Triplet quenching by onium salts in polar and nonpolar solvents

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Abstract

The triplet quenching of several sensitizers (thioxanthone (TX), 2-chlorothioxanthone (CTX), xanthone (X), benzophenone (BP), pyrene (PY), benzil (BZ), and phenothiazine (PT)) was investigated with lipophilic substituted onium salts (iodonium $I_{(1)}$ and sulfonium salts $S_{(1)}$) in benzene, n-heptane, and mixtures of these. Moreover, the triplet quenching of these sensitizers was also studied in acetonitrile with onium salts $I_{(2)}$ and $S_{(2)}$, with a similar pattern of substitution to the lipophilic salts.

Using the determined half-wave reduction potential of the onium salts, one can show that an efficient triplet quenching by electron transfer is possible with the exception of BP and BZ. The quenching constants obtained fit the theoretical Rehm–Weller plot. The quality of the fit is better in acetonitrile than in n-heptane. Using TX and CTX cation radicals are detectable, which support a triplet quenching by electron transfer. Nevertheless, the triplets of BP and BZ were also efficiently quenched by the onium salts.

The quenching reaction by sulfonium salt is hardly influenced from the polarity of the solvent used. However, the iodonium salt shows a strong dependence on the polarity: for instance in benzene the rate is one order of magnitude higher than in n-heptane. Moreover, the magnitude of triplet quenching in benzene is for the iodonium salt one order higher than for the sulfonium salt. Surprisingly, we found (with exception of PT and PY) in n-heptane no strong differences in quenching between iodonium and the sulfonium compounds. © 1997 Elsevier Science S.A.

Keywords: Triplet quenching; Electron transfer; Half-wave potentials; Photochemistry; Onium salts

1. Introduction

Onium salts (On$^+$ = sulfonium and iodonium salts) in combination with several sensitizers (Sens) are important initiators of cationic photopolymerizations [1]. There have been many investigations of their sensitized photoreactions in polar solvents [1–5]. As has been shown, under these circumstances the quenching mechanism is an electron transfer to give the radical cation of the sensitizer and the neutral radical of the onium salt if this is thermodynamically feasible. Additionally, using iodonium and sulfonium salts an effective triplet energy transfer is thermodynamically allowed in many cases [1c].

However, in technical applications, cationic polymerizations are carried out in nonpolar solvents, the monomer usually being the reaction medium ($\varepsilon = 4$–6) as well. A recent study [2] shows that the kinetics of the singlet sensitized

photolysis depends on the solvent polarity. Yet, so far no mechanistic investigations have been reported about the photoreaction of excited triplet sensitizer with onium salts in nonpolar solvents.

In this work, we therefore studied the photoreactions of lipophilic onium salts with excited sensitizers in the triplet state in different solvents (acetonitrile, benzene, n-heptane, and mixtures of the latter two solvents). The onium compounds investigated are shown in Scheme 1 with their abbreviations adopted in this work; if not marked they were employed as their SbF$_6^-$ salts, which eliminates complications caused by participation of nucleophilic and/or oxidizable anions in these reactions. The following compounds have been used as triplet sensitizers: thioxanthone (TX), 2-chlorothioxanthone (CTX), xanthone (X), benzophenone (BP), pyrene (PY), benzil (BZ), and phenothiazine (PT). The triplet energies of this sensitizer vary between approximately 200 kJ mol^{-1} (PY) and 310 kJ mol^{-1} (X). Moreover, the oxidation potentials range from 0.6 V (PT) to 2.7 V (BP).

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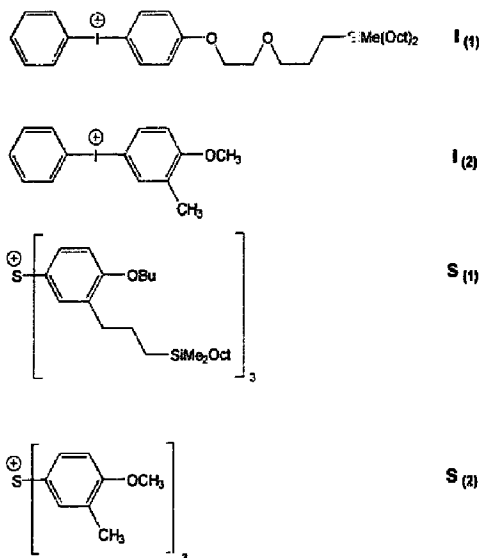
Scheme 1.

2. Experimental

All onium salts (see Scheme 1) were a gift (experimental products) from Wacker Chemie, Burghausen. The synthesis of these products has been described elsewhere [6]. $Ph_2I^+SbF_6^-$ and $Ph_3S^+SbF_6^-$ were prepared from the chlorides (Fluka) by anion exchange. They were purified by precipitation from a solution in isopropanol by adding n-heptane (50% v/v). All other chemicals and solvents were obtained commercially in the highest available purity. The solvents (Fluka, Aldrich) are used as received. The sensitizers used were recrystallized.

The experimental set up of the time-resolved laser spectroscopy and instrumentation used has been described on principle elsewhere [7]. The system used is hard- and software modified. The sample is excited by a short pulse of light (3 ns) delivered by a Nd/YAG laser operating at $\lambda = 355$ nm. The analysis of the transients is carried by using a time-resolved colorimetric device. The reaction cell (1 cm × 1 cm) was deaerated by argon bubbling. All measurements were made at room temperature (20 °C). The concentration of the sensitizer was adjusted to give on the irradiation wavelength (355 nm) an optical density 0.5.

energetic considerations
Scheme 2.
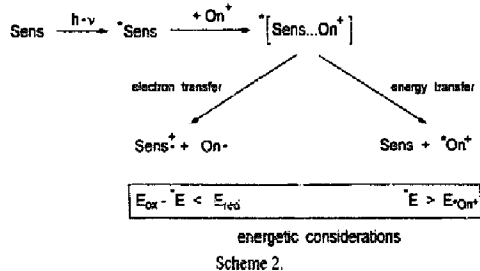
The voltammetric experiments were performed with a GWP 986 Polarograhic Analyzer (Lab. of Academy of Science) equipped with x–y plotter (ENDIM620.02) for current–potential curve registration. The cell consists of a thermostated sample kit of about 5 ml volume with inert gas and electrode fittings. A 0.77 mm^2 glass-sealed platinum disk acts as working electrode. The auxiliary electrode consisted of a BNC-contacted Pt wire. A platinum foil pseudo-reference electrode completed the three-electrode arrangement. The ohmic drop was compensated electronically by positive-feedback under oscillographic control (Voltcraft 2040).

All voltammetric data were referred to the standard potential of the ferrocene/ferrocenium redox couple, added to sample solution at the end of the measuring procedure (10–50 µl 0.3 M ferrocene in THF) and rescaled to SCE potential.

The sample and supporting electrolyte solutions were deaerated with purified argon. To prevent traces of moisture the supporting electrolytes were filtered over a column filled with activated alumina (neutral Al_2O_3 (Merck) for acetonitrile, basic Al_2O_3 (Aldrich) for tetrahydrofurane) according with Heinze [8].

3. Results and discussion

3.1. Electrochemical investigations

The sensitized photolysis of onium salts can occur through energy or electron transfer governed by thermodynamic requirements, see Scheme 2. Electron transfer from the excited sensitizer to onium salts is thermodynamically possible if the free energy obtained from the Rehm–Weller relationship is negative:

$$\Delta G = E_{ox} - E_{red} - {}^*E \qquad (1)$$

where ΔG^1 is the free energy of the electron transfer, E_{ox} is the half-wave oxidation potential of the sensitizer, E_{red} is the half-wave reduction potential of the onium salt, ${}^*E$ is the energy of the excited sensitizer (E_T = triplet energy; E_S = singlet energy).

The knowledge of the half-wave reduction potential of the onium salt is one of the basic conditions for the discussion of the mechanism of the sensitized photolysis. Therefore, we have carried out cyclic voltammetric investigations of all substituted onium salts under identical conditions. Acetonitrile and tetrahydrofurane were used as polar and nonpolar solvent, respectively. The results of these investigations are summarized in Table 1. Table 1 contains also the measured potentials of the unsubstituted iodonium and sulfonium hexafluoroantimonate.

Generally, all onium salts exhibit similar electrochemical behaviour. The reduction of the onium salt is irreversible, resulting in carbon–iodine or carbon–sulfur bond cleavage.

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[1] It is not necessary to include a coulombic term in Eq. (1) because only a positive charge is transferred from the onium salt to the sensitizer.

Table 1
Cyclovoltammetric determined half wave potentials of the onium salt hexafluoroantimonates in volt vs. SCE

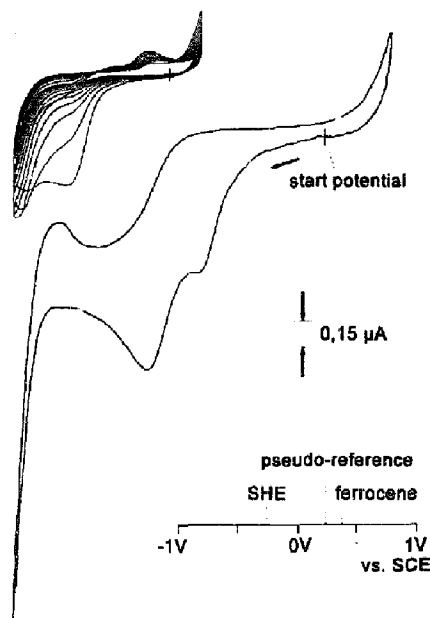| Solvent	Ph_2I^+	$I_{(2)}$	$I_{(1)}$	Ph_3S^+	$S_{(2)}$	$S_{(1)}$
Acetonitrile	I: +0.02	I: −0.04	I: −0.47	I: −1.01	I: −0.16	I: [a]
	II: −0.64	II: −0.61	II: −0.84	II: −1.46	II: −0.71	II: −1.67
			III: −1.39			
Tetrahydrofurane	[b]	I: −0.39		[b]	I: −0.48	I: −1.15
		II: −0.98	II −0.89		II: −1.01	II: −2.10
			III: −1.52			

[a] Not detectable.
[b] Not determined

Fig. 1. First scan of a typical cyclovoltammogram of $I_{(2)}$ in dry tetrahydro-furane (electrolyte, tetrahexylammoniumtetrafluoroantimonate; scan rate, 0.1 V s^{-1}; inset, second and subsequent scans).

Typical cyclic voltammograms are given in Fig. 1. From Fig. 1 it can be deduced that the onium salts will be reduced in more waves, which is determined by several processes [1,9,10b]. Nevertheless, a passivation of the electrode was observed for all systems used and is independent of the solvent used [9].

The definition of E_{red} from the observed peaks is difficult without knowledge of the electrochemistry. Bachofner [11] and Peters [12] agree that the value at about −0.6 V (all values versus SCE) is the potential for the reduction of soluble diphenyliodonium cation. This value corresponds to our observed more negative peak ($E_{1/2} = -0.64$ V). Moreover, −0.7 V [13] is consistent with observed electron transfer reactions [1,13b]. The cyclovoltammogram of $I_{(2)}$ is similar to the unsubstituted product. Under this assumption one can suspect that the more negative peak ($E_{1/2} = -0.61$ V) corresponds too, with E_{red}. Surprisingly, no influence of the

alkoxy group on the peak potential was found. From diazonium salts it is well known that donator substituents cause a decrease of E_{red} (0.3 V and respectively 0.14 for the unsubstituted and p-MeO-substituted benzene diazonium salt [14]).

In the cyclovoltammogram of $I_{(1)}$ three waves were observed [9]. However, the resolution of cyclovoltammogram is bad caused by the irreversibility of the e$^-$ transfer step. The second step ($E_{1/2} \approx -0.84$ V) reflects presumable the reduction potentials. Surprisingly, the lipophilic alkoxy substituent acts on the reduction potential of the iodonium salt. The observed negative shift from 200 mV to the unsubstituted product agree with the above diazonium salt results. Moreover, our findings show well that the solvent polarity influence also the positions of the steps, see Table 1. The reduction of the studied system $I_{(1)}$ and $I_{(2)}$ is more difficult in tetrahydrofurane than in acetonitrile. Interestingly, this effect is stronger for $I_{(2)}$ than for $I_{(1)}$, see Table 1. Nevertheless, in tetrahydrofurane one can observe for $I_{(2)}$ also a third step at stronger negative potentials [9].

The early work from McKinny [10] describes well the electrochemistry of triphenylsulfonium cations. Their reduction gives two waves in the polarogramm depending upon several parameters. The first wave ($E_{1/2} = -1.1...-1.2$ V) involves the formation of an unstable triphenylsulfonium radical. The second wave ($E_{1/2} \approx -1.4$) reflects the reduction of the primary products. Our cyclic voltammogram for triphenylsulfonium hexafluoroantimonate agrees well with the irreversible two-step mechanism. The first step ($E_{1/2} = -1.01$ V) corresponds to the reduction potential. Moreover, the second step ($E_{1/2} = -1.46$ V) describes the second polarographic wave.

From the results of iodonium salts one can expect that the m-Me and the p-MeO substituents have no significant influence on the reduction potential. Nevertheless, our findings show that the reduction of $S_{(2)}$ follows a more simple net reduction process than the reduction of the triphenylsulfonium salt; see Table 1.

In comparison with $S_{(2)}$ the reduction of $S_{(1)}$ is more difficult. The shift between the unsubstituted product and $S_{(1)}$ ranges in the same order (−0.21 V) as the shift between the Ph_2I^+ and $I_{(1)}$ (−0.2 V). However, in the case of $S_{(1)}$ one can observe in acetonitrile only one cathodic peak potential.

Table 2
Thermodynamic data (E_T, E_{ox}) and triplet state quenching rate constants (in 10^7 l mol^{-1} s^{-1}) of different sensitizer by onium salts in acetonitrile

Sensitizer	PY	BZ	PT	TX	CTX	BP	X
E_T (kJ mol^{-1}) [19d]	201.8	227.3	239 [a]	274.2	280.7 [b]	289.7	310.2
E_{ox} (V) [20]	1.16 [b]	2.4 [c]	0.6	1.7	1.52 [d]	2.7	1.8
$(E_{ox}-E_T)$ (kJ mol^{-1}) [e]	−89.9	4.3	−181.6	−110.3	−134.0	−29.2	−136.5
$I_{(2)}$, SbF$_6^-$	13.5	2.7	2314	1310	256	135.6	1100
$I_{(2)}$, tos$^-$	–	–	–	–	236	65.5	–
$S_{(2)}$, SbF$_6^-$	5.8	5.6	203.5	188	21.1	12.9	208
$S_{(2)}$, Cl$^-$	–	–	–	–	69.9	22.1	–

[a] From Ref. [20].
[b] From Ref. [21].
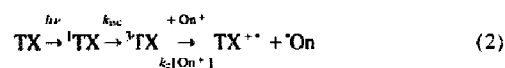[c] From IP (9.1 eV) of BZ [22], converted using $E_{ox} = 0.89 IP - 5.7$ [23].
[d] from Ref. [24].
[e] the value 96.5 converts E_{ox} into kJ mol^{-1} [19c].

Interestingly, a recent study [15] presents for the triphenyl-sulfonium cation a cylovoltammogram with only one cathodic peak potential ($E_{pc} = -1.52... -1.58$ V, in acetonitrile). Nevertheless, in tetrahydrofurane one can detect for $S_{(1)}$ two potentials where the first step ($E_{1/2} = -1.15$) is more negative than the reduction potential of the triphenyl-sulfonium salt in acetonitrile. Generally, it is observed that the reduction of the sulfonium compounds is in tetrahydro-furan more difficult than in acetonitrile.

3.2. Triplet quenching

3.2.1. Influence of the sensitizer

Thioxanthone (TX) and substituted thioxanthones are well-known triplet sensitizers of onium salt photolysis [16–18]. In polar solvents the quenching mechanism for the unsubstituted iodonium and sulfonium salt is an electron transfer to give the radical cation of the TX and the neutral radical of the onium salt [17,18], see Eq. (2). The rate constant of this reaction k_r can be determined by means of the Stern–Volmer relationship (3). Assumed the triplet quenching is the result of an electron transfer (k_q is equal k_e; normally it was found $k_q > k_e$).

$$TX \xrightarrow{h\nu} {}^1TX \xrightarrow{k_{isc}} {}^3TX \xrightarrow[k_c[\text{On}^+]]{+\text{On}^+} TX^{+\bullet} + {}^\bullet On \qquad (2)$$

$$\frac{1}{\tau} = \frac{1}{\tau_o} + k_q[\text{On}^+] \qquad (3)$$

where τ_o and τ are the triplet lifetimes in the absence and in the presence of the onium salt, $[\text{On}^+]$ is the onium salt concentration, and k_q is the rate constant of triplet quenching ($k_q \geq k_e$).

Our results show that triplet thioxanthone also reacts effectively with the substituted onium compounds; see Table 2 and Fig. 2. In acetonitrile is the triplet quenching more effective for $I_{(2)}$ than for the sulfonium compound $S_{(2)}$. Interestingly, k_q is for $I_{(2)}$ a magnitude higher than the k_e value determined in acetonitrile for TX and Ph$_2$I$^+$Cl$^-$
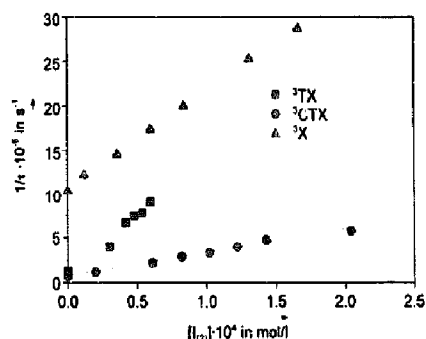

Fig. 2. Stern–Volmer plots of several triplet sensitizer and $I_{(2)}$ as quencher (solvent: acetonitrile; $I_{(2)}$ as hexafluoroanimonate).

(2×10^9 l mol^{-1} s^{-1}) [16]. The triplet quenching of CTX with $I_{(2)}$ and $S_{(2)}$ results in formation of a new transient with an absorption maximum at 450 nm. The spectra agree well with the cation radical of chlorothioxantone, absorbing in acetonitrile between 400 and 500 nm [17,18]. From this observation one can deduce that the triplet quenching is based on electron transfer for both onium salts.

The thermodynamic conditions of the electron transfer are given by Eq. (1). For a given sensitizer ΔG was determined using the reduction potential of the onium salt. The electron transfer step approaches the rate of diffusion as ΔG values ≤ -40 kJ mol^{-1}, see Fig. 3. Moreover, at higher ΔG values the rate constant of the electron transfer k_e decrease with increasing ΔG values [19]. The calculated ΔG value about approximately -50 kJ mol^{-1} for the TX/$I_{(2)}$ systems (determined with the cyclovoltametric potential $E_{1/2} = E_{red} = -0.61$ V ≈ -59 kJ mol^{-1}) corresponds well to measured rate constants of triplet quenching near the diffusion control ($k_{diff} = 1.9 \times 10^{10}$ l mol^{-1} s^{-1} in acetonitrile). However, by means of the determined potentials of $S_{(2)}$, one cannot explain the observed low rate constant for the triplet quenching of TX. Nevertheless, it is amazing that E_{red} of $S_{(2)}$ is lower than E_{red} of Ph$_3$S$^+$, whereas one would expect that the methoxy substituent causes a decreasing of E_{red}. According
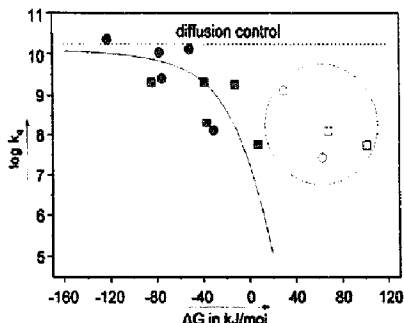
Fig. 3. Rehm–Weller fit of the determined triplet quenching rate constants (solvent: acetonitrile; circles: $I_{(2)}$; squares: $S_{(2)}$; all salts as hexafluoroantimonate; sensitizers: PT; X; CTX; TX; PY; BP; BZ; from left to right for each onium salt).

to the words of DeVoe et al. [1b] "care must be exercised when using reported reduction potentials ... for electron transfer thermodynamics ...", the potential of the Ph_3S^+ and the resulting ΔG value (≈ -11 kJ mol^{-1}) correlate well with the low rate constant observed. Presumably, it is an effect of the observed strong adsorption of $S_{(2)}$ on the electrode, which falsifies the real reduction potential of $S_{(2)}$ [9].

For a given onium salt ΔG depends on the oxidation power ($E_T - E_{ox}$) of the sensitizer. Therefore, we have also studied the triplet quenching also with 2-chlorothioxanthone (CTX), xanthone (X), benzophenone (BP), pyrene (PY), benzil (BZ), and phenothiazine (PT), which are well-known triplet sensitizers. Their triplet energies vary between 310 and 200 kJ mol^{-1}. The half-wave oxidation energies vary between 0.6 and 2.7 V; see Table 2.

The results of triplet quenching with these sensitizers are summarized in Table 2. The rate constants obtained reach the magnitude of related systems in acetonitrile. The following examples show that the reactivity of the used onium salts is comparable with known results. For instance: (a) the rate constants determined for CTX and $I_{(2)}$ is of the same order as that for CTX and (p-MeO-C_6H_4)$PhI^+AsF_6^-$ (2.1×10^9 l mol^{-1} s^{-1} [17]) respectively $Ph_2I^+AsF_6^-$ ($2.9\ 10^9$ l mol^{-1} s^{-1} [18]) as quencher; (b) CTX was quenched by $Ph_3S^+PF_6^-$ at 1.4×10^8 l mol^{-1} s^{-1} [25], which is nearly the same as for quenching by $S_{(2)}$; (c) the triplet quenching of PY by (p-MeO-C_6H_4)$PhI^+AsF_6^-$ (4.5×10^8 l mol^{-1} s^{-1} [17]) is of the same magnitude as that by $I_{(2)}$. Nevertheless, the k_c values for BP and $Ph_2I^+Cl^-$ (2.0×10^7 l mol^{-1} s^{-1} [16]) and respectively X and $Ph_2I^+Cl^-$ (1.4×10^9 l mol^{-1} s^{-1} [16]) are one order of magnitude lower than the values estimated by triplet quenching. The sensitized photolysis of onium salts can occur through energy or electron transfer governed by energetic considerations or by thermodynamic requirements; see Scheme 2. Presumably, the observed triplet quenching corresponds to mixed energy and electron transfer quenching. Mixed quenching was observed in polar solvents for BP and X using Ph_2I^+ [26]. It was estimated from the product dis-

tribution that X gave 25% and that BP gave 30% triplet sensitized photoproducts. Moreover, the triplet sensitized photolysis were also described for X and Ph_3S^+ [1,27c]. The missing formation of the sensitizer cation radical, which was observed only for PY and TX and both onium salts respectively for CTX and $I_{(2)}$ support this assumption.

For triplet quenching by electron transfer, the rate constant of quenching can be calculated by means of Eq. (4) [19e]:

$$k_q = \frac{k_d}{1 + A[\exp(\Delta G^{\ddagger}/RT) + \exp(\Delta G/RT)]}$$

with $A = \dfrac{k_d}{k_0 V_K}$ (4)

where k_d is the rate constant of diffusion in the solvent used, $\Delta G^{\ddagger}$ is the activation enthalpy of the electron transfer reaction, ΔG is the free reaction enthalpy of the electron transfer reaction, k_0 is a general frequency factor $\approx 10^{11}$–10^{14} s^{-1} [19], which depend on the solvent [28], V_K is the volume of the solvent cage ≈ 0.86 l mol^{-1} [19c].

Using the Weller theory one can calculate $\Delta G^{\ddagger}$ according Eq. (5):

$$\Delta G^{\ddagger} = \frac{\Delta G}{2} + \sqrt{\left(\frac{\Delta G}{2}\right)^2 + (\Delta G_0^{\ddagger})^2}$$ (5)

where $\Delta G_0^{\ddagger}$ is $\Delta G^{\ddagger}$ at $\Delta G = 0$ kJ mol^{-1} [19].

The theoretical plot of k_q versus ΔG according to Eq. (4) is given in Fig. 3. The used values for $A = 0.22$ ($k_d = 1.9 \times 10^{10}$ l mol^{-1} s^{-1}; $k_0 = 10^{11}$ l mol^{-1} s^{-1}; $V_K = 0.86$) and $\Delta G_0^{\ddagger} = 20$ kJ mol^{-1} are typical values for many low viscous solvents [19]. Fig. 3 also includes the measured triplet quenching values for all sensitizer and onium salts used. From Fig. 3 one can deduce that the most measured k_q values fit the theoretical plot. Nevertheless, the high values obtained for BP and BZ do not correlate with an electron transfer reaction. The high k_q values and the high E_T value of BP account for an energy transfer. However, the measured high k_q value does not correlate with an endergonic energy transfer. The cause of that triplet quenching is not clear until to now.

3.2.2. Triplet quenching in nonpolar solvents

Our results demonstrate that substituted onium salts react effectively with exited sensitizers in polar solvents. However, the technical applications of the onium salts take place in aprotic nonpolar solvents, the monomer ($\varepsilon = 4$–6) usually being the reaction medium as well. We therefore also studied the photoreactions of onium salts with excited sensitizer in n-heptane. Owing to the poor solubility of the short chain substituted salts the quenching experiments were carried out using the lipophilic products $I_{(1)}$, and $S_{(1)}$ with a similar pattern of substitution to the products $I_{(2)}$ and $S_{(2)}$.

One can observe that the absorption maxima of the TX, CTX and BZ triplets undergo a bathochromic shift of about 20–40 nm on changing from the polar acetonitrile to the nonpolar n-heptane. A hypsochromic shift of about 30–50 nm
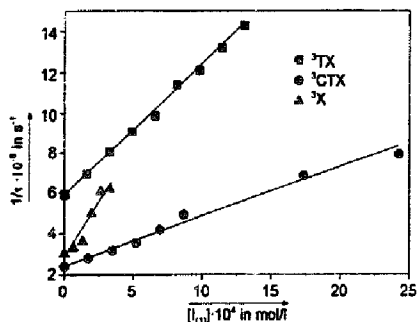
Fig. 4. Stern–Volmer plots of several triplet sensitizer and the lipophilic $I_{(1)}$ as quenchers (solvent: n-heptane; $I_{(1)}$ as hexafluoroanimonate).

Table 3
Triplet state quenching rate constants (in 10^7 l mol^{-1} s^{-1}) of different sensitizer by onium salts in n-heptane

Sensitizer	PY	BZ	PT	TX	CTX	BP	X
$I_{(1)}$ SbF$_6^-$	1.2	8.4	43.7	64.4	23.7	16.3	110
$I_{(1)}$ tos$^-$	–	–	69.3	69.4	20.6	20.5	–
$S_{(1)}$ SbF$_6^-$	0.2	5.6	1020	58.0	22.2	18.3	154
$S_{(1)}$ PF$_6^-$	–	–	731	68.3	19.3	17.7	–
$S_{(1)}$ Cl$^-$	–	–	618	85.7	51.7	19.0	–

was observed for X and PT. BP and PY show no solvatochromic effects. Nevertheless, most of the excited triplet sensitizers react with the lipophilic sulfonium and iodonium salts. Fig. 4 gives typical Stern–Volmer plots of several sensitizers and the lipophilic iodonium salt $I_{(1)}$. The rate constant of triplet quenching determined from the Stern–Volmer plot are summarized in Table 3.

A comparison of Tables 2 and 3 shows that the efficiency of triplet quenching differs in acetonitrile and n-heptane, the influence being stronger for the iodonium salt ($I_{(1)}/I_{(2)}$) than for the sulfonium salts ($S_{(1)}/S_{(2)}$). In n-heptane X the most reactive sensitizer for $I_{(1)}$. However, the sulfonium salt reacts better with PT. Pyrene has the lowest triplet energy for the quenching reaction of the lipophilic onium salts in the nonpolar solvent. Moreover, with exception of PT and PY there are no strong differences in quenching between iodonium and the sulfonium compounds.

In polar solvents the quenching mechanism of TX is electron transfer. The triplet quenching in n-heptane results in formation of a new transient with an absorption maximum at 530 nm (studied for $I_{(1)}$ and $S_{(1)}$). Under the assumption that the observed transient is TX$^{+\cdot}$, the triplet quenching is based on electron transfer.

Our results show that cyclovoltametrically determined half-wave potentials decrease with decreasing solvent polarity; see Table 1. Using the values obtained in tetrahydrofurane ($I_{(1)}$, −0.89 V; $S_{(1)}$, −1.15 V versus SCE) one can calculate ΔG values ($\approx$ −23 kJ mol^{-1} and $\approx$ 2 kJ mol^{-1} for TX with $I_{(1)}$ and with $S_{(1)}$), respectively, which agree with an electron transfer reaction. Nevertheless,
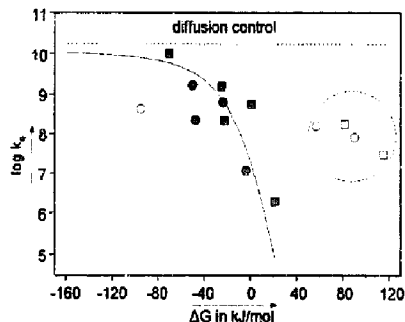

Fig. 5. Rehm–Weller fit of the determined triplet quenching rate constants (solvent: n-heptane; circles: $I_{(1)}$; squares: $S_{(1)}$; all salts as hexafluoroantimonate; sensitizers: PT; X; CTX; TX; PY; BP; BZ; from left to right for each onium salt).
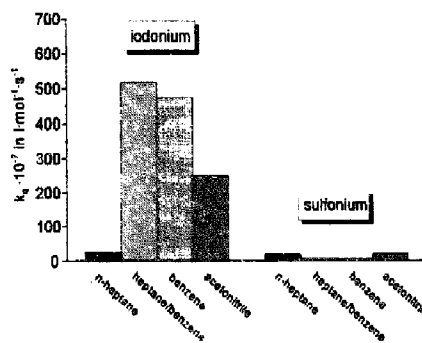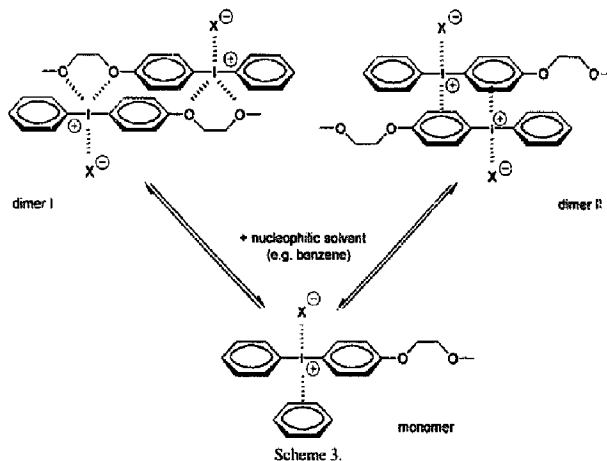

Fig. 6. Rate constant of triplet quenching as function of the solvent polarity (sensitizer: CTX; the lipophilic onium salts $I_{(1)}$ and $S_{(1)}$ were used in heptane, heptane/benzene and benzene; in acetonitrile $I_{(2)}$ and $S_{(2)}$ was used as quencher).

remarkably the iodonium and sulfonium salts show no differences in reactivity towards triplet quenching although ΔG differs for both salts.

The theoretical plot of k_q versus ΔG according to Eq. (4) is given in Fig. 5. The values used are as follows: $A = 0.19$ ($k_d = 1.6 \times 10^{10}$ l mol^{-1} s^{-1}; $k_0 = 10^{11}$ l mol^{-1} s^{-1}; $V_K = 0.86$), $\Delta G_0^{\ddagger} = 20$ kJ mol^{-1}. The figure also includes the measured triplet quenching values in n-heptane for all sensitizer and onium salts used. From Fig. 5 one can see that the determined values fit the theoretical plot poorly. The behaviours of BP and BZ towards both onium compounds are similar to those in acetonitrile. Nevertheless, the evidence of electron transfer is the formation of the short-lived sensitizer cation radical. A new transient absorption has been observed only for CTX and $I_{(1)}$ ($\lambda_{max} = 540$ nm) and the above TX systems.

To study the specifics of the solvent n-heptane the triplet quenching of ^{3}CTX was carried out in different solvent mixtures; see also Ref. [29]. The results of these studies are summarized in Fig. 6. From Fig. 6 one can see that the two onium salts react differently on changing of the solvent properties. The quenching reaction of the sulfonium salt is hardly influenced by the polarity of the solvent used. The iodonium salt shows a strong dependence on the polarity. In comparison

Scheme 3.

with n-heptane the rate constant increases in benzene by one order of magnitude. Moreover, the magnitude of triplet quenching in benzene for $I_{(1)}$ is one order of magnitude higher than that for $S_{(1)}$. The calculated k_q values for the CTX/onium salts systems $(2.7 \times 10^9 \, \text{l mol}^{-1} \, \text{s}^{-1}$; $5.4 \times 10^8 \, \text{l mol}^{-1} \, \text{s}^{-1}$ for $I_{(1)}$ and $S_{(1)}$) respectively agree well with measured rate constants of triplet quenching in benzene. A similar dramatic solvent effect between n-heptane and toluene was observed for singlet quenching of anthracene using $I_{(1)}$ and $S_{(1)}$ [29].

Presumably, the observed strong solvent effect for $I_{(1)}$ is an effect of the solvation of the lipophilic iodonium salts. It is well known that the iodonium salts crystallizes as a dimer [30]. Maybe, a dimer of $I_{(1)}$ exists in n-heptane and can be destroyed by means of electron donating solvents; see Scheme 3. By means of this theory one can explain that the triplet quenching in benzene has the same magnitude than in acetonitrile.

3.2.3. Influence of the anion

The cationic polymerization requires weakly nucleophilic anions. Nevertheless, with a view to finding a possible influence of the anion on the triplet quenching, we also studied the triplet quenching with onium salts having different counterions, PF_6^-, Cl^-, tos^- (tosylate). PT, CTX and TX were used as typical electron transfer sensitizers. Moreover BP serves as sensitizer where electron and energy transfer is possible. The results of these findings in n-heptane are summarized in Table 3.

In general one can expect that the triplet quenching of the sensitizers used depends in different ways on the onium salt and anion used. The triplet quenching of TX is nearly independent of the anion used. The metal halide anions have no influence on quenching of the CTX and BP triplets. Nevertheless, using PT k_q decreases when the metal halide anion changes from SbF_6^- to PF_6^-. The influence of the nucleophilic anions Cl^- and tos^- on the rate constant is also different. In comparison with SbF_6^- one can observe a increase of k_q using

the $PT/I_{(1)}/tos^-$, and $CTX/S_{(1)}/Cl^-$. A decrease of k_q was also observed for $PT/I_{(1)}/Cl^-$. The behaviour in acetonitrile for the $I_{(2)}/tos^-$ and $S_{(2)}/Cl^-$ systems studied is similar to that of the lipophilic salts in n-heptane; see Tables 2 and 3. Interestingly, with the $BP/I_{(2)}/tos^-$ system one can observe a decrease of the rate constant.

The reason for the observed influence is unknown at this time. Nevertheless, the behaviour in acetonitrile and n-heptane differs from literature findings where $Ph_2^+ Cl^-$ and $Ph_2I^+ AsF_6^-$ do not show any marked influence in methanol on the triplet quenching rate constant of substituted thioxanthones [25].

Acknowledgements

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