Electron Donor–Acceptor Complexes – Key Intermediates in the Thermal and Photoinduced Reduction of Aromatic Nitro Compound in Donor Solvents

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Electron donor–acceptor (EDA) complexes are shown to be key intermediates in the photolysis and thermolysis of *sym*-trinitrobenzene and its chloro-substituted derivatives in methylbenzenes.

Photolysis of aromatic nitro compounds in homogeneous systems, with nitroxyl radicals as intermediates, is well documented in the literature.[1–5] Direct excitation of a nitro compound into the triplet state followed by hydrogen abstraction from a donor molecule is usually supposed to be the primary stage of the process:

$$\mathrm{Ar{-}NO_2(S_0)} \xrightarrow{h\nu} \mathrm{Ar{-}NO_2^*(S_1)} \qquad (1)$$

$$\mathrm{Ar{-}NO_2^*(S_1)} \longrightarrow \mathrm{Ar{-}NO_2^*(T_1)} \qquad (2)$$

$$\mathrm{Ar{-}NO_2^*(T_1) + CH_3{-}Ar'} \longrightarrow \mathrm{Ar{-}N(O^{\cdot}){-}OH + {}^{\cdot}CH_2{-}Ar'} \qquad (3)$$

Unstable "primary" Ar–N($\dot{\mathrm{O}}$)–OH and "secondary" Ar–N($\dot{\mathrm{O}}$)–OR radicals are recorded only at low temperatures.[5] On increasing the temperature they transform into more stable Ar–N($\dot{\mathrm{O}}$)–R radicals. It is essential that the same radicals are formed during thermolysis in analogous systems.[6]

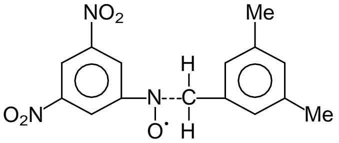
Aromatic nitro compounds, being good electron acceptors, are known to form EDA complexes with donor solvents.[7] However, to our knowledge, no relationship of these properties with photo- and thermal formation of radicals in such systems exists to date. At the same time, many other chemical reactions in homogeneous systems proceed through the excited state of EDA complexes.[8]

We have shown earlier[9] that formation of radicals stabilized on γ-Al_2O_3 during nitrobenzene reduction on surface donor sites of the catalyst proceeds through excitation of EDA complexes between active surface sites and adsorbed molecules. Photoreduction of aromatic nitro compounds in solution can also be supposed to result from excitation of EDA complexes and not from direct excitation of nitro compounds, as is usually considered to be the case.

This proposition could be substantiated by observation of a dependence of the photoreduction red edge on the ionization potential of solvents for any chosen nitro compound. In our study we used *sym*-trinitrobenzene (TNB), *sym*-trichlorotrinitrobenzene (TCTNB) and 1-chloro-2,4,6-trinitrobenzene (CTNB) as acceptors and methyl substituted benzenes as donor solvents.

Solutions (10^{-2} mol dm^{-3}) of the nitro compounds in toluene, *o*-xylene and mesitylene were irradiated with monochromatic light directly in the cavity of an "ERS-221" EPR spectrometer. A high pressure 1 kW mercury lamp was used as a light source, mercury lines being picked out with a monochromator.

During illumination of a TNB solution in mesitylene at 290 K radical particles were observed, and their spectrum is presented in Fig. 1 (*a*). According to refs. 4–6, they can be interpreted as nitroxyl radicals resulting from mesitylene addition to TNB:



Similar spectra were also obtained with *o*-xylene and toluene as solvents. EPR spectral parameters in all three solvents were almost identical with those obtained in a study[5] of TNB photolysis in toluene. A simulated spectrum is shown in Fig. 1 (*b*).

As has already been mentioned, substitution of the toluene donor molecule for mesitylene has practically no effect on the EPR spectra of the radicals. However, the red edge of the photoreduction is substantially shifted towards lower photon energies. The use of a stronger acceptor (TCTNB) produces the same effect (see Table 1). One should also note that the red edge for the radical formation process during CTNB photolysis is determined by the absorption of the EDA complexes and is not connected with the intrinsic absorption of this molecule near 3.0 eV observed in hexane solution.

Table 1 Dependence (eV) of the red edge for photoinduced formation of radicals on the ionization potential of solvents.

Acceptor	Toluene $I_\mathrm{p} = 8.78$ eV	*o*-Xylene $I_\mathrm{p} = 8.56$ eV	Mesitylene $I_\mathrm{p} = 8.40$ eV
TNB	3.4	3.04	2.85
CTNB	3.4	3.04	–
TCTNB	3.04	2.85	–

The results obtained testify that the photoreduction of nitro compounds in solution proceeds through excitation of EDA comlexes:

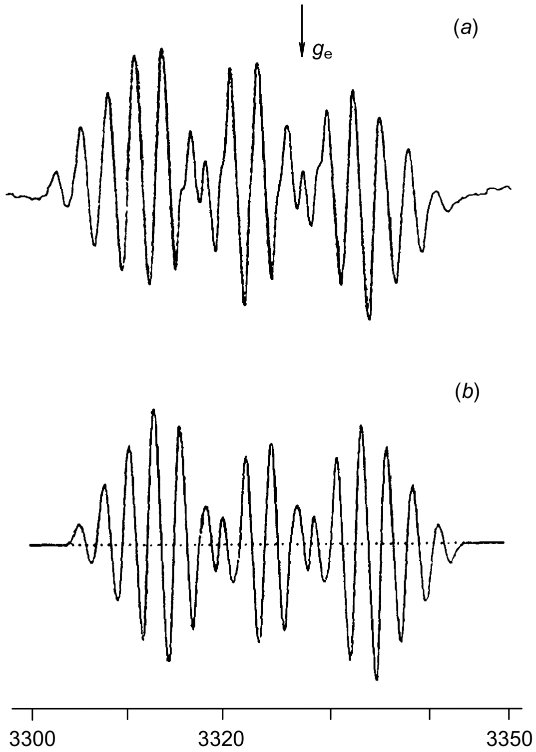


Fig. 1 EPR spectrum observed during photolysis of TNB in mesitylene at 295 K (*a*) and a simulated spectrum computed with the following parameters: $g = 2.0061$, $A_\mathrm{N}^1 = 9.52$ G, $A_\mathrm{N}^2 = 0.20$ G (two nuclei), $A_\mathrm{H}^1 = 5.36$ G (two nuclei), $A_\mathrm{H}^2 = 2.68$ G (three nuclei) (*b*).

$$\mathrm{NB} + \mathrm{D} \rightleftarrows [\mathrm{NB}\cdot\mathrm{D}] \overset{h\nu}{\rightleftarrows} [\mathrm{NB}^{-}\cdot\mathrm{D}^{+}]^{*} \longrightarrow \mathrm{R}^{\cdot} \qquad (4)$$

and not through direct excitation of the nitro compounds (reaction 1), as is usually considered to be the case.

As well as illumination, thermal treatment is also known to result in the excitation of EDA complexes.[7] So, reaction (4) can be expected to proceed at higher temperatures without illumination. We failed to observe TNB thermolysis in the solvents studied due to their low boiling temperature, so we therefore studied the TNB–hexamethylbenzene (HMB) system. Its thermolysis at 180–240 °C with the formation of radical intermediates was studied earlier.[6]

We managed to observe the same radicals produced by thermolysis and photolysis in this system (Fig. 2). The fact that similar radicals are formed strongly supports the supposition that thermal and photoinduced formation of nitroxyl radicals in this system follows an analogous mechanism that can be described as:

$$\mathrm{NB} + \mathrm{D} \rightleftarrows [\mathrm{NB}\cdot\mathrm{D}] \overset{h\nu, kT}{\rightleftarrows} [\mathrm{NB}^{-}\cdot\mathrm{D}^{+}]^{*} \longrightarrow \mathrm{R}^{\cdot} \qquad (5)$$

If the thermolysis really proceeds through the excitation of EDA comlexes then the ionization potential of donor molecules and the acceptor strength of nitro compounds must be the main factor influencing the activation energy of the process and so its temperature interval. With the donor fixed, the use of compounds with higher electron affinities should decrease the characteristic temperatures of the reaction.

Thermolysis of chloro-substituted trinitrobenzenes that are stronger acceptors than TNB in HMB was indeed shown to begin at substantially lower temperatures. For example, we observed equal concentration of radicals at 130 °C during CTNB thermolysis in HMB and at 170 °C in the case of TNB.

After HMB substitution with a weaker donor mesitylene no radicals were observed even with the strongest acceptor TCTNB at the temperatures available (mesitylene boils at 164 °C).

The results of this study make it possible to conclude that EDA complexes are key intermediates in the thermal and photoinduced reduction of aromatic nitro compounds in donor solvents.

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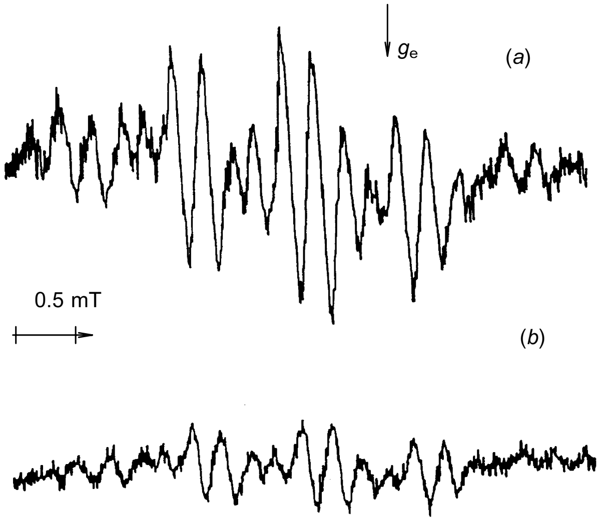

Fig. 2 EPR spectra obtained in TNB–HMB corresponding to stationary radical concentrations at 403 K under illumination $\lambda = 436$ nm (*a*) and in the dark (*b*).

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