RADICAL INTERMEDIATES IN PHOTOCHEMICAL AND REDOX INITIATED DECOMPOSITION OF THIOAZO COMPOUNDS (AN EPR AND CYCLOVOLTAMMETRIC STUDY)

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The cathodically and photochemically induced decomposition of thioazo compounds $XC_6H_4–N_2–S–C_6H_4CH_3$ and their polymers with X = NO_2, COOH, and SO_3H were investigated. The formation of carbon-centered $XC_6H_4^{\bullet}$ and sulfur-centered $^{\bullet}S–C_6H_4Y$ radicals was confirmed using spin-trap technique. These reactive radicals either abstract hydrogen from CH_3CN solvent molecule forming $^{\bullet}CH_2CN$ radical or they recombine to cage products $XC_6H_4–S–C_6H_4CH_3$ eliminating N_2. The decomposition rate of the investigated thioazo compounds is characterized by a formal half-life time of 5 to 10 s.
Key words: Photolysis; Free radicals; Electrochemically initiated decomposition; Spin trap.

Thioazo compounds are relatively stable thermally, and consequently represent a suitable source of radicals in photochemically, electrochemically and redox-initiated radical reactions. Those radical reactions have been studied in detail, in particular polymers with pendant ArN=NSAr, ArSN=NAr (where Ar is for aryl) have been applied as polymeric initiators for grafting reactions[1,2]. Polymers with –N=NS– group in the main chain are of some interest as wall forming material of micro capsules and in the resist technology[3–5].

Therefore, the mechanism of fragmentation of thioazo compounds as well as the structure of radicals formed attract much attention. Suehiro and co-workers[6] investigated the formation and properties of aryldiazenyl radicals ($ArN_2^{\bullet}$) formed in the photolysis of thioazo compounds $Ar^1N_2SAr^2$ in cyclopropane at low temperatures (166 K) by

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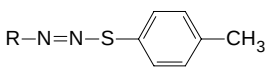
EPR. The present paper deals with the radicals generated in the photochemically and electrochemically initiated decomposition of thioazo compounds and their oligomeric analogues at 295 K. The radicals formed were identified by means of spin-trap technique.

EXPERIMENTAL

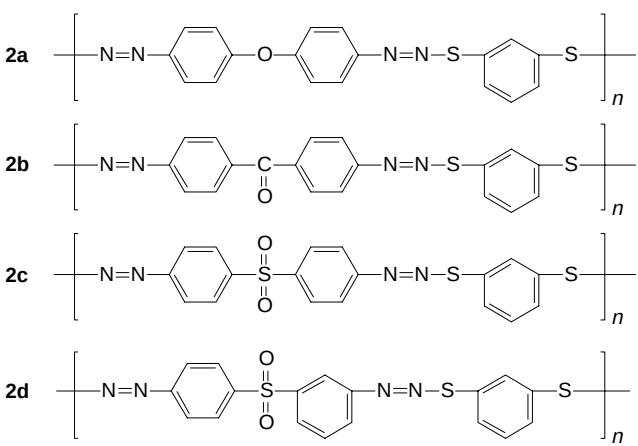
Materials. The investigated thioazo compounds **1** and their oligomer analogues **2** were prepared as described in refs[3,4]. The spin-trap nitrosodurene (ND) was obtained from Oklahoma Medical Research Foundation U.S.A.; 5,5-dimethylpyrroline-*N*-oxide (DMPO), tetrabutylammonium perchlorate (TBAP) and acetonitrile were purchased from Sigma.

Apparatus. The electrochemical investigations were performed in an electrolyte containing 0.001 mol l^{-1} substrate and 0.1 mol l^{-1} TBAP under argon. The cyclovoltammetric studies were carried out using platinum electrodes and an electrochemical system PAR 270 with saturated calomel electrode (SCE) as a reference. The surface of the working electrode was 4 mm^2. To investigate the radicals formed during the electrochemical redox reactions, the amperostatic electrolysis was carried out in an EPR spectrometer in a Varian electrolytic cell.

The photochemical investigations were also performed in a flat cell directly in the cavity of EPR spectrometer in acetonitrile solutions in the presence of spin trap. Medium pressure mercury lamp



1	R
a	4-$NO_2C_6H_4$
b	3-$NO_2C_6H_4$
c	2-$NO_2C_6H_4$
d	3-$(HO_2C)C_6H_4$
e	3,5-$(HO_2C)_2C_6H_3$
f	4-$(HO_3S)C_6H_4$



(Applied Photophysics, U.K.) with the radiation flux of 2.9 . 10^{-9} mol s^{-1}, measured directly in the EPR cavity by means of ferioxalate actinometry[7], served as an irradiation source. The wavelengths below 300 nm were cut off using a Pyrex filter 2 mm thick. In all investigations Bruker Spectrometer 200 D equipped with an Aspect 2000 computer was used to measure and to simulate the obtained EPR spectra.

RESULTS AND DISCUSSION

Electrochemical Measurements

Cyclic voltammetry. The cyclovoltammetric parameters for the forward ($E_{pc}^{\rightarrow}$) and reverse ($E_{pc}^{\leftarrow}$) scans are summarized in Table I.

Figure 1a illustrates the cyclic voltammograms obtained for azo compound **1c** and Fig. 1b for polymer **2c**. Most of compounds **1** showed one reduction peak in the potential region from –0.8 to –1.3 V, except for compound **1a** which exhibits two peaks and compound **1d**, for which no reduction peak was observed.

TABLE I
Peak potentials $E_{pc}^{\rightarrow}$, $E_{pa}^{\leftarrow}$ for forward and $E_{pc}^{\leftarrow}$, $E_{pa}^{\rightarrow}$ for reverse scan (in V) and the reversibility found in 0.001 mol l^{-1} solution of sample probe, 0.1 mol l^{-1} TBAP in acetonitrile and scan rate of 500 mV s^{-1}

Sample	$E_{pc}^{\rightarrow}$	Reversibility	$E_{pc}^{\leftarrow}$	$E_{pc}^{\leftarrow}$	$E_{pa}^{\leftarrow}$	Reversibility	$E_{pa}^{\rightarrow}$
1a	–0.887	irrev.		0.015	1.365	irrev.	0.207
	–1.258	[a]	–1.058		1.491	irrev.	
					1.808	irrev.	
1b	–1.126	[a]	–0.962	0.017	1.733	irrev.	
					1.943	irrev.	
1c	–1.303	[a]	–1.088	–0.023	1.878	irrev.	0.146
1d	–						
1e	–1.284	irrev.	–1.135		1.609	irrev.	
1f	–0.783	irrev.			1.693	irrev.	
2a	–1.077	irrev.			1.457	irrev.	
	–1.803	irrev.	–1.043				
2b	–0.907	irrev.	–0.487		1.161	irrev.	
	–1.450	irrev.	–1.212				
2c	–0.973	irrev.	–0.543		1.111	irrev.	
2d	–1.136	irrev.	–0.398		1.585	irrev.	
	–1.205	irrev.			1.905	irrev.	–0.186

[a] The contribution of consecutive product to the reverse peak strongly dominates.

The analysis and interpretation of cyclic voltammograms is complex. Considering the EPR spectra, which are in more details presented below, we suggest following explanation. The informations extracted from EPR data are summarized in Scheme 1 using compound **1a**. In the first reduction step an unstable anion radical of parent compound **1** is formed. It decomposes under N_2 elimination to radicals $O_2NC_6H_4^{\bullet}$ and $^{\bullet}S–C_6H_4CH_3$. They are very reactive and terminate either by abstraction of proton from solvent forming $O_2NC_6H_5$ or recombine to a cage product $O_2NC_6H_4–S–C_6H_4CH_3$. Both consecutive products were identified in EPR. Thus the cyclic voltammogram can be interpreted in a following way: The first cathodic peak represents the reduction of original azo compound. By the reverse scan only a negligible part of parent anion is present and the corresponding counter peak represents the oxidation of nitrobenzene anion formed as a consecutive product. The potential of the first reverse peak corresponds to the oxidation of nitrobenzene anion while the potential of second reverse peak can be assigned to the sulfur substituted nitrobenzene and consequently to the cage product $O_2NC_6H_4–S–C_6H_4CH_3$. Considering the data we have, the first reduction process cannot be classified as reversible. However, a plausible explanation for observed electrochemical behaviour cannot be given at present.

Thioazo polymers **2a**, **2b**, and **2d** undergo electrochemical reduction in two irreversible peaks in the potential region from –1 to –1.8 V. On the reverse scan a consecutive product was found at the potential shifted up to 0.70 V. The second peak apparently represents rapidly formed product and the peak observed at the reverse scan corresponds to its oxidation. Its limited stability is indicated by the scan rate dependent peak height ratio.

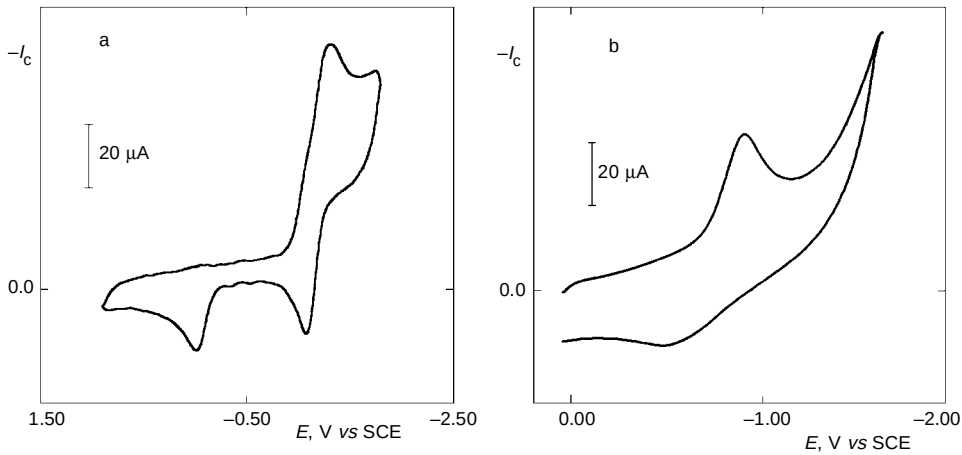
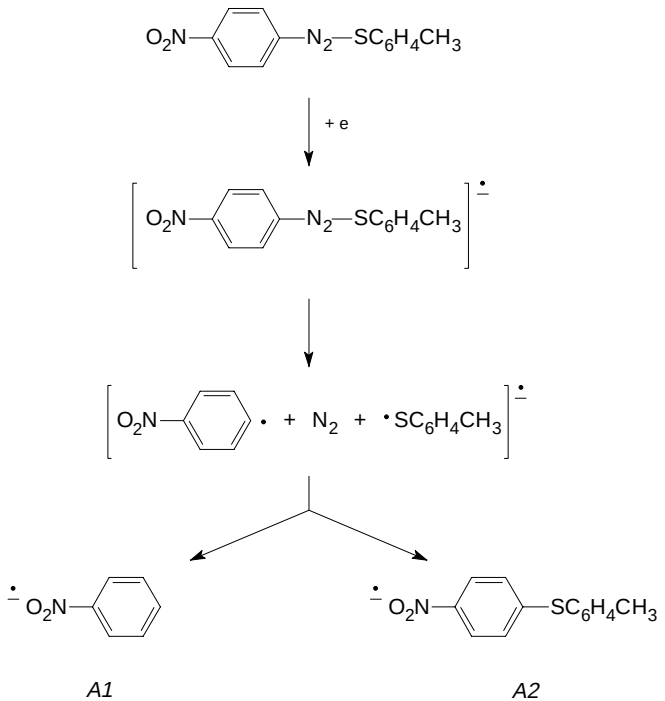


FIG. 1

The cyclic voltammograms obtained for compound **1c** a and **2c** b in 0.001 mol l^{-1} solution of sample, 0.1 mol l^{-1} TBAP acetonitrile solution with a scan rate of 500 mV s^{-1}

The cyclic voltammogram of polymer **2c** coresponds to an irreversible reaction characterized by only one cathodic peak at –0.973 V as shown in Fig. 1b.

The electrochemical oxidation of thioazo compounds **1** as well as polymers **2** is more complex. Almost all of them are irreversibly oxidized in the potential region from 1.1 V to 1.9 V yielding various numbers of peaks; oxidation of compound **1a** proceeds with 3 peaks, **1b** and **2d** with 2 peaks and the remaining compounds are oxidized in just one peak. No oxidation peak was found for compound **1d**. On the reverse scan an anodic peak shifted more than 1 V to negative potentials was observed for compounds **1a**, **1c** and **2d**, indicating consecutive products.



SCHEME 1

EPR investigations. The *in situ* EPR investigations with the resolution of minutes on time scale implied the formation of anion radicals of parent compounds **1a–1c** in the region of the first peak, but their spectra were increasingly superimposed with the spectra of further consecutive products. Therefore an unambiguous identification of the primary radical products by means of EPR spectroscopy was not possible. In the course of time, well resolved EPR spectra of two relatively stable consecutive products appeared.

The first one was simulated with g = 2.0045 and splitting constants $a_H(3,5)$ = 0.108 mT, $a_H(2,6)$ = 0.336 mT, $a_H(4)$ = 0.369 mT, $a_N(NO_2)$ = 1.042 mT and can be assigned to nitrobenzene anion radical according to similar reaction scheme as stated in our previous investigation[8].

In addition to it, after 10–20 min when the electrolysis was stopped, spectra of stable cage products survived as shown in Fig. 2a and 2b.

The experimental EPR spectrum of radical *A2* obtained from compound **1a** is shown in Fig. 2a. The spectrum was simulated with splitting constants given in Table II. Analogously, Fig. 2b shows spectrum of radical *A3* obtained from compound **1b** simulated with splitting constants summarized in Table II. The results indicate the formation of nitrobenzene anion radical with an EPR silent substituent in its *para* (*A2*) and *meta* (*A3*) position. Evidently, a cage product is formed after nitrogen elimination, and consequently, the corresponding R substituent is most probably 4-$H_3CC_6H_4S^{\bullet}$.

Noteworthy, in the case of radical *A2*, the considerable differences can be found in the non-equivalence of hydrogen nuclei $a_H(3,5)$ = 0.09 mT and 0.124 mT, $a_H(2,6)$ = 0.287 mT and 0.372 mT, indicating the hindered rotation of *para*-positioned substituents. This phenomenon is already described for anion radicals of nitrobenzenes substituted by oxygen in *para* position[9]. Such effect is less pronounced in the case of radical *A3* (Fig. 2) where the corresponding substituent is placed in the *meta* position. Similar behaviour was also observed for other azo compounds, but mixed spectra and limited stability prevented us from expanding these studies.

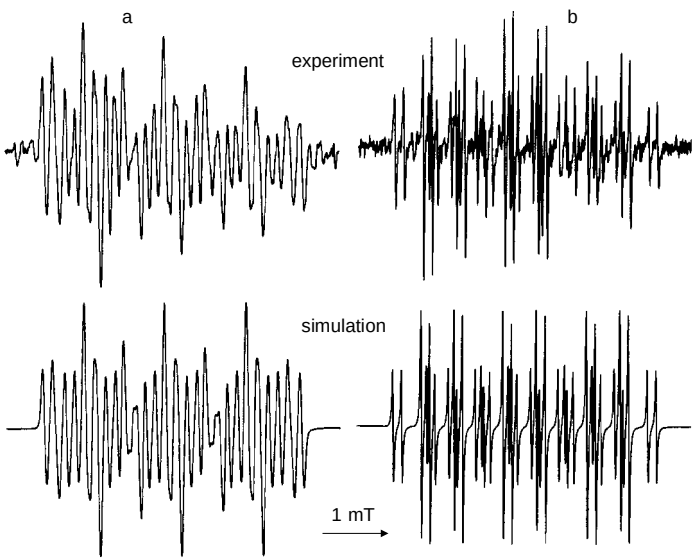
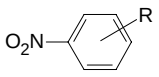
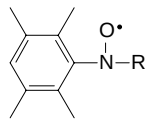


FIG. 2
EPR spectra of anion radical obtained in acetonitrile solution by electrolysis of **1a** a and **1b** b

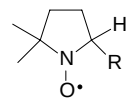
Also, there is the remarkable difference between the *g*-values of radicals *A2* and *A3* substituted with $-SC_6H_4CH_3$ in Fig. 2. The *meta*-substituted radical *A3* with $g = 2.0045$ has a characteristic *g*-value generally attributed to nitrobenzene anions, whereas $g = 2.0065$ of *para*-substituted anion radical *A2* is unusually high. This points to a significant participation of a sulfur atom on the distribution of unpaired spin density, and it also contributes to the hindered rotation mentioned above.

A 

	R
A1	-
A2	4-X_1
A3	3-X_2

B 

	R
B1	$NCCH_2$
B2	4-$CH_3C_6H_4S$
	3-XSC_6H_4S
B3	4-$(HO_3S)C_6H_4$
B4	3-$(HO_2C)C_6H_4$
B5	3,5-$(HO_2C)_3C_6H_3$
B6	3-$XSO_2C_6H_4$
B7	3-$XSO_2C_6H_4$

C 

	R
C1	C
C2	XS

Whereas compounds **1a–1c** gave defined well resolved spectra of their consecutive products, remaining reducible compounds **1e** and **1f** were EPR silent, possible due to their protolytic character.

The thioazo polymers **2** showed an irreversible behaviour both in electrochemical reduction and oxidation and no radical products were found in similar amperostatic EPR experiments as described for compounds **1**.

Photolytic Measurements

On irradiation of solid samples **1** and **2** and their solutions in acetonitrile, methanol or benzene in the EPR measurements *in situ*, no significant radical concentrations were observed. Therefore, further investigations were carried out in the presence of ND or DMPO spin traps.

A characteristic spectrum found by the irradiation of nitro substituted compounds **1a–1c** in the presence of ND spin trap is shown in Fig. 3a. From the simulation of superimposed spectra two radicals are evident. One spectrum with the splitting constants $a_H(CH_2) = 0.977$ mT, $a_N(NO) = 1.343$ mT and $g = 2.0061$ can be attributed to *B1* (Table II) and the second one, with $a_N = 1.63$ mT and $g = 2.0065$ attributed to adduct

B2 (Table II); similar parameters for such radicals are reported in the literature[10]. The stability of the sulfur-centered adduct was very limited with a half-life time $t_{1/2}$ = 3 s. In the background of the superimposed spectra (Fig. 3a) a rich hyperfine structure is evident, but due to the low concentration of the corresponding radical, its unambiguous identification was not possible. The formation of nitrophenyl adduct to ND is possible: Spectra similar to those found for **1a** were also observed by the irradiation of *meta*- and *ortho*- substituted probes **1b** and **1c**.

The EPR spectrum observed by the irradiation of sample **1f** is shown in Fig 3b. The results obtained here were similar to those yielded by the previous experiments with **1a–1c**. Radical adducts *B1* and *B2* (Table II) were also found here. Additionally a superimposed spectrum of *B3* adduct with splitting constants $a_H(3,5)$ = 0.106 mT, $a_H(2,6)$ = 0.283 mT and $a_N(NO)$ = 1.03 mT (Table II) was identified. Similar spectra were also obtained for compounds **1d**, and **1e**. The splitting constants for the corresponding adducts *B4* and *B5* obtained in the simulation are summarized in Table II.

The thioazo polymers **2** showed behaviour analogous to the monomer compounds **1**. Two characteristic EPR spectra observed due to the irradiation of polymers with *meta*- (**2d**) and *para*-substituted (**2b**), phenyl groups are shown in Fig. 4. In Fig. 4a, where the compound **2d** was used, an adduct *B6* was found in addition to *B1*. In Fig. 4b, using

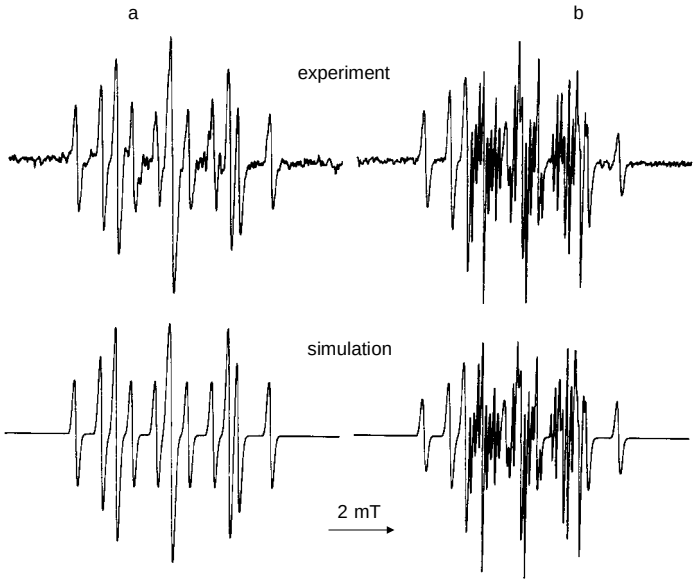


FIG. 3

Characteristic EPR spectra of $^{\bullet}$ND–R adducts found during the irradiation of acetonitrile solution in the presence of ND spin trap using compounds **1a–1c**, R = $CNCH_2$, 4-$CH_3C_6H_4S$ (a) and **1f**, R = $CNCH_2$, 4-$CH_3C_6H_4S$, and 4-$HO_3SC_6H_4$ (b)

compound **2b**, also *B2* and *B7* appeared in addition to *B1*. The spectral parameters of the corresponding adducts are summarized in Table II.

Additionally, we also carried out the photolytically induced decomposition of **1** and **2** in the presence of DMPO spin trap. In agreement with the above described results, EPR spectra of carbon-centered adduct *C1* with a_H = 2.182 mT, a_N(NO) = 1.484 mT and sulfur-centered adduct *C2*, with a_H = 1.482 mT and a_N(NO) = 1.34 mT were observed (Table II). The time evolution of the carbon-centered radical with the increased irradiation time in the case of probe **1e** is shown in Fig. 5. The reaction was completed after approximately 25 s and the resulting formal half life time was 5–10 s. Similar half-life times were found also for other compounds.

In previous investigations of thioazo compounds $R^1N_2SR^2$ described by Suehiro *et al.*[6], at 160 K (Scheme 2), R^1 was mostly represented with various substitutions of phenyl

TABLE II
Structure of radicals and their EPR parameters splitting constants in mT and *g*-values found in photolytically and electrochemically induced decomposition of thioazo compounds **1** and **2** in acetonitrile solutions

Compound	Splitting constants			Value	Generation method/from
A1	$a_N(NO_2)$ 1.042	a_H(2,6) 0.336 a_H(4) 0.369	a_H(3,5) 0.108	2.0045	+e/**1a**
A2	$a_N(NO_2)$ 0.782	a_H(2) 0.287 a_H(6) 0.372	a_H(3) 0.09 a_H(5) 0.124	2.0065	+e/**1a**
A3	$a_N(NO_2)$ 0.996	a_H(2,6) 0.335) a_H(4) 0.402	a_H(3) 0.105	2.0045	+e/**1b**
B1	a_N(NO) 1.343	$a_H(CH_2)$ 0.977		2.0061	irr./solv.
B2	a_N(NO) 1.630			2.0065	irr./**1**,**2**
B3	a_N(NO) 1.030	a_H(2,6) 0.283	a_H(3,5) 0.106	2.0059	irr./**1f**
B4	a_N(NO) 1.076	a_H(2,6) 0.285 a_H(4) 0.306	a_H(3) 0.096	2.0057	irr./**1d**
B5	a_N(NO) 1.054	a_H(2,6) 0.275 a_H(4) 0.295		2.0057	irr./**1e**
B6	a_N(NO) 0.999	a_H(2,6) 0.280 a_H(4) 0.285	a_H(3) 0.093	2.0057	irr./**2d**
B7	a_N(NO) 0.966	a_H(2,6) 0.277	a_H(3,5) 0.101	2.0057	irr./**2b**
C1	a_N(NO) 1.484	a_H 2.182		2.0057	irr./**1**,**2**
C2	a_N(NO) 1.340	a_H 1.482		2.0060	irr.**1**,**2**

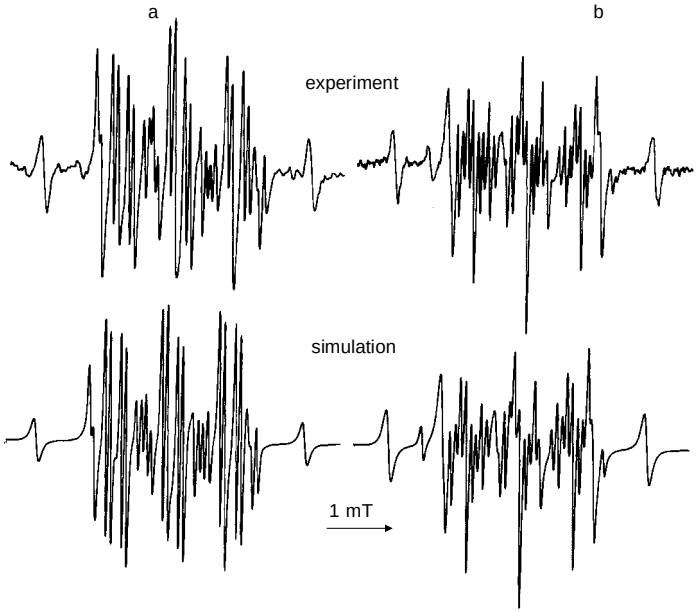


FIG. 4

Experimental and simulated EPR spectra of nitrosodurene adducts $^{\bullet}$ND–R obtained during the irradiation of acetonitrile solutions of thioazo polymers **2d**, R = $CNCH_2$, 3-XSO_2–C_6H_4 (a) and **2b**, R = $CNCH_2$, 3-XSC_6H_4S, and 4-$XCOC_6H_4$ (b)

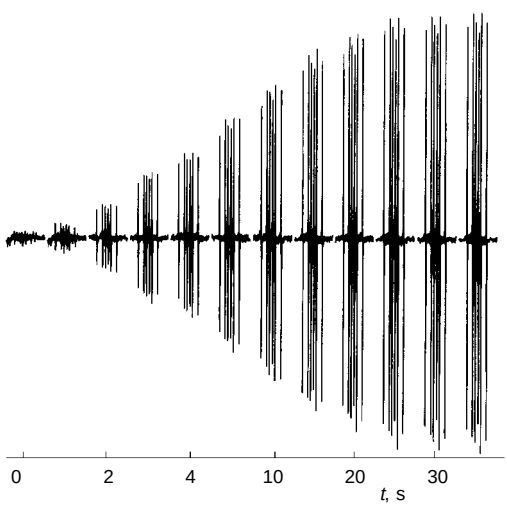
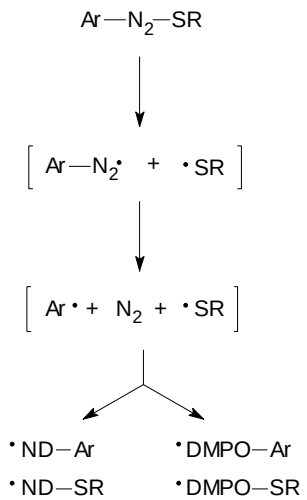


FIG. 5

The development of EPR spectra of $^{\bullet}$DMPOR adduct with the increased irradiation time using acetonitrile solution of sample **1e**. The simulation yielded following parameters: a_N(NO) = 1.484 mT and a_H = 2.182 mT. R in $^{\bullet}$DMPOR is carbon-centered radical

groups and R^2 was sulfur centered radical ($^{\bullet}S–C_6H_4CH_3$). The formation of aryldiazenyl radicals $ArN_2^{\bullet}$ confirmed non-symmetric splitting as a primary step. According to our investigations carried out at 298 K, this primary step is coupled with a rapid decomposition of the aryldiazenyl radicals according to the Scheme 2: The formation of the assumed radicals was confirmed in our investigations with the observation of the corresponding radical adducts: $^{\bullet}$ND–Ar, $^{\bullet}$ND–SR and $^{\bullet}$DMPO–Ar, $^{\bullet}$DMPO–SR.



SCHEME 2

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