Electronic Substituent Effects in Quenching of $^1O_2$ by Diaryl Tellurides

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Singlet-oxygen quenching by a series of substituted diaryl tellurides was investigated in 10% aqueous methanol by monitoring the competitive inhibition of oxidation of 1,3-diphenylisobenzofuran. The extent of quenching of the sensitizer triplet state was determined by repeating the analysis in both air- and O_2-saturated solutions and by laser flash-photolysis experiments. A Hammett analysis of the rate of quenching as a function of substituent constant (σ) gave a ρ value of −0.5, which is significantly lower than the ones reported for other chalcogenides. Although this value does not dispute the existence of a charge-transfer intermediate, it suggests that a strong contribution from the heavy-atom effect of Te is present and that Te is relatively insensitive to inductive electronic substituent effects. The efficiency of chemical quenching in the system was estimated to be 2−9% of the overall quenching of $^1O_2$.

Introduction

Singlet oxygen ($^1O_2$, the electronically excited $^1\Delta_g$ state of dioxygen) is implicated in a number of biological processes associated with oxidative stress *in vivo.*[1] In addition to lipid peroxidation[2] and activation of the mutagenicity of polycylic aromatic hydrocarbons,[3] $^1O_2$ mediates the destruction of tumors during photodynamic therapy (PDT), which represents a therapeutically beneficial use of $^1O_2$.[4] In PDT, an excited triplet state of a photosensitizer reacts with ground state oxygen to produce $^1O_2$.

The lifetime of $^1O_2$ in aqueous solution is on the order of 3−4 μs.[5] Several mechanisms have been demonstrated for the quenching of $^1O_2$ in solution, including (1) electronic energy transfer from $^1O_2$ to nearly isoenergetic vibrational overtones of solvent molecules,[6] (2) electronic energy transfer from $^1O_2$ to a lower-lying electronic state of a quencher molecule,[7] (3) charge transfer or reversible coordination between $^1O_2$ and the quencher resulting in intersystem crossing of $^1O_2$ to the ground state, e.g., with 1,4-diazabicyclo[2.2.2]octane (DABCO),[8] or chemical oxidation, e.g., 2,5-diphenylfuran.[9]

Several organotellurium compounds show promise as sensitizers for PDT due to the heavy-atom effect of the Te atom,[10] which is observed in the increased rates of intersystem crossing and in increased quantum yields for singlet-oxygen generation relative to O-, S-, and Se-containing analogues.[11] However, the benefits of organotellurium compounds are moderated by faster rates of reaction with $^1O_2$ to give the corresponding telluroxides or their hydrates.[11]

Organotellurium sensitizers serve two roles in PDT, which are diametrically opposed. In one role, the heavy-atom effect promotes intersystem crossing in the excited state to give high quantum yields of triplets, which then react with ground-state oxygen to *generate* $^1O_2$. In the other role, the Te-containing sensitizer acts as a chemical *quencher* of $^1O_2$ to produce ground-state oxygen through relaxation and to produce telluroxides via reaction with $^1O_2$.

Little is known about the effects of substituents on the quenching processes and, consequently, about the latitude of structural variation available in the design of more efficient Te-containing sensitizers for PDT. In a series of organochalcogen compounds, the quenching efficiencies followed the order PhTeMe > PhSeMe > PhSMe > PhOMe[12a] and it was subsequently found that the quenching constants and the rates of intersystem crossing in organochalcogenides followed identical functions of Z^4 (where Z is the atomic number of the heaviest atom(s) in the molecules).[12b] Thus, spin−orbit effects associated with heavy atoms will promote *both generation and quenching* of $^1O_2$.

The electronic effects from substituents on processes that are Z^4-dependent would be expected to be subtle.

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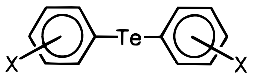
Scant information is available with respect to organoselenium and organotellurium compounds. However, the electronic effects of substituents on the singlet-oxygen quenching constants, $k_Q{}^O$, for a series of thioanisoles have been described with excellent correlation with σ_p [$\rho = -(1.6-1.7)$].[13] In this manuscript, we examine the effects of substituents on $k_Q{}^O$ for a series of *p*- and *m*-substituted diaryl tellurides **1**−**10**. In addition, we report quenching constants for the reaction of the Rose Bengal triplet state with diaryl tellurides.



1, X = *p*-NMe$_2$
2, X = *p*-NH$_2$
3, X = *p*-OH
4, X = *p*-OMe
5, X = H
6, X = *p*-F
7, X = *m*-OMe
8, X = *p*-Cl
9, X = *m*-Cl
10, X = *p*-COCH$_3$

Experimental Section

Reagents. Methanol was HPLC grade (Fisher) and was used without further purification. Water used for the experiments was doubly distilled. 1,3-Diphenylisobenzofuran (DPBF), Rose Bengal, methylene blue, tellurium granules, *m*-bromoanisole, and 3-chlorobromobenzene were purchased from Aldrich and used as received.

Preparation of Diaryl Tellurides. *p*-Substituted diaryl tellurides **1**−**4**, **6**, **8**, and **10** and diphenyl telluride **5** were prepared according to literature procedures.[14] The *m*-substituted diaryl tellurides were prepared according to the procedures described below.

Preparation of *m*-Methoxyphenyl Telluride (7). A solution of *m*-bromoanisole (1.87 g, 10.0 mmol) in 25 mL of anhydrous tetrahydrofuran (THF) was heated at reflux under an argon atmosphere with 0.29 g (12 mmol) of magnesium turnings. Following consumption of the magnesium, tellurium granules (1.40 g, 12 mmol) were added and the resulting mixture was heated until consumption of tellurium was complete. The reaction mixture was poured into 100 mL of a saturated ammonium chloride solution. The products were extracted with ether (3 × 50 mL). The combined ether extracts were washed with brine, dried over MgSO$_4$, and concentrated. The residual oil (a mixture of mono- and ditellurides) was dissolved in 25 mL of toluene, and 1 g of copper powder was added. The resulting mixture was heated at reflux for 15 h. The reaction mixture was filtered through a small pad of Celite, and the filtrate was concentrated. The *m*-methoxyphenyl telluride (**7**) was recrystallized from hexanes to give the diaryl telluride in 66% yield as pale yellow crystals, mp 42−44 °C.

For **7**: ^{1}H NMR (CDCl$_3$) δ 7.26 (t × d, 2 H, J = 1, 8 Hz), 7.25 (d × d, 2 H, J = 1.5, 2.5 Hz), 7.12 (t, 2 H, J = 8 Hz), 6.80 (d × d × d, 2 H, J = 1.5, 2.5, 8 Hz), 3.74 (s, 6 H); ^{13}C NMR (CDCl$_3$) δ 159.95, 130.31, 130.25, 123.30, 115.27, 113.91, 55.25; FDMS, *m/z* 344 ($C_{14}H_{14}O_2{}^{130}Te$).

Anal. Calcd for $C_{14}H_{14}O_2Te$: C, 49.18; H, 4.13. Found: C, 49.37; H, 4.19.

Preparation of *m*-Chlorophenyl Telluride (9). 3-Chlorobromobenzene (3.82 g, 20.0 mmol) and magnesium turnings (0.60 g, 25 mmol) were heated at reflux in 75 mL of anhydrous THF. After the magnesium was consumed (~1 h), the reaction mixture was cooled to ambient temperature and bis(*N,N*-diethyldithiocarbamato)tellurium(II) (4.24 g, 10.0 mmol) was added as a powder. The resulting mixture was heated at reflux for 1 h. The reaction mixture was diluted with 100 mL of water, and the products were extracted with ether (3 × 75 mL). The combined ether extracts were washed with brine, dried over MgSO$_4$, and concentrated. The residue was purified via chromatography on silica gel eluted with CH$_2$Cl$_2$ to give 2.81 g (80%) of telluride **9** as a pale yellow oil.

For **9**: ^{1}H NMR (CDCl$_3$) δ 7.68 (t, 2 H, J = 2 Hz), 7.54 (t × d, 2 H, J = 1, 8 Hz), 7.26 (d × d × d, 2 H, J = 1, 2, 8 Hz), 7.14 (t, 2 H, J = 8 Hz); ^{13}C NMR (CDCl$_3$) δ 137.58, 136.07, 135.15, 130.65, 128.49, 115.38; FDMS, *m/z* 352 ($C_{12}H_8{}^{35}Cl_2{}^{130}Te$).

A crystalline derivative was prepared by the oxidative addition of iodine (0.110 g, 0.433 mmol) to telluride **9** (0.150 g, 0.427 mmol) in 5 mL of acetone at ambient temperature. Stirring produced bright orange microcrystals of $C_{12}H_8Cl_2TeI_2$, which were collected by filtration, washed with cold acetone, and dried to give 0.191 g (74%) of the Te(IV) derivative, mp 181−183 °C: ^{1}H NMR (CDCl$_3$) δ 8.09 (br s, 2 H), 8.03 (br d, 2 H, J = 8 Hz), 7.41 (br d, 2 H, J = 8 Hz), 7.36 (br t, 2 H, J = 8 Hz).

Anal. Calcd for $C_{12}H_8Cl_2TeI_2$: C, 23.84; H, 1.33. Found: C, 24.05; H, 1.53.

Measurements. The studies of the quenching of singlet oxygen were carried out in a stopped-flow spectrophotometer (Applied Photophysics, Ltd.; SX18). The output beam of a 150 W Xenon arc lamp was passed through a monochromator (0.25 mm slits) to separate the 410 nm radiation and directed into the mixing chamber (approximate volume 100 μL) via a flexible optical fiber to provide the excitation for DPBF. The excitation beam entered the chamber through a port that provides a 2 mm path length. The fluorescence of DPBF was monitored at a 90° angle to the excitation beam via a photomultiplier tube (PMT) (Hamamatsu) close-coupled to the chamber assembly. The fluorescence light was passed through a 460 nm interference filter (Oriel) placed in front of the PMT window. The photolysis radiation was supplied by a 100 W QTH lamp (Oriel). The output of the lamp was passed through 530 nm long pass and 560 nm interference filters (both Oriel) and focused onto an input window of a flexible optical fiber. The photolysis light via the fiber reached the mixing chamber by entering through the 10 mm path length port.

The solution of the sensitizer and the solution of DPBF and the quencher were prepared separately to prevent the sample degradation and were injected into the mixing chamber that was kept at 25.0 ± 0.1 °C by a circulating water bath. The decay of the fluorescence of DPBF was then observed on a 200 or 500 s scale. Representative traces are shown in Figure 1. If the experiments required saturation of the samples with oxygen, both solutions were purged by O$_2$ through a needle for approximately 5 min prior to injection.

Laser flash-photolysis experiments were carried out using a setup at Bowling Green State University based on a Nd:YAG laser with a pulse width of 6−7 ns (Continuum). The detailed arrangement has been described previously.[15]

Rate constants for the oxidation of the quenchers by $^1O_2$ were measured by comparing the yield of the disappearance of DPBF to the yield of the disappearance of the quencher when irradiated in solutions containing identical concentrations of Rose Bengal. The concentration of DPBF was monitored by absorbance at 411 nm ($\epsilon = 2.65 \times 10^4$ cm^{-1} M^{-1}). The concentrations of **1**, **5**, and **10** were monitored by absorption at 350, 345, and 333 nm, respectively. The rate constant (k_c) was determined using the methodology developed by Detty and Merkel.[11]

Analysis. The fluorescence decays were analyzed using the routine provided with the stopped-flow instrument software package by fitting them to a first-order exponential decay function with a floating endpoint. A total of three measure-

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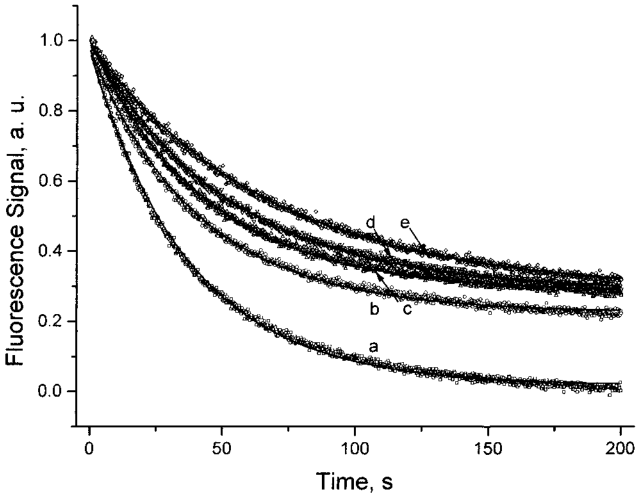
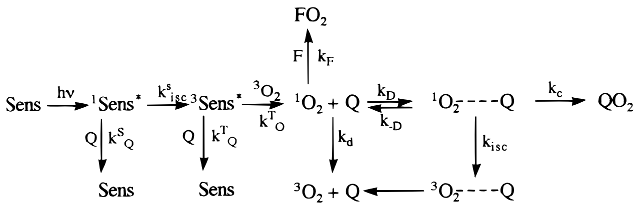


Figure 1. Quenching of the decay of fluorescence of DPBF in oxygen-saturated solutions containing 4.6 μM Rose Bengal and (a) 0, (b) 26.8, (c) 53.6, (d) 134, and (e) 268 μM quencher **2**. The solid lines represent the best fits to first-order single-exponential decay function with slopes *S* equal to (a) 0.02630, (b) 0.02423, (c) 0.02264, (d) 0.01909, and (e) 0.01476 s^{-1}.

Scheme 1



ments were recorded for each sample, and the results were averaged to obtain a mean value for the decay rate. The linear plots of the ratios of the decay slopes were fit using linear regression analysis. The first point ([Q] = 0) was excluded from the fit.

Results and Discussion

Scheme 1 summarizes the processes responsible for the fate of the $^1O_2$ species in solution.[16,17] Irradiation of the sensitizer (Sens) produces singlet sensitizer (^{1}Sens*) which can undergo intersystem crossing (with the rate constant $k_{isc}{}^S$) to the triplet sensitizer (^{3}Sens*). The reaction of ^{3}Sens* with ground-state oxygen ($^3O_2$) gives $^1O_2$ (and Sens) with a rate constant of $k_O{}^T$. Both the singlet and triplet excited states of the sensitizer can be quenched by the quencher (Q), with rate constants of $k_Q{}^S$ and $k_Q{}^T$, respectively.

Under continuous irradiation, a steady-state concentration of $^1O_2$ is established that at a constant light intensity, sensitizer and ground-state O_2 concentration is dependent on the rate at which this intermediate is removed from the system. The processes that deplete the concentration of $^1O_2$ include the relaxation of $^1O_2$ to the ground state and transformations that occur through bimolecular interactions of $^1O_2$ with the quencher. It is, therefore, possible to measure the rate constant of singlet-oxygen quenching by monitoring the steady-state concentration of $^1O_2$ at different concentrations of the quencher. One of the ways of accomplishing this goal was devised by Young et al.[18] and involves observing the decay of a species known to react efficiently with $^1O_2$.[19] The probe (F in Scheme 1) commonly used for this purpose is 1,3-diphenylisobenzofuran (DPBF) whose strong fluorescence can, in most systems, be monitored at 460 nm. DPBF is oxidized irreversibly into an *endo*-peroxide intermediate upon reaction with $^1O_2$ at a rate of 1×10^9 M^{-1} s^{-1} (k_F in Scheme 1) in methanol.[5,20] The decay of fluorescence that accompanies DPBF oxidation in a system where $^1O_2$ is produced at a constant rate can be described by eq 1,[18] where K_T is the rate of production of sensitizer triplet and $k_Q{}^O$ (eq 2) is the rate constant of singlet-oxygen quenching,[8b] where k_D is the

$$-\frac{d[\mathrm{F}]}{\mathrm{dt}} = K_T\left(\frac{k_O{}^T[O_2]}{k_O{}^T[O_2] + k_Q{}^T[Q]}\right)\left(\frac{k_F[F]}{k_d + k_Q{}^O[Q]}\right) \qquad (1)$$

$$k_Q{}^O = k_D\,\frac{k_{isc} + k_c}{k_{-D} + k_{isc} + k_c} \qquad (2)$$

diffusion rate constant, k_{-D} is the rate of dissociation of the complex (^{1}O---Q) formed between $^1O_2$ and the quencher, k_{isc} is the rate of intersystem crossing of the complex, and k_c is the rate constant of the processes that lead to the oxidation products. Equation 2 will be discussed later.

Equation 1 is only valid when $k_F[F] \ll k_d$ ([F] < 1 μM in methanol, $k_d = 1.34 \times 10^5$ s^{-1})[5] and describes a first-order decay process when K_T, [O_2], and [Q] are constant. Singlet-state lifetimes of commonly used sensitizers of $^1O_2$ are short (nanosecond range), and therefore, quenchers in the concentration range usually employed cannot intercept sensitizer singlets. Therefore, K_T is not affected by the change in the quencher concentration. It can be assumed that the quenching of the sensitizer excited states by the probe F is negligible since the probe concentrations employed are low. The assumption of the constancy of [O_2] and [Q] throughout the irradiation is based on the fact that the process leading to the formation of the oxidation products (k_c) was estimated to be inefficient compared to the overall quenching constant ($k_Q{}^O$) for the quenchers used in the study (*vide infra*). The ratio of the slopes of this decay in the absence (S_0) and presence (S) of a quencher is given by eq 3.

$$\frac{S_O}{S} = \frac{k_O{}^T[O_2] + k_Q{}^T[Q]}{k_O{}^T[O_2]}\left(1 + \frac{k_Q{}^O}{k_d}[Q]\right) \qquad (3)$$

When the rate of quenching of the excited states of the sensitizer by Q is negligible compared to the rate of energy transfer from ^{3}Sens to ground-state oxygen, the first term on the right side of the eq 3 reduces to unity

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[16] Foote, C. S. In *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic: New York, 1979; pp 139−171.

[17] Gorman, A. A. In *Advances in Photochemistry*; Volman, D. H., Hammond, G. S., Neckers, D. C., Eds.; John Wiley & Sons: New York, 1992; Vol. 17, pp 217−274.

[18] Young, R. H.; Wehrly, K.; Martin, R. L. *J. Am. Chem. Soc.* **1971**, *93*, 5774−5779.

[19] The use of this technique was questioned by the reviewers due to the availability of a newer procedure that involves direct time-resolved monitoring of $^1O_2$ via its emission at 1270 nm. The costly laser and detection equipment was not available to us, however, and we do not have direct access to existing setups. Therefore, the use of the "Young's technique" that was shown to give reliable data by many investigators was warranted.

[20] Krinsky, N. I. In *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic: New York, 1979; pp 597−641.

and the plot of the ratio (S_0/S) vs quencher concentration is a straight line. The rate constant for the quenching of $^1O_2$ can then be obtained from the slope of the plot and the known lifetime of $^1O_2$ in the solvent used. It has been found, however, that quenchers of $^1O_2$ are often also capable of quenching triplet states of the sensitizers in the range of concentrations commonly used.[21] In that case, appropriate corrections to the values of the slope ratios need to be employed, which requires the knowledge of $k_Q{}^T$. These values can be obtained from the measurement of the slopes of the first-order decays of the DPBF fluorescence in air- and oxygen-saturated solutions containing identical concentrations of the quencher, according to eq 4,[21] where $[O_2]$ is the concentration of oxygen in the solvent saturated with the gas.

$$k_Q{}^T = \frac{k_O{}^T[O_2](1 - (S_{air}/S_{ox}))}{5[Q](S_{air}/S_{ox}) - [Q]} \tag{4}$$

Alternatively, the rate constant for the triplet quenching can be found by measuring the rate of the decay of the sensitizer triplet state with various concentrations of quencher in a laser flash-photolysis experiment.

Using the described methodology, the interaction of $^1O_2$ with a series of substituted diaryl tellurides was investigated in methanol containing 10% water. Since oxidation of Te centers is known to be sensitive to the presence of water,[11] use of the mixed rather than neat solvent was chosen to eliminate the need for drying the solvent. Rose Bengal (RB) was used as the sensitizer in most experiments. Decay of the fluorescence of DPBF was analyzed and fitted with a first-order exponential decay function. Although some deviation from the first-order behavior of the decays was observed, it was relatively insignificant and dependent on neither the presence nor concentration of the quencher (See Figure 1). The deviation can be attributed to the possible depletion of the sensitizer through side reactions. On the other hand, DPBF is known to undergo self-sensitized oxidation under irradiation.[22] Adjusting the kinetic treatment for that process, however, did not improve the fits.

In order to determine the extent of quenching of the sensitizer triplet state by some of the tellurides, the measurements of the rate of decay of DPBF fluorescence in air-equilibrated samples were compared to the measurements in oxygen-saturated solutions. The bimolecular rate constant for this process was determined according to eq 4 using $k_O{}^T = 1.2 \times 10^9$ M^{-1} s^{-1} and $[O_2] = 9.3$ mM.[5,23] The triplet-quenching rate constants were determined by this technique only for the more efficient quenchers, since it was found that the effect was insignificant and hard to detect when $k_Q{}^T$ became lower than 1.0×10^7 M^{-1} s^{-1}. A representative series of linear quenching plots obtained from the fluorescence decay data is shown in Figure 2. The results are compiled in Table 1.

The data for triplet quenching obtained with the procedure described above was confirmed by laser flash-photolysis experiments. Rose Bengal was excited by 532-nm 8-ns pulses of a Nd:YAG laser in deoxygenated solutions, and the decay of the 600-nm transient absorption signal in the presence of various concentrations of diaryl tellurides was analyzed.[24] The resulting values for the rate constants for triplet quenching agreed reasonably well with the ones obtained by the method described above (Table 1).

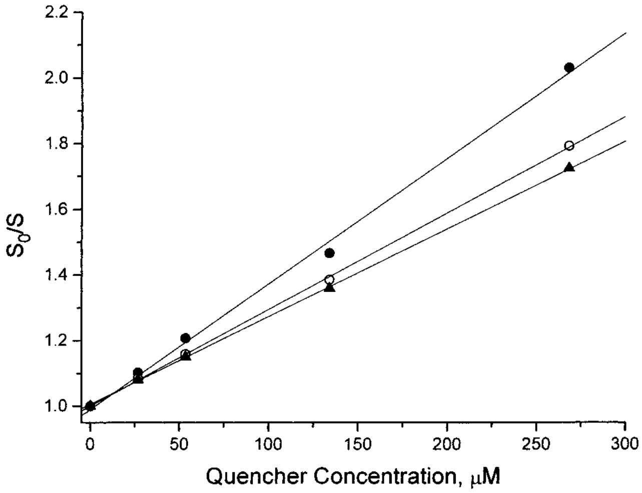

Figure 2. Quenching of the oxidation reaction of DPBF by **2** in 10% aqueous methanol. Data points are for an air-equilibrated solution (●, slope = 3822 ± 160, r = 0.9982) and oxygen-saturated solution (○, slope = 2940 ± 43, r = 0.9998), corrected for sensitizer triplet quenching (▲, slope = 2672 ± 25, r = 0.9999). [RB] = 4.6 μM, [DPBF] = 0.9 μM.

Table 1. Electronic Substituent Constant (σ), Rate Constant for Quenching of RB Triplet ($k_Q{}^T$), and Rate Constant of Quenching of Singlet Oxygen ($k_Q{}^O$) for a Series of Substituted Diaryl Tellurides in a 1:9 H_2O/MeOH Mixture at 25 °C

quencher[a]	σ[b]	$k_Q{}^T$, $\times 10^8$ M^{-1} s^{-1}[c]	$k_Q{}^O$, $\times 10^7$ M^{-1} s^{-1}[d]
1	−0.83	33.4 ± 2.1 (41.5 ± 2.8)	48.1
2	−0.66	16.5 ± 4.2	35.8
3	−0.37	6.63 ± 2.34 (8.88 ± 0.09)	17.9
4	−0.27	2.05 ± 0.78 (4.78 ± 0.11)	15.9
5	0	0.39	7.3
6	0.06	0.27 ± 0.1	5.2
7	0.12	0.23	7.3
8	0.23	*e*	3.8
9	0.37	*e*	3.7
10	0.50	*e* (0.052 ± 0.009)	2.2

[a] See Introduction. [b] Reference 23. [c] Numbers in parentheses are the results from the flash photolysis experiments. [d] Error in values is ±5%. [e] Not measured.

In order to obtain a better understanding of the interplay of all the components in the kinetic scheme and to confirm the validity of the treatment, the rate constant for chemical oxidation (k_c) was estimated for quenchers **1**, **5**, and **10**, with the highest, median, and lowest quenching efficiencies, respectively. The values of 1.0×10^7 M^{-1} s^{-1} for **1**, 5.0×10^6 M^{-1} s^{-1} for **5**, and 2.0×10^6 M^{-1} s^{-1} for **10** were obtained. Therefore, chemical quenching represents 2−9% of the overall $^1O_2$ quenching for the diaryl tellurides studied. The assumption of the constancy of [Q] and $[O_2]$ throughout the experimental runs is, consequently, a valid one. The results also confirm that quencher-induced intersystem

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(24) Mills, A.; Lawrence, C.; Douglas, P. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 2291−2303.

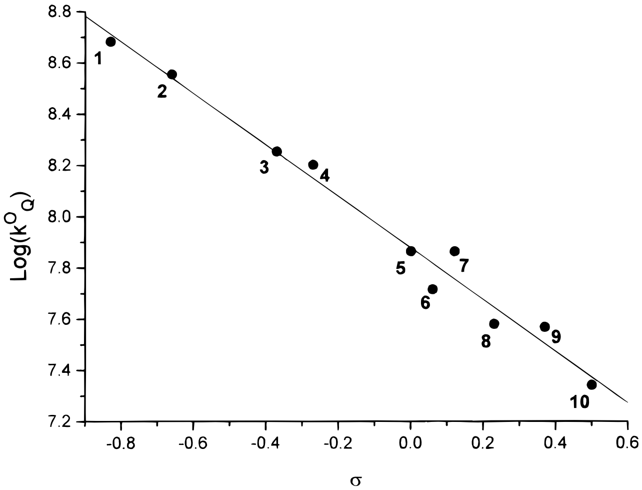

Figure 3. Hammett plot for $^1O_2$ quenching by substituted diaryl tellurides (slope = −1.01 ± 0.05, $r = 0.99$; $\rho = -0.5$). Data from Table 1.

crossing is a dominating process of the deactivation of $^1O_2$ in the system studied.

Knowing $k_Q{}^T$, the data obtained for the singlet-oxygen quenching can be corrected to yield true values for the rate constant. The rate constants obtained for the series of quenchers are compiled in Table 1. It can be seen from the table that there is a trend in the rate constants for singlet-oxygen quenching that is consistent with the changing electron-donating ability of substituents. A linear fit to the data plotted according to the Hammett equation yields a slope of −1.0 (Figure 3). Dividing the slope by two to accommodate the fact that two substituents are being changed per quencher yields a ρ value of −0.5. It has been observed that the quenching of $^1O_2$ by amines,[21] sulfides,[13] and phenols[25] shows similar dependencies of the rate constants on the electron-donating ability of substituents. Such a low ρ value from the diaryl tellurides, however, is significantly different from the ones reported for substituted *N*,*N*-dimethylanilines (−1.72),[21] thioanisoles (−1.6),[13b] and 2,6-di-*tert*-butylphenols (−1.72).[25]

The dependence of the rate constant for the quenching of $^1O_2$ on the electron-donating ability of the substituents can be rationalized in terms of the stability of an exciplex that is formed between $^1O_2$ and the quencher. The existence of such an exciplex has been documented in a number of systems in the literature.[17] It is assumed that the formation of the exciplex involves some degree of charge transfer from the quencher to the oxygen molecule. The complex that is initially formed in a singlet state may undergo intersystem crossing to the triplet manifold and subsequently dissociate to form the quencher and ground state of oxygen. The exciplex may also undergo a chemical transformation to yield oxidation products of the quencher. Dissociation of the complex occurs in competition with these two main processes and leads to repopulation of $^1O_2$. The overall rate constant for the quenching of $^1O_2$ ($k_Q{}^O$) is described by eq 2. Depending on the relative magnitude of the rate parameters in eq 2, the quenching process may be either diffusion controlled ($k_{-D} \ll k_{isc} + k_c$), eq 5,[8b] or lie in the pre-equilibrium regime ($k_{-D} \gg k_{isc} + k_c$), eq 6.

$$k_Q{}^O = k_D \tag{5}$$

$$k_Q{}^O = (k_D/k_{-D})(k_{isc} + k_c) \tag{6}$$

Most of the quenchers that cannot undergo energy transfer reaction with $^1O_2$ do not quench this species at the diffusion-controlled rate at room temperature.[5] The fastest rate constant in this study was found to be 4.8 × 10^8 M^{-1} s^{-1}. In the pre-equilibrium regime, k_{-D} and k_{isc} are the rate constants that are expected to be most affected by the electron-donating ability of the substituents on the quencher. k_{-D} is decreased as the substituent becomes more electron-donating through the stabilization of the positive charge that develops on the heteroatom (Te) in the exciplex. Electron donation is also known to increase spin−orbit coupling, thus promoting intersystem crossing of the complex.[17] On the basis of the large heavy-atom effect projected by Te onto the system, it is expected that the substituent effects on k_{isc} would be small. In the examples studied, k_c is larger with more electron-donating substituents, but the exact mechanism of the process of oxidation of diaryl tellurides is not known. It is thought that the first intermediate formed in the process (pertelluroxide or telluradioxirane) is attacked by a second molecule of the quencher to form two telluroxides.[11]

Higher ρ values for the quenching of $^1O_2$ are usually taken to indicate partial charge transfer within the exciplex. It would seem, therefore, that the ρ value of −0.5 obtained in this study is evidence of a smaller degree of charge transfer between the oxygen species and the telluride quencher relative to amines,[21] sulfides,[13] and phenols.[25] It is reasonable to expect, however, since Te is more electropositive than O, S, or N, that Te would be more prone to transfer its electrons to oxygen. On the other hand, the size of the outer orbitals of Te might prevent an efficient interaction of the heteroatom with the π-systems of the phenyl rings.[26] The electron density on the tellurium atom, therefore, will not be affected to a large extent by the substituents on the rings. Additionally, the contribution of the heavy-atom effect of Te to the intersystem crossing rate of the exciplex may increase k_{isc} to the extent that it will compete with k_{-D}. Both the aforementioned factors can be invoked to explain the low sensitivity of the singlet oxygen quenching reaction to the electron-donating ability of the substituents on the ring.

Conclusion

The dependency of the rate constant for singlet-oxygen quenching by a series of substituted diaryl tellurides on the electron-donating ability of the substituents was investigated in 10% aqueous methanol. The low negative ρ value (−0.5) found in the study is consistent with partial electron transfer from Te to O in the exciplex. The small magnitude of the ρ-value can be explained by the fact that the heavy-atom effect of Te is expected to enhance the intersystem crossing rate of the exciplex, which would allow this process to compete effectively with the exciplex dissociation. Additionally, a poor overlap of the outer orbitals of Te with

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the π-system of the phenyl rings may contribute to the low sensitivity of the heteroatom to the electronic effects of the substituents.

These results are important in the design of organotellurium compounds to be used in PDT. While substituents attached to the π-framework may affect the electronic absorption properties of the dyes or their stability to hydrolysis, these substituents will not significantly alter the properties induced by the presence of the heavy heteroatom. Namely, the rates of intersystem crossing and the rates of the reaction with $^1O_2$ will be minimally affected by substituent changes.

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Supporting Information Available: Figures of the quenching of the decay of fluorescence of DPBF in air-equilibrated and oxygen-saturated solutions, ratio of slopes of the first-order decay of DPBF fluorescence, decay of Rose Bengal triplet state, and observed rate constant for decay of the Rose Bengal triplet state (5 pages). Ordering information is given on any current masthead page.

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