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The Photochemically Induced Oxidation of Aniline by Hydroperoxides: An Electron Paramagnetic Resonance Study. Part II.[1]

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Abstract : The oxidation reaction of aniline by tertiary hydroperoxides, induced photochemically, was studied. The peculiar radical intermediates, nitroxides and peroxy radicals, involved in the reaction mechanism were detected and identified by EPR spectroscopy. The presence of these intermediates confirm that PhNO is the first product of the oxidation of aniline and the PhNH· radical as its precursor.

Introduction

A study of the oxidation mechanism of aniline promoted by different peroxy compounds has been reported recently.[1] However, among the oxidants, the hydroperoxides and the peroxides do not react spontaneously.

It is known that hydroperoxides can perform the aniline oxidation if catalytic amount of certain metal compounds are present,[2] nevertheless, the aim of the research was to discover whether a possible oxidative process could be induced photochemically, *via* a homolytic radical mechanism.[3]

I want to discuss here the reaction mechanism of this process and in particular the nature of the detected radical intermediates. These results can in fact support a mechanism which leads to the consideration that the nitroso benzene is the first oxidative product of aniline and the phenylaminyl is its radical precursor. Experiments were then performed with both hydroperoxides and peroxides, but only the former succeed to oxidize aniline.

Results and Discussion

When a solution of aniline (1), in different solvents , is photolyzed in the presence of *ter*-butyl hydroperoxide (2) or cumyl hydroperoxide (3), within the cavity of an EPR spectrometer at different temperatures, the formation of radical species is observed. In particular, at room temperature, the phenyl *ter*-butoxyl nitroxide (4) and the phenyl cumyl nitroxide (5) are detected when (2) and (3) are respectively the oxidants. Since the EPR spectra show these two nitroxides to be different in structure (see Table), it seems reasonable to suppose that they are formed following a different reaction pathway. Based on these experimental evidences and the literature data,[4-7] the most conceivable mechanism might be represented by Scheme 1, SCHEME 1

$$\mathrm{R{-}OOH} \xrightarrow{h\nu} \mathrm{R{-}O\cdot + \cdot OH} \qquad [1]$$

$$\mathrm{R{-}OO{-}H + R{-}O\cdot/\cdot OH} \longrightarrow \mathrm{R{-}OO\cdot + R{-}OH / H_2O} \qquad [2]$$

$$\mathrm{PhNH_2 + R{-}O\cdot/\cdot OH} \longrightarrow \mathrm{PhNH\cdot + R{-}OH / H_2O} \qquad [3]$$

$$\mathrm{PhNH\cdot + \cdot OO{-}R} \longrightarrow \mathrm{PhNO + R{-}OH} \qquad [4]$$

$$\mathrm{PhNO + RO\cdot} \longrightarrow \mathrm{PhN(O\cdot)OR} \qquad [5]$$

$\mathrm{R = Bu^t,\ PhC(CH_3)_2}$

which, however, could account only for the detection of (4) but not (5).
Nevertheless, the formation of radical (5) could be justified following this scheme, if further reaction-steps are taken into account.[4]

Table . Hyperfine Splitting Constants[a] (Gauss) of Detected Radicals.

entry	Radical	a_N	$a_H(m)$	$a_H(o,p)$	a_H	g-factor
(4)	$\mathrm{PhN(O\cdot)OBu^t}$	14.62	0.95	3.00		2.0052
(5)	$\mathrm{PhN(O\cdot)C(CH_3)_2Ph}$	11.25	0.87	2.50		2.0057
(6)	$\mathrm{PhN(O\cdot)OC(CH_3)_2Ph}$	14.75	1.00	3.00		2.0050
(7)	$\mathrm{PhN(O\cdot)CH_3}$	10.20	0.95	2.70	9.60 ($\mathrm{CH_3}$)	2.0057
(12)	$\mathrm{PhN(O\cdot)H}$	9.20	1.00	2.87	12.20 (NH)	2.0058
(13)	$\mathrm{Ph(CH_3)_2COO\cdot}$					2.0153
(14)	$\mathrm{Bu^tOO\cdot}$					2.0153

a) Small change in the h.f.c. are depending on the solvent and the temperature.

For instance, if phenyl cumyloxyl nitroxide (6) is assumed to be initially formed, reaction [5], due to its low stability at room temperature it could rapidly rearrange to $\mathrm{PhNO_2}$ and cumyl radical which when trapped by PhNO leads to (5), i.e.,

$$\mathrm{PhN(O\cdot)OC(CH_3)_2Ph} \xrightarrow{\circ} \mathrm{PhNO_2 + \cdot C(CH_3)_2Ph} \qquad [6]$$

$$\mathrm{PhNO + \cdot C(CH_3)_2Ph} \longrightarrow \mathrm{PhN(O\cdot)C(CH_3)_2Ph} \qquad [7]$$

Actually, a photochemical experiment conducted in continuos flow at -70 °C, with a solution of aniline and cumyl hydroperoxide in 1-butene oxide, directly in the cavity of the EPR spectrometer, allowed one to detect besides the radical (5) its radical precursor (6), Fig.1, as hypothesized by the reactions [6] and [7]. This result definitely is in favour of the reaction scheme proposed. It is also noteworthy to point out the presence, in some experiments at room temperature, of the phenyl methyl nitroxide (7): in fact, the rearrangement of cumyloxyl radical leads to acetophenone and methyl radical which is trapped by PhNO. However, it was necessary to get more experimental evidence to support such a mechanism: for instance, verifying the possible involvement of the radical PhNH(•) (8) and then the presence of PhNO (9).

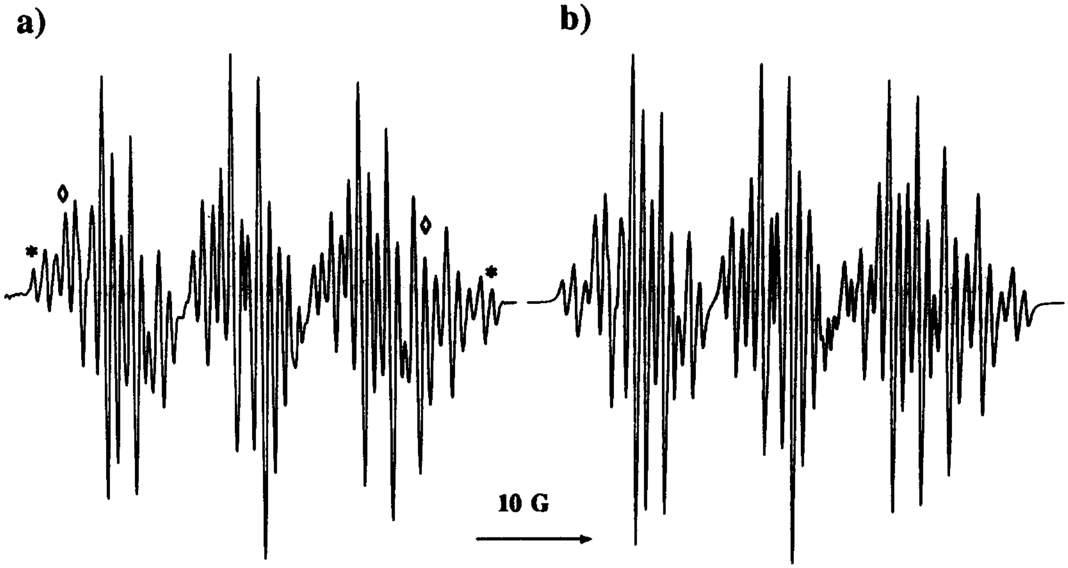

Fig. 1 (a) EPR spectrum , at -70 °C in 1-butene oxide, showing both radicals (6)(*) and (5)(◊). (b) Computer simulation with ratio between the radical species of 40:60.

To prove the presence of (9) and the role played by it in the formation of the detected nitroxides its direct interaction with (2) and (3) has been studied: both react almost instantaneously, no UV.- irradiation is necessary, and lead to the formation of (4) and (5) respectively. In particular, when (3) is used at low temperature, the radical (6) can be detected, confirming its low thermodynamic stability; at room temperature, beside the radical (5) the nitroxide (7) is evident. For these reactions, the pathway previously partly suggested,[4] could be:

$$\mathrm{R{-}OOH + (9) \longrightarrow [PhN(OOR)OH]^{*} \xrightarrow{\Omega} PhN(O\bullet)OH + \bullet OR} \qquad [8]$$

followed by reaction [5] or reactions [5], [6] and [7] depending on the hydroperoxide.

Further experimental evidence for strengthening the correct spectroscopic identification of the radical species, in particular (5) and (6), were obtained from the reaction of (9) with both cumene (10) and cumyl peroxide (11). The reaction between (9) and (10) is spontaneous and leads to the detection of two radical species, PhN(O•)H (12) and (5): reaction [9] followed by [5].

$$PhNO + HC(CH_3)_2Ph \longrightarrow PhN(O\cdot)H + \cdot C(CH_3)_2Ph \qquad [9]$$

On the contrary, the reaction between (9) and (11) has to be induced photochemically;

$$[PhC(CH_3)_2O]_2 \xrightarrow{h\nu} 2\ PhC(CH_3)_2O\cdot \qquad [10]$$

nevertheless, it leads, depending on the temperature, to the same radical species (6), (5) and (7) detected when the correspondent hydroperoxide (3) was used.

A direct and definitive confirmation of the correct assignment of the structure, based on spectral parameters, to radical (5) and indirectly to (6), was obtained through the oxidation of the parent secondary amine, i.e., the N-cumylaniline (15). In fact when (15) was allowed to react, in benzene solution at room temperature, with *m*-chloro perbenzoic acid it was possible to detect a radical species with the same spectroscopic parameters perceived for radical (5).

As suggested by Scheme1, the formation of PhNO is from the oxidation of the phenylaminyl radical (8), and then further support to the proposed mechanism could come from the knowledge of the behaviour of this radical. In principle, radical (8) can be obtained from benzanilide by hydrogen abstraction following reaction [1] and then [11];

$$PhNHC(O)H \xrightarrow{-H} PhNHC(O)\cdot \xrightarrow{\alpha} PhNH\cdot \qquad [11]$$

so, through reaction [4], the formation of nitroso benzene might be accounted for.

To check this hypothesis, i.e., the formation of (9) via radical (8), the photolysis of benzanilide in the presence of (3) or (2) was conducted directly in the cavity of the EPR spectrometer at low temperature in isooctane solution. These experiments allowed to detect the radical (4) along with the *ter*-butylperoxy radical

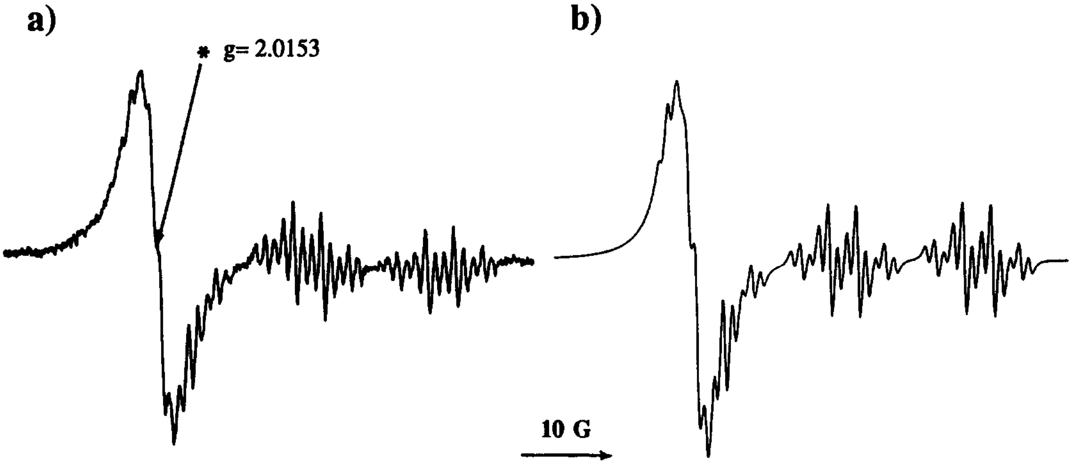

Fig. 2. (a) EPR spectrum, at -63 °C in isooctane, showing both radicals (6) and (13)(*). (b) Computer simulation with ratio between the radical species of 20:80.

(14) and the nitroxide **(6)** along with the cumylperoxy radical **(13)**, Fig.2, respectively. The presence of these radical species definitely is in favour of the reaction scheme proposed.

In summary, it has been shown how EPR spectroscopic results can account for a general mechanism of oxidation of aniline *via* a homolitic radical process leading to the formation of aminyl radical and then nitroso benzene; a reaction mechanism similar to that in the amine inhibited decomposition of hydroperoxides.[5,6] It also comes out that whilst hydroperoxides failed in the direct oxidation of aniline, most likely due to the redox potential[8] too low to induce a spontaneous E.T. process, in this case, peroxy radicals can definitely be considered responsible for the aniline oxidation.

Experimental

N-cumylaniline **(15)**. To a solution of 3.62 g. of 2-bromo-2-phenylpropane in 100 ml. of CCl_4 was added Et_3N (2.53 ml.) and $PhNH_2$ (1.70 ml). The mixture was allowed to stand at room temperature for 6 h, then filtered and chromatographed. Elution with petroleum ether / Et_2O (100:1) on neutral alumina column gave the title product (2.0 g. 80%). It was purified in 85% by distillation under reduced pressure, b.p. 37°C / 0.2 mm.; δ_H 1.63 (6H, s), 3.6 (1H,br s), 6.55-7.45 (10H, m); (Found: M^+, 211).

2-bromo-2-phenylpropane.[9] 18.0 g. of N-bromosuccinimide were dissolved in 125 ml of CCl_4 and a catalytic amount of benzoyl peroxide was added. The mixture was refluxed and then 14.0 ml of cumene were added dropwise under vigorous stirring for 10 min.. After cooling the solvent was removed and the residue was distilled under reduced pressure, 6.12 g. 85% of title product was recovered. b.p. 60°/1 mm.; δ_H 2.18 (6H, s), 7.3-7.6 (5H, m).

EPR spectra were recorded on Varian E-104 X-band spectrometer, with a 100KHz modulation. ^1H NMR spectra were measured on Varian 200 (200 MHz) spectrometer, and are for $CDCl_3$ solutions with $SiMe_4$ as internal standard. GC-MS analyses were carried out with a Carlo Erba QMD 1000 instrument. The dynamic EPR experiments were performed using a 50ml gastight SGE syringe driven by a INFORS Precidor.

All the products were purified by distillation or recrystallisation before use.

EPR Experiments. Solutions of aniline and oxidant in benzene, isooctane, 1-butene oxide were photolysed within the cavity of the EPR spectrometer, equipped with a variable temperature control system, using both a standard quartz sample tube, for static experiments, and a flat cell arrangement (0.3 mm cell width) for dynamic experiments: for these, the flow rate was ranging between 0.1 and 0.6 ml/min. The solutions were deaerated prior to use, with the freeze-thaw technique or by purging with N_2-gas (flow experiments) for 50-60 min.. The light source was an OSRAM HBO 500W/2 Hg-lamp, the light of which was focused onto the sample by an elliptical mirror and two quartz lenses. The g-value for the radical species were determined by comparison with the g-value (2.0037) of DPPH.

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