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Photochemically and Electrochemically Initiated Radical Decomposition of Sulfonium Salts (A Spin Trap Study)

Andrej Staško*, **Peter Rapta, Vlasta Brezová,**

Faculty of Chemistry, Slovak Technical University, SK-812 37 Bratislava, Slovakia

Oskar Nuyken[a] **and Rainer Vogel**

Macromolecular Chemistry, University Bayreuth, D-8580 Bayreuth, Germany

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Abstract: Sulfonium salts $R^1 R^2 R^3 S^+A^-$, where R^1, R^2, R^3 is C_6H_5-, *p*(Me-, ^{t}Bu-)C_6H_4-, $C_6H_5CH{=}CH$- and A^- is mostly BF_4^- or PF_6^- dissolved in acetonitrile are cathodically reduced in an irreversible one-electron step in the potential region from -1.3 to -1.6 V *vs.* saturated calomel electrode and form mainly phenyl, then $^{\cdot}CH_2CN$ from solvent and $^{\cdot}CHX^1CH_2X^2$ from support salt, radicals as identified by 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) and ^{t}Bu-NO spin traps. The UV irradiation initiates the decomposition of sulfonium salts with the formation of phenyl radicals. Further radical products identified are $^{\cdot}CH_2CN$ and $PhS^{\cdot}$ using DMPO and nitrosodurene spin traps.

Introduction

In aprotic medium, sulfonium cations, after one-electron transfer, are known to be rapidly cleaved into aryl or alkyl free radicals and sulfide, but radical intermediates were directly not identified so far. Various mechanisms of their cleavage are assumed as formation of π-ligand radical anion and sulfonium cation[1] or a synchronous electron transfer and bond cleavage[2]. At low temperature sulfuranyl radicals have been observed by EPR from the sulfonium cations in which a heteroatom was attached to sulfur[3]. By spin trap experiments alkyl and aryl radicals have been assumed, but identified only by indirect reduction processes[4]. In the photolysis of sulfonium salts, cage escape sulfide products[5] and acid formation in cage fragmentation-recombination reactions[6,7] are discussed. Evidence exists for $R_2S^{+\cdot}$ formation in the photolysis of sulfonium salts peresters[8] and photo induced cleavage with subsequent molecular rearrangement has been reported[9]. By pulse radiolysis within a resolution time of 0.1 μs, the $R_3S^{\cdot}$ radical was not observed[10] and in laser flash photolysis, cleavage products such as $Ph_2S^{+\cdot}$ were not found[11].

The aim of this work is to investigate the radical intermediates formed during the cathodic reduction as well as photolysis of new prepared sulfonium salts using various spin traps enabling to identify further radical intermediates. Choice of suitable experimental conditions enabled us selectively to trap Ph˙ intermediates.

Experimental Section

The investigated sulfonium salts listed in Table 1 were prepared as described[12]. The solvent, acetonitrile (ACN) of analytical purity, was dried over molecular sieves and then over P_2O_5 and vacuum distilled. Spin traps nitroso-*tert*-butane (^{t}BuNO) and nitrosodurene (ND) were commercial products from Aldrich. 5,5-dimethylpyrroline N-oxide (DMPO), purchased from Sigma, was freshly distilled at 75°C and 0.5 Torr and stored at -25°C before use. Phenyl sulfide, Ph_2S **(11)**, was a commercial product from Janssen Chimica and *tert*-butyl peroxide (TBP) was purchased from Fluka. Ph-S-CH=CHPh **(12)** was prepared as described[12].

The electrochemical reduction was performed in acetonitrile solutions containing 10^{-3} mol dm^{-3} of substrate and 10^{-1} mol dm^{-3} tetrabutylammonium perchlorate (TBAP) under argon. Investigations were carried out in an electrolytic cell using platinum working and platinum counter electrodes. Saturated calomel electrode (SCE) served as a reference electrode. Voltammetric curves were recorded with electrochemical system PAR 270.

In situ electrochemical EPR experiments were carried out in a Varian flat cell on a Bruker 200 D spectrometer on line with an Aspect 2000 computer. EPR spectra were simulated employing Bruker standard program.

In the photochemical experiments the ACN containing 10^{-3} mol dm^{-3} of substrate was saturated with argon and pumped into a flat cell and irradiated directly in a cylindrical cavity. A 500 W high pressure mercury lamp from Narva (Germany) with an in house constructed power supply was employed as the irradiation source. The cavity was continuously flushed with argon at 20°C to eliminate overheating of the cavity.

Results and Discussion

Electrochemical investigations

All of the previously listed sulfonium salts exhibited similar electrochemical behaviour. A representative cyclic voltammogram is presented in Fig.1 with an irreversible peak in the potential region of -1.5 V *vs.* SCE. The extracted cathodic peak potentials E_{pc} derived from cyclovoltammetric investigations are summarised in Table 1. According to their values the investigated substrates can be divided into two groups: i) structures **1-3** with triphenyl-sulfonium cation Ph_3S^+ have averaged value $E_{pc} \cong -1.55$ V, ii) structures **4-10** with diphenyl,phenyl-vinyl- sulfonium cation $Ph_2S^+CH{=}CHPh$, have $E_{pc} \sim -1.3$ V. The difference in E_{pc} corresponds well to the donor-acceptor properties of PhCH=CH- and Ph- groups.

Further electrochemical investigations were carried out in the cavity of the EPR spectrometer. No radical products were observed by the cathodic reduction at room temperature and at 240 K. Therefore, spin traps were employed. A limiting factor in their application was the low reduction potential resulting in the

Table 1. Sulfonium Salts prepared, their Cyclovoltammetric Cathodic Peak Potentials, E_{pc}, found in ACN Solutions (10^{-3} mol dm^{-3} TBAP, Pt electrode, SCE reference, scan rate 100 mV s^{-1}).

		$R^1 R^2 R^3 S^+ X^-$			
Substrate	R^1	R^2	R^3	X^-	$-E_{pc}$
1	C_6H_5	C_6H_5	C_6H_5	BF_4^-	1.52
2	C_6H_5	C_6H_5	C_6H_5	PF_6^-	1.58
3	C_6H_5	C_6H_5	C_6H_5	$CF_3SO_3^-$	1.55
4	C_6H_5	C_6H_5	$CH=CHC_6H_5$	BF_4^-	1.30
5	C_6H_5	C_6H_5	$CH=CHC_6H_5$	PF_6^-	1.30
6	C_6H_5	C_6H_5	$CH=CHC_6H_5$	$AsPF_6^-$	1.34
7	C_6H_5	C_6H_5	$CH=CHC_6H_5$	$SbPF_6^-$	1.28
8	C_6H_5	C_6H_4-*p*-^{t}Bu	$CH=CHC_6H_5$	BF_4^-	1.35
9	C_6H_5	C_6H_4-*p*-^{t}Bu	$CH=CHC_6H_5$	PF_6^-	1.36
10	C_6H_5	C_6H_4-*p*-Me	$CH=CHC_6H_5$	PF_6^-	1.36

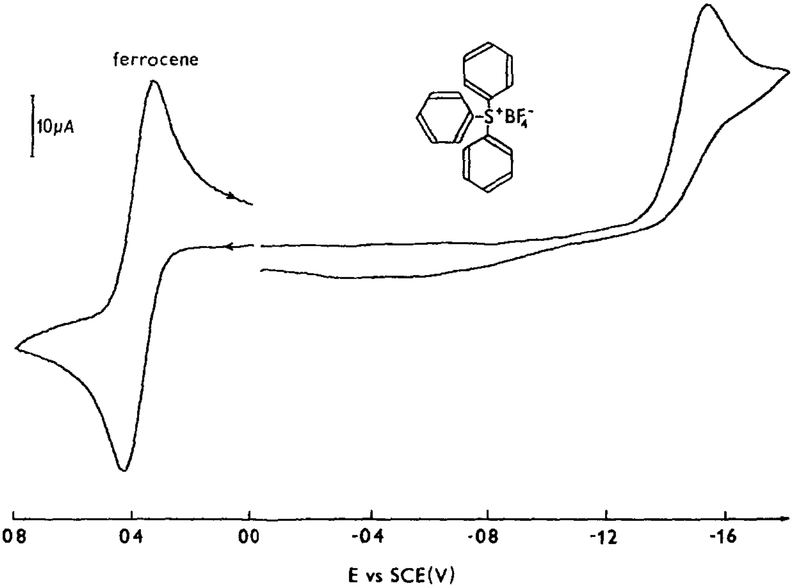

Fig.1. Cyclic Voltammograms of 0.001 M $Ph_3S^+BF_4^-$ and 0.001 M Ferrocene in 0.1 M TBAP ACN solutions. Potentials are referred in Volts *vs*. SCE.

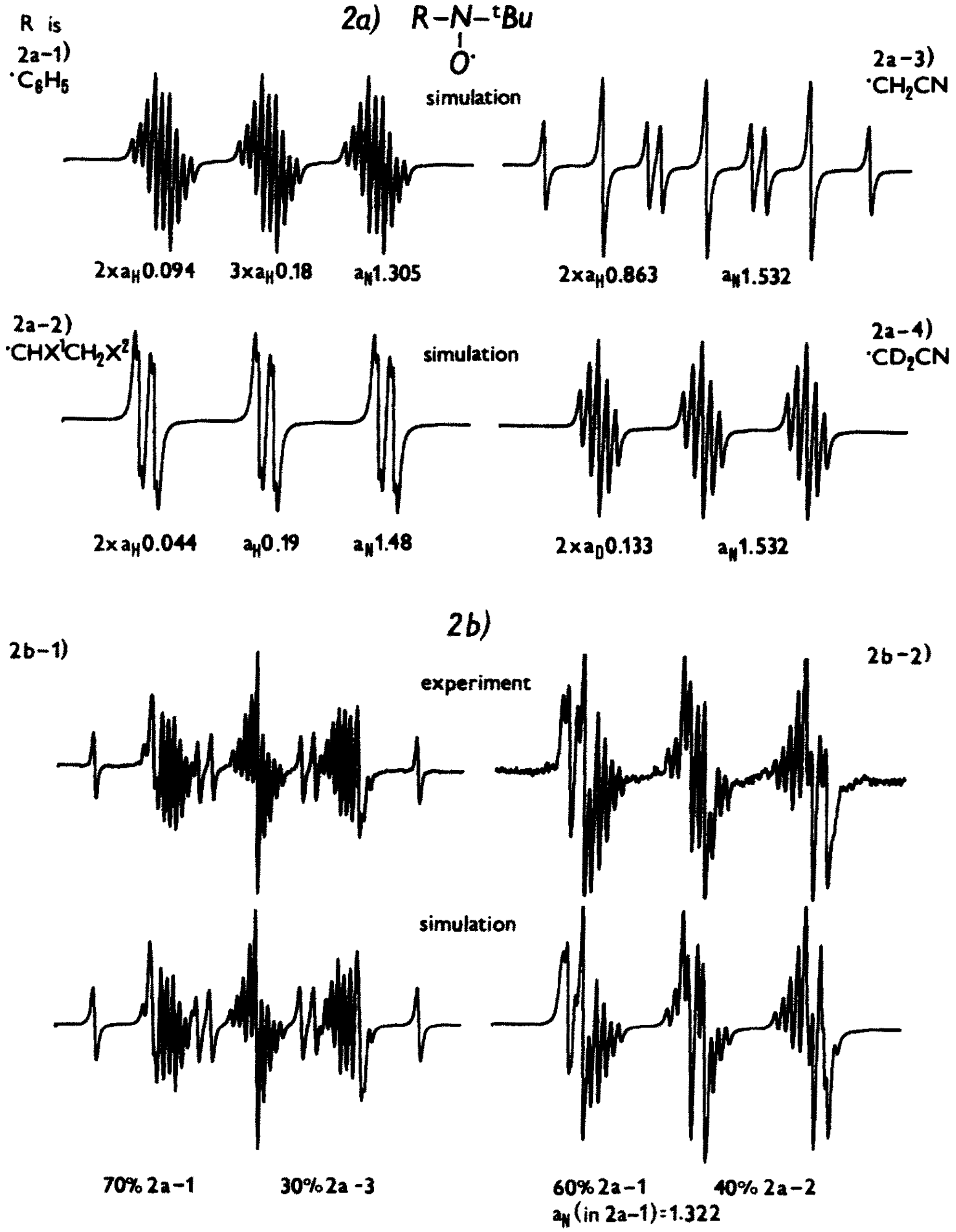

Fig.2. EPR Spectra observed by the Cathodic Reduction of $Ph_3S^+BF_4^-$ in ACN in the presence of ᵗBu-NO trap, 2a) Simulated Spectra of individual Spin Adducts, 2b) Experimental and Simulated Spectra of Radical Mixture employing $Ph_3S^+BF_4^-$ (b-1) or TBAP (b-2) as the Support Salt.

formation of their anion radicals. Thus in the case of nitrosodurene (ND) we were not able to eliminate its anion radical by an indirect reduction with 2,6-dinitro-anthracene as it was already suggested[4]. However, using the ${}^tBuNO$ spin trap, frequent, superimposed spectra were observed as illustrated in Figs.2b-1 and 2. The simulation extracted spectra of individual radicals are presented in Figs.2a1-4. The ratio of the radicals trapped depends on the concentration of the spin trap, nature of the solvent, the support salt employed and on the time of electrolysis. Generally, at the beginning of the electrolysis, in an excess of spin trap (${}^tBuNO$) whose concentration exceeding 0.01 M, the phenyl adduct prevailed with the spectrum as depicted in Fig.2a-1. The ratio of additional by-products depends on the type of support salt. The sulfonium salts, actually our substrate, in high concentrations can also function as a support salt. In such systems, on prolonged electrolysis, the spectrum of the phenyl adduct 2a-1 is increasingly superimposed with adduct 2a-3 as illustrated in Fig.2b-1. This further adduct with $a_N = 1.532$ mT and 2 x $a_H = 0.863$ mT (g=2.0066) was assigned to CH_2CN- ${}^tBuNO^{\cdot}$ where ${}^{\cdot}CH_2CN$ is formed from the solvent by H-abstraction initiated by the radical intermediates generated during the electrolysis. This was confirmed when CD_3CN was used as solvent. The spectrum shown in Fig.2a-4 was observed and simulated on replacing 2 x $a_H = 0.863$ mT in 2a-3 by the deuterium parameters (2 x $a_D = 0.133$ mT). If TBAP was used as a support salt, adducts 2a-3 and 2a-2 (Fig.2a-2) were formed in addition to 2a-1. The experimental and simulated superimposed spectra of 2a-1 and 2a-2 are shown in Fig.2b-2. The splitting constants of adduct 2a-2 with $a_H = 0.19$ mT, 2 x $a_H = 0.044$ mT and $a_N = 1.48$ mT, (g=2.0067) according to the literature[13] correspond well to the radical ${}^{\cdot}CHX^1CH_2X^2$ added to ${}^tBuNO$, where X^1 and X^2 are phenyl or alkyl groups which are EPR silent in this structure. Formation of 2a-2 was observed only in the presence of TBAP or other tetraalkylammonium support salts with longer alkyl chains (e.g. tetraoctylammonium). The radical ${}^{\cdot}CHX^1CH_2X^2$ is probably formed from alkyl of Bu_4N^+ in the reaction with electrolytically generated intermediates from sulfonium. The reaction mechanism is not obvious, but this assumption is supported by the following observation. The adduct is not observed if alkyl R in R_4N^+ is Me- or Et- or if a support salt like $Ph_3S^+X^-$ was employed. In all cases, the formation of radicals like ${}^{\cdot}CHX^1CH_2X^2$ from R is hardly possible. It is worth while to mention that the splitting constant $a_N = 1.305$ mT (spectrum 2a-1) of the phenyl adduct with ${}^tBuNO$ increased to $a_N = 1.322$ mT (spectrum 2b-2) in an experiment in the presence of TBAP.

The formation of a further adduct, with spectral parameters $a_N = 1.474$ mT, $a_H = 0.285$ mT, was observed in all electrolytic experiments at very advanced stages of electrolysis and is assumed to be a modified product of ${}^tBuNO$ spin trap.

Photochemical investigations

On the irradiation of solid samples or their solutions, no EPR spectrum was observed at the room temperature and 240 K. Therefore, the solutions were irradiated in the presence of the spin trap agents. Fig.3b illustrates the superimposed experimental spectra of DMPO and ND adducts along with their simulation and Fig.3a shows the simulated spectra of the individual radicals employed in simulation of Fig.3b. DMPO forms two adducts (Fig.3b-1). The first adduct, observed immediately upon initiation of irradiation, with $a_N = 1.44$ mT, $a_H = 2.124$ mT and g = 2.0059, is evidently a carbon centred radical. Detailed specifications are given below. The second adduct, whose concentration was increased at an advanced stage of photolysis, has the following parameters: $a_N = 1.342$ mT, $a_H = 1.482$ mT, g = 2.0062 and half-life $t_{1/2} = 1.4$ s. It was assigned to the sulfur centred radical ($PhS^{\cdot}$) according to[14] and according to our additional

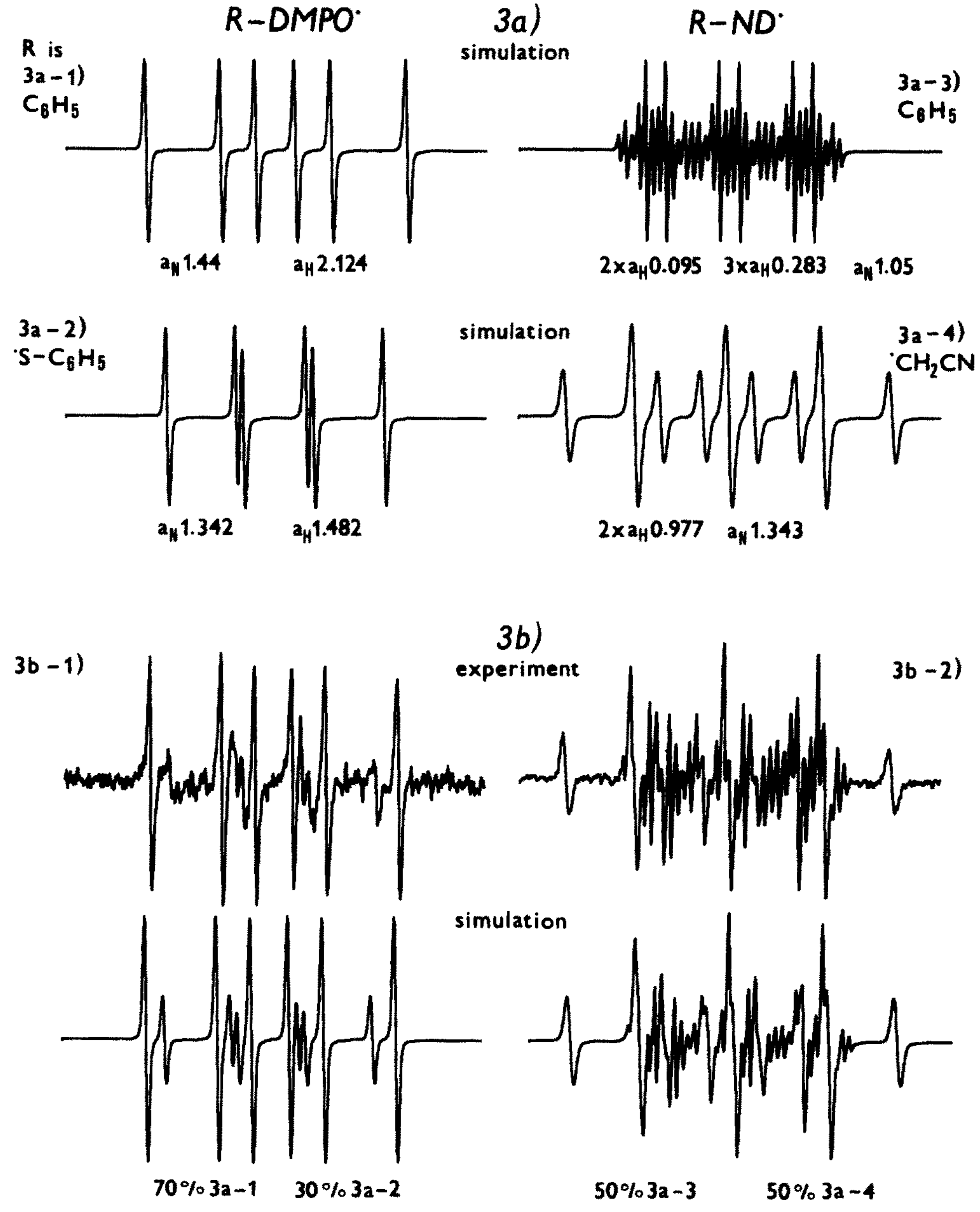

Fig.3. EPR Spectra observed by the Photolysis of $Ph_3S^+BF_4^-$ in ACN employing DMPO and ND Spin Traps. 3a) Simulated Spectra of individual Spin Adducts, 3b) Experimental and Simulated Spectra of Radical Mixture employing DMPO (b-1) and ND (b-2).

experiments with Ph_2S described below. In a few cases, in the first stage of photolysis, a stable adduct with parameters a_N = 1.357 mT, a_H = 1.201 mT and g = 2.0060 was observed in low concentrations. The parameters are similar to oxygen centred radicals but its formation is not clear at this time.

Closer specification of the carbon centred radical in the DMPO adduct was elucidated in experiments with ND where EPR spectra shown in 3b-2 were observed. They consist of two superimposed adducts 3a-3 and 3a-4. The first one, 3a-3, with a_N = 1.05 mT, $a_H^{o,o,p}$ = 0.283 mT, $a_H^{m,m}$ = 0.095 mT and g = 2.0058 is evidently phenyl adduct and the second one with a_N = 1.343 mT and 2 x a_H = 0.977 mT (g=2.0062) is $^{\cdot}CH_2CN$ adduct to ND as already identified in the electrochemical investigations above. The experiments with ND imply that to the spectrum of carbon centred adduct in Fig.3b-1 may contribute both $^{\cdot}$Ph and $^{\cdot}CH_2CN$ radicals. To clarify this, the following experiments were performed. The $^{\cdot}CH_2CN$ radical was photochemically generated in 0.1 mol dm^{-3} TBP acetonitrile solution. In the presence of ND, the CH_2CN-ND$^{\cdot}$ adduct was found, but in the presence of DMPO, no carbon centred radical was observed. If additional $Ph_3S^+BF_4^-$ was present in the DMPO system, a carbon centred radical as shown in Fig.3a-1 was found. Therefore, it may be concluded that the contribution to the carbon centred adduct in DMPO system originates from $^{\cdot}$Ph radical. This spectrum was used in the kinetic investigations of the $^{\cdot}$Ph formation as it will be described elsewhere.

Table 2. The EPR Parameters of Spin Adducts observed in Photochemically (hν) and Electrochemically (+e$^-$) Initiated Decomposition of Sulfonium Salts **1-10** and Sulfides **11,12** in ACN Solutions.

Spin Trap	Adduct	Splitting constants (mT)	Generation	Substrate
^{t}BuNO	$^{\cdot}$Ph	a_N 1.305 2 x a_H 0.094 3 x a_H 0.18	+e$^-$	1-12
^{t}BuNO	$^{\cdot}CH_2CN$	a_N 1.532 2 x a_H 0.863	+e$^-$	1-12
^{t}BuNO	$^{\cdot}CHX^1CH_2X^2$	a_N 1.48 2 x a_H 0.044 a_H 0.19	+e$^-$	1-12
^{t}BuNO	$^{\cdot}$X	a_N 1.474 a_H 0.285	+e$^-$	1-12
DMPO	$^{\cdot}$Ph	a_N 1.44 a_H 2.124	+e$^-$, hν	1-11
DMPO	$^{\cdot}$S-Ph	a_N 1.342 a_H 1.482	hν	1-12
DMPO	$^{\cdot}$X	a_N 1.357 a_H 1.201	hν	1-10
ND	$^{\cdot}$Ph	a_N 1.05 2 x a_H 0.095 3 x a_H 0.283	hν	1-11
ND	$^{\cdot}CH_2CN$	a_N 1.343 2 x a_H 0.977	hν	1-11
ND	$^{\cdot}$S-Ph	a_N 1.63	hν	11, 12

If substrate **1** (where R_3S^+ is Ph_3S^+) was exchanged e.g. by **4**, (where R_3S^+ is $Ph_2S^+CH=CHPh$), the same carbon centred radical (presumably $^{\cdot}$Ph) was observed with DMPO and the $^{\cdot}$Ph and $^{\cdot}CH_2CN$ adducts were identified with the ND trap. To obtain more information on the PhS$^{\cdot}$ and PhCH=CH$^{\cdot}$ intermediates, the photolysis with Ph_2S and Ph-S-CH=CHPh in the presence of DMPO and ND was carried out. By irradiation of Ph_2S in the presence of DMPO, the superimposed spectra shown in 3a-1 and 3a-2 (i.e. $^{\cdot}$Ph- and PhS-DMPO$^{\cdot}$ adducts) at the ratio about 1:1 were observed. In the presence of ND, three spin adducts were found with the ratio $^{\cdot}$Ph : $^{\cdot}CH_2CN$: PhS$^{\cdot}$ ≅ 1 : 1 : 10. The parameters of PhS-ND$^{\cdot}$ adduct are a_N = 1.63 mT,

$t_{1/2}$ = 0.6 s and g =2.0071. Irradiating the solution of Ph-S-CH=CHPh in the presence of DMPO, a carbon centred spin adduct with a negligible concentration (if compared with analogous Ph_2S solutions) was found and its splitting constants a_N = 1.455 mT, a_H = 2.173 mT are slightly different from those observed with Ph_2S (a_N = 1.43 mT, a_H = 2.115 mT). In experiments with ND and Ph-S-CH=CHPh, no phenyl, but only $^{\cdot}CH_2CN$ and $^{\cdot}PhS$ radicals with the ratio $^{\cdot}CH_2CN$: $PhS^{\cdot}$ ≅ 1:10 were observed. However, phenyl radicals were found in high concentration in Ph_2S system. This implies that the leaving group in Ph-S-CH=CHPh photolysis is the $^{\cdot}$CH=CHPh radical, but not detectable by the spin trap employed. The radical adducts observed in the electrochemical and photochemical experiments are summarised in Table 2.

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[a] new address: Macromolecular Chemistry, Technical University Munich, Lichtenbergstr. 4, D-8046 Garching, Germany