Table I. Selected Structural Parameters in the $MoS_9{}^{2-}$-Dianion

	Bond Lengths, Å		
Mo–S_1	2.128 (1)	S_2–S_3	2.166 (1)
Mo–S_2	2.331 (1)	S_3–S_4	2.012 (1)
Mo–S_5	2.387 (1)	S_4–S_5	2.107 (1)
Mo–S_3	3.735 (1)	S_2–S_5	3.345 (1)
Mo–S_4	3.535 (1)	S_2'–S_5	2.984 (1)
	Bond Angle, deg		
S_2–Mo–S_5	90.32 (3)	Mo–S_2–S_3	112.28 (3)
S_2'–Mo–S_5	78.45 (3)	Mo–S_5–S_4	103.59 (3)
S_1–Mo–S_2	110.83 (3)	S_2–S_3–S_4	100.17 (4)
S_1–Mo–S_5	105.88 (3)	S_3–S_4–S_5	101.83 (5)
S_2–S_3–S_4/S_3–S_4–S_5 dihedral angle = 50.48 (6)			

sorption at 316 nm (ϵ 15 750) and shoulders at 470, 405, and 340 nm. The Mo=S stretching vibration in the IR spectrum obtained in a KBr pellet occurs at 525 cm^{-1}.

Single crystals of I can be obtained by the slow diffusion of diethyl ether into a DMF solution of I.[7] X-ray diffraction data on a single crystal of I were collected on a Picker-Nuclear FACS-I automatic diffractometer using the θ–2θ scan technique and employing graphite monochromatized Mo Kα radiation (λ = 0.7107 Å, $2\theta_m$ = 12.2°). The data (full sphere to 2θ = 50°) corrected for Lorentz, polarization, and absorption effects were used for the solution of the structure by conventional, Patterson, direct methods, and Fourier techniques. Refinement was carried out by full-matrix least-squares methods. All hydrogen atoms were included at their calculated positions (C–H = 0.95 Å) but were not refined. Refinement on 145 parameters on 2146 data [$F_o^2 \geq 3\sigma(F_o^2)$] has converged to a conventional R factor of 0.025. All anisotropic temperature factors are normal and show no evidence for disorder or highly anisotropic thermal motions.

The structure of the anion in I (Figure 1) shows the $Mo{=}S^{2+}$ unit coordinated by two $S_4{}^{2-}$ bidentate chelates. In the distorted square-pyramidal MoS_5 unit, the molybdenum atom is displaced from the basal plane of its square-pyramid toward S_1 by 0.73 Å. The $MoS_9{}^{2-}$ anion[8] is situated on a crystallographic twofold axis (at 0, $^1/_4$, z) that contains the Mo=S unit. The Mo=S distance at 2.128 (1) Å is near the upper end of the range for doubly bonded Mo–S distances[9] (1.937–2.129 Å). The "basal" Mo–S_5 and Mo–S_2 distances at 2.387 (1) and 2.331 (1) Å differ significantly from each other. At this time we do not have a satisfactory explanation for this difference;[10] however, a similar difference in chemically equivalent Mo–S bond lengths has been reported[11] for the anti form of $Mo_2S_4(S_2C_2H_4)_2{}^{2-}$ with Mo–S bridge bonds of 2.298 (3) and 2.344 (3) Å. The mean value of the basal Mo–S bonds in I, 2.36 (3) Å, is considerably shorter than the corresponding value reported for the oxobis(di-*n*-propyldithiocarbamato)molybdenum(IV) complex [2.413 (3) Å].[12]

The tetrasulfide ligand in I shows an interesting alternation in the lengths of the S–S bonds (Table I). Thus the two "terminal" S–S bonds (S_2–S_3, S_4–S_5) of 2.166 (1) and 2.107 (1) Å, respectively, are significantly longer than the $\overline{\text{S–S}}$ bond in orthorhombic sulfur[13] [2.037 (5) Å]. The S_3–S_4 "central" bond in I is significantly shorter than any of the above values at 2.012 (1) Å. This alternation in the S–S bond lengths is not observed for the $S_4{}^{2-}$ dianion in the structure[14] of $BaS_4{\cdot}H_2O$ ($\overline{\text{S–S}}$ = 2.069 (2) Å).

An alternation in the S–S bond lengths has also been observed for the $S_4{}^{2-}$ ligand in the structure of the $(C_5H_5)_2MoS_4$ complex[15] and has been rationalized as a result of significant $Mo(d_\pi)$–$S(d_\pi)$ interactions. The rather short Mo(IV)–S bond lengths in I and the alternation in the S–S bond lengths within the $S_4{}^{2-}$ ligands could be rationalized in terms of a similar argument involving $Mo(d_\pi)$–$S(d_\pi)$ and $S(d_\pi)$–$S(d_\pi)$ interactions.[16]

In dimethyl sulfoxide solution, I is diamagnetic, as expected for a five-coordinate Mo(IV) complex with a $d_{xy}{}^2$ ground state in a pseudo C_{4v} geometry. Preliminary studies on the chemical reactivity of I indicate that the $MoS_9{}^{2-}$ anion is a rather reactive species. Upon refluxing in air, CH_3CN or DMF solutions of I slowly develop a green color. Golden green crystals of $(Et_4N)_2MoOS_8$ (II) can be isolated from these solutions following addition of ether to incipient crystallization and standing. Anal. Calcd for $MoS_8OC_{16}H_{40}N_2$ (M_r 629.1): C, 30.57; H, 6.37; N, 4.46. Found: C, 30.35; H, 6.46; N, 4.37.

The X-ray powder patterns of I and II are identical, and the infrared spectrum of II obtained in a KBr pellet shows a strong band at 930 cm^{-1} and no absorption at 525 cm^{-1}. We assign the 930-cm^{-1} absorption in II to the $Mo{=}O_t$ stretching vibration in a $(S_4)_2MoO^{2-}$ anion, isostructural to $(S_4)_2MoS^{2-}$.

The formation of the $MoS_9{}^{2-}$ anion from $MoS_4{}^{2-}$ under apparently oxidizing conditions is intriguing. At present we can only speculate that the $S_4{}^{2-}$ chelating ligands and the Mo(IV) ion in I have been obtained as a result of intramolecular electron transfer in a $S_2Mo^{VI}(S_2)_2{}^{2-}$ unit. Such a unit could have been formed following S^0 addition to the $MoS_4{}^{2-}$ anion.

The $(S_4)_2MoO^{2-}$ dianion appears to be a suitable model for dithionite-reduced sulfite oxidase. Both the oxidation state and the nature of the ligands encompassing the molybdenum agree with the EXAFS studies.[17] The apparent coordination unsaturation of the complex may allow for the interaction of a sixth ligand with the molybdenum atom. The molecular structure, redox properties, and reaction chemistry of this very interesting molecule are at present under study.

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Supplementary Material Available: Observed structure factors for $(Et_4N)_2MoS_9$ and a table of atomic parameters (10 pages). Ordering information is given on any current masthead page.

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[7] Crystal data for $(Et_4N)_2MoS_9$: cell dimensions, a = 15.594 (3), b = 13.264 (4), c = 27.577 (5); space group *Ibca*; Z = 8; d_{calcd} = 1.502 g cm^{-3}; d_{obsd} = 1.49 (2) g cm^{-1}; μ = 10.89 cm^{-1}.

[8] The two tetraethylammonium cations lie on crystallographic twofold axes at x, 0, $^1/_4$ and 0, $^1/_4$, z. The four independent C–N bond lengths span the range from 1.515 (3) to 1.520 (3) Å with a mean value of 1.517 (2) Å. Similarly the four independent C–C bonds are in the range between 1.502 (4) and 1.511 (4) Å with a mean value of 1.507 (4) Å.

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[10] Essentially the same differences in Mo–S and S–S bond lengths were found at the end of the isotropic refinement of the structure. Refinement on 718 data ($2\theta_{max}$ = 35°) conveyed to a conventional R value of 0.076. All of the isotropic temperature factors at this stage were small, in the range of 2.6–5.0 $Å^2$. The Mo–S_2 and Mo–S_5 bond lengths were 2.338 (5) and 2.382 (5) Å, respectively. The S_2–S_3, S_4–S_5, and S_3–S_4 bond lengths were 2.162 (8), 2.100 (7), and 2.021 (7) Å, respectively.

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Chemistry of Singlet Oxygen. 34. Unexpected Solvent Deuterium Isotope Effects on the Lifetime of Singlet Molecular Oxygen ($^1\Delta_g$)

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In recent years it has become increasingly evident that the lifetime of singlet molecular oxygen ($^1\Delta_g$) is solvent dependent.[1-3]

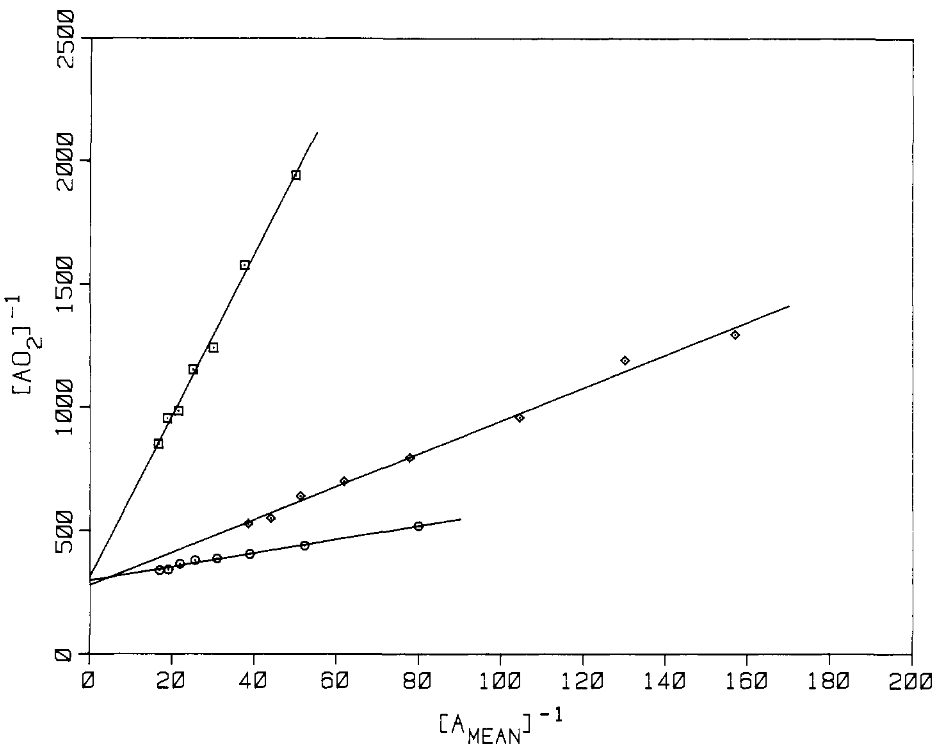

Figure 1. Rose bengal sensitized photooxygenation of 1-methylcyclohexene in acetone-d_6 (○), a mixture of acetone-d_6 and -h_6 (◇), and acetone-h_6 (□).

It has been shown that the lifetime may differ by a factor of several hundred in spanning the range of common organic solvents. In addition, solvent deuterium isotope effects have been reported by several investigators.[1,2] Recent results in our laboratories[4,5] prompted us to reinvestigate the effect of solvent deuteration on the lifetime of singlet molecular oxygen. We report dramatic solvent deuterium isotope effects for acetone, acetonitrile, benzene, and chloroform, which are much larger than earlier published results.[1,2]

In an attempt to quantify the effect of solvent deuteration on dye-sensitized photooxygenations, a kinetic scheme was used in which an acceptor (A) quenches (k_q) or reacts with (k_a) singlet oxygen generated by energy transfer from a sensitizer in its triplet state. By use of the usual steady-state treatment and adjustment of the concentration of the acceptor A such that the rate constant for the decay of singlet oxygen (k_d) is much larger than (k_a + k_q)[A], the disappearance of the acceptor is expressed by eq 1 where K is the rate of formation of singlet oxygen.

$$\ln([A]/[A]_0) = -K(k_a/k_d)t = k_{obsd}t \qquad (1)$$

For the acceptors rubrene and 1,3-diphenylisobenzofuran (DPBF), if it is assumed that fluorescence intensity is directly proportional to the concentration of acceptor in solution, first-order plots determined according to Young's technique[3a] should be linear with a slope of k_{obsd}. Values of the relative rate constant (k_{obsd}) obtained from parallel experiments in protiated and deuterated solvents can then be compared to yield values of a solvent isotope effect if the reasonable assumption[1,6] is made that k_a changes negligibly upon solvent deuteration. A similar assumption, however, may not hold for terms which are incorporated into K. Independent experiments discussed below, however, suggest that K does not change significantly upon solvent deuteration. Any changes, therefore, in k_{obsd} are manifestations of changes in the lifetime ($1/k_d$) of singlet oxygen.

First-order plots are linear (correlation coefficient >0.999), occasionally showing only slight curvature at high concentrations of acceptor.[7] Table I lists the average values of the ratios of k_{obsd} taken from subsequent runs. The errors for these values are 95% confidence limits. The isotope effects observed for chloroform at first appeared to be substrate dependent, rubrene yielding a value approximately three times larger than that obtained from DPBF. However, upon the addition of 2,4,6-tri-*tert*-butylphenol (TBP), a radical-chain inhibitor, very similar isotope effects were found for both substrates. These results suggest that photooxygenation of both rubene and DPBF in chloroform can involve processes other than singlet oxygen addition if care is not taken to suppress them.

[†] National Science Foundation Trainee, 1978–1979.

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(7) Mallinckrodt spectrograde solvents were used for the protio experiments. 99.5% d acetone (Aldrich), 99.0% d acetonitrile (Aldrich), 99.8% d chloroform (Merck Sharp and Dohme), and 99.5% d benzene (Alfa) were used in the deuterio experiments. The general features of the spectrofluorometer used have been described elsewhere.[8] However, for these experiments the frequency of the fluorescence excitation lamp was modulated with a Heath model EUW-27 sine-square wave generator whose signal was amplified by a Dynaco audio amplifier. Fluorescence was detected by an RCA-1P28A photomultiplier tube powered by a Fluke 415B power supply. Signals were amplified by an Ithaco Dynatrac 391A lock-in amplifier. Rose bengal (1.0 × 10^{-5} M) and methylene blue (1.0 × 10^{-5} M) solutions were photolyzed through Corning CS 3-68 and CS 2-63 filters, respectively. Rubrene (1.0–2.0 × 10^{-6} M) fluorescence was excited at 490 or 460 nm and monitored at 550 nm. DPBF (1.0 × 10^{-6} M) fluorescence was excited at 410 nm and monitored at 477 nm. Photooxygenation of an acceptor in a protiated solvent was immediately followed by reaction in a deuterated solvent, thereby minimizing the effects of any changes in experimental conditions (e.g., lamp intensities). Absorption spectra were taken to ensure that the amount of sensitizing dye present in each case was identical.

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Table I. Experimentally Determined Solvent Isotope Effects[7]

solvent	substrate	sensitizer	$k_{\mathrm{obsd}}{}^{\mathrm{d}}/k_{\mathrm{obsd}}{}^{\mathrm{h}}$ [a]
acetone	rubrene	rose bengal	19.9 ± 1.3
	DPBF	rose bengal	17.0 ± 3.8
	DPBF	methylene blue	17.8 ± 2.0
acetonitrile	rubrene	rose bengal	8.7 ± 1.0
	DPBF	rose bengal	7.2 ± 1.6
benzene[b]	rubrene	methylene blue	15.9 ± 2.1
	DPBF	methylene blue	16.8 ± 1.0
chloroform	rubrene	methylene blue[d]	15.6 ± 1.6
	DPBF	methylene blue	5.8 ± 2.6
	rubrene/TBP[c]	methylene blue	10.4 ± 1.2
	DPBF/TBP[c]	methylene blue	9.8 ± 0.9

[a] Equivalent to $k_{\mathrm{decay}}{}^{\mathrm{h}}/k_{\mathrm{decay}}{}^{\mathrm{d}}$. See text. [b] Contained 0.8% MeOH in order to dissolve methylene blue. [c] 2.0–4.0 × 10^{-5} M TBP. [d] During the period of photolysis methylene blue bleached significantly (~20%) in $CDCl_3$ but showed negligible changes in concentration in $CHCl_3$. Consequently, $CDCl_3$ solutions were prepared with a slightly greater amount of methylene blue than $CHCl_3$ solutions. The average concentration of methylene blue in $CDCl_3$ during photolysis was then equivalent to that in $CHCl_3$. The addition of TBP had no effect on the bleaching of methylene blue.

For a test of the assumption that K is invariant, β values (k_d/k_a) for 2,3-dimethyl-2-butene were determined[9] in both acetonitrile-d_3 and -h_3. The ratio of these values yielded a solvent isotope effect (8.0 ± 1.0) within the error limits of the k_{obsd} values for rubrene and DPBF (8.7 and 7.2, respectively). Similarily, the ratio of β values determined[10] for 1-methylcyclohexene in both acetone-d_6 and acetone-h_6 yielded a solvent isotope effect (11.8 ± 4.3) only slightly lower than those determined from the k_{obsd} values for the other substrates (approximately 18).[12]

Upon the addition of a quencher to the photooxygenation of a substrate (A) by singlet oxygen, two limiting cases are obtained.[11] In the first, the added quencher affects the lifetime of ^{3}Sens and/or ^{1}Sens but does not deactivate singlet oxygen. In this case, plots of $[AO_2]^{-1}$ vs. $[A]^{-1}$ have intercepts (K^{-1}) which are dependent on the quencher concentration. If, however, the quencher does not affect the lifetime of either ^{3}Sens or ^{1}Sens but deactivates only singlet oxygen, the plots yield a common intercept, independent of the quencher concentrations used. Since the data in Table I suggest that singlet oxygen is longer lived in deuterated solvents, the corresponding protiated solvent may be considered as a quencher. Plots of $[AO_2]^{-1}$ vs. $[A]^{-1}$ for the photooxygenation of 1-methylcyclohexene are given in Figure 1. The constant intercept is excellent corroborating evidence that the lifetime of ^{3}Sens is independent of solvent deuteration. There is ample precedent in the literature for the conclusion that $\tau^{1}{}_{\mathrm{Sens}}$ does not change upon solvent deuteration.[5,14,15]

Our observations suggest that the approach taken by Kearns[1a] does not provide an adequate description for the quenching of singlet oxygen by solvent interactions. In particular, a direct correlation was not found between solvent isotope effects on the lifetime of singlet oxygen and the optical densities of the solvent in regions that correspond to the transitions $[^1\Delta_g(v = 0) \rightarrow {}^3\Sigma_g{}^-]$ where oxygen is left in its ground electronic state with varying amounts of vibrational quanta.[16] Further work needs to be done, therefore, in the development of a satisfactory theory for the quenching of singlet oxygen by solvent interactions. Such work is presently being undertaken. The results of experiments in which the lifetime of singlet oxygen is determined directly from the decay of singlet oxygen luminescence should provide significant insight into the problem.[17] In fact, it has long been recognized that for solvents in which the rate constant for singlet oxygen decay (k_d) is small, the currently accepted indirect methods for determining singlet oxygen lifetimes cannot be used with any reasonable degree of accuracy.[3b] Byteva[17d] has noted that values for the lifetime of singlet oxygen in solution determined by the indirect method[1-3] are significantly smaller than values determined from the direct luminescence of singlet oxygen. This conclusion supports the results reported in this communication.

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(9) Determined by using Young's technique.[3a] The experimental apparatus is identical with that outlined in ref 7. DPBF decay curves were analyzed by a DEC PDP-11/45 computer using a program originally written by Dr. J. V. V. Kasper and Dr. R. W. Wake and revised by Dr. L. Levine and P. R. Ogilby.

(10) Calculated from the data shown in Figure 1.[12] 1-Methylcyclohexene was distilled prior to use. Samples were photooxygenated by a tungsten lamp in a merry-go-round apparatus. After having been reduced with triphenylphosphine, the samples were chromatographed on a Hewlett-Packard 5880A flame ionization gas chromatograph using a 6.0-ft × 0.085-in. column of 10% UCW 98 on a support of WHP. 1,4-Dimethoxybenzene was used as internal standard.

(11) C. S. Foote, ref 1e, p 139.

(12) It is important to recognize that in both types of β-value determinations (Young's method and the reciprocal plots of Figure 1), the formation constant for singlet oxygen (K) is canceled internally.[3,11,13] In taking the ratio of β values, therefore, the only assumption is that k_a is invariant to solvent deuteration. The large error in the isotope effect determined by using methylcyclohexene reflects the error in the intercepts in the plots of $[AO_2]^{-1}$ vs. $[A]^{-1}$.

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Chiral Discrimination in the Energetics of Ion Aggregation[†]

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Tables I and II present the first data known to us which compare directly the energetics of aggregation of chiral ions in solution to make diastereomeric ion pairs. It has been obvious since the principles of stereochemistry were first established over a century ago that diastereomers should differ in all of their physical properties, including heats of formation. However, until recently[1] the methods of purification and measurements were not sufficiently sensitive to detect the differences between diastereomeric solvates or ion pairs in solution[2] with certainty.

Tables I and II give unequivocal evidence that diastereomeric ion pairs formed by aggregation of even rather simple chiral ions can differ by 200–350 cal/mol in their heats of formation from the free ions—a factor sufficient to account for the difference between a 50:50 yield in a reaction and a 60:40 yield, for example. Highly purified solutions of the bases shown were titrated with solutions of mandelic acid. The compounds were chosen because the configurations of both enantiomers were well established[3] and (in addition to their pharmacological relevance) because both were readily available in high purity. This permitted us to apply the absolute method of cross-chiral checks between enantiomeric ion pairs [e.g., *R*,*R* vs. *S*,*S* or *R*,*S* vs. *S*,*R*].

Thermometric titration of (*R*)- or (*S*)-α-phenethylamine with (*R*)- or (*S*)-mandelic acid in water yielded a single value regardless of the configuration of the acid or base. Since only free ions should be formed in this solvent over the concentration range of the

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[†] Work done at the University of Pittsburgh.

(1) Horeau, A.; Guette, J. P. *Tetrahedron* **1974**, *30*, 1923–1931. This reference discusses many early attempts to measure such small energetic differences and has shown that most reported values may be rejected for one reason or another.

(2) It is widely realized that the structures and lattice energies of diastereomeric compounds and salts differ considerably in the crystalline state.

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