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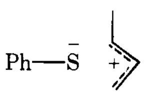
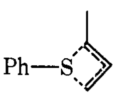
Assessment of the Thioallylic Rearrangement by a Simplified Technique for High-Precision Measurement of Isotope Effects

Sir:

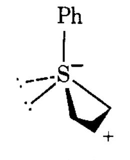
The thermal thioallylic rearrangement has received extensive study in these laboratories. The results involving correlations of rate with solvent and substituent effects[1] indicate that the sulfur seat of reaction in the transition state has experienced a considerable increase in electron density. Three 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 ($\Delta P < 0.1 \times 10^{-6}$

Table I. Precision of Measurements for Various Ions as a Function of the Magnitude of the Isotope Ratio

Compound	Ions monitored	Abundance of 2d as % of 1st ± 1σ	1σ/abundance × 100 = % precision
α-Methylallyl phenyl sulfide	164, 166	5.173 ± 0.009	0.18[a]
1,1,2-Trichloroethane	132, 134	93.82 ± 0.07	0.08[b]
	134, 136	31.80 ± 0.03	0.10[b]
	132, 130	5.483 ± 0.012	0.22[b]
Benzyl acetate	150, 152	1.014 ± 0.004	0.35[b]

[a] Based on 60 000 determinations of the isotope ratio. [b] Based on 10 000 determinations of the isotope ratio.

Torr/h) and reproducible source pressures (2×10^{-6} Torr).

The actual data acquisition was controlled by the computer using specially developed software. The objective was to sample the voltages corresponding to the parent and isotope peaks sufficiently close together in time to approximate simultaneous detection and to sample frequently enough to average out short term fluctuations in the electron beam or ion current. This was achieved by a technique of real time data collection in which the computer positioned the mass filter at the top of each peak and sampled the voltage of the ions in the order mass I, mass II, mass II, mass I. The voltages were summed, periodically verified against a set of threshhold conditions and stored for later retrieval and analysis. Following this procedure it is possible to make approximately 60 readings at each mass per second or 10 000–60 000 determinations of the isotope ratio in less than 20 min. This rate of data acquisition was limited only by the time required for equilibration of the detector when changing to a new mass setting. For a jump between two masses differing by 2 amu, the dead time was ~3 ms.

These data were evaluated off-line by means of a standard error analysis and a statistical treatment presented. A representative selection of isotope ratios for several compounds studied is presented in Table I. In general, statistics from individual runs and groups of determinations on a given day indicate a remarkable degree of instrument stability. This precision is characterized by a standard deviation (σ) of less than 0.2% for most measurements. It is only where the intensities of the ions being compared were greatly different from each other that the degree of precision deteriorates. Still, this precision is somewhat better than that found by Caprioli et al.[8] and far superior to that of Schoeller and Hayes.[9]

The question of accuracy, in the sense of absolute isotope ratio measurements, presented a problem for two reasons, isotope fractionation occurring during sample preparation, and mass discrimination resulting from the dependence of the quadrupole system's performance on tuning parameters (repeller voltage). For the α-methylallyl phenyl sulfide study, the difficulty was obviated by always referencing the ratio to that found in the starting material i.e.,

$$\text{fractionation} = \frac{{}^{34}S_0/{}^{32}S_0}{{}^{34}S_t/{}^{32}S_t}$$

Because the parent ion was used in the determinations, the isotope peak (p + 2) had to be corrected for ^{13}C and ^{2}H contributions. The data in Table II take this correction into account.

In this way, an average sulfur isotope effect of 1.0040 ± 0.0016 at 198° was calculated from the experimental fractionation and equilibrium data. When compared with the theoretical evaluation, the findings indicate a transition state of an associative nature (model 3) in which a clear increase in bonding is experienced by the sulfur seat of reaction. Moreover, the inverse equilibrium isotope effect of $K_{32}/K_{32} = 0.9956$, which has been determined, corresponds to a zero point energy difference of 4 cal/mol at 198°.

Table II. Variation of the Kinetic Isotope Effect with Approach to Equilibrium Composition of the Thioallylic Rearrangement

t (min)	% reaction	$^{34}S_0/^{32}S_0/^{34}S_t/^{32}S_t \pm 1\sigma)$[a]
12.6	2.5	1.0041 ± 0.0027
25.5	5.0	1.0049 ± 0.0022
52.4	10.0	1.0036 ± 0.0025
80.9	15.0	1.0011 ± 0.0031
$\infty = (10t_{1/2})$[b]	equilibrium	0.99 ± 0.0027
$\infty = (20t_{1/2})$[b]	equilibrium	0.9959 ± 0.0024

[a] The value of 1.0040 ± 0.0016 is calculated for each % reaction listed when correcting for the inverse equilibrium isotope effect measured, $K_{32}/K_{34} = 0.9956$. [b] $t_{1/2}$ = a half life of reaction.

These findings are offered to demonstrate a simple, new technique the availability of which could permit widespread application of the heavy atom isotope criterion of reaction mechanism. With the precision now realizable through use of the method described herein, it should be generally possible for one, previously deterred by instrumental limitations, to subject mechanistic proposals to the most searching "substituent effect" test for an unequivocal answer, namely, the kinetic isotope effect criterion. This applies particularly to reaction centers lighter than sulfur where the kinetic effects are much larger. Elaboration of this approach, presently under development in our laboratories, gives promise of improvements in the precision of measurement almost by another order of magnitude. This should make possible applications to reaction centers even heavier than sulfur.

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A New Diisocyanide of Novel Ring Structure from a Sponge

Sir:

Recent reports of the occurrence of sesquiterpene[1-5] and diterpene isocyanides[4] from sponges prompt us to report the structure of a diisocyanide obtained from a sponge of the genus *Adocia* collected near Townsville, Australia, on the Great Barrier Reef.

Concentration of the combined cold petroleum ether extracts of the milled freeze-dried sponge gave 2% of a crystalline