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The quenching of short-lived S_2 states of aromatic thioketones by hydrocarbons. I. Important contributions of the transient effect from steady-state measurements

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Abstract

The very efficient fluorescence quenching of seven aromatic thioketones in the second excited singlet state S_2 (lifetime τ_{S_2} = 53–857 ps in inert perfluoro-1,3-dimethylcyclohexane) has been examined by quantum yield and/or intensity measurements. Five *n*-alkanes (C_6H_{14}, C_8H_{18}, C_8D_{18}, $C_{10}H_{22}$ and $C_{16}H_{34}$) as well as 2,2,4,4,6,8,8-heptamethylnonane, cyclohexane, benzene and their deuterated derivatives were used as quenchers.

The contribution of the transient effect to the quenching rate constant k_q, which depends on the S_2-thioketone lifetime as well as on the size and diffusion coefficient of the quencher, has been investigated. The role of the transient effect in the quenching process was found to be very significant. Taking the transient effect into account, the quenching rate constants calculated from the Stern–Volmer relation ranged from 0.2×10^{10} M^{-1} s^{-1} to the very large value of 12×10^{10} M^{-1} s^{-1}.

These experimental results have been rationalized by assuming the Smoluchowski–Collins–Kimball model. A comparison has been made between the measured and calculated values of k_q for almost 40 donor–quencher systems in perfluoro-1,3-dimethylcyclohexane.

Keywords: Quenching; S_2 states; Aromatic thiketones; Steady-state measurements

1. Introduction

Short-lived aromatic thioketones exhibit unique reactivity in the S_2 excited state [1–3]. Because of this many alkane solvents (ALs), including 3-methylpentane, quench short-lived S_2-thiones at diffusion-controlled rates [1,3]. This, in turn, enables experimental investigations of the transient effect in quenching [4–9] to be made within the system. To study such phenomena, it is necessary to use solvents such as perfluoroalkanes (PFs) [1–3] which are exceptionally inert.

The influence of the quenching mechanism, and the properties of the excited donor (D*), quencher (Q) and solvent on the contribution of the transient effect to the quenching process, has been discussed in numerous publications [4–21]. Relatively few of these papers have reported experimental studies of this effect, by either dynamic or steady-state methods [7,22–34]. Moreover, except for the cases described in our earlier papers [25,26], the contribution of the transient effect to the quenching process has never been large. It has therefore been difficult to estimate quantitatively the contribution of the transient effect to the quenching processes. These difficulties have been compounded by the fact that data on the diffusion coefficient *D* and the molecular radii *R* of the donors and quenchers studied have not been readily accessible.

Recently [25] we showed that the quenching of the S_2 state of xanthione by five *n*-alkanes (C_6H_{14}, C_8H_{18}, $C_{10}H_{22}$, $C_{13}H_{28}$ and $C_{16}H_{34}$) in perfluoro-1,3-dimethylcyclohexane (PFDMCH) has a large rate constant $k_q = (1–5)\times10^{10}$ M^{-1} s^{-1}, owing to the large contribution of the transient effect to the quenching process. A satisfactory explanation of the results for the quenching of six other excited aromatic thiones by hexadecane was also provided by assuming a decisive role of the transient effect in the quenching process. The influence of a change in the viscosity of the PF solvent (in the range from 0.46 to 5.6 cP) on the k_q value was explained. For most of the D*–Q–solvent systems studied, relatively good agreement between the experimental values of k_q and the values calculated from the time-dependent Smoluchowski equation (see below Eq. (10)) was found [25].

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The aim of the paper is to examine further and to discuss the role of the transient effect in the quenching process using S_2-thione fluorescence quenching by saturated linear, branched and cyclic hydrocarbons and by benzene in PF solvents as model systems. In these investigations we have used seven aromatic thioketones of quite short S_2 lifetime ($\tau_{S_2} = 53$–857 ps) as donors. The quenchers employed differ in size ($R_Q = 3.0$–11.0 Å) and in molecular structure as well as in their C–H bond energies. We anticipated that such a selection of donor and quencher properties (involving also D isotope substitution for H) would permit an examination of the mechanism and kinetics of quenching under conditions to which the transient effect made a large and widely varying contribution. This paper also aims to test whether the most frequently used theoretical models by Smoluchowski [35] and Collins-Kimball [36] provide a satisfactory description of our experimental results.

2. The transient effect in bimolecular quenching

The theory of bimolecular diffusion-controlled process kinetics has been the subject of many papers [4–21,35–39], most of which assume the continuum model for the medium. Experimentally, one of the most useful ways of examining the kinetics of bimolecular processes involves studies of the quenching of the fluorescence of electronically excited molecules D* by quenchers Q. In such systems, the following are usually assumed (following [19,24,35–38]),

(a) D* and Q are spherical and have radii of R_D and R_Q respectively.

(b) Donors and quenchers are randomly distributed in the solution.

(c) An encounter between D* and Q results in quenching when the distance between their centers of mass is equal to $R = R_D + R_Q$.

(d) For a separation distance $r > R$, not interaction between D* and Q occurs.

(e) The concentration of Q is considerably higher than that of D*, i.e. $[Q] \gg [D^*]$.

Consider the overall quenching process

$$D^* + Q \longrightarrow \text{product} \qquad (1)$$

Smoluchowski [35] derived the general expression for the measured rate constant of the reaction described by

$$k = \frac{4\pi R^2 N' D \{\partial[Q](r,t)/\partial r\}|_{r=R}}{[Q]} \qquad (2)$$

Here $D = D_{D*} + D_Q$ is the sum of diffusion coefficients of D^* and Q, $\{\partial[Q](r,t)/\partial r\}|_{r=R}$ is the gradient of the concentration of quencher molecules on the surface of sphere of radius R, N' is Avogadro's constant divided by 1000, and k is the observed rate constant for process (1). The $[Q](r,t)$ function can be calculated from Fick's second law:

$$\frac{\partial[Q](r,t)}{\partial t} = D\nabla_r^2[Q](r,t), \qquad (3)$$

where

$$\nabla_r^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right)$$

This equation was solved for the following (Smoluchowski–Collins–Kimball) conditions.

(i) $[Q](r,0) = [Q]$ for $r > R$.

(ii) $[Q](r,0) = 0$ for $r \leqslant R$, with the boundary conditions as follows

(iii) $[Q](\infty,t) = [Q]$.

(iv) $(\partial/\partial r)[Q](r,t)|_{r=R} = (k_r/4\pi R^2 D)[Q](r,t)$.

If the intermolecular attraction–repulsion potential is neglected, then according to the Smoluchowski–Collins–Kimball model the rate coefficient is given by:

$$k(t) = \frac{4\pi R D N'}{1 + 4\pi R D}\left(1 + \frac{k_r}{4\pi R D}\exp(x^2)\,\mathrm{erfc}(x)\right) \qquad (4)$$

where $x = [(Dt)^{1/2}/R](1 + k_r/4\pi RD)$ and k_r ($\mathrm{M}^{-1}\,\mathrm{s}^{-1}$) is a specific quenching rate constant.

The quenching of D* may be measured by both dynamic and steady-state methods. In the presence of a quencher the expression describing the decay of D* fluorescence has the form

$$I(t) = I_0 \exp\left[\left(-\frac{t}{\tau}\right) - [Q]\int_0^t k(t)\,\mathrm{d}t\right] \qquad (5)$$

As Ware and Novros [24] showed, if $k_r \rightarrow \infty$ and the transient effect is taken into account, the fluorescence quantum yield ratio Φ_F^0/Φ_F exhibits a non-linear dependence on [Q]:

$$\frac{\Phi_F^0}{\Phi_F} = \int_0^\infty \exp\left(-\frac{t}{\tau}\right)\mathrm{d}t \Big/ \int_0^\infty \exp\Bigl[-\Bigl(\frac{1}{\tau} + k_{\mathrm{diff}}[Q]\Bigr) \times t - k_{\mathrm{diff}}\frac{2R}{(\pi D)^{1/2}}[Q]t^{1/2}\Bigr]\mathrm{d}t \qquad (6)$$

$$= \frac{1 + k_{\mathrm{diff}}\tau[Q]}{1 - \frac{1}{2}u\pi^{1/2}\exp(\frac{1}{4}u^2)\,\mathrm{erfc}(\frac{1}{2}u)} \qquad (7)$$

where $u = (2/\pi^{1/2})\{k_{\mathrm{diff}}\tau[Q)/(1 + k_{\mathrm{diff}}\tau[Q])^{1/2}\}[R/(D\tau)^{1/2}]$.

As a rule, Φ_F^0/Φ_F vs. [Q] is positively curved when the transient effect is significant. However, Ware and coworkers [24,40] and Birks and coworkers [4] have shown that for small [Q] this curvature may be slight and hard to detect. Thus, for small concentrations of the quencher, Eq. (7) may be expanded as a function of [Q] in a Taylor series to give [4,24,37,40]:

$$\lim_{[Q]\to 0}\left(\frac{\Phi_F^0}{\Phi_F}\right) = 1 + k_{diff}\left(1+\frac{R}{(D\tau)^{1/2}}\right)\tau[Q] \qquad (8)$$

where $k_{diff} = 4\pi RDN'$. Thus, if $R/(D\tau)^{1/2}$ is a significant fraction of unity, it should be possible to study the transient effect using steady-state fluorescence quenching measurements. It is useful to introduce the quantity TT (cf. for example [4,40]) describing the contribution of the transient effect to the quenching process:

$$\mathrm{TT} = \frac{R}{(D\tau)^{1/2}} \qquad (9)$$

The rate constant for the quenching of D* by Q, for small values of [Q], may thus be written

$$k_{diff}^{SV} = k_{diff}(1+\mathrm{TT}) \qquad (10)$$

where k_{diff}^{SV} may be compared with the observed quenching rate constant k_q which is determinable from Stern–Volmer plots.

Eqs. (9) and (10) following directly from Eq. (8) are suitable for determination of fluorescence quenching rate constants. They will be used in the following discussion of our experimental results. Taking a typical value (in our studies) of TT = 3 and the maximum concentration used, [Q] = 0.1 M, we see that the values of Φ_F^0/Φ_F calculated with eqs. (7) and (8) differ only by about 4%. Given typical measuring errors (±5%), it seems reasonable to use the simpler expression, Eq. (10), to evaluate k_q. As was shown by Szabo [9] for steady-state properties, e.g. the fluorescence intensity, the Smoluchowski approach is essentially equivalent to the mean field theory in two and higher dimensions and for low quencher concentrations.

3. Experimental details

The thioketones employed were synthesized and purified as described in [1]. Hexane, octane, decane, hexadecane, 2,2,4,4,6,8,8-heptamethylnonane (7MeN), cyclohexane, benzene and their deuterated derivatives (Merck, Aldrich, Fluka, PAN-ICHF) of spectroscopic and/or gas chromatography purity were used as quenchers. PFDMCH, purified by column chromatography and repeated distillation, was used as a solvent.

Absorption and emission spectra were measured using an M-40 spectrophotometer (C. Zeiss) and a modified MPF-3 spectrofluorometer (Perkin–Elmer) respectively.

For the fluorescence quenching measurements, the experimental conditions were selected so that radiation was absorbed only by the thioketone. The inner filter effect and photolysis of thiones were kept to a minimum. Quenchers C_6H_{14}, C_8H_{18}, $C_{10}H_{22}$, 7MeN, c-C_6H_{12} and C_6H_6 were used in concentrations of 0.1 M or less, and $C_{16}H_{34}$ in concentrations of 0.02 M or less. The thioketone concentration was of the order of 10^{-5} M and absorbance at λ_{exc} was always lower than 0.15. All measurements were made at room temperature using non-deoxygenated samples. The reported values of k_q are the averages of at least three independent measurements of Φ_F^0/Φ_F.

4. Results

Seven aromatic thioketones (Fig. 1) were used as donors to study the efficiency of the quenching process and the role of the transient effect. Consistent with the main aim of the paper, we selected donors which exhibit short but widely differing S_2-state lifetimes ($\tau_{S_2} = 53$–857 ps [1,41,42]). These thioketones exhibit a relatively wide range of S_2 energies ($E_{S_2} = 62$–83 kcal mol^{-1}) but have similar sizes and structures. In PF solvents, the selected thioketones exhibit $S_2 \rightarrow S_0$ fluorescence (Fig. 2), with quantum yields Φ_F^0 varying from 0.002 to 0.14 [1,41], making it possible to study quenching by simple measurements of Φ_F^0/Φ_F or I_F^0/I_F.

The common alkanes proved to be unusually efficient quenchers of S_2-thiones [1,25,42]. For convenience, we used four n-alkanes, C_6H_{14}, C_8H_{18}, $C_{10}H_{22}$ and $C_{16}H_{34}$, which differed in their van der Waals radii along the carbon chain (long axis of the molecule) in the range $R_Q = 4.9$–11.0 Å. 7MeN ($R_Q = 6.7$ Å) and cyclohexane ($R_Q = 3.3$ Å) were also used as quenchers. The only active bonds in all these quenchers are C–H bonds. In benzene ($R_Q = 3.0$ Å) used as a quencher, the aromatic ring should be responsible for the quenching.

PFs were used as solvents because they are chemically inert and exhibit unusually weak solvent–solute interactions [1–3,41–44]. Only if PFs were applied in our earlier work could we obtain intramolecular properties of S_2-thiones almost unmodified by interactions with a solvent in fluid solution, at room temperature. According to our best knowledge, all the available theories, beginning with the description of quenching given by Smoluchowski, treat solvents as an unreacting continuum. Thus PFs seem to be the only group of solvents fulfilling this assumption, as we have proven [2,42–44] concerning solvent spectral shift in PFs.

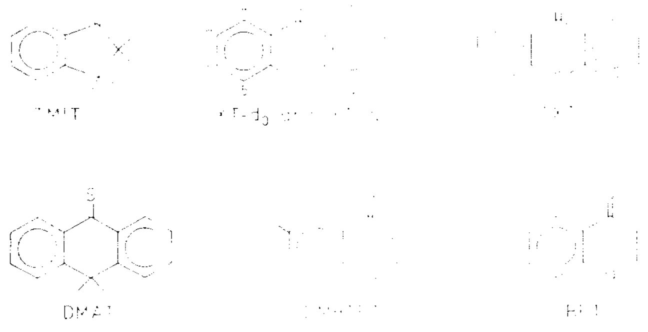

Fig. 1. Structures of the thioketones used in this study: TMIT, 2,2,3,3-tetramethylindanethione; BPT, 4H-1-benzopyran-4-thione; XT-d_0, xanthione; XT-d_6, xanthione deuterated at positions 1,3,4,5,6,8; TXT, thioxanthione; DMBTPT, 2,6-dimethyl-4H-1-benzothiopyran-4-thione; DMAT, 9,9-dimethylantrathione.

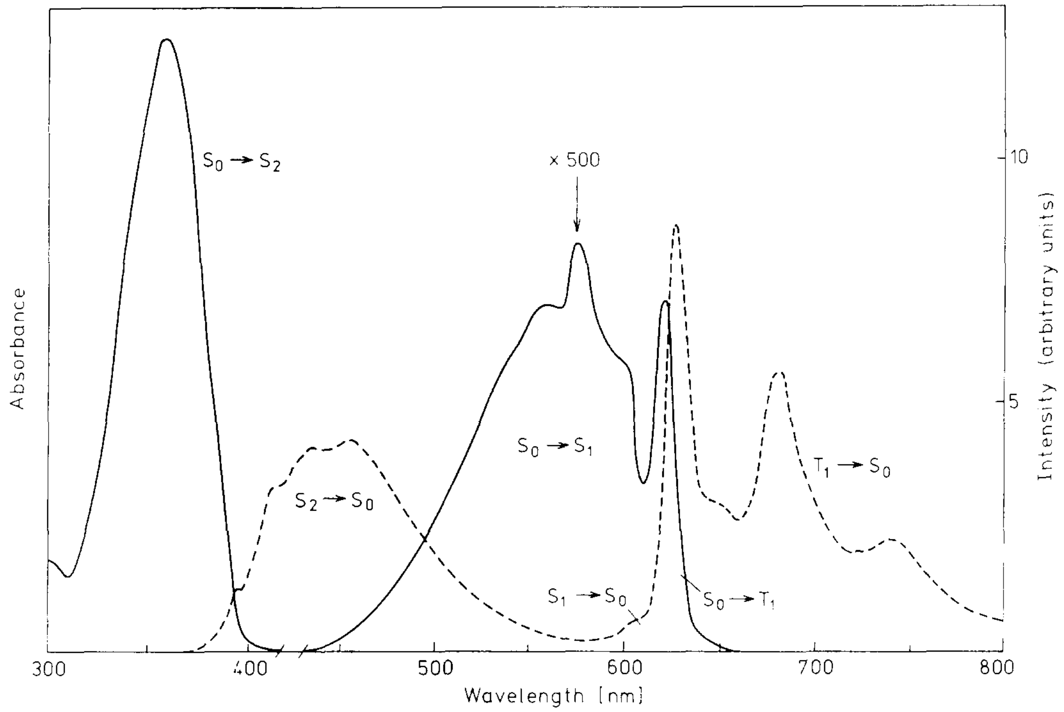

Fig. 2. Absorption and emission spectra of 4H-1-benzopyran-4-thione in perfluoro-1,3-dimethylcyclohexane at room temperature.

The value of k_q determined for S_2-thione fluorescence quenching using steady-state methods may be affected not only by the transient effect, but also by pseudoquenching (i.e. ground-state complex formation), static quenching, long-range energy transfer and inner filter effects. Because the wavelength range of the $S_2 \rightarrow S_0$ thione emission ($E_{S_2} < 83$ kcal mol^{-1}) and the wavelength range of the $S_0 \rightarrow S_1$ quencher absorption band ($E_{S_1} > 105$ kcal mol^{-1}) differ greatly, the contribution of the two latter effects may be totally neglected. Quencher concentrations 0.1 M or less were employed, so that the contribution of static quenching to the overall quenching process was also low (10% or less). However, ground-state complex formation is difficult to prove and this problem was therefore addressed more thoroughly.

The following evidence is offered in support of our conclusion that ground-state interactions between the thioketones (Fig. 1) and the hydrocarbon quenchers employed in this study were too weak for complexes to be formed in significant amounts at room temperature.

(1) UV–visible absorption and emission spectra were measured at thione (10^{-6}–10^{-4} M) and quencher (10^{-3}–10^{-1} M) concentrations higher (a factor of more than 10 in some cases) than those employed in the quenching measurements, so as to obtain the highest possible concentration of any ground-state complex. However, no changes in the absorption and emission spectra which would indicate the presence of such ground-state complexes were observed. Relatively low concentration of quenchers and very small concentrations of thiones are used in the quenching measurements (owing to a solubility problem in PFs). Nevertheless, the UV–visible spectrum should be a relatively sensitive test of complex formation in these systems because the thiones absorb over a broad spectral range (200–700 nm) encompassing at least five well-resolved absorption bands (often with readily observable vibrational structure in PF solvents) and because, except for benzene, none of the quenchers and solvents absorbs at $\lambda > 200$ nm.

(2) Except for a small solvent shift, the UV–visible spectra of XT-d_0, XT-d_6 and TXT are each identical in C_6H_{14}, $C_{10}H_{22}$ and $C_{16}H_{34}$. However, significantly different values of k_q are obtained when the same alkanes are used as quenchers in PFDMCH (Tables 1–3).

(3) To our knowledge, no evidence of ground-state complex formation between aromatic thiones and alkanes has been reported in the literature.

Under $S_0 \rightarrow S_2$ excitation the $S_2 \rightarrow S_0$ fluorescence intensity I_F, the $S_2 \rightarrow S_0$ fluorescence quantum yield Φ_F and the thione S_2 lifetime τ_{S_2} all decreased with increasing quencher concentration [25,42,43]. A typical result illustrating the dependence of $\Phi_F{}^0/\Phi_F$ on the concentration of the quencher is presented in Fig. 3. At $[Q] < 10^{-1}$ M, for which $\Phi_F{}^0/\Phi_F \leqslant 1.4$, all such plots are almost linear. The values of k_q for S_2-thiones quenched by the linear alkanes, hexane, decane and hexadecane, are given in Tables 1–3 together with the values of TT and $k_{diff}{}^{SV}$ calculated from Eqs. (9) and (10). For reference the values of τ_{S_2} for the thiones in PFDMCH, and their S_2 energies E_{S_2} are listed in Table 1. Determination of the quencher molecule radii R_Q may be a problem. Although AL molecules are not rigid, their shape is similar to that of propane, pentane and decane molecules [45,46]. In view of that, we decided to adopt the same way for calculating their molecular radii assuming they had a linear effective structure and their diffusion coefficients D_Q in

Table 1
Values of the transient term TT and the rate constant k_q for the quenching of thiones with various S_2 lifetimes by hexane in perfluoro-1,3-dimethylcyclohexane at room temperature

Thione [a]	τ_{S_2} [b] (ps)	E_{S_2} [b] (kcal mol^{-1})	TT	$k_q \times 10^{-10}$ (M^{-1} s^{-1})	$k_{diff}^{SV} \times 10^{-10}$ (M^{-1} s^{-1})	k_q/k_{diff}^{SV}
TMIT	857	83.0	0.95	0.62	1.15	0.54
XT-d_6	600	68.2	1.14	0.70	1.26	0.56
DMAT	467	68.1	1.29	0.63	1.35	0.47
BPT	221	72.8	1.88	1.05	1.70	0.62
XT-d_0	178	68.3	2.04	0.98	1.79	0.55
DMBTPT	73	66.4	3.22	1.52	2.49	0.61
TXT	53	62.2	3.83	0.87	2.85	0.31

$D_Q = 0.38 \times 10^{-5}$ cm^2 s^{-1}; $R_Q = 4.9$ Å; $D_{thione} = 0.52 \times 10^{-5}$ cm^2 s^{-1}, $R_{thione} = 3.8$ Å; $k_{diff} = 0.59 \times 10^{10}$ M^{-1} s^{-1} (calculated from Eq. (12)).
[a] [Thione] $\leqslant 10^{-5}$ M.
[b] From [42].

Table 2
Values of the transient term TT and the rate constant k_q for the quenching of thiones with various S_2 lifetimes by decane in perfluoro-1,3-dimethylcyclohexane at room temperature

Thione	TT	$k_q \times 10^{-10}$ (M^{-1} s^{-1})	$k_{diff}^{SV} \times 10^{-10}$ (M^{-1} s^{-1})	k_q/k_{diff}^{SV}
TMIT	1.38	1.04	1.55	0.67
XT-d_6	1.65	1.62	1.72	0.94
DMAT	1.86	1.47	1.86	0.85
BPT	2.72	1.95	2.42	0.81
XT-d_0	2.93	2.39	2.55	0.94
DMBTPT	4.71	5.26	3.06	1.72
TXT	5.55	3.62	4.26	0.85

$D_Q = 0.25 \times 10^{-5}$ cm^2 s^{-1}; $R_Q = 7.4$ Å; values of τ_{S_2}, E_{S_2}, D_{thione} and R_{thione} are given in Table 1; $k_{diff} = 0.65 \times 10^{10}$ M^{-1} s^{-1}.

Table 3
Values of the transient term TT and the rate constant k_q for the quenching of thiones with various S_2 lifetimes by hexadecane in perfluoro-1,3-dimethylcyclohexane at room temperature

Thione	TT	$k_q \times 10^{-10}$ (M^{-1} s^{-1})	$k_{diff}^{SV} \times 10^{-10}$ (M^{-1} s^{-1})	k_q/k_{diff}^{SV}
TMIT	1.92	1.72	2.34	0.74
XT-d_6	2.30	2.63	2.64	1.00
DMAT	2.60	2.34	2.88	0.81
BPT	3.79	3.99	3.83	1.04
XT-d_0	4.10	4.87	4.08	1.19
DMBTPT	6.59	14.53	6.07	2.39
TXT	7.75	14.98	7.00	2.14

$D_Q = 0.17 \times 10^{-5}$ cm^2 s^{-1}; $R_Q = 11$ Å; values of τ_{S_2}, E_{S_2}, D_{thione} and R_{thione} are given in Table 1; $k_{diff} = 0.8 \times 10^{10}$ M^{-1} s^{-1}.

PFDMCH are also given in the footnotes to these tables. The latter values were calculated as in [25] using the diffusion coefficient for anthracene measured in perfluorohexane as a reference [47]. Diffusion coefficients of the donors and quenchers were also calculated from the Stokes–Einstein equation [4,6,47,48]:

$$D_{SE} = \frac{k_B T}{4\pi\eta R_{SE} f} \qquad (11)$$

where D_{SE} is D_D or D_Q, k_B is the Boltzmann constant, and R_{SE} is R_D or R_Q. The "slip" limit was assumed for the solvent, i.e. a factor of 4 is used in Eq. (11) because of the properties of liquid PFs [2,50]. The structure of the solvent medium surrounding the diffusing molecule was taken into account by using the coefficient of microfriction [4,49,51]: $f = 0.16 + 0.4(R_{solute}/R_{solvent})$. The values of D_D and D_Q obtained from Eq. (11) are about 20–30% higher than those determined using data for the diffusion of anthracene. We used the former in the calculation of k_{diff} and TT as we believed that we would get more accurate results in this way (see below).

The values of D_{thione} were determined similarly. A value of $R_{thione} = 3.8$ Å was assumed because this is the van der Waals radius along the axis of the molecule on which the C=S group responsible for S_2-thione quenching is located [1,3,52,53]. With the values of τ_{S_2}, $D = D_{thione} + D_Q$ and $R = R_{thione} + R_Q$ in hand, the value of TT was then calculated using Eq. (9) (Tables 1–3). It was then possible to estimate the contribution of the transient effect to the values of k_q

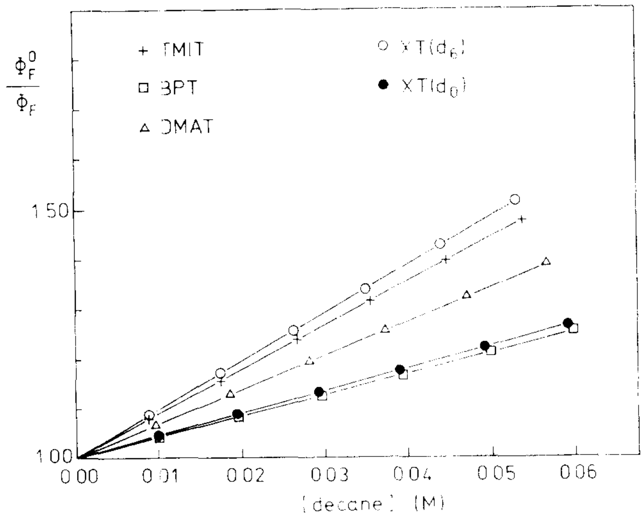

Fig. 3. Stern–Volmer plot for the quenching of the second excited singlet state of several thiones by decane in perfluoro-1,3-dimethylcyclohexane at room temperature ([thione] ≈ 10^{-5} M).

Table 4
Values of the transient term TT and the rate constant k_q for the quenching of thiones with various S_2 lifetimes by 2,2,4,4,6,8,8-heptamethylnonane in perfluoro-1,3-dimethylcyclohexane at room temperature

Thione	TT	$k_q \times 10^{-10}$ ($M^{-1} s^{-1}$)	$k_{diff}^{SV} \times 10^{-10}$ ($M^{-1} s^{-1}$)	k_q/k_{diff}^{SV}
XT-d_6	1.60	1.3	1.48	0.88
XT-d_0	2.86	2.0	2.20	0.91
TXT	5.42	5.4	3.66	1.48

$D_Q = 0.19 \times 10^{-5}$ cm^2 s^{-1}; $R_Q = 6.7$ Å; values of τ_{S_2}, E_{S_2}, D_{thione} and R_{thione} are given in Table 1; $k_{diff} = 0.57 \times 10^{10}$ M^{-1} s^{-1}.

Table 5
Values of the transient term TT and the rate constant k_q for the quenching of thiones with various S_2 lifetimes by cyclohexane in perfluoro-1,3-dimethylcyclohexane at room temperature

Thione	TT	$k_q \times 10^{-10}$ ($M^{-1} s^{-1}$)	$k_{diff}^{SV} \times 10^{-10}$ ($M^{-1} s^{-1}$)	k_q/k_{diff}^{SV}
TMIT	0.72	0.69	1.05	0.66
XT-d_6	0.86	0.83	1.13	0.73
DMAT	0.98	0.68	1.21	0.56
XT-d_0	1.54	0.82	1.55	0.53
DMBTPT	2.47	1.66	2.12	0.78
TXT	2.91	0.97	2.39	0.41

$D_Q = 0.60 \times 10^{-5}$ cm^2 s^{-1}; $R_Q = 3.3$ Å; values of τ_{S_2}, E_{S_2}, D_{thione} and R_{thione} are given in Table 1; $k_{diff} = 0.61 \times 10^{10}$ M^{-1} s^{-1}.

Table 6
Values of the transient term TT and the rate constant k_q for the quenching of thiones with various S_2 lifetimes by benzene in perfluoro-1,3-dimethylcyclohexane at room temperature

Thione	TT	$k_q \times 10^{-10}$ ($M^{-1} s^{-1}$)	$k_{diff}^{SV} \times 10^{-10}$ ($M^{-1} s^{-1}$)	k_q/k_{diff}^{SV}
XT-d_6	0.80	1.07	1.10	0.97
XT-d_0	1.47	1.59	1.51	1.05
TXT	2.73	3.32	2.28	1.46

$D_Q = 0.66 \times 10^{-5}$ cm^2 s^{-1}; $R_Q = 3$ Å; values of τ_{S_2}, E_{S_2}, D_{thione} and R_{thione} are given in Table 1; $k_{diff} = 6.1 \times 10^9$ M^{-1} s^{-1}.

Table 7
The influence of D isotope substitution for H in the quencher, on the rate constant k_q for the quenching of S_2-xanthione (d_0) in perfluoro-1,3-dimethylcyclohexane at room temperature

Quencher	TT	$k_q \times 10^{-10}$ ($M^{-1} s^{-1}$)	k_q/k_{diff}^{SV}	k_H/k_D
C_8H_{18}	2.56	1.54	0.70	1.75
C_8D_{18}	2.56	0.88	0.40	
c-C_6H_{12}	1.54	0.86	0.55	2.15
c-C_6D_{12}	1.54	0.40	0.26	
C_6H_6	1.47	1.67	1.05	1.07
C_6D_6	1.47	1.56	1.02	

For octane, $k_{diff} = 6.2 \times 10^9$ M^{-1} s^{-1}.

determined from the slope of the Stern–Volmer plots and to compare them with the values of the quenching rate constants k_{diff}^{SV}, calculated from Eq. (10).

Table 4 presents the analogous results for three thiones with significantly different values of τ_{S_2}, when a branched alkane, 7MeN, with steric hindrance and a relatively rigid structure was employed as a quencher.

The results of quenching by c-C_6H_{12} in PFDMCH (Table 5) provide an additional illustration of the role of transient effects in the quenching process. We used benzene as a quencher (Table 6) to obtain more data on the mechanism of S_2-thione quenching. To elucidate the role of C–H bonds and of phenyl ring in the quenching process, we also performed measurements using deuterated quenchers and these results are presented in Table 7.

5. Discussion

In previous experimental studies of the transient effect, the values of k_q have been obtained from steady-state measurements of Φ_F^0/Φ_F while D and R for both donor and quencher have been determined from dynamic experiments. In these studies the value of TT ranged between 0.2 and 1.0 [7,22–24,27–34].

Since reliable values of D_{D*} and D_Q are scarce in the literature and it is rather difficult to determine R_{D*} and R_Q and the efficiency of the quenching accurately, these relatively small values of TT have made it difficult to determine quantitatively the role of the transient effect in the systems studied to date. Note that the interpretations of the role of the transient effect is inconsistent even in the most thoroughly studied system; 1,2-benzanthracene (S_1) quenched by CBr_4, for which, in propane-1,2-diol, TT ≈ 0.57 [7,27,32,34,54–56]. On the contrary, many theoretical papers have appeared in which the nature of the transient effect and its role in the quenching processes are discussed [4–21]. These papers, however, report no experimental results for the quenching of short-lived donors ($\tau_{D*} < 1$ ns) for which one could expect a large contribution of the transient effect. Therefore the major aim of our study was to investigate a number of systems which could be used to test the various theoretical models [5,8,13,21,24,35–37,54] which describe the time-dependent quenching processes.

For the approximately 40 donor–quencher combinations (all in PFDMCH) which we have chosen, the values of TT calculated from Eq. (9) ranged from 0.7 to 7.7 (Tables 1–7). The use of low concentrations of quenchers ([Q] < 0.1 M) enabled us to obtain a linear dependence of Φ_F^0/Φ_F on [Q] (see above), to minimize the role of static quenching, and to eliminate the competitive effect mentioned in [56,57]. We are also able to neglect variations in viscosity, refractive index and other properties of the solution with changing [Q] which would affect both k_{diff} and Φ_F^0/Φ_F (for example through the dependence of the radiative rate constant on the refractive index of the medium).

Because these systems yield large values of TT it is reasonable to expect that the transient effect should significantly influence the values of k_q [5,6,20,21,24–26,56]. Indeed, the values of k_q obtained in the present fluorescence quenching experiments are very large (Tables 1–7), and almost always much bigger than the values of k_{diff} calculated from Eq. (12)

$$k_{diff} = 4\pi DRN' \qquad (12)$$

A clear correlation between the value of TT and the measured value of k_q is found.

Stationary fluorescence quenching measurements which yield values of k_q in excess of k_{diff} can also be indicative of static quenching, pseudoquenching, long-range energy transfer, or the inner filter effects. However, as we have shown in Section 4, the contribution of all these effects except for the first one may be excluded. The fact that the ground state complexes between thiones and quenchers are not formed in fluid PFDMCH solution at room temperature has been additionaly confirmed by previous studies of thione triplet quenching [58–60]. The same value of the self-quenching rate constant (k_{self}) is obtained from both dynamic [59] and steady-state [60] measurements. In these cases $k_{self} \approx k_{diff}$ because the triplets are long-lived and the transient effect is negligible. If ground-state complexation occurred between pairs of thione molecules the value of k_{self} obtained via a steady-state method would be expected to be larger than that obtained via a dynamic method. In addition, k_{self} would be greater than k_{diff}. Therefore we proceed on the assumption that complex formation between aromatic thiones and alkanes is unimportant in the present cases.

On the basis of the above consideration we conclude that the transient effect is responsible for the exceptionally large values of k_q obtained in the present study. As τ_{S_2} of the thiones decrease and R_Q for the alkanes increase the expected increase in k_q appears. For a given thione, as we proceed from *n*-hexane (Table 1) through *n*-octane (Table 7) and *n*-decane (Table 2) to *n*-hexadecane (Table 3), the observed excess of k_q over k_{diff} may be seen to be due not only to an increase in TT but also to a different efficiency of quenching described by k_q/k_{diff}^{SV} [4–8,33,37,56,62]. In the following we discuss this problem in more detail.

There is generally good agreement between the measured values of k_q and the values of k_{diff}^{SV} calculated from Eq. (10). The k_{diff}^{SV} data are calculated assuming that quenching is a diffusion-controlled process, and therefore values of k_q which are considerably lower than k_{diff}^{SV} indicate that this assumption fails in the case of quenching by hexane (Table 1). In fact, except for TXT, $k_q \approx 0.5k_{diff}^{SV}$ for all the thiones quenched by hexane, implying that approximately every second collision results in quenching. When *n*-decane is used as a quencher, the k_q/k_{diff}^{SV} ratio increases significantly for all thiones (Table 2). This trend continues when a larger molecule, hexadecane, is used as a quencher (Table 3). In the latter case, the largest values of TT are obtained and this is also true of the k_q/k_{diff}^{SV} ratio. Note that, for XT-d_0, DMBTPT and TXT quenched by hexadecane in PFDMCH, over 80% of the observed fluorescence quenching is the result of the transient effect. To our knowledge this is the greatest contribution of the transient effect to the total yield of quenching ever found experimentally. The contribution could be even greater in solvents of higher viscosity [25,44].

In order to explain the fact that quenching efficiency is considerably lower for hexane than it is for longer alkanes, it is necessary to discuss the mechanism of S_2-thione quenching by ALs. The *n*-alkane exhibit an increase in polarizability [63] and size of molecules, a decrease in diffusion rate and an increase in the number of lower energy secondary C–H bonds with increasing chain length. All these factors may contribute to the observed increase in the k_q/k_{diff}^{SV} ratio as we proceed from *n*-hexane to *n*-hexadecane.

Our results are in qualitative agreement with those of Motyka and Topp [58], who showed that in a supersonic jet the yield of S_2-thione–AL van der Waals complexation decreases in the order: decane > heptane > pentane. Topp and coworkers [61] also showed that τ_{S_2} for XT diminishes with increasing alkane size, from $\tau_{S_2} = 28$ ps in pentane, to $\tau_{S_2} = 21$ ps in undecane, and suggested that a reversible chemical quenching mechanism was responsible. We have also suggested that chemical interactions might be responsible for the considerable shortening of the S_2 lifetime of XT in ALs compared with PFs [1]. Topp and coworkers [61] noted that the rate of a possible reversible H atom abstraction process in a quencher molecule should vary in the order primary < secondary < tertiary, in keeping with their results. However, our results for the quenching of several thiones by 7MeN (Table 4) show that, despite the greater number of primary C–H bonds in this quencher, the k_q values obtained are large and nearly equal to k_{diff}^{SV}. The results demonstrate that it is the energy of C–H bonds and not their order that should be taken into account. The primary C–H bonds energy is smaller in 7MeN than the secondary C–H bond energy in a linear AL [64] owing to steric crowding in the former.

Note also the significantly lower value of k_q/k_{diff}^{SV} for the hexane quenching of TXT compared with the other thiones (Table 1). Since TXT and XT have similar structures and properties, their physical interactions with AL should also be alike [26]. Yet, a considerably lower value of E_{S_2} for TXT (Table 1) suggests that a reversible abstraction of hydrogen atom from AL molecule may be an endothermic process [52,60]. As a result, the rate of chemical quenching and, at the same time, its contribution decrease. This explanation was also supported by a lower value of k_q/k_{diff}^{SV} for TXT quenched by decane (Table 2) and cyclohexane (Table 5).

The results of quenching by c-C_6H_{12} are similar to those obtained for C_6H_{14}, except that the values of k_q/k_{diff}^{SV} (Table 5) are slightly larger for the cycloalkane. This may be due to a slightly lower C–H bond energy in c-C_6H_{12} [64]. The significantly more efficient quenching by benzene, $k_q/k_{diff}^{SV} = 1$ (Table 6), is a consequence of their stronger interaction and, probably, S_2-exciplex formation. This is suggested by the essentially different paths of deactivation of S_2-XT in PFs and in C_6H_6 [1–3] and by the transient absorption spectra measured for the latter system at 6 ps, 33–100 ps [65] and a hundred nanoseconds after laser excitation [66]. The relatively strong interaction between these excited thiones and benzene is also indicated by the very short $\tau_{S_2} = 10 \pm 2$ ps for XT-d_0 in pure C_6H_6 [61,66].

The results of D substitution for H in the quenchers suggest that the mechanisms of S_2-thione quenching are entirely different in the alkanes compared with arenes [1,26,61] (Table 7). The substitution of deuterium for hydrogen does not affect the values of k_q/k_{diff}^{SV} for XT quenched by benzene because the aromatic ring plays a decisive role in their interaction with the excited thio group. On the contrary, for the hydrocarbon quenchers, deuterium substitution results in $k_H/k_D \approx 2$, which is consistent with a mechanism involving reversible hydrogen atom abstraction [1,3,52].

In an earlier paper we assumed [25] that S_2thione quenching occurred according to the Smoluchowski model, as most of the results concerned the quenching by hexadecane for which $k_q/k_{diff}^{SV} \approx 1$. The results obtained in this paper for smaller ALs and c-C_6H_{12} imply that the radiation boundary condition according to the Collins–Kimball model should be applied for their interpretation [24,36]. Although the interaction of S_2-thiones with S_0-AL or S_0-C_6H_6 leads to efficient quenching, the energy of this interaction is relatively small [1,42], and only a weak complex is formed [1,58]. The values of k_q for the quenching of DMBTPT and TXT by hexadecane are a factor of about 2 larger than k_{diff}^{SV}. Regarding the very short τ_{S_2} and extremely high TT values (6.6 and 7.75 respectively), the disagreement seems to result from violation of the condition of continuity of the medium [6,8,21,40,57] and from non-diffusive dynamic behavior of D* and Q molecules [56]. Moreover, it can be a consequence of the k_q dependence on the non-uniform radial distribution function and the correlation distance in agreement with the work of Keizer [8,12,57], Ware and coworkers [28,40,55] and Andre and coworkers [21,56]. Also, extremely low solubility of hexadecane in PFs ($c \leqslant 0.02$ M) caused additional inaccuracies in k_q determination, restricting the measuring range and reducing the magnitude of the quenching effect ($\Phi_F^0/\Phi_F \leqslant 1.2$).

6. Conclusions

Quenching of short lived S_2-aromatic thione by ALs and other saturated hydrocarbons is of remarkably high efficiency. Therefore the study of this process in PF solvents provides a unique possibility for experimental verification of the role of transient effect in quenching processes by means of simple measurements of Φ_F^0/Φ_F. A large number of S_2-thione–S_0-quencher–PF systems, significantly differing in the values of τ_{S_2}, R_Q and viscosity of PFs, for which a good agreement between k_q and k_{diff}^{SV} values have been reached [25,26,43], corroborates the obtained results.

The studied systems also show some other advantages: high and highly differentiated values of TT; the use of exceptionally weakly interacting PF [2,42–44] as solvents, owing to which the assumptions taken in theoretical models, which concern for example the continuity of medium, are well met [5,35,36]; the existence of only one quenching path (the complex formation), which should make it easier to determine appropriate values of R_D and R_Q for the applied donors and quenchers [4]; the ability to use quenchers having only C–H reactive bonds but of different sizes, shapes, steric hindrances, C–H bond energies and energies of interactions with donors.

As a result of the above properties we can study systems of considerable contribution of transient effect, and moreover both of diffusion-limited rate ($k_q/k_{diff}^{SV} \approx 1$) and of different contribution of activation (chemical) limited rate contribution which enables the quantitative determination of k_r [5,42,43]. For the above-mentioned reasons, the systems that we studied are particularly well suited to verification of the theoretical models describing time-dependent quenching processes. Moreover, we would like to stress that the results of the dynamic quenching experiments [42,43] for these systems have confirmed the results of the presented steady-state measurements. It should also be pointed out that, when the contribution of transient effect to the quenching process is high enough, a direct dependence of k_q on the inverse of solvent viscosity should not be expected to occur, as has already been shown in [25].

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