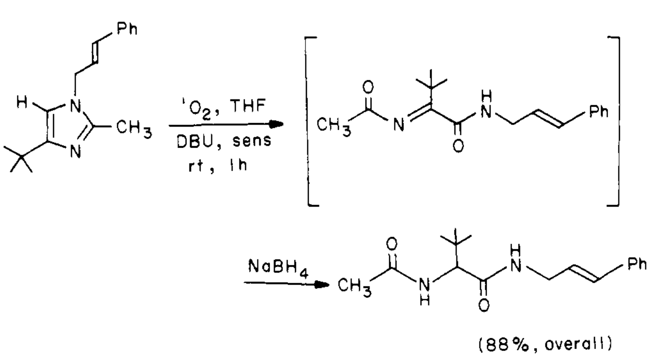

of a new and efficient photooxidative transformation of imidazoles. Curiously, excess DBU is required, in spite of the well-known ability of amines to efficiently quench singlet oxygen.[15] Both diamides and dipeptides (cf. entry 4) may be unmasked using this three-step protocol. Chiral products with high ee's result from hydrogenations using an optically active Rh(I)/DIPAMP combination as catalyst. Application of this technology[16] to the generation of $\alpha$-alkylated amino acids,[17] as well as the phencyclopeptines,[4] will be reported in due course.

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**Registry No.** 2,4-Dimethyl-1-(phenylmethyl)-1*H*-imidazole, 52726-31-5; 2-methyl-4-(1-methylethyl)-1-[2-[4-(phenylmethyl)phenyl]ethyl]-1*H*-imidazole, 88336-71-4; 2-methyl-4-(1-methylethyl)-1-(phenylmethyl)-1*H*-imidazole, 54416-18-1; ethyl 2-methyl-4-(1-methylethyl)-1*H*-imidazole-1-acetic acid, 88336-72-5; 2-methyl-4-(2-methylpropyl)-1-(phenylmethyl)-1*H*-imidazole, 88336-73-6; 2,4-dimethyl-1-[2-[4-(phenylmethoxy)phenyl]ethyl]-1*H*-imidazole, 86921-46-2; 2-methyl-1,4-bis(phenylmethyl)-1*H*-imidazole, 88336-74-7; 2-(acetylamino)-*N*-(phenylmethyl)propanamide, 86921-48-4; 2-(acetylamino)-3-methyl-*N*-(phenylmethyl)butanamide, 88336-75-8; 2-(acetylamino)-3-methyl-*N*-[(ethoxycarbonyl)methyl]butanamide, 88336-76-9; 2-(acetylamino)-4-methyl-*N*-(phenylmethyl)pentanamide, 88336-77-0; 2-(acetylamino-*N*-[2-[4-(phenylmethoxy)phenyl]ethyl]propanamide, 88336-78-1; 2-(acetylamino)-*N*-(phenylmethyl)benzenepropanamide, 67509-08-4.

**Supplementary Material Available:** IR, NMR, mass spectral and high-resolution MS analytical data and physical constants for selected intermediates **2**, **3**, and **4** (3 pages). Ordering information is given on any current masthead page.

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(15) Foote, C. S. In "Singlet Oxygen"; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; Chapter 5. The appropriate control reactions (i.e., i, no light; ii, no sensitizer) clearly established that singlet oxygen is the reactive reagent.

(16) A typical procedure for the photooxidation/isomerization/hydrogenation sequence is illustrated using 1-benzyl-2-methyl-4-isobutylimidazole (Table I, entry 5). A solution of the imidazole (217 mg, 0.95 mmol) in 10 mL of dry THF containing 121 $\mu$L (1.44 mmol) of DBU and ca. 5 mg of hematoporphyrin is fitted with a gas dispersion tube through which dry oxygen is continuously passed.[18] The solution is cooled with a stream of tap water (20–25 °C) and irradiated externally with a 275-W sunlamp for 2.25 h. Following consumption of starting material (as monitored by TLC) the mixture was concentrated in vacuo, diluted with 5 mL of dry THF, and placed under Ar. To the crude imine (**2**, R = $CH(CH_3)_2$; R′ = H) dissolved in 5 mL of THF was added a solution of KH (108 mg, 35% in oil, 1.0 mmol) and 136 mg (2.0 mmol) of *tert*-butyl alcohol in 5 mL of dry THF. The mixture was maintained at room temperature until complete by TLC. Extractive workup (EtOAc) followed by drying ($MgSO_4$) and chromatography on $SiO_2$ (1:1 EtOAc/$Et_2O$) gave 205 mg (83%) of the *N*-acetyldehydroleucine *N*-benzylamide as a white solid, mp 124–126 °C. A flask charged with 13.7 mg (0.053 mmol) of the dehydroamino acid diamide and 3 mL of degassed MeOH is placed under 1 atm of $H_2$. A solution of ca. 1 mg of Rh(NBD)Cl dimer and ca. 0.5 mg of (*R*,*R*)-DIPAMP in 2 mL of degassed MeOH is prehydrogenated (1 atm) for 10 min. The resulting solution is then syringed into the dehydrodiamide in MeOH and monitored by TLC over time. Upon completion, the mixture was concentrated in vacuo, diluted with 3 mL of dry THF, and filtered through a short plug of $SiO_2$ affording 13.6 mg (98%) of the desired material. The enantiomeric excess of 95% in the above mixture was determined via $Eu(hfc)_3$-perturbed[19] 300-MHz NMR, by measuring the relative peak heights of the acetyl methyl and/or the benzyl singlets, both of which were easily resolved and viewed using a stacked plot program.

(17) For a recent approach to these materials, see: Seebach, D., Boes, M., Naef, R., Schweizer, W. B. *J. Am. Chem. Soc.* **1983**, *105*, 5390.

(18) For a description of the apparatus, see: Foote, C. S.; Vickers, R. S. *Chem. Pharm. Bull.* **1970**, *109*, 599.

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## Induced Internal Redox Processes in Molybdenum-Sulfur Chemistry: Conversion of $MoS_4^{2-}$ to $Mo_2S_8^{2-}$ by Organic Disulfides

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In molybdenum–sulfur chemistry redox usually involves either changes in the metal oxidation state[1,2] or in a few cases changes in the oxidation state of the sulfur ligands.[3,4] However, in some complex reactions[5-7] both Mo- and S-based redox occur. In this paper, we report and rationalize a simple albeit counterintuitive reaction in which both molybdenum and sulfur change their oxidation states.

The tetrathiomolybdate ion, $MoS_4^{2-}$, has molybdenum in its maximal hexavalent oxidation state. We find that this ion can nevertheless be readily *oxidized* by organic disulfides to give the dinuclear complex, $Mo_2S_8^{2-}$, containing *reduced* pentavalent molybdenum. This stoichiometrically simple reaction involves induced internal electron transfer[8] from sulfide to molybdenum, and its documentation and implications are the subjects of this communication.

The stoichiometry of reaction I has been established to be

$$2MoS_4^{2-} + RSSR \rightarrow Mo_2S_8^{2-} + 2RS^- \qquad (I)$$

Reaction of 2 equiv of $(NH_4)_2MoS_4$ with 1 equiv of $C_6H_5SSC_6H_5$ in DMF at 90 °C for ~1 h results in the formation of $Mo_2S_8^{2-}$. The anion has been isolated in >80% yield as the $P(C_6H_5)_4^+$ salt by precipitation with diethyl ether/isopropyl alcohol. The organic product was detected and quantitated as RSH by reversed-phase HPLC.[9] The conversion of $MoS_4^{2-}$ to $Mo_2S_8^{2-}$ can also be effected at 90 °C by $C_6H_5SeSeC_6H_5$ or at room temperature with $p$-$O_2NC_6H_4SSC_6H_4$-$p$-$NO_2$. Salts of $Mo_2S_8^{2-}$ display analytical[10] and spectral[11] data consistent with their formulation. The product is identical with one formed in good yield by the reaction of $Mo_2(S_2)_6^{2-}$ with 8 equiv of thiolate.[4]

Single crystals suitable for X-ray diffraction were obtained by vapor diffusion of diethyl ether into an acetonitrile solution of

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(9) Reverse-phase HPLC, Altex Ultrasphere ODS column, 4.6 mm × 15 cm, 1:1 MeOH/$CH_3CN$ (1% acetic acid), 1 mL $min^{-1}$, UV–vis detection (250 nm).

(10) For the $[N(C_2H_5)_4]_2Mo_2S_8$ complex analysis for $C_{16}H_{40}N_2Mo_2S_8$ gives, calcd, C, 27.1, H, 5.69, N, 3.95, found, C, 27.1, H, 5.46, N, 3.74.

(11) Infrared spectra in KBr disk of $[N(C_2H_5)_4]_2Mo_2S_8$ shows bands at 520, 535, 460, and 350 $cm^{-1}$ assignable to molybdenum-sulfur vibrational modes. The electronic spectrum in $CH_3CN$ displays bands at 573 ($\epsilon$2590), 467 (2130), and 295 nm.

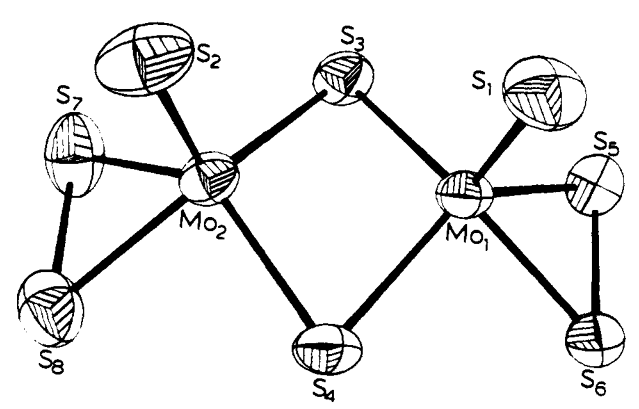

**Figure 1.** The structure of $Mo_2S_8^{2-}$ as determined in its $(C_6H_5)_4P^+$ salt. Bond distances and angles in the anion are: $Mo_1$–$Mo_2$ = 2.821 (1), $Mo_2$–$S_2$ = 2.108 (1), $Mo_1$–$S_1$ = 2.128 (1), $S_5$–$S_6$ = 2.051 (2), $S_7$–$S_8$ = 2.072 (3), $Mo_2$–$S_7$ = 2.391 (1), $Mo_2$–$S_8$ = 2.405 (2), $Mo_1S_5$ = 2.403 (1), $Mo_1$–$S_6$ = 2.375 (2), $Mo_2$–$S_3$ = 2.314 (1), $Mo_2$–$S_4$ = 2.313 (1), $Mo_1$–$S_3$ = 2.306 (1), $Mo_1$–$S_4$ = 2.308 (2) Å; $S_4$–$Mo_2S_3$ 101.0 (1)°, $S_4$–$Mo_1$–$S_3$ 101.4°, $Mo_1$–$S_3$–$Mo_2$ 75.3 (1)°, $Mo_1$–$S_4$–$Mo_2$ 75.2 (1)°.

$[(C_6H_5)_4P]_2[Mo_2S_8]$ in the dark. X-ray diffraction analysis[12-15] confirmed the presence of the binuclear $Mo_2(S)_2(\mu\text{-}S)_2(S_2)_2^{2-}$ ion shown in Figure 1. The complex anion is isostructural to the previously reported $Mo_2O_2(\mu\text{-}S)_2(S_2)_2^{2-}$ ion.[16,17] The *syn*-$Mo_2S_4^{2+}$ core has dimensions very close to those of related pentavalent dinuclear complexes.[18] The two disulfur ligands with S–S distances of 2.05 and 2.07 Å are, as in related complexes,[19] formulated as persulfide ($S_2^{2-}$) ligands.

The formation of $Mo_2S_8^{2-}$ from two $MoS_4^{2-}$ anions involves a net two-electron oxidation with no overall gain or loss of sulfur atoms, i.e., $Mo_2S_8^{2-}$ is the dimer of the one-electron oxidation product of hexavalent $MoS_4^{2-}$. Despite this net oxidation, the $Mo_2S_8^{2-}$ product contains pentavalent Mo and belongs to the well-established class of pentavalent dinuclear complexes containing the $Mo_2O_xS_{4-x}^{2+}$ core ($x$ = 0–4). Clearly, oxidation of the complex has caused reduction of the metal.

Reaction I can be fruitfully represented as involving induced internal electron transfer from $S^{2-}$ to Mo(VI). Induced internal electron transfers in chemical systems had previously only been well established[8,20-22] for mononuclear cobalt complexes in which Co(III) is *reduced* to Co(II) upon reaction with an external one-electron *oxidant* such as Ce(IV). A concomitant net two-electron oxidation of the ligand is required (e.g., $C_2O_4^{2-} \rightarrow 2CO_2$). In the present case the external oxidant, RSSR, takes up two electrons and each of two Mo atoms takes up one electron. This requires, and we observe, a four-electron oxidation of the ligands, i.e., the conversion of four $S^{2-}$ ligands to two $S_2^{2-}$ ligands. The ease with which internal electron transfer occurs in this and related systems is a manifestation of the ability of sulfide/polysulfide ligand systems to exhibit energy levels both above and below the 4d levels of molybdenum.[23] This closeness of energy levels may also be responsible for the unusual reactivity of the related molecule $Mo_2O_2(\mu\text{-}S)_2(S_2)_2^{2-}$ toward activated alkynes,[24] which involves insertion of the alkyne into the $Mo(S_2)$ group forming a vinyl disulfide ring containing both Mo–C and S–C bonds.

The induced internal redox concept may be applied toward conceptual understanding of the remarkable reaction of $MoS_4^{2-}$ with $S_8$ to yield $MoS_9^{2-}$.[6,7] Here, formation of the Mo(IV) product is viewed as a result of internal redox from $S^{2-}$ to Mo(VI) induced by the external oxidant $S_8$. Clearly, in other multisulfidometal complexes, particularly where the metal is in a high formal oxidation state, the possibility of effecting net metal atom *reduction* by external *oxidants* must be considered.[25] Such manner of electronic structural and internal redox flexibility may be important in Mo enzymes such as nitrogenase and in Mo–S industrial catalysts.

**Supplementary Material Available:** Tables of atomic coordinates, thermal parameters, bond lengths and bond angles, and structure factors (55 pages). Ordering information is given on any current masthead page.

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[12] The complete structure determination was carried out by Dr. C. S. Day of Crystalytics Co., Lincoln, NB.

[13] Crystal Data: space group $P\bar{1}$-$C_i^1$ (No. 2), with $a$ = 13.277 (6) Å, $b$ = 18.933 (9) Å, $c$ = 10.959 (5) Å, $\alpha$ = 100.28 (4)°, $\beta$ = 110.39 (4)°, $\gamma$ = 104.23°, $V$ = 2395 (2) Å$^3$, and $Z$ = 2. Calculated density 1.56 g cm$^{-3}$. Unit cell dimensions were determined from least-squares refinement of 15 reflections with $2\theta > 25°$.

[14] The data was corrected for absorption ($\Psi$ scan); transmission factors 0.718–1.000. The structure was solved using direct methods (SHELLxTL Direct Methods Programs), difference Fourier synthesis, and cascade block diagonal least-squares refinement. $R_F$ = 0.043, $Rw_F$ = 0.041 for 8126 independent diffracted intensities ($I > 3.0\sigma(I)$) with $3° < 2\theta < 55°$ (Mo K$\alpha$ radiation). Anisotropic thermal parameters were utilized for all non-hydrogen atoms.

[15] Further details of the structure analysis, including tables of atomic coordinates, thermal parameters, bond lengths, bond angles, and structure factors, are available as supplemental material.

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[23] Theoretical calculations by J. Bernholc of our laboratory (to be published) on $Mo_2S_8^{2-}$ confirm the delocalized nature of the highest filled and lowest empty orbitals in this complex.

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[25] The reaction of $MoS_9^{2-}$ with 2 equiv of $^-SCH_2CH_2S^-$ leads to the formation of $MoS_4^{2-}$. This reaction appears to be an example of an induced redox process in which an external *reductant* ($^-SCH_2CH_2S^-$) leads to *oxidation* of the Mo(IV) to Mo(VI) concomitant with reduction of the polysulfide ligands to sulfide ligands. It is, thus, an induced internal redox in the opposite sense (L → M) to that of equation I.

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## p$K_a$ and Keto-Enol Equilibrium Constant of Acetone in Aqueous Solution

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Recent interest in the chemistry of simple enols has led to a number of estimates of the keto–enol equilibrium constant for acetone in aqueous solution,[1,2] as well as the dissociation constant of this substance as a carbon acid in this medium.[2b,3,4] These estimates, however, are all necessarily approximate, for each depends upon an assumed value for at least one unknown quantity, e.g., the magnitude of a rate constant thought to be encounter controlled or the value of an unknown parameter in a thermodynamic cycle. We wish to report that we have now determined the keto–enol equilibrium constant as well as the acid dissociation

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