EPR study of the arylnitro anion radicals formed in the reaction between some aminoarenes, sodium nitrite and ascorbate

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By EPR spectroscopy it was shown that stable free radicals are formed at room temperature in reaction mixtures containing sodium nitrite and aminoarenes such as 4-aminobenzoic acid, sulfanilic acid, 3,5-dimethoxyaniline 3,4,5-trimethoxyaniline, 3,5-dibromo-4-aminobenzenesulfonic acid, aminobenzene, 4-fluoroaniline or 4-methoxybenzenediazonium ions together with ascorbic acid when first dissolved in water followed by the addition of NaOH to an alkaline pH. The radicals appeared without any previous irradiation with UV light. The EPR spectra exhibited an interaction of the unpaired electron with one nitrogen nucleus and the hydrogen nuclei of the parent aminoarenes. By use of [^{15}N]nitrite it was found that the nitrogen atom of the radicals was derived from the nitrite ion. It is suggested that the radicals are arylnitro anion radicals $ArNO_2^{\bullet -}$. The reaction involves the formation of aryldiazonium ions $Ar\overset{+}{N}\equiv N$ (acidic conditions) in the reaction with nitrite, followed by their reduction to aryl radicals $Ar^{\bullet}$ in the reaction (alkaline conditions) with ascorbic acid. The radicals $Ar^{\bullet}$ combine with nitrite ions to give the observed arylnitro anion radicals $ArNO_2^{\bullet -}$.

Nitrogen oxides such as $NO^{\bullet}$, $NO_2^{\bullet}$, N_2O_3, nitrite and nitrate ions and their photochemically induced interconversion products, are important environmental pollutants. Many of these species are free radicals. One of the most reactive intermediates of the nitrite–H_2O photolysis is the $^{\bullet}OH$ radical which possesses a strong oxidative power. Nitrogen oxide, $NO^{\bullet}$, is rather stable and less reactive, but can be oxidized easily by oxygen to nitrogen dioxide, $NO_2^{\bullet}$, which seems to be the next most important transient intermediate of the nitrite photolysis after $^{\bullet}OH$. The photochemistry of these nitrogen species has recently been studied by the technique of EPR and spin trapping.[1,2]

In connection with studies of nitrite reactions, it has now been found, by use of EPR spectroscopy, that radicals are formed at room temperature in reaction mixtures of sodium nitrite, a number of aminoarenes and ascorbic acid when first dissolved in water followed by the addition of NaOH to an alkaline pH. The radicals appeared almost immediately without any previous irradiation with UV light. The radicals studied here were obtained in reactions with 4-aminobenzoic acid, sulfanilic acid, 3,5-dimethoxyaniline, 3,4,5-trimethoxyaniline, 3,5-dibromo-4-aminobenzenesulfonic acid, aniline, 4-fluoroaniline or 4-methoxybenzenediazonium ions. The EPR spectra (Figs. 1–3) indicate an interaction of the unpaired electron with one nitrogen nucleus and hydrogen or fluoro nuclei of the ring of the parent aminoarenes. It was shown by use of [^{15}N]nitrite that the nitrogen atom is derived from the nitrite ion. It is suggested that the radicals very probably are arylnitro anion radicals, $ArNO_2^{\bullet -}$.

Experimental

The EPR spectra were recorded using a Varian E-9 EPR spectrometer at 20 °C with a microwave power of 1–5 mW and a 100 kHz modulation amplitude of 0.01–0.05 mT. The samples were contained in a flat aqueous solution cell. Hyperfine splitting constants were measured by comparison with the splitting of Fremy's radical (a_N = 1.3 mT). The *g*-value of the radicals was evaluated by comparison with that of $Bu^t{}_2NO^{\bullet}$ simultaneously present in some of the reaction mixtures. The chemicals were obtained from Aldrich or Fluka AG. Sodium [^{15}N]nitrite was from ICON Inc.

Results and discussion

The parent aminoarenes and the coupling constants of the observed radicals are collected in Table 1. The EPR spectra are shown in Figs. 1–3. The highest yield of radicals was obtained when equimolar amounts of the aminoarene, sodium nitrite and ascorbic acid were simultaneously dissolved in water, and in some cases together with a small amount of ethanol to bring the aminoarene into solution. The radicals appeared subsequent to the addition of 0.5 mol dm^{-3} NaOH in water to bring the pH of the reaction mixtures from *ca.* 3 to *ca.* 10.5. The radicals were formed at room temperature without any previous irradiation with UV light.

The EPR spectra indicated an interaction of the unpaired electron with one nitrogen nucleus and hydrogen nuclei of the ring of the parent aminoarenes. By use of [^{15}N]nitrite [see Table 1 and Figs. 1(*b*)–3(*b*)], it was found that the nitrogen atom of the radicals was derived from the nitrite ion. It is suggested that the radicals are arylnitro anion radicals $ArNO_2^{\bullet -}$. It is considered that the reactions leading to the observed radicals take place as shown in eqns. (1)–(3a) or (3b).

$$\underset{\mathbf{1}}{ArNH_2} \xrightarrow[\text{Acid pH}]{\text{Nitrite}} \underset{\mathbf{2}}{Ar\overset{+}{N}\equiv N} \qquad (1)$$

$$\underset{\mathbf{2}}{Ar\overset{+}{N}\equiv N} \xrightarrow[\text{Alkaline pH}]{\text{Ascorbic acid}} \underset{\mathbf{3}}{Ar^{\bullet}} + N_2 \qquad (2)$$

$$\underset{\mathbf{3}}{Ar^{\bullet}} + {}^{14}NO_2^{-} \longrightarrow \underset{\mathbf{4a}}{Ar^{14}NO_2^{\bullet -}} \qquad (3a)$$

$$\underset{\mathbf{3}}{Ar^{\bullet}} + {}^{15}NO_2^{-} \longrightarrow \underset{\mathbf{4b}}{Ar^{15}NO_2^{\bullet -}} \qquad (3b)$$

Alternatively, the aryl cation Ar^+ is formed from the aryldiazonium ion **2**. Ar^+ combines subsequently with NO_2^- to form nitroarenes ($ArNO_2$) which are reduced to the radical $ArNO_2^{\bullet -}$.

The reaction mechanism [eqns. (1)–(3)] includes three steps. The first takes place at an acidic pH which allows the formation of a diazonium ion **2**. The second one is carried out at an alkaline pH in which aryl radical $Ar^{\bullet}$ is formed by reduction

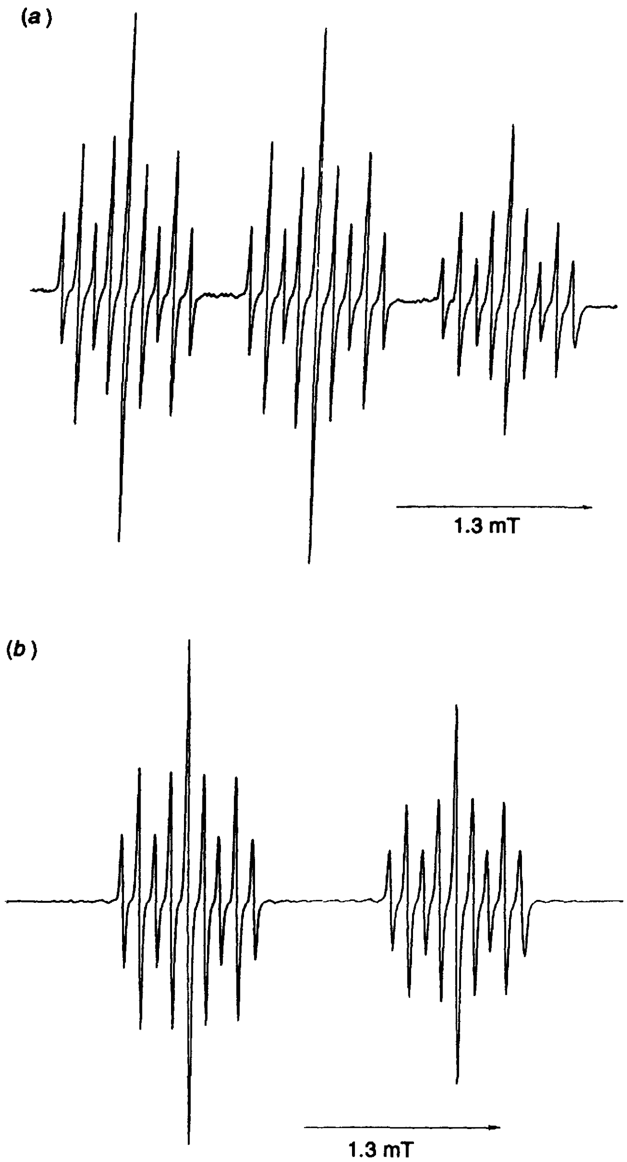


Fig. 1 EPR spectra of the radicals formed in the reaction between sodium nitrite, 4-aminobenzoic acid and ascorbic acid: (*a*) with [^{14}N]nitrite; (*b*) with [^{15}N]nitrite

with ascorbic acid. In the third step the aryl radical Ar$^\bullet$ (**3**) is trapped by nitrite ions to give the observed radicals **4**. Evidently, ascorbic acid has a double function, *i.e.* to produce an acidic reaction which is a prerequisite for the diazotation[3] in the first step and as a reductant in the second step at an alkaline reaction. The nitrite ions have also a double function, *i.e.* the formation of the diazonium ions and the trapping of the aryl radicals [eqn. (3)].

The mechanism suggested in eqns. (1)–(3) is supported by the results obtained in the reaction between 4-methoxybenzenediazonium tetrafluoroborate, sodium nitrate and ascorbic acid when dissolved in an alkaline water solution. The EPR spectra of the reaction mixture indicated that the radical 4-MeO–PhNO$_2^{\bullet-}$ was formed. The coupling constants are given in Table 1. There is an interaction also with the three hydrogen nuclei of the methoxy group in addition to those with one nitrogen and two sets of hydrogen nuclei of the aromatic ring. When the reaction was carried out with [^{15}N]nitrite, the spectrum indicated that the nitrogen atom of the radical was derived from the nitrite ion in analogy with the findings for the other members of this series.

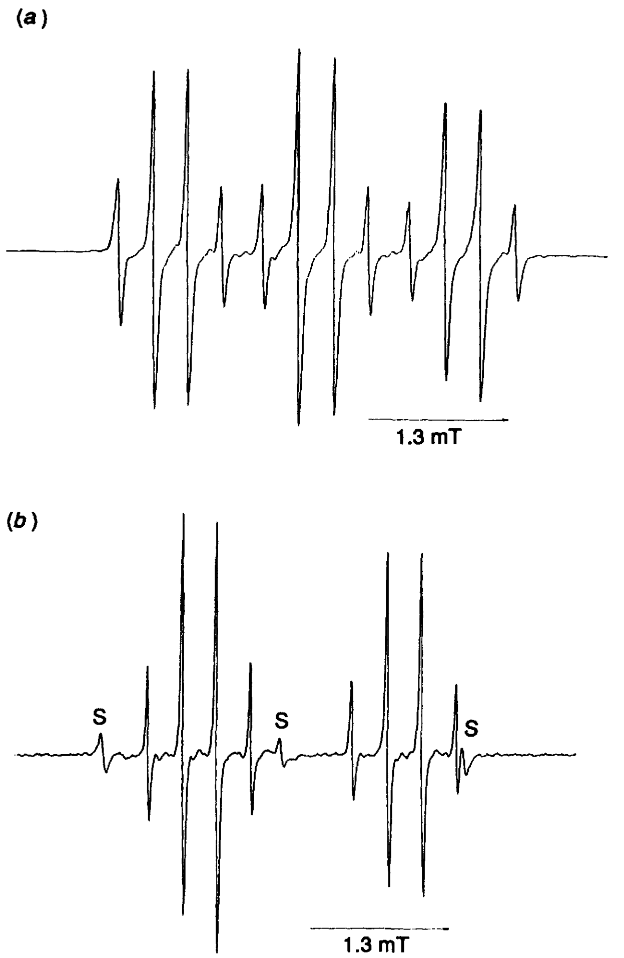


Fig. 2 EPR spectra of the radicals formed with 3,5-dimethoxyaniline: S = 3 × 1 line spectrum of the radical Bu$^t{}_2$NO$^\bullet$: (*a*) with [^{14}N]nitrite; (*b*) with [^{15}N]nitrite

It has recently been found by the technique of spin trapping that 4-methoxybenzenediazonium ions (4-MeO–Ph$\overset{+}{N}{\equiv}$N) are reduced to the aryl radical 4-MeO–Ph$^\bullet$ by melanin precursors and substances such as dihydroxybenzenes.[4] These findings support the suggested mechanism of the present reactions, eqns. (1)–(3).

The nitrogen coupling constant of the radical derived from 3,5-dibromo-4-aminobenzenesulfonic acid, *i.e.* $a_{^{14}N}$ = 2.10 mT, was intermediate between those of the other members of this series, *i.e.* 1.2–1.4 mT and the nitrogen coupling constants of iminoxyl radicals R^{1}R^{2}C=N–O$^\bullet$ (R^1, R^2 = aryl, alkyl), *i.e.* 2.6–3.2 mT.[5] This might indicate an admixture of structures with s-character (sigma-radicals) possibly connected with a steric influence brought about by the bromine atoms in the *ortho*-position.

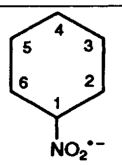
The *g*-value was evaluated for some of the radicals by comparison with the position of the lines of added Bu$^t{}_2$NO$^\bullet$. With the *g*-value of the latter radical taken to be 2.0055, the value of *g* was 2.0044 for the radical derived from 3,5-dimethoxyaniline [*cf.* Figs. 2(*b*) and 3(*a*)]. The same value (2.0044) was given for the *g*-value of nitrobenzene anion radical.[6]

Arylnitro anion radicals ArNO$_2^{\bullet-}$ have been prepared by reduction of the corresponding nitro compounds by a number of different methods including polarographic methods, dithionite, or alkali metals (tetrahydrofuran).[6–9] The EPR spectra of these radicals exhibited an interaction with one nitrogen nucleus and the hydrogen nuclei of the aromatic ring. The coupling constants a_H were solvent dependent, with the largest

Table 1 Coupling constants of the radicals formed in the reaction between sodium nitrite (^{14}N and ^{15}N) and some aminoarenes together with ascorbic acid

Parent aminoarene or diazonium compound	$[^{14/15}N]$Nitrite	$a_{^{14}N}$	$a_{^{15}N}$	a_{H^1}	a_{H^2}	a_{H^3}	a_F
4-Aminobenzoic acid	14	1.27 (1 N)		0.312 (2 H)	0.17 (2 H)		
4-Aminobenzoic acid	15		1.79 (1 N)	0.312 (2 H)	0.17 (2 H)		
4-Aminobenzenesulfonic acid	14	1.27 (1 N)		0.312 (2 H)	0.17 (2 H)		
3,5-Dimethoxyaniline	14	1.34 (1 N)		0.312 (3 H)			
3,5-Dimethoxyaniline	15		1.87 (1 N)	0.312 (3 H)			
3,4,5-Trimethoxyaniline	14	1.35 (1 N)		0.328 (2 H)			
3,4,5-Trimethoxyaniline	15		1.85 (1 N)	0.328 (2 H)			
3,5-Dibromo-4-aminobenzenesulfonic acid	14	2.10 (1 N)		0.074 (2 H)			
3,5-Dibromo-4-aminobenzenesulfonic acid	15		3.00 (1 N)	0.074 (2 H)			
4-Methoxybenzenediazonium tetrafluoroborate	14	1.44 (1 N)		0.331 (2 H)	0.105 (2 H)	0.04 (3 H)	
4-Methoxybenzenediazonium tetrafluoroborate	15		2.04 (1 N)	0.331 (2 H)	0.105 (2 H)	0.04 (3 H)	
Aminobenzene		1.35 (1 N)		0.338 (2 H)	0.325 (1 H)	0.104 (2 H)	
4-Fluoro-1-aminobenzene		1.38 (1 N)		0.34 (2 H)	0.11 (2 H)		0.80 (1 F)

[a] Arylnitro anion radical:



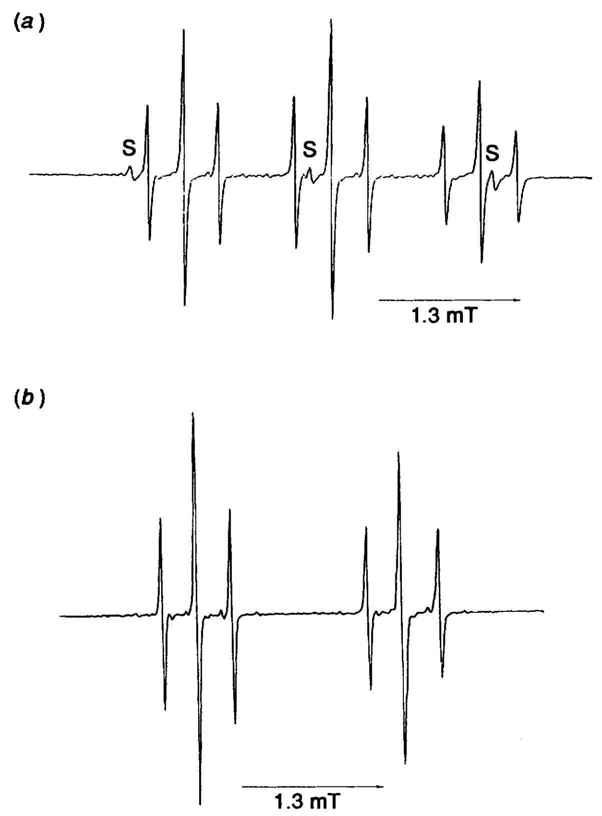


Fig. 3 Spectra obtained with 3,4,5-trimethoxyaniline: S = 3 × 1 line of $Bu^t_2NO^\bullet$; (a) with $[^{14}N]$nitrite; (b) with $[^{15}N]$nitrite

values observed for water. Generally, the a_N values were between 1.0 and 1.3 mT. The coupling constants observed for the anion radical derived from nitrobenzene in water and those recorded here for the radical formed in the reaction between aminobenzene, sodium nitrite and ascorbate (*cf.* Table 1) were close to each other:[8] nitrobenzene–aminobenzene: a_N = 1.33/1.35; a_{H^1} = 0.34/0.338; a_{H^2} = 0.340/0.325; a_{H^3} = 0.09/0.104 mT. For 4-fluoronitrobenzene–4-fluoroaniline the following values were noted:[9] a_N = 1.38/1.38; a_{H^1} = 0.34/0.34; a_{H^2} = 0.11/0.11; a_F 0.80/0.80, *i.e.* identical values. These values refer to water solutions. The findings support the suggestion that the radicals are arylnitro anion radicals $ArNO_2^{\bullet -}$. The reaction [eqn. (3)] leading to the radicals $ArNO_2^{\bullet -}$ might be classified as a $S_{RN}1$ reaction.

Acknowledgements

The author is indebted to Professor Lennart Eberson for valuable discussions. This work was supported by grants from *Adlerbertska Forskningsfonden* and The Royal Society of Arts and Sciences in Gothenburg.

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Paper 4/06089J
Received 5*th October* 1994
Accepted 24*th November* 1994