

216. The Radical-anions of *para*-Substituted Aromatic Nitro-compounds.

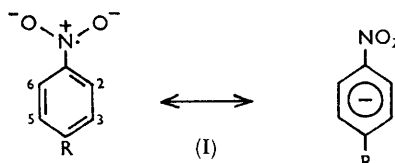
By P. L. KOLKER and WILLIAM A. WATERS.

The reduction of *para*-substituted nitrobenzenes by alkaline sodium dithionite in a flow apparatus has been used to generate radical-anions, $(p\text{-R}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)^-$, which have been investigated by electron spin resonance spectroscopy. Many of the spectra also show a signal due to $(\cdot\text{SO}_2)^-$.

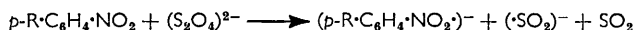
Analysis of the electron spin resonance spectra shows that the ^{14}N coupling constants a_{N} vary with the solvent used whereas a_{H} values are almost unaffected. The a_{N} values for the radical-anions can be correlated with the partial rate factors, f_p^{R} , for *para*-nitration of the corresponding molecules $\text{R}\cdot\text{C}_6\text{H}_5$ and, less accordantly, with various σ factors in current use for aromatic compounds.

Theoretical implications of this correlation are discussed.

THE addition of an electron to an aromatic nitro-compound yields a radical-anion, which is a resonance hybrid (I):

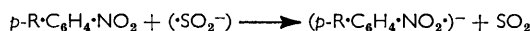


Such radical-ions have a sufficiently long life for investigation by electron spin resonance (e.s.r.) spectroscopy when generated by electrolytic reduction in a suitable solvent within the spectrometer cell,^{1,2} by reduction with an alkali metal,³ or, as briefly reported by us, by reduction with alkaline sodium dithionite, using a flow technique.⁴ The latter method, which is described in the Experimental section, often yields spectra which are different from those obtained by electrolytic reduction, in that the centre of the spectrum has superimposed on it a single broad line (see Fig. 1). This we ascribe to the radical-anion $(\cdot\text{SO}_2)^-$ derived from the dithionite, which clearly must act as a one-electron reducing agent:



as has been indicated by polarographic studies.⁵

A similar line, also with a g -value of *ca.* 2.01, can be observed with alkaline solutions of sodium dithionite which have been exposed to the air, and corresponds to that noticed by Hodgson, Neaves, and Parker⁶ for solid sodium dithionite. We have been unable to obtain any such signal from sulphite, bisulphite, or thiosulphate solutions. This central peak does not appear in all our spectra; it would not be observable if the $(\cdot\text{SO}_2)^-$ radical-anion were removed very rapidly by a following reaction:



Many of the e.s.r. spectra of the *para*-substituted radical-anions (I) clearly exhibit three symmetrically spaced groups of lines of equal intensity due to interaction of the odd electron with the nitrogen nucleus ($I = 1$). Within each group of lines is observed triplet splitting, with an intensity ratio of 1 : 2 : 1, due to interaction of the odd electron with the

¹ Maki and Geske, *J. Amer. Chem. Soc.*, 1961, **83**, 1852.

² Piette, Ludwig, and Adams, *J. Amer. Chem. Soc.*, 1962, **84**, 4212.

³ Ward, *J. Chem. Phys.*, 1959, **30**, 852.

⁴ Kolker and Waters, *Proc. Chem. Soc.*, 1963, 55.

⁵ Holleck, *Z. Naturforsch.*, 1952, **7a**, 282.

⁶ Hodgson, Neaves, and Parker, *Nature*, 1956, **178**, 489.

ortho-hydrogen nuclei, and often further triplet splitting due to interaction with the *meta*-hydrogen nuclei. Fig. 2 shows the analysis of a representative spectrum.

Table 1, which amplifies the data of our preliminary report⁴ and gives, for comparison, values reported by other workers, summarises the results of the analysis of the spectra of those radicals which we have obtained by dithionite reduction in dilute aqueous acetone. It includes, when possible, coupling constants relating to the substituent R. Thus with R = alkyl and R = CH₂X, coupling with the α -hydrogens has been evaluated by assuming that the coupling with the *ortho*- and *meta*-hydrogens remains

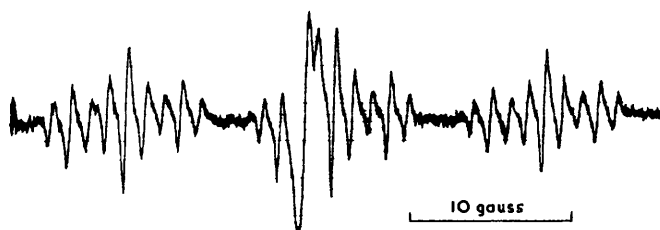


FIG. 1. Electron spin resonance spectrum of the radical-anion (I; R = I), showing the (SO_2)⁻ signal in the centre, with no distortion of the two side peaks.

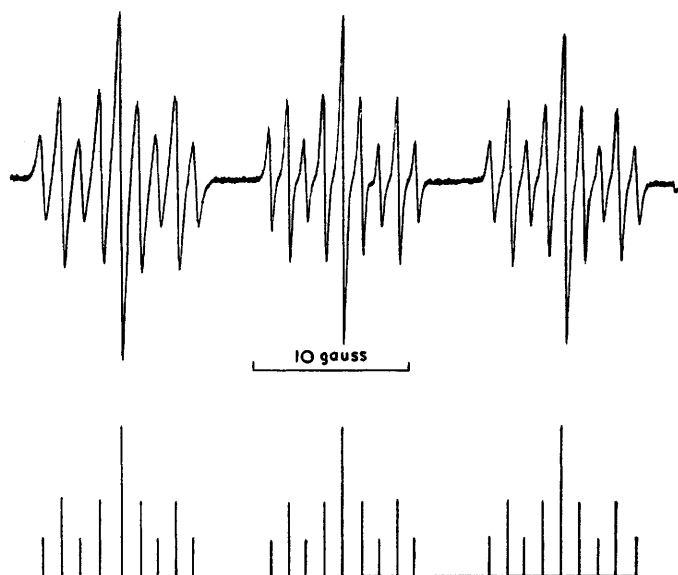


FIG. 2. Electron spin resonance spectrum and theoretical reconstruction for radical-anion (I; R = OPh); no splitting from the protons of the ⁻OPh group was observed.

unaltered; this data is collected separately in Table 2. For (I; R = F), the large interaction with the ¹⁹F nucleus ($I = \frac{1}{2}$) dominates the spectrum, but for [I; R = Cl ($I = \frac{3}{2}$)], the corresponding interaction is too small to be observed. Attempts to obtain an e.s.r. spectrum by reduction of *p*-nitrophenol were unsuccessful, but its ethers gave symmetrical spectra; α -hydrogen coupling has been evaluated for (I; R = OMe) and (I; R = OEt), but no such coupling was evident for (I; R = OPh) (see Fig. 2).

Coupling with a second nitrogen nucleus has been evaluated for (I; R = NO₂) and (I; R = CN), and also for the radical-anion of 4-nitropyridine 1-oxide.

Solvent Effects.—Table 1 shows that the coupling constants a_N which we have evaluated often differ from those of other workers by amounts which exceed possible experimental

errors. Since the a_N values for radicals formed in water are all much larger than those for radicals formed in dry methyl cyanide, it follows that radical-solvent interactions cause changes in the electron-density distribution within the radicals. Table 3(a) shows how the coupling constants for the methyl *p*-nitrobenzoate radical-anion, formed electrolytically, vary for methyl cyanide-water mixtures. These figures amplify data reported by Piette, Ludwig, and Adams² for three similar systems. A small percentage of water increases the a_N coupling constant considerably, but in solutions containing more than 50% of water the coupling constants are almost the same as in pure water. This is also the case for

TABLE 1.
Coupling constants (in gauss) for radical-anions (I), $(p\text{-R}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)^-$.

R	a_N	a_o^f	$-a_m^f$	$a_{p\text{-subst.}}$	$a_o + a_m$	R	a_N	a_o^f	$-a_m^f$	$a_{p\text{-subst.}}$	$a_o + a_m$
F	13.20	3.40	1.15	7.95 ^e	2.25	CN	11.10	3.25	1.05	—	2.20
	^a 10.76	3.56	1.16	8.41 ^e	2.40	^b	9.51	3.51	1.17	5.05 ^d	2.34
Cl	12.90	3.30	0.90		2.40	NH ₂	14.65	3.35	1.10		2.25
	^a 9.83	3.46	1.17		2.29	^a	12.18	3.36	1.12	$a_H = a_N =$ 1.12	2.24
Br	12.80	3.40	1.00		2.30	^b	15.30	3.36	1.12	$a_H = a_N =$ 2.24	2.24
	^a 9.70	3.43	1.15		2.28						
I	13.15	3.35	1.10		2.25	CO ₂ H	12.60	3.40	1.15		2.25
OMe	14.25	3.45	1.15	0.40 ^g	2.30	^c	12.79	3.32	2.32		1.00
	^a 11.57	3.43	1.11	0.30 ^g	2.32	CO ₂ Me	11.45	3.20	1.05		2.15
	^b 14.48	3.31	1.01	0.32 ^g	2.30	^a	7.73	3.11	—		—
OEt	14.40	3.45	1.10	0.40 ^f	2.35	CO ₂ Et	11.50	3.25	1.05	0.20 ^f	2.20
OPh	13.75	3.45	1.15		2.30	CONH ₂	11.95	3.30	1.10		2.20
H	13.30	3.40	0.90	3.40 ^e	2.50	^a	8.37	3.20	0.98		2.22
	^a 10.32	3.39	1.09	3.97 ^e	2.30	COMe	12.15	3.35	1.10		2.25
	^b 13.87	3.30	1.12	3.52 ^e	2.18	^a	7.02	2.95	0.66	0.66 ^g	2.29
NO ₂	4.65	1.10	—1.10	4.65	2.20	CHO	12.85	3.30	1.15	1.75 ^e	2.15
						^a	5.83	3.10 ^e	2.37 ^e	1.23 ^e	0.44

^a Ref. 1, measurements in methyl cyanide. ^b Ref. 2, measurements in water. ^c Ref. 2, measurement in 40% aqueous propanol. ^d Interaction with ring nitrogen of pyridine. ^e Interaction with one spin of $I = \frac{1}{2}$. ^f Interaction with two spins of $I = \frac{1}{2}$. ^g Interaction with three spins of $I = \frac{1}{2}$.
^h Radical-anion of 4-nitropyridine *N*-oxide.

TABLE 2.
Coupling constants (in gauss) for radical-ions (I; R = alkyl or substituted alkyl).

R	a_N	a_o^c	$-a_m^c$	$a_{p\text{-subst.}}$	$a_o + a_m$	R	a_N	a_o^c	$-a_m^c$	$a_{p\text{-subst.}}$	$a_o + a_m$
Me	14.10	3.50	1.10	3.80 ^d	2.40	CH ₂ ·COOEt	13.65	3.25	1.10	2.50 ^c	2.15
	^a 10.79	3.39	1.11	3.98 ^d	2.28	CH ₂ ·CN	13.20	3.25	0.95	3.25 ^c	2.30
Et	14.15	3.45	1.15	3.05 ^c	2.30	CH ₂ ·Cl	13.25	3.25	0.95	2.25 ^c	2.30
Pr [†]	14.20	3.40	1.15	1.80 ^b	2.25	CH ₂ ·Br	13.25	3.25	1.00	2.25 ^c	2.25
Bu [†]	14.25	3.40	1.10		2.30	CH ₂ ·OH	13.70	3.40	1.15	2.75 ^c	2.25

^a Ref. 1, measurements in methyl cyanide. ^b Interaction with one spin of $I = \frac{1}{2}$. ^c Interaction with two spins of $I = \frac{1}{2}$. ^d Interaction with three spins of $I = \frac{1}{2}$.

TABLE 3.
(a) The a_N coupling constants (in gauss) of $(p\text{-MeO}_2\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)^-$ in methyl cyanide-water mixtures. Radicals formed electrolytically.

x	7.20	2.62	1.61	0.496	0
% (v/v) water...	0	7.06	17.55	25.71	52.90
a_N	7.91	9.08	9.81	10.02	10.88
a_o	3.10	3.10	3.15	3.15	3.20
a_m	1.15	1.15	1.13	1.10	1.05

x = Moles methyl cyanide : moles water.

(b) The a_N coupling constants (in gauss) of $(p\text{-HO}_2\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)^-$ in acetone-water mixtures. Radicals formed in flow apparatus.

% (v/v) water...	50.0	60.0	70.0	80.0	90.0	100
a_N	12.52	12.55	12.58	12.58	12.61	12.60
a_o	3.39	3.40	3.38	3.39	3.42	3.40
a_m	1.15	1.16	1.14	1.14	1.15	1.15

acetone–water mixtures [see Table 3(b)] and hence our data in Table 1, which have been measured in 10–15% aqueous acetone, give comparable information concerning the structures of the radical-anions in water. In aqueous methyl cyanide, the e.s.r. spectra are still comprised of sharp lines, rather than diffuse or doubled bands, and hence discrete solvates cannot be equilibrating slowly, *i.e.*:



but rather the whole electronic structure of the radical must depend on the bulk solvent environment. Comparison of Tables 1 and 3(a) shows that the a_N coupling constant in water for (I; R = CO₂Me) is the same for radical production by chemical or by electrolytic reduction. It can be seen (Table 1) that the coupling constants for the aromatic protons are scarcely affected by the solvent so that, as suggested by Gendell, Freed, and Fraenkel,⁷ the solvent must be modifying the geometry or the electronegativity of the (–NO₂)[–] group. Similar changes in a_N have been observed for the hydrazyl group of $\alpha\alpha$ -diphenyl- β -picryl-hydrazyl in a range of solvents (Table 4).

TABLE 4.

Values of a_N coupling constant (in gauss) from hydrazyl group of $\alpha\alpha$ -diphenyl- β -picryl-hydrazyl in various solvents.

Solvent	1,4-Dioxan	Benzene	Chloroform	Nitrobenzene	Cyclohexane
a_N	8.21	8.89	8.86	8.86	8.76

The changes do not seem to be related to any individual physical property of the solvent, such as its dielectric constant or dipole moment.

DISCUSSION

Coupling with Nuclear Protons.—Table 1 shows that $a_o + a_m = 2.3 \pm 0.1$ gauss for all the radicals of formula (I), it being assumed that a_m is a measure of negative spin density at C-3 and C-5 in the aromatic ring. This constancy of the sum of the *ortho* and *meta* coupling constants has also been noted for aryloxy radicals $p\text{-R}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot$,^{8,9} and indicates that, though in both series of radicals the spin densities at C-4 (and presumably C-1) can be influenced by the nature of the attached substituent, R, which may attract or repel electronic charge from the functional group, (–NO₂)⁺ or –O[•], any change in spin density at C-2 or C-6 is drawn from the adjacent *meta*-positions C-3 and C-5. Thus the linear pull, or push, of electronic charge to or from R is not dissipated by any net charge transference to the side (*ortho* or *meta*) carbon atoms. Thus one can validly discuss (below) the polar effect of a *para*-substituent on the electron density of an aromatic radical, in simple electrostatic terms.

The theoretical relationship $a_H = Q_{\text{O-H}} \times \rho_{\text{O-H}}$ where a_H is the measured spin coupling constant, $\rho_{\text{O-H}}$ is the local electron-spin density, and $Q_{\text{O-H}}$ is the interaction parameter (evaluated⁹ as –23.7 gauss), indicates that for the unsubstituted nitrobenzene radical-anion (I; R = H) the total spin density associated with the C₆H₅ group is only 0.35. Consequently, for the radical-anions (I), most of the odd electron density remains in the region of the nitro-group.

The ¹⁴N Hyperfine Splitting Constants, a_N .—For a number of heterocyclic radicals it has been shown that the magnitude of the splitting constant due to the interaction of an odd electron with a ¹⁴N nucleus is a measure of the electron density at the nitrogen atom.¹⁰ Thus for the radical-anions (I), the values of a_N given in Table 1, for our own observations in water as solvent, are a measure of the interaction between the (–NO₂)[–] group and the

⁷ Gendell, Freed, and Fraenkel, *J. Chem. Phys.*, 1962, **37**, 2832.

⁸ Stone and Waters, *J.*, 1964, 213.

⁹ Karplus and Fraenkel, *J. Chem. Phys.*, 1961, **35**, 1312.

¹⁰ Carrington and Veiga, *Mol. Phys.*, 1962, **5**, 21.

electrons of the aromatic ring, and so give a measure of the electronic effect of the substituent R. It is seen that a_N values differ, at most, by 20% from that for (I; R = H).

In our preliminary communication,⁴ we drew attention to the correlation between a_N for $(p\text{-R}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)^-$ and the logarithm of the partial rate factor, $\log f_p^R$, for *para*-nitration of $\text{C}_6\text{H}_5\cdot\text{R}$. Fig. 3 illustrates this correlation for a larger number of compounds and shows that correlations with the Hammett σ factor¹¹ and the Brown σ^+ factor¹² are both less satisfactory. The statistical correlation coefficients for a number of kinetic factors that have been used in discussion of quantitative aspects of heterolytic aromatic substitution are given in Table 5. None is widely discordant, as in the case for correlation with partial rate factors for homolytic aromatic substitution. The solvent dependence of $\log f_p^R$ and the various σ -values is still a moot point. It may affect numerically our correlation coefficients, but not the shapes of the plots of Fig. 3, each of which refers to one

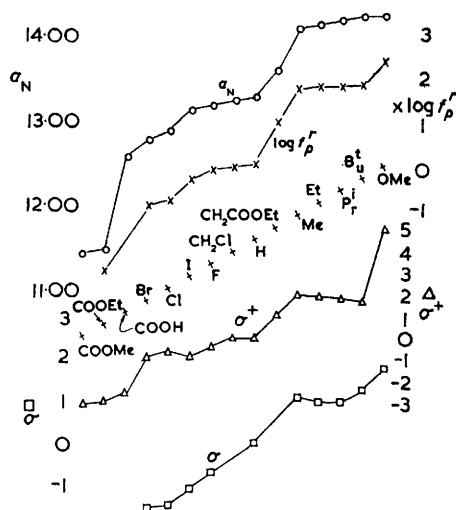
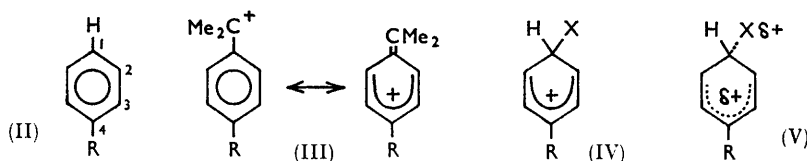


FIG. 3. Correlation of a_N for the radical-anion $(p\text{-R}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)^-$ with kinetic constants for heterolytic aromatic substitution of $\text{C}_6\text{H}_5\cdot\text{R}$.

particular solvent. Further consideration as to why electron-spin densities for a series of nitrogen-containing aromatic radicals with *para*-substituents, R, should be such excellent measures of the heterolytic reactivity of $\text{C}_6\text{H}_5\cdot\text{R}$ towards one particular reagent (NO_2^+) is thus merited.



The σ_G values of Knowles, Norman, and Radda¹³ and the σ^N values of van Bekkum, Verkade, and Wepster¹⁴ are claimed to give a measure of the polar effect of a substituent R on the ground state of the *para*-carbon atom, C-1, in a normal molecule, $\text{C}_6\text{H}_5\cdot\text{R}$ (II), which has six electrons. Very closely similar is the function of Hammett which can be used in connection with both homolytic and heterolytic side-chain reactions. These functions do not follow variations of a_N R = alkyl, but are in accord for the halogens. The σ^+ function of Brown, calculated from the ease of formation of ions (III), is taken to

¹¹ Jaffé, *Chem. Rev.*, 1953, **53**, 191.

¹² Brown and Stock, *J. Amer. Chem. Soc.*, 1962, **84**, 3298.

¹³ Knowles, Norman, and Radda, *J.*, 1960, 4885.

¹⁴ van Bekkum, Verkade, and Wepster, *Rec. Trav. chim.*, 1959, **78**, 815.

represent energy levels in Wheland intermediates (IV) in heterolytic aromatic substitution, and deviates considerably from a_N both for $R = \text{alkyl}$ and $R = \text{halogen}$.

TABLE 5.
Correlation of a_N with kinetic functions of aromatic substitution.

Function	No. of values	Correlation coefficient	Function	No. of values	Correlation coefficient
$\log f_p^{\text{NO}_2}$	12	0.993	σ	9	0.965
$\log f_p^{\text{Br}}$	9	0.958	σ^n	7	0.974
σ^+	14	0.961	σ_G	5	0.989

According to current theories of electrophilic aromatic substitution the reactivity-determining transition state for nitration, (V; $X = \text{NO}_2$), is considered to be structurally more like (II) than (IV), with a scarcely formed $\text{C}_{(1)}\text{-NO}_2$ bond, whereas for bromination, (V; $X = \text{Br}$) is considered to more closely resemble (IV), which has only four π electrons.

With regard to the polarisation of the π electrons of the aromatic rings, the radical-ions (I) resemble the transition-state structures (V) in that some of the π -electron density has been drawn out to balance the odd electron of the $(\text{-NO}_2)^-$ group, but since, as we have pointed out above, most of the unpaired electron density is still localised in the $(\text{-NO}_2)^-$ group, the perturbation of (I) from the ground state (II) is small and the six aromatic electrons can still be assigned to π orbitals. Viewed in this way, the correlation of a_N with $\log f_p^R$ for nitration, but not for bromination, is rational. If there were no conjugative perturbation of the π -electron distribution in a molecule $\text{C}_6\text{H}_5\cdot\text{R}$ on substituting $(\text{-NO}_2)^+$ for the *para*-hydrogen, then the electrostatic effect of R on the odd electron would still operate and one would anticipate that a_N should vary with the ground-state factors σ_G or σ^n . When small conjugative effects must be included, the Hammett σ function becomes more appropriate as has been found for side-chain homolytic substitution,¹⁵ just as for heterolytic side-chain reactions. We suggest that correlations between physical properties of aromatic molecules and their chemical reactivity can rationally be attempted if the aromatic sextet is perturbed, but not disrupted, by the addition, with π bonding, of either a cation or a radical.

EXPERIMENTAL

The aromatic nitro-compounds were crystallised before use, and had melting points in accord with literature values. They were dissolved in a 0.1M-solution of sodium hydroxide in 25% aqueous acetone, to give 10^{-2}M -solutions. These solutions were mixed with 10^{-2}M -solutions of sodium dithionite in 0.1M-sodium hydroxide (in water) in the flow apparatus which has already been described.^{16,17} The e.s.r. spectra were observed *ca.* 1×10^{-2} — 5×10^{-2} sec. after the instant of mixing of the two solutions in an aqueous-solution cell of a Varian V 4500 e.s.r. spectrometer, using a magnetic field sweep of about 5.8 gauss/min. The amplitude of the 100 kc./sec. modulation was kept as low as possible, so as to minimise line broadening. The spectra were all calibrated by reference to the hyperfine splitting constants of *p*-benzosemiquinone (2.37 gauss), by passing an alkaline solution of this radical through the apparatus immediately after each reaction mixture. The average liquid flow rate used was 0.2 l./min.

The technique for effecting electrochemical reduction of aromatic nitro-compounds in an e.s.r. spectrometer cell has already been described.^{1,18} The data given in Table 3(a) were obtained with solvent mixtures of distilled water and methyl cyanide (purified by refluxing followed by fractionation, both over phosphorus pentoxide). Methyltri-*t*-butylammonium iodide, m. p. 181° , in 0.1M-solution, was used as the supporting electrolyte.

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¹⁵ Kooyman, Van Helden, and Bickel, *Proc. k. ned. Akad. Wetenschap.*, 1953, B56, 75.

¹⁶ Stone and Waters, *Proc. Chem. Soc.*, 1962, 253.

¹⁷ Dixon and Norman, *J.*, 1963, 3119.

¹⁸ Kolker and Waters, *Chem. and Ind.*, 1963, 1205.