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Direct Photophysical Evidence for Quenching of the Triplet Excited State of 2,4,6-Triphenyl(thia)pyrylium Salts by 2,3-Diaryloxetanes

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The thiapyrylium salt **1b** is an efficient electron-transfer photosensitizer in the preparative irradiation of *trans,-trans*-2,3-diphenyl-4-methyloxetane (**2a**). Previously, the reaction has been assumed to occur through the triplet excited state of **1b**, which has a very high intersystem crossing yield ($\phi_{ISC} = 0.97$). In the present report, direct evidence for triplet quenching in the oxidative cycloreversion of the 2,3-diaryloxetanes is provided. The rate constants $k_q(T_1)$ and the free energy changes of the electron transfer $\Delta G_{ET}(T_1)$ have been determined for the reaction between **1b** and oxetanes **2a−d** and **2a′**. The process has been found to be exergonic in all cases except for **2d**; this agrees with the fact that no photoproduct was obtained in the preparative irradiation of **1b** in the presence of **2d**. Good correlation between $k_q(T_1)$ and $\Delta G_{ET}(T_1)$ was observed, confirming the involvement of the excited triplet state in the reaction mechanism.

Introduction

Photoinduced electron transfer (PET) processes have attracted growing interest in the last two decades.[1] It is well-known that their mechanism involves exchange of one electron between the excited state of the sensitizer (singlet or triplet) and the ground state of the substrate. In general, the synthetic utility of PET is limited by deactivation of the resulting radical ion pairs via back electron transfer (BET).[1c,d]

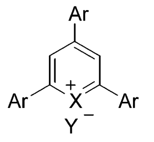
The effect of spin multiplicity on PET reactions has been discussed as one of the most important factors from the viewpoint of charge separation.[2] The high efficiency of reactions occurring from the triplet as opposed to the singlet has two main causes: (a) the triplet states are long-lived, making it possible for the reactants to diffuse and collide with each other and (b) back electron transfer is slow within the triplet radical ion pairs, allowing efficient escape of the partner ions. By contrast, singlet excited states are very short-lived and the radical ion pairs derived therefrom undergo back electron transfer very fast. This makes PET for the excited singlets less effective, despite their higher oxidizing ability.

Recently, the PET cycloreversion (CR) of oxetanes has attracted considerable interest as it is involved in the photoenzymatic repair of the (6−4) photoproducts of the DNA dipyrimidine sites by photolyase.[3] Besides, this process entails cleavage of two bonds and may yield formal metathesis products.[4]

Prior to our work, only two reports have appeared on the CR of oxetane radical cations.[5] In both cases, cyanoaromatic compounds were used as electron-transfer photosensitizers, and the cycloreversion was assumed to occur through the excited singlet state. Although the mechanism was explained via formation of radical cations, no intermediate of this type was detected.

Pyrylium salts are well-established PET sensitizers;[6] they can be selectively excited in the presence of a variety of substrates, because of their absorption in the visible, and are extremely good photooxidizing agents (Table 1). Depending on the substitution pattern and the reaction conditions, pyrylium salts can generate radical ion pairs of different multiplicity (singlet or triplet);[7−9] hence, they may be the sensitizers of choice to study the influence of this factor on the reaction.

TABLE 1: Redox and Photophysical Properties of Pyrylium Salts 1a−d



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sensitizer	X	Y	Ar	$E(S_1)^a$	$E(T_1)^a$	$\phi_{ISC}{}^b$	$E_{(A/A^{-}\bullet)}{}^{c,d}$
1a	O	BF_4	Ph	66	53^d	0.53	−0.29
1b	S	ClO_4	Ph	66	52^d	0.94	−0.21
1c	O	BF_4	*p*-Br−C_6H_4	63	n.a.[e]	0.67	−0.19
1d	O	BF_4	*p*-MeO−C_6H_4	58	51^d	0.03	−0.52

[a] $E(S_1)$, singlet energy; $E(T_1)$, triplet energy (given in kcal/mol). [b] ϕ_{ISC}, intersystem crossing quantum yield, in acetonitrile, in the absence of quencher; ($\phi_{ISC} = 1\text{-}\phi_F$). [c] In V, vs SCE. [d] Taken from the literature.[6] [e] n.a., not available.

The 2,4,6-triphenyl derivative **1a** is the most studied pyrylium salt. Its triplet excited-state sensitizes the oxygenation[7a] and isomerization[7b] of stilbenes. Other reactions, such as the oxygenation of arylfurans,[8a] adamantylideneadamantanes,[8b] and diarylethylenes,[8c] appear to be photosensitized both from the singlet and the triplet of **1a**. Finally, in some cases the only possibility considered is reaction from the singlet excited state[9] (for instance, in the PET ring opening of epoxides).[9a]

The only example of pyrylium sensitized CR of oxetanes has been recently reported by our group.[10] Different results were obtained in the preparative irradiation of model 2,3-diphenyloxetanes **2a** and **2a′** depending on the employed photosensitizers. Thiapyrylium salt **1b**, with the highest intersystem

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crossing quantum yield (ϕ_{ISC}),[11] was found to be the most efficient photosensitizer; by contrast, irradiation in the presence of methoxy salt **1d**, with the lowest ϕ_{ISC} value,[6a] did not result in the formation of any photoproduct.

From these preparative studies, electron-transfer CR was assumed to proceed through the triplet sensitizer. This was supported by the fact that intersystem crossing was found to be efficient enough even at high oxetane concentration. However, direct photophysical evidence for quenching of the triplet excited state of pyrylium salts by oxetanes is still missing.

In view of the results obtained in the CR of model diphenyloxetane **2a**,[10a,b] thiapyrylium salt **1b** was chosen as the most suitable PET sensitizer to explore the feasibility of oxidative CR of oxetanes from the triplet excited state. Besides, the thiapyranyl radical (the one-electron reduced species) does not absorb in the 500−600 nm region,[11c] so it does not interfere with the typical triplet−triplet absorption of **1b** (460 and 600 nm).

In the present work, electron transfer between the thiapyrylium salt **1b** and diphenyloxetane **2a** has been studied in detail, and the photophysical parameters of the involved processes have been determined. These studies have provided clear evidence for triplet quenching. The quenching rate constant $k_q(T_1)$ and the free energy change of the electron-transfer process $\Delta G_{ET}(T_1)$ have been calculated. The study has been extended to oxetanes **2a′** and **2b**−**d** with electron releasing or electron withdrawing substituents attached to the aryl group(s), which modify the oxidation potential of the model oxetane. A good correlation between $k_q(T_1)$ and $\Delta G_{ET}(T_1)$ has been obtained, which confirms the electron-transfer mechanism from the triplet excited state.

Experimental Section

Chemicals. Sensitizer **1a** was commercially available. Its analogue **1b** was synthesized according to the procedure described by Wizinger and Ulrich,[12] whereas **1c** and **1d** were obtained following the method described by Steckhan and coworkers.[6b]

Oxetane **2a** and **2b** were prepared via the Paterno-Büchi photocycloaddition of benzaldehyde and *trans*-β-methylstyrene,[13a] or *trans*-anethole,[13b] respectively. A similar procedure was followed in the synthesis of **2c** and **2d**. Briefly, solutions of the aryl olefin and the aldehyde (ca. 0.5 M) derivatives were placed in Pyrex tubes and irradiated for 72 h under argon atmosphere with a high-pressure mercury lamp (400 W). After irradiation, the solvent was evaporated and the reaction mixture was purified by silica gel column chromatography using hexane:ethyl acetate as eluent (gradient from 99:1 to 95:5 v/v).

All known compounds were characterized by ^{1}H and ^{13}C NMR spectra, which were recorded on 300 and 75 MHz, respectively. Data were consistent with those found in the literature.

***trans,trans*-4-Methyl-2-(4-methylphenyl)-3-phenyloxetane (2c).** ^{1}H NMR (δ, ppm): 1.57 (d, J 6.0 Hz, 3H), 2.34 (s, 3H), 3.58 (t, J 7.5 Hz, 1H), 5.02 (dq, J 7.5 Hz, J 6.0 Hz, 1H), 5.63 (d, J 7.5 Hz, 1H), 7.2−7.4 (m, 9 H). ^{13}C NMR (δ, ppm): 21.2 (CH_3), 23.2 (CH_3), 57.7 (CH), 80.7 (CH), 85.0 (CH), 125.5 (CH), 127.2 (CH), 128.7 (CH), 129.0 (CH), 129.2 (CH), 136.0 (C), 139.0 (C), 140.0 (C). MS (m/z (%)): 194 (42), 180 (6), 179 (45), 178 (38), 165 (7), 152 (5), 119 (31), 118 (100), 117 (55), 105 (4), 91 (20), 77 (5). Exact mass (EI): required for $C_{17}H_{18}O$: 238.1358 (M^+); found: 238.1325.

***trans,trans*-2-(4-Cyanophenyl)-4-methyl-3-phenyloxetane (2d).** ^{1}H NMR (δ, ppm): 1.56 (d, J 6.0 Hz, 3H), 3.49 (t, J 7.5 Hz, 1H), 5.09 (dq, J 7.5 Hz, J 6.0 Hz, 1H), 5.72 (d, J 7.5 Hz, 1H), 7.31−7.44 (m, 5H), 7.50 (d, J 8.4, 2H),), 7.66 (d, J 8.4, 2H). ^{13}C NMR (δ, ppm): 23.2 (CH_3), 57.7 (CH), 81.6 (CH), 84.0 (CH), 112.1 (C), 119.4 (C), 126.2 (CH), 127.8 (CH), 128.2 (CH), 129.6 (CH), 133.0 (CH), 138.8 (C), 148.5 (C). MS (m/z (%): 205 (24), 204 (25), 203 (11), 190 (11), 176 (5), 165 (3), 151 (2), 130 (5), 118 (100), 117 (66), 102 (8), 91 (12), 76 (4). Exact mass (CI): required for $C_{17}H_{16}NO$: 250.1232 (MH^+); found: 250.1236.

***trans,trans*-2,3-Diphenyl-4-hydroxymethyloxetane (2a′).** ^{1}H NMR (δ, ppm): 3.83 (dd, J 12.8 Hz, J 3.7 Hz, 1H), 3.92 (dd, J 3.4 Hz, J 12.8 Hz, 1H), 4.13 (t, J 7.7 Hz, 1H), 4.95 (ddd, J 7.6 Hz, J 3.7 Hz, J 3.4 Hz, 1H), 5.75 (d, J 7.7 Hz, 1H), 7.31−7.49 (m, 10H). ^{13}C NMR (δ, ppm): 49.7 (CH_2), 64.8 (CH), 84.3 (CH), 85.5 (CH), 125.5 (CH), 127.3 (CH), 128.5 (CH), 128.5 (CH), 138.6 (C), 141.4 (C). MS (m/z (%)): 240 (<1, [$M^{+\bullet}$]), 222 (<1), 180 (92), 179 (100), 178 (74), 165 (51), 152 (15), 134 (96), 105 (34), 92 (92), 78 (29). Exact mass (CI): required for $C_{16}H_{17}O_2$ 241.1229 (MH^+); found: 241.1182.

Cycloreversion Reactions. Solutions of oxetanes **2a**−**d** and **2a′** (4×10^{-2} M) with photosensitizer **1b** (10^{-3} M) in CD_3CN (0.8 mL) were placed in NMR tubes and bubbled with argon. Then, the solutions were irradiated during 20 min in a multilamp photoreactor, using 8 W lamps (4×) with emission maximum at $\lambda = 350$ nm. The reaction was followed by ^{1}H NMR, which was recorded before and after the irradiation. Control experiments showed that photocycloreversion does not take place in the dark or in the absence of photosensitizer.

Cyclic Voltammetry. The redox potentials were measured using the cyclic voltammetry technique. All measurements were made in acetonitrile containing tetrabutylammonium perchlorate (0.1 M) as supporting electrolyte, using a glassy carbon working electrode and ferrocene in acetonitrile (5 mg in 30 mL) as standard, $E_{Pa} = 423$ mV and $E_{Pc} = 345$ mV. The scan rate was 400 mV/s. Potentials are reported with respect to the saturated calomel electrode (SCE) as reference.

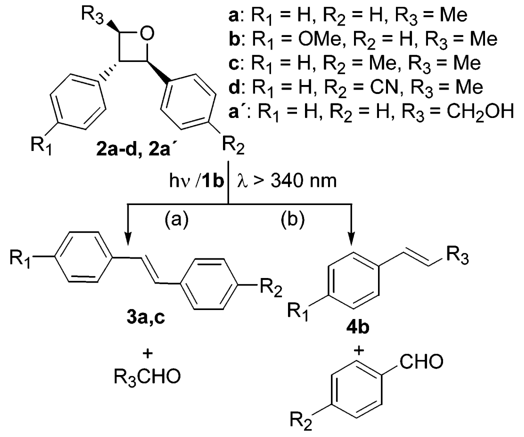
Fluorescence Spectroscopy. The steady-state fluorescence spectra were obtained with a FS 900 spectrofluorimeter equipped with a 450 W xenon lamp. The samples were placed into quartz cells of 1 cm path length. The pyrylium salt concentration was fixed adjusting the absorbance of the solutions at arbitrary concentration between 0.2 and 0.3.

Time-Resolved Absorption Spectroscopy. The laser flash photolysis system was based on a pulsed Nd:YAG SL404G-10 Spectron Laser Systems, using 355 nm as excitation wavelength. The single pulses were ca. 10 ns duration and the energy was ca. 20 mJ/pulse. A Lo255 Oriel xenon lamp was employed as detecting light source. The laser flash photolysis apparatus consisted of the pulsed laser, the Xe lamp, a 77200 Oriel monochromator, an Oriel photomultiplier (PMT) system made up of 77348 side-on PMT tube, 70680 PMT housing, and a 70705 PMT power supply. The oscilloscope was a TDS-640A Tektronix. The output signal from the oscilloscope was transferred to a personal computer for study.

Results and Discussion

Singlet Quenching vs Triplet Population. Oxetanes **2a**−**d** and **2a′** were synthesized according to the Paterno-Büchi cycloaddition, following the procedure described in the literature.[13] Preparative irradiations were carried out in the presence of catalytic amounts of thiapyrylium salt **1b**. The reaction pathway was different depending on the substitution pattern of the oxetane: stilbenes (**3a**,**c**) and acetaldehyde were obtained in the CR of **2a,c** (pathway a, Scheme 1),[10a,b] whereas *trans*-

SCHEME 1



anethole (**4b**) and benzaldehyde were found in the case of **2b** (pathway b, Scheme 1);[14d] no photoproduct was detected in the PET irradiation of **2d**. The hydroxymethyl derivative **2a′** also followed pathway a, leading to stilbene **3a** and the hydroxyacetaldehyde dimer.[10c] As stated above, the reaction was assumed to occur from the triplet excited state of the thiapyrylium salt.

To make sure that the triplet of **1b** was formed in sufficient amount, even at high concentration of oxetane, it appeared necessary to determine the relative intersystem crossing yield under the employed reaction conditions. Estimations were made taking into account the main deactivation mechanisms of the singlet excited state: fluorescence emission, fluorescence quenching, and intersystem crossing. Competition between them should be governed by the respective rate constants and by the quencher concentration.

The rate constant of fluorescence emission (k_f) and intersystem crossing (k_{ISC}) are intrinsic properties of the photosensitizer. The values for **1b** were calculated from eqs 1 and 2 and were $k_f = 0.1 \times 10^8$ s^{-1} and $k_{ISC} = 2.1 \times 10^8$ s^{-1}, respectively

$$\tau_f k_f = \phi_f \tag{1}$$

$$\tau_f k_{ISC} = \phi_{ISC} \tag{2}$$

The rate constants for quenching of the thiapyrylium salt **1b** fluorescence $k_q(F)$ by **2a**−**d** and **2a′** were obtained from the Stern−Volmer analysis (eqs 3 and 4)

$$\phi_0/\phi = 1 + K_{SV}[\text{oxetane}] \tag{3}$$

$$K_{SV} = \tau_f k_q(F) \tag{4}$$

Their values are given in Table 2, together with the relative contributions of the different singlet deactivation pathways at two oxetane concentrations.

From these data, it is clear that the main deactivation route is intersystem crossing, except when high concentrations of **2b** are present. That means that, even at high quencher concentrations, the triplet excited state of the photosensitizer is sufficiently populated and may photosensitize the electron-transfer reaction.

Evidence for Triplet Quenching. Laser flash photolysis ($\lambda_{exc} = 355$ nm) of thiapyrylium salt **1b** resulted in a broad transient absorption between 460 and 600 nm, with a lifetime of ca. 4.2 μs in acetonitrile, which was assigned to the known T−T transition of **1b**.[11c] Depletion of the ground state of the sensitizer was also observed between 390 and 440 nm. In the presence of oxetanes **2a**−**c** and **2a′**, a faster decay of the triplet was observed. Concomitantly, transients were formed corresponding to olefin radical cations resulting from the cycloreversion of oxetanes. As expected, no band related to the thiapyranyl radical was found, because this species does not absorb in the recorded spectral window.[11c]

TABLE 2: Relative Contribution of the Different Pathways Resulting in Deactivation of the Excited Singlet of 1b at Two Concentrations of Oxetane

oxetane	$10^{-9} \times k_q(S_1)^a$	[**2**] (M)^b	F (%)^c	Q(%)^d	ISC (%)^e
2a	6.9	10^{-2}	3	25	72
		10^{-4}	5	1	94
2b	16.6	10^{-2}	3	54	43
		10^{-4}	5	1	94
2c	13.9	10^{-2}	3	48	59
		10^{-4}	5	1	94
2d	5.4	10^{-2}	4	19	77
		10^{-4}	5	1	94
2a′	4.1	10^{-2}	4	16	80
		10^{-4}	5	1	94

[a] Rate constant for quenching of the fluroescence of **1b** by **2a**−**d** and **2a′** (given in M^{-1} s^{-1}). [b] Oxetane concentration. [c] F, Residual fluorescence. [d] Fluorescence quenching. [e] ISC, Intersystem crossing.

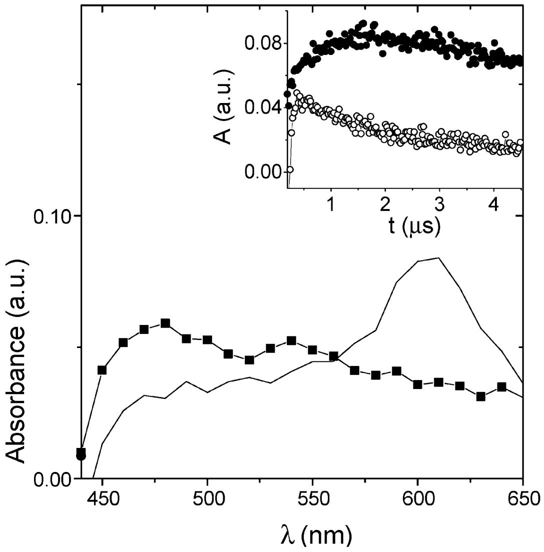


Figure 1. Transient spectra obtained upon LFP ($\lambda = 355$ nm) of **1b** (0.75×10^{-4} M), in acetonitrile, under argon: (a) in the absence of quenchers (■) and (b) in the presence of 1.25×10^{-4} M of **2b** (—). Spectra recorded 1 μs after the laser pulse. Insert: growth and decay of the bands at 600 nm (●) and at 470 nm (○).

For example, when **1b** was submitted to LFP in the presence of **2b**, triplet quenching (measured at 470 nm) was accompanied by the appearance of a new transient with absorption maximum at 600 nm (Figure 1). The latter can be safely assigned to the radical cation of *trans*-anethole ($\mathbf{4b}^{+\bullet}$), on the basis of the literature data.[14] The insert of Figure 1 shows that, under the employed experimental conditions (low concentration of oxetane), growth of the 600 nm band occurs in the submicrosecond time scale together with the decay at 470 nm.

The rate constants for triplet quenching of **1b** in the presence of **2a**−**c** and **2a’**were measured by monitoring the decay of the T−T transition at different concentrations of oxetane. The wavelength was selected case by case, to avoid interference with species due to other transients. Thus, it was previously established by our group that PET cycloreversion of **2a** follows pathway a of Scheme 1 and leads to *trans*-stilbene radical cation ($\mathbf{3a}^{+\bullet}$), which has an absorption maximum at 470 nm;[10a,b] hence,

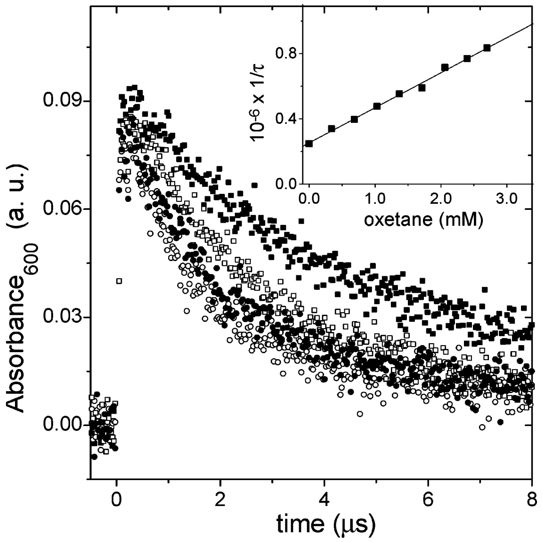


Figure 2. Decay traces of the T−T absorption of **1b** (1.25×10^{-4} M) measured at 600 nm in the presence of increasing amounts of **2a**: 0 M (■), 0.68×10^{-3} M (□), 1.37×10^{-3} M (●), 2.40×10^{-3} M (○). Insert: Stern−Volmer plot to obtain $k_q(T_1)$. The insert also includes results obtained at oxetane concentrations for which the decay traces are not shown.

the quenching experiments were measured at 600 nm. In the case of **2b**, CR exhibits a different regioselectivity (pathway b in Scheme 1) and proceeds through the radical cation of *trans*-anethole (**4b**$^{+\bullet}$).[14] As this species displays a band with maximum at 600 nm (Figure 1), quenching experiments were followed at 470 nm.

When LFP of **1b** was performed in the presence of **2c**, CR occurred following the same pathway as in the case of **2a**. A band with maximum at ca. 490 nm (4-methylstilbene radical cation, **3c**$^{+\bullet}$) was recorded, so quenching experiments were measured at 600 nm.

In the LFP of mixtures of **1b** and **2d**, neither deactivation of the triplet nor formation of new bands was detected, so no quenching measurements could be done.

The triplet quenching rate constants, $k_q(T_1)$ were determined from the decay traces obtained for the T−T absorption of **1b** in the presence of increasing amounts of oxetane. Such traces are shown in Figure 2 for **2a** as a typical case. By plotting the reciprocal lifetimes ($1/\tau$) against the concentration of oxetane, Stern−Volmer linear relationships were obtained (see insert of Figure 2). The slopes of the straight lines correspond to $k_q(T_1)$ as deduced from Equation 5. Data are collected in Table 3 and good correlation coefficients were found in all cases

$$1/\tau = k_0 + k_q(T_1) \qquad (5)$$

It is noteworthy that the $k_q(T_1)$ values were markedly influenced by the substitution pattern of the aryl groups in the oxetanes. They show that electron transfer occurs at almost diffusion controlled rate for oxetanes **2b** and **2c** (with electron releasing groups) while no triplet quenching was observed for oxetanes with electron withdrawing substituents (cf. **2d**).

Correlation between Thermodynamics and Kinetics of the Electron-Transfer Reaction. The free energy changes associated with electron transfer from the triplet excited states of the sensitizers were calculated using the Weller[16] equation (eq 6)

$$\Delta G_{ET}(\text{kcal/mol}) = 23.06[E_{(D^{+\bullet}/D)} - E_{(A/A^{-\bullet})}] - E^*_A \quad (6)$$

TABLE 3: Thermodynamics and Kinetics of the Photosensitized ET Reaction from the Triplet Excited State of 1b

oxetanes	$10^{-9} \times k_q(T_1)^a$	$E_{(D^{+\bullet}/D)}{}^b$	$\Delta G_{ET}(T_1)^c$
2a	0.21	1.86^d	−4
2b	3.98	1.48	−13
2c	2.60	1.75^e	−7
2d	0.00	2.30	+6
2a′	0.29	n.a.^{f}	n.a.^{f}

[a] Rate constant for quenching of triplet **1b** by oxetanes **2a**−**d** and **2a′**, given in M^{-1} s^{-1}. [b] Given in V vs SCE. [c] Given in kcal/mol. [d] Obtained after the first scan. Previously, a value of 1.42 V has been reported; however, this value was obtained after several scans, where some stilbene ($E_{(D^{+\bullet}/D)} = 1.45$ V vs SCE)[15] resulting from CR of **2a** could be already present. [e] Value calculated using *p*-xylene as a model, because cyclic voltametry of **2c** was unclear, probably due to decomposition of the sample. [f] n.a.: not available.

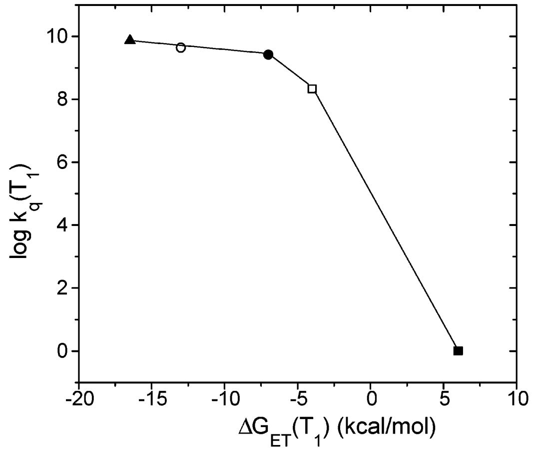


Figure 3. Correlation between log $k_q(T_1)$ and $\Delta G_{ET}(T_1)$ for quenching of triplet **1b** by several donors: oxetanes **2a** (□), **2b**(○) **2c** (●), **2d** (■), and *trans*-anethole **4b** (▲).

The oxidation potentials $E_{D^{+\bullet}/D}$ were measured by cyclic voltammetry in acetonitrile. Their values (Table 2) were found to depend on the substitution pattern of the aryl groups. As anticipated, electron withdrawing substituents increase the oxidation potential, while the reverse is true for electron releasing groups. Thus, the $E_{D^{+\bullet}/D}$ values decreased in the order: **2d** >**2a** > **2c** > **2b**.

As the $E_{A/A^{-\bullet}}$and the triplet energy of **1b** have been previously measured (Table 1), the $\Delta G_{ET}(T_1)$ values were obtained by fitting the above data into eq 6. The results are given in Table 3. According to them, the reaction would be possible in all cases, except for oxetane **2d**. The most exergonic reaction would be expected in the case of the methoxy substituted derivative **2b**.

A plot of the logarithm of the triplet quenching rate constants log $k_q(T_1)$ against $\Delta G_{ET}(T_1)$ is shown in Figure 3. The resulting correlation is typical for electron-transfer processes.[11e,17] It presents two clearly defined regions: for slightly exergonic processes (from 0 kcal/mol to ca. −5 kcal/mol), the more negative is $\Delta G_{ET}(T_1)$, the higher is the rate of triplet quenching. However, for $\Delta G_{ET}(T_1)$ more negative than ca. −7 kcal/mol, the curve reaches a plateau. In this region, the electron transfer process progressively approaches diffusion control. The figure also includes the experimental values obtained for *trans*-anethole **4b** (the photoproduct of **2b**) under the same conditions.

Conclusions

Cycloreversion of 2,3-diaryloxetanes **2a**−**c** and **2a′** follows an electron-transfer mechanism through the triplet excited state of the thiapyrylium salt. The rate constants for quenching of the triplet of **1b** $k_q(T_1)$ by the oxetanes have been determined; they exhibit a marked dependence on the substitution at the phenyl groups. Free energy changes $\Delta G_{ET}(T_1)$ have also been calculated, and the reaction has been found to be exergonic in all cases except for PET between **1b** and **2d**. Accordingly, in this case, no photoproduct was found in the preparative irradiation. A good correlation between $k_q(T_1)$ and $\Delta G_{ET}(T_1)$ is observed, as a confirmation of the electron transfer between the triplet excited state of the thiapyrylium salt **1b** and the 2,3-diphenyloxetanes.

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