# Photoinduced Electron-Transfer Cycloreversion of Thietanes: The Role of Ion−Molecule Complexes

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**ABSTRACT**
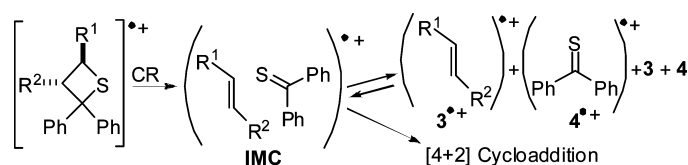


Cycloreversion (CR) of thietane radical cations leads to formation of thiobenzophenone and the corresponding alkenes, eventually followed by secondary [4 + 2] cycloaddition. Final product distribution depends on the ability of fragments to escape from ion−molecule complexes (IMCs).

Cycloreversion (CR) of oxetane/azetidine radical ions has attracted considerable interest in connection with its possible role in the photoenzymatic repair of DNA by photolyases.[1] Our research group has extensively studied both the anionic and the cationic pathways of this reaction using model systems in order to gain insight into the mechanistic aspects.[2]

In comparison, few examples have been reported regarding photoinduced electron-transfer (PET) CR of thietanes, which mimic the key oxetane intermediates in the repair reaction. Carell and co-workers have studied the reductive CR of thietane models, obtaining photoproducts derived from cleavage of the four-membered ring.[3] Previously, PET-mediated ring splitting of 2,2-diarylthietane derivatives was investigated using 9,10-dicyanoanthracene (DCA) as sensitizer. On the basis of fluorescence-quenching studies, an electron-transfer to the DCA singlet excited state was proposed to generate undetected sulfide radical cations and ultimately the corresponding 1,1-diarylethenes as photoproducts.[4] In connection with mechanistic evidence for the oxidative PET CR of thietanes, there seems to be no report

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focusing on the direct detection of intermediates by means of laser flash photolysis (LFP). Likewise, the dependence of CR regioselectivity on the thietane structure as a mechanistic fingerprint has not been investigated.

With this background, the aim of the present work is to study in detail the behavior of model thietanes under PET conditions, with special attention to mechanistic elucidation by LFP measurements. Specifically, 2,2,3-triarylthietanes **1** were chosen as models and thiapyrylium salt **2** as PET photosensitizer[5,6] (Figure 1).
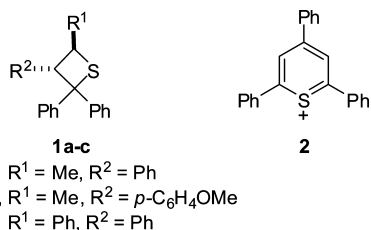


**Figure 1.** Chemical structures of thietanes **1a**−**c** and photosensitizer **2**.

Reactions under study are shown in Scheme 1. *Trans* 4-methyl-2,2,3-triphenylthietane (**1a**) was totally consumed

**Scheme 1.** Direct and Sensitized Photolysis of **1a**−**c**
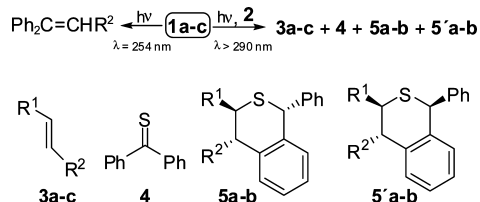


after 30 min irradiation in the presence of thiapyrylium salt (**2**), giving cyclic products **5a** and **5′a** in high yield (Table 1, entry 1). The presence of an electron-releasing group in *trans*-2,2-diphenyl-3-(4-methoxyphenyl)-4-methylthietane (**1b**) was associated with a decreased yield of **5b** and **5′b**, together with formation of anethole (**3b**) and thiobenzophenone (**4**) (Table 1, entry 2). Products **5a,b** and **5′a,b**, previously described,[7] were analyzed by HPLC. Interestingly, *trans*-2,2,3,4-tetraphenylthietane (**1c**) gave cleanly the fragments *trans*-stilbene (**3c**) and **4** under the same reaction conditions (Table 1, entry 3). Thus, although $C_2-C_3$ bond scission occurred in all cases, the ratio $(3 + 4)/(5 + 5′)$ strongly depended on the thietane structure. It is remarkable

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**Table 1.** Photoinduced Reactions of **1** in the Presence of Thiapyrylium Salt (**2**)[a]

| entry | thietane | product distribution[b,c] (%) | | | | | |
|---|---|---|---|---|---|---|---|
| | | **3** | **4** | **5a** | **5′a** | **5b** | **5′b** |
| 1 | **1a** | | | 48 | 52 | | |
| 2 | **1b** | 26 | 28 | | | 33 | 39 |
| 3 | **1c** | 100 | 85 | | | | |
| 4[d,e] | **1a** | | | 38 | 39 | 11 | 12 |
| 5[d,f] | **1b** | 51[g] | | 37 | 41 | 10 | 12 |

[a] **1**, 0.05 M; **2**, 0.002 M, $CH_3CN$, nitrogen atmosphere. Irradiation for 30 min with a high-pressure mercury lamp at room temperature (effective irradiation wavelength between 300 and 500 nm). [b] Conversions were nearly 100%, except in the crossover experiments, where it was kept below 50%. Mass balance was in general higher than 95%. [c] Determined by HPLC. [d] Determined by GC analysis, using biphenyl as internal standard. [e] In the presence of 0.05 M of anethole, **3b**. [f] In the presence of 0.05 M of *trans*-β-methylstyrene, **3a**. [g] Yield of anethole, **3b**.

that the yield of [4 + 2] cycloadduct decreased with increasing charge and spin delocalization in the purported alkene radical cation intermediate.

In the absence of photosensitizer, CR occurred with the reverse regioselectivity, leading always to the corresponding 2-aryl-1,1-diphenylethenes (see Scheme 1 as well as the Supporting Information, Scheme S1 and Table S1).

To investigate the possible involvement of ion−molecule complexes, such as $(3/4)^{•+}$, as opposed to free ions ($3^{•+}$ or $4^{•+}$), crossover experiments were performed. Thus, when a mixture of **1a** and **2** was irradiated in the presence of **3b** under the usual conditions, **5a** and **5′a** were still formed together with lower amounts of the crossed products **5b** and **5′b** (Table 1, entry 4). Conversely, in the analogous experiment using a mixture of **1b** and **2** in the presence of added **3a** (Table 1, entry 5), the crossed products **5a** and **5′a** were now the major ones, whereas the direct products **5b** and **5′b** were obtained in smaller amounts.

In order to obtain direct mechanistic evidence based on detection of possible reaction intermediates, LFP measurements were carried out on **2** in the presence of **1a**−**c**, using 355 nm as the excitation wavelength. As the intersystem crossing quantum yield of **2** is very high ($\Phi_{ISC} = 0.94$), the triplet excited state (detectable as a broad T−T band with a flat maximum at ca. 450 nm) was assumed to be involved in the CR process.[5] Indeed, triplet quenching was observed in all cases; rate constants were determined by application of the Stern−Volmer equation[8] and found to be $1.2 \times 10^9$ $M^{-1}$ $s^{-1}$ (**1a**), $2.6 \times 10^9$ $M^{-1}$ $s^{-1}$ (**1b**), and $1.4 \times 10^9$ $M^{-1}$ $s^{-1}$ (**1c**). From these data, it was established that thietanes **1a**−**c** quench the triplet excited state of **2** at a nearly diffusion-controlled rate.

Concomitantly with the disappearance of the T−T band, a new transient peaking at 500 nm was detected in the presence of **1a** and **1b** (Figure 2). This species was tentatively assigned to the radical cations of **5a** and **5b**, respectively. In the case of **1b**, an absorption band around 600 nm was also

(8) *IUPAC Compendium of Chemical Terminology*, 2nd ed.; McNaught, A. D., Wilkinson, A., Eds.; Royal Society of Chemistry: Cambridge, 1997.
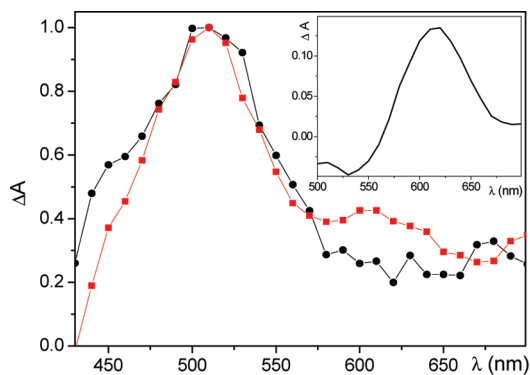
**Figure 2.** Normalized transient absorption spectra obtained upon LFP ($\lambda$ = 355 nm) of **2** (0.06 mM) in the presence of 1 mM **1a** (●) and 1 mM **1b** (■) in acetonitrile, under argon. Spectra recorded 0.4 $\mu$s after the laser pulse. Inset: Difference spectrum of both transient absorption traces (smooth curve fitting).



**Figure 3.** Decay kinetics monitored at 470 nm after 355 nm LFP of **2** (0.06 mM) in the presence of increasing amounts of **1c**: 0 M (black line), 0.05 mM (red line), 0.1 mM (green line), and 0.2 mM (blue line). Inset: Transient absorption obtained for **2** (0.06 mM) in the absence (■) and in the presence of **1c** (1 mM) (●) recorded at 0.4 $\mu$s after the laser pulse.

observed (Figure 2, inset); it was safely ascribed to anethole radical cation (**3b•+**) on the basis of reported literature data.[2h] To confirm assignment of the 500 nm band, **5a•+** and **5b•+** were independently generated from their neutral precursors. For example, the transient spectrum obtained upon 355 nm LFP of **2** in the presence of **5a** (see the Supporting Information, page S7) was similar to that of the intermediate formed from **1a**.
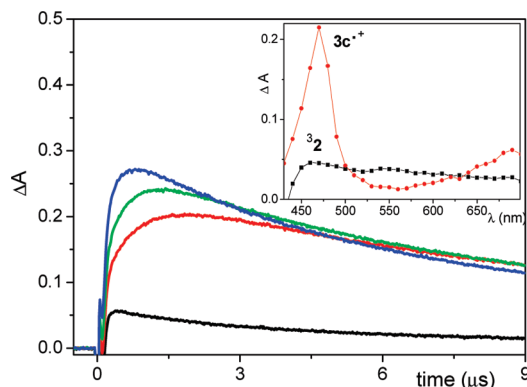
Sulfide radical cations are known to dimerize in solution, giving rise to detectable species. To obtain further pieces of evidence supporting assignment of **5•+**, LFP of **2** was carried out in the presence of increasing amounts of **5** (see the Supporting Information, for the cases of **5a**, **5′a**, and **5b**). A small but significant reduction of the 500 nm signal, with concomitant growth of a new band around 700 nm (dimeric radical cation),[9] was observed in all cases.

As shown in Table 1 (entry 3), the CR of thietane **1c•+** was much cleaner, and accordingly, LFP studies provided straightforward information. Thus, excitation of **2** at 355 nm in the presence of **1c** resulted in the formation of a sharp and intense band centered at 470 nm (inset of Figure 3), which was assigned to stilbene radical cation (**3c•+**) on the basis of literature data.[10]

When the kinetics of the 470 nm trace obtained for various concentrations of **1c** was monitored, a progressive formation of **3c•+** was clearly observed (Figure 3). As a general trend, higher concentrations of **1c** were associated with faster growth of the signal (indicating smaller lifetimes of the precursor species) and with higher values of the top absorbance at 470 nm. This observation, combined with the above-mentioned triplet quenching data, unambiguously confirm that the electron-transfer process takes place from the triplet excited state of **2**.

Complementary experiments were carried out to investigate the reactivity of cyclic sulfides **5** upon irradiation in the presence of **2**. Starting from **5a**, isomerization to **5′a** (20%) was the only observed process; it can be explained by deprotonation of radical cation **5a•+**, followed by protonation and back-electron transfer (BET).[11] However, under the same conditions, sulfide **5b•+** underwent cycloreversion to **3b** and **4** in 18% and 12% yield, respectively, together with isomerization to **5′b** (8%). This is in agreement with detection of anethole radical cation (**3b•+**) after LFP of **2** in the presence of **5b** (see the Supporting Information).

Overall, combined photoproduct studies and transient absorption measurements on the photo-oxidative CR of thietanes strongly support the reaction mechanism outlined in Scheme 2. After formation of **1•+** through PET from its neutral precursor to the triplet excited state of **2** (process a), ring-splitting is completed through C$_2$–C$_3$/C$_4$–S bond scission, giving an ion–molecule complex (IMC) (process b). Escape of the free radical ions (**3•+** or **4•+**) from this complex (process c) constitutes a critical event. Back-electron transfer (process d) leads to the neutral fragments, namely alkenes **3** plus thiobenzophenone **4**. However, an alternative pathway from the IMC is a [4 + 2] cycloaddition reaction to give **6•+** (process e), followed by 1,3 H migration to give **5•+** (process f) and back-electron transfer with formation of cycloadducts **5** and **5′** as final products (process g). Competition between escape and [4 + 2] cycloaddition at the IMC stage (process c vs e) would depend on the relative energy barriers (see inset of Scheme 2): the former would be clearly favored in the case of **1c**, whereas the latter would largely predominate with **1a** as starting material. The situation for **1b** would be intermediate, with a reasonable balance between both processes. Thus, effective delocalization of charge and spin in **3b•+** and **3c•+** results in a less exothermic formation of IMCs, and therefore, radical cations are capable of

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(11) Ioele, M.; Steenken, S.; Baciocchi, E. *J. Phys. Chem. A* **1997**, *101*, 2979–2987.

## Scheme 2. Proposed Reaction Mechanism
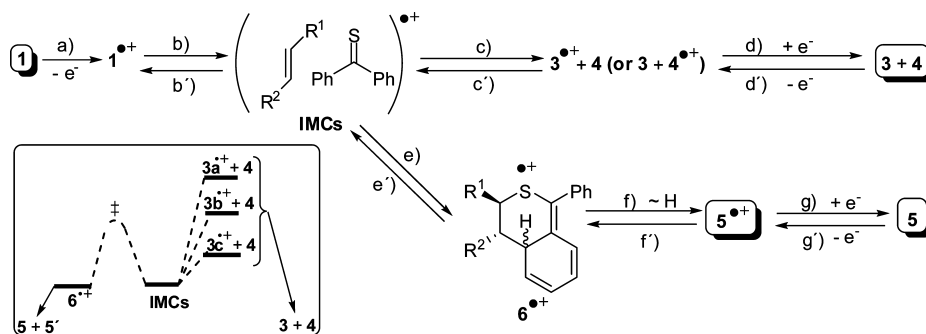


escaping from the complex to afford higher yields of cycloreversion products.[12]

Most of the above processes are reversible. Thus, it is known that long-wavelength irradiation of a mixture of thiobenzophenone and arylalkenes **3a** or **3b** in the presence of thiapyrylium salt **2** leads to **5a,b** and **5′a,b** (pathway d′ + c′ + e + f + g).[7] According to DFT calculations,[13] this reaction follows an asynchronous concerted mechanism through formation of IMCs.

On the other hand, irradiation of compound **5b** in the presence of thiapyrylium salt **2** led to **3b** (pathway g′+ f′+ e′+ c + d). Interestingly, the results from LFP experiments using **2** as photosensitizer were in agreement with the preparative data: (i) for **1a** and **5a** only the radical cation of the cycloadduct (**5a•+**) was observed, (ii) **1b** and **5b** gave a mixture of **3b•+** and **5b•+**, and (iii) **1c** gave only rise to a strong absorption characteristic of **3c•+**. Thus, the role of IMCs explains not only the photoproduct distribution but also the selectivity observed in crossover experiments and the nature of the transient intermediates detected in LFP.

In summary, the oxidative PET CR of thietanes has been studied in detail. Mediation of radical cations has been confirmed by LFP experiments. The photoproducts ratio (**3 + 4**)/(**5 + 5′**) has been found to be dependent on the ability of fragment radical ions to escape from the corresponding ion−molecule complexes.

**Supporting Information Available:** General methods, ^{1}H NMR and ^{13}C NMR spectra of **1c**, and additional schemes, table, and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Oxidation potentials (vs SCE): **3a**, 1.7 V; **3b**, 1.2 V; **3c**, 1.5 V; **4**, 1.7 V.

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