Photochemical Electron-Transfer Reactions between Sulfides and Tetranitromethane. Oxidation vs Fragmentation of the Sulfide Radical-Cation Intermediate

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Oxidation and/or *fragmentation* products are observed in the photochemical reaction of the alkyl phenyl sulfides **1a**−**d** with tetranitromethane (TNM). The product distribution depends markedly on the substrate structure. Thus, methyl phenyl sulfide (**1a**) and benzyl phenyl sulfide (**1b**) give only the corresponding sulfoxides (oxidation). However, when the radical cation **1b**$^{\bullet+}$ is generated by chemical oxidation with triarylaminium salts ($Ar_3N^{\bullet+}$) in acetonitrile, in addition to oxidation fragmentation is also observed, and with an excess of $Ar_3N^{\bullet+}$ oxidation is facilitated and no fragmentation is produced. For the photoreaction of diphenylmethyl phenyl sulfide (**1c**) with TNM, fragmentation is the main reaction, while for triphenylmethyl phenyl sulfide (**1d**) only this process is observed. The ease of C−S bond scission in these sulfur-centered radical cations **1**$^{\bullet+}$ follows the ease of alkyl cation formation, i.e., Ph_3C > Ph_2CH > $PhCH_2$ > CH_3.

Introduction

Oxidation of sulfides may be achieved by a variety of methods; the most common is the two-electron oxidation of the sulfur with concomitant atom transfer.[1] In contrast to this electrophilic substitution on the sulfur center, electron-transfer oxidation produces a sulfur radical cation as intermediate. These reactive intermediates, which are important in biochemical transformations,[2] can be generated in different ways: by electrochemical oxidation of sulfides,[3] by chemical oxidation with cerium(IV) ammonium nitrate (CAN),[4] $K_5CoW_{12}O_{40}$,[5] Mn(III),[6] Cr(VI),[7] cytochrome P-450,[8] peroxidases,[9] triarylaminium salts ($Ar_3N^{\bullet+}$),[10] and antimony pentachloride,[11] by radiolysis,[12] by photosensitized oxidation,[13] and by irradiation of the charge-transfer complex of sulfides with tetracyanoethylene (TCNE)[14] and tetranitromethane (TNM).[15] The latter novel oxygen-transfer process is illustrated for TNM in Scheme 1.

These reactions proceed through initial formation of a charge-transfer complex, followed by light-induced, dissociative electron transfer to lead to the triad of reactive species, namely the sulfide radical cation, the radical nitrogen dioxide, and the nitroform anion. Coupling of the two former and subsequent loss of nitrosyl cation gives the corresponding sulfoxide (pathway a oxidation, Scheme 2).

Alternative transformations of the sulfide radical cation are the pathways b−d in Scheme 2. In pathway b, C−S bond cleavage[16] occurs to produce a thiyl radical and a carbocation, the radical dimerizes to the corresponding disulfide **3**, and the cation is trapped by a nucleophile to give product **4**. During pathway c, C_α−H deprotonation to form a carbon-centered radical takes place, which after reaction with a nucleophile and oxidation gives product **5**. Finally, in pathway d, nucleophilic attack at the aromatic ring proceeds to form a carbon radical, which after oxidation and protonation results in product **6**.

In view of this complexity in the potential fate of the intermediary sulfide radical cations in such photoinitiated electron-transfer, oxidation of sulfide by TNM, it was of mechanistic interest to conduct a detailed product study for a related set of alkyl phenyl sulfides. For this purpose, the sulfides **1a**−**d** were chosen, in which the alkyl group comprises the series CH_3, $PhCH_2$, Ph_2CH, and Ph_3C, well suited for mechanistic elucidation of competitive reaction channels. Presently, we report the

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(16) For C−S bond cleavage of the (1-phenyl)ethyl phenyl sulfide radical cation, see ref 5.

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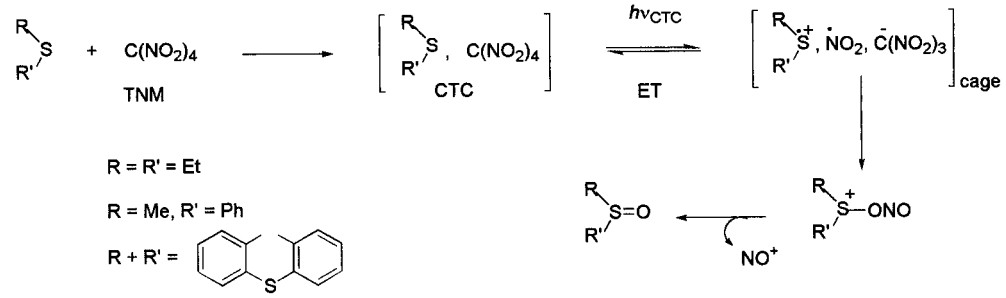
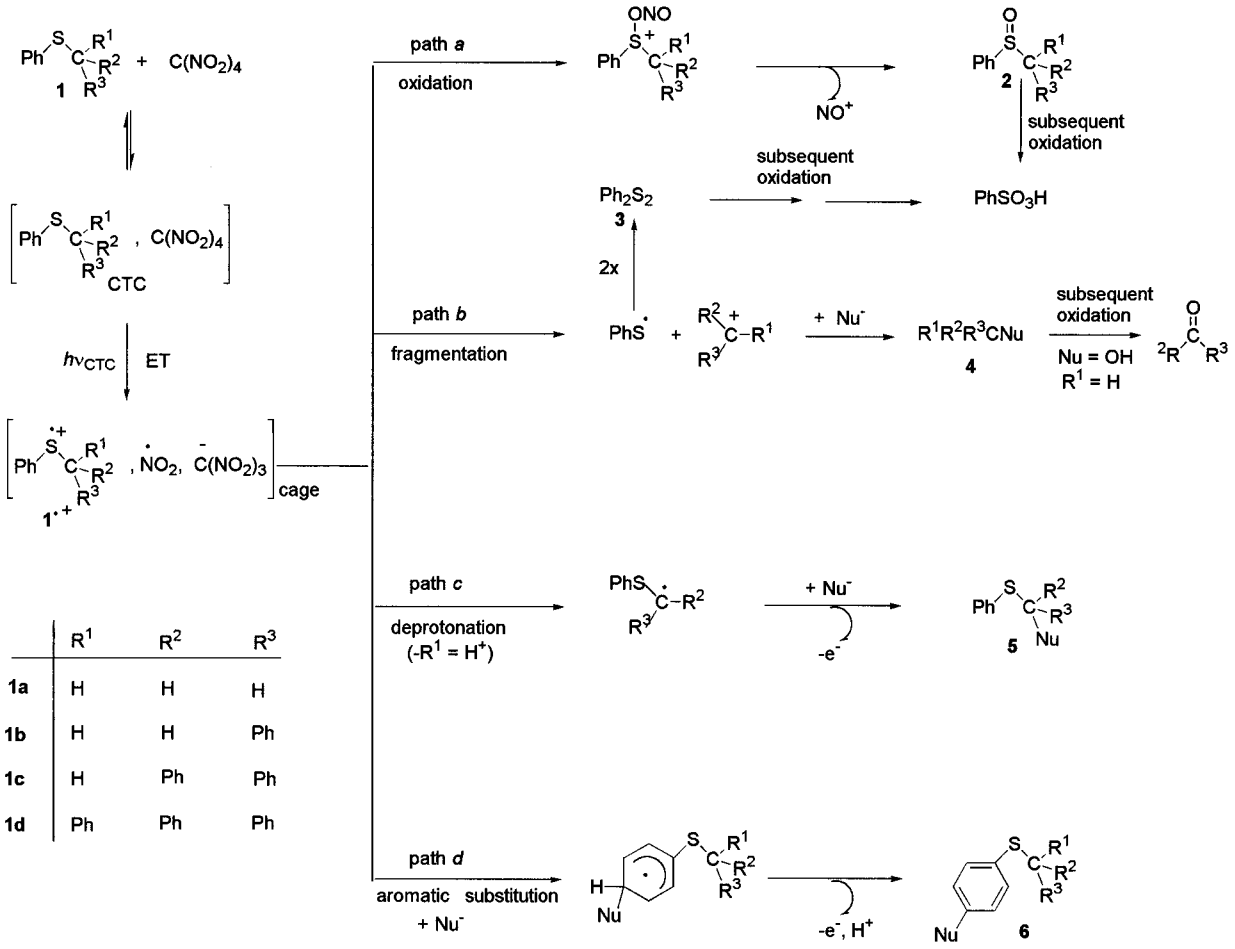
Scheme 1



Scheme 2



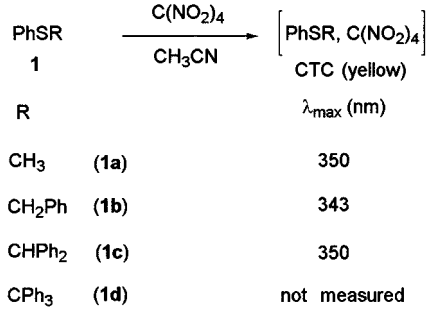
	R^1	R^2	R^3
1a	H	H	H
1b	H	H	Ph
1c	H	Ph	Ph
1d	Ph	Ph	Ph

details of this product study, which reveals that of the four possible reaction channels in Scheme 2 the sulfide radical cations compete effectively only between the oxidation pathway a and the fragmentation pathway b for this set of sulfides **1**.

Results

Photochemical Reactions of the Charge-Transfer Complexes. When TNM was added to a solution of the sulfides **1a**−**d** in acetonitrile (CH_3CN), a yellow color immediately developed (Scheme 3). The formation of the charge-transfer complex (CTC) was confirmed by UV−vis spectroscopy, which showed absorption bands with a maximum at 343−350 nm that extended to 550 nm. The solubility of **1d** was too low to detect the CTC. These results are in agreement with the data previously reported for the CT complex between TNM and sulfides.[15]

Scheme 3



R		λ_{max} (nm)
CH_3	**(1a)**	350
CH_2Ph	**(1b)**	343
$CHPh_2$	**(1c)**	350
CPh_3	**(1d)**	not measured

When a solution of the CTC was kept in the dark under an argon atmosphere, no products were observed. After irradiation of the CTC with a filtered mercury high-pressure lamp (150 W, short cutoff filter, $\lambda > 400$ nm), and aqueous workup, the products were isolated by silica

Table 1. Product Data for the Reaction of the Sulfides 1 with Tetranitromethane (TNM) and Control Experiments[a]

				product composition[b]				
				oxidation[c] (path a) **2**[e]	fragmentation (path b)[c]			
						$R^1R^2R^3CNu$ (**4**), Nu =		
entry	substrate	reaction conditions solvent, *t* (min), *T* (°C)	convn[d] (%) [MB (%)]		Ph_2S_2 (**3**) ($PhSO_3Na$)[f]	OH (Ph_2CO)[g]	$NHCOCH_3$	$C(NO_2)_3$
1	**1a**	CH_3CN, 90, −5	100[h] [100]	100				
2	**1b**	CH_3CN, 180, −5	91 [100]	91[i]				
3	**1b**	CH_3CN, 120, 40	100 [100]	100				
4	**1b**	CH_3CN, 180, −5[j]	0 [85][k]					
5	**1b**	CH_3CN, 5, −5[l]	50 [100]	17	33		21[m]	
6	**1b**	CH_3CN, 5, 25[l,n]	62 [92]	6	51		17[m]	
7	**1b**	CH_3CN, 30, 22[n−p]	65 [95]	62				
8	**1c**	CH_3CN, 180, −5	100 [100]		73	7 (6)	33	55
9	**1c**	CH_2Cl_2, 180, −5	100 [91]		17 (55)	(68)		23
10	**1c**	CH_2Cl_2, 30, 25[q]	17 [100]	6	9 (2)	12 (*r*)		<1
	1c	CH_2Cl_2, 60, 25	42 [100]	3	19 (20)	13 (*r*)		*r*
	1c	CH_2Cl_2, 120, 25	80 [100]	2	47 (31)	39 (*r*)		28
	1c	CH_2Cl_2, 180, 25	95 [100]	1	36 (58)	25 (*r*)		43
11	**1c**	CH_2Cl_2, 180, 25[s]	17 [88]	2	13	7 (5)		
12	**1d**	CH_3CN, 180, −5	100 [94]		94	90		
13	**1d**	CH_2Cl_2, 150, 0	100[h] [95]		37 (15)	81 (13)[t]		
14	**1d**	CH_2Cl_2, 150, 0[s]	37 [95]		24	35		
15	**2c**	CH_3CN, 180, 25	90 [85]	10	(38)	20 (5)	10	40
16	**3**	CH_2Cl_2, 60, 25	20 [70]		80 (14)			
17	**4c** (Nu = OH)	CH_2Cl_2, 180, 25	17 [99]			83 (16)		
18	**4d** (Nu = OH)	CH_2Cl_2, 60, 25	37[h] [22]			(6)[u]		
19	**4d** (Nu = OH)	CH_2Cl_2, 60, 25[v]	20[h,w] [20]					

[a] Performed under argon or nitrogen atmosphere; equimolar amounts of TNM and 0.1 M sulfide solutions were used; irradiations were performed at $\lambda > 400$ nm with a mercury high-pressure lamp (150 W). [b] The reaction products were quantified by isolation by silica gel chromatography unless otherwise indicated, absolute yields of isolated material (error 5% of stated values). [c] Cf. Scheme 2. [d] Conversion determined by quantification of the unreacted substrate, mass balance (MB). [e] $R^1R^2R^3CSOPh$. [f] Diphenyl disulfide isolated as subsequent oxidation product (in parentheses) (cf. Scheme 2). [g] Ph_2CHOH isolated as subsequent oxidation product (in parentheses) (cf. Scheme 2). [h] Quantified by gas−liquid cromatography, error 5%. [i] 9% of substrate **1b** was recovered. [j] TCNE as oxidant. [k] Recovered substrate, no product was detected. [l] $Ar_3N^{\bullet+}$ (Ar = 2,4-dibromophenyl) as oxidant. [m] Together with PhCOOH and PhCHO, these were not quantified. [n] Under air atmosphere. [o] $Ar'_3N^{\bullet+}$ (Ar′ = 4-bromophenyl) as oxidant. [p] In acetonitrile with 0.5% H_2O, oxidant:sulfide ratio of 2.4. [q] Reaction of $PhSCHPh_2$ (**1c**) with TNM monitored first after 30 min and then every 60 min, product composition evaluated by ^1H NMR spectroscopy, detection limit <1%. [r] Not quantified. [s] This reaction was performed with 0.17 equiv of TNM. [t] Together with <1% Ph_3CH. [u] Together with ca. 2% Ph_3CH. [v] In the absence of TNM. [w] Ca. 4% Ph_3CH as only product.

gel chromatography and identified by comparison with authentic samples or by spectral analysis. The product yields were determined by GC analysis, ^1H NMR spectroscopy, or by isolation (Table 1). In the aqueous layer, the presence of the nitroform anion was confirmed by UV−vis spectroscopy according to literature.[17]

Methyl Phenyl Sulfide (1a). The photochemical oxidation of sulfide **1a** by TNM was repeated in order to check previous results.[15] Indeed, 100% conversion to the corresponding sulfoxide **2a** was confirmed (Table 1, entry 1).

Benzyl Phenyl Sulfide (1b). Irradiation of a solution of sulfide **1b** with TNM in CH_3CN led to the corresponding sulfoxide **2b** in 91% yield and a recovery of 9% of the substrate (Table 1, entry 2). When this reaction was performed at 40 °C, the conversion to the sulfoxide **2b** was complete and no fragmentation products were observed (Table 1, entry 3).

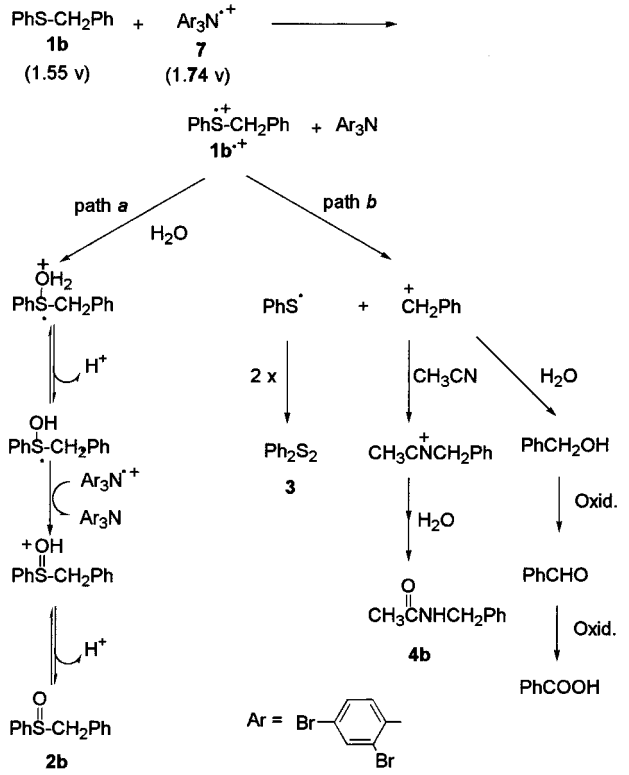
To test whether under other conditions the chemically generated radical cation of sulfide **1b** renders fragmentation products (pathway b, **Scheme 2**), we performed a number of alternative reactions. Thus, the dark-red charge-transfer complex between the sulfide **1b** and TCNE in CH_3CN, confirmed by UV spectroscopy (λ_{max} = 483 nm), was photochemically inert on irradiation at $\lambda > 400$ nm, since the starting materials were recovered by silica gel chromatography (Table 1, entry 4). If photochemical electron transfer has taken place for the CTC complex between this sulfide **1b** and TCNE,[14] presumably electron back-transfer is so efficient that diffusion out of the cage and subsequent product formation are suppresed.

When the radical cation **1b**$^{\bullet+}$ was generated by chemical electron transfer with stoichiometric amounts of triarylaminium hexachloroantimonates **7** (E_{ox} = 1.74 V vs NHE)[18] in CH_3CN at −5 °C under an argon atmosphere or at room temperature and in the presence of molecular oxygen, the main products (**Scheme 4**) were the sulfoxide **2b**, diphenyl disulfide (**3**), and benzylacetamide (**4b**, Nu = CH_3CN), with benzaldehyde and benzoic acid as the minor products (Table 1, entries 5 and 6). Thus, the main transformation is the fragmentation of the radical cation intermediate (pathway b, Scheme 2), which increases as the temperature rises. However, the reaction of sulfide **1b** with an excess of the aminium salt (2.4 equiv) in CH_3CN and the presence of $NaHCO_3$ as a base gave only the sulfoxide **2b** (Table 1, entry 7), i.e., oxidation (pathway a, Scheme 2).

Diphenylmethyl Phenyl Sulfide (1c). Irradiation of a solution of sulfide **1c** and TNM in CH_3CN at −5 °C led to a complex product mixture (Table 1, entry 8), with diphenyl disulfide (**3**), $Ph_2CHNHCOCH_3$ (**4c**, Nu = CH_3CN), and $Ph_2CHC(NO_2)_3$ (**4c**, Nu = $(NO_2)_3C^-$) as major and Ph_2CHOH and Ph_2CO as minor products. Thus, for this substrate, fragmentation of the radical cation (pathway b, Scheme 2) prevails since not even traces of the sulfoxide **2c** were detected.

(17) Sankararaman, S.; Haney, W. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 7824.

Scheme 4



In dichloromethane (Table 1, entry 9), the amount of benzophenone considerably increased and sodium benzenesulfonate was also present. The Ph_2S_2 was found to be consumed in this reaction medium, with a recovery of only 17%. The product distribution of this reaction was time-monitored by NMR spectroscopy (Table 1, entry 10). Thus, the sulfoxide **2c** was detected at shorter reaction times and its concentration decreased as the reaction proceeded with simultaneous increase of the amount of sodium benzenesulfonate, as subsequently oxidized product. Also, the yields of Ph_2S_2 and Ph_2CHOH decreased with time. In contrast, in the reaction of sulfide **1c** with a catalytic amount (0.17 equiv) of TNM, 17% of conversion and a good mass balance were observed to afford traces of the sulfoxide **2c**, the Ph_2S_2 as major product, together with Ph_2CHOH and benzophenone (Table 1, entry 11). These results indicate that also under these conditions the fragmentation of the radical cation prevails, but some oxidation takes place in dichloromethane (pathways a and b, Scheme 2).

Triphenylmethyl Phenyl Sulfide (1d). Irradiation of a solution of sulfide **1d** and TNM in CH_3CN gave only the fragmentation products (pathway b, Scheme 2) diphenyl disulfide (**3**) and triphenylcarbinol (**4d**, Nu = OH), isolated by silica gel chromatography (Table 1, entry 12). In the nonpolar dichloromethane, besides the expected products **3** and **4d** (Nu = OH), benzophenone and sodium benzenesulfonate were also found (Table 1, entry 13). Moreover, traces of triphenylmethane and $PhS(O)_2SPh$ were detected by GC−mass spectrometry. In the reaction of sulfide **1d** in CH_2Cl_2 with a catalytic amount (0.17 equiv) of TNM, 37% conversion was observed to afford products **3** and **4d**, but no benzophenone (Table 1, entry 14).

Product Stability. Some control experiments were carried out in order to check the stability of the products under the reaction conditions. The photosensitized reaction of the diphenylmethyl phenyl sulfoxide (**2c**) with TNM in CH_3CN (Table 1, entry 15) gave the products **4c** from diverse nucleophilic trapping of the diphenylmethyl cation and sodium benzenesulfonate (pathways a and b, Scheme 2). Further control experiments confirmed that diphenyl disulfide (**3**) and Ph_2CHOH were also oxidized by TNM in CH_2Cl_2 to benzenesulfonic acid (isolated as the sodium salt, Table 1, entry 16) and to benzophenone, respectively (Table 1, entry 17). When TNM is added to a solution of Ph_3COH in CH_2Cl_2, it remained colorless. After irradiation (Table 1, entry 18), benzophenone and triphenylmethane were obtained in low yields, whereas on irradiation in the absence of TNM (Table 1, entry 19), only triphenylmethane was found.

Mechanistic Discussion

The products observed in the photolysis of the charge-transfer complexes (CTC) between the sulfides **1** and TNM (Table 1) may be readily rationalized in terms of the sulfide radicals cation $\mathbf{1}^{\bullet+}$, generated together with the NO_2 radical and $(NO_2)_3C$ anion on electron transfer (Scheme 2). Of the possible competitive reaction pathways a−d for the sulfide radical cations, only the oxidation (pathway a) and fragmentation (pathway b) reactions apply under our conditions. Thus, we shall analyze mechanistically the trends in the product distribution (Table 1) in terms of the competition between these pathways as a function of sulfide structure and mode of electron transfer.

The radical cations $\mathbf{1a,b}^{\bullet+}$ gave only the sulfoxides **2a,b** as the oxidation products from geminate coupling with the NO_2 radical in the solvent cage (pathway a, Scheme 2), with no carbon−sulfur bond cleavage. Thus, for these derivatives such geminate coupling is very fast ($k \approx 10^8$−10^{10} M^{-1} s^{-1})[19] and suppresses effectively fragmentation of the radical cation $\mathbf{1}^{\bullet+}$ or diffusion from the cage. This is in contrast to previous reports that in the anodic oxidation of sulfide **1b** at 30−40 °C in CH_3CN, which contained 0.5% of water and lithium perchlorate, some (32%) fragmentation of the radical cation intermediate was observed, together with the sulfoxide **2b** as the main product (64%).[3a] In fact, under similar conditions, as much as a 74% yield of fragmentation products (only 26% of the sulfoxide **2b**) was reported for this substrate.[3b]

Products derived from both oxidation and fragmentation of the radical cation $\mathbf{1b}^{\bullet+}$ were obtained when sulfide **1b** was treated with stoichiometric quantities of triarylaminium hexachloroantimonates (Table 1, entries 5 and 6) as chemical electron-transfer agents. In analogy to the triarylamine-catalyzed anodic oxidation of sulfides,[10] the formation of the sulfoxide **2b** may be explained by nucleophilic attack of water (present in traces in the CH_3CN) on the sulfur-centered radical cation $\mathbf{1b}^{\bullet+}$ (pathway a, Scheme 4)[3c] and further oxidation by the triarylaminium salt. The diphenyl disulfide (**3**) and benzylacetamide (**4b**) derive from C−S bond fragmentation of the radical cation $\mathbf{1b}^{\bullet+}$ (pathway b, Scheme 4), in which the former arises from dimerization of the thiyl radical and the latter through the Ritter reaction of the benzyl cation with CH_3CN. The fragmentation process is completely suppressed when an excess of the triarylaminium salt is

(18) Schmidt, W.; Steckhan, E. *Chem. Ber.* **1980**, *113*, 577.
(19) Free Radicals; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, Chapters 2, 4, and 7.

used followed by trapping by H_2O, and the sulfoxide **2b** is the only product (Table 1, entry 7). Thus, the presence of an excess of aminium salts facilitate oxidation and the C−S bond cleavage in the sulfide radical cation **1b**$^{\bullet+}$ is not observed. These conditions in the chemical electron-transfer simulate the photochemical process for the **1b**/TNM charge-transfer complex (pathway a, Scheme 2) in that only oxidation to the sulfoxide **2b** is observed. Nevertheless, for the photoreaction, the oxidation is more effective because, after electron transfer, the oxygen-atom donor (NO_2) is directly present in the solvent cage.

The sulfide **1c** gave a complex mixture of fragmentation and oxidation products in the photochemical process, which depended on the solvent (Table 1). In CH_3CN, the photopersistent Ph_2S_2 (coupling of the PhS radicals) is indicative of the fragmentation process (pathway b, Scheme 2), which is the main reaction pathway. The benzhydryl cation fragment shows up as the nucleophilic trapping products **4c** [$Ph_2CHNHCOCH_3$, $Ph_2CHC(NO_2)_3$, Ph_2CHOH] and Ph_2CO. Some oxidation (pathway a, Scheme 2) to the sulfoxide **2c** (not observed) must have also taken place, but control experiments (Table 1, entry 15) revealed that **2c** is further oxidized and, thus, not persistent under these photochemical conditions. This problem is still more serious in CH_2Cl_2, for which it is difficult to recognize whether the fragmentation or the oxidation processes predominate because the primary products Ph_2S_2 and $PhSOCHPh_2$ are efficiently further oxidized under these reaction conditions. Besides TNM, also nitrosotrinitromethane, generated by coupling of the nitrosyl cation with the nitroform anion, may serve as additional oxidant for the primary products [**2c**, **3**, and **4c** (Nu = OH)].[15]

Finally, the sulfide **1d** gave only fragmentation products **3** and **4d** (Nu = OH) in acetonitrile. While these products persist under these reaction conditions, in dichloromethane they are further oxidized to sodium benzenesulfonate and benzophenone. The sodium benzenesulfonate derives from the oxidation of diphenyl disulfide through the intermediary $PhS(O)_2SPh$ (traces detected), as documented by the fact that sodium benzenesulfonate is a product of the electrooxidation of diphenyl disulfide.[3c] The benzophenone is presumably produced by oxidation of the carbinol **4d** (Nu = OH) by TNM, probably through β fragmentation of the corresponding Ph_3CO radical.[20]

Conclusions

Oxidation and/or *fragmentation* products (pathways a and b in Scheme 2) were observed in the photoreaction of sulfides **1** with TNM, and the relative proportions are given in Table 2. No products from deprotonation (pathway c) of the sulfide radical cation **1b**$^{\bullet+}$ intermediate were detected, a process which requires the presence of a base, as established in previous work.[3b] The fact that no nucleophilic substitution (pathway d) was observed on the aromatic ring suggests that the positive charge in the radical cation **1b**$^{\bullet+}$ is localized on the sulfur atom.

The product distribution depends markedly on the substrate structure. Thus, methyl phenyl sulfide (**1a**) and benzyl phenyl sulfide (**1b**) gave only the corresponding sulfoxides **2** (oxidation). For the methyl sulfide **1a**, the lack of C−S bond cleavage is expected, but for the benzyl derivative **1b** this suggests that in-cage coupling of the radical cation intermediate with the nitrogen dioxide radical is faster than diffusion. The other extreme represents phenyl triphenylmethyl sulfide (**1d**), for which exclusively C−S bond scission is observed presumably through dissociative electron transfer, as documented in its electrochemical oxidation.[3] Not surprisingly, for the diphenylmethyl derivative (**1c**) both pathways compete with the fragmentation as the main reaction. Thus, the driving force for the carbon−sulfur bond cleavage in the sulfide radical cation intermediate **1**$^{\bullet+}$ follows the stabilization of the carbenium ion produced through phenyl conjugation, i.e., the established sequence $CH_3^+ < PhCH_2^+ < Ph_2CH^+ < Ph_3C^+$, such that fragmentation process dominates in this order.

Table 2. Oxidation vs Fragmentation for the Photoinduced Electron Transfer of Sulfides 1 with Tetranitromethane (TNM)[a]

	product distribution[b] (%)	
sulfides	oxidation	fragmentation
$PhSCH_3$ (**1a**)[c]	100	0
$PhSCH_2Ph$ (**1b**)	100	0
$PhSCHPh_2$ (**1c**)	27[d]	73[e]
$PhSCPh_3$ (**1d**)	0	100

[a] In acetonitrile at −5 °C; irradiations were performed at $\lambda >$ 400 nm with a mercury high-pressure lamp (150 W) for 180 min, unless otherwise indicated. [b] Relative yields normalized to 100%, determined from the product data of Table 1. [c] Irradiation for 90 min. [d] The primary oxidation product $PhSOCHPh_2$ (**2c**) does not photopersist these reaction conditions; since the conversion was complete, the amount of oxidation was approximated as the difference between 100% conversion and 73% of fragmentation. [e] Yield of the photopersistent product Ph_2S_2 (**3**).

Experimental Section

General Methods. ^1H and ^{13}C NMR spectra were recorded on a Bruker 200 spectrometer, and all spectra are reported in δ (ppm) relative to Me_4Si, with $CDCl_3$ as solvent. Gas chromatographic analyses were performed on a Hewlett-Packard 5890 Series II with a flame-ionization detector and the data system Spectra Physics 4290 on a 5 m capillary column coated with methyl silicone gum of a 0.53 mm × 2.65 μm film thickness. The column chromatography was performed on silica gel (70−230 mesh ASTM). The UV spectra were recorded on a UV−vis recording spectrophotometer Shimadzu UV-260. Melting points were obtained on a Büchi 510 apparatus and are not corrected.

Materials. Tetranitromethane, tetracyanoethylene, methyl phenyl sulfide (**1a**), diphenyl disulfide, triphenylcarbinol, and benzophenone were commercially available (Aldrich) and used as received. CH_3CN (Merck) and CH_2Cl_2 (Merck) were dried according to standard procedures and stored over molecular sieves (4 Å). Benzyl phenyl sulfide (**1b**)[21] and diphenylmethyl phenyl sulfide (**1c**)[22] were synthesized by the reaction of the benzenethiolate anion, prepared from PhSH (Merck), and $PhCH_2Cl$ (Aldrich) or Ph_2CHCl (Aldrich) with potassium *tert*-butoxide (Fluka) in dimethylformamide (DMF) (Merck) at 25 °C for 30 min. Triphenylmethyl phenyl sulfide (**1d**)[23] was prepared by the reaction of PhSH with Ph_3Cl (Aldrich) in benzene under reflux for 1 h. The triarylaminium hexachloroantimonates salts were generated from the triarylamines and $SbCl_5$ according to the literature.[18] The products were identified by spectral comparison with authentic samples of the known compounds prepared by standard procedures. The

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sulfoxides $PhS(O)CH_2Ph$ (**2b**)[24] and $PhS(O)CHPh_2$[25] (**2c**) were synthesized by oxidation of the corresponding sulfides by H_2O_2 or CrO_3. $PhCH_2NHCOCH_3$[26] and $Ph_2CHNHCOCH_3$[27] were produced from the corresponding amines by acylation with acetic anhydride and sodium acetate.

Photoreaction of Sulfides 1b with TNM. General Procedure. The photochemical reaction was carried out in a 10-mL, three-necked Schlenk tube, equipped with argon or nitrogen gas inlets, a condenser with a cooling jacket, and a magnetic stirrer. The tube was charged with argon and then with 5 mL of dried CH_3CN, and 106 mg (0.5 mmol) of $PhSCH_2$-Ph (**1b**) and an equimolar amount of TNM were added. The reaction mixture was cooled to −5 °C and irradiated for 180 min at $\lambda > 400$ nm. The reaction mixture was treated with 10 mL of water and 30 mL of ethyl ether and the ethereal layer separated and submitted to GC analysis. Only $PhS(O)$-CH_2Ph (**2b**) was observed as product by comparison with authentic samples,[24] of which 134 mg (91%) was isolated by silica gel chromatography (Table 1, entry 2).

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1,1,1-Trinitro-2,2-diphenylethane was isolated in 55% yield by silica gel chromatography with petroleum ether/ethyl ether (25:75) as eluent of the crude reaction product of sulfide **1c** and TNM (Table 1, entry 8): ^{1}H NMR ($CDCl_3$) δ 5.80 (s, 1H), 7.20−7.36 (m, 6H), 7.36−7.52 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 56.26 (d, CH), 128.90 (d, C_4 Ar), 129.49−129.63 (d, C_2−C_3 Ar), 133.63 (s, C_1 Ar); MS (70 eV) *m*/*z* 43 (12.6), 51 (35.5), 63.1 (15.5), 76 (32.1), 77 (64.9), 78 (11), 89 (28.1), 105.1 (80.6), 152.1 (42.6), 165.1 (88.3), 166.1 (55.0), 167.1 (74.4), 168.1 (26.4), 178.1 (100), 179.1 (73), 180.1 (22.1), 182.1 (26.30), 183.1 (15.7), 184.1 (9.0), 193.1 (32.0), 194.1 (39.9), 208.1 (13.2), 225.0 (4.25), 271.1 (1.2), 317.1 (68.9), 318.1 (12.2); HRMS (EI+) calcd 317.0648, found 317.0649.

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