New Evidence on the Mechanism of the Decomposition of *N*-Nitrosoacetanilide in Solution: Detection of a New Radical

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Summary The detection by e.s.r. of a new radical believed to be PhN:NO• (σ) during the title reaction, coupled with the observed partial or sometimes complete suppression of the signal due to the radical PhNAc·NPh·O• in certain solvents, supports Rüchardt and Freudenberg's rather than Perkins and Chalfont's mechanism for the reaction.

IN 1964, Rüchardt and Freudenberg[1] suggested what appeared to be a satisfactory mechanism (Scheme 1) for a reaction which had been a puzzle for 60 years, *viz.* the decomposition of *N*-nitrosoacetanilide (NNA) in benzene.

$$\mathrm{PhN(NO)Ac} \rightarrow \mathrm{PhN{:}NOAc} \rightarrow \mathrm{PhN_2^+\ AcO^-}$$

$$\mathrm{PhN{:}NOAc} + \mathrm{AcO^-} \rightarrow \mathrm{Ac_2O} + \mathrm{PhN{:}NO^-}$$

$$\mathrm{PhN_2^+} + \mathrm{PhN{:}NO^-} \rightarrow \mathrm{PhN_2{\cdot}O{\cdot}N_2Ph} \rightarrow$$
$$\mathrm{Ph{\bullet}} + \mathrm{N_2} + \mathrm{PhN{:}NO{\bullet}} \qquad \mathrm{(I)}$$

$$\mathrm{Ph{\bullet}} + \mathrm{PhH} \rightarrow [\mathrm{PhC_6H_5H}]{\bullet} \xrightarrow{\mathrm{(I)}} \mathrm{Ph_2} + \mathrm{PhN{:}NOH}$$

$$\mathrm{PhN{:}NOH} + \mathrm{AcO^-} \rightarrow \mathrm{PhN{:}NO^-} + \mathrm{AcOH}$$

$$\mathrm{PhN{:}NO^-} + \mathrm{PhN_2^+} \rightarrow \textit{et seq.}$$

SCHEME 1

It was stated[2,3] that this mechanism was supported by e.s.r. studies which revealed a long-lived free radical, claimed to be the aryldiazotate π-radical (I). Chalfont and Perkins[4] then suggested an alternative mechanism (Scheme 2) based on their contention that the observed e.s.r. signal was due to the stable radical PhNAc·NPh·O• (II), an assignment which was supported by independent synthesis of the radical.[4,5]

$$\mathrm{PhN(NO)Ac} \rightarrow \mathrm{PhN{:}NOAc} \rightarrow \mathrm{Ph{\bullet}}$$

$$\mathrm{Ph{\bullet}} + \mathrm{PhN(NO)Ac} \rightarrow \mathrm{PhNAc{\cdot}NPh{\cdot}O{\bullet}} \qquad \mathrm{(II)}$$

$$\mathrm{Ph{\bullet}} + \mathrm{PhH} \rightarrow [\mathrm{Ph\ C_6H_5H}]{\bullet} \xrightarrow{\mathrm{(II)}}$$
$$\mathrm{Ph_2} + \mathrm{PhNAc{\cdot}NPh{\cdot}OH}$$

$$\mathrm{PhNAc{\cdot}NPh{\cdot}OH} + \mathrm{AcO^-} \rightarrow \mathrm{AcOH} + \mathrm{PhNAc{\cdot}NPh{\cdot}O^-}$$

$$\mathrm{PhNAc{\cdot}NPhO^-} + \mathrm{PhN_2^+} \rightarrow \mathrm{PhNAc{\cdot}NPh{\cdot}O{\cdot}N_2Ph}$$

$$\mathrm{PhNAc{\cdot}NPh{\cdot}O{\cdot}N_2Ph} \rightarrow \mathrm{Ph{\bullet}} + \mathrm{N_2} + \mathrm{(II)} \rightarrow \textit{et seq.}$$

SCHEME 2

In view of this conflict we have examined the e.s.r. spectra resulting from the decomposition of *N*-nitrosoacetanilide in a variety of solvents. We find (Table) that the

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signal attributed to the radical (II) (Figure 1) ($a_N = 11{\cdot}6$ gauss) is *not* present in all solvents used and that the intensity of this signal, when it appears, is very weak in all solvents having an easily abstractable hydrogen atom. Further we find that in *all* solvents used there is a *second*, weak, signal (Figures 2, 3) consisting of 9 lines arranged as a 1 : 1 : 1 triplet of 1 : 1 : 1 triplets, indicating the presence, in all cases, of a new radical (III) containing two nitrogen atoms. (a_{N-1} 30·5 gauss; a_{N-2} 2·3 gauss; g 2·0017). No further splittings are observed with lower modulation amplitude. Thus, in benzene the signal resulting from (II) is intense and almost obliterates that from (III). The latter becomes clear at lower modulation amplitude (Figures 1 and 2) and for this reason, presumably, it was overlooked by previous workers. In mesitylene the signal resulting from (III) is dominant (Figure 3).

TABLE

E.s.r. signals from PhN(NO)Ac *in solvents*

Solvent	Signal (II)	Signal (III)
PhH	intense	weak
PhMe	v. weak	weak
PhEt	v. weak	weak
$PhPr^{i}$[a]	absent	weak
$PhBu^{t}$	intense	weak
Mesitylene	almost absent	weak
p-Xylene	v.v. weak	weak

[a] A 1 : 1 : 1 triplet (a_N 15·0 gauss) attributed[6] to dicumyl nitroxide was also observed.

$$PhN(NO)Ac \longrightarrow NO; NO + 2PhCMe_2\cdot \longrightarrow [PhCMe_2]_2NO$$

Assuming that the same decomposition mechanism is operable in each solvent, the implication of these observations is that the Chalfont and Perkins radical (II) is *not* the required chain carrier, but that it is a relatively unimportant side product, possibly irrelevant to the production of phenyl radicals from NNA, and that Scheme 2 is not operable. This side product (II) is suppressed in solvents which give stabilised benzyl-type radicals by abstraction of side-chain hydrogen atoms by phenyl radicals either through scavenging of the radical (II) by the benzyl radical[7] in a chain termination step, and/or because the removal of phenyl radicals by the combined reactions of side-chain abstraction and nuclear addition becomes more important than removal by their reaction with unchanged NNA.

In the light of this new evidence Rüchardt and Freudenberg's mechanism (Scheme 1) is worthy of consideration as is the possibility, which we now raise, that our observed radical (III) is the elusive radical (I) essential to Scheme 1, with the exception that it is a σ- rather than the π- radical, suggested by Rüchardt. This follows by analogy with the splitting constants previously recorded[8] for the closely related σ- iminoxy-radicals, *viz. syn*-PhCH:NO•, a_N 29·2; *anti*-PhCH:NO•, a_N 31·6; Ph_2C:NO•, a_N 31·4. In support of this, our theoretical calculations (CNDO/2) on the parent radical, HN:NO• and the related CH_2:NO, show that these should exist as σ-radicals.

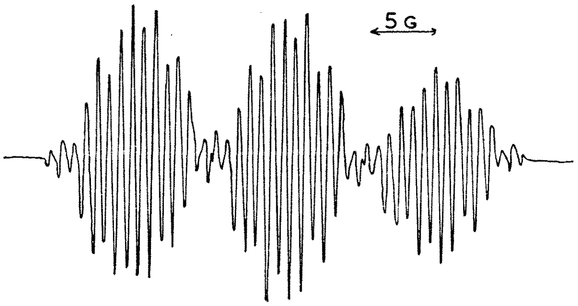

FIGURE 1. *Signal from NNA in benzene, apparently due to* PhNAc·NPh·O• (*modulation amplitude* 0·04 *gauss*).

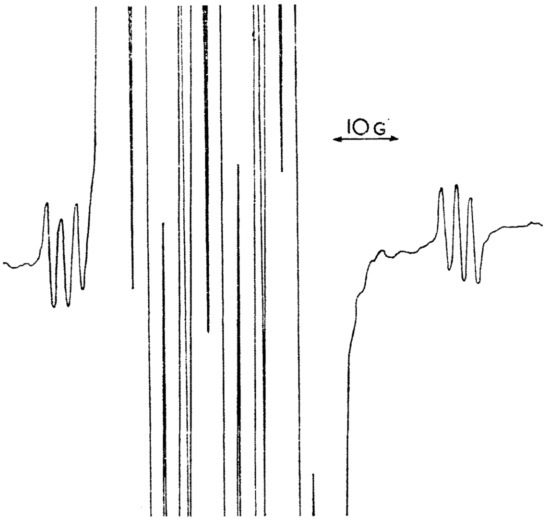

FIGURE 2. *Remodulated signal recorded in Figure* 1, *showing the presence of radical* (III) (*modulation amplitude* 1·3 *gauss*).

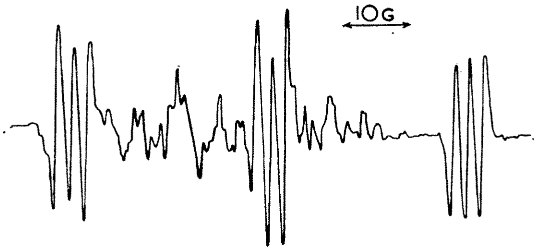

FIGURE 3. *Signal due to radical* (III) *from NNA in mesitylene* (*modulation amplitude* 1·3 *gauss*).

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