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ELECTRON PARAMAGNETIC RESONANCE AND SPIN TRAPPING STUDY OF RADICALS FORMED DURING REACTION OF AROMATIC AMINES WITH *iso*AMYL NITRITE UNDER APROTIC CONDITIONS

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Diazotization of primary aromatic amines with isoamyl nitrite in benzene at room temperature was studied employing EPR and spin trapping techniques. Nitrosodurene (ND), 2-methyl-2-nitrosopropane (MNP), and 5,5-dimethyl-pyrroline N-oxide (DMPO) were used as spin trapping agents. Aryl radicals were detected employing ND and MNP. Using DMPO as a spin trap most of the amines produced EPR spectra ascribed to adducts with aniline-type radicals (N-centred radicals). The assignments were verified using ^{15}N-labeled anilines. Similar spectra of DMPO adducts were recorded from amines treated with benzoyl peroxide or benzophenone plus UV. Possible mechanisms of formation of these adducts (radical trapping versus nucleophilic addition to DMPO followed by oxidation) during treatment of the amines with isoamyl nitrite are discussed.

KEY WORDS: Aryl radicals, arylaminyl radicals, aromatic amines diazotization, EPR, spin trapping.

ABBREVIATIONS: iAmONO, isoamyl nitrite; BP, benzophenone; BePo, benzoyl peroxide; DME, ethylene glycol dimethyl either; DMPO, 5,5-dimethyl-1-pyrroline N-xide; MNP, 2-methyl-2-nitrosopropane; PBN, phenyl N-*tert*-butylnitrone; ND, nitrosodurene.

INTRODUCTION

The reaction of primary aromatic amines with isoamyl nitrite (iAmONO) under aprotic conditions at elevated temperatures has long been recognized as a convenient method of aromatic arylation.[1,2] Analysis of product distribution from such a process together with model reactions, employing aroyl peroxide decomposition, indicated that phenyl radicals are the major arylating agents.[1,2] Intermediacy of other radical species, such as diazotate Ar–N=NO•, phenylcyclohexadienyl PhPhH•, aryldiazenyl Ar–N=N•, pentyloxyphenylnitroxyl, diphenylnitroxyl, alkoxyl and hydroxyl radicals, has also been invoked.[1-7]

Formation of aryl radicals from aromatic amines treated with iAmONO occurs *via* the formation and subsequent homolysis of a diazoanhydride (Scheme I).

Aryl radicals can dimerize, abstract hydrogen from suitable donors, or add to solvent molecules or a spin trapping agent.

In an earlier report on the reaction of an arylalkyl-sulfoxide **11**, with iAmONO at room temperature formation of a nitrogen centred radical was demonstrated using EPR and spin trapping methods.[5] We have extended our studies to include other

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$$\begin{array}{c} \text{Ar-NH}_2 + \text{iAmO-N=O} \\ \downarrow \\ \text{Ar-NH-N=O} \\ \downarrow \\ \text{Ar-N=N-OH} \\ \downarrow\uparrow \\ \text{Ar-N=N-O-N=N-Ar} \\ \downarrow \\ \text{Ar, Ar-N=N-O, N}_2\text{, other (non) radical products} \end{array}$$

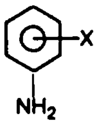
SCHEME I

primary aromatic amines, listed in Table 1, and have employed other type of spin traps (ND and MNP) as presented in this report. Additionally EPR/spin trapping study of radicals produced from certain anilines treated with benzoyl peroxide (BzPo) or benzophenone (BP) + UV, are described. The data presented permit a more detailed interpretation of the previous results[5] and identification of a key intermediate in these processes as an aryl radical.

MATERIALS AND METHODS

Aniline (**1**) was from Mallinckrodt. 4-Aminobenzonitrile (**4**), 4-nitroaniline (**3**), o-anisidine (**5**), p-toluidine (**2**), p-chloroaniline (**6**), 2,5-di-*tert*-butyl aniline (**14**), isoamyl nitrite, DMPO, MNP, benzene, ethylene glycol dimethyl either (DME) and benzoyl peroxide were purchased from Aldrich (Milwaukee, WI). ^{15}Labeled aniline (**1a**) was purchased from Terochem Laboratories Ltd. (Alberta). 4-Nitro-aniline($^{15}N_2$) was from Cambridge Isotope Laboratories and benzophenone from Fisher Scientific. Arylalkyl thioethers (**7–9**) sulfoxides (**10, 11**) and sulfones (**12, 13**) were synthesized as described previously.[5] DMPO and aniline were purified by distillation under reduced pressure. ND was prepared according to the procedure described earlier.[8] All other compounds were used as received.

TABLE 1
Primary aromatic amines studied in this work



Amine	X	
1 (aniline)	H	
2	*p*-CH_3	
3	*p*-NO_2	
4	*p*-CN	
5	*o*-OCH_3	
6	*p*-Cl	
7	*o*-S	OH
8	*o*-S	OCH_3
9	*o*-S	OAc
10	*o*-S(O)	OCH_3
11	*o*-S(O)	OAc
12	*o*-S(O_2)	OH
13	*o*-S(O_2)	OAc
14	2,5-di-*tert*-butyl	

Stock solutions of the amines (0.1 M or 0.2 M), iAmONO (70 mM and 140 mM), ND (10 mM), MNP (11.5 mM) and BePo (100 mM) were prepared in benzene. Amine **3** was dissolved in DME due to its poor solubility in benzene. Samples were prepared adding 10, 20 or 50 μL of AmONO to 450 μL of the amine solutions containing DMPO (usually 10–100 mM), or ND (5 mM) or MNP (6 mM) in quartz test-tubes (internal diameter 3 mm). Samples for the UV activation containied BP (10 mM). Solutions were saturated with argon for 25 min and sealed tightly. EPR spectra were measured using a Bruker ER-400 spectrometer operating at 9,3 GHz with 100 kHz modulation frequency. The following instrumental settings were generally employed: microwave power 20 mW, modulation amplitude 0.5 G, time constant 0.2 or 0.5 sec, scan rate 500 or 1000 sec and the appropriate gain level. Magnetic field calibration was achieved using the known distance between the h.f. components of the EPR spectrum of Fremy salt in 50 mM K_2CO_3. All measurements were performed at room temperature.

RESULTS

Incubation of aromatic amines **1–14** (0.1 M) with iAmONO (1.4 mM–16 mM) in deaerated benezene did not generate any EPR signals. However, when the spin trap ND was introduced into this system strong and persistent spectra were recorded. The latter were assigned to ND adducts with aryl radicals (Ar) derived from amines **1,4–6, 10–14**. An example is given in Figure 1A which shows the spectrum recorded in the presence of **13**, and Figure 1B shows simulated spectrum. No radicals were trapped

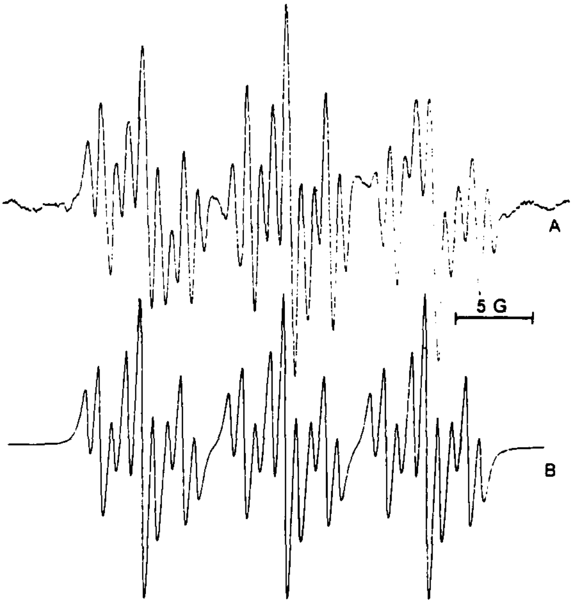


FIGURE 1 (A) EPR spectrum of ND-Ar spin adduct from system containing amine 13 (0.1 M), ND (5 mM), and iAmONO (3.5 mM) in deaerated benzene at room temperature. (B) Simulated spectrum using hf couplings from Table 2.

TABLE 2
Hyperfine coupling constants (G) from EPR spectra of ND-Ar radicals in benzene at room temperature

Source of Ar radical	Hyperfine coupling constants		
	a_N	other	
1	10.10	2.8 (*o*-, *p*-H)	0.95 (m-H)
	10.11[a]	2.78[a]	0.95[a]
4[b]	9.7	2.6 (*o*-H)	0.8 (m-H)
5[b]	9.8	2.8 (*o*-H)	1.0 (m-H)
	10.0[c]	2.52[c]	0.88[c]
6[d]	9.42[c]	2.72 (2H)[x]	1.35 (2h)[c]
11	9.7	2.99 (*o*-H)	1.01 (m-H)
13	9.6	2.7 (*o*-H)	0.75 (m-H)
14	10.3	2.26 (2H)	0.9 (1H)

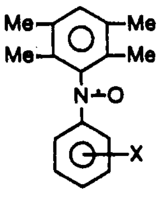
[a] from ref.[9]; [b] approximate values of hf couplings due to poor resolution of EPR spectra; [c] from ref.[11]; [d] strong signal recorded however due to poor resolution couplings were not extracted.

TABLE 3
Hyperfine splitting constants (G) from EPR spectra of MNP-Ar radicals in benzene at room temperature

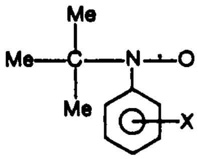
Source of Ar radical	Hyperfine coupling constants	
	a_N	other
1	12.3	1.9 (*o*-,*p*-H) 0.9 (m-H)
	12.45[a]	1.9[a] 0.9[a]
4	10.7	2.2 (*o*-H) 0.9 (m-H) 0.31 (a_N^{CN})
6	11.85	2.1 (*0*-H) 1.0 (m-H)

[a] from ref.[10].

with ND upon treatment of arylalkyl thioethers **7–9** with iAmONO. Aryl radicals derived from amines **1, 6, 8** and **13** treated with iAmONO, were detected with MNP as a spin trap. In these cases strong components from di-*tert*-butyl nitroxide overlap with the lines arising from the MNP-Ar adducts. Simulated spectra, obtained using couplings to appropriate aromatic ring hydrogens for a given amine, agreed with the recorded spectra, thereby confirming the assignments. Hyperfine coupling constants for ND- and MNP- adducts are given in Table 2 and 3 respectively. Comparison of those couplings with values reported by other workers shows satisfactory agreement in those cases for which such references are available.[9-11] No spectra corresponding to ND or MNP adducts with N-centred radicals were detected.



(a)
ND-Ar



(b)
MNP-Ar

With DMPO as a spin trap quite different types of spectra were obtained. Figure 2 shows examples of such spectra recorded for ^{14}N-aniline, **1** (A), ^{15}N-aniline, **1a** (B), p-Cl-aniline, **6** (C) and p-CN-aniline, **4** (D). Upper traces are control scans and were recorded before iAmONO addition. The spectra were interpreted as doublets of triplets split further into triplets (Figures 2A, C, D) and can be attributed to DMPO-arylaminyl radicals, DMPO-NHAr. In the case of ^{15}N-labeled aniline the spectrum (2B) was interpreted as a doublet of triplets split further into doublets. The second doublets result from interaction of the unpaired election with the ^{15}N nucleus of nuclear spin 1/2. These spectra are similar to those of DMPO adducts with ^{14}N- and ^{15}N-labeled azidyl radicals (N_3), produced upon radiolysis of aqueous solutions of $Na^{14}N_3$ and $Na^{15}N_3$.[12] Hyperfine splitting constants were obtained from computer simulations and they are listed in Table 4. They are close to h.f. splittings reported for DMPO-NH (n-Bu) radical.[13,14]

Amine **3** was examined in DME due to its poor solubility in benzene. A strong EPR spectrum of the same type as shown in Figure 2A, was observed even without any activator (iAmONO, BzPo, or BP + UV). It is likely that reaction of peroxide contaminants, present in the solvent, with the amine, or its DMPO adduct, is responsible for formation of this radical. Similarly, 4-$^{15}NO_2$-^{15}N-aniline in DME produced an EPR spectrum of the same type as shown in Figure 2B.

When BzPo was used instead of iAmONO with amines **1**, **1a**, **4** and **6**, EPR spectra similar to those obtained in the presence of the nitrite were recorded (Figure 2).

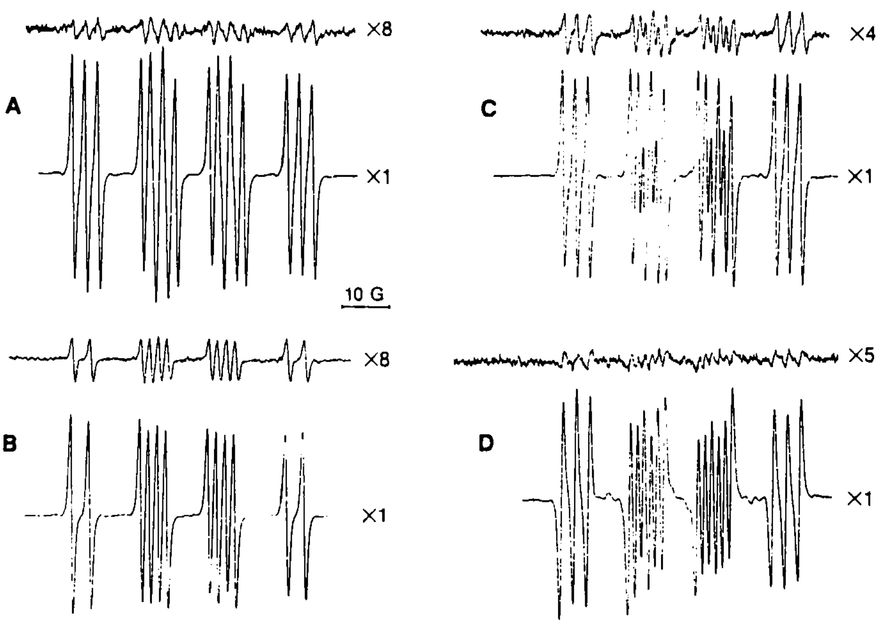


FIGURE 2 EPR spectra of DMPO-NHAr radicals from samples containing aromatic amine (0.1 M), DMPO 100 mM), and iAmONO (2.8 mM) in argon-saturated benzene at room temperature. (A)- ^{14}N-aniline, (B)- ^{15}N-labeled aniline, (C)-*p*-Cl-aniline, (D)-p-CN aniline. Numbers of the right side of the spectra indicate relative gain level. Upper traces represent control scans recorded before addition of iAmONO.

TABLE 4
Hyperfine splitting constants (G) from EPR spectra of arylaminyl-DMPO and aryl-DMPO radicals in benzene

	Hyperfine coupling constants		
Aromatic amine	$a_N{}^1$	a_H	a^{N2}
1 (aniline)	14.0	15.82	2.6
1a (^{15}N-aniline)	14.2	15.9	3.6 (^{15}N)
2	13.9	16.3	2.5
3‡	13.8	15.0	2.9
4	13.9	15.3	2.8
5	14.0	15.2	2.8
6	14.3	16.1	2.7
7	14.0	15.2	2.7
8	13.9	14.1	2.9
10	13.7	13.9	3.2
11	13.7	13.9	3.2
14	14.1	16.8	2.3
12	14.5	22.2	-
13	14.1	21.2	-

‡in DME

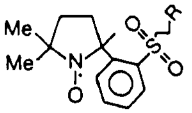
UV-irradiation of a sample containing **1**, (or **1a** or **6**) BP and DMPO, produced spectra similar to those shown in Figure 2A, B, C.

It is known that amines may form nonparamagnetic adducts DMPOH–NHAr, *via* nucleophilic addition to DMPO (Scheme II). Oxidation of such an adduct by oxygen or other mild oxidizing agent, could conveivably be a potential source of radicals.[13-16] The following control experiment was performed to examine if an EPR spectrum, similar to those shown in Figure 2, could be produced *via* such a mechanism. A sample containing $PhNH_2$ and DMPO in benzene was saturated with oxygen and incubated for 30 min at room temperature. Subsequently the sample was deoxygenated by purging with argon for 30 min and the EPR measurement was performed. The recorded spectrum corresponds to the DMPO–NHPh radical, but its intensity was

FIGURE 3 EPR spectrum of DMPO-Ar spin adduct from system containing amine **13** (0.1 M), DMPO (10 mM) and iAmONO (3.5 mM) in deaerated benezne. HF coupling constants are given in Table 3.

close to that of the control scan shown in Figure 2A. Apparently DMPOH–NHPh, if formed, is not readily oxidized by dissolved oxygen. However, upon addition of iAmONO or BzPo a strong EPR signal was generated similar to that shown in Figure 2A. (An experiment, suggested by a referee, in which $Fe(CN)_6^{-3}$ was used as an oxidizing agent, with the intention of differentiating between $PhNH_2$ and DMPOH–NHPh oxidation in CH_3CN/N_2O (1:1 vol/vol) solution, was inconclusive). Although the experiment with O_2 oxidation was negative it would be premature to exclude completely the latter pathway as the main mechanism of formation of the DMPO–NHAr species under diazotizating conditions.

Amines **12** and **13** upon treatment with iAmONO, produced EPR spectra characteristic of DMPO adducts with carbon-centred radicals (Figure 3, Table 4). They were assigned to DMPO–Ar radicals following earlier investigation with ND as a spin trapping agent, which is more sensitive to radical structure than DMPO.



DMPO-Ar
R:OAc; OH

DISCUSSION

EPR and spin trapping techniques have been employed to detect radicals produced during aprotic diazotization of aromatic primary amines with isoamyl nitrite. In the absence of spin trapping agents we did not observe radical formation, although other workers reported EPR spectra of radicals produced in similar processes employing very high concentrations of amines and isoamyl nitrite.[6,7]

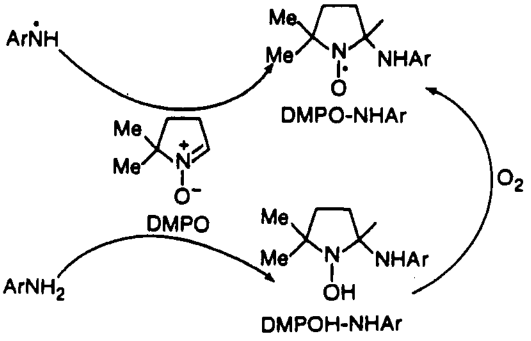
In this work we have recorded the EPR spectra of ND- and MNP-spin adducts of aryl radicals formed in reactions similar to that shown in the Scheme I above, confirming that the process is an excellent source of aryl radicals.

Spin adducts of ND with Ar radicals derived from *o*-substituted anilines (**5, 11, 13**), produced EPR spectra which resemble those obtained from para-substituted amines in the sense that in both cases their hf structures originate from couplings of an unpaired electron to two pairs of equivalent hydrogens (Table 2). Although this may be a coincidence, an alternative explanation of this could be that the most stable resonance form of the Ar radicals, from both *o*- and *p*-substituted anilines, is the one with the unpaired electron in the para position and accordingly this form is trapped by ND (and perhaps by other spin traps). In this case the larger values of hf couplings (Table 2) for adducts with Ar form **5, 11, 13**, should also be assigned to the ortho-hydrogens, and the smaller couplings to meta-hydrogens in the Ar moiety.

DMPO is an efficient scavenger of carbon-centred radicals including aryl radicals.[14,17] However all the amines studied in this work, (except **12** and **13**), when treated with iAmONO in the presence of DMPO, afforded EPR spectra corresponding to DMPO–NHAr radicals. Unambiguous identification of these species has been accomplished using ^{15}N-labeled anilines, which produced spectra clearly confirming contribution of the amine nitrogen to the hyperfine structure.

There are two pathways which could lead to production of these types of adducts

(Scheme II). First, in which free arylaminyl radicals are trapped by DMPO. Second, a pathway in which a hydroxylamine DMPOH-NHAr, produced by nucleophilic addition of an amine to DMPO, undergoes oxidation to a nitroxide radical.



SCHEME II

Control experiments have not provided convincing evidence for or against either of those two pathways. One can speculate that oxidizing species, formed during the diazotization process, such as aryl and alkoxy radicals,[1-5] could abstract hydrogen from NH_2 groups of the amines yielding arylaminyl radicals. At the same time however the same species are likely to abstract a hydrogen atom from hydroxylamine. BzPo and BP/UV can function in a similar manner, oxidizing amines [18-23] and hydroxylamines. Therefore simultaneous operation of those two mechanisms can not be excluded at the present time, although Cadogan's observation[1] that no products arising from the reaction of arylaminyl radicals were detected in experiments with isoamyl nitrite favors the alternative mechanism of formation of the DMPO-NHA species.

In accord with the latter argument is the lack of any EPR evidence suggesting formation of ND or MNP adducts with aminyl radicals during the diazotization process. Other workers demonstrated that nitroso spin traps, including ND and MNP, are capable of trapping N-centred racials.[24-26] The failure to detect such adducts in this study may be a consequence of either the absence or low concentration of aminyl radicals in the present system, or poor reactivity of the nitroso spin traps towards aminyl radicals in comparison with aryl radicals.

Amines **12** and **13** are unique in the sense that upon reaction with iAmONO they produce carbon centred radicals both with the nitroso spin traps as well as with DMPO. Possible reasons for the different behavior of these amines could include either (i) their inability to add to DMPO to form DMPOH-NHAr hydroxylamine, owing to steric hindrance (i.e. the presence of the bulky $S(O)_2CH_2CH_2R$ groups ortho to NH_2), or (ii) reduced nucleophilicity of these amines due to the presence of a strong electron- withdrawing group in the chromophore. The observation that another heavily substituted amine, **14**, produces an EPR spectrum characteristic of the DMPO-NHAr radical, similar to those shown in Figure 2, excludes steric hindrance as a decisive factor preventing formation of the DMPOH-NHAr adduct. Therefore the presence of an electron withdrawing group may play an essential role affecting nucleophilic addition of these amines to the spin trap.

In conclusion, the nitroso spin traps, ND and MNP, appeared to be superior to the nitrone trapping agent, DMPO, in studying diazotization processes under aprotic conditions. The former traps do not add readily to the primary aromatic amines and are more sensitive to the structure of the trapped radicals. The ambiguity of the data obtained from DMPO renders this spin trap ill-suited to study reactions of primary aromatic amines. In our previous paper[5] the EPR spectrum recorded during treatment of aryl alkyl sulfoxide *11* with iAmONO in the presence of DMPO was tentatively ascribed to the DMPO-aryldiazenyl spin adduct (ArN=N-DMPO). In the light of the results presented in this report the EPR spectrum should be reassigned to a DMPO-arylaminyl radical.

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