-nitro-2-furaldehyde diacetate	THF[b] (MTHF)[b]	N	1.266 (1.189)
		H	0.597 (0.546)
		2H	0.124
		H	(0.143)
		H	(0.098)
		H[a]	0.038
2-nitrothiazole	THF[c] (MTHF)[d]	N	1.294 (1.254)
		H	0.332 (0.325)
		N	0.241 (0.248)
		H	0.097
		H[a]	0.033
2-chloro-5-nitro-pyridine	THF[b]	N	1.369
		N	0.091
		2H	0.284
		H	0.193
2-chloro-3-nitro-pyridine	THF[b]	N	1.614

[a] hyperfine splittings from solvent hydrogen; [b] sample temperature of 233 K; [c] sample temperature of 278 K; [d] sample temperature of 261 K.

Spectra attributable to alkoxynitroxide radicals were recorded when heterocyclic nitro compounds were photolyzed (see table 3). In general, lower radical concentrations were obtained compared with those from nitrobenzene compounds: this

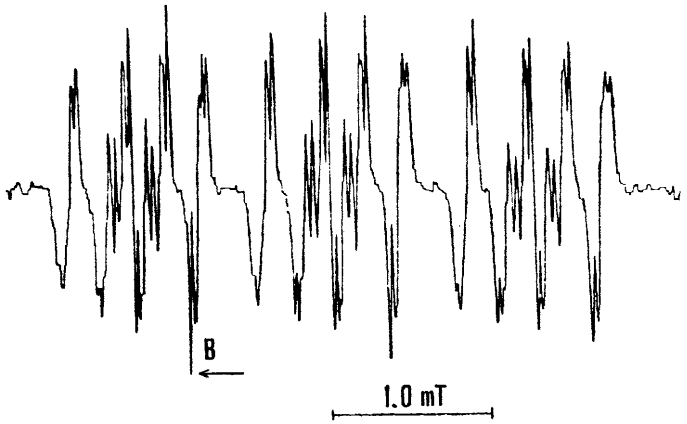


FIG. 5.—E.s.r. spectrum obtained *during* u.-v. photolysis at 278 K of 2-nitrothiazole dissolved in tetrahydrofuran.

necessitated the use of lower sample temperatures (fig. 4). An exception is 2-nitrothiazole which gives an intense e.s.r. signal when photolyzed near room temperature (fig. 5). The spectrum observed from 2-nitrothiophene diminished in intensity after 30-min photolysis and became undetectable shortly afterwards; during the photolysis the colour of the solution changed from pale to bright yellow. No e.s.r. signals could be detected upon ultra-violet irradiation of 2-nitropyrrole, 2-bromo-5-nitrothiazole or anti-5-nitro-2-furfurylidine oxime dissolved in tetrahydrofuran.

TABLE 4.—ACTIVATION ENTHALPIES ΔH^* AND PRE-EXPONENTIAL FACTORS A FOR FIRST-ORDER DECAYS OF ARYLALKOXYNITROXIDE RADICALS IN TETRAHYDROFURAN

parent nitro compound	ΔH^* (kJ mol^{-1})	$\log_{10}A$	temp. range (K)
2,3,5,6-tetrachloronitrobenzene	79.3 ± 7.4	13.2 ± 1.3	265.0-306.0
5-nitro-isophthallic acid	54.5 ± 5.0	9.1 ± 0.9	257.0-300.0
3-nitrobenzoic acid	51.8 ± 7.5	8.2 ± 1.3	257.5-308.0
4-nitrophthallic acid	33.1 ± 1.5	5.0 ± 0.4	267.0-305.0

Rates of decay were measured for the arylalkoxynitroxide radicals derived from solutions of the four following compounds dissolved in tetrahydrofuran: 2,3,5,6-tetrachloronitrobenzene, 3-nitrobenzoic acid, 5-nitroisophthallic acid and 4-nitrophthallic acid. First-order rate and energy data are given in table 4. Several general observations can be made from the kinetic measurements. (i) The increase of stationary-state radical concentration with lowering of temperature is less than would be expected from the enthalpy of activation—assuming that steps (1), (2) and (4) have lower enthalpies of activation. (ii) The presence of secondary radicals during ultra-violet photolysis and also in the dark period became less apparent at the lower temperatures. (iii) The e.s.r. line widths of some arylalkoxynitroxide radicals depend upon the nitrogen nuclear spin quantum number, the lines of the high-field group being broader than those of the low-field group which in turn were broader than those of the central group. This selective broadening became more apparent at the lower temperatures. Similar effects have been noted in the e.s.r. spectra of nitrobenzene anion radicals [12] and have been explained in terms of the anisotropy of nitrogen hyperfine couplings and g-tensors.[13, 14] The effects we have observed for the arylalkoxynitroxide radicals are smaller than those for the corresponding anion radicals.[15]

DISCUSSION

The previous [11] inexplicable failure of certain substituted nitrobenzenes to form detectable concentrations of arylalkoxynitroxide radicals has recurred in this work. It may be seen that the substrates involved possess substituents which can donate readily electrons into the aromatic π-system, for example, OH, NH_2 and $NHNH_2$. The inclusion of the CH_2Br substituent into this group appears to be anomalous, but it has been noted previously [7] that bromonitrobenzenes fail to form arylalkoxynitroxide radicals. An explanation has been put forward [7] that either a hydrogen-abstracting excited state is lacking or that reaction (4) is inhibited after hydrogen abstraction. When electron-donating substituents are present (π,π^*) excited triplet states may be lowered in energy relative to the more effective hydrogen-abstracting (n,π^*) triplet state.[16, 18] Alternatively, such substituents may hinder addition to the nitro group of a free radical originating from the solvent (by alpha-hydrogen abstraction).

Spin-trapping experiments have demonstrated [7] that hydrogen atoms are abstracted from tetrahydrofuran during the ultra-violet photolysis of 4-nitrophenol, but no arylalkoxynitroxide radicals were detected. We have observed these radicals when di-tertiarybutyl peroxide is added to the system and their e.s.r. spectra have also been recorded from rapid flow measurements in which Ti(III)/H_2O_2 was the hydrogen abstracting agent.[17] From all these observations there is no reason to modify the reaction scheme given in the introduction; thus failure to detect the arylalkoxynitroxide radicals of 4-nitrophenol is due to a low stationary-state concentration.

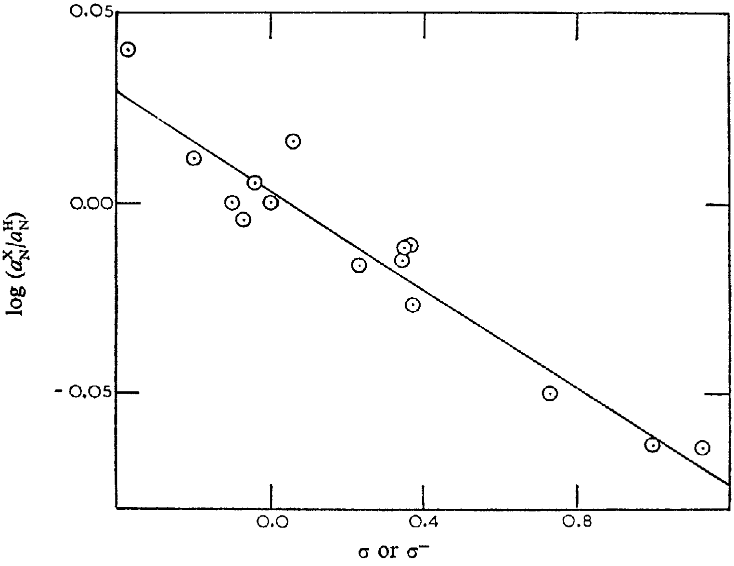


FIG. 6.—Least-squares plot of $\log_{10}(a_N^X/a_N^H)$ against Hammett σ constants for some arylalkoxynitroxide radicals.

TABLE 5.—NITROGEN COUPLING CONSTANTS a_N^X OF ARYLALKOXYNITROXIDE RADICALS FROM U.-V. PHOTOLYSIS OF MONOSUBSTITUTED NITROBENZENES IN TETRAHYDROFURAN AND HAMMETT σ (OR σ⁻) CONSTANTS OF THE SUBSTITUENTS

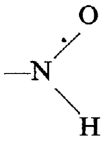
substituent	a_N^X (mT)	$\log_{10}(a_N^X/a_N^H)$	σ (or σ⁻)	ref.
H	1.506	0.0000	0.00	5
3-COOH	1.466	−0.0118	0.35	this work
4-COOH	1.342	−0.0501	0.73 (σ⁻)	this work
4-CHO	1.298	−0.0646	1.13 (σ⁻)	this work
4-CN	1.301	−0.0636	1.00 (σ⁻)	this work
3-$Si(CH_3)_3$	1.525	0.0055	−0.04	9
4-$Si(CH_3)_3$	1.492	−0.0041	−0.07	9
3-$C(CH_3)_3$	1.506	0.0000	−0.10	9
4-$C(CH_3)_3$	1.548	0.0119	−0.20	9
3-Cl	1.415	−0.0271	0.37	5
4-Cl	1.451	−0.0162	0.23	5
4-OH	1.654	0.0407	−0.37	this work
3-F	1.453	−0.0155	0.34	23
4-F	1.563	0.0161	0.06	23
3-CHO	1.467	−0.0114	0.36	23

Inspection of the arylalkoxynitroxide hyperfine splittings given in table 1 shows that ring-hydrogen splittings are insensitive to substituent effects—apart from some orthosubstituted compounds. A similar observation has been made for substituted nitrobenzene anion radicals.[19] However, the nitrogen hyperfine splittings are sensitive to substitution and we have attempted to correlate them with Hammett σ constants (σ^- for 4-COOH, 4-CN or 4-CHO substitution). Fig. 6 shows a least-squares plot of $\log_{10}(a_N^X/a_N^H)$ against σ_X, where a_N^X and a_N^H are the nitrogen hyperfine splittings for the substituted and unsubstituted compounds respectively; σ_X is the substituent Hammett constant. The data used are summarized in table 5. The gradient of the line shown in fig. 6 is $-(6.47 \pm 0.54) \times 10^{-2}$ which is considerably lower than values obtained from similar treatment of nitrobenzene free radical anion data.[20] This is in agreement with the assertion [21] that charged radicals are more sensitive than uncharged radicals to substituent effects.

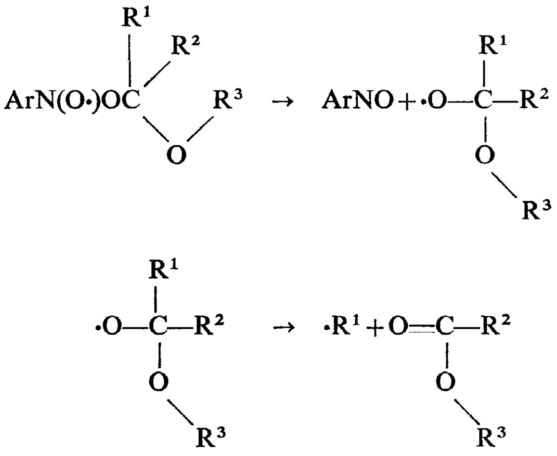
It is interesting to compare the nitrogen hyperfine couplings for a substituent in the meta or para position. Fluorine atoms,[22, 23] chlorine atoms [5] and $Si(Me)_3$ groups [9] are examples of substituents which produce inductive effects along sigma bonds in opposition to pi-type resonance interactions. The attenuation of the latter effect on meta substitution is particularly well illustrated; the a_N values for meta and para substituted radicals being 1.453 and 1.563 mT, 1.415 and 1.451 mT, and 1.525 and 1.492 mT respectively.

The influence of steric hindrance on a_N when an ortho substituent affects alkoxynitroxide groups in arylalkoxynitroxide radicals is paralleled by similar behaviour in nitroaromatic free radical anions.[5] Steric hindrance is shown to be important by comparing first the nitrogen hyperfine splittings of the arylalkoxynitroxides of 2- and 4-cyanonitrobenzenes (in tetrahydrofuran), they are 1.346 and 1.301 mT respectively, thus there can be little steric hindrance.

Now, the values for the corresponding nitrobenzoic acids are 1.614 and 1.342 mT respectively, suggesting that the carboxylic group gives rise to steric effects when it is in the ortho position. The nitrogen hyperfine splitting increases further to 1.806 mT when carboxylic groups are present in both the 2 and 6 positions. The steric effect of this group is also seen (see table 1) for the substrates 3-nitrophthallic acid, nitroterephthallic acid, 2-nitro-5-chlorobenzoic acid and 2-nitro-4-chlorobenzoic acid. The steric influence of the acetyl group is apparent in the a_N values of the alkoxynitroxide radicals obtained from 2- and 4-nitroacetophenone in tetrahydrofuran, the values being 1.548 and 1.316 mT [23] respectively.

The formation of the secondary phenyl nitroxide in the dark period can be understood since they can be produced by ultraviolet photolysis of hydroxylamines.[24] The latter occur in the systems under study as a result of photoreduction of the nitro compounds.[24, 25] The  $-N(\dot{O})H$ structure may be identified from the relative magnitudes of the hydrogen and nitrogen hyperfine splittings; Barbarella and Rassat [26] found that a_H^{NH}/a_N only varied from 1.32 to 1.35. In our work this range is 1.33 to 1.50 (see table 2).

It has been suggested that the decay mechanism of alkoxynitroxides, derived from sterically-hindered nitrobenzenes, proceeds via a homolytic fission which is followed by beta-fission of the resulting alkoxy radical [6]:



$$ArNO + R\cdot^{1} \rightarrow PhN(O\cdot)R^{1}$$

The ΔH^* and A values for this homolytic fission are listed in table 4 for 2,3,5,6-tetrachloronitrobenzene in tetrahydrofuran. However, from the wide divergence of the ΔH^* and A values and of the nature of the secondary radicals, it seems that the other three systems studied (which involve non-hindered nitro groups) follow a different mechanism. We have no evidence to suggest what this mechanism might be.

The results obtained for the heterocyclic nitro compounds (see table 3 and fig. 4 and 5) suggest that the reaction scheme applies equally to these compounds. Anion radicals of thiophene [27, 28] and furan [29] derivatives show similar spin distributions in their ring systems to those of the corresponding alkoxynitroxides. There are similarities in behaviour between heterocyclic nitrocompounds which on photolysis failed to give alkoxynitroxide radicals, and nitrobenzene substrates: (i) 2-nitropyrrole does not photoreduce [30] hence it is unlikely that alkoxynitroxide radicals would be formed since common hydrogen abstraction processes are involved; (ii) bromine derivatives do not yield alkoxynitroxides; (iii) donation of electrons into the pi aromatic system prevents alkoxynitroxide formation. Here, the CH=NOH group donates electrons into the furan ring.

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