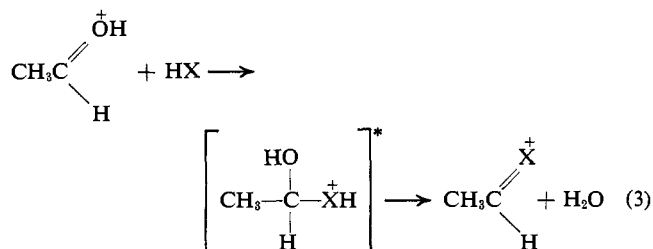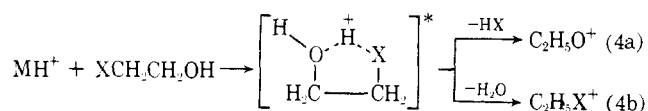Reactions 1 and 2 are not specific for PH_3 in that they occur as well with other hydrides. For example, in a mixture of ethylene oxide and hydrogen sulfide, reactions 1 and 2 (HX = H_2S) are observed to produce an ion at m/e 61 corresponding to $C_2H_5S^+$. In contrast to the behavior observed with ethylene oxide, in mixtures of acetaldehyde with PH_3 and H_2S, reactions corresponding to the generalized process 3 are not

$$CH_3C\overset{\overset{+}{OH}}{\diagdown}_H + HX \longrightarrow$$

$$\left[\begin{array}{c} HO \\ | \\ CH_3-C-\overset{+}{XH} \\ | \\ H \end{array} \right]^* \longrightarrow CH_3C\overset{\overset{+}{X}}{\diagdown}_H + H_2O \quad (3)$$

observed. In mixtures of 1,2-dimethoxyethane with PH_3 and H_2S, the $C_2H_5O^+$ isomer III does not lead to a condensation product at m/e 61. Clearly reaction 1 serves to identify the protonated oxirane structure II, distinguishing it from I and III.[21]

In comparing reactions 1 and 3, the replacement of oxygen by phosphorus or sulfur in the three-membered rings is likely to be favored on energetic grounds, there being considerably less strain energy with the second-row atom.[22] In contrast, replacement of oxygen with phosphorus or sulfur in reaction 3 is unfavorable since π bonding to carbon is ineffective in the product ion.[23] In fact it is highly probable that reaction 3 proceeds favorably in the reverse direction in accordance with recently proposed rules for nucleophilic attack on substituted carbonium ions.[24]

Our observations bear an interesting relationship to the recent study of gas-phase ion chemistry of β-substituted alcohols reported by Caserio and coworkers.[16] They identified the preferred product in reaction 4 for

$$MH^+ + XCH_2CH_2OH \longrightarrow \left[\begin{array}{c} H\diagdown_{O^+}\diagup^{\overset{+}{H}}\diagdown_X \\ | \quad | \\ H_2C----CH_2 \end{array} \right]^* \begin{array}{c} \overset{-HX}{\longrightarrow} C_2H_5O^+ \quad (4a) \\ \overset{-H_2O}{\longrightarrow} C_2H_5X^+ \quad (4b) \end{array}$$

various proton donors MH^+ to involve loss of HX for X = F and Cl and loss of H_2O for X = Br, OR, SR, SH, and NH_2. Their suggestion that product stability is a major factor determining the mode of dissociation is corroborated by our experiments, in which similar intermediates are postulated, the mode of formation being via the reverse of reaction 4a.

In addition to providing ion structural information and being of mechanistic interest, studies such as those reported above have interesting implications relating to the stability of strained cyclic ions. We are currently investigating the occurrence and preferred direction of reactions involving nucleophilic attack on strained cyclic ions containing oxygen, nitrogen, sulfur, phosphorus, and halogen heteroatoms.

(21) The reactant ion in process 1 may not be the initially formed $C_2H_5O^+$ since this species may undergo further collisions with C_2H_4O prior to reactions with PH_3.

(22) Thermochemical estimates in ref 15 indicate that reaction 1 is $\sim$32 kcal/mol exothermic for HX = H_2S.

(23) B. G. Keyes and A. G. Harrison, *J. Amer. Chem. Soc.*, 90, 5671 (1968).

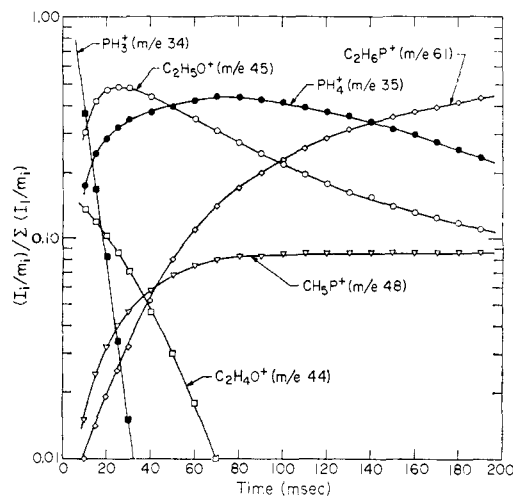(24) J. H. Cook and J. L. Beauchamp, *J. Amer. Chem. Soc.*, submitted for publication.

Figure 1. Variation of ion abundance with time for a mixture of ethylene oxide (3.3 $\times$ 10^{-6} Torr) and phosphine (3.7 $\times$ 10^{-6} Torr) at an electron energy of 12 eV. Ionic species less than 5% of the total ionization are not shown.

(25) Earle C. Anthony Predoctoral Fellow, 1973–1974.
(26) NDEA Predoctoral Fellow, 1970–1973.
(27) Camille and Henry Dreyfus Teacher–Scholar, 1971–1976.

Ralph H. Staley, Reed R. Corderman[25]
Michael S. Foster,[26] **J. L. Beauchamp***[27]

Contribution No. 4787
Arthur Amos Noyes Laboratory of Chemical Physics
California Institute of Technology
Pasadena, California 91109
Received November 14, 1973

The Nature of Electron Delocalization in a Heteropoly "Blue" Anion. Evidence for Valence Trapping at Low Temperatures

Sir:

A number of heteropoly oxo complexes of molybdenum(VI) and tungsten(VI) are reducible to a series of mixed valence (V, VI) complexes known as heteropoly blues.[1] In most cases the several reducible metal atoms in a heteropoly complex are structurally equivalent, and as a result there is some uncertainty as how best to describe the electronic structures of the reduced substances. We report here the electron spin resonance (esr) spectrum of a heteropoly anion at temperatures between 6 and 300°K. The spectra reveal a valence oscillation that can be described as an intramolecular electron hopping process, and we can show that the electron becomes trapped on a single metal atom at very low temperatures. Although such a thermal electron delocalization has been postulated for other mixed valence systems,[2] the present results constitute the first demonstration of temperature-dependent valence trapping in a polynuclear complex. The temperature be-

(1) M. T. Pope, *Inorg. Chem.*, 11, 1973 (1972).
(2) See, for example, W. H. Morrison, Jr., S. Krogsrud, and D. N. Hendrickson, *Inorg. Chem.*, 12, 1998 (1973).

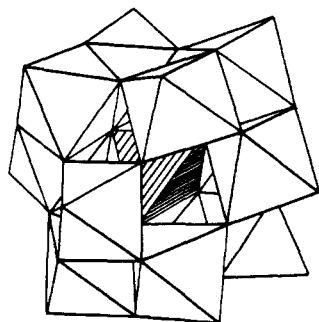**Figure 1.** Representation of the Keggin structure of $PMo_{12}O_{40}{}^{3-}$ as an arrangement of edge- and corner-shared MoO_6 octahedra surrounding a central PO_4 tetrahedron (shaded). The molybdenum atoms are displaced from the centers of their respective octahedra toward the terminal (unshared) oxygen atoms.
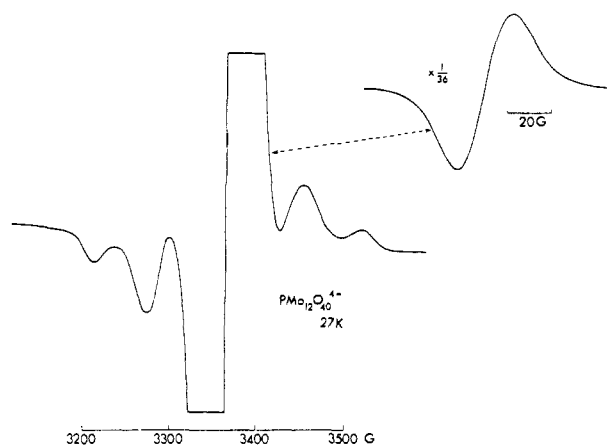

Figure 3. Polycrystalline esr spectrum of isotopically enriched $(98\% \ {}^{95}Mo) \ PMo_{12}O_{40}{}^{4-}$ in $(Bu_4N)_4SiW_{12}O_{40}$ at $28\,°K$.

Figure 2. Polycrystalline esr spectrum of $PMo_{12}O_{40}{}^{4-}$ in $(Bu_4N)_4$-$SiW_{12}O_{40}$ at $27\,°K$.

havior further distinguishes heteropoly blues from other mixed valence clusters, e.g., $Nb_6Cl_{12}{}^{3+}$, in which electron delocalization appears to be described in terms of multicenter molecular orbitals.[3]

The complex that we have studied is the one-electron reduction product of the 12-molybdophosphate anion, $PMo_{12}O_{40}{}^{3-}$, the structure of which is shown in Figure 1. In aqueous media 12-molybdophosphate is largely hydrolyzed and in mixed protonic solvents undergoes two-electron reductions[4] to diamagnetic blues, H_n-$PMo_{12}O_{40}{}^{3-}$. We have found that, as a tetrabutylammonium salt in an aprotic solvent such as acetonitrile or propylene carbonate, the anion is stable indefinitely and undergoes a one-electron reduction at a platinum electrode. The reduced salt, $(Bu_4N)_4PMo^{V,VI}{}_{12}O_{40}$, may also be prepared by interaction of $PMo_{11}O_{39}{}^{7-}$ and $MoOCl_4{}^-$ in an aprotic solvent.[5] Both chemically and electrolytically produced salts gave satisfactory analyses and identical infrared and esr spectra. *Anal.* Calcd: C, 27.52; H, 5.19; N, 2.00. Found: C, 27.40; H, 5.04; N, 1.96. The heteropoly blue salt is isomorphous with the corresponding tetrabutylammonium salts of other $4-$ Keggin anions ($SiMo_{12}O_{40}{}^{4-}$, $PMo^VW_{11}O_{40}{}^{4-}$, etc.); it is not isomorphous with the oxidized salt.[5]

Esr measurements were made at X-band on powdered solid solutions (1%) of the blue salt in $(Bu_4N)_4SiW_{12}O_{40}$,

using a JEOL MES-3X spectrometer. The temperature of the sample could be held to within a degree at any temperature between 6 and 300°K by means of an Air Products Heli-Tran LTD-3 system.

At 298°K the spectrum consisted of a broad (525 G) Lorentzian line. As the temperature was lowered the line narrowed considerably and, below 140°K, an increasing admixture of a Gaussian component could be detected. At 77°K the line was about 25% Gaussian and was 26 G peak-to-peak. Below 77°K the line width did not change, but hyperfine satellites developed at *ca.* 64°K and these grew in intensity as the temperature was further lowered. A typical low-temperature spectrum is shown in Figure 2. The central line in this spectrum is seen to be completely isotropic; it remained so down to 6°K, the lowest temperature studied. That the hyperfine lines were indeed part of an isotropic six-line spectrum (with $a = 61$ G) is confirmed by the spectrum of the isotopically enriched $(98\% \ {}^{95}Mo, I = {}^5/_2)$ anion shown in Figure 3. The positions of the outer lines in this spectrum correspond exactly with those in Figure 2. The component lines are broader in the spectrum of the enriched material, and this may be due to unresolved superhyperfine interactions with neighboring ${}^{95}Mo$ atoms.

Computer simulation of the spectrum of the isotopically enriched material at 6°K, which differs very little from that shown in Figure 3, can only be achieved by mixing a broad (186 G) line with the six hyperfine components. It was not possible to determine from spectra of the enriched complex if the relative intensities of the broad line and the hyperfine spectrum varied with temperature or if the hyperfine lines merely broadened until they were no longer detectable (at *ca.* 64°K). However, the better-resolved hyperfine spectrum of the nonenriched complex clearly increased in intensity as the temperature was lowered, although the presence of the underlying line prevented accurate intensity measurements.

The 12 equivalent metal atoms in the Keggin structure (Figure 1) occupy axially distorted (*ca.* C_{4v}) sites,[6] and the esr spectrum of polycrystalline $(Bu_4N)PMo^V$-$W_{11}O_{40}$, for example, is fully resolved into parallel and

(3) R. A. Mackay and R. F. Schneider, *Inorg. Chem.*, **6**, 549 (1967).
(4) J. M. Fruchart and P. Souchay, *C. R. Acad. Sci., Ser. C*, **266**, 1571 (1968).
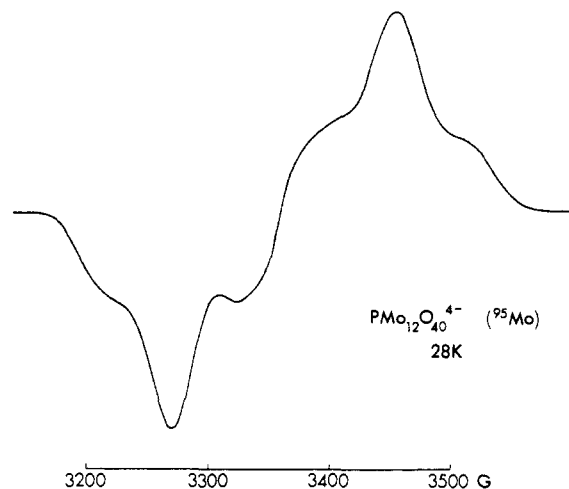(5) P. T. Meiklejohn and M. T. Pope, in preparation.
(6) D. P. Smith, H. So, J. Bender, and M. T. Pope, *Inorg. Chem.*, **12**, 685 (1973).

perpendicular components [$g_{||}$ = 1.918, $g_\perp$ = 1.937, $a_{||}$ = 81.3 G, $a_\perp$ = 33.2 G] at room temperature. The isotropy of the esr spectrum of $PMo_{12}O_{40}{}^{4-}$ indicates therefore that the unpaired electron in this complex is still very mobile even at 6°K.

The above results are consistent with a model for the electron structures of heteropoly blues in which the valence electrons oscillate between a number of metal atoms in identical sites. To a large extent the electron delocalization appears to be thermally activated.[7] Although further discussion of delocalization processes in heteropoly blues is beyond the scope of this communication, we note that the theoretical model of Hush[8] would predict an activation energy for thermal delocalization that is much too large (ca. 6 kcal/mol) to account for the degree of trapping observed here.

(7) Laser irradiation of glassy samples at 6328 Å during the esr measurements had no detectable effects on the spectra.

(8) N. S. Hush, *Progr. Inorg. Chem.*, **8**, 391 (1967). The activation energy is predicted to be 25% of the energy of the optical intervalence band which occurs at 8000–10,000 cm⁻¹ in reduced molybdophosphate.

Ronald A. Prados, Paul T. Meiklejohn, Michael T. Pope*
*Department of Chemistry, Georgetown University
Washington, D. C. 20007*

Keteneimmonium and 2-Azabutadiene Complexes from Reactions of α-Chloroenamines with Metal Carbonyl Anions

Sir:

α-Chloroenamines (I; R = CH_3 or R_2 = $(CH_2)_5$), unlike normal vinylic halides but like certain polycyanovinyl halides,[1] are very reactive toward nucleophiles.[2-4] Reactions of these α-chloroenamines (I) with various metal carbonyl anions[5] have now been found to yield new transition metal organometallic compounds including several species with novel structural features. In particular, the first transition metal complexes of keteneimmonium[4,6] and 2-azabutadiene systems have been prepared and characterized. The neutral unit $(CH_3)_2C=C(NR_2)$ derived from the α-chloroenamines has been found to bond to transition metals in five different ways: one way as a one-electron donor, three ways as a three-electron donor, and one way as a five-electron donor.

Some reactions of the α-chloroenamines with metal carbonyl anions give relatively simple products in which the chlorine of the α-chloroenamine is replaced with a metal carbonyl residue. For example, reaction[7]

(1) R. B. King and M. S. Saran, *J. Amer. Chem. Soc.*, **94**, 1784 (1972); **95**, 1811 (1973).

(2) L. Ghosez, B. Haveaux, and H. G. Viehe, *Angew. Chem., Int. Ed. Engl.*, **8**, 454 (1969).
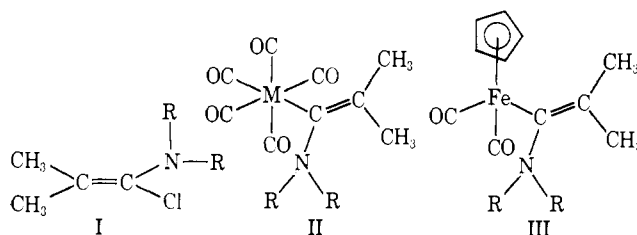
(3) M. Rens and L. Ghosez, *Tetrahedron Lett.*, 3765 (1970).

(4) J. Marchand-Brynaert and L. Ghosez, *J. Amer. Chem. Soc.*, **94**, 2869 (1972).

(5) R. B. King, *Accounts Chem. Res.*, **3**, 417 (1970).

(6) J. Marchand-Brynaert and L. Ghosez, *J. Amer. Chem. Soc.*, **94**, 2870 (1972).

(7) These reactions were carried out at ambient temperatures in the tetrahydrofuran solutions in which the metal carbonyl anions were prepared.

of $(CH_3)_2C=C[N(CH_3)_2]Cl$ with $NaRe(CO)_5$ gives yellow crystalline[8] $(CH_3)_2C=C[N(CH_3)_2]Re(CO)_5$ (II; M = Re, R = CH_3): mp 40–41°; infrared $\nu(CO)$ in hexane 2088 (m, A_1), 2021 (w, B_1), 1972 (vs, E), and 1940 (s, A_1) cm⁻¹; proton nmr[9] in $CDCl_3$ [$N(CH_3)_2$] τ 7.04 and [$=C(CH_3)_2$] 8.15 and 8.33. Reaction[7] of $(CH_3)_2C=C[N(CH_3)_2]Cl$ with $NaFe(CO)_2C_5H_5$ gives air-sensitive brown liquid $(CH_3)_2C=C[N(CH_3)_2]Fe(CO)_2$-$C_5H_5$ (III; R = CH_3): infrared $\nu(CO)$ in hexane 2000 (s) and 1949 (s) cm⁻¹; proton nmr[9] in $CDCl_3$ (C_5H_5) τ 5.31, [$N(CH_3)_2$] 7.79, and [$=C(CH_3)_2$] 8.20 and 8.35. In these complexes the neutral $(CH_3)_2C=C(NR_2)$ unit acts as a one-electron donor.

Two types of keteneimmonium transition metal complexes have been prepared from reactions of $(CH_3)_2$-$C=C[N(CH_3)_2]Cl$ with other metal carbonyl anions. Reaction[7] of $(CH_3)_2C=C[N(CH_3)_2]Cl$ with $NaCo(CO)_4$ gives the air-sensitive yellow liquid[8] [$(CH_3)_2C=C=N$-$(CH_3)_2]Co(CO)_3$: bp 30–35° (0.5 mm) by evaporative distillation; infrared $\nu(CO)$ in hexane 2038 (s) and 1961 (vs) cm⁻¹; proton nmr[9] in $CDCl_3$ [$N(CH_3)_2$] τ 6.63 and 6.79 and [$=C(CH_3)_2$] 8.46. Reaction[7] of $(CH_3)_2C=C[N(CH_3)_2]Cl$ with $NaMo(CO)_3C_5H_5$ gives a 12% yield of yellow crystalline[8, 10] [$(CH_3)_2C=C=N$-$(CH_3)_2]Mo(CO)_2C_5H_5$: mp 120–122°; infrared $\nu(CO)$ in CH_2Cl_2 1930 (s) and 1832 (s) cm⁻¹; proton nmr[9] in $CDCl_3$ (C_5H_5) τ 4.84, [$N(CH_3)_2$] 7.38, and [$=C(CH_3)_2$] 8.10 and 8.14. In both of these compounds the neutral $(CH_3)_2C=C=N(CH_3)_2$ unit acts as a three-electron donor. The distinct differences in the nmr spectra of the protons in the $(CH_3)_2C=C=N(CH_3)_2$ units of the cobalt and molybdenum complexes suggest different modes of bonding of this three-electron ligand in the two complexes. If the geometry of the $(CH_3)_2C=C=N$-$(CH_3)_2$ ligand approximates that of tetramethylallene with a linear central sp carbon atom, postulation of structures IV (M = Co, R = CH_3) and V (M = Mo, R = CH_3) for these complexes can account for the nmr equivalence of the two C-methyl groups and the nmr nonequivalence of the two N-methyl groups in the cobalt complex as well as the nmr equivalence of the two N-methyl groups and the nmr nonequivalence of the two C-methyl groups in the molybdenum complex. These observations suggest that a keteneimmonium ligand such as $(CH_3)_2C=C=N(CH_3)_2$ can bond to transition metals either through the carbon–carbon or the carbon–nitrogen double bond.

Cyclic acyl derivatives in which a carbonylated neutral $(CH_3)_2C=C[N(CH_3)_2]C(O)-$ unit acts as a three-electron donor have also been prepared. Reaction[7] of $(CH_3)_2C=C[N(CH_3)_2]Cl$ with $NaMn(CO)_5$ gives a 60% yield of air-stable yellow crystalline[8] $(CH_3)_2C=C[N$-$(CH_3)_2]C(O)Mn(CO)_4$: mp 90–92°; infrared $\nu(CO)$ in

(8) These new compounds were characterized by correct elemental analyses for at least carbon, hydrogen, nitrogen, and oxygen.

(9) All of the resonances in these proton nmr spectra were singlets.

(10) The mass spectrum of this compound exhibited a molecular ion and ions corresponding to the stepwise loss of the carbonyl groups.