

Electron Transfer from alpha-Keggin Anions to Dioxygen

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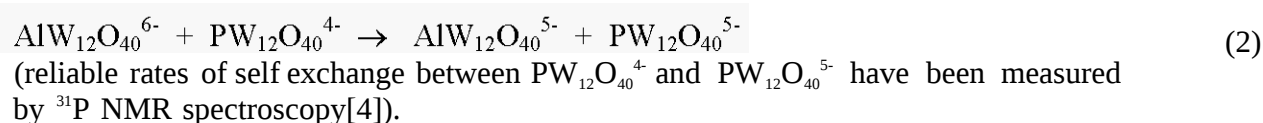
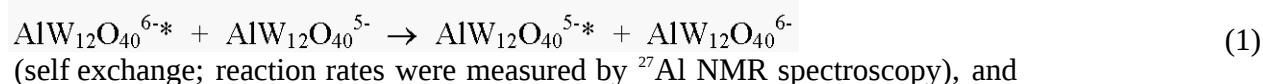
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Polyoxometalates. Polyoxometalates (POMs), of which alpha-Keggin anions are representative, are a diverse and rapidly growing class of water-soluble cluster–anion structures with applications ranging from molecular catalysis to materials.[1] POMs are inexpensive, minimally or non-toxic, negatively charged clusters comprised of early-transition-metals, usually in their d^0 electronic configurations (e.g. W(VI), Mo(VI), V(V), Nb(V), Ti(IV)), bridged by oxygens (formally oxide, or occasionally hydroxide ions). POMs have a number of attributes that render them attractive for applications in catalysis[2] and other technologies. For example, POMs exhibit extensive reversible redox processes,[3] and their reduction potentials, acidities, and other properties relevant to catalysis and materials science can be extensively yet readily altered by the elemental composition of the POM unit itself. For all the above reasons, yearly citations of articles on POMs have been growing steadily and, for each of the past three years, have outnumbered articles on fullerenes.

Electron Transfer from POMs to O_2 . The mechanism of O_2 reduction by POMs is of fundamental importance to all POM-catalyzed O_2 oxidations. Prior to the studies described here, it had been reported that isopoly- and heteropolytungstates in their reduced forms ($H_2W_{10}O_{32}^{4-}$ and $P_2W_{18}O_{62}^{7-}$) reduce O_2 without incorporation of ^{17}O into the POM products. While not unequivocal, these data are consistent with a mechanism that does not involve intermediate covalent W–O bonds and therefore, as in certain other POM reductions, is likely outer sphere. (In contrast, reaction of reduced *polymolybdates* with O_2 had been proposed for years, and was recently demonstrated by Neumann to proceed by an inner-sphere Mars van Krevelen-type mechanism).

We now provide: (1) detailed kinetic data that unequivocally demonstrate that 1e--reduced alpha-Keggin anions, $X^{n+}W_{12}O_{40}^{(7-n)-}$ ($X = Al(III), Si(IV), P(V)$) reduce O_2 by an outer-sphere mechanism, and (2) the first systematic and quantitative evaluation of the role of heteroatom, X, on the reorganization energies, λ_{in} , of alpha-Keggin anions. The reorganization energy, λ_{in} is the sum of the energies associated with changes in atomic coordinates (bond lengths and angles) upon reversible electron transfer to or from the POM anion. This parameter, λ_{in} , is important because it determines electron-transfer rates and is thus central to the use of POMs in redox catalysis and as catalysts for selective oxidations by O_2 .

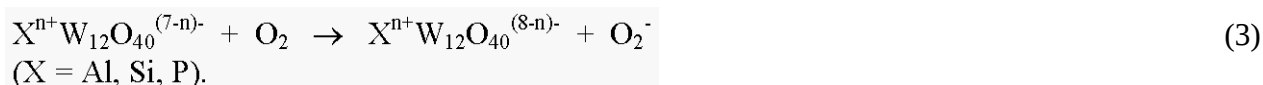
Kinetic Data. Marcus parameters. Fundamental parameters associated with electron-transfer reactions of the $AlW_{12}O_{40}^{5-/6-}$ pair were obtained using stopped-flow kinetic methods and ^{27}Al NMR spectroscopy. Two reactions were studied:



It was first determined that both reactions obeyed the Debye-Hückel relationship (prescribed changes in rate constants with ionic strength, μ). Next, the reorganization energy, λ , associated with the $AlW_{12}O_{40}^{5-/6-}$ pair was directly determined from rate data obtained by linewidth analysis of ^{27}Al NMR spectra of mixtures of the two anions (eq 1). The λ value

calculated from the reaction in eq 1 was confirmed by the cross reaction in eq 2, by recourse to published data for the $\text{PW}_{12}\text{O}_{40}^{5-/4-}$ pair (experimental and theoretical[5] values were 10 and $2\text{M}^{-1}\text{s}^{-1}$, respectively).

Electron transfer to dioxygen. Kinetic data were then obtained for the following elementary reactions (the first, and in each case, rate-limiting step in the 2e reduction of O_2 and 2H^+ to H_2O_2):



The reactions were studied by stopped-flow kinetic methods using visible spectroscopy to measure the time-dependent decrease in the concentrations of $\text{X}^{n+}\text{W}_{12}\text{O}_{40}^{(7-n)-}$. The reactions in eq 3 are, in each case rate-limiting (they are followed by rapid disproportionation of O_2 to peroxide and O_2), and are first order in both reactants. Experimental rate constants were, respectively, 55, 90 and $5\text{M}^{-1}\text{s}^{-1}$ for X = Al, Si and P. Using the published rate constant for the self-exchange reaction of the $\text{PW}_{12}\text{O}_{40}^{5-/4-}$ pair ($k_{11(\text{P})} = 1.1 \times 10^5$), and our experimentally determined rate constant for the self-exchange reaction in eq 1 ($k_{11(\text{Al})} = 3.3 \times 10^{-3}$), the Marcus cross relation was used to calculate theoretical values for the respective reactions in eq 3.[6] Experimental and theoretical rate constants were, for 55 and $24\text{M}^{-1}\text{s}^{-1}$ for X = Al, and for 5 and $3\text{M}^{-1}\text{s}^{-1}$ for X = P. This close agreement between theory and experiment made it possible to rely upon the Marcus cross relation to estimate, by fitting, the self-exchange rate constant, $k_{11(\text{Si})}$, for the $\text{SiW}_{12}\text{O}_{40}^{5-/4-}$ pair. A fitted value of $k_{11(\text{Si})} = 1.33 \times 10^2$ corresponded to a theoretical rate constant for eq 3 of $43\text{M}^{-1}\text{s}^{-1}$, close to the experimental value of $90\text{M}^{-1}\text{s}^{-1}$.

Determination and Variation of λ_{in} Values. The semi-classical method of Sutin[7] was then used to calculate λ_{in} values for the three $\text{X}^{n+}\text{W}_{12}\text{O}_{40}^{(7-n)-/(8-n)-}$ pairs. The three experimentally-determined self-exchange rate constants, k_{11} , obtained as described above, were used other parameters were as previously described. [4] Reorganization-energy, λ_{in} , values of 8.4, 12.6 and 17.1kcal mol^{-1} , respectively, for X = Al, Si and P, were calculated for the three $\text{X}^{n+}\text{W}_{12}\text{O}_{40}^{(7-n)-/(8-n)-}$ pairs.

Role of Heteroatom, X, in Electron-Transfer Reactions of Heteropolyanions. Alpha-Keggin anions may be viewed as clathrate structures in which tetrahedral $\text{X}^{n+}\text{O}_4^{(8-n)-}$ moieties are encapsulated within neutral $\text{W}_{12}\text{O}_{36}$ shells. Moreover, it has been shown that X- μ_4 -O bond lengths decrease and corresponding μ_4 -O-W bond lengths increase as X is varied from Al to Si to P.[8] Hence, λ_{in} , the energy associated with changes in W-O bond lengths upon addition of an electron to the $\text{W}_{12}\text{O}_{36}$ shell, should increase as μ_4 -O-W bonds decrease in length. One index associated with variation in X- μ_4 -O bond lengths is simply the electronegativity of the heteroatom, X. Notably, λ_{in} values, determined here for the first time, bear a remarkably linear correlation when plotted against the electronegativity of the heteroatom as X is varied from Al to Si to P.

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