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Short Communication

Bimolecular quenching of the second excited singlet state of tetramethylindanethione

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Aromatic thiones are numbered among the few polyatomic molecules which fluoresce with high efficiency in fluid solution at room temperature from excited electronic states higher than S_1 or T_1 [1]. Using picosecond laser techniques we have recently shown that 3-methylpentane and benzene, which have previously been used as solvents in photochemical and photophysical studies of thiones and which are commonly considered to be chemically inert, quench the second excited singlet states of aromatic thiones at nearly diffusion-controlled rates [2, 3]. In contrast, perfluoroalkane solvents appear to act as efficient heat sinks for vibrational relaxation of excited thione solutes without significantly modifying their electronic radiationless transition probabilities [4]. These solvents are also capable of dissolving relatively large amounts of oxygen and other non-polar substances including the thiones themselves. It is therefore possible to measure directly the rate constants for the bimolecular quenching of the second excited singlet states of a number of aromatic thiones in fluid perfluoroalkane solutions at room temperature in the absence of complicating chemical interactions between the solvent and the excited solute. We report here the rate constants for the bimolecular quenching of the second excited singlet state of 2,2,3,3-tetramethylindanethione (TMIT) by itself, by oxygen and by acetonitrile, ethanol and cyclohexane together with their perdeutero analogues.

TMIT was prepared as described previously [5, 6]. Perfluoroalkane solvents were purified by long-term UV irradiation of aerated samples, followed by repeated fractional distillation. Gas chromatography with flame ionization detection revealed that they contained no more than 0.2 mol.% impurities containing C—H bonds. Most experiments except those involving oxygen quenching employed deoxygenated perfluoromethylcyclohexane or perfluoro-*n*-hexane solutions at room temperature. When oxygen quenching rate constants were measured, both oxygen-saturated and air-saturated solutions were used and oxygen concentrations were obtained from previously reported solubilities [7, 8].

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Subnanosecond fluorescence lifetimes were measured with a synchronously pumped cavity-dumped frequency-doubled R6G dye laser excitation source ($\lambda_{ex} \approx 300$ nm), using the previously described pulse shape mimic technique to effect the deconvolution of the instrument response function from the measured fluorescence decay [9]. A Fresnel double rhomb which rotates the plane of polarization of the exciting radiation to the "magic angle" and a calcite polarization analyser were employed to eliminate distortion of the fluorescence decay curves due to rotational depolarization [10]. In all cases individual sample fluorescence decays were described very well by single-exponential functions. Excited state lifetimes longer than 30 ps could be measured in this way with a precision of ±10 ps.

Excitation at about 300 nm populates the second excited singlet state of TMIT, of $^1(\pi,\pi^*)$ character, which radiates directly to the ground state in the spectral window between the $S_2 \leftarrow S_0$ and $S_1 \leftarrow S_0$ absorption systems [5]. We have previously shown that the quantum yield of net photodecomposition of TMIT is less than 10^{-4} in degassed perfluoroalkane solvents and that the emission lifetimes, quantum yields and spectra are independent of excitation wavelength within the $S_2 \leftarrow S_0$ absorption system. The following simple kinetic scheme therefore adequately describes the quenching of the vibrationally relaxed second excited singlet state of TMIT by ground state TMIT or by added quencher Q:

$$S_0 + h\nu \longrightarrow S_2 \tag{1}$$

$$S_2 \xrightarrow{k_r} S_0 + h\nu_f \tag{2}$$

$$S_2 \xrightarrow{k_{nr}} S_1, S_0, T_n \tag{3}$$

$$S_2 + S_0 \xrightarrow{k_{sq}} 2S_0 \tag{4}$$

$$S_2 + Q \xrightarrow{k_q} S_0 + Q \tag{5}$$

It should be noted that eqn. (5) represents an overall quenching process which could proceed in several steps or by different mechanisms for different quenchers. Bimolecular quenching constants k_q can be obtained directly from standard Stern–Volmer plots. Such plots are shown in Fig. 1 and the rate constants obtained from them are collected in Table 1. Steady state fluorescence quenching experiments in combination with the measured value of $\tau^0 = 880$ ps yielded the same results, but with a larger statistical error.

Initial experiments in which decay times were measured as a function of thione concentration established that $k_{sq} = (2.4 \pm 0.2) \times 10^{10}$ M^{-1} s^{-1} in perfluoro-*n*-hexane at 296 K. Because the lifetimes of TMIT S_2 are in the subnanosecond domain, self-quenching therefore contributes negligibly to the total decay rate when thione concentrations lower than about 10^{-3} M are employed. For all subsequent measurements of k_q, thione concentrations were no larger than 10^{-5} M.

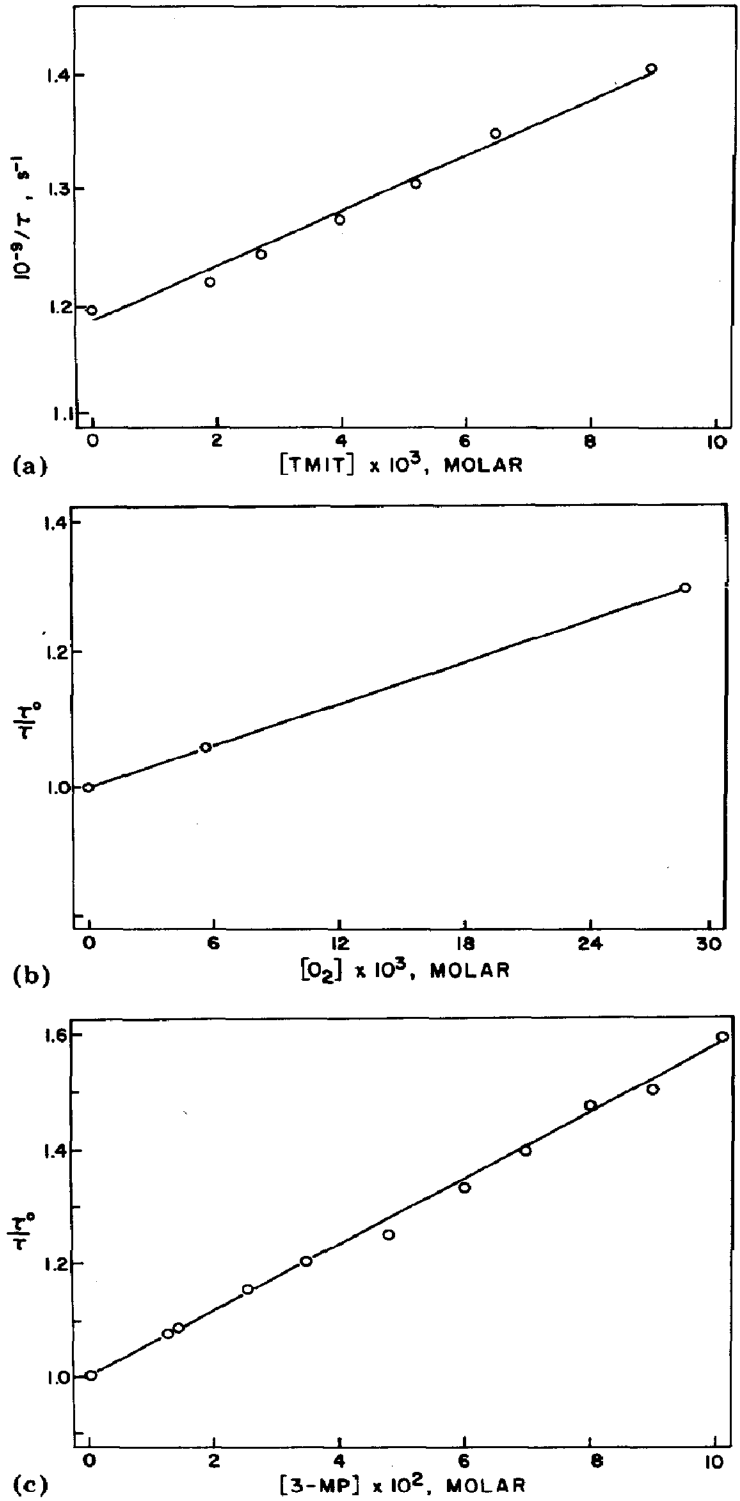

Fig. 1. (a) $1/\tau$ *vs.* [TMIT] in air-saturated perfluoro-*n*-hexane (τ^0 = 840 ps); (b) τ^0/τ *vs.* [O_2] in perfluoro-*n*-hexane; (c) τ^0/τ *vs.* [3-methylpentane] in degassed perfluoro-*n*-hexane.

TABLE 1

Rate constants for the bimolecular quenching of the second excited singlet state of 2,2,3,3-tetramethylindanethione in perfluoroalkane solutions at room temperature

Quencher	O_2	Acetonitrile	Ethanol	Cyclohexane[a]	3-methylpentane[b]
k_q [c] ($M^{-1} s^{-1}$)	1.16×10^{10}	1.66×10^{10}	1.65×10^{10}	7.0×10^9	6.8×10^9
k_q^H/k_q^D [d]	—	1.00	1.23	1.49	—

[a] In perfluoromethylcyclohexane; all others in perfluoro-*n*-hexane.

[b] k_q for 3-methylpentane in perfluoromethylcyclohexane is 4.6×10^9 M^{-1} s^{-1} reported previously in ref. 2.

[c] The error limits are ±8%.

[d] k_q^H is for the perhydro compound; k_q^D is for the perdeutero compound.

Oxygen quenches TMIT S_2 with a rate constant of 1.16×10^{10} M^{-1} s^{-1}. It is important to note (see Fig. 1) that both k_q and the oxygen concentration (5.7×10^{-3} M [7]) are sufficiently large that oxygen quenching contributes significantly to the decay of TMIT S_2 in air-saturated perfluoro-*n*-hexane at room temperature, even though the decay occurs on a subnanosecond time scale. We also note that the S_2 thione–O_2 quenching rate constant is within a factor of 2 of the diffusion-controlled value and is nearly identical with those for the quenching of the triplet states of *N*-methylthioacridone and other thiones by oxygen [11]. However, no experiments to elucidate the nature of the S_2 thione–O_2 interaction have been performed to date and no further comments on this aspect of the work appear to be warranted at this time.

The rate constants for the quenching of the second excited singlet state of TMIT by acetonitrile, ethanol, cyclohexane and 3-methylpentane are all large. Several potential quenching mechanisms should be considered. Quenching by exothermic or thermoneutral electronic energy transfer is not possible because the lowest excited singlet state energies of these quenchers are all higher than that of TMIT S_2 (83 kcal mol^{-1}). No correlation between k_q and the ionization potentials or electron affinities of the quenchers is apparent, given the limited data available, so that quenching by a general charge transfer mechanism is eliminated. There is also no spectroscopic evidence for the formation of either ground or excited state complexes in any of the TMIT–quencher combinations investigated. However, results of previous photochemical studies in several thione systems and the present isotope effect results do provide some insight into possible mechanisms of the excited state quenching process.

de Mayo [12] has shown that the second excited singlet ($^1(\pi,\pi^*)$) states of thiones are highly reactive. Aralkyl, diaryl and alicyclic thiones excited to S_2 undergo an apparently general cycloaddition to the cyano group, leading ultimately to *N*-thioacylketimine products [13]. The large value of k_q for the quenching of TMIT S_2 by acetonitrile, the absence of a deuterium isotope effect and the lack of excimer emission all suggest that the interaction in this case occurs at the nitrile function and that quenching occurs via a short-lived dark exciplex. The fact that TMIT excited to S_2 in acetonitrile solvent exhibits a quantum yield of net photodecomposition of less than 10^{-3} suggests that such an exciplex yields distinguishable photoproducts with a low efficiency.

S_2 thiones have also been shown to be among the most indiscriminate intermolecular and intramolecular hydrogen abstractors known [14 - 20]. This propensity is confirmed by the present results in which large values of k_q and modest deuterium isotope effects are found for the interaction of TMIT S_2 with ethanol and cyclohexane. These results lend support to the model proposed by Law and coworkers [16, 17] for the abstraction of hydrogen from cyclohexane by adamantanethione S_2 and the subsequent reactions of the resulting caged and diffusing radicals. From a comparison of ethanol and cyclohexane, the smaller isotope effect and the larger k_q are found for quenching by ethanol, in which the availability of more readily abstractable hydrogen atoms leads to a greater reaction exothermicity and an "earlier" transition state. k_H/k_D values of 1.5 or less suggest that the heats of reaction in these cases are exothermic by more than 25 kcal mol^{-1} [21].

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