A peculiar quenching concentration dependence of photoinduced fragmentation in dithiane–carbonyl adducts: A mechanistic experimental and theoretical study

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ABSTRACT

Photoinduced fragmentation in methyldithiane–benzaldehyde adduct, which is externally sensitized by electron transfer sensitizers such as benzophenone, shows a peculiar Stern–Volmer quenching dependence when quenched by diethyl sulfide or DABCO. At lower diethyl sulfide concentration not only negative curvature but also negative slope is observed. At higher concentration the slope of the plot is conventionally positive. This atypical behavior is rationalized in terms of co-sensitization by the quencher at low concentrations. Ab initio and DFT computations were carried out to support the suggested mechanistic rationale. Also the partitioning of the dithianyl radical and benzophenone ketyl radical between the productive disproportionation channel and the recombination channel is determined to be 1:1 at low conversion. These findings provide critical experimental and theoretical insights into the mechanism of this photoinduced fragmentation.

1. Introduction

Photoinduced fragmentations in dithiane–carbonyl adducts [1] require external sensitizers, for example benzophenone, and follow the mechanism shown in Scheme 1 [2].

Such externally sensitized fragmentations can be made contingent on a molecular recognition event, which brings the two parts of a binary photolabile system – the dithiane adduct and the sensitizer – into the close proximity of each other, effectively "arming" the system [3]. This offers a platform for the development of useful bioanalytical methods, where molecular recognition events can be detected by monitoring the results of the fragmentation. One area where this methodology was successfully tested is in the encoding and screening of solution phase combinatorial libraries [4]. The sensitivity of such detection can be further improved with photoinduced signal amplification through controlled externally sensitized fragmentation in masked sensitizers [5]. This last advance required somewhat tightly packed or more concentrated dithiane adducts to ensure propagation of the amplification effect through a two-dimensional array of immobilized adducts or in a 3D compartmentalized volume. In order to improve the overall efficiency of this propagation one needs better understanding of the concentration dependence of the fragmentation and the effects of external competitive quenchers on the quantum yields. In this paper we report a peculiar concentration dependence of quenching the photofragmentation channel with dialkyl sulfides. We also clarified the role of radical recombination *vs.* disproportionation, as this has a direct impact on the apparent quantum efficiency of the fragmentation.

2. Materials and methods

The 2-methyl-[1,3]-dithiane adduct of benzaldehyde was prepared as described earlier and purified by column chromatography [1]. The reagents were purchased from Sigma–Aldrich: diethyl sulfide and DABCO (diazabicyclo[2.2.2]octane) were used as is; benzophenone was recrystallized three times from ethyl acetate–hexane.

Relative quantum yields of photoinduced fragmentation were measured at 50 mM benzaldehyde–dithiane adduct and 10 mM benzophenone as an electron transfer sensitizer. In a typical quenching experiment diethyl sulfide was added to 12 Pyrex vials, containing CH_2Cl_2 solutions of 50 mM benzaldehyde–dithiane adduct and 10 mM benzophenone. Appropriate amounts of diethyl sulfide were added to cover a 0–1 M concentration range; the vials were degassed by 3–4 freeze–thaw cycles and irradiated in a carousel Rayonet reactor with RPR-3500 lamps (broadband 300–400 nm UV source with max. emission at 350 nm) to

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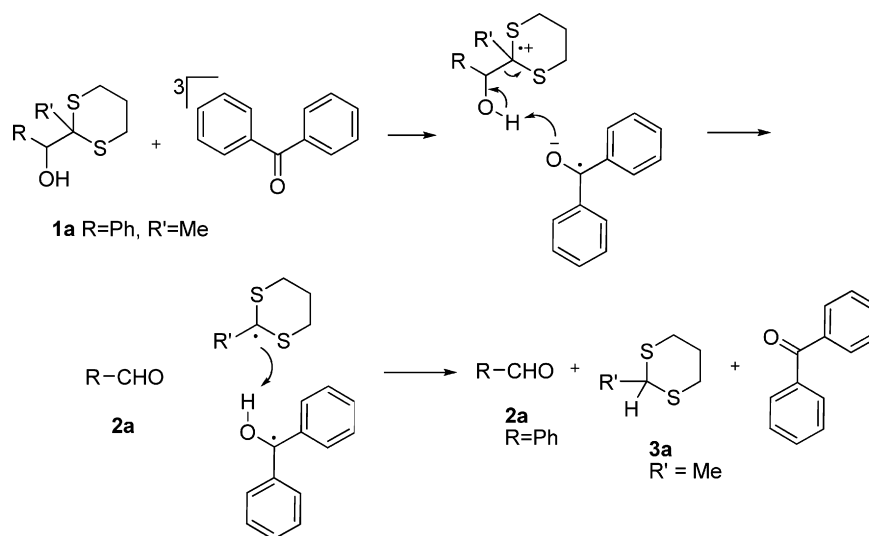
Scheme 1.
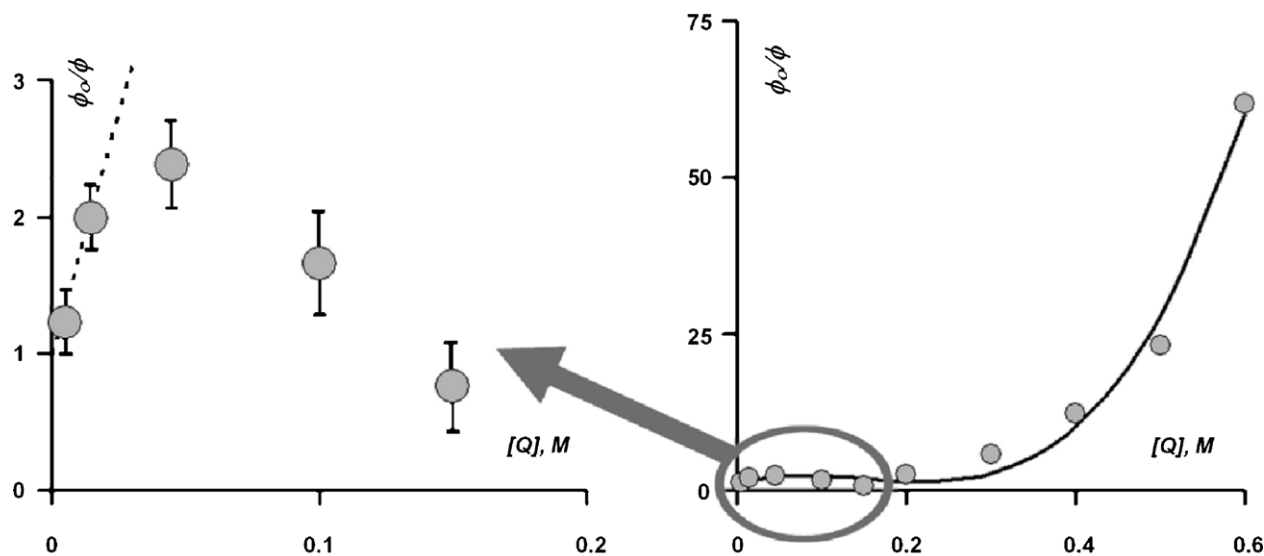
Fig. 1. Markedly non-linear Stern–Volmer plot for diethyl sulfide quenching of the fragmentation in **1a**.

5–15% conversion. All experiments were carried out at 25 °C. The reaction was followed by the calibrated GCMS monitoring of the released 2-methyldithiane. A similar quenching experiment was carried out with DABCO. The results are shown in Figs. 1 and 5.

The NMR monitoring of the recombination–disproportionation ratios was carried out in CD_3CN with systematically diluted benzaldehyde–methyldithiane adduct **1a** @ 105.5 mM, 62.3 mM, 51.9 mM, 39.3 mM, 28.6 mM, 10.4 mM, 8.2 mM, and 6.3 mM, while keeping the sensitizer (benzophenone) concentration at 100 mM. The samples were irradiated in the Rayonet reactor with RPR-3500 lamps. The results are tabulated in Table 1.

Laser Flash Photolysis (LFP) experiments were run using Applied Photophysics nanosecond LFP system with 2–3 ns resolution. The concentration of dimethyl sulfide was varied in this series from 10 mM to 50 mM; lifetime of triplet benzophenone was measured as a transient absorption decay at 525 nm [6]. This concentration series yielded the bimolecular quenching rate constant of $2 \times 10^9 \, mol \, L^{-1} \, s^{-1}$.

3. Calculations

Density Functional Theory (DFT) calculations were carried out using Gaussian 03, Rev. C.02. All geometries were pre-optimized at the AM1 level and then fully optimized at the B3LYP/6-31G(d) followed by vibrational analysis to test for imaginary frequencies. All geometries were found to be true minima (i.e. no imaginary frequencies were found). The DFT energies were ZPE-corrected before calculating the ionization potentials (IPs). Geometry optimizations for the dimeric and trimeric dialkyl sulfide radical cations were performed using dimethyl sulfide for simplicity. The lowest energy conformation of the ground state dimeric radical cation $[Me_2SSMe_2]^{\bullet+}$ has C_{2H} symmetry. The geometry optimization was not initially constrained to any particular symmetry but converged on a C_{2H} structure shown below. The bond dissociation energy (for mesolytic fragmentation) of the three-electron two-center S–S bond calculated in this study was 29.4 kcal/mol. This compares favorably with previously reported [7] 29.3 kcal/mol at the MP2/6-31G(d) or 32.3 kcal/mol at the MP2/6-311G(2df,p) level of theory.

The bond length of 2.895 Å obtained in this study is somewhat longer than the MP2-calculated bond length of 2.795 Å.
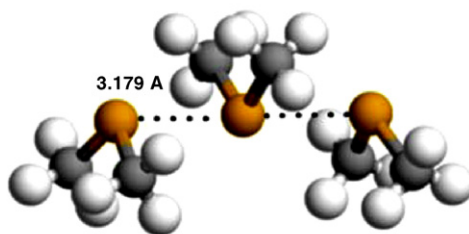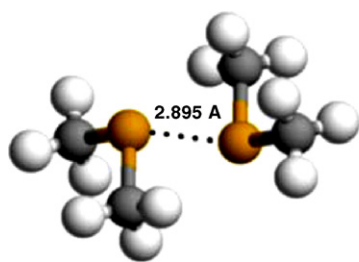
The trimer has C_{2V} symmetry with S–S bond lengths of 3.179 Å as shown. Its mesolytic fragmentation into the dimeric radical cation and dimethyl sulfide is 7.8 kcal/mol uphill. The calculated energies for the formation of heterodimers and oligomers are summarized in Fig. 3.

For evaluation of vertical excitation energy in dimeric and trimeric radical cations CASSCF(6,6)/6-311++G(3df) energies for the DFT ground state geometries were calculated: (1) dimeric radical cation: $E_{CAS}(S_0) = -953.36191$ Hartree, $E_{CAS}(S_1) = -953.26047$ Hartree; $\Delta E = 2.76$ eV or 449 nm; (2) trimeric r.-c.: $E_{CAS}(S_0) = -1430.1182$ Hartree, $E_{CAS}(S_1) = -1430.0441$ Hartree; $\Delta E = 2.02$ eV, or 615 nm.

4. Results and discussion

4.1. Stern–Volmer quenching of the externally sensitized fragmentation with diethyl sulfide

The results of Stern–Volmer quenching experiments are shown in Fig. 1. The release of 2-methyl-[1,3]-dithiane **3a** from its benzaldehyde adduct **1a** in dichloromethane upon benzophenone sensitization was monitored by GCMS as a function of the quencher (dimethyl sulfide) concentration. The total ion count in the mass detector (A) was used to calculate the quantum yield ratios: $\varphi/\varphi_0 = A/A_0$. At high dilution of the quencher, the first two points produced an initial quenching slope, which corresponds to the Stern–Volmer constant K_{SV} of 63.7 L mol^{-1} (dashed line, Fig. 1). Given that the triplet lifetime of benzophenone in non-polar benzene is 6.9 μs [8], it follows from $K_{SV} = \tau k_q$ that the rate constant of quenching in dichloromethane is on the order of 10^7 L mol^{-1} s^{-1}. This is about an order of magnitude lower than expected [2]. However, even this shallow slope does not last long: for the next few points the curve levels off and then the slope becomes negative, recovering only at concentrations 0.2 M and higher (Fig. 1). Eventually, the reaction is quenched more than 90% at concentrations exceeding 0.4 M. Clearly the simple Stern–Volmer rationale of diethyl sulfide independently competing with the dithiane adduct **1a** for bimolecular electron transfer quenching of triplet benzophenone needed a major revision.

A formal fitting of this peculiar quenching dataset is shown in the right panel of Fig. 1. The solid line represents a linear first order Stern–Volmer function augmented with a negative quadratic and a positive cubic term:

$$\frac{\phi_0}{\phi} = 1 + K_{SV}[Q] - K'[Q]^2 + K''[Q]^3$$

where $K_{SV} = 37.4$ M^{-1} L, $K' = 311.7$ M^{-2} L^2, and $K'' = 688.9$ M^{-3} L^3.

The quadratic term amounts to co-sensitization, while the cubic is another quenching term. It is conceivable that higher order quenching terms are needed to fit the experimental data at concentrations above 1 M, although the experimental error in determining very small concentrations of dithiane resulting from the over-

whelming amount of quencher does not allow us to make a certain conclusion.

We suggest that the formation of a dimeric radical cation, $[R_2S\overset{\cdot}{\cdot}SR_2]^{\bullet+}$ and its higher oligomers can provide a plausible mechanistic rationale for co-sensitization at intermediate concentrations of the quencher and eventual quenching at the higher concentrations. Asmus reported a rate constant of 3×10^9 mol^{-1} L s^{-1} for dimerization of methyl sulfide radical cation [9], and from his experimental data [10] the equilibrium constant for $Me_2S^{\bullet+} + Me_2S \rightleftarrows [Me_2S\overset{\cdot}{\cdot}SMe_2]^{\bullet+}$ is derived to be 2×10^5 mol^{-1} L. This value was later adjusted to $1-5 \times 10^4$ mol^{-1} L by Merényi and co-workers [11], who also measured the one electron reduction potentials for $Me_2S^{\bullet+}$ (1.66 V vs. NHE) and the dimer $[Me_2S\overset{\cdot}{\cdot}SMe_2]^{\bullet+}$ (1.40 V vs. NHE). Asmus observed experimentally that the dimer is capable of direct oxidation of thiols, i.e. it does not have to undergo dissociation into the monomeric radical cation [12]. According to Glass, most substituted dithianes oxidize below 1 V vs. SCE (approx. 1.24 V vs. NHE) [13], which implies that the dimeric radical cation of the dialkyl sulfide quencher should be capable of oxidizing dithiane, i.e. acting as a co-sensitizer.

Thus we hypothesized (Scheme 2) that at low concentrations of the quencher, the initial ion radical pair ($Et_2S^{\bullet+}/BP^{\bullet-}$), formed in competition with the dithiane oxidation, undergoes fast wasteful back electron transfer (BET) with $k'_{BET} > k_{BET}$ due to low stability of the monomeric radical cation of diethyl sulfide as compared with more stable dithiane-based radical cation.

As the concentration of the quencher increases, the initial diethyl sulfide radical cation forms more stable dimer $[Et_2S\overset{\cdot}{\cdot}SEt_2]^{\bullet+}$ which has a better chance of diffusing away, escaping the BET (i.e. k''_{BET} is sufficiently slower than k'_{BET}, making it competitive with k_{BET}), and acting as a co-sensitizer. Further increase of concentration produces tri- or higher oligomers, which are too stable, so they are not capable of oxidizing the dithiane adduct and initiating the fragmentation. This regime corresponds to higher polynomial quenching terms.

Trimeric organic radical cations are certainly not unprecedented in the literature [14] although we did not find any data on oligomerization of dialkyl sulfide-based radical cations. The dimeric radical cation of dimethyl sulfide has an absorption band at 465 nm [15]. Our CASSCF (Complete Active Space Self-Consistent Field) calculation of vertical excitation gap yielded 2.76 eV, which corresponds to an absorption band at approximately 450 nm—a good agreement with the experimental value. The calculated CASSCF vertical excitation energy for the corresponding trimer was 2.02 eV, or 615 nm. Unfortunately, in the experimental laser flash photolysis this region overlaps with absorption of benzophenone anion radical making any assignments ambiguous. Experimentally we were not able to detect any evidence for the trimeric cation radical in the laser flash photolysis, which in this series gave a triplet benzophenone quenching constant of 2×10^9 mol L^{-1} s^{-1}. This rate constant is somewhat lower than the diffusion controlled, but otherwise the system behaves conventionally. Thus the anomaly in the Stern–Volmer plot shown in Fig. 1 is not due to anomalous quenching of triplet benzophenone.
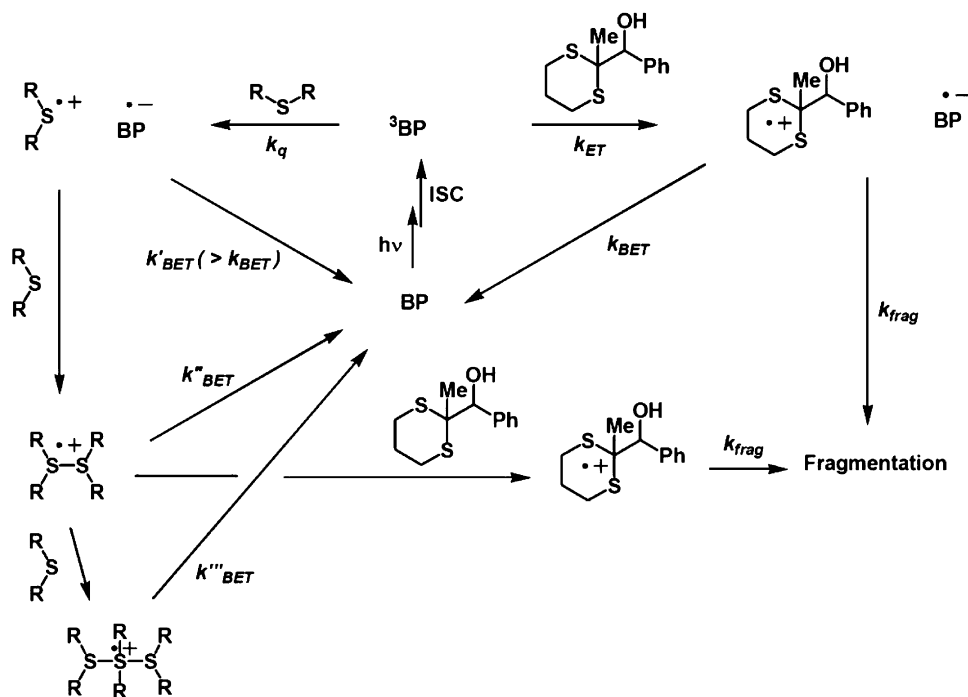
Scheme 2.

For the mechanism shown in Scheme 2 to be plausible, the ionization potential of the dithiane should fall between the IPs for the dimeric and trimeric dialkyl sulfide. In order to gain additional insight into the mechanism, we have carried out DFT computations assessing the relative stability of radical cations potentially involved in the fragmentation/quenching processes. For simplicity, dialkyl sulfide quencher was modeled as dimethyl sulfide and 2-methyldithiane was used as a model for methyldithiane adducts.

Fig. 2 shows non-vertical ionization potentials for oligomeric $(Me_2S)_n$ radical cations as a function of n (i.e. the degree of oligomerization). For $n = 1$ (i.e. monomeric dimethyl sulfide) the IP value is 8.54 eV. It decreases by 0.9 eV for the dimer ($n = 2$, 7.27 eV) and then further decreases to 6.93 eV for the trimer. The IP value for 2-methyldithianyl radical cation lies at 7.66 eV, i.e. between the monomer and the dimer. However, the heterodimer dimethyl sulfide–dithiane has an IP of 7.10 eV, which lies between the dimer and the trimer of Me_2S. We therefore hypothesize that the actual mechanism for the rate enhancement at intermediate concentrations of the dialkyl sulfide quencher is realized via the 1:1 heterodimer of the benzaldehyde–methyldithiane adduct **1a** and the quencher (Fig. 2, inset).
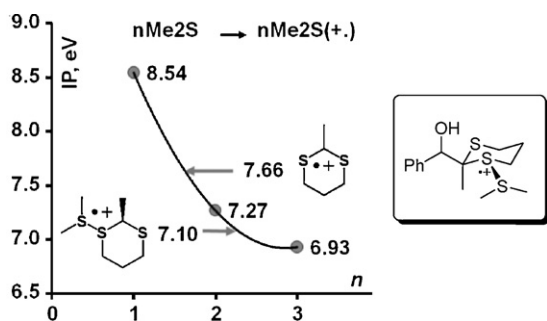
Potentially, this heterodimer can be formed by reaction of (i) [**1a**]$^{\bullet+}$ with the quencher, (ii) the neutral **1a** with the radical cation of the quencher, or (iii) the neutral **1a** with the radical cation of the quencher dimer. According to the calculated DFT energies (Fig. 3), all these reactions are spontaneous. However, for the trimer radical cation (last entry in Fig. 3) oxidation of methyldithiane is an uphill reaction, i.e. the formation of the trimer is the dead end which decreases the overall quantum efficiency of the fragmentation reaction and potentially accounts for the third order quenching dependence at higher concentration of the quencher. The co-sensitization effect is expected to exhibit a second order (fitted plot, Fig. 1) only in case the oxidation of the dithiane adduct **1a** with the dimeric radical cation of the quencher is irreversible. Direct oxidation of the dithiane by the radical cation of the monomeric quencher is potentially possible but unlikely, as the back electron transfer from the benzophenone radical anion to the monomeric radical cation of the quencher is expected to prevail. At higher concentration of the quencher, dimerization of the radical cation competes with such back electron transfer, ensuring that enough dimers escape the cage to co-sensitize the fragmentation.

If this rationale is correct, one might expect a similar dependence of the overall quantum efficiency of the fragmentation on the concentration of substrate **1a** itself (i.e. in the absence of external quenchers), with the reservation that due to different steric conditions the absolute range of concentrations should be different. Fig. 4 summarizes our experimental findings. The substrate **1a** was systematically diluted while the sensitizer concentration was kept constant, as described in Section 2. Three outcomes were monitored by NMR after 5 min of irradiation: (i) the disappearance of the starting material, (ii) the appearance of benzaldehyde, and (iii) the appearance of 2-methyldithiane. The relative quantum yields were calculated based on NMR integration.

The concentration dependence of the overall quantum yield of the fragmentation clearly shows a maximum at 40 mM. The dithiane and the aldehyde accumulation is contingent on their survival in the presence of the sensitizer. It is plausible that the "delayed" maxima for the benzaldehyde and methyldithiane are due to their shielding each other from the secondary oxidative degradation by

Fig. 2. B3LYP/6-311++G(3df) ionization potentials for oligomeric radical cations as a function of n (degree of oligomerization). Inset: The heterodimer (**1a·Me₂S**)$^{\bullet+}$.
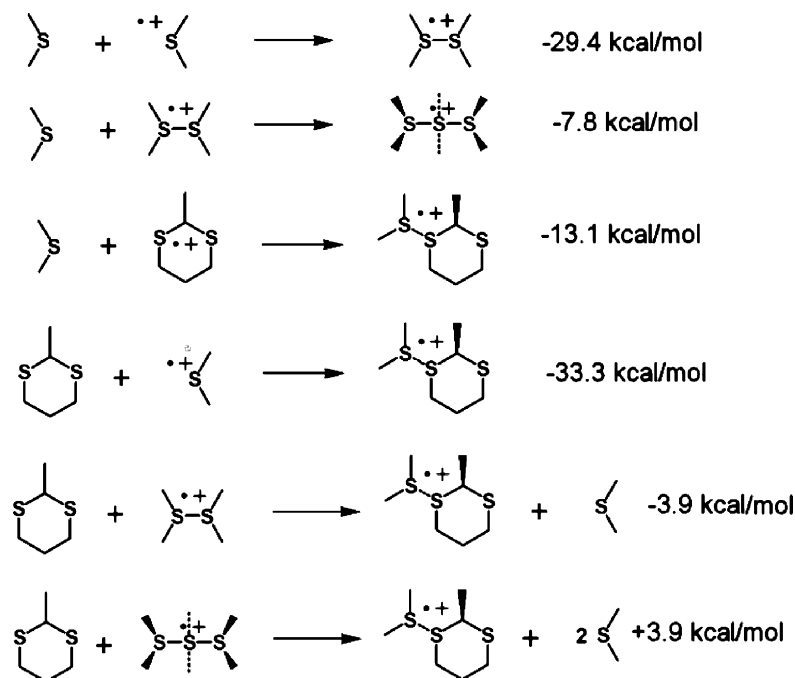
Fig. 3. B3LYP/6-311++G(3df) heats of oligomerization for radical cations.

excess sensitizer. The practical conclusion here is that for each dithiane–carbonyl adduct there must be an optimal concentration of the substrate which ensures highest quantum efficiency.

The quenching of fragmentation in **1a** by DABCO also exhibits similar anomaly, Fig. 5. While the Stern–Volmer plot in this case does not show negative slope per se, there is a clear lack of apparent quenching at low concentrations (<50 mM).

4.2. Recombination–disproportionation partitioning and its effect on the overall quantum yield

The second important issue addressed in this study is the partitioning of the two radicals – benzophenone ketyl and 2-methyldithianyl radical – at the final step of the fragmentation. The two radicals are produced as a result of C–C bond fragmentation concomitant with the release of RCHO. The net result of the fragmentation (Scheme 1) is the formation of dithiane and the regeneration of the benzophenone sensitizer via the hydrogen transfer from the ketyl radical to dithiane (i.e. disproportiona-

tion). The side reactions include dimerization of ketyl radicals—trace amount of tetraphenylpinacol is always detected. These side processes can be kept in control by dilution. However, recombination of the dithianyl and benzophenone ketyl radicals is beyond such control and depends solely on the intrinsic propensity to disproportionate or recombine. We note that recombination does not change the ultimate outcome of the reaction: the transient benzophenone–methyldithiane adduct **4a** undergoes similar benzophenone-sensitized fragmentation and eventually regenerates free benzophenone, releasing methyldithiane (Scheme 3). It is important, however, to estimate the recombination–disproportionation partitioning ratio, because recombination affects the overall quantum efficiency of the fragmentation.

It is generally known that the substitution shifts the partitioning in radical pairs toward disproportionation at the expense of recombination [16]. However, little information is available for heteroatom-substituted radicals. Utilization of methyldithiane allowed us to monitor the partitioning shown in Scheme 3 by NMR, because the prominent methyl singlet in the benzophenone adduct **4a** (δ = 1.9 ppm) is found far apart from the methyl singlet in the benzaldehyde adduct **1b** (δ = 1.31 ppm) and the prominent doublet of
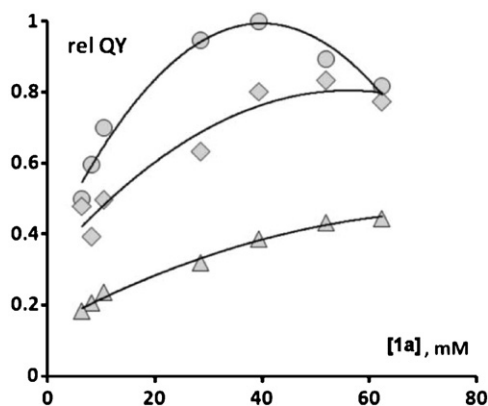

Fig. 4. Dependence of the relative quantum yield of the fragmentation on the concentration of **1a**: disappearance of **1a** (circles); release of benzaldehyde (diamonds); release of methyldithiane (triangles).
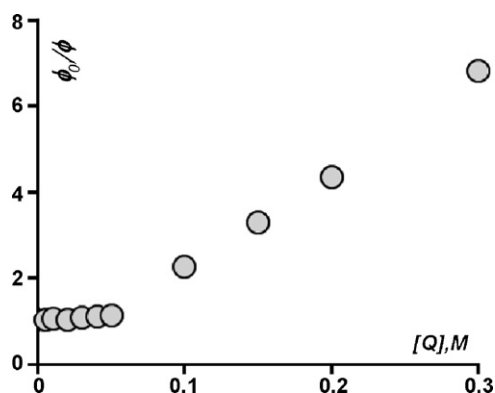

**Fig. 5.** DABCO quenching of fragmentation in **1a**.

Table 1
Dilution of **1a** series with fragmentation sensitized by a 100 mM benzophenone.

1a, mM[a]	Relative integrated intensity of Me group (%)			Recombination–disproportionation ratio	Mass balance[b] (%)
	in **4a**	in **3a**	in **1a**		
105.5	5	4	91	1.15	109
62.3	8	7	85	1.04	87
51.9	10	9	81	1.04	87
39.3	13	13	74	1.02	81
28.6	17	15	68	1.10	76
10.4	(29)[c]	43	29	(0.68)[c]	38
8.2	(29)[c]	53	18	(0.55)[c]	29
6.3	(23)[c]	71	6	(0.32)[c]	18

[a] Benzophenone concentration is kept at 100 mM, all samples were irradiated for 5 min.
[b] Calculated based on integration of combined aromatic protons as a reference; at high conversion poor mass balance is due to irreversible degradation of methyl dithiane.
[c] At high conversion the ratio reflects subsequent fragmentation of the benzophenone adduct.
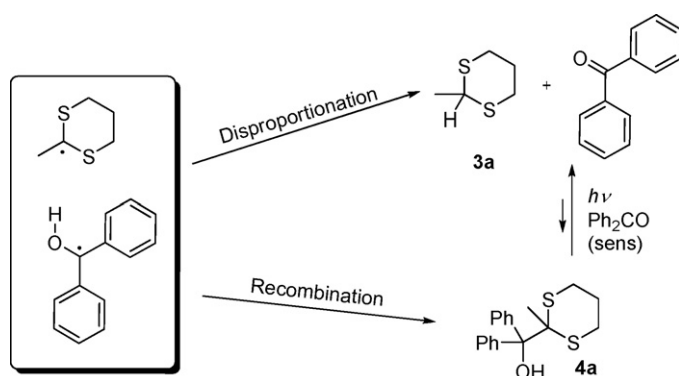
Scheme 3.

the methyl group in the free methyldithiane (δ = 1.41 ppm). These signals do not overlap with the CH_2 protons of dithiane, allowing for accurate integration. The recombination–disproportionation ratio is therefore the ratio of integrated intensity of the methyl peaks in methyldithiane and the transient methyldithiane adduct of benzophenone. The cumulative integrated intensity of the three peaks (in **1a**, **3a**, and **4a**) is used to calculate conversion.

We found that when the fragmentation reaction of benzaldehyde–methyldithiane adduct **1a** was run to a small conversion, the benzophenone–methyldithiane was clearly forming as an intermediate product. At high conversion it disappeared as expected. An alternative disproportionation product, 2-methylidene-1,3-dithiane was not detected.

The recombination–disproportionation ratio at small conversions stayed constant at approximately 1:1.1 (see Table 1). This implies that even with negligible back electron transfer the absolute quantum yield for the release of dithiane cannot exceed $1/\sum_{k=0}^{\infty} 2^{-k}$ or 50%. In practice, methyldithiane recovery never exceeds 40–60% due to secondary irreversible oxidation of it by the sensitizer, meaning that the apparent quantum yields for dithiane release are always below 25%.

An alternative explanation for the formation of **4a** is based on benzophenone reacting with the released methyldithiane. We examined this possibility and ruled it out based on the following observations. We irradiated an equimolar mixture of benzophenone and methyldithiane at a 100 mM concentration, which produced only 7% of **4a**. Excited triplet benzophenone oxidizes methyldithiane in acetonitrile [2] with the near diffusion controlled rate of 1.5×10^9 mol L^{-1} s^{-1}. If the efficient hydrogen transfer were to follow the electron transfer in this pair, the content of **4a** would grow until the rate of fragmentation **4a** becomes equal to the rate of its formation. The electron transfer quenching of triplet benzophenone with methyldithiane is at least twice as fast as quenching with **4a**, yet **4a** survives in only 1:15 ratio to

methyldithiane. This implies that the relative quantum efficiency of **4a** formation from benzophenone and methyldithiane under the circumstance cannot exceed 3.5% of that for the fragmentation. That is, the contribution from the direct reaction of benzophenone with methyldithiane to the recombination–disproportionation ratio is negligible. The analysis of Table 1 further confirms this observation. The recombination–disproportionation ratio does not change much from the first entry (low conversion with little free methyldithiane available) to higher conversions. The ratio actually becomes smaller, not larger as more methyl dithiane becomes available. It is clear that the recombination–disproportionation ratio in Table 1 is the result of the primary fragmentation mechanism, shown in Scheme 1, and reflects the intrinsic properties of the two involved radicals. The nearly 1:1 partitioning between the productive disproportionation channel and the recombination channel (which is effectively delaying the release of 2-methyldithiane) can potentially be rationalized in terms of stability of both radicals, which makes the dithianyl radical not as effective for hydrogen abstraction.

In our prior laser flash photolysis studies, we have shown that the rate of the initial electron transfer decreases with increased substitution in dithiane–ketone adducts [2]. At the same time the quantum yield of fragmentation systematically increases with the length of the alkyl tail on dithiane [17]. It is plausible that substitution improves the recombination–disproportionation ratio, although the effect is not as pronounced: 2–3% improvement in quantum yield per additional CH_2 group in lower alkyls, leveling off for 2-hexyldithiane.

5. Conclusions

We have shown that diethyl sulfide utilized as a quencher of the photoinduced ET-sensitized fragmentation in dithiane–carbonyl adducts can act as a co-sensitizer when added in a certain concentration range. The plausible mechanism for such co-sensitization involves the formation of a heterodimeric radical cation possessing a two-center three-electron S–S bond. DABCO exhibits a similar effect on the Stern–Volmer quenching curve, attesting to the generality of this phenomenon.

Additionally, the partitioning between the (productive) disproportionation and the recombination channel at the final step of this fragmentation is found to be approximately 1:1. This ratio is governed by the properties of the involved radicals and can be improved by the steric bulk of the substituent in position 2 of dithiane.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2009.05.016.

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