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Evidence in Support of the Corey–Kahn Mechanism of Quenching of Singlet Oxygen with Organometallic Compounds. Oxophilicity and Rates of Intersystem Crossing in Organochalcogen Compounds

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Summary: The Corey–Kahn mechanism of single oxygen quenching requires a donor–acceptor interaction between the heavy-atom nucleophile and electrophilic singlet oxygen and heavy-atom-promoted intersystem crossing in the organometallic quencher. The "oxophilicity" (as determined by comparative rates of oxidation) of the chalcogen atoms in chalcogenapyrylium dyes **1** is similar for two different electrophilic oxidants (singlet oxygen and hydrogen peroxide) that react at the chalcogen atom. A plot of log $k(H_2O_2)$ as a function of $k(^1O_2)$ for the dyes **1** is linear (R = 0.99) with a slope of 2.42, suggesting that chalcogen nucleophilicity is important in oxidations with electrophilic reagents. In the case of singlet oxygen reacting with chalcogenapyrylium dyes **1**, the encounter complex must form with a rate constant approaching that of diffusion control. If the encounter complexes between the Corey–Kahn phenyl methyl chalcogenides and singlet oxygen form at nearly a diffusion-controlled rate, quenching constants will be limited by the rate of intersystem crossing. The rate constants of intersystem crossing for chalcogenapyrylium dyes **1** have been calculated from other photophysical properties of these dyes. The Corey–Kahn quenching constants for phenyl methyl chalcogenides and the rate constants for intersystem crossing in chalcogenapyrylium dyes **1** are identical functions of Z^4, where Z is the chalcogen atomic number.

The quenching of singlet oxygen in solution has been demonstrated for three distinct processes whose mechanisms include (1) electronic energy transfer from singlet oxygen to nearly isoenergetic vibrational overtones of solvent molecules (from C–H and O–H bonds),[1] (2) electronic energy transfer from singlet oxygen to a lower-lying electronic state of a quencher molecule,[2] and (3) electron transfer and/or reversible coordination between singlet oxygen and the quencher.[3] For the electron-transfer mechanism, the ionization potential of the quencher correlates well with electron-transfer quenching both in solution[4] and in the gas phase.[5]

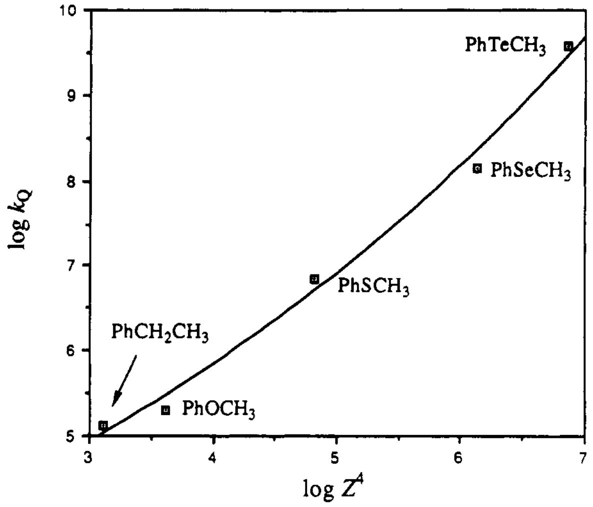

Figure 1. Quenching constants (k_Q) as a function of atomic number (Z) in diorganochalcogenides.

A fourth mechanism, with consequences for organometallic chemistry, has been proposed in two papers by Corey and Kahn which derives from a combination of two physical effects—heavy-atom-induced electron spin–orbit coupling and donor–acceptor-type interactions between the heavy atom as nucleophile and singlet oxygen as electrophile.[6,7] It was proposed that the large quenching constants for singlet oxygen (10^7 M^{-1} s^{-1}) observed in organogold(I) complexes might arise from heavy-atom-promoted increases in rates of intersystem crossing. Spin–orbit coupling ought to be significant for gold (Z = 79), since the efficiency of this process increases as Z^4.[6] In addition, simultaneous operation of "chemical" quenching with gold(I) is possible via either electron transfer or a donor–acceptor interaction between gold(I) and singlet oxygen involving d-orbitals of the former and π-orbitals of the latter. This reasoning was extended to include a series of organochalcogen complexes in which the quenching efficiencies followed the order $R_2Te > R_2Se > R_2S > R_2O$ and in which the quenching efficiencies increased as Z^4 as shown in Figure 1.[7,8]

The Corey–Kahn mechanism assumes that the heavy atoms are good nucleophiles for electrophilic singlet oxygen, perhaps leading to unstable oxidative addition products, and that the magnitude of spin–orbit coupling is directly related to the heavy-atom effect on quenching constants. This note presents experimental evidence in support of the Corey–Kahn mechanism and the two assumptions described via "chemical" quenchers of singlet oxygen and rates of intersystem crossing within these quenchers incorporating oxygen, sulfur, selenium, and tellurium.

Results and Discussion

Heavy-Atom–Singlet Oxygen Encounter Complex. The importance of the nucleophilicity of the heavy atom

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(8) The exponential curve in Figure 1 is of the form $y = 2.9705e^{0.1687x}$, where R^2 = 0.991.

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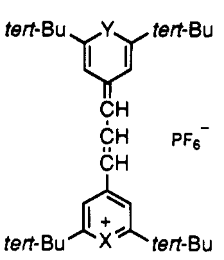
Table I. Rate Constants for Reaction of Singlet Oxygen [$k(^1O_2)$] and Hydrogen Peroxide [$k(H_2O_2)$] with Chalcogenapyrylium Dyes 1 and Rates of Intersystem Crossing (k_{isc}) for Dyes 1

compd	$k(^1O_2)$,[a] M^{-1} s^{-1}	$k(H_2O_2)$,[b] M^{-1} s^{-1}	k_{isc},[c] s^{-1}
1a	$(3 \pm 1) \times 10^6$	$(1.04 \pm 0.05) \times 10^{-4}$	2×10^6
1b	$(1.3 \pm 0.1) \times 10^7$	$(1.81 \pm 0.03) \times 10^{-3}$	8×10^6
1c	$(4 \pm 1) \times 10^6$	$(7.65 \pm 0.07) \times 10^{-4}$	
1d	$(5 \pm 1) \times 10^6$	$(4.68 \pm 0.06) \times 10^{-4}$	7×10^8
1e	$(9.4 \pm 0.9) \times 10^7$	1.04 ± 0.01	
1f			2×10^{10}
1g	$(1.8 \pm 0.1) \times 10^8$	2.26 ± 0.02	4×10^{10}

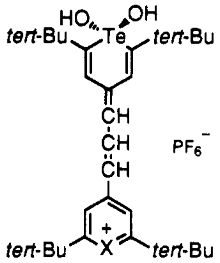
[a] Values in 50% methanol from ref 9. [b] In distilled water with 1% added methanol. [c] Values in methanol from ref 9.

in the quenching of singlet oxygen might be probed via the kinetics of irreversible reactions of heavy atoms with singlet oxygen. The observed quenching constants for such reactions would then be greater than or equal to the rate of reaction of the heavy atom with singlet oxygen.

The reaction of chalcogenapyrylium dyes 1 with singlet oxygen has been described.[9] The dyes 1 are bleached upon exposure to singlet oxygen



1a; X=Y=O
1b; X=Y=S
1c; X=Se,Y=O
1d; X=Y=Se
1e; X=Te,Y=O
1f; X=Te,Y=Se
1g; X=Y=Te



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with the second-order rate constants, $k(^1O_2)$, given in Table I.[9] From the stoichiometry of reaction, the tellurium-containing dyes **1e–g** react with singlet oxygen to give some oxidized intermediate. This intermediate reacts with a second dye molecule and water to give the dihydroxytelluranes **2**. (Tellurane is appropriately used for the saturated six-membered ring. Tellurane is being used in this paper in a broader sense to include both forms.) Similar products are not observed with pyrylium dye **1a**, thiapyrylium dye **1b**, and selenapyrylium dyes **1c**, and **1d**. The chalcogenapyrylium dyes **1** illustrate the increased reactivity of tellurium-containing species relative to oxygen-, sulfur-, and selenium-containing species toward singlet oxygen. Furthermore, the products of reaction of singlet oxygen and tellurapyrylium dyes are tellurium(IV) species generated by direct attack of singlet oxygen on the tellurium atoms. With the lighter chalcogens, rates of reaction are slower and similar products derived from oxidation of sulfur or selenium in the chalcogenapyrylium dyes are not observed. Since the rate constant for bleaching of **1g** with singlet oxygen (in water, 8×10^8 M^{-1} s^{-1}; in 50% methanol, 1.8×10^8 M^{-1} s^{-1})[9] is approaching that of diffusion control, the initial encounter complex of singlet oxygen and tellurium must also form with a rate constant approaching that of diffusion control.

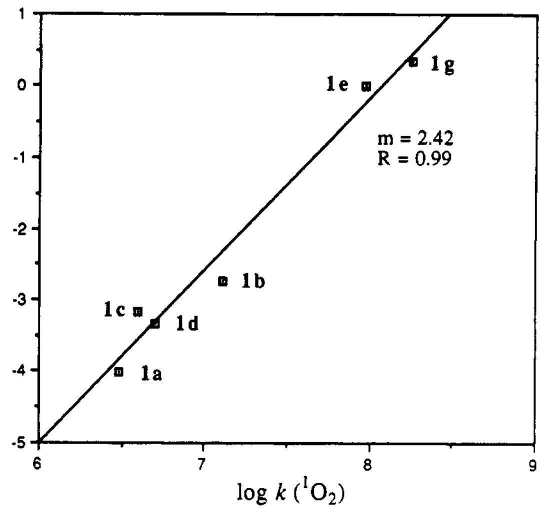
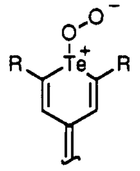
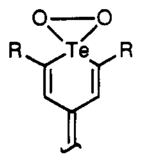


Figure 2. Plot of log $k(H_2O_2)$ as a function of log $k(^1O_2)$ for the chalcogenapyrylium dyes 1.

Possible encounter complexes between tellurium and singlet oxygen are the pertelluroxide or telluradioxirane structures



Pertelluroxide



Telluradioxirane

Similar intermediates—persulfoxides and thiadioxiranes—have been proposed for the oxidation of neutral diorganosulfides to sulfoxides[10] with singlet oxygen. Corresponding perselenoxides and selenadioxiranes might also be proposed for the oxidation of selenides to selenoxides with singlet oxygen. Although products of direct oxidation of sulfur or selenium with singlet oxygen in the chalcogenapyrylium dyes **1a–d** were not observed,[9] an initial adduct might be reversible [perhaps regenerating **1** and ground-state ($^3O_2$) oxygen] and/or might lead to oxidation at another atom in the molecule (as is observed for dihydroxytelluranes **2**).[11]

If the nucleophilicity of the heavy atom were important in reactions with singlet oxygen, then similar trends in reactivity should be observed with other electrophilic oxidants, such as hydrogen peroxide, which is an electrophilic oxidant in neutral or acidic media. Second-order rate constants, $k(H_2O_2)$, for the bleaching of the dye chromophore of chalcogenapyrylium dyes **1** were measured under pseudo-first-order conditions with hydrogen peroxide and are compiled in Table I. The oxidation of tellurapyrylium dyes **1e–g** with hydrogen peroxide gave the dihydroxytelluranes **2** as the only observed product.

Singlet oxygen is much more reactive than hydrogen peroxide and, consequently, is much less selective toward the dyes **1** than hydrogen peroxide as an oxidant. However, a plot of log $k(H_2O_2)$ as a function of log $k(^1O_2)$ is linear as shown in Figure 2, with a slope of 2.42 ($R = 0.99$). The slope of this plot indicates that the difference in selectivity of the two oxidants is roughly 250-fold while the linear relationship indicates that the "oxophilicity" within

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[9] Detty, M. R.; Merkel, P. B. *J. Am. Chem. Soc.* **1990**, *112*, 3845–3855.

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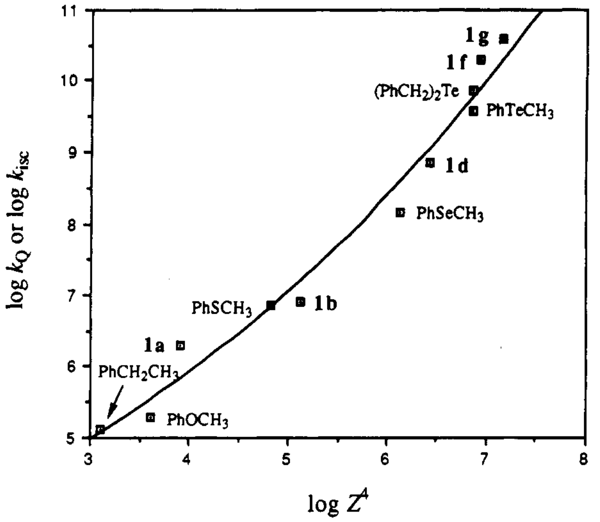

Figure 3. Quenching constants (k_Q) for the diorganochalcogenides and rates of intersystem crossing (k_{isc}) for the chalcogenapyrylium dyes 1 as functions of atomic number (Z).

the heteroatom series is similar for the two reagents. These data suggest that the nucleophilicity of the heteroatoms is similarly important in both "chemical" quenching of singlet oxygen with dyes 1 and in oxidative addition of hydrogen peroxide with dyes 1.

Heavy-Atom Effects. The second issue in Corey–Kahn mechanism is the importance of spin–orbit coupling to the rate of quenching. If the encounter complex between singlet oxygen and the heavy atom is assumed to form at a diffusion-controlled rate in the phenyl methyl chalcogenide series of Corey and Kahn,[7] then rates of intersystem crossing should be both rate limiting for the electronic quenching of singlet oxygen with these molecules (up to the limit of diffusion control) and identical to the rate constants for intersystem crossing. Values of the quenching constant, k_Q, for this series are 1.3×10^5 M^{-1} s^{-1} for $PhCH_2CH_3$, 2.0×10^5 M^{-1} s^{-1} for $PhOCH_3$, 7.1×10^6 M^{-1} s^{-1} for $PhSCH_3$, 1.4×10^8 M^{-1} s^{-1} for $PhSeCH_3$, 3.8×10^9 M^{-1} s^{-1} for $PhTeCH_3$, and 7.26×10^9 M^{-1} s^{-1} for $(PhCH_2)_2Te$.[7]

For the chalcogenapyrylium dyes 1, values of the rate constants for intersystem crossing, k_{isc}, have been calculated from other photophysical properites of these dyes and are compiled in Table I.[9] Spin–orbit coupling of the heavy atoms with the excited electron is the primary contributor to increased rates of intersystem crossing with increasing chalcogen atomic number in these dyes.[9]

The heavy-atom contributions to both k_Q and k_{isc} should be similar in diorganochalcogenide systems described here. However, as shown in Figure 3, the points defined by log k_Q and the points defined by log k_{isc} are on the same curve as functions of log Z^4.[12,13]

The agreement in k_Q and k_{isc} as functions of Z^4 suggests that the rate of intersystem crossing is the dominant factor and that electron-transfer quenching is of minimal importance in the observed rates of singlet oxygen quenching with the phenyl methyl chalcogenides. Electron transfer may play a role in the formation of the encounter complex, but singlet oxygen quenching via electron transfer is slow relative to quenching via intersystem crossing in these organometallic compounds.[14]

Experimental Section

UV–visible–near-infrared spectra and spectroscopic kinetic runs were recorded on a Perkin-Elmer Lambda 9 spectrophotometer equipped with constant-temperature cell holders. Dyes 1 were prepared as described in ref 9.

Determination of Second-Order Rate Constants for the Oxidative Addition of Hydrogen Peroxide to Dyes 1. Stock solutions of hydrogen peroxide at 1.0, 0.10, and 0.010 M were prepared in water by serial 10-fold dilution of 30% hydrogen peroxide. Stock solutions of dyes 1 at $\sim 1.0 \times 10^{-3}$ M in methanol were prepared. A 0.030-mL aliquot of the dye solution was added to 3.00 mL of the 1.0 M peroxide solution for dyes **1a**, **1c**, and **1d**, to 3.00 mL of the 0.10 M peroxide solution for dye **1b**, and to 3.00 mL of the 0.010 M peroxide solution for dyes **1e** and **1g**. The decrease in absorbance of the dye was monitored as a function of time. The pseudo-first-order rate constants obtained (between $\sim 10^{-4}$ and 2×10^{-2} s^{-1}) were divided by hydrogen peroxide concentration to give the apparent second-order rate constants. Values given in Table I are the average of duplicate runs.

Registry No. **1a**, 133433-91-7; **1b**, 126876-68-4; **1c**, 126876-70-8; **1d**, 126876-74-2; **1e**, 124620-16-2; **1f**, 141089-57-8; **1g**, 126876-77-5; O, 17778-80-2; H_2O_2, 7722-84-1.

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[12] In the dyes 1, log Z^4 is defined as log $(Z_X{}^4 + Z_Y{}^4)$ where Z_X and Z_Y are the atomic numbers of the chalcogen atoms X and Y in structures 1. For the exponential curve shown, $y = 2.9464e^{0.1731x}$, where $R^2 = 0.978$.

[13] One reviewer of this paper noted that a similar correlation with ionization potential rather than Z^4 would be observed. Although values of ionization potential (IP) for the cationic dyes 1 are not available, gas-phase ionization potentials for the dimethyl chalcogenides decrease with Z^4 with Me_2O (10.04 eV) > Me_2S (8.71 eV) > Me_2Se (8.40 eV) > Me_2Te (7.89 eV),[7] suggesting an inverted correlation of k_Q and k_{isc} with IP. However, a nonnucleophilic series of related compounds [with ionization potentials similar to the dimethyl chalcogenides relative to Z^4 (PhF, PhCl, PhBr, PhI)] shows similar values of k_Q (approximately 10^5 M^{-1} s^{-1})[7] for the entire range of Z^4, indicating that IP, alone, does not adequately describe the behavior of these compounds.

[14] The contribution of electron-transfer quenching to k_Q would be expected to be small in organic solvents where the reduction potential of $^3O_2$ is approximately −0.80 V (vs SCE). With $^1O_2$ approximately 1 eV higher in energy than $^3O_2$, exothermic electron transfer would require oxidation potentials for the quenchers to be more negative than +0.2 V (vs SCE), which are not observed for the compounds described in this report.