ELECTRON SPIN RESONANCE STUDIES ON THE RADICALS PRODUCED IN THE PHOTOREDUCTION OF NITROBENZENE BY ALIPHATIC AMINES

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Summary

An electron spin resonance study on the radicals produced in the photolysis of nitrobenzene–amine systems was made. The nature and characteristics of the different radicals produced with six different amines are discussed. A correlation is attempted between the structure of the amine and the type of radical formed.

1. Introduction

Electron spin resonance (ESR) studies on the radicals produced in the various types of reductions of nitrobenzene have been useful in mechanistic elucidations. In general, nitrobenzene anion radical is formed in these cases and this anion has been well studied by means of the ESR technique [1, 2]. Secondary radicals such as $PhNOH$ (Ph $\equiv$ phenyl) and its derivatives are also formed as a result of the subsequent transformation of $PhNO_2^-$. In the oxidation of aromatic amines, phenylhydroxylamines etc. $PhNHO$ has been observed. ESR work on these has been reviewed by Ayscough [3]. Radicals produced in the photoreduction of nitrobenzene by neutral organic substrates have been studied in detail, but studies with Lewis base reactants such as aliphatic amines have not received much attention. In this paper work on the radicals produced in the photoreaction of nitrobenzene–amine systems is described.

2. Experimental details

Nitrobenzene and the amines are purified by standard techniques [4, 5]. In typical experiments a solution containing nitrobenzene and an amine in a suitable solvent in the concentration range 0.1 - 0.5 M is taken in a Pyrex tube and irradiated with a 900 W xenon arc lamp for about 30 min,

and the ESR spectra of the radicals produced are recorded with a Varian E4 spectrometer using a quartz cell.

The concentration of the radicals is calculated from the area of the peaks, the area being converted to units of concentration by using an internal standard (2,2-diphenyl-1-picrylhydrazyl) in the ESR cavity and normalizing. By this method it was found that 1 cm^2 corresponds to a radical concentration of approximately 4.75×10^{-6} M.

3. Results and discussion

Two types of signals are observed for different amines in the photolysis of nitrobenzene: a triplet signal with (a) diethanolamine, (b) piperidine, (c) dipropylamine and (d) triethylamine and a quartet signal with cyclohexyl-amine. The triplet signal has $g \approx 2.019$ and the quartet signal has $g \approx 2.0155$. The triplet is assigned the structure PhṄOH and the quartet is assigned PhNHȮ. These assignments are made on the basis of the values of the hyperfine splitting constant and also on the basis of the splitting patterns etc. already reported by Ayscough et al. [6] (Table 1). It should be noted that, except for cyclohexylamine where PhNHO is formed, in all the other amines only PhṄOH is formed. Previous workers [3, 6 - 9] who have made extensive ESR investigations of the photoreductions of nitrobenzene have invariably detected PhṄOH and its derivatives while PhNHȮ has been detected in the oxidations of aniline, phenylhydroxylamine etc. [7]. Thus the results of the present study more or less confirm the definitive work of the previous workers in all cases except that with cyclohexylamine as the reactant.

A study of the dependence of the concentration of the radicals on the concentration of the substrates etc. presents many interesting features although no quantitative correlation could be reached. With the exception of cyclohexylamine, which produces PhNHO, the radical concentration for the amines is in the following order: triethylamine > dipropylamine > piperidine > diethanolamine > tert-butylamine. The photoreactivities of the amines towards nitrobenzene judged from the quantum yields are in the following order: triethylamine > dipropylamine > piperidine > cyclohexylamine > diethanolamine > tert-butylamine. Thus a general agreement between the photoreactivity and the radical yield is noted. The yield of the radical in-

TABLE 1

Hyperfine splitting constant a_N of the radicals

Radical	a_N	
	Experimental value (G)	Value from ref. 6 (G)
PhṄOH	10.5	10.6
PhNHȮ	12.0	11.9

creases with increases in the amine concentration but is independent of the nitrobenzene concentration as observed in the quantum yield measurements (Tables 2 and 3).

TABLE 2

Effect of [triethylamine] on the [PhṄOH] produced

[triethylamine] (M)	[PhṄOH] (M)
0.33	5.2×10^{-5}
0.17	4.1×10^{-5}
0.07	2.7×10^{-5}
0.03	1.8×10^{-5}

[nitrobenzene] = 0.17 M; photolysis period, 30 min.

TABLE 3

Effect of [cyclohexylamine] on the [PhNHȮ] produced

[cyclohexylamine] (M)	[PhNHȮ] (M)
0.33	7.1×10^{-5}
0.17	5.1×10^{-5}
0.07	2.2×10^{-5}
0.03	—

[nitrobenzene] = 0.17 M; photolysis period, 30 min.

Studies made of the change in the radical in the dark yield some interesting details. For PhṄOH radical, when the irradiation is discontinued, there is a slight increase in the concentration of the radical with time (within 20 min) to reach an almost steady value. For PhNHO radical, obtained for cyclohexylamine, there is a first-order decay with time in the dark (Table 4) with a rate constant of about 1.1×10^{-5} s^{-1}. These details give some indication of the mechanism of the reaction. The excited nitrobenzene forms an exciplex with the amine RCH_2NHR' (R, R' ≡ alkyl). Formation of the exciplex is followed by electron transfer from the amine to the nitro group, yielding an ion pair ($PhNO_2^- \ldots \ldots RCH_2^+NHR$). Within the ion pair, proton transfer occurs from the amine to the nitrobenzene anion radical yielding a radical pair complex ($PhNȮ_2H \ldots \ldots R\dot{C}HNHR'$). Radicals such as PhṄOH arise from further reactions between the two radicals and from reactions involving the intermediate $PhN(OH)_2$. It is important to note that the ESR study did not reveal the presence of $PhNO_2^{\cdot-}$ radical in detectable amounts. This shows that protonation of $PhNO_2^{\cdot-}$ within the ion pair is more important than ion pair dissociation.

For amines which produce PhṄOH, the radical yield in benzene solvent (3.4×10^{-5} M) is much higher than the yield in isopropanol (1.4×10^{-5} M). This is due to the high reactivity of PhṄOH. PhṄOH can combine with

TABLE 4

Decay of PhNHȮ radical

Time elapsed after irradiation (min)	[radical](M)
—	11.0×10^{-5}
18	10.3×10^{-5}
34	9.0×10^{-5}
56	8.1×10^{-5}
73	6.5×10^{-5}

[cyclohexylamine] = 0.167 M; [nitrobenzene] = 0.167 M.

$(CH_3)_2\dot{C}OH$ radical formed in the isopropanol system to yield a radical complex which forms PhNHOH and $(CH_3)_2CO$ in a fast process. Furthermore, in irradiated solutions, $PhN\dot{O}_2H$ can also combine with $PhNOH$ to give a diamagnetic adduct which decomposes slowly in the dark to re-form the reactants:

$$PhNOH + PhN\dot{O}_2H \underset{dark}{\overset{h\nu}{\rightleftharpoons}} adduct \qquad (1)$$
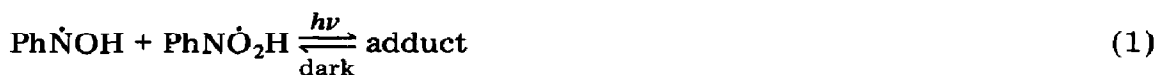
A similar explanation has been offered by Sleight and Sutcliffe [7] who have also observed the increase in ArNOH (Ar ≡ aryl) concentration with time in the dark for substituted nitrobenzenes in alcohols. The radicals PhNOH and $PhN\dot{O}_2H$ can also decay by the following pathways:

$$PhNOH + PhN\dot{O}_2H \longrightarrow PhNHOH + PhNO_2 \qquad (2)$$

$$PhNOH + amine \longrightarrow PhNHOH + radical\ from\ amine \qquad (3)$$

It is noted that process (1) produces PhNOH and processes (2) and (3) account for the radical destruction in the dark. Thus the concentration of PhNOH remains stationary to some extent over a period of time.

   Tert-butylamine, which is the least reactive amine, produces no radical at all. Cyclohexylamine produces PhNHȮ whereas the other amines produce PhNOH. These facts suggest that the nitrogen atom of the amine must approach the nitrogen atom of $PhNO_2$ or $PhN\dot{O}_2H$ and form a complex. In this arrangement, the ease with which the complex is formed and the manner in which the complex reorganizes into the radicals are dependent on the ionization potential of the amine as well as on the steric and conformational aspects. A highly sterically crowded substrate such as *tert*-butylamine is almost inert. Furthermore, it does not have an α hydrogen atom which can react. Cyclohexylamine in its chair conformation will probably approach the nitro moiety in such a manner that the α CH_2 group of the cyclohexylamine avoids the oxygen atoms of the NO_2 group. Thus it is noted that in this case a hydrogen atom is transferred to the nitrogen atom and not to the oxygen atom.

4. Conclusion

All the amines used gave PhṄOH except cyclohexylamine which gave PhNHȮ. *Tert*-butylamine did not give any radical. These results show that the structure and reactivity of the amines used are important in the formation of different radicals in the photolysis of nitrobenzene–amine systems.

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