2-Methyl-2-nitro-1-decyne. Reaction of 1-octyne and 2-chloro-2-nitropropane gave material: bp 62–64 °C (0.1 Torr); $n^{20}{}_D$ 1.4452; ^{1}H NMR (CCl_4) δ 0.90 (t, 3, J = 6.1 Hz), 1.30 (m, 8), 2.12 (t, 2, J = 6.1 Hz), 1.78 (s, 6).

Anal. Calcd for $C_{11}H_{19}NO_2$: C, 66.97; H, 9.71; N, 7.10. Found: C, 66.97; H, 9.75; N, 6.80.

Reaction of 2-Cyano-2-nitropropane with 1-Pentynyllithium. To 0.05 mol of 1-pentynyllithium in THF at −50 °C was added 5.7 g (0.05 mol) of 2-cyano-2-nitropropane.[23,24] After 1 h at −50 °C the reaction mixture was diluted with water and extracted with hexane to give 3.9 g of material, bp 30–40 °C (0.1 Torr). By GC–mass spectrum tetramethylsuccinonitrile (M^+ 114) and 2-hexynenitrile (major product) [m/e (rel intensity) 93 (M^+, 88), 89 (27), 71 (121), 58 (28), 57 (56), 55 (33), 50 (20)] were present. Repeated distillations gave 2.8 g (60%) of 2-hexynenitrile: bp 51–53 °C (20 Torr); $n^{25}{}_D$ 1.4385; $n^{20}{}_D$ 1.4416 (lit.[25] bp 34–36 (11 Torr); $n^{20}{}_D$ 1.4444); ^{1}H NMR (CCl_4) δ 1.07 (t, 3, J = 6 Hz), 1.3–1.9 (m, 2), 2.35 (t, 2, J = 6 Hz); IR (neat) 2320 ($C\equiv N$), 2260 ($C\equiv C$), 1575, 1465, 1345 cm^{-1}.

Reaction of 2-Cyano-2-nitropropane with 1-Hexynyllithium. To the hexynyllithium obtained from 4.1 g (0.05 mol) of 1-hexyne in 40 mL of THF at −50 °C, 5.7 g (0.05 mol) of 2-cyano-2-nitropropane was added slowly as the temperature increased to −30 °C. After 30 min at −30 °C the reaction mixture was quenched with water and extracted with hexane. Distillation at 1 Torr gave a fraction in which 2-cyano-2-nitropropane ($M^+ - 46 = 68$), tetramethylsuccinonitrile (M^+ 114) and 2-heptynenitrile (major component) were detected by GC–mass spectrum. The mass spectrum of 2-heptynenitrile gave m/e (rel intensity) 108 ($M^+ + H$, 10), 107 (M^+, 2.6), 106 ($M^+ - H$, 27), 92 ($M^+ - CH_3$, 81), 80 ($M^+ - HCN$, 41), 79 ($M^+ - C_2H_4$, 41), 78 ($M^+ - C_2H_5$, 12), 65 ($M^+ - C_3H_6$, 100), 56 (C_4H_8, 14), 51 (C_3HN, 40), 50 (C_3N, 27).

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References and Notes

(1) Reactions of Resonance Stabilized Anions. 35. This work was supported by a grant from the National Science Foundation.
(2) G. A. Russell and W. C. Danen, *J. Am. Chem. Soc.*, **88**, 5663 (1966); **90**, 347 (1968).
(3) G. A. Russell, R. K. Norris, and E. J. Panek, *J. Am. Chem. Soc.*, **93**, 5839 (1971).
(4) J. J. Zeiktra and J. B. F. N. Engberts, *Recl. Trav. Chim. Pays-Bas*, **92**, 954 (1973); N. Kornblum, S. D. Boyd, and N. Ono, *J. Am. Chem. Soc.*, **96**, 2580 (1974).
(5) J. K. Kim and J. F. Bunnett, *J. Am. Chem. Soc.*, **92**, 7463 (1970).
(6) G. A. Russell, *Pure and Appl. Chem., Suppl., Int. Congr. Pure Appl. Chem., 23rd*, **4**, 67 (1971).
(7) G. A. Russell and G. Kaupp, *J. Am. Chem. Soc.*, **91**, 3851 (1969).
(8) M. Simonetta, G. Fevini, and S. Carra, *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.*, **17**, 375 (1954); *Chem. Abstr.*, **49**, 10832*g* (1955).
(9) W. H. Baarshers and T. L. Loh, *Tetrahedron Lett.*, 3483 (1971).
(10) M. Makosza and M. Jawdosiuk, *Chem. Commun.*, 648 (1970); M. Makosza, J. M. Jagusztyn-Grochowska, M. Ludwikow, and M. Jawdosiuk, *Tetrahedron*, **30**, 3723 (1974).
(11) R. D. Gutherie, D. P. Wesley, G. W. Pendygraft, and A. T. Young, *J. Am. Chem. Soc.*, **98**, 5870 (1976).
(12) G. A. Russell and L. A. Ochrymowycz, *J. Org. Chem.*, **34**, 3618 (1969).
(13) G. M. Whitesides, J. SanFilippo, Jr., C. P. Casey, and E. J. Panek, *J. Am. Chem. Soc.*, **89**, 5302 (1967).
(14) G. A. Russell and R. F. Bridger, J. Am. Chem. Soc., **85**, 3754 (1963).
(15) The $S_{RN}1$ process with 2-cyano-2-nitropropane leads to coupling products in which the nitro group has been displaced.[3]
(16) A similar process was suggested for the reaction of diaryliodonium salts with anions of 1,3-indandiones: F. M. Beringer, S. A. Galton, and J. J. Huang, *J. Am. Chem. Soc.*, **84**, 2819 (1962).
(17) S_N2 displacement of the nitro group from nitromethane has been reported to occur in HMPA, THF, or DMF solution: M. Benn and A. C. M. Meesters, *J. Chem. Soc., Chem. Commun.*, 597 (1977).
(18) K. Deuchert, U. Hertenstein, and S. Hünig, *Synthesis*, 777 (1973).
(19) G. Stork and L. Maldonado, *J. Am. Chem. Soc.*, **93**, 5286 (1971).
(20) E. J. Corey and D. Seebach, *Angew. Chem.*, **77**, 1135 (1965).
(21) W. S. Johnson, J. W. Petersen, and W. P. Schneider, *J. Am. Chem. Soc.*, **69**, 74 (1947).
(22) G. M. Mkryan, S. M. Gaspuryan, N. K. Mekonyan, and A. A. Nazanyan, *J. Org. Chem. USSR* (*Engl. Transl.*), **6**, 917 (1970).
(23) J. R. Tilney-Bassett and W. A. Waters, *J. Chem. Soc.*, 3129 (1957). This preparation involves the decomposition of 2-azoisobutyronitrile in the presence of nitrogen dioxide in benzene. Distillation of the product at 30 Torr gives a vigorous exothermic reaction with evolution of gas at ~90 °C which can result in a serious explosion. Apparently the crude product contains the nitrite ester of 2-cyano-2-propanol.[24]
(24) B. G. Gowenlock, J. Pfab, and G. Kresze, *Justus Liebigs Ann. Chem.*, 1903 (1975).
(25) S. T. D. Gough and S. Trippett, *J. Chem. Soc.*, 2333 (1962); R. A. Van der Welle and L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, **92**, 667 (1973).

Electron Transfer Processes. 19. Reaction of Aryl Radicals with Anions in Aqueous Solution[1]

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Abstract: Phenyl radicals and a variety of substituted phenyl radicals are readily trapped in aqueous solution by the anions of nitromethane, -ethane, or -propane to yield the radical anions which can be detected by ESR spectroscopy. Nitrite ion will also capture a variety of phenyl radicals in the absence of any heavy-metal ions. The p-nitrophenyl radical can be trapped only by oxidation-resistant anions, such as nitrite or cyanide. The trapping of radicals by anions is greatly facilitated by the presence of a nitro group which will stabilize the resulting radical anion. In the absence of a trapping agent aryldiazonium ions and sodium dithionite form a variety of unstable paramagnetic species.

The reaction of a radical with an anion to form a radical anion with a new bond, particularly a carbon–carbon bond, had not received serious consideration prior to 1966, when it was suggested as a key step in the reaction of the anion of 2-nitropropane with 2-halo-2-nitropropanes or p-nitrobenzyl chloride.[2] The coupling reaction has been demonstrated to occur by a free radical chain process that is most reasonably formulated as reactions 1-3,[2] and has been given the label $S_{RN}1$.[3]

$$R\cdot + (CH_3)_2C{=}NO_2^- \rightarrow RC(CH_3)_2NO_2\cdot^- \qquad (1)$$

$$R - X + RC(CH_3)_2NO_2\cdot^- \rightarrow RX\cdot^- + RC(CH_3)_2NO_2 \qquad (2)$$

$$RX\cdot^- \rightarrow R\cdot + X^- \qquad (3)$$

A number of reactions involving radicals and heavy metal salts have at times been formulated as involving addition of the

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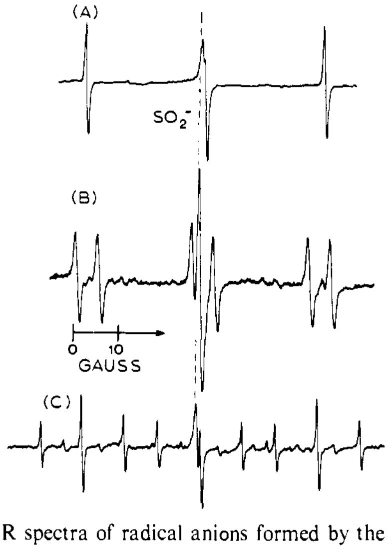
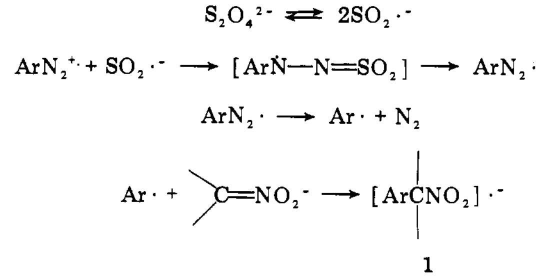


Figure 1. ESR spectra of radical anions formed by the addition of *p*-chlorophenyl radicals to anions of nitroalkanes: (a) from 2-nitropropane; (b) from nitroethane; (c) from nitromethane.

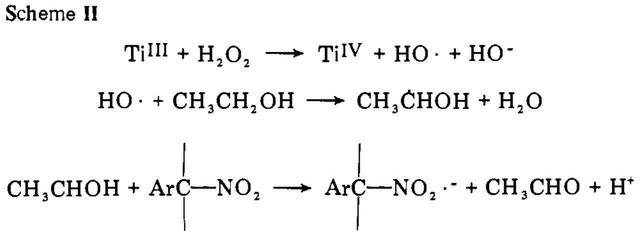
Table I. ESR Hyperfine Splitting Constants for **1**, H_2O, 25 °C

radical anion	a^N, G	a^H, G
$C_6H_5CH_2NO_2\cdot^-$	25.88	9.31 (2 H)
p-$^-O_2CC_6H_4CH_2NO_2\cdot^-$	25.82	9.24 (2 H)
m-$^-O_2CC_6H_4CH_2NO_2\cdot^-$	25.87	9.39 (2 H)
p-$ClC_6H_4CH_2NO_2\cdot^-$	25.92	9.26 (2 H)
p-$CH_3OC_6H_4CH_2NO_2\cdot^-$	26.02	9.43 (2 H)
$C_6H_5CH(CH_3)NO_2\cdot^-$	25.92	7.16
p-$^-O_2CC_6H_4CH(CH_3)NO_2\cdot^-$	25.88	7.10
m-$^-O_2CC_6H_4CH(CH_3)NO_2\cdot^-$	25.94	7.08
p-$ClC_6H_4CH(CH_3)NO_2\cdot^-$	25.99	6.92
p-$CH_3OC_6H_4CH(CH_3)NO_2\cdot^-$	26.03	6.65
$C_6H_5CH(C_2H_5)NO_2\cdot^-$	25.43	5.11
p-$^-O_2CC_6H_4CH(C_2H_5)NO_2\cdot^-$	25.40	5.09
m-$^-O_2CC_6H_4CH(C_2H_5)NO_2\cdot^-$	25.46	5.07
p-$ClC_6H_4CH(C_2H_5)NO_2\cdot^-$	25.52	4.90
p-$CH_3OC_6H_4CH(C_2H_5)NO_2\cdot^-$	25.55	4.74
$C_6H_5C(CH_3)_2NO_2\cdot^-$	26.22	
p-$^-O_2CC_6H_4C(CH_3)_2NO_2\cdot^-$	26.22	
m-$^-O_2CC_6H_4C(CH_3)_2NO_2\cdot^-$	26.26	
p-$ClC_6H_4C(CH_3)_2NO_2\cdot^-$	26.24	
p-$CH_3OC_6H_4C(CH_3)_2NO_2\cdot^-$	26.28	

Scheme I



Scheme II



radical to the anion,[4] but the timing of the electron transfer is difficult to determine experimentally.[5]

Since our original description of reaction 1 examples of this process have been reported by workers in the field of ESR spectroscopy. In the presence of Ti^{III} the anions of nitroethane or 2-nitropropane trap hydroxyl,[6] amino,[6] or methyl radicals.[7] Hydroxy radicals have also been trapped by the anions of nitromethane[8,9] as have a variety of hydroxyalkyl radicals.[10]

A major driving force for these reactions must be the stability of the nitroalkane radical anion. In fact, this type of radical anion can also be generated by the addition of radicals to nitrite ion:

$$R\cdot + NO_2^- \rightarrow RNO_2\cdot^- \qquad (4)$$

Reaction 4 has been observed with R = phenyl,[10] *p*-nitrophenyl,[12] and a variety of photochemically generated radicals[11] including $CO_2\cdot^-$, $\cdot CH_2CO_2^-$, $CH_3\dot{C}HCO_2^-$, $CH_3COCH_2\cdot$, $HOCH_2\cdot$, $NH_2COCH_2\cdot$, $NH_2\dot{C}HCH_3$, and $(CH_3)_2NCH_2\cdot$. Reaction 1 has been implicated by ESR spectroscopy in oxidative dimerization of a variety of nitroalkane anions by the titanium(III)-persulfate redox system.[12] There has also been presented extensive evidence for the reduction by Ti^{III} of α-halo nitroalkanes to α-nitroalkyl radicals which attack the anions of the nitroalkanes or the aci form of the nitroalkane.[13]

We will first discuss experiments wherein phenyl radicals have been trapped by a variety of anions in the absence of heavy-metal ions and at a pH where the presence of the conjugate acid of the anion can be excluded. In the final section we will consider a series of paramagnetic species formed from aryldiazonium ions and sodium dithionite in the absence of a phenyl-radical trap.

Reaction of Benzenediazonium Ions with Sodium Dithionite in the Presence of the Anions of Nitroalkanes. Reaction of benzenediazonium ions with sodium dithionite and anions of nitroalkanes (nitromethane, nitroethane, 1- and 2-nitropropane) at pH 13–14 gave from 0.1 s to several minutes after mixing strong ESR signals of the aryl-substituted nitroalkane radical ion (**1**) formed according to Scheme I.

Well-resolved ESR spectra (e.g., Figure 1) were observed for Ar = phenyl, *p*-carboxyphenyl, *m*-carboxyphenyl, *p*-chlorophenyl, and *p*-methoxyphenyl. Table I lists the observed hfsc observed in the trapping experiments. The parent α-nitrotoluene radical anions (**1**, Ar = C_6H_5) were independently synthesized using the technique of McMillan and Norman[7] (Scheme II).

Coupling products **1** were not formed for Ar = *p*-nitrophenyl or *p*-cyanophenyl. We were at first surprised that the *p*-nitrophenyl radical was not trapped by the nitronate anions since both the 2-nitro-2-propyl radical and the *p*-nitrobenzyl radical are readily trapped by the anions of 2-nitropropane.[2] However, it has been demonstrated that *p*-nitrohalobenzenes react with easily oxidized anions to yield the carbanion dimerization product rather than the crossed coupling product[14,15] (Scheme III).

Apparently the *p*-nitro- or *p*-cyanophenyl radical has a sufficiently high electron affinity that electron transfer (a) takes preference to the addition reaction (b) (Scheme IV).

Reaction of Aryl Radical with other Anions. We thus turned to anions with low oxidizability which should be resistant to process (b) (Scheme IV) but which could still react by process (a). As expected, the *p*-nitrophenyl radicals or the *p*-cyanophenyl radical was trapped by nitrite ion and the *m*- or *p*-nitrophenyl radical trapped by cyanide ion. Thus, the *p*-cyanonitrobenzene radical anion (Figure 2) is readily generated by any of the three routes in Scheme V.[16] A number of other known nitrobenzene radical anions were formed from the corresponding diazonium salts and the appropriate anion including $[C_6H_5NO_2]\cdot^-$, $[p\text{-}O_2CC_6H_4NO_2]\cdot^{2-}$, $[m\text{-}O_2CC_6H_4NO_2]\cdot^{2-}$, $[p\text{-}ClC_6H_4NO_2]\cdot^-$, $[m\text{-}NO_2C_6H_4NO_2]\cdot^-$, and

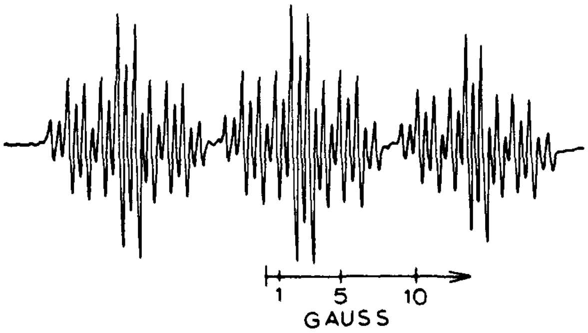


Figure 2. ESR spectrum of *p*-cyanonitrobenzene radical anion.

Scheme III

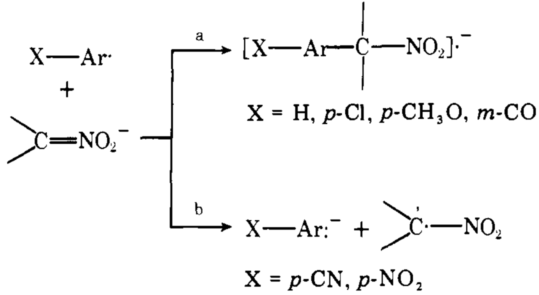
$$[p\text{-NO}_2\text{C}_6\text{H}_4\text{X}]\cdot^- \longrightarrow p\text{-NO}_2\text{C}_6\text{H}_4\cdot + \text{X}^-$$

$$p\text{-NO}_2\text{C}_6\text{H}_4\cdot + \text{A}^- \longrightarrow p\text{-NO}_2\text{C}_6\text{H}_4\!:^- + \text{A}\cdot$$

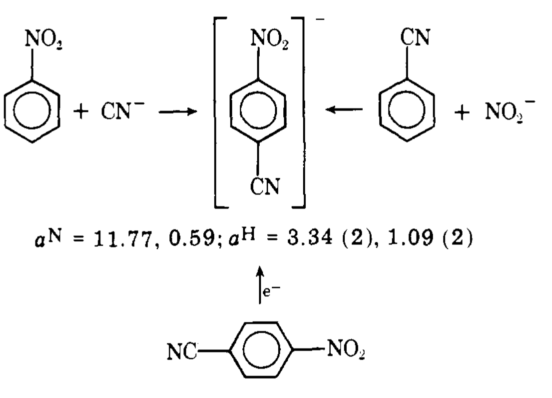
$$2\text{A}\cdot \longrightarrow \text{A-A}$$

$$p\text{-NO}_2\text{C}_6\text{H}_4\!:^- + \text{H}^+ \longrightarrow p\text{-NO}_2\text{C}_6\text{H}_5$$

Scheme IV



Scheme V



$a^{N} = 11.77, 0.59; a^{H} = 3.34\ (2), 1.09\ (2)$

[*p*-$NO_2C_6H_4NO_2$]$\cdot^-$. Values of the hfsc agreed perfectly with the published values.[18-20]

The *p*-methoxyphenyl radical was not trapped to yield a detectable radical anion by nitrite ion. This suggests that the trapping reaction is either rather sensitive to polar effects or that the reaction is reversible. However, we have found no evidence for reversibility such as that outlined in Scheme VI under the reaction conditions using *p*-chlorophenyl radicals. The *p*-nitrophenyl radical was not trapped by either chloride or fluoride ions under the reaction conditions, although the *p*-halophenyl radicals were readily trapped by nitrite ions.

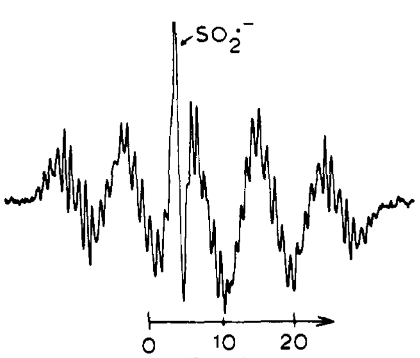


Figure 3. ESR spectrum of first detected radical species in the reaction of benzenediazonium ion with sodium dithionite.

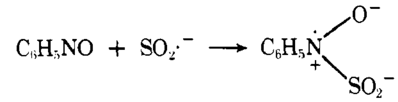
Scheme VI

$$p\text{-ClC}_6\text{H}_4\cdot + \text{NO}_2^- \rightleftarrows [p\text{-ClC}_6\text{H}_4\text{NO}_2]\cdot^-$$

$$[p\text{-ClC}_6\text{H}_4\text{NO}_2]\cdot^- \rightleftarrows p\text{-NO}_2\text{C}_6\text{H}_4\cdot + \text{Cl}^-$$

$$p\text{-NO}_2\text{C}_6\text{H}_4\cdot + \text{NO}_2^- \rightarrow [p\text{-NO}_2\text{C}_6\text{H}_4\text{NO}_2]\cdot^-$$

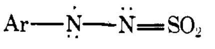
Reaction of Aryldiazonium Ions with Sodium Dithionite. In the absence of a trapping reagent the benzenediazonium ion is reduced by dithionite (0.1 s between mixing and detection) to yield a five-line spectrum (~1:2:3:2:1), $g = 2.0035$, $a^{N} \sim 9.2$ (2 N) G (Figure 3), a radical previously observed by others.[21] The suggestion[21] that this is the benzenediazonium radical ($C_6H_5N_2\cdot$) is inconsistent with CIDNP results which indicate a very rapid loss of nitrogen from $C_6H_5N_2\cdot$.[22] The radical $C_6H_5N{=}NO\cdot$ can also be excluded since for this species $a^{N} = 30.5, 2.3$; $g = 2.0017$.[23] The a^{N} and g values of the unknown radical are rather similar to the values observed for triarylhydrazyl radicals which typically have $a^{N} = 8\text{–}9$ G, $g = 2.0035$. However, the fine structure observed for the unknown quite clearly indicates the presence of only one conjugated phenyl ring with $a^{H} = 1.40$ for 3 H (*o*-, *o′*-, *p*-) and 0.60 for 2 H (*m*-, *m′*-). The unknown radical is observed in the presence of $SO_2\cdot^-$ as shown in Figure 3. This suggests that possibly the species is a coupling product between $C_6H_5N_2^+$ and $SO_2\cdot^-$ analogous to the addition product formed between nitrosobenzene and $SO_2\cdot^-$ (reaction 5).[24] Addition of $SO_2\cdot^-$,



$$\text{C}_6\text{H}_5\text{NO} + \text{SO}_2\cdot^- \longrightarrow \text{C}_6\text{H}_5\overset{+}{\dot{\text{N}}}(\text{O}^-)(\text{SO}_2^-) \qquad (5)$$

$a^{N} = 11.3$
$a^{H} = 2.40$ (2 H), 0.90 (2 H)

or direct reaction between the diazonium ions and $S_2O_4^{2-}$, could lead to either adducts **2** or **3**, both of which could decompose to SO_2, N_2, and the phenyl radical. Spectra with two approximately equivalent nitrogen atoms with $a^{N} \approx 9$ G were also observed from the reaction of *p*-chloro-, *p*-methoxy-, *p*-carboxy-, and *m*-carboxybenzenediazonium ions with sodium dithionite in the absence of a trapping agent for phenyl radicals.[25]



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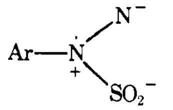

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p-Cyano- and *p*-nitrobenzenediazonium ions gave fairly stable species observable in the absence of $SO_2\cdot^-$ with hfs by three nitrogen atoms. *p*-Cyanobenzenediazonium ions formed a species with $a^{N} = 7.6, 5.3, 0.6$, $a^{H} = 3.2, 3.2, 0.8, 0.8$ G. *p*-Nitrobenzenediazonium ion gave at least two well-defined paramagnetic species. At fast flows (0.1 s) the spectrum of Figure 4a was observed with $a^{N} = 8.0, 2.7, 2.7$, $a^{H} = 0.6, 0.6$ G. At slower flows (Figure 4b), or when the *p*-nitrobenzenediazonium ion had been first treated with hydroxide ion

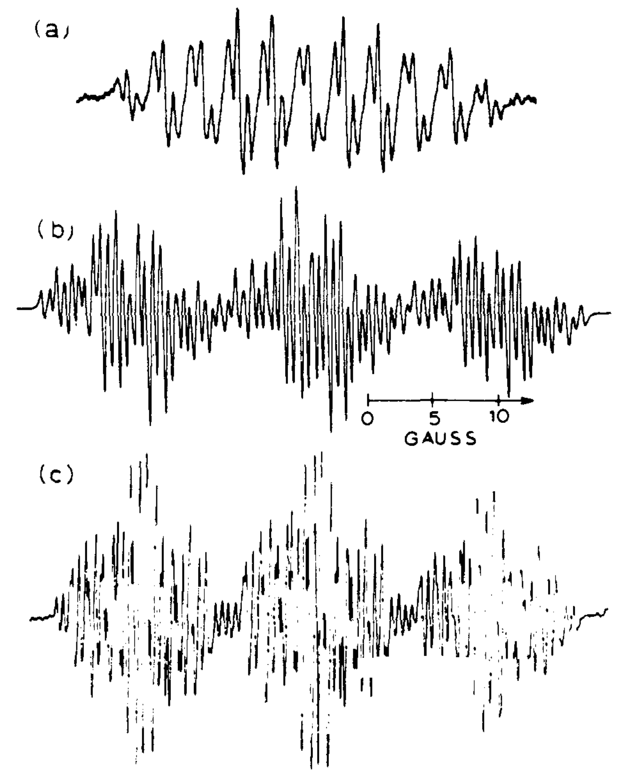
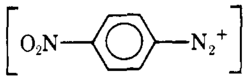


Figure 4. ESR spectra of reaction products of *p*-nitrobenzenediazonium ion with dithionite: (a) 0.1 s between mixing and detection; (b) radical anion observed at slower flow rates; (c) reaction product of dithionite and preformed *p*-nitrobenzenediazotate anion.

to form the diazotate ion (Figure 4c), the spectra were quite typical of a nitrobenzene radical anion with $a^N \sim 13.5$ G ($C_6H_5NO_2\cdot^-$ in H_2O has $a^N = 13.87$, $a^H = 3.52$ (1 H), 3.30 (2 H), 1.12 (2 H) G).[18] The first-formed species might be neutral radical **4**, wherein extensive delocalization may lead to a decreased rate of nitrogen loss. At slower flow rates **5**, or perhaps the product of coupling with the phenol (**6**), may be



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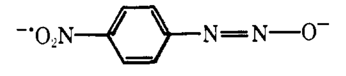

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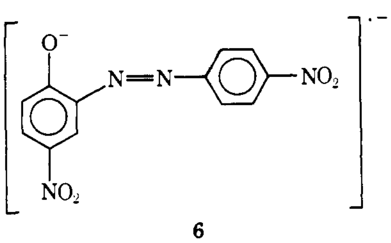


6

involved. Figure 4c can be analyzed as a species with $a^N = 13.43, 1.24, 0.51$, $a^H = 3.42$ (2 H), 1.24 (2 H) G, which certainly seems to require the fragment $-N{=}NC_6H_4NO_2\cdot^-$. The spectrum of Figure 4b may be a composite of Figures 4a and 4c, or perhaps different species are formed under the different reaction conditions. Spectrum 4b can also be detected in the presence of nitrite ion at high pH, whereas at lower pH the reaction with dithionite leads cleanly to *p*-dinitrobenzene radical anion.

With *p*-nitrobenzenediazonium ion and dithionite ion in flow or stopped-flow systems we have never detected a radical anion containing only a single nitrogen hfs. If hydroxide or sulfite ion can trap the *p*-nitrophenyl radical under the reaction conditions, the resulting radical dianions ($p\text{-}O_2NC_6H_4O\cdot^{2-}$, $p\text{-}O_2NC_6H_4SO_3\cdot^{2-}$) must be quite short lived, which is not surprising in view of their highly reduced state.[26] Alternately hydroxide and sulfite ions may be ineffective in trapping the *p*-nitrophenyl radical (as are chloride and fluoride ions) in competition with other possible trapping reactions, for example, reaction with SO_2 or $SO_2\cdot^-$.

Experimental Section

Aqueous hydrochloric acid solutions of a diazotized aniline (0.5 M) at 0 °C were mixed with an aqueous basic solution of sodium dithionite (~0.075 M). Both solutions were thoroughly deoxygenated. Unless otherwise mentioned the concentration of base was adjusted so that the mixed solutions had a final pH of 13–14 (~1 M hydroxide ion). Substrates (~0.15 M) expected to trap the phenyl radical were added to the aqueous dithionite solution. Mixing and ESR detection occurred in a Varian V-4549A cell having a volume of ~0.05 mL between the point of mixing and detection. ESR spectra were recorded ~0.1 s after mixing using a Varian V-4500 spectrometer.

References and Notes

(1) This work was supported by a grant from the National Science Foundation.

(2) (a) G. A. Russell and W. C. Danen, *J. Am. Chem. Soc.*, **88**, 5663 (1966); **90**, 347 (1968); (b) N. Kornblum, R. E. Michael, and R. C. Kerber, *ibid.*, **88**, 5662 (1966).

(3) J. K. Kim and J. Bunnett, *J. Am. Chem. Soc.*, **92**, 7463, 7464 (1970).

(4) For example, $Ar\cdot + Cu^{2+} + X^- \rightarrow ArX + Cu^+$: W. A. Waters, *J. Chem. Soc.*, 266 (1942).

(5) For a review see G. A. Russell, *Chem. Soc., Spec. Publ.*, **No. 24**, 271 (1970).

(6) D. J. Edge and R. O. C. Norman, *J. Chem. Soc. B*, 182 (1969).

(7) M. McMillan and R. O. C. Norman, *J. Chem. Soc. B*, 590 (1968).

(8) K. D. Asmus and I. A. Taub, *J. Phys. Chem.*, **72**, 3382 (1968).

(9) K. Eiben and R. W. Fessenden, *J. Phys. Chem.*, **72**, 3387 (1968).

(10) A. L. J. Beckwith and R. O. C. Norman, *J. Chem. Soc. B*, 403 (1969).

(11) H. Zeldes and R. Livingston, *J. Am. Chem. Soc.*, **90**, 4540 (1968).

(12) E. J. Edge, R. O. C. Norman, and P. M. Storey, *J. Chem. Soc. B*, 1096 (1970).

(13) N. H. Anderson, M. McMillan, and R. O. C. Norman, *J. Chem. Soc. B*, 1075 (1970).

(14) G. A. Russell, R. K. Norris, and E. J. Panek, *J. Am. Chem. Soc.*, **93**, 5839 (1971).

(15) W. H. Baarschers and T. L. Loh, *Tetrahedron Lett.*, 3483 (1971).

(16) The results are in complete agreement with the electrochemical studies of Bartak, Danen, and Hawley[17] which have suggested the following reaction sequence:

$$p\text{-}NO_2C_6H_4I + e^- \rightarrow [p\text{-}NO_2C_6H_4I]\cdot^- \rightarrow p\text{-}NO_2C_6H_4\cdot + I^-$$

$$p\text{-}NO_2C_6H_4\cdot + CN^- \rightarrow [p\text{-}NO_2C_6H_4CN]\cdot^- \xrightarrow{-e^-} p\text{-}NO_2C_6H_4CN$$

(17) D. E. Bartak, W. C. Danen, and M. D. Hawley, *J. Org. Chem.*, **35**, 1206 (1970).

(18) L. H. Piette, D. Ludwig, and R. W. Adams, *J. Am. Chem. Soc.*, **84**, 4212 (1962).

(19) P. Kolker and W. A. Waters, *J. Chem. Soc.*, 1136 (1964).

(20) W. E. Griffiths, C. J. W. Gutch, G. F. Longster, J. Myatt, and P. F. Todd, *J. Chem. Soc. B*, 785 (1968).

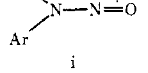
(21) W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 4857 (1964).

(22) A. Rieker, P. Niederer, and D. Leibfritz, *Tetrahedron Lett.*, 4287 (1969); A. Rieker, P. Niederer, and H. B. Stegman, *ibid.*, 3873 (1971).

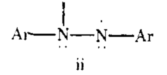
(23) J. I. G. Cadogan, R. M. Paton, and C. Thomson, *Chem. Commun.*, 615 (1969).

(24) B. Lakatos, B. Turešanyi, and F. Tüdős, *Acta Chim. Acad. Sci. Hung.*, **70**, 225 (1971); D. Mulvey and W. A. Waters, *J. Chem. Soc., Perkin Trans. 2*, 772 (1974).

(25) Addition of the aryl radical to the diazotate ion (or addition of the aryl radical to the diazonium ion followed by reaction with hydroxide ions) could form i or ii. Both seem inconsistent with the spectrum of Figure 3, which has hfs



i



ii

by a single aryl group. Attempts to form ii by reduction of azoxybenzene with dithionite have been unsuccessful.

(26) 2-Nitro-2-propyl radicals can be trapped by sulfite ions. This process is important in the $S_{RN}1$ reaction between 2-chloro-2-nitropropane and sulfite ion to form 1-methyl-1-nitroethanesulfonic acid (unpublished results with Mr. J. Hershberger). In the dithionite reductions sulfite was not investigated as an added anion, and with an excess of sulfite anion the detection $p\text{-}NO_2C_6H_4SO_3{}^{2-}\cdot$ remains a possibility.