teristic of those observed in powder spectra for axially symmetric hyperfine tensors. From the clearly separated parallel and perpendicular features corresponding to the outermost (±3, 3) components, corrected values of $A_{\parallel}$ = 143.3 G and $A_{\perp}$ = 130.3 G were calculated. The derived isotropic coupling, a_F = 135 G, is in satisfactory agreement with the value of 137 G obtained directly from the completely isotropic spectrum of $C_6F_6^-$ in the adamantane matrix at 218 K.[19]

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The Role of the Excited Singlet State of Dyes in Dye Sensitized Photooxygenation Reactions

Sir:

The role of the triplet state of dyes in dye sensitized photooxygenation reactions has been the subject of much discussion.[1] There is now no doubt that in many oxygenation reactions the triplet dye acts as a source of energy for the formation of the highly reactive species, singlet oxygen ($^1\Delta_gO_2$). In other oxygenation reactions, the triplet dye has been shown to react with a substrate to generate radicals which subsequently react with oxygen to give oxidation products derived from the substrate. In very few instances has the role of the excited singlet state of the dye been discussed apart from its relevance to the process of intersystem crossing.

Examination of the excited singlet states of common sensitizing dyes such as rose bengal and methylene blue is facilitated by the fact that these dyes fluoresce. Thus, substrate-singlet dye interactions can be quantitatively assessed by measuring the effectiveness of quenching the dye fluorescence by the substrate. We have previously shown that triethylamine quenches the excited singlet state of rose bengal.[2]As can be seen from Table I, many other amines quench the fluorescence of the dyes. In accordance with the view that the quenching occurs via a charge-transfer process, i.e.,

$$\text{Dye}_{S_1} + \text{Am} \rightarrow \text{Dye}\cdot^- + \text{Am}\cdot^+$$

where Am = amine, the lower the ionization potential of the amine, the more effective a quencher it becomes. Another feature of the quenching process is that its efficiency is solvent dependent (see Table II). However, until singlet lifetimes for rose bengal in a variety of solvents have been determined, the solvent dependency of the K_{SV} values cannot be analyzed. However, the K_{SV} values do show how the part played by the excited singlet state of the dyes in the sensitized oxidation of amines is very dependent upon the solvent which is employed.

The K_{SV} values determined for aliphatic amines such as DABCO show that the quenching of the excited singlet state of the dye is important when high concentrations of amines are used (>5 × 10^{-2} M). It is therefore most important that this fact be borne in mind when amines are being used to test for the participation of singlet oxygen in oxygenation reactions. In order to be certain that the retardation of an oxygenation reaction is not due to any quenching of the excited singlet state of the dye, the amine concentration should be kept below 5 × 10^{-3} M. Another hazard of using high amine concentrations is that the triplet state of the dye may be appreciably quenched.

Aromatic amines such as *N,N*-dimethylaniline are remarkably efficient quenchers of the fluorescence of the dyes. It is therefore not surprising that indoles are also very efficient quenchers (see Table I). Thus any photooxidation of indoles carried out at >10^{-3} M substrate concentration will involve the excited singlet state of the dye and makes attempts to relate observed products to particular reactive intermediates a precarious business.[4] A further consequence of the quenching process is that the rate of photooxidation of indoles does not markedly increase with increase in indole concentration. In those cases where the dyes become adsorbed to a substrate (e.g., a protein) the quenching process will become very important if a tryptophyl residue is near the site of adsorption.

Table I. Stern–Volmer Constants[a] for Quenching of the Fluorescence of Rose Bengal and Methylene Blue

Substrate	K_{SV} (M) Rose bengal[b]	 Methylene blue[b]
N,N-Dimethylaniline	32.5[c]	20.6[c]
Tribenzylamine		5.0[c]
1,4-Diazabicyclo[2.2.2]octane	6[c]	2.6[c]
Triethylamine	1.1[c]	1.0[c]
3-Methylindole	23.0[c]	24.0[c]
Tryptamine	23.0[c]	17.0[c]
Sodium iodide	2.0[d]	14.6,[d] 15.4[e]
Sodium bromide	0.1[d]	0.8[e]
Sodium chloride		0.2[e]
Sodium azide	0.6[d]	3.6[e]
Sodium thiosulfate		3.1[e]
2,5-Diphenylisobenzofuran		57[c]
β-Carotene		57[f]

[a] Calculated from $\phi_0/\phi = 1 + K_{SV}[Q]$ where ϕ_0 = quantum yield of fluorescence in absence of quencher, ϕ = quantum yield of fluorescence when quencher present at concentration [Q], and $K_{SV} = k_q\tau$ where k_q = bimolecular quenching rate constant and τ = fluorescence lifetime of the dye. In all cases aerated solutions were used. Maximum error in K_{SV} is estimated at ±10%. [b] Optical density of dyes = 0.1 at λ_{excit}. [c] Methanol. [d] Methanol/water (50:50 V/V). [e] Methanol/water (20:80 V/V). [f] Methanol-benzene (20:80 V/V), corrections applied for absorption by *β*-carotene at λ_{excit} and λ_{emis} of dye.

Table II. Stern–Volmer Constants for the Quenching of Rose Bengal Fluorescence by Triethylamine in Various Solvents

Solvent	K_{SV} (M)	Solvent	K_{SV} (M)
Methanol	1.1	Acetone	0.4
Methanol-water	1.3	Acetonitrile	~1.5[b]
Water	4–5[a,b]	Ethanol	1.5
Pyridine	0.25		

[a] Minimum amount of methanol added to aid solubility (~1%). [b] Some curvature was observed in the Stern–Volmer plot.

The quenching of the excited singlet states of dyes by anions[5] is particularly relevant to the report[6] by Fenical, Kearns, and Radlick, that addition of azides to photooxygenation reactions of olefins leads to azido–hydroperoxide formation. The azide ion is a powerful quencher of the excited singlet state of methylene blue and, at an azide concentration of 1.0 M, quenching is ~78% efficient. Electron transfer from the anion to the excited dye will produce azide radicals which can subsequently react with the olefin in the presence of oxygen to give the observed products. Gollnick has previously demonstrated the feasibility of the radical anion.[7] The azide ion has also been shown[8] to be a quencher of singlet oxygen. If therefore it is to be used for testing for the intermediacy of singlet oxygen by adding varying amounts of the anion to a reaction, its concentration must be kept relatively low.

Azide ions, like halogen anions quench the fluorescence of rose bengal far less efficiently than methylene blue fluorescence. This lower quenching efficiency can be attributed to the fact that the dye molecule is an anion and consequently the quenching process requires the close approach of two anions, i.e., the development of an unfavorable Coulombic interaction.

The excited singlet state of methylene blue is efficiently quenched by *β*-carotene and 2,5-diphenylisobenzofuran. *β*-Carotene, like DABCO, has been proposed as being a suitable quencher for use in a diagnostic test for the participation of singlet oxygen in oxygenation reactions.[3b] The high K_{SV} value indicates that the β-carotene concentration should be kept 10^{-3} M in order to avoid quenching the excited singlet state of the dye. However, in practice, it is necessary to employ much lower concentrations ($\sim 10^{-5}$ M) since the carotene is also a very efficient quencher of the triplet states of dyes.[9]

Although the K_{SV} value for quenching by the isobenzofuran is high, it is unlikely that the quenching process interferes with the methods recently described[10] for the determination of absolute rate constants for reaction of compounds with singlet oxygen.

The described results show that care has to be taken in using amines and β-carotenes in tests for participation of singlet oxygen in dye sensitized oxygenation reactions. Furthermore the use of high substrate concentrations make it impossible to draw any conclusions about the participation of singlet oxygen from product studies.

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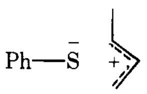
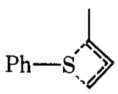
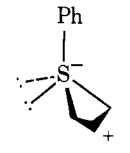
Assessment of the Thioallylic Rearrangement by a Simplified Technique for High-Precision Measurement of Isotope Effects

Sir:

The thermal thioallylic rearrangement has received extensive study in these laboratories. The results involving correlations of rate with solvent and substituent effects[1] indicate that the sulfur seat of reaction in the transition state has experienced a considerable increase in electron density. Three transition state structures, modeled after the intermediate configurations **1**, **2**, and **3** (below), could be considered on the basis of these data pertaining to the rearrangement of α-methylallyl to crotyl phenyl sulfide.[1b]


dissociative
(ion-pair)
1


concerted (bond
making-breaking)
2


associative
(triagonal-bipyramid
or tetragonal pyramid)
3

A basis for distinction between the models could be found in the heavy atom isotope effect[2] which has been previously applied to sulfur for identifying dissociative mechanisms.[3-5] An example of an associative mechanism has also been discussed where increased bonding has created an electron deficient sulfur in the transition state.[6] Instances of octet expansion and the development of an additional bond to sulfur in the transition state have not been investigated previously by means of the heavy atom isotope effect. However, the same principles should apply, i.e., any change in the ratio of naturally occurring isotope fractionation from reactant ($^{34}S_0/^{32}S_0$) to product ($^{34}S_t/^{32}S_t$) should give a measure of the difference in rates at which the two reacted. The experimental extent of fractionation at any time, t, could therefore be calculated.

In order to interpret the experimental results, theoretical isotope effects corresponding to each of the proposed transition state models were calculated on the basis of the Bigeleisen–Mayer equation[2] describing the relative rates of reaction of molecules containing light (L) and heavy (H) isotopes:

$$k_L/k_H = \left(\frac{m_H^*}{m_L^*}\right)^{1/2} \times \left[1 + \sum_{i}^{3n-6} G(\mu_i)\Delta\mu_i - \sum_{i}^{3n'-6} G(\mu_i)^{\dagger}\Delta\mu_i^{\dagger}\right]$$

The temperature-independent term, $m_H^*/m_L^{*1/2}$, was estimated to be 1.008 on the basis of Slater's model[7] which describes the breaking of an isolated bond in a large molecule in terms of an imaginary diatomic bond rupture. With regard to the temperature-dependent terms (within the large bracket). the simplifying assumption made is that only those stretching frequencies of bonds to the central isotopic species that will be made or broken in the transition state need be considered. In this case, the C–S–C stretch in the Raman is found at 711 cm^{-1}. On these grounds, the values (k_{32}/k_{34}) calculated for each of the models are: **1**, 1.012; **2**, 1.008; **3**, 1.004. Clearly, if distinctions between the alternative transition states are to be drawn on the basis of measurements of these sulfur isotope effects, experimental precision of a very high order is required. This has now been realized through application of a new approach[8,9] developed independently in these laboratories to accommodate this requirement through use of a computer controlled mass spectrometer.

In the past, most isotope ratio measurements were made on gaseous degradation products of a parent molecule[10,11] using a magnetic deflection double-detector mass spectrometer.[6,12,13] Recently several authors[8,9] have demonstrated that computer techniques can be employed to improve the performance of nonspecialized instruments. Our approach to this problem was to take advantage of available instrumentation (Hewlett-Packard 5930A mass spectrometer and 5932 data system) and, through appropriate software modification, attempt to simulate the high precision of the double detector system while avoiding the requirement for low molecular weight gas samples. Our instrument was a modified quadrupole (duodecapole) mass analyzer system. Data of the highest precision was realized by maintaining the ionization potential (70 eV), emission current (0.3 mA), mass filter temperature (90 °C), and ion source temperature (150 °C) at the specified levels throughout the course of the work. The ion source tuning parameters (repeller, draw-out, ion focus, etc.), which are known to be invariant over an 8-h period, were adjusted for maximum sensitivity with minimum noise in the region of the spectral pattern of interest for each compound measured. The inlet system of choice was a stainless steel, direct introduction probe fitted with a stainless steel metering valve and glass sample container. This system provided constant ($\Delta P < 0.1 \times 10^{-6}$