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Photoinduced hydrogen- and electron-transfer processes between chloranil and aryl alkyl sulfides in organic solvents. Steady-state and time-resolved studies

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Received 29th November 1999, Accepted 14th February 2000
Published on the Web 17th March 2000

The photochemical behavior of three aryl alkyl sulfides, thioanisole (TA), benzyl phenyl sulfide (BPS) and 4-methoxybenzyl phenyl sulfide (MBPS), sensitized by triplet chloranil (CA), was investigated by nanosecond laser flash photolysis and steady-state irradiation in CH_2Cl_2 and MeCN. The nature of the transients detected upon 355-nm laser excitation was independent of the molecular structure of the aryl alkyl sulfides but strongly affected by the solvent polarity. In particular, in CH_2Cl_2 the quenching process of triplet CA by aryl alkyl sulfides was accompanied by H-transfer, with formation of the $CAH^{\cdot}$ and $TA(-H)^{\cdot}/BPS(-H)^{\cdot}/MBPS(-H)^{\cdot}$ radicals. In contrast, a charge transfer process between triplet CA and aryl alkyl sulfides, with formation of the radical anion $CA^{\cdot-}$ and radical cations of aryl alkyl sulfides, occurred in MeCN. In this solvent, a transient detected at long delay time was tentatively assigned to the anion CAH^- formed by H-transfer between radical ions. In all experiments, transient species were characterized in terms of second-order decay rate constants and quantum yields of formation. Steady-state irradiation of the CA/TA system led to the stable photoadduct $C_6H_5SCH_2OC_6Cl_4OH$ in both CH_2Cl_2 and MeCN with quantum yields of 0.033 and 0.27, respectively. In contrast, aldehydes, thioacetals, and disulfides were the main products obtained upon irradiation of the CA/BPS and CA/MBPS systems. The photoaddition products were not observed, probably owing to their low stability. The nature of the photoproducts formed by irradiation of CA/aryl alkyl sulfides was independent of solvent properties, even though the reactivity was higher in MeCN than in CH_2Cl_2.

1 Introduction

Organic sulfur compounds are known to undergo fast one-electron oxidation reactions, owing to their relatively low ionization potentials. Thus, suitable oxidants can remove an electron from a lone pair on the sulfur atom, the likely site of the oxidative attack, to produce molecular radical cations, important intermediates in a great variety of chemical processes, extending from those of industrial importance to the biological ones.[1–3] Most investigations have been carried out to provide information on the main reaction pathways of dialkyl sulfide radical cations, while much less attention has been given to radical cations from aromatic sulfides.[1a,4–8]

The radical cations of sulfides decay through competitive pathways whose relative rate constants depend strongly on the structure of the substrate and on experimental conditions (solvent polarity, additives, *etc.*). In particular, deprotonation at a C_α–H bond, C–S fragmentation, oxidation, aromatic substitution, and dimerization have been investigated after generation of the radical cation by photoinduced electron transfer, radiolysis or chemical and electrochemical oxidation.[1–8]

The aim of this work was a detailed investigation of the reactivity and photokinetic behavior of three aryl alkyl sulfides sensitized by triplet chloranil in organic solvents of different polarity at room temperature. Nanosecond time-resolved measurements and steady-state irradiations were carried out to identify the transient species produced upon light absorption, their decay pathways, and final photoproducts. As recently shown for alkyl aromatic radical cations when the counter ion has a relatively low basicity,[9] a homolytic C_α–H bond cleavage is likely to occur in the interaction between the chloranil radical anion and aromatic radical cations of sulfides.

2 Experimental

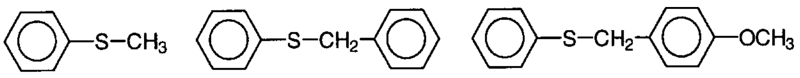
2.1 Starting materials

Chloranil (CA, Fluka) was recrystallized from acetone and sublimed under vacuum; thioanisole (TA, Aldrich), was distilled; benzyl phenyl sulfide (BPS, Aldrich) was recrystallized from $EtOH–H_2O$; 4-methoxybenzyl phenyl sulfide (MBPS) was prepared by reaction of 4-methoxybenzyl chloride with thiophenol as previously described.[10] The structures of TA, BPS and MBPS are shown in Scheme 1. MeCN and CH_2Cl_2 were Aldrich solvents of spectrophotometric grade, used as received. Tetrachlorohydroquinone (Sigma) and $Me_4NOH \cdot 5H_2O$ (Aldrich) were used as received.

2.2 Laser flash photolysis

The excitation wavelength of 355 nm from a Nd:YAG laser (Continuum, third harmonic) was used in nanosecond flash photolysis experiments (pulse width *ca.* 7 ns and energy <3 mJ per pulse).[11] The transient spectra were obtained by a point-to-point technique, monitoring the absorbance changes (ΔA) after the flash at intervals of 5–10 nm over the spectral range 300–850 nm, averaging at least 10 decays at each wave-

DOI: 10.1039/a909372i



thioanisole
(TA)

benzyl phenyl sulfide
(BPS)

4-methoxybenzyl phenyl sulfide
(MBPS)

Scheme 1

length. The $t_{1/2}$ values (the time at which the initial signal is halved) are reported for transients showing second-order kinetics. The quantum efficiencies of transient formation were measured by calibrating the experimental set-up with optically matched solutions of benzophenone (B) in MeCN. The following relationship between quantum yields (ϕ), absorption coefficients (ε), and absorbance changes (ΔA), measured at the corresponding absorption maxima of the transient (Tr) and the triplet benzophenone [$\phi_T(B) = 1$ and $\varepsilon_T(B) = 6500$ M^{-1} cm^{-1} at 520 nm],[12] was used to obtain transient quantum yields:

$$\phi_{Tr} = \phi_T(B)\,\frac{\varepsilon_T(B)}{\varepsilon_{Tr}}\,\frac{\Delta A_{Tr}}{\Delta A(B)} \qquad (1)$$

The experimental errors on $t_{1/2}$ were estimated to be ±10% and those on ε_{Tr} and ϕ_{Tr} to be ±15%.

All solutions were flowed through a quartz photolysis cell while argon was bubbling through them. All measurements were carried out at 22 ± 2 °C.

2.3 Photochemical reactions

A solution of CA (2×10^{-2} M), the TA, BPS and MBPS substrates (2×10^{-2} M) in CD_3CN or CH_2Cl_2, contained in a Pyrex vessel, was capped with a rubber septum, flushed with argon and irradiated without cooling at the instrumental operating temperature in a Rayonet photoreactor (λ_{exc} = 310–390 nm). After irradiation for 60 min (TA) or 30 min (BPS and MBPS), an internal standard was added and the raw photolysate was analyzed by GLC, GC-MS and ^{1}H-NMR (directly, for experiments in CD_3CN, or after evaporation of the solvent and addition of CD_3CN, for experiments in CH_2Cl_2). All products formed were identified by comparison with authentic specimens: benzaldehyde, 4-methoxybenzaldehyde and diphenyl disulfide were commercial products; benzaldehyde diphenyldithioacetal and 4-methoxybenzaldehyde diphenyldithioacetal were synthesized according to literature procedures.[13] The adduct $PhSCH_2OC_6Cl_4OH$ formed by CA and TA was isolated from the oxidation system on a preparative scale and characterized on the basis of the following spectral data: MS m/z (rel. intensity) M$^+$ 370,123(100),77,45; ^{1}H-NMR δ 7.5–7.3 (m, 5H, ArH), 5.96 (s, 1H, OH), 5.51 (s, 2H, CH_2). Quantitative analysis of reaction products was performed by GLC and ^{1}H-NMR. A good mass balance was obtained in all experiments (>90%). Prolonged irradiation of BPS and MBPS led to a decrease in the [dithioacetal] : [benzaldehyde] ratio of the two compounds.

2.4 Quantum yields

A 2.5 ml solution of CA (8.5×10^{-3} M in MeCN and 1.0×10^{-2} M in CH_2Cl_2) and TA (2×10^{-3} and/or 1.0×10^{-2} M), de-aerated by bubbling with argon, was placed in a quartz cuvette and irradiated with a high pressure Hg lamp (λ_{exc} = 366 nm, selected by a Balzer interference filter). To minimize the inner filter, the conversion to photoproduct was kept below 10%. To obtain the percentage of conversion, the solvent of the irradiated solution was evaporated and the residue was dissolved in $CDCl_3$ before analysing it by ^{1}H-NMR spectrometry and/or GC. Bibenzyl was used as an internal standard. Light intensity was measured by use of potassium ferrioxalate actinometry.[14] The photoreaction quantum yields were averages of at least three independent experiments (mean deviation *ca.* 7%).

For BPS and MBPS, quantum yields could not be measured because the relative amount of photoproducts depends on irradiation time, even at small conversion percentages.

Ground state absorption spectra were recorded by a UVKON 923 double-beam spectrophotometer.

3 Results and discussion

3.1 Laser flash photolysis

The lowest triplet state of CA was efficiently quenched by aryl alkyl sulfides in both CH_2Cl_2 and MeCN; decay rate constants k_{obsd} measured at different TA concentrations are shown in Fig. 1. From the linear plots of k_{obsd} *vs.* concentration of aryl alkyl sulfides, quenching rate constants k_q close to the diffusional limit (k_q = 0.49–1.32 × 10^{10} M^{-1} s^{-1}, Table 1) were obtained. It has to be noted that, within experimental error, the quenching process of triplet CA in CH_2Cl_2 did not show any isotope effect, at least for TA. In fact, k_q obtained with both TA and $PhSCD_3$ was 1.1 × 10^{10} M^{-1} s^{-1}; hence,

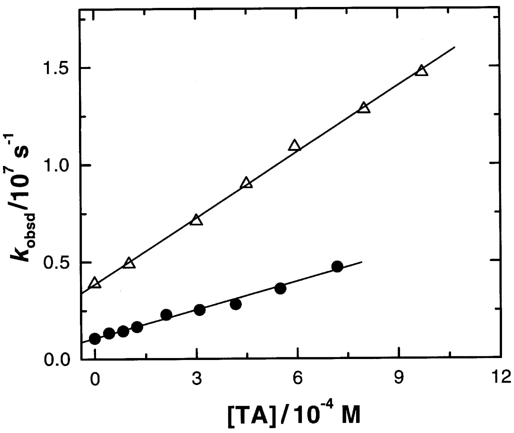


Fig. 1 First-order decay rate constant (k_{obsd}) of ^{3}CA* in CH_2Cl_2 (△) and MeCN (●) at different TA concentrations, recorded at 520 nm (λ_{exc} = 355 nm).

Table 1 Quenching rate constants (k_q) of triplet CA by TA, BPS and MBPS in CH_2Cl_2 and MeCN

Compound	Solvent	k_q/10^{10} M^{-1} s^{-1}
TA	CH_2Cl_2	1.10
	MeCN	0.49
BPS	CH_2Cl_2	1.32
	MeCN	0.65
MBPS	CH_2Cl_2	1.07
	MeCN	0.92

the main bimolecular deactivation process of triplet CA does not involve a H-transfer process, even if the isotope effect could be hidden by high quenching rate constants.

Laser photolysis of oxygen-free CH_2Cl_2 solutions of CA (4.0×10^{-3} M) was carried out by exciting at 355 nm in the presence of aryl alkyl sulfides (1.0×10^{-2} M). Under these experimental conditions, the lifetime of triplet CA ($\lambda_{max} = 520$ nm)[15] was too short to be detected ($\tau \leqslant 10$ ns). Indeed, small signals were recorded just after the laser pulse with absorption maxima at 340–360, 420(sh) and 435 nm (see Fig. 2 for the CA/TA system), very similar to those previously reported for $CAH^{\bullet}$,[16,17] $TA(\text{-H})^{\bullet}$,[7] and the radicals $PhCH^{\bullet}SPhCH_2SO_3^-$ and $4\text{-}MeOPhCH^{\bullet}SPhCH_2SO_3^-$.[7] Taking also into account the small effect of the $-CH_2SO_3^-$ group on the absorption spectra of similar radicals,[7] the transient species were assigned to radicals produced by a fast H-transfer process from aryl alkyl sulfides to CA within a short-lived triplet complex.

The properties of the radicals $CAH^{\bullet}$, $TA(\text{-H})^{\bullet}$, $BPS(\text{-H})^{\bullet}$ and $MBPS(\text{-H})^{\bullet}$ are summarized in Table 2. The absorption spectrum of $TA(\text{-H})^{\bullet}$ is centered at *ca.* 340 nm (Fig. 2), to be compared with the λ_{max} of 330 nm previously reported for the same transient in water,[7] while the main absorption bands of $BPS(\text{-H})^{\bullet}$ and $MBPS(\text{-H})^{\bullet}$ are overlapped with the first absorption of $CAH^{\bullet}$ ($\lambda_{max} = 360$ nm).

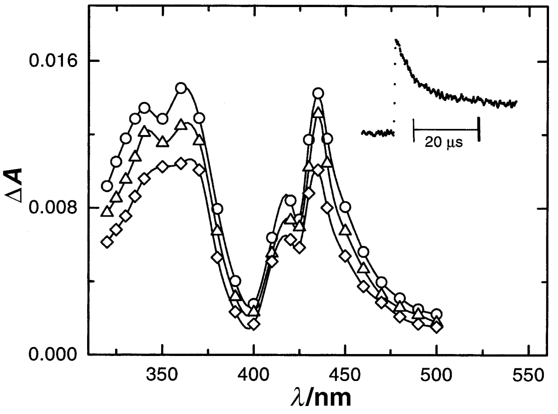


Fig. 2 Time-resolved absorption spectra obtained by laser photolysis of 4.0×10^{-3} M CA in the presence of 1.0×10^{-2} M TA in CH_2Cl_2, recorded 0.22 (○), 1.9 (△) and 8.0 (◇) μs after the laser pulse ($\lambda_{exc} = 355$ nm). Inset: changes in absorbance recorded at 435 nm.

The product $\varepsilon_{Rad}\phi_{Rad}$ for the radical $CAH^{\bullet}$ in CH_2Cl_2 was obtained by a comparison between the absorbance changes (ΔA) recorded at 435 nm (maximum absorption for $CAH^{\bullet}$) upon laser excitation of CA in the presence of aryl alkyl sulfides, and that recorded at 520 nm (maximum triplet–triplet absorption) for an optically matched solution of benzophenone in MeCN (see experimental section). A value of 0.06 was obtained for quantum yields of formation of the radical $CAH^{\bullet}$, by use of the absorption coefficient $\varepsilon_{Rad} = 7300$ M^{-1} cm^{-1} (ref. 16 and 18) for $CAH^{\bullet}$ at 435 nm. The quantum yields of formation of the radicals $TA(\text{-H})^{\bullet}$, $BPS(\text{-H})^{\bullet}$ and $MBPS(\text{-H})^{\bullet}$ (ϕ_{Rad}) were obviously taken to be equal to those of $CAH^{\bullet}$. It has to be noted that ϕ_{Rad} is rather low and remains constant for the three systems investigated. In fact, also the rate constant of radical formation ($k \sim 7 \times 10^8$ M^{-1} s^{-1}) does not change with the structure of aryl alkyl sulfides (see below). These results are likely related to a transition state of the C–H homolytic cleavage which is close to the structure of the reagents. The possibility that, in the presence of high concentrations of aryl alkyl sulfides, the radical $CAH^{\bullet}$ is formed by H-abstraction from the solvent is ruled out by the very short lifetime of triplet CA ($\tau_T < 10$ ns to be compared with $\tau_T \approx 3$ μs in the absence of aryl alkyl sulfides) and by the presence of the partner radicals [$TA(\text{-H})^{\bullet}$, $BPS(\text{-H})^{\bullet}$ and $MBPS(\text{-H})^{\bullet}$] which absorb at 340–360 nm.

The ΔA values measured at λ_{max} for $TA(\text{-H})^{\bullet}$, $BPS(\text{-H})^{\bullet}$ and $MBPS(\text{-H})^{\bullet}$ (340 or 360 nm, depending on the sulfide) were used to obtain the absorption coefficient ε_{Rad} of each radical by use of eqn (2):

$$\varepsilon_{Rad} = \frac{\Delta A_{\lambda}}{\Delta A_{520}(B)} \frac{\varepsilon_T \phi_T}{\phi_{Rad}} - \varepsilon_{\lambda}(CAH^{\bullet}) + \varepsilon_G(CA) \qquad (2)$$

where $\Delta A_{520}(B)$ is the absorbance change recorded at 520 nm for the optically matched solution of benzophenone (B) in acetonitrile, the product $\varepsilon_T\phi_T = 6500$ M^{-1} cm^{-1} refers to the triplet–triplet absorption of B at 520 nm,[12] $\varepsilon_{\lambda}(CAH^{\bullet})$ is the absorption coefficient of $CAH^{\bullet}$ at the wavelength of analysis (equal to 2400 and 7800 M^{-1} cm^{-1} at 340 and 360 nm, respectively)[19] and $\varepsilon_G(CA)$ is the absorption coefficient of chloranil in the ground state. It has to be noted that at these wavelengths $\varepsilon_G(CA) \approx 200$ M^{-1} cm^{-1} and, therefore, the effect of ground state absorption on ε_{Rad} is within the experimental error (±15%).

The ε_{Rad} values measured in this work (in the range 4400–9000 M^{-1} cm^{-1}, see Table 2) are similar to those previously

Table 2 Spectral and kinetic properties and quantum yields of the transients sensitized by triplet CA[a] in the presence of aryl alkyl sulfides[b]

Compound	Solvent	λ_{max}/nm	$t_{1/2}{}^c$/μs	$2k_2/10^{10}$ M^{-1} s^{-1}	ε^d/M^{-1} cm^{-1}	ϕ_{Tr}	Transient
TA	CH_2Cl_2	340	14	1.1	4400	0.06	$PhSCH_2^{\bullet}$
		360, 420(sh), $\underline{435}$	13	1.7	7300[e]	0.06	$CAH^{\bullet}$
	MeCN	325, 430(sh), $\underline{450}$	3.5	3.1	9700[f]	1.0	$CA^{\bullet-}$
		530	2.9	3.8	6100[g]	1.0	$PhSCH_3^{\bullet+}$
		330, 360, $\underline{450}$	13.5	3.5	13500	0.24	CAH^-
BPS	CH_2Cl_2	360	13	1.3	8200	0.06	$PhSCH^{\bullet}Ph$
		360, 420(sh), $\underline{435}$	10	1.7		0.06	$CAH^{\bullet}$
	MeCN	325, 430(sh), $\underline{450}$	3.5	3.4		0.83	$CA^{\bullet-}$
		320, $\underline{530}$	3.0	3.8	4800	0.83	$PhSCH_2Ph^{\bullet+}$
		330, 360, $\underline{450}$	14	3.5		0.22	CAH^-
MBPS	CH_2Cl_2	360	116	0.34	9000	0.06	$MeOPhCH^{\bullet}SPh$
		360, 425(sh), $\underline{435}$	123	0.23		0.06	$CAH^{\bullet}$
	MeCH	325, 430(sh), $\underline{450}$	3.9	3.4		0.75	$CA^{\bullet-}$
		330, $\underline{520}$	3.0	4.5	4500	0.75	$MeOPhCH_2SPh^{\bullet+}$
		330, 360, $\underline{450}$	12	3.8		0.23	CAH^-

[a] [CA] = 4.0×10^{-3} and 3.6×10^{-3} M in CH_2Cl_2 and MeCN, respectively. [b] 1.0×10^{-2} M aryl alkyl sulfides in CH_2Cl_2 and MBPS in MeCN and 2.0×10^{-3} M TA and BPS in MeCN. [c] $t_{1/2}$ is the time at which the initial signal was halved. [d] Absorption coefficient at the underlined maximum. [e] From ref. 16 and 18. [f] From ref. 16 and 17. [g] From ref. 23.

obtained by pulse radiolysis of TA and sulfonate derivatives of BPS and MBPS in aqueous solutions,[7] thus indicating that the medium does not affect significantly the transition probabilities of these transients.

The transient absorptions recorded at any wavelength (see, *e.g.*, inset of Fig. 2) decayed by second-order laws, with half-lives ($t_{1/2}$) on the microsecond timescale and second-order rate constants ($2k_2$) in the range 10^9–10^{10} M^{-1} s^{-1}. The decay rate constant of the radicals is very close for TA(-H)$^{\bullet}$ and PS(-H)$^{\bullet}$ ($t_{1/2} = 10$–14 μs and $2k_2 = 1.1$–1.7×10^{10} M^{-1} s^{-1}) and decreases by about one order of magnitude for MBPS(-H)$^{\bullet}$ ($t_{1/2} \approx 120$ μs and $2k_2 \approx 0.3 \times 10^{10}$ M^{-1} s^{-1}), thus indicating that the methoxy group stabilizes significantly the radical species. The second-order decay kinetics recorded for the radicals CAH$^{\bullet}$, TA(-H)$^{\bullet}$, BPS(-H)$^{\bullet}$ and MBPS(-H)$^{\bullet}$, together with the lack of further transients in the absorption spectra, suggests that CAH$^{\bullet}$ recombines with the counterpart radical to produce stable products (see below).

The photochemical behavior of CA in the presence of aryl alkyl sulfides investigated in CH_2Cl_2 is in general agreement with that reported for chloranil-sensitized oxidation of aromatic hydrocarbons in benzene and 1,2-dichloroethane,[16,17,20] where CAH$^{\bullet}$ was the main transient produced after the decay of charge-transfer complexes in the triplet manifold.

Photolysis of CA (3.6×10^{-3} M) in Ar-saturated MeCN was carried out in the presence of aryl alkyl sulfides (2.0×10^{-3} M), conditions where triplet CA was efficiently quenched ($\tau \leqslant 150$ ns). The time-resolved absorption spectra recorded for the CA/TA system are reported in Fig. 3. Two transients appeared on the absorption spectra just after the decay of triplet CA; absorption bands with $\lambda_{max} = 325$, 430(sh) and 450 nm were confidently attributed to the anion radical CA$^{\bullet-}$ (ref. 16 and 18) while the broad band centered at 520–530 nm was assigned to the radical cations of aryl alkyl sulfides.[7] Remarkably, the presence of the radicals CAH$^{\bullet}$ and $PhSCH_2^{\bullet}$, the transients recorded in CH_2Cl_2, can be clearly excluded in MeCN, if one compares the time-resolved absorption spectra of CA/TA (Fig. 3) with that of CAH$^{\bullet}$ in MeCN (Fig. 4).[21]

At long delay time, the absorptions of the ion radicals were replaced by that of a further transient with maxima at 330, 360(sh) and 450 nm (Fig. 3, spectrum recorded 40 μs after the pulse). This spectrum resembles that of CA$^{\bullet-}$, but the much longer decay time shows that it must be assigned to another transient. The absorption spectrum of CAH^{-}, produced both by (a) photolysis of CA/bis(4-methoxyphenyl)methane in MeCN[9] and (b) deprotonation of tetrachlorohydroquinone (CAH_2, 1×10^{-4} M) in the presence of the base $Me_4NOH \cdot 5H_2O$ (2.4×10^{-4} M) in MeCN (see Fig. 5), also resembles the longer-lived transient that was, therefore, tentatively assigned to the anion CAH^{-}. The absorption spectra of CA$^{\bullet-}$ and CAH^{-} are similar to each other. This was confirmed by quantum mechanical calculations carried out with the INDO/1-CI model (ZINDO module of the Cerius^2 package, rel. 3.8) on molecular structures optimized by use of the set of bases 3–21G (Gaussian 98).[23]

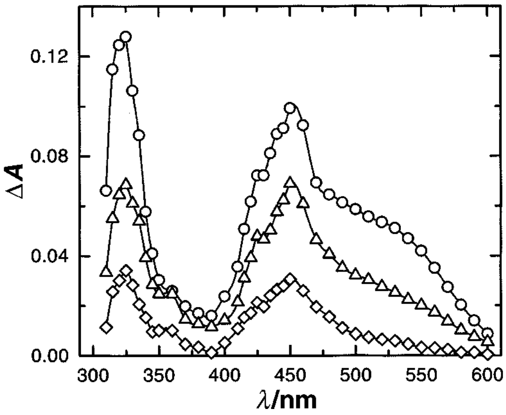


Fig. 3 Time-resolved absorption spectra obtained by laser photolysis of 3.6×10^{-3} M CA in the presence of 2.0×10^{-3} M TA in MeCN, recorded 0.5 (○), 3.5 (△) and 40 (◇) μs after the laser pulse ($\lambda_{exc} = 355$ nm).

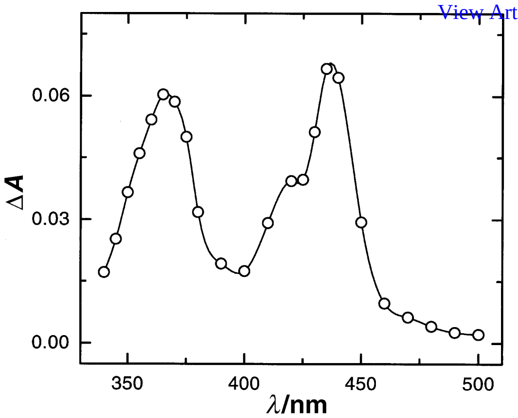


Fig. 4 Absorption spectrum of CAH$^{\bullet}$ obtained by photolysis of CAH_2 (0.025 M) and di-*tert*-butyl peroxide (1 M) in MeCN ($\lambda_{exc} =$ 355 nm).

Configuration interaction (CI) calculations including singly excited configurations built from 20 highest occupied and 20 lowest virtual molecular orbitals have shown that the energies of the allowed $S_0 \rightarrow S_n$ transitions do not change significantly for CA$^{\bullet-}$ and CAH^{-} and that, except for the forbidden n,π* states, the two species have the same state order.

Because of the strong overlap between transient absorptions in the 300–550 nm range, the kinetic analysis of signals recorded at any wavelength could not give direct information on the formation process of CAH^{-} but, by analogy with CA/bis(4-methoxyphenyl)methane in MeCN,[9] the ions CAH^{-} and TA(-H)$^{+}$/BPS(-H)$^{+}$/MBPS(-H)$^{+}$ were probably formed by H-transfer from the radical cations of the aryl alkyl sulfides to CA$^{\bullet-}$. It has to be noted that the cations were not detected in the photolysis experiments, because they absorb only at short wavelengths (see below).

The formation quantum yields of CA$^{\bullet-}$ in MeCN were determined by calibrating the experimental set-up with an optically matched solution of benzophenone in the same solvent and by use of the absorption coefficient $\varepsilon = 9700$ M^{-1} cm^{-1} at 435 nm for CA$^{\bullet-}$ (Table 2). For CA/TA, also the formation quantum yield of the radical cation TA$^{\bullet+}$ was

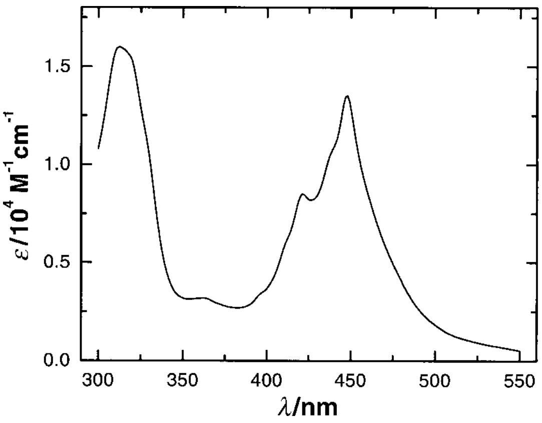


Fig. 5 Absorption spectrum of 1×10^{-4} M tetrachlorohydroquinone and 2.4×10^{-4} M $Me_4NOH \cdot 5H_2O$ in MeCN.

obtained by use of its absorption coefficient at 530 nm (6100 M^{-1} cm^{-1}).[24] However, since the ε values of $BPS^{\cdot +}$ and $MBPS^{\cdot +}$ in MeCN are unknown, their formation quantum yields were taken to be equal to the corresponding values of $CA^{\cdot -}$; this assumption allowed the absorption coefficients of these radical cations to be obtained (Table 2) by relationship (3):

$$\varepsilon_{RC} = \varepsilon_{RA} \frac{\Delta A_{RC}}{\Delta A_{RA}} \qquad (3)$$

where ΔA_{RC} and ΔA_{RA} represent the absorbance changes measured at the absorption maxima of the radical cation of an aryl alkyl sulfide and $CA^{\cdot -}$, respectively. The ε_{RC} values obtained in this way (4800 and 4500 M^{-1} cm^{-1} for $BPS^{\cdot +}$ and $MBPS^{\cdot +}$, respectively) are of the same order of magnitude as those previously reported for similar radical cations in water.[7] In all cases, the radical ions were produced with high efficiency ($\phi_{RI} \geqslant 0.75$, see Table 2).

The high values of the formation quantum yield of CAH^- ($\phi_{An} = 0.24$–0.30, see Table 2) show that, surprisingly, the hydrogen transfer process competes efficiently with other possible decay channels. It is known that radical ions of aryl alkyl sulfides are able to undergo deprotonation and/or C–S cleavage.[3,5,6,8] However, such processes were not operative under our experimental conditions. In fact, the lack of the typical absorption band at *ca.* 360 nm (characteristic of $CAH^{\cdot}$) in the time-resolved spectra of CA/aryl alkyl sulfides recorded in MeCN (see Fig. 3, as an example) excludes the occurrence of an efficient proton transfer process between $CA^{\cdot -}$ and radical cations of aryl alkyl sulfides to give the corresponding radicals $CAH^{\cdot}$ and $TA(-H)^{\cdot}/BPS(-H)^{\cdot}/MBPS(-H)^{\cdot}$.[21] As pointed out in a previous work,[9] this is likely due to the low basicity of $CA^{\cdot -}$ in MeCN ($pK_a = 6.8$) which is not able to deprotonate radical cations of aryl alkyl sulfides. Furthermore, the inefficiency of C–S cleavage for $BPS^{\cdot +}$ and $MBPS^{\cdot +}$ was supported by both time-resolved and steady-state investigations. In fact, neither absorption bands characteristic of $PhS^{\cdot}$ ($\lambda_{max} = 300$ and 460 nm)[7] nor photoproducts attributable to the cations $PhCH_2^+$ and $4\text{-}MeOPhCH_2^+$ (alcohols and acetamides) were obtained by time-resolved and steady-state investigations, respectively, of CA/BPS and CA/MBPS in MeCN.

The concentrations of TA and BPS in MeCN were kept at 2×10^{-3} M to avoid formation of dimer radical cations which would make the reaction mechanism more complicated; strong absorptions in the 600–850 nm range, due to dimers, were observed at higher concentrations.[24] Instead, analogously with 4-methoxythioanisole,[24] dimer radical cations of MBPS were not detected even at a concentration of 1×10^{-2} M. It has to be noted that the presence of the dimer does not affect the reactivity of the system, since the quantum yield of CAH^- (ϕ_{An}) and of the final photoadduct (ϕ_P) are virtually independent of TA concentration: in fact, almost constant ϕ_{An} and ϕ_P values were obtained at 2×10^{-3} and 1×10^{-2} M TA.

The decay kinetics of radical ions (see Fig. 6 for decays of CA/TA recorded at 450 and 530 nm) were well fitted by second-order laws with half-lives on the microsecond timescale ($t_{1/2} = 2.9$–3.9 μs) and decay rate constants close to the diffusional limit ($2k_2 = 3.1$–4.5×10^{10} M^{-1} s^{-1}) (Table 2). The anion CAH^- also decayed by second-order kinetics with a half-life of 12–14 μs, longer than those observed for radical ions, and a diffusion controlled decay rate constant ($2k_2 \sim 3.5 \times 10^{10}$ M^{-1} s^{-1}, see Table 2). These results show that there is no significant effect of the sulfide structure on decay rate constants of charged transients, thus suggesting that their behavior is flattened by chloranil properties.

The formation quantum yields and decay rate constants of charged species produced in MeCN and of $CAH^{\cdot}$ in CH_2Cl_2 remained virtually unchanged in air-equilibrated solutions, while the radicals $TA(-H)^{\cdot}$, $BPS(-H)^{\cdot}$, and $MBPS(-H)^{\cdot}$ formed in CH_2Cl_2 were quenched by molecular oxygen ($k_q \sim 1 \times 10^7$ M^{-1} s^{-1}).

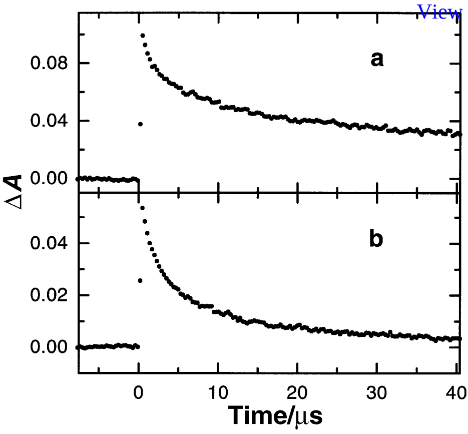


Fig. 6 Changes in absorbance with time following photolysis of 3.6×10^{-3} M CA and 2.0×10^{-3} M TA in MeCN solution at (a) 450 and (b) 530 nm.

3.2 Absorption spectra of cations

In the time-resolved absorption spectra of CA/aryl alkyl sulfides there is no absorption that can confidently be ascribed to the counterpart cation $TA(-H)^+/BPS(-H)^+/MBPS(-H)^+$. Since to our knowledge, the absorption spectra of these cations have not been reported in the literature, quantum mechanical calculations were performed to predict transition energies and probabilities. The geometry of $TA(-H)^+$, $BPS(-H)^+$, and $MBPS(-H)^+$ was optimized at a semi-empirical level by use of the AM1 method (Gaussian 98) followed by geometry optimization with an *ab initio* calculation by use of the set of bases 3–21G (Gaussian 98).[23] The transition energies and oscillator strengths (f) were calculated by the INDO/1-CI model (ZINDO module of the Cerius^2 package, rel. 3.8) including solute–solvent interactions in the Hamiltonian by use of a self-consistent reaction field (SCRF) model;[25] configuration interaction (CI) calculations included singly excited configurations built from 20 highest occupied and 20 lowest virtual molecular orbitals. Calculations predicted main absorption maxima at 204 nm ($f = 0.21$), 312 nm ($f = 0.93$) and 328 nm ($f = 1.0$) for $TA(-H)^+$, $BPS(-H)^+$, and $MBPS(-H)^+$, respectively. It has to be noted that the errors on these absorption maxima are likely to be in the range of some tens of nanometers. On the basis of these predictions, cations are therefore expected to absorb essentially below 350 nm, in regions where our experimental set-up is not sensitive or where strong absorptions of other transients and of the ground state molecule can make it difficult to distinguish their presence.

3.3 Steady-state irradiation

Photolysis of CA/aryl alkyl sulfides in Ar-saturated solutions of CH_2Cl_2 and MeCN was carried out by steady-state irradiation at $\lambda_{exc} = 310$–390 nm, where only CA absorbs. The results of these experiments are compiled in Table 3. In particular, for the CA/TA system the photoreaction was clean and led exclusively to the photoadduct $PhSCH_2OC_6Cl_4OH$, while for BPS and MBPS different photoproducts were obtained, namely benzaldehyde (or 4-methoxybenzaldehyde), benzaldehyde diphenyldithioacetal (or 4-methoxybenzaldehyde diphenyldithioacetal) and diphenyl disulfide (Table 3). These products might derive from hydrolysis of unstable photoadducts $[ArCH(SPh)OC_6Cl_4OH]$ that produce CAH_2 and

Table 3 Products formed in the CA-sensitized photolysis of TA, BPS and MBPS in CH_2Cl_2 and MeCN together with the chemical yields

Compound	Solvent	Product	Chemical yield[a] (%)
TA[b,c]	CH_2Cl_2	$PhSCH_2OC_6Cl_4OH$	7.3
	MeCN	$PhSCH_2OC_6Cl_4OH$	38.5
BPS[b,d]	CH_2Cl_2	PhCHO	3.0
		$PhCH(SPh)_2$	1.1
		PhSSPh	0.9
	MeCN	PhCHO	15
		$PhCH(SPh)_2$	4.7
		PhSSPh	4.5
MBPS[b,d]	CH_2Cl_2	$4\text{-}CH_3OPhCHO$	5.3
		$4\text{-}CH_3OPhCH(SPh)_2$	3.8
		PhSSPh	0.8
	MeCN	$4\text{-}CH_3OPhCHO$	33.1
		$4\text{-}CH_3OPhCH(SPh)_2$	11.6
		PhSSPh	9.0

[a] Yields referred to the substrate. Average of at least two determinations. The error is ±10%. [b] [TA] = [BPS] = [MBPS] = 0.01 M. [c] Irradiation time of 60 min. [d] Irradiation time of 30 min.

hemithioacetals [ArCH(OH)SPh] which in turn lead to benzaldehydes and thiophenol. A reaction between the latter products might lead to dithioacetal, while thiophenol can be oxidized to the disulfide.

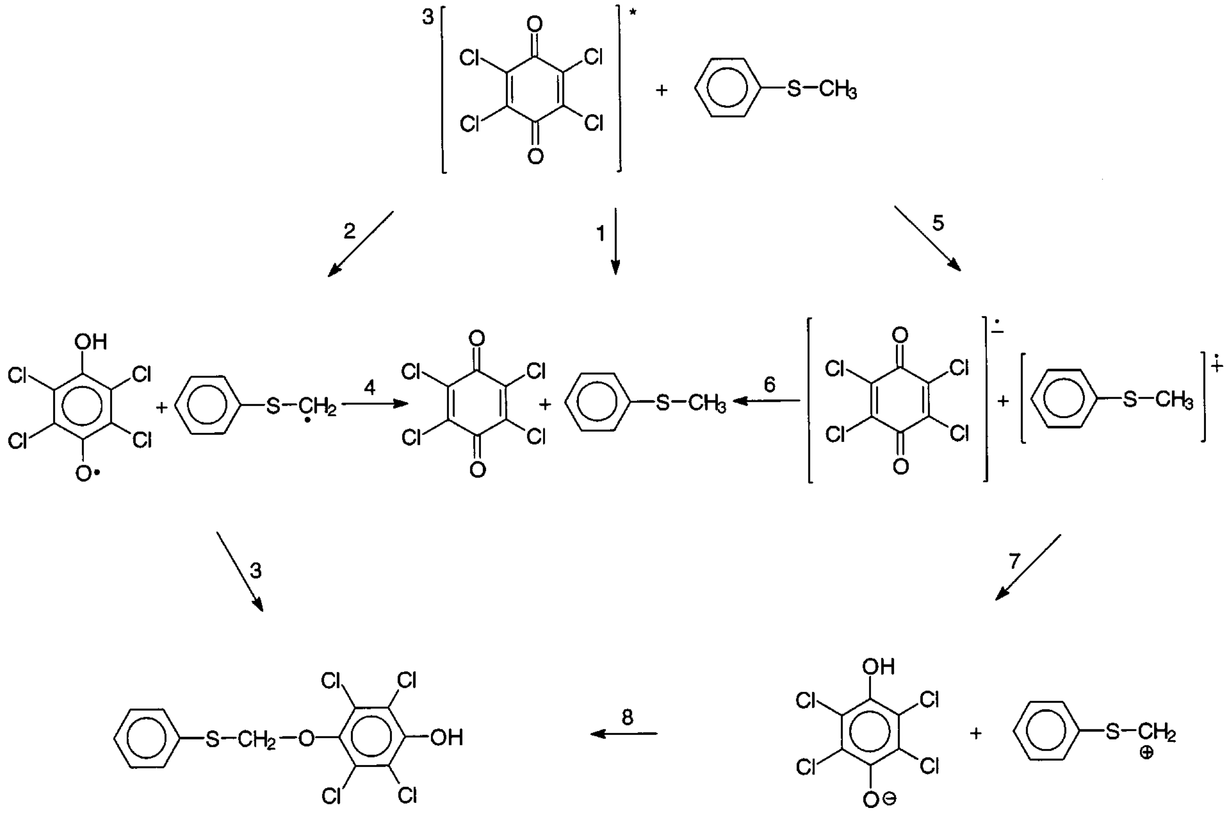
For the CA/TA system, reaction quantum yields (ϕ_P) of 0.033 and 0.27 were obtained in CH_2Cl_2 and MeCN, respectively, by exciting at 366 nm. In MeCN, ϕ_P were measured at two TA concentrations (2×10^{-3} and 1×10^{-2} M) without observing any appreciable change. It was not possible to measure ϕ_P of the other two sulfides because the relative amount of photoproducts was strongly dependent on the irradiation time, thus indicating that the primary products were not photostable. Indeed, when benzaldehyde diphenyldithioacetal, PhSCH(SPh)Ph (2×10^{-2}M), was irradiated in the presence of CA (2×10^{-2}M) in MeCN, a partial oxidation of this substrate to give benzaldehyde and diphenyl disulfide was observed.

3.4 Photoreaction mechanisms

On the basis of the above assignments, the results of the time-resolved and steady-state measurements on the photochemical behavior of CA/TA, the only system where a stable photoproduct was formed, can be rationalized in terms of the reaction kinetics shown in Scheme 2. Steps 1–4 refer to the less polar CH_2Cl_2 and steps 5–8 to the more polar MeCN. The efficiency $\varphi(i)$ and the second-order rate constant $2k_2(i)$ (with $i = 1$–8) of each step are compiled in Table 4.

In CH_2Cl_2, the quenching process of triplet CA is mainly followed by return to the ground state (step 1), with very high quantum efficiency [$\varphi(1) = 1 - \varphi(2) = 1 - \phi_{Rad} = 0.94$] and $2k_2(1)$, corresponding to the product $k_q\varphi(1)$, close to the diffusional limit. In contrast, the parallel formation of radical species (step 2) is rather inefficient [($\varphi(2) = \phi_{Rad} = 0.06$)] and the corresponding rate constant [$2k_2(2) = k_q\varphi(2)$] is about one order of magnitude smaller than $2k_2(1)$ (Table 4). This is confirmed by the lack of a deuterium isotope effect on the quenching rate constant of triplet CA by TA. The radical recombination can give both the final photoadduct [step 3, with $\varphi(3) = \phi_P/\phi_{Rad}$] and the return H-transfer process [step 4, with $\varphi(4) = 1 - \varphi(3)$] with rate constants [$2k_2(3) = 2k_2(\mathrm{CAH^\bullet})\varphi(3)$ and $2k_2(4) = 2k_2(\mathrm{CAH^\bullet})\varphi(4)$] slightly smaller than the diffusional limit.

In MeCN, the bimolecular interaction between TA and triplet CA produces radical ions (step 5) with unitary efficiency and rate constant $2k_2(5) = k_q\varphi(5) = 0.49 \times 10^{10}$ M^{-1} s^{-1}. The main decay pathway of the radical ions $CA^{\bullet-}$ and $TA^{\bullet+}$ is return electron transfer [step 6, $\varphi(6) = 1 - \varphi(7) = 1 - \phi_{An} = 0.76$] which occurs with a very high rate constant [$2k_2(6) = 2k_2(\mathrm{RI})\varphi(6) = 3.45 \times 10^{10}$ M^{-1} s^{-1}, where $2k_2(\mathrm{RI})$ is the average of decay rate constants of radical ions]. At this point one should expect the occurrence of proton transfer from $TA^{\bullet+}$ to $CA^{\bullet-}$, however, the absence of the signal at *ca.*



Scheme 2

Table 4 Quantum efficiencies (φ) and second-order rate constants ($2k_2$) of reactions 1–4 (in CH_2Cl_2) and 5–8 (in MeCN), see Scheme 2

	TA		BPS		MBPS	
Step	φ	$2k_2/10^{10}$ M^{-1} s^{-1}	φ	$2k_2/10^{10}$ M^{-1} s^{-1}	φ	$2k_2/10^{10}$ M^{-1} s^{-1}
1	0.94	1.03	0.94	1.24	0.94	1.01
2	0.06	0.07	0.06	0.08	0.06	0.06
3	0.55	0.94				
4	0.45	0.77				
5	1.0	0.49	0.83	0.54	0.75	0.69
6	0.76	3.45	0.73	2.63	0.70	2.76
7	0.24	1.2	0.27	0.97	0.30	1.2
8	1.0	1.25				

360 nm which is characteristic of $CAH^{\bullet}$ clearly excludes the deprotonation process. Thus, a H-transfer process from $TA^{\bullet +}$ to $CA^{\bullet -}$ probably occurs, by analogy with CA/bis(4-methoxyphenyl)methane in MeCN, and, accordingly, evidence of the absorption spectrum of CAH^- has been found at long delay times ($t_{1/2} \sim 13$ μs). On the basis of Scheme 2, one expects that the half-life of the cation species must be equal to that of CAH^-. This value, which might appear particularly high,[26] is affected by the remarkable stabilization of the methyl cation induced by the phenylthio substituent as shown by the kinetic data for the hydrolysis of aryl chloromethyl sulfides.[28]

The H-transfer process [step 7, $\varphi(7) = \phi_{An} = 0.24$] is a reaction slightly slower than return electron transfer and competes efficiently in the decay of radical ions to produce the ions CAH^- and TA^+. The final product is probably formed by recombination of ions [step 8, $\varphi(8) = \phi_R/\phi_{An}$ and $2k_2(8) = 2k_2(CAH^-)\varphi(8)$].

From the kinetic point of view (nature of transients, quantum efficiencies and rate constants), no significant changes were obtained by use of BPS and MBPS, instead of TA, as quencher of triplet CA. Only slightly smaller values of $\varphi(5)$ were obtained by use of BPS and MBPS (0.83 and 0.75, respectively). In contrast, a remarkable change in photochemical products was observed by replacing TA with BPS and MBPS. In our opinion, this is probably due to the instability of the photoadduct, the precursor of the stable photoproducts obtained by irradiation of CA/BPS and CA/MBPS (Table 3).

In conclusion, it has been clearly shown that, even though solvent polarity does not modify the nature of the products obtained by chloranil-photosensitization of aryl alkyl sulfides, the reaction mechanism operative in the two solvents is completely different. In fact, only radical transients were detected in the less polar CH_2Cl_2, while charged species were formed in the polar MeCN. Furthermore, radical cations of aryl alkyl sulfides do not give deprotonation or fragmentation when they react with the chloranil radical anion, but a H-transfer process is likely to be operative.

The above results have shown the lack of structural effects on the primary steps of the chloranil sensitized reactivity of TA, BPS and MBPS, in line with the high rate constants of the decay channels of radicals (in CH_2Cl_2) and radical ions (in MeCN). This suggests a transition state very close to the reagent structure.

Acknowledgement

Thanks are due to Professor E. Baciocchi for his advice and to the Italian Consiglio Nazionale delle Ricerche and Ministero della Università e della Ricerca Scientifica e Tecnologica (Programma di Ricerca di Interesse Nazionale) for financial support.

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Paper a909372i