

## Photochemical decomposition of triazenes. (Electron paramagnetic resonance study)

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### SUMMARY:

In the photochemical decomposition of triazene  $R-N=N-NR^1R^2$  in  $CH_3CN$  solutions, where R was (3-HOOC-, di-3,5-HOOC-, 4-HOOC-, 4-CN-)phenyl and  $R^1$ ,  $R^2$  were  $-CH_3$ ,  $-C_2H_5$ ,  $-CH(CH_3)_2$ ,  $-CH_2CH_2OH$ , the corresponding phenyl-substituted radicals were identified as 5,5-dimethyl-1-pyrroline N-oxide (DMPO) or  $(CH_3)_3CNO$  adducts. The reaction is described by a first-order kinetics with a half lifetime of 7 s. If R was di-3,5-CON<sub>3</sub>-C<sub>6</sub>H<sub>3</sub>-, a nitrogen-centred radical was found on radiation in the solid state as well as in  $CH_3CN$  solution with DMPO as spin trap.

### Introduction

Triazene, compounds with the functional  $-N=N-N<$  group, have found widespread use in chemical synthesis<sup>1)</sup>. Few cases are known in which triazenes have been used to start a radical polymerization<sup>2)</sup>. Recently triazenes have been applied for the promotion of polymer ablation by ultraviolet irradiation<sup>3-5)</sup>. Therefore, in a similar way as described previously<sup>6-8)</sup> for azo compounds, we investigated the photochemical behaviour of the aryldialkyltriazenes  $X^1X^2C_6H_3-N=N-NR^1R^2$  1-9 by a spin-trap technique presented in this paper (Tab. 1).

Tab. 1. List of aryldialkyl triazenes 1-9

$X^1X^2C_6H_3-N=N-NR^1R^2$	$X^1$	$X^2$	$R^1$	$R^2$
1	3-COOH	H	$-C_2H_5$	$-C_2H_5$
2	3-COOH	H	$-CH_3$	$-CH_2CH_2OH$
3	3-COOH	H	$-CH(CH_3)_2$	$-CH(CH_3)_2$
4	3-COOH	H	$-CH_2CH_2CH_3$	$-CH_2CH_2CH_3$
5	3-COOH	5-COOH	$-C_2H_5$	$-C_2H_5$
6	3-COOH	5-COOH	$-CH_2CH_2OH$	$-CH_2CH_2OH$
7	3-CON <sub>3</sub>	5-CON <sub>3</sub>	$-C_2H_5$	$-C_2H_5$
8	4-COOH	H	$-C_2H_5$	$-C_2H_5$
9	4-CN	H	$-C_2H_5$	$-C_2H_5$

## Experimental part

The investigated triazenes **1–9** were prepared from the corresponding substituted anilines via their diazonium salts which reacted then with the amines  $R^1R^2NH$  according to the procedure described in ref. <sup>9</sup>.

The solvents  $CH_3OH$ ,  $C_2H_5OH$ ,  $(CH_3)_2CHOH$ ,  $CH_3(CH_2)_3OH$ , benzene, acetone of p. a. degree were employed without further purification. The spin trap agent 5,5-dimethyl-1-pyrroline *N*-oxide from Sigma Chemicals was freshly distilled (0,5 mmHg and 75 °C) and stored at  $-25$  °C before use, nitrosodurene (3-nitroso-1,2,4,5-tetramethylbenzene) from TU Dresden and  $(CH_3)_3CNO$  from Sigma were used without further procedures.

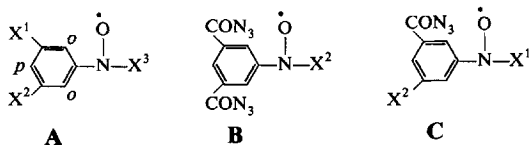
Because of very limited solubility, saturated solutions of substances **1–9** (first without, then with  $10^{-2}$  mol/L of spin trap) were prepared, flushed with argon, pumped into the standard tube (in non-polar) or flat cell (in polar solvents) and then irradiated directly in the cavity of the electron paramagnetic resonance (EPR) spectrometer with a high-pressure mercury lamp, without or with a pyrex glass filter cutting off the region below 330 nm.

The EPR spectra were recorded after an irradiation time of few seconds up to few minutes using a Bruker 200 D spectrometer operating in the X-band region, equipped with an Aspect 2000 computer.

## Results and discussion

No paramagnetic species were found in the pure solid samples of compounds **1–9**. If those were mixed with NaCl (otherwise they exploded) and then irradiated, the singlet spectra of radicals, with peak-to-peak widths of 1,5 mT and  $g = 2,0040$  were observed, in low concentrations from compounds **1**, **4**, and **7**. The radicals were stable for a few minutes. During irradiation the triazene samples were converted into a dark and insoluble residue.

Irradiation of samples **1–9** in various solvents, at 295 K or at lower temperature down to 100 K, generally, did not result in significant electron paramagnetic resonance (EPR) spectra. Only in the case of compound **7**, here already without irradiation, and increasingly after irradiation, a spectrum characterized by the splitting constants  $2 \times a_H^o = 0,36$  mT,  $a_H^m = 0,42$  mT,  $a_N(NO) = 1,29$  mT and a  $g$ -value of 2,0057 was found. The yield of radical increased in the presence of oxygen. The spectral data correspond well to the common structure of a nitroxyl radical described by formula **A**, where  $X^1$ ,  $X^2$  and  $X^3$  are EPR-silent substituents.



The splitting constants are assigned to the ortho- and meta-protons and to the nitrogen of the nitroxyl group, as specified above.

The conversion of substrate **7** to the nitroxyl radical type **A** is not obvious. Probably aminyl intermediates of **7** are involved, which terminate and are oxidized to nitroxyl

radicals. Two alternatives **B** and **C** may be suggested. To form structure **B** a splitting of the triazene group has to be assumed. A mesomeric form, suitable for such a fragmentation as well as splitting products corresponding to such aminyl ( $R_2N^*$ ) intermediates were described in ref.<sup>10</sup>. Also the splitting of an azido group  $N_3$  via aminyl products leading to structure **C** has been reported<sup>11</sup>. From our results no preference for alternative **B** or **C** can be elucidated.

Due to the short life time of the radicals produced in the photochemical decomposition of the investigated triazenes spin traps have been employed. A characteristic spectrum of the 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) adduct formed by irradiation of **8** in its methanol solution is shown in Fig. 1a. The splitting constants  $a_H = 2,175$  mT and  $a_N = 1,495$  mT extracted by the simulation and  $g = 2,0058$  confirm the addition of a carbon-centred radical to DMPO. Similar spectra were observed if substrates **1–9** were used in various solvents, except for substrate **7** (Fig. 1b). This will be discussed in a later section.

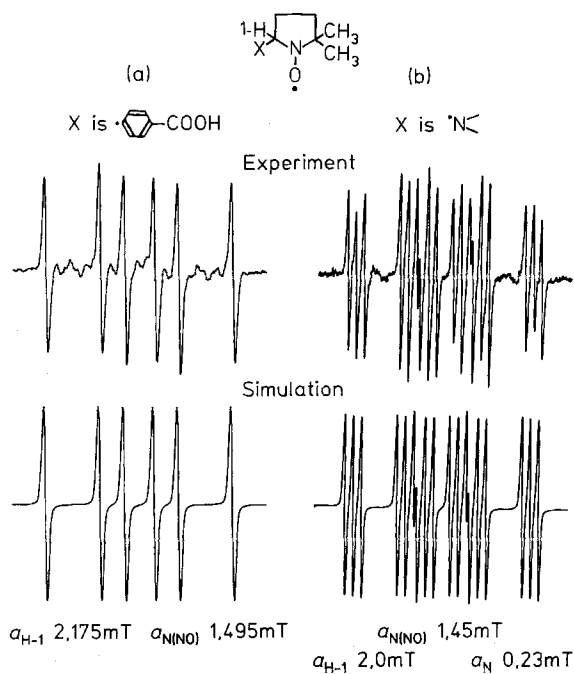


Fig. 1. Experimental and simulated electron paramagnetic resonance (EPR) spectra of 5,5-dimethyl-1-pyrroline-*N*-oxide adducts obtained by irradiation of compounds **1–4** (a) and **7** (b) in acetonitrile solutions

A closer description of the carbon-centred radical observed was possible if nitroso-durene (3-nitroso-1,2,4,5-tetramethylbenzene) was employed as spin trap. The so observed spectra are shown in Fig. 2a, b. From the hyperfine structure of the spectrum in Fig. 2a, with splitting constants  $a_H^m = 0,096$  mT,  $a_H^o(2) = 0,285$  mT,  $a_H^o = 0,306$  mT and  $a_N = 1,076$  mT indicate the presence of a meta-substituted phenyl adduct. This corresponds very well with the expected 3-HOOC-C<sub>6</sub>H<sub>4</sub> radical. In agreement with

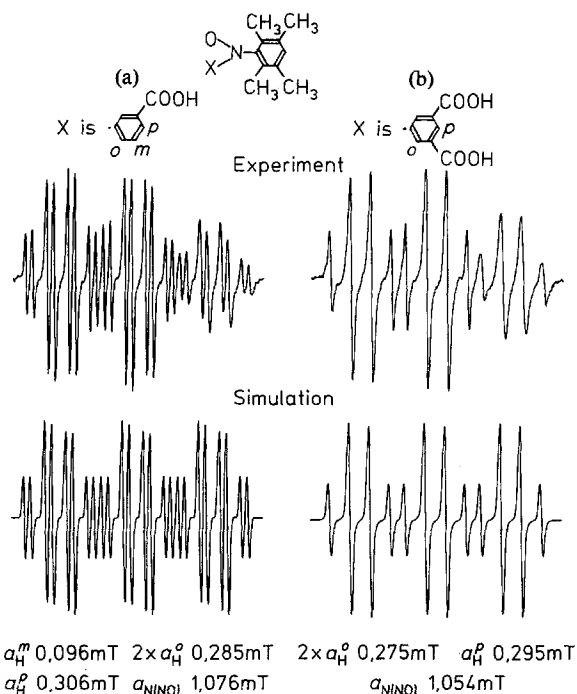


Fig. 2. Experimental and simulated electron paramagnetic resonance (EPR) spectra of nitrosodurene adducts obtained by irradiation of compounds 1–4 (a) and 5–7 (b) in acetonitrile solutions

this interpretation, equal spectra were observed from compounds 1–4. By decomposition of 5 and 6 in the presence of nitrosodurene a spectrum as shown in Fig. 2b was found. The splitting constants of two hydrogens with  $a_H^o(2) = 0,275$  mT, one hydrogen with  $a_H^p = 0,296$  mT and one nitrogen with  $a_N = 1,054$  mT correspond well with a di-3,5-HOOC—C<sub>6</sub>H<sub>3</sub><sup>•</sup>-radical added to nitrosodurene.

Radical products di-3,5-HOOC—C<sub>6</sub>H<sub>3</sub><sup>•</sup> and 3-HOOC—C<sub>6</sub>H<sub>4</sub><sup>•</sup> were also identified when (CH<sub>3</sub>)<sub>3</sub>CNO was employed as spin trap. However, the observed spectra were strongly superimposed by the one of [(CH<sub>3</sub>)<sub>3</sub>C]<sub>2</sub>NO formed from (CH<sub>3</sub>)<sub>3</sub>CNO during irradiation.

As already mentioned above for substrate 7 a spectrum depicted in Fig. 1b was found, indicating that the trapped radical is nitrogen-centred. The structural assignment of this radical, is more complex as there are more alternatives for its formation from compound 7. One alternative is the splitting off of N<sub>3</sub><sup>•</sup> from the —CON<sub>3</sub> group in the meta-position of the phenyl ring. This is not likely as the spectrum of N<sub>3</sub><sup>•</sup> trapped to DMPO is characterized<sup>[12,13]</sup> by a lower  $a_H = 1,6$  mT (2 mT here) and higher  $a_N = 0,3$  mT (0,23 mT here). Furthermore the elimination of N<sub>2</sub> from a CON<sub>3</sub>-group is well established according to the literature<sup>[12]</sup>. The data observed fit well with the aminyl adduct to DMPO<sup>[13,14]</sup>. There are more nitrogen-centred fragments from compound 7 possible such as (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>N<sup>•</sup>, 3,5-(N<sub>3</sub>OC)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N<sup>•</sup>X, 3-(N<sub>3</sub>OC)—,

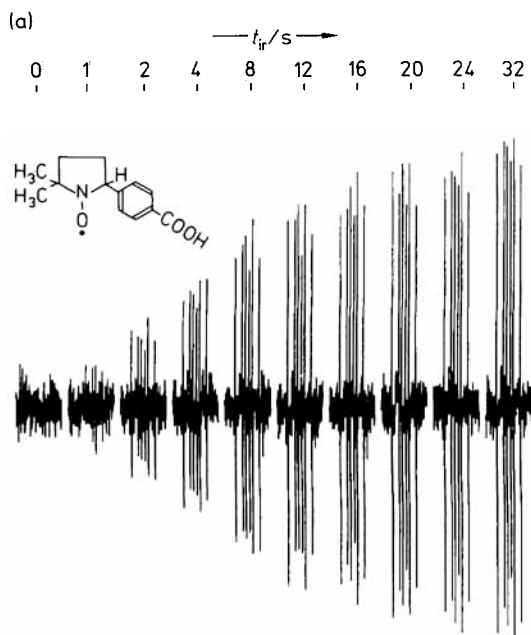
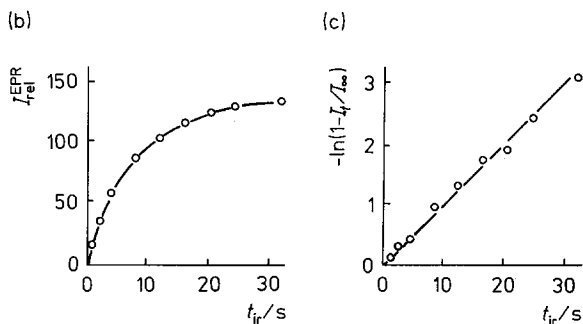
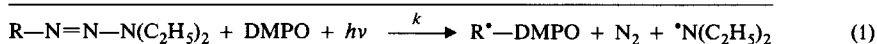
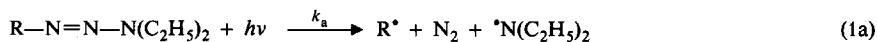


Fig. 3. Experimental spectra of 5,5-dimethyl-1-pyrroline *N*-oxide recorded after various irradiation times,  $t_{ir}$ , of **1** in acrylonitrile (a), the relative intensities of electron paramagnetic resonance (EPR) line,  $I_{rel}^{EPR}$ , plotted vs.  $t_{ir}$  (b) and logarithmic plot of  $1 - I_t^{EPR}/I_{\infty}^{EPR}$  vs.  $t_{ir}$  (c);  $t = \infty$  end of reaction



5-X—C<sub>6</sub>H<sub>3</sub>N<sup>+</sup>X, and eventually 3,5-di-N<sub>3</sub>OC—C<sub>6</sub>H<sub>3</sub>—N<sub>2</sub><sup>+</sup> or (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>N—N<sub>2</sub><sup>+</sup>, which are compatible with the adduct observed (X are unknown EPR-silent substituents).

The EPR spectrum already described in Fig. 1a was measured after various irradiation intervals as shown in Fig. 3a in order to estimate the kinetic parameters in the photochemical decomposition. As the line width remained constant during the whole experiment the relative peak heights,  $I_{rel}^{EPR}$ , are proportional to the adduct concentration [R<sup>+</sup>-DMPO], where R<sup>+</sup> stands for *m*-HOOC—C<sub>6</sub>H<sub>4</sub>. Relative intensities  $I_{rel}^{EPR}$  are shown as a function of the irradiation time  $t_{ir}$  in Fig. 3b. The reaction can be described by the following simplified scheme:



Reaction Eq. (1b) is rapid and the photochemical decomposition of  $\text{R}-\text{N}=\text{N}-\text{N}(\text{C}_2\text{H}_5)_2$ , considering only  $\text{R}^*-\text{DMPO}$  formation, was described by Eq. (1), where Eq. (1) = Eq. (1a) + Eq. (1b). The decay rate  $d[\text{R}-\text{N}=\text{N}-\text{N}(\text{C}_2\text{H}_5)_2]/dt$  is given by Eq. (2)

$$-d[\text{R}-\text{N}=\text{N}-\text{N}(\text{C}_2\text{H}_5)_2]/dt = d[\text{R}^*-\text{DMPO}]/dt = k[\text{R}-\text{N}=\text{N}-\text{N}(\text{C}_2\text{H}_5)_2][\text{DMPO}]\phi(\nu) \quad (2)$$

As  $\phi(\nu)$  was constant and sufficiently high, the initial concentration,  $[\text{DMPO}]_0$ , is few magnitudes higher than the radical concentrations  $[\text{R}^*]$  or adduct concentration  $[\text{R}^*-\text{DMPO}]$ , then Eq. (2) can be modified to Eq. (3)

$$d[\text{R}^*-\text{DMPO}]/dt = k'[\text{R}-\text{N}=\text{N}-\text{N}(\text{C}_2\text{H}_5)_2] \quad (3)$$

The stability of the  $[\text{R}^*-\text{DMPO}]$  adduct is sufficiently high to neglect its decay during irradiation. Then, the concentration  $[\text{R}-\text{N}=\text{N}-\text{N}(\text{C}_2\text{H}_5)_2]_t$  at time  $t$  was approximated by the adduct concentration  $[\text{R}^*-\text{DMPO}]_t$  at  $t$  and  $[\text{R}^*-\text{DMPO}]_\infty$  after the end of the reaction ( $[\text{R}-\text{N}=\text{N}-\text{N}(\text{C}_2\text{H}_5)_2]_t \approx [\text{R}^*-\text{DMPO}]_\infty - [\text{R}^*-\text{DMPO}]_t$ ) and Eq. (3) was reformulated to Eq. (4)

$$d[\text{R}^*-\text{DMPO}]_t/dt = k'([\text{R}^*-\text{DMPO}]_\infty - [\text{R}^*-\text{DMPO}]_t) \quad (4)$$

After integration of Eq. (4) and replacing  $[\text{R}^*-\text{DMPO}]$  by  $I^{\text{EPR}}$  with  $I_t^{\text{EPR}}$  for the irradiation time  $t_{\text{ir}}$  and with  $I_\infty^{\text{EPR}}$  for  $t_{\text{ir}} \rightarrow \infty$

$$\ln(1 - I_t^{\text{EPR}}/I_\infty^{\text{EPR}}) = k' \cdot t_{\text{ir}} \quad (5)$$

On quoting  $\ln(1 - I_t^{\text{EPR}}/I_\infty^{\text{EPR}})$  upon the irradiation time  $t_{\text{ir}}$  as shown in Fig. 3c, a linear dependence was found with a correlation coefficient  $r = 0,996$ , and the estimated half lifetime of the reaction is 7 s.

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