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HEAVY ATOM QUENCHING OF THE SINGLET DELTA DIOXYGEN MOLECULE ($^1\Delta g\ O_2$)

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Summary: Evidence is provided from quenching experiments that heavy atom spin-orbit coupling and donor-acceptor interactions can both contribute to deactivation of $^1\Delta g\ O_2$, and that heavy atom quenching is ineffective for poor electron donors.

Three distinct mechanisms have been demonstrated experimentally for the quenching of singlet delta dioxygen molecules ($^1\Delta g\ O_2$) in solution: (1) electronic energy transfer from singlet oxygen to nearly isoenergetic vibrational overtones of the solvent molecules, e.g. C-H and O-H bonds;[1-3] (2) electronic energy transfer from singlet oxygen to a lower lying electronic state of a quencher molecule, e.g. quenching by β-carotene;[4] and (3) charge transfer or reversible coordination between singlet oxygen and the quencher, e.g. 1,4-diazabicyclo[2.2.2]octane (DABCO) quenching.[5] As expected, charge transfer interaction correlates well with the ionization potential of the quencher, observed in both solution[6] and gas phase studies.[7] This paper provides evidence for a different quenching process which derives from a combination of two physical effects, heavy-atom induced electron spin-orbit coupling and donor-acceptor type interaction. A previous publication from this laboratory demonstrated that antiarthritic gold (I) compounds of the type $RSAuPEt_3$, exemplified by the commercial antiinflammatory agent Auranofin, are highly effective inactivators of $^1\Delta g\ O_2$ (quenching constants on the order of $10^7\ M^{-1}\ sec^{-1}$).[8] It was proposed that such quenching could result from heavy atom-promoted intersystem crossing by spin-orbit coupling which ought to be significant for gold ($Z = 79$) since the efficiency of this process increases as Z^4. In addition, a donor acceptor interaction between Au(I) and $^1\Delta g\ O_2$ involving *d* orbitals of the former and π-orbitals of the latter could further enhance the rate of quenching. From this line of analysis it was reasoned that organotellurium compounds such as R_1TeR_2 ($Z = 52$ for Te) ought to function as effective quenchers for $^1\Delta g\ O_2$ and ought to be more efficient than the comparably nucleophilic selenium, sulfur or oxygen analogs. The series $PhTeCH_3$, $PhSeCH_3$, $PhSCH_3$, $PhOCH_3$, and $PhCH_2CH_3$ was therefore selected for study (Series I). Rate constants for the quenching of $^1\Delta g\ O_2$ by the members of the Series I ($PhXCH_3$) were determined by generating $^1\Delta g\ O_2$ from 1,4-dimethylnaphthalene-1,4-endoperoxide through spontaneous decomposition at 23°C in CCl_4 solution and measuring the steady state concentration of $^1\Delta g\ O_2$ from the emission $O_2(^1\Delta g) \rightarrow O_2(^3\Sigma g)$ at

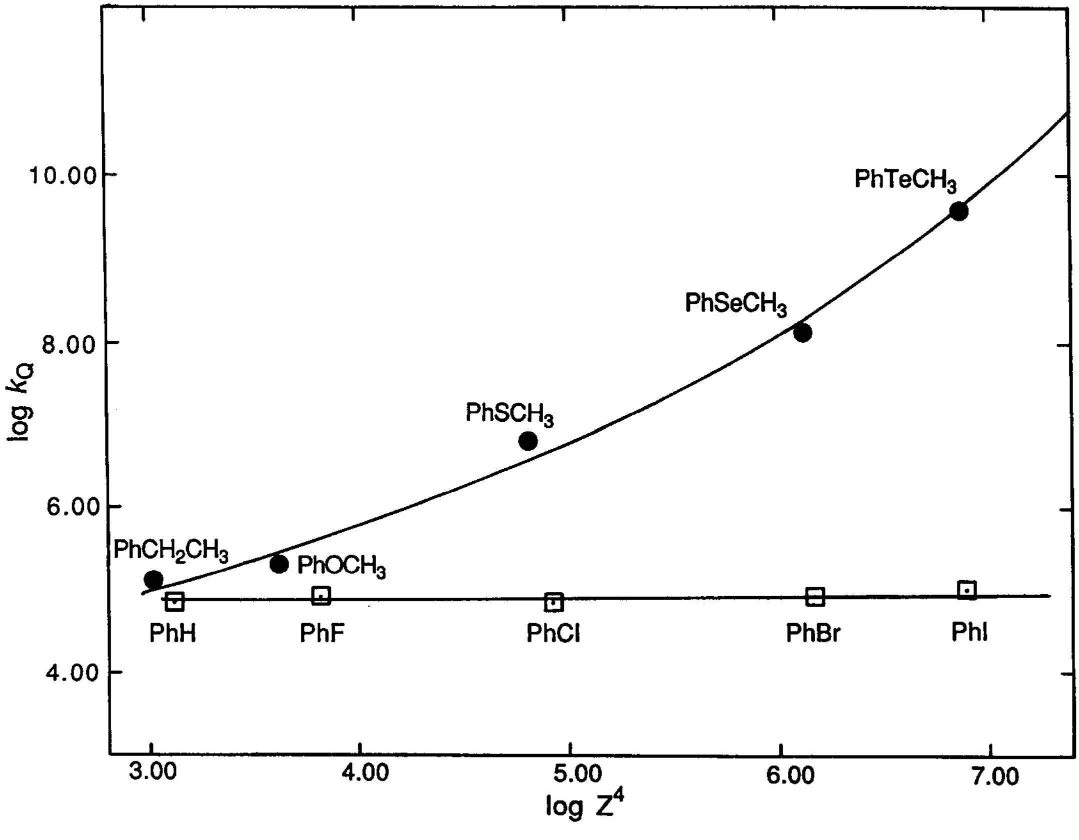
1268 nm as a function of quencher concentration, [Q]. A typical experiment consisted of adding 100 μl of an ice-cold CCl_4 solution of 1,4-dimethylnaphthalene-1,4-endoperoxide to 10 ml of CCl_4 in an optical cell at 23°C, to give final concentration of the endoperoxide of approximately 10^{-5} *M*. The optical cell was located at the slit of an ultrasensitive near IR spectrometer, described in detail elsewhere.[9] The endoperoxide dissociates at 23°C to $^1\Delta g\ O_2$ with a half life of *ca.* 30 h.[10,11] The duration of the quenching experiments was approximately 1000 sec. After the 1268 nm emission attained a steady value, I_0, 100 μl of solution of the quencher in CCl_4 at 23°C was added to the solution in the optical cell, reducing the emission to a new steady state value, I_Q. In total four 100 μl aliquots of quencher solution was added to the solution of endoperoxide. The quenching constant, k_Q, was evaluated from the Stern-Volmer equation[12] $I_0/I_Q = 1 + (k_Q/k_{Sol})[Q]$, where the value of $k_{Sol} = 1.7 \times 10^3$, an average value for CCl_4 determined by Wilkinson and Brummer.[13] The measured quenching constants for the compounds of Series I and also for β-carotene as reference were as follows:

Quencher	k_Q $(M^{-1}\ \text{sec}^{-1})$
β-carotene	1.0×10^{10}
$PhTeCH_3$	3.8×10^9
$PhSeCH_3$	1.4×10^8
$PhSCH_3$	7.1×10^6
$PhOCH_3$	2.0×10^5
$PhCH_2CH_3$	1.3×10^5

β-Carotene was included in this study because it is the most efficient quencher known for singlet oxygen, the rate of quenching being essentially diffusion controlled.[4,14] It is evident from our data that $PhTeCH_3$ is also an excellent quencher and that quenching efficiency does fall off with atomic number in Series I. The plot of log Z^4 vs log k_Q for Series I which is shown in Figure 1 indicates that the heavy atom Z^4 effect may significantly enhance the rate of quenching. Another determinant of quenching, electron availability at the heavy atom, is likely also to be involved, since such electron availability decreases in the order Te > Se > S > O, as indicated by ionization potentials, which are as follows (in ev): Me_2Te, 7.89; Me_2Se, 8.40; Me_2S, 8.71; Me_2O, 10.04.[15,16] In order to ascertain whether heavy atom quenching is effective for compounds in which the heavy atom is essentially non-nucleophilic another set of related compounds PhH, PhF, PhCl, PhBr and PhI (Series II) were investigated as quenchers of $^1\Delta g\ O_2$. All of the compounds of Series II showed similar quenching ability, $k_Q \cong 10^5\ M^{-1}\ \text{sec}^{-1}$; see also Figure 1. The lack of heavy atom quenching for iodo- and bromobenzene is an indication that the basicity of the halogen substituent is probably too low to allow an effective donor-acceptor interaction between $^1\Delta g\ O_2$ and the aryl halide.[17]

As expected, other nucleophilic organotellurium compounds are good quenchers of $^1\Delta g\ O_2$. The quenching constants measured in CCl_4 solution for three members of the series PhXXPh are as follows: PhTeTePh, 1.1×10^8; PhSeSePh, 1.2×10^6; PhSSPh, $3.0 \times 10^5\ M^{-1}\ sec^{-1}$. The value of k_Q found for the nonconjugated telluride $PhCH_2TeCH_2Ph$ was $7.26 \times 10^9\ M^{-1}\ sec^{-1}$, almost diffusion controlled.[18]

Amines of approximately the same ionization potential (IP) as RTeR derivatives are less effective as quenchers of $^1\Delta g\ O_2$.[21] For example trimethylamine, for which IP = 7.82 ev and $k_Q \cong 10^7$ (in CCl_4), is *ca.* 10^2 slower as a quencher than the organotellurides of similar donor ability. The difference in quenching efficiency can reasonably be ascribed to a heavy atom effect. Thus, the fast quenching rates for RTeR derivatives can be viewed as the result of the concurrent operation of charge transfer and heavy atom quenching mechanisms. On the other hand, the heavy atom effect alone clearly does not produce enhanced quenching in the absence of any intermolecular charge-transfer interaction, as indicated by the results in the aryl halide series.[22]



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