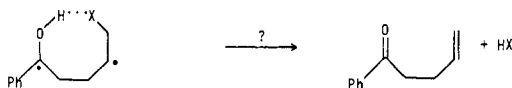certed mechanism can compete with radical cleavage except possibly for the worst leaving groups.

Relative rates of β cleavage can be obtained directly from the product ratios, given the plausible assumption that k_s is largely independent of X.[16] Recent measurements[17] indicate that $k_s = 1 \times 10^7$ s^{-1}; so a k_{-X} value of 2.7×10^5 s^{-1} is indicated for X = n-BuS. Actual rate constants for β elimination in solution have not been reported previously. The 7.5-kcal activation energy estimated for β-bromoethyl radical[18] is certainly consistent with our estimated $k_{-Br} = 1 \times 10^8$ s^{-1}, given an A factor of 10^{13} s^{-1}.

Comparison of the relative k_{-X} values is revealing. As expected, I > Br > Cl and PhS $\gg$ n-BuS[19] as leaving groups. The order RSO $\gg$ RS, RSO$_2$ confirms Kice's suggestion[20] that sulfinyl radicals have the greatest relative kinetic stability of the three. That SCN $\gg$ SCOCH$_3$ may reflect the known weak conjugative stabilization in α-keto radicals[21] and further indicates that δ-X leaves as a radical rather than an anion.

The most surprising result is that Cl is eliminated more rapidly than thiyl radicals. Kineticists usually assume a much smaller value of k_{-X} for β-chloroethyl[22] than we estimate. Therefore it is possible that the cyclic concerted mechanism contributes for X = Cl. However, the amount of Cl loss in the radical addition of mercaptans to allyl chloride[23] is consistent with our separate observations that loss of δ-Cl and trapping by mercaptans[14a] compete comparably with type II cleavage. It is not inconceivable that studies on monoradicals have indicated too low a value for k_{-Cl} because of rapid reverse addition. Our k_{-X} values are *minimum* values uncorrected for reverse addition. However, since the diradicals can generate caged radical pairs, in-cage radical–radical reactions are probably faster even than addition of Cl atoms to double bonds and thus minimize the effects of reversibility on relative k_{-X} values.

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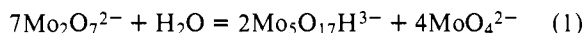**Michael J. Lindstrom**
Department of Chemistry, Michigan State University
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Synthesis and Characterization of the Pentamolybdate Ion, Mo$_5$O$_{17}$H^{3-}
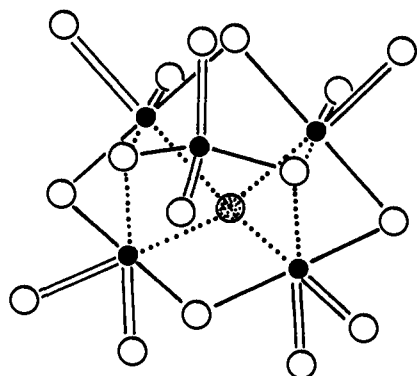
Sir:

We recently reported the synthesis and characterization of the dimolybdate ion, Mo$_2$O$_7$$^{2-}$, as a tetrabutylammonium salt.[1] This compound contains the most basic polymolybdate ion isolated to date and is reactive toward a wide variety of reagents. We report here its reaction with water to form a labile pentamolybdate ion:

$$7Mo_2O_7{}^{2-} + H_2O = 2Mo_5O_{17}H^{3-} + 4MoO_4{}^{2-} \quad (1)$$

The instability of this novel, protonated isopolymolybdate in nonaqueous solution provides new insights into the kinetics and mechanism of polymolybdate transformations.

Although addition of water to a CH$_3$CN solution of [(n-C$_4$H$_9$)$_4$N]$_2$Mo$_2$O$_7$ (1) produces no significant change in its solution IR spectrum,[1] the pentamolybdate ion can be synthesized according to eq 1 by forcing the equilibrium to the right using two different approaches. In the first approach, the low solubility of the pentamolybdate ion in CH$_3$CN/(C$_2$H$_5$)$_2$O is exploited. Slow addition ($\sim$15 mL/min) of 80 mL of (C$_2$H$_5$)$_2$O to a clear solution of 1.0 g of 1 and 1.0 mL of H$_2$O in 10 mL of CH$_3$CN with rapid stirring yields 190 mg of an amorphous precipitate having the empirical formula[2] [(n-C$_4$H$_9$)$_4$N]$_3$Mo$_5$O$_{17}$H (2). In the second approach, the high solubility of [(n-C$_4$H$_9$)$_4$N]$_2$MoO$_4$ in H$_2$O relative to 1 and 2 is exploited. When a suspension of 1.0 g of 1 in 10 mL of pH 5–6 aqueous HCl is stirred for $\sim$1 min and filtered, compound 2 (460 mg) is obtained as an amorphous powder.
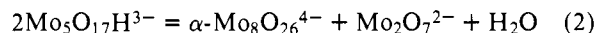
Structural characterization of 2 is rendered difficult by its instability in solution (see below) which has thus far ruled out recrystallization, conductivity measurements, and the measurement of ^{17}O NMR parameters. Nonetheless, elemental analysis[2] and IR spectroscopy strongly suggest the anion structure for 2 shown in Figure 1, where MoO$_4$$^{2-}$ and OH$^-$ groups are connected to opposite sides of an Mo$_4$O$_{12}$ ring by weak (>2.2 Å) Mo–O bonds yielding the structural formula[3] (MoO$_4$$^{2-}$)(OH$^-$)(Mo$_4O_{12}$). This structure is closely related to the (CH$_3$)$_2$AsMo$_4$O$_{15}$H^{2-} structure[4] by replacement of the bidentate MoO$_4$$^{2-}$ subunit with a bidentate (CH$_3$)$_2$AsO$_2$$^-$ group.[5] Structural isomorphism between the anions in 2 and [(n-C$_4$H$_9$)$_4$N]$_2$(CH$_3$)$_2$AsMo$_4$O$_{15}$H (3) should imply similar IR spectra for the two compounds in the 500–4000-cm^{-1} region with the exception of absorptions characteristic of the MoO$_4$$^{2-}$ and (CH$_3$)$_2$AsO$_2$$^-$ subunits. Such a similarity is in fact observed. Both 2 and 3 exhibit sharp OH absorptions at 3610 cm^{-1} and their spectra in the 500–1000-cm^{-1} region (see Figure 2a and 2b) bear a striking resemblance outside of the 725–850-cm^{-1} region. In the 725–850-cm^{-1} region, 3 displays

Figure 1. Proposed, C_{2v} idealized structure for $Mo_5O_{17}H^{3-}$. Small filled circles represent molybdenum atoms, large open circles represent oxygen atoms, and the shaded large circle represents a hydroxyl group. Molybdenum-oxygen distances <1.75 Å are represented by double lines, 1.75 Å < d_{Mo-O} < 1.95 Å by single lines, and d_{Mo-O} > 2.2 Å by dotted lines.

$\bar{\nu}(\text{cm}^{-1})$

Figure 2. IR spectra of (a) $[(n\text{-}C_4H_9)_4N]_3Mo_5O_{17}H$ (2) in KBr pellet, (b) $[(n\text{-}C_4H_9)_4N]_2(CH_3)_2AsMo_4O_{15}H$ (3) in KBr pellet, (c) 2 in CH_3CN at equilibrium, (d) 2 in 1,2-$C_2H_4Cl_2$ <2 min after dissolution (e) 2 in 1,2-$C_2H_4Cl_2$ 30 min after dissolution. Spectra c–e were measured in ZnS (IRTRAN-2) cells.
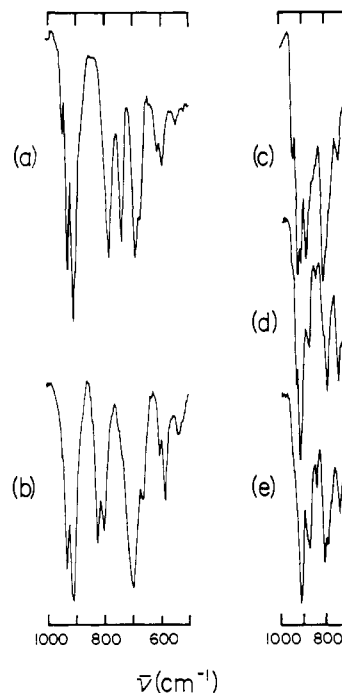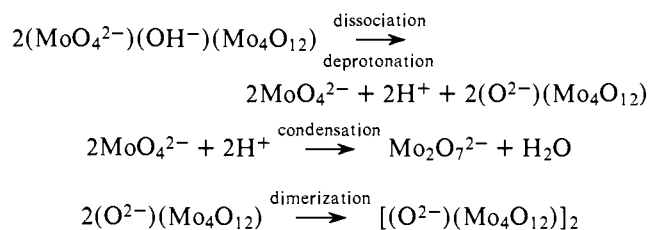
characteristic[8] As–O absorptions at 803 and 826 cm^{-1} and 2 displays absorptions at 786 and 740 cm^{-1} which may be assigned to tetrahedral molybdate.

When 2 is dissolved in CH_3CN, its solution IR spectrum in the 700–1000-cm^{-1} region (see Figure 2c) taken <2 min after dissolution shows absorptions characteristic of 1[1] at 880 and 786 cm^{-1} and α-$[(n\text{-}C_4H_9)_4N_4Mo_8O_{26}$ (4)[9,10] at 950, 920, 905, 850, 808, and 740 cm^{-1}, but no pattern of absorptions characteristic of 2. An analogous spectrum in 1,2-$C_2H_4Cl_2$ (see Figure 2d), however, shows absorptions due to pentamolybdate 2 at 954, 934, 913, 786, and 740 cm^{-1} in addition to weaker absorptions characteristic of di- and octamolybdate. When this dichloroethane solution is allowed to equilibrate, precipitation of 4 is accompanied by an increase in intensity of the absorptions for 1 and 4 and a concomitant decrease in intensity of the absorptions for 2 (see Figure 2e). These observations imply the following equilibrium
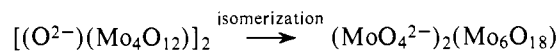
$$2Mo_5O_{17}H^{3-} = \alpha\text{-}Mo_8O_{26}^{4-} + Mo_2O_7^{2-} + H_2O \quad (2)$$

which is rapid and favors decomposition products in CH_3CN, but is slower and less displaced toward decomposition products in 1,2-$C_2H_4Cl_2$.

Two features of the $(MoO_4^{2-})(OH^-)(Mo_4O_{12})$ structure account for its instability in solution. First, the presence of an OH^- subunit offers the potential for generation of protons in solution capable of reacting with basic molybdate species to form condensation products. ^1H NMR measurements confirm the lability of this proton in that addition of CH_3OH to a solution of 2 in 1,2-$C_2H_4Cl_2$ causes the δ 2.12 ppm resonance for 2 to disappear.[12] Second, the presence of a weakly bound MoO_4^{2-} subunit implies facile dissociation of the MoO_4^{2-} group in a fashion analogous to that observed for $(MoO_4^{2-})_2(Mo_6O_{18})$.[3] Dynamic ^{17}O NMR experiments designed to confirm this lability have been unsuccessful since room temperature spectra cannot be accumulated before equilibration is complete and low temperature spectra yield resonances broadened beyond recognition by quadrupole relaxation. These two features suggest a simple, four-step mechanism for the decomposition reaction given in eq 2:

$$2(MoO_4^{2-})(OH^-)(Mo_4O_{12}) \xrightarrow[\text{deprotonation}]{\text{dissociation}} 2MoO_4^{2-} + 2H^+ + 2(O^{2-})(Mo_4O_{12})$$

$$2MoO_4^{2-} + 2H^+ \xrightarrow{\text{condensation}} Mo_2O_7^{2-} + H_2O$$

$$2(O^{2-})(Mo_4O_{12}) \xrightarrow{\text{dimerization}} [(O^{2-})(Mo_4O_{12})]_2$$

$$[(O^{2-})(Mo_4O_{12})]_2 \xrightarrow{\text{isomerization}} (MoO_4^{2-})_2(Mo_6O_{18})$$

In the initial step, dissociation and deprotonation yield monomolybdate ions, protons, and $(O^{2-})(Mo_4O_{12})$ fragments. The protons are utilized in the second step to condense monomolybdate ions into dimolydbate ions. In the third step, the $(O^{2-})(Mo_4O_{12})$ fragments dimerize to form $[(O^{2-})(Mo_4O_{12})]_2$, i.e., β-$Mo_8O_{26}^{4-}$. Finally, β-$Mo_8O_{26}^{4-}$ undergoes facile isomerization to α-$Mo_8O_{26}^{4-}$ via the mechanism proposed in ref 9.

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(13) Fellow of the Alfred P. Sloan Foundation, 1976–1978.

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