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Cation and Pressure Effects on the Electrochemistry of 12-Tungstocobaltate and 12-Tungstophosphate Ions in Acidic Aqueous Solution

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The effects of supporting electrolytes and of pressure on the electrode reactions of the aqueous $CoW_{12}O_{40}^{5-/6-}$ couple at 25 °C are reported, together with limited data on $PW_{12}O_{40}^{3-/4-}$ and $PW_{12}O_{40}^{4-/5-}$. The half-wave potentials $E_{1/2}$ for the CoW_{12} couple become moderately more positive with increasing electrolyte concentration and cationic charge, and also in the sequences $Li^+ \approx Na^+ < NH_4^+ \leq H^+ < K^+ < Rb^+ < Cs^+$ and $Na^+ < Mg^{2+} < Ca^{2+} < Eu^{3+}$. The mean diffusion coefficients for CoW_{12} with the 1:1 electrolytes are independent of electrolyte concentration and rise only slightly from Li^+ to Cs^+, averaging $(2.4 \pm 0.3) \times 10^{-6}$ cm^2 s^{-1}. Neither the volumes of activation for diffusion $\Delta V_{diff}^{\ddagger}$ (average –0.9 ± 1.1 cm^3 mol^{-1}) nor the electrochemical cell reaction volumes $\Delta V_{Ag/AgCl}$ (average –22 ± 2 cm^3 mol^{-1}) for the CoW_{12} couple show significant dependence on electrolyte identity or concentration. For the $PW_{12}^{3-/4-}$ and $PW_{12}^{4-/5-}$ couples, $\Delta V_{Ag/AgCl} = -14$ and –26 cm^3 mol^{-1}, respectively, suggesting a dependence on $\Delta(z^2)$ (z = ionic charge number) as predicted by the Born–Drude–Nernst theory of electrostriction of solvent, but comparison with $\Delta V_{Ag/AgCl}$ for CoW_{12} and other anion–anion couples shows that the Born–Drude–Nernst approach fails in this context. For aqueous electrode reactions of CoW_{12}, as for other anionic couples such as cyanometalates, the standard rate constants k_{el} show specific cation catalysis ($Na^+ < K^+ < Rb^+ < Cs^+$), and $\Delta V_{el}^{\ddagger}$ is invariably positive, in the presence of supporting electrolytes. For the heavier group 1 cations, $\Delta V_{el}^{\ddagger}$ is particularly large (10–15 cm^3 mol^{-1}), consistent with a partial dehydration of the cation to facilitate catalysis of the electron-transfer process. The positive values of $\Delta V_{el}^{\ddagger}$ for the CoW_{12} couple cannot be attributed to rate control by solvent dynamics, which would lead to $\Delta V_{el}^{\ddagger} \leq \Delta V_{diff}^{\ddagger}$, i.e., to negative or zero $\Delta V_{el}^{\ddagger}$ values. These results stand in sharp contrast to those for aqueous cationic couples, for which k_{el} shows relatively little influence of the nature of the counterion and $\Delta V_{el}^{\ddagger}$ is always negative.

Introduction

The importance of polyoxometalates as catalysts and as multivalent redox reagents is well recognized.[1−5] Among the most familiar examples are the 12-tungstocobaltate ($CoW_{12}O_{40}^{n-}$, $n = 4-8$; "CoW_{12}")[5] and 12-tungstophosphate ions ($PW_{12}O_{40}^{n-}$, $n = 3-5$; "PW_{12}"),[6] which, as ordinarily prepared, have the α-Keggin structure[1] wherein the central Co or P atom is tetrahedrally coordinated by four oxygens and which behave as "hard" bases. Our particular interest in the $CoW_{12}O_{40}^{5-/6-}$ couple, which is robust, unprotonated,[4] and substitution inert[7] in dilute acidic aqueous solution and has convenient kinetic[8] and thermodynamic[9] characteristics, stems from our desire to extend our investigations of cation and pressure effects on the electron-transfer chemistry of anions to couples other than cyanometalates,[10−14] which could

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(1) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: New York, 1983.

(2) Pope, M. T.; Müller, A. *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*; Kluwer Academic Publishers: Dordrecht, 1994.

(3) *Polyoxometalate Chemistry: From Topology via Self-Assembly to Applications*; Pope, M. T., Müller, A., Eds.; Kluwer Academic Publishers: Dordrecht, 2001.

(4) Weinstock, I. A. *Chem. Rev.* **1998**, *98*, 113−170.

(5) Saha, S. K.; Ali, M.; Banerjee, P. *Coord. Chem. Rev.* **1993**, *122*, 41−62.

(6) Pope, M. T.; Varga, G. M., Jr. *Inorg. Chem.* **1966**, *5*, 1249−1254.

(7) Geier, G.; Brubaker, C. H., Jr. *Inorg. Chem.* **1966**, *5*, 321−322.

(8) Rasmussen, P. G.; Brubaker, C. H., Jr. *Inorg. Chem.* **1964**, *3*, 977−980.

(9) Carloni, P.; Eberson, L. *Acta Chem. Scand.* **1991**, *45*, 373−376.

(10) Zahl, A.; van Eldik, R.; Swaddle, T. W. *Inorg. Chem.* **2002**, *41*, 757−764.

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arguably represent special cases because of the "softness" conferred by the π-acceptor action of the cyano ligands. The $PW_{12}O_{40}{}^{3-/4-}$ couple offers similar properties except that it is stable in aqueous solution only at pH <1.5,[6] its self-exchange electron-transfer rate is much faster,[15] and the added electron is delocalized over the W_{12} framework rather than associated with the central atom as in the Co case. The essentially spherical shape of the 12-tungstometalates, and their inward polarization resulting in a lack of strong interactions with solvent or solute species,[15] also allows for simpler theoretical interpretations of experimental observations.

For cyanometalate couples, the observed rate constants k_{ex}'s for self-exchange in homogeneous solution are completely dominated by pathways involving catalysis by the counterion,[12] and indeed the direct observation of the uncatalyzed pathway in $Fe(CN)_6{}^{3-/4-}$ required sequestration of the cation (K^+) by a cryptand or crown ether.[10] For the $Mo(CN)_8{}^{3-/4-}$, $W(CN)_8{}^{3-/4-}$, and $Os(CN)_6{}^{3-/4-}$ self-exchange pathways catalyzed by alkali metal ions, the volumes of activation $\Delta V_{ex}^{\ddagger}$ $(= -RT(\partial \ln k_{ex}/\partial P)_T)$ are all markedly positive,[12] in contrast to the negative values predicted for the uncatalyzed paths from an adaptation of Marcus theory (and observed for $Fe(CN)_6{}^{3-/4-}$).[10] For pathways catalyzed by tetraalkylammonium cations R_4N^+, however, $\Delta V_{ex}^{\ddagger}$ is negative.[12] The interpretation given[12] is that aqueous alkali metal cations M^+ must be at least partially desolvated to act as catalysts for electron transfer, whereas R_4N^+ ions are very poorly solvated to begin with. Indeed, the catalytic power of $M^+(aq)$ is found to increase in the sequence Li < Na < K < Rb < Cs, which is the order of increasing (i.e., less negative) heats of hydration.[12] For the corresponding electrode reactions, the rate constants k_{el} and activation volumes $\Delta V_{el}^{\ddagger}$ show these same trends,[11] as do the rate constants for many net redox reactions of cyanometalates.[12]

Heteropolyoxometalate anions are much larger, less polarizable, and less basic than cyanometalates or, indeed, most other anionic metal complexes for which the electron-transfer characteristics have been studied. Thus, the effects of factors such as protonation, Coulombic interactions, and solvent dynamics that can complicate the interpretation of experimental data are much reduced. Nevertheless, marked cation effects have been reported on reduction potentials of heteropolyoxometalates in aqueous,[16] organic,[17] and aqueous–organic[9,18,19] media, and also on the rates of self-exchange[8,20] and of net redox reactions,[4,5,16,21] although it has not always been clear whether the effects observed are cation specific or arise in a general way from ionic strength. Moreover, even the qualitative nature of the cation effects cannot be simply summarized; for example, in the *oxidation* of *p*-methoxytoluene by $Co^{III}W_{12}{}^{5-}$ in acetic acid/water, the rate constants increased in the order $Dec_4N^+ < Hex_4N^+ < Pr_4N^+ < Bu_4N^+ < Me_4N^+ < Na^+ < Li^+ < K^+ < Rb^+ < Ca^{2+} < Cs^+ < Sr^{2+}$,[16] whereas in the *reduction* of CBr_4 by $Co^{II}W_{12}{}^{7-}$ or $Co^{II}W_{12}{}^{8-}$ in acetonitrile/water the rate constants increased in the sequence $Cs^+ < K^+ < Na^+ \sim Li^+ < Bu_4N^+ < Me_4N^+$.[21] Rasmussen and Brubaker[8] studied the kinetics of the outer-sphere self-exchange reaction of the $CoW_{12}{}^{5-/6-}$ couple in acidic aqueous solution at 0 °C by a precipitation method using ^{60}Co radiotracer and with LiCl or KCl to maintain constant ionic strength. They found that k_{ex} was independent of $[H^+]$ but was about 10 times greater in KCl relative to comparable concentrations of LiCl. Detailed interpretation of their observations may be inappropriate, however, as Weinstock[4] has pointed out that the ionic strengths were incorrectly calculated and that some of the data may have been flawed; unfortunately, since both the $Co^{II}W_{12}$ and $Co^{III}W_{12}$ are paramagnetic, a check on the results by dynamic NMR methods is not feasible. Nevertheless, it is clear that the $CoW_{12}{}^{5-/6-}$ self-exchange rate is much slower than that of $PW_{12}{}^{3-/4-}$, which approaches diffusion control.[15,22] This is evidently because the transferred electron goes to the Co center in the former couple, resulting in retardation through a substantial Franck–Condon effect amplified by Jahn–Teller distortions of the polytungstate cage, whereas in PW_{12} the electron is delocalized over all the W centers.[15,22] It was hoped that the present study would throw further light upon this contrast in behavior. The $PW_{12}O_{40}{}^{3-}$ ion, however, is unstable in aqueous solution except at pH 1.5 or less,[6] and even at such high acidities it is, in our experience, precipitated on addition of significant concentrations of cations other than Li^+ or Na^+. Accordingly, the present report focuses on the effects of cations and pressure on the electrode kinetics and potentials of the $CoW_{12}{}^{5-/6-}$ couple, and only a superficial report on the $PW_{12}{}^{3-/4-}$ and $PW_{12}{}^{4-/5-}$ electrode reactions is included for comparison.

Experimental Section

Materials. Distilled water was further purified on a Barnstead E-pure train. $K_6CoW_{12}O_{40}\cdot xH_2O$ ($x \sim 16$) was prepared by the method of Nolan et al.[23] and recrystallized twice from water. Some lattice water was lost on drying on a Schlenk line ($x \sim 7$, molar mass 3268, on the basis of the visible spectrum; molar absorbance 214 L mol^{-1} cm^{-1} at 625 nm[23]). $H_3PW_{12}O_{40}$ (Strem, >99%), $HClO_4$ (Baker Analyzed Reagent), LiCl, KCl, NH_4ClO_4, $Mg(ClO_4)_2$ (Fisher Reagent Grade), NaCl, $NaClO_4\cdot H_2O$ (BDH Analytical Reagent), $CaCl_2$ (MCB), RbCl (ICN, 99%), CsCl (Ventron, 99.9%), and $Eu(NO_3)_3\cdot 6H_2O$ (Alfa, 99.9%) were used as received. $LiClO_4\cdot 3H_2O$ (Aldrich) was recrystallized twice from water. Addition of $SrCl_2$, $BaCl_2$, $[(CH_3)_4N]Cl$, and $[(C_4H_9)_4N]Cl$ to CoW_{12} solutions caused precipitation.

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[11] Fu, Y.; Swaddle, T. W. *Inorg. Chem.* **1999**, *38*, 876–880.

[12] Metelski, P.; Swaddle, T. W. *Inorg. Chem.* **1999**, *38*, 301–307.

[13] Swaddle, T. W.; Tregloan, P. A. *Coord. Chem. Rev.* **1999**, *187*, 255–289.

[14] Fu, Y.; Swaddle, T. W. *J. Am. Chem. Soc.* **1997**, *119*, 7137–7144.

[15] Kozik, M.; Baker, L. C. W. *J. Am. Chem. Soc.* **1990**, *112*, 7604–7611.

[16] Eberson, L. *J. Am. Chem. Soc.* **1983**, *105*, 3192–3199.

[17] Himeno, S.; Takamoto, M.; Ueda, T. *J. Electroanal. Chem.* **2000**, *485*, 49–54.

[18] Grigoriev, V. A.; Cheng, D.; Hill, C. L.; Weinstock, I. A. *J. Am. Chem. Soc.* **2001**, *123*, 5292–5307.

[19] Grigoriev, V. A.; Hill, C. L.; Weinstock, I. A. *J. Am. Chem. Soc.* **2000**, *122*, 3544–3545.

[20] Kirby, J. F.; Baker, L. C. W. *Inorg. Chem.* **1998**, *37*, 5537–5543.

[21] Eberson, L.; Ekström, M. *Acta Chem. Scand. B* **1988**, *42*, 101–112.

[22] Kozik, M.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1986**, *108*, 7627–7630.

[23] Nolan, A. L.; Burns, R. C.; Lawrance, G. A. *J. Chem. Soc., Dalton Trans.* **1998**, 3041–3047.

Electrochemical Measurements. All sample solutions were prepared under Ar, CoW_{12} solutions with at least 0.001 mol L^{-1} $HClO_4$ and PW_{12} solutions with at least 0.2 mol L^{-1} $HClO_4$ to suppress decomposition of the heteropolytungstate species. Cyclic voltammograms (CV) and alternating current voltammograms (ACV) were obtained at variable applied pressure (0−204 MPa, ±1 MPa) at 25.0 ± 0.1 °C, using an EG&G Model 273 potentiostat and Model 5208 lock-in amplifier as described previously.[11,14,24] The counter electrode was Au wire, and the reference electrode was Ag/AgCl/NaCl(satd) (the customary KCl[11,13,14] could not be used with perchlorate or PW_{12} solutions[6]). The Pt wire working electrode used for measurements on the $CoW_{12}^{5-/6-}$ couple at the half-wave potential $E_{1/2} \sim 900$ mV and $PW_{12}^{3-/4-}$ at ~40 mV was cleaned before each pressure cycle by polishing with a suspension of 0.05 μm Al_2O_3, followed by a brief sonication in $K_2S_2O_8$/concentrated H_2SO_4 and then in water. When a Au/Hg working electrode was used, the two-electron $CoW_{12}^{6-}/H_2CoW_{12}^{6-}$ and $H_2CoW_{12}^{6-}/H_4CoW_{12}^{6-}$ couples could also be observed at about −400 and −530 mV, respectively,[6] but variable pressure experiments were not attempted with these highly reducing couples. For PW_{12}, the $PW_{12}^{4-/5-}$ couple[6] was detectable at $E_{1/2} \sim -220$ mV with either Au or Pt working electrodes. In all cases, the average electrochemical transfer coefficient α over a pressure cycle lay between 0.45 and 0.55.

Results

Values of $E_{1/2}$ and the diffusion coefficient D were obtained from CVs, and standard electrode rate constants k_{el} were obtained from ACVs, as described previously.[14,24] Weaver[25] warned that the effects of uncompensated resistance R_u can masquerade as electrode kinetics. Our k_{el} calculations were therefore carefully corrected using experimental R_u values measured at 10 kHz. The R_u values were, however, fairly small (38−178 Ω at 0.1 MPa) and decreased by only about 10% from 0 to 204 MPa, so that the impact of any incomplete correction on $\Delta V_{el}^{\ddagger}$ would be negligible. For pressure cycles (from 0 to 204 MPa and back), only those data sets in which a final $E_{1/2}$ or k_{el} measurement agreed with the initial one at the same pressure (within the experimental uncertainty of ±2 mV in $E_{1/2}$ and ±5% in k_{el}) were accepted. Because $E_{1/2}$ for CoW_{12} increased with both supporting electrolyte concentration (especially for the 2:1 and 3:1 electrolytes) and pressure, the anodic wave maxima in CVs for some 1.0 mol L^{-1} electrolytes encroached upon O_2 evolution potentials, so that D and especially $\Delta V_{diff}^{\ddagger}$ values obtained for 1.0 mol L^{-1} $CaCl_2$ and $Eu(NO_3)_3$ from current maxima in CVs were deemed unreliable. In the ACV technique, a small ac voltage was imposed upon a dc voltage ramp and the ratio of in-phase and 90° out-of-phase was measured to obtain k_{el}; only in cases where this ratio lay between 1.2 and about 5 could reliable k_{el} values be extracted, which meant that for the fastest electrode reactions (RbCl or CsCl > 0.1 mol L^{-1}) only a lower limit of ~0.1 cm s^{-1} could be set. For $[Eu(NO_3)_3] = 0.1$ or 0.2 mol L^{-1} at pH 3, R_u was too high for accurate measurement of k_{el}. Added to these limitations was the low solubility of CoW_{12} when [CsCl] > 0.2 mol L^{-1}. Consequently, there are several gaps in Tables 1−4 and Tables S1 and S2 in the Supporting Information.

Table 1. Half-Wave Potentials $E_{1/2}$/mV[a] at a Pt Electrode for the Aqueous $CoW_{12}O_{40}^{5-/6-}$ Couple Relative to Ag/AgCl/NaCl(satd)

	concn of supporting electrolyte/mol L^{-1}			
medium	0.10	0.20	0.50	1.00
$HClO_4$	877	890	916	939
$HClO_4$[b]	927	933	934	939
NH_4ClO_4[c]	877	888	907	927
$LiClO_4$[c]	870	883	899	914
$NaClO_4$[c]	871	880	895	917
KCl[c]	882	901	916	946
RbCl[c]	885	899	925	943
CsCl[c]	902	912	*d*	*d*
$Mg(ClO_4)_2$[c]	898	905	929	953
$CaCl_2$[c]	902	912	938	962
$Eu(NO_3)_3$[e]	934	939	970	986

[a] At 0.1 MPa, 25.0 °C, $[K_6CoW_{12}] = 1.0$ mmol L^{-1}; from intercepts of $E_{1/2}$ vs P plots, with precision ±2 mV or better; reference electrode ~200 mV vs NHE. [b] Ionic strength adjusted to 1.00 mol L^{-1} with $NaClO_4$. [c] With 0.001 mol L^{-1} $HClO_4$ present. [d] Cs_6CoW_{12} insufficiently soluble. [e] With 0.10 mol L^{-1} $HClO_4$ present.

Table 2. Volumes of Reaction $\Delta V_{Ag/AgCl}$/cm^3 mol^{-1} for the Aqueous $CoW_{12}O_{40}^{5-/6-}$ Couple Relative to Ag/AgCl/NaCl(satd)[a]

	concn of supporting electrolyte/mol L^{-1}			
medium	0.10	0.20	0.50	1.00
HClO4	−23.8 ± 0.9	−22.7 ± 0.8	−19.0 ± 0.7	−17.2 ± 0.8
HClO4[b]	−22.2 ± 0.7	−19.3 ± 0.9	−18.9 ± 0.8	(−17.2 ± 0.8)
NH_4ClO_4[c]	−24.5 ± 0.5	−21.4 ± 0.6	−22.0 ± 0.9	−21.1 ± 1.5
$LiClO_4$[c]	−22.9 ± 1.6	−23.6 ± 0.5	−22.8 ± 0.9	−25.3 ± 0.9
$NaClO_4$[c]	−24.5 ± 1.0	−24.4 ± 1.1	−22.7 ± 0.8	−24.2 ± 0.4
KCl[c]	−24.3 ± 0.9	−22.5 ± 1.1	−22.5 ± 1.0	−23.4 ± 0.5
RbCl[c]	−23.2 ± 0.6	−21.8 ± 1.2	−21.5 ± 1.1	−22.7 ± 2.0
CsCl[c]	−21.4 ± 0.7	−23.5 ± 1.5	*d*	*d*
$Mg(ClO_4)_2$[c]	−22.7 ± 0.9	−21.8 ± 1.7	−19.5 ± 1.1	−22.3 ± 1.0
$CaCl_2$[c]	−23.0 ± 1.1	−22.6 ± 1.0	−23.1 ± 1.0	−22.0 ± 1.0
$Eu(NO_3)_3$[e]	−19.6 ± 0.8	−20.0 ± 0.6	−19.6 ± 0.9	−18.5 ± 1.0

[a] At 0−204 MPa, 25.0 °C, $[K_6CoW_{12}] = 1.0$ mmol L^{-1}; from linear $E_{1/2}$ vs P regression. [b] Ionic strength adjusted to 1.00 mol L^{-1} with $NaClO_4$. [c] With 0.001 mol L^{-1} $HClO_4$ present. [d] Cs_6CoW_{12} insufficiently soluble. [e] With 0.10 mol L^{-1} $HClO_4$ present.

Table 3. Standard Electrode Reaction Rate Constants $k_{el}/10^{-2}$ cm s^{-1} for the Aqueous $CoW_{12}O_{40}^{5-/6-}$ Couple[a]

	concn of supporting electrolyte/mol L^{-1}			
medium	0.1	0.2	0.5	1.0
$HClO_4$		1.8 ± 0.1	1.8 ± 0.1	*b*
$HClO_4$[c]	1.6 ± 0.1	1.0 ± 0.1	1.6 ± 0.1	(*b*)
NH_4ClO_4[d]	0.8 ± 0.1			
$LiClO_4$[d]			0.8 ± 0.1	
$NaClO_4$[d]			0.7 ± 0.1	0.7 ± 0.1
KCl[d]	0.9 ± 0.1	1.6 ± 0.1	2.8 ± 0.1	9.9 ± 0.6
RbCl[d]	2.5 ± 0.1	≥10[e]	>10[e]	>10[e]
CsCl[d]	8.3 ± 0.1	>10[e]	*f*	*f*
$CaCl_2$[d]	0.8 ± 0.1			
$Eu(NO_3)_3$[g]			1.5 ± 0.1	

[a] At 0.1 MPa, 25.0 °C, $[K_6CoW_{12}] = 1.0$ mmol L^{-1}; from intercepts of ln k_{el} vs P plots. [b] Visible degeneration of electrode surface. [c] Ionic strength adjusted to 1.00 mol L^{-1} with $NaClO_4$. [d] With 0.001 mol L^{-1} $HClO_4$ present. [e] Too fast for accurate measurement by ACV. [f] Cs_6CoW_{12} insufficiently soluble. [g] With 0.10 mol L^{-1} $HClO_4$ present.

Within the limits of experimental uncertainty, $E_{1/2}$, ln D, and ln k_{el} were found to be linear functions of the pressure (as exemplified by Figure 1), the slopes of which therefore gave, respectively, mean values of the volume of reaction relative to Ag/AgCl/NaCl(satd)$\Delta V_{Ag/AgCl}$

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(24) Fu, Y.; Cole, A. S.; Swaddle, T. W. *J. Am. Chem. Soc.* **1999**, *121*, 10410−10415.

(25) Weaver, M. J. *Chem. Rev.* **1992**, *92*, 463−480.

Table 4. Volumes of Activation $\Delta V_{el}^{\ddagger}$/cm^3 mol^{-1} for the Aqueous $CoW_{12}O_{40}^{5-/6-}$ Electrode Reaction[a]

	concn of supporting electrolyte/mol L^{-1}			
medium	0.1	0.2	0.5	1.0
$HClO_4$		4.4 ± 0.7	3.7 ± 0.6	*b*
$HClO_4$[c]	5.3 ± 0.4	5.8 ± 0.5	4.4 ± 0.7	(*b*)
NH_4ClO_4[d]	6.5 ± 0.5			
$LiClO_4$[d]			6.2 ± 0.3	
$NaClO_4$[d]			11.1 ± 0.8	10.4 ± 0.5
KCl[d]	15.1 ± 0.7	13.1 ± 0.6	11.7 ± 0.3	12.0 ± 1.3
RbCl[d]	13.7 ± 1.0	*e*	*e*	*e*
CsCl[d]	12.0 ± 0.3	*e*	*f*	*f*
$CaCl_2$[d]	10.6 ± 1.1			
$Eu(NO_3)_3$[g]			2.6 ± 0.4	

[a] At 0−204 MPa, 25.0 °C, $[K_6CoW_{12}] = 1.0$ mmol L^{-1}; from slopes of ln k_{el} vs P plots. [b] Visible degeneration of electrode surface. [c] Ionic strength adjusted to 1.00 mol L^{-1} with $NaClO_4$. [d] With 0.001 mol L^{-1} $HClO_4$ present. [e] Too fast for accurate measurement by ACV. [f] Cs_6CoW_{12} insufficiently soluble. [g] With 0.10 mol L^{-1} $HClO_4$ present.

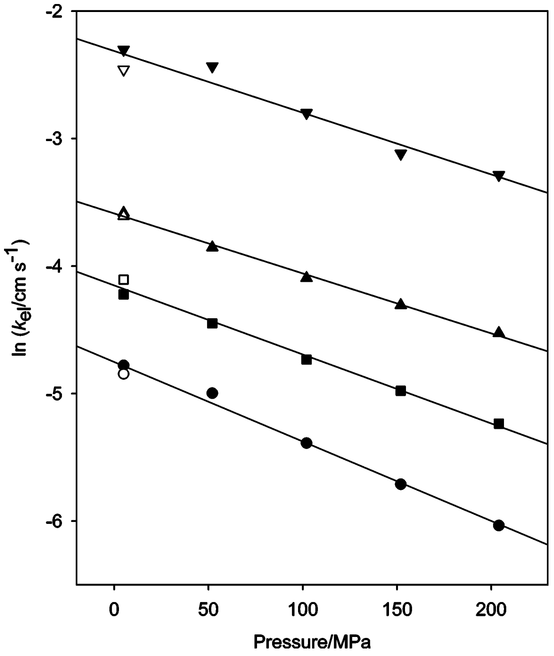

Figure 1. Pressure and supporting electrolyte concentration dependences of rate constants k_{el} for the $CoW_{12}O_{40}^{5-/6-}$ electrode reaction in aqueous KCl at 25.0 °C. [KCl] = 0.10 (●), 0.20 (■), 0.50 (▲), and 1.00 (▼) mol L^{-1}; hollow symbols represent return to low pressure after the pressure cycle. $[K_6CoW_{12}O_{40}] = 1.0$ mmol L^{-1}.

($= -F(\partial E_{1/2}/\partial P)_T$), the volume of activation for diffusion $\Delta V_{diff}^{\ddagger}$ ($= -RT(\partial \ln D/\partial P)_T$), and the volume of activation $\Delta V_{el}^{\ddagger}$ ($= -RT(\partial \ln k_{el}/\partial P)_T$) of the electrode reaction for the aqueous $CoW_{12}O_{40}^{5-/6-}$ couple, over the pressure range 0−204 MPa. Error limits given in this article are standard deviations.

12-Tungstocobaltate. Table 1 shows that $E_{1/2}$ becomes more positive as the concentration of a particular supporting electrolyte increases, and tends to be higher with multiply charged cations. The volumes of reaction $\Delta V_{Ag/AgCl}$, however, show no clear trends (Table 2), although the $HClO_4$ data become slightly more positive with increasing $HClO_4$ content, even at constant ionic strength I, and the $Eu(NO_3)_3$ results are about 2 cm^3 mol^{-1} more positive than the overall average, which is −22.0 ± 1.9 cm^3 mol^{-1}.

Table 5. Half-Wave Potentials and Volumes of Reaction for the Aqueous $PW_{12}O_{40}^{3-/4-}$ and $PW_{12}O_{40}^{4-/5-}$ Couples Relative to Ag/AgCl/NaCl(satd)[a]

couple	$[HClO_4]$/ mol L^{-1}	$[LiClO_4]$/ mol L^{-1}	$E_{1/2}$[b]/mV	$\Delta V_{Ag/AgCl}$[c]/ cm^3 mol^{-1}
$PW_{12}O_{40}^{3-/4-}$	1.0	0.0	32 ± 1[d]	−16.4 ± 0.7[d]
	0.2	0.8	40 ± 1[e]	−13.5 ± 0.4[e]
$PW_{12}O_{40}^{4-/5-}$	0.2	0.8	−218 ± 2[e]	−25.5 ± 0.5[e]

[a] At 25.0 °C; each entry is the average of two experiments. [b] At 0.1 MPa. [c] At 0−202 MPa. [d] At Au electrode; $[H_3PW_{12}] = 2.2$ mmol L^{-1}. [e] At Pt electrode; $[H_3PW_{12}] = 1.0$ mmol L^{-1}.

For 1:1 supporting electrolytes and $Mg(ClO_4)_2$, the mean diffusion coefficients D for the CoW_{12} complexes show no significant variation with the concentration of the supporting electrolyte and only a slight variation with its identity, ranging from 1.9×10^{-6} to 2.7×10^{-6} cm^2 s^{-1} in the sequence $LiClO_4 < NaClO_4 < KCl \approx HClO_4 \approx NH_4ClO_4 \approx Mg(ClO_4)_2 < RbCl < CsCl$ with an average of $(2.4 \pm 0.3) \times 10^{-6}$ cm^2 s^{-1}. For the electrolytes $CaCl_2$ and $Eu(NO_3)_3$ up to 0.5 mol L^{-1}, D averaged 1.6×10^{-6} and 1.7×10^{-6} cm^2 s^{-1}, respectively. In all cases, the dependence of D on pressure was slight, and $\Delta V_{diff}^{\ddagger}$ showed no systematic variations with the electrolytes, averaging −0.9 ± 1.1 cm^3 mol^{-1}. Details are given in Tables S1 and S2 (Supporting Information).

As is commonly found,[13] the standard (i.e., zero overpotential) electrode reaction rate constants k_{el} (Table 3) were dependent to some degree on the nature and history of the working electrode surface, but because these factors are insensitive to pressures in the 0−200 MPa range, $\Delta V_{el}^{\ddagger}$ values (Table 4) generally showed good reproducibility. The values of k_{el} at 0.1 MPa listed in Table 3 were obtained from linear least-squares regressions of ln k_{el} on P, and the error limits cited are the corresponding standard deviations rather than a measure of reproducibility from run to run, which was sometimes as poor as ±60%. For some runs (0.1 and 1.0 mol L^{-1} $HClO_4$, 0.1 mol L^{-1} $Mg(ClO_4)_2$) data scatter over the pressure cycle was excessive; for 1.0 mol L^{-1} $HClO_4$, the problem was associated with the visible degradation of the working electrode surface over the course of the measurements. In such cases, no k_{el} or $\Delta V_{el}^{\ddagger}$ value is reported. Nevertheless, it is evident from Table 3 that k_{el} increases in the order $Li^+ \sim Na^+ < K^+ < Rb^+ \ll Cs^+$ for a given cation concentration, and with increasing electrolyte concentration for K^+ at least. Multiply charged cations showed no significant rate enhancement relative to H^+, Li^+, or Na^+.

12-Tungstophosphate. Solubility and hydrolysis limited studies of the $PW_{12}^{3-/4-}$ and $PW_{12}^{4-/5-}$ electrode reactions to $[H^+] > 0.1$ mol L^{-1} and Li^+ as the only other cation in high concentration. Even so, no reproducible diffusion coefficients or rate constants could be obtained for either couple. Nevertheless, $E_{1/2}$ was accurately reproducible between experiments, as was its linear dependence on pressure. Values of $E_{1/2}$ at atmospheric pressure and $\Delta V_{Ag/AgCl}$ were obtained from regressions of $E_{1/2}$ on P and are listed in Table 5. The $E_{1/2}$ data at 0.1 MPa are in good agreement with those of Pope and Varga,[6] allowing for the different medium (1.0 mol L^{-1} sulfate) and reference electrode.

Discussion

Potentials. Table 1 shows that the half-wave potentials $E_{1/2}$ for the $CoW_{12}{}^{5-/6-}$ couple become more positive with increasing electrolyte concentration and cationic charge, and (for alkali metal counterions) with decreasing *hydrated* anion–cation contact distances as inferred from activity coefficients for aqueous alkali metal halides (contact distance LiX > NaX > KX > RbX > CsX).[26] The much-reduced upward trend in $E_{1/2}$ with $[H^+]$ for the various $HClO_4/NaClO_4$ mixtures with constant $I = 1.0$ mol L^{-1} implies that this is primarily an ionic strength effect. In accordance with this interpretation, $E_{1/2}$ is higher for the 2+ and especially the 3+ cations at a given concentration C, since $I = C$, $3C$, and $6C$ for 1:1, 2:1, and 3:1 electrolytes, respectively. The effect, however, is not large, and detailed analysis with (for example) extended Debye–Hückel theory is not warranted in this concentration regime, but the observations can be understood qualitatively on the basis of CoW_{12}–cation interactions, implicit in the theory, which will stabilize the more highly charged $Co^{II}W_{12}{}^{6-}$ anion relative to $CoW_{12}{}^{5-}$.

Diffusion Coefficients. The lack of any substantial dependence of the diffusion coefficients D on pressure (average $\Delta V_{diff}{}^{\ddagger} = -0.9 \pm 1.1$ cm^3 mol^{-1}) is attributable through the Stokes–Einstein relation ($D = k_BT/6\pi\eta a$, where a is the radius of the diffusing particle and η is the viscosity of the medium) to the fact that, at near-ambient temperatures, the viscosity of water is very nearly independent of pressure.[24] This arises because the pressure-induced breakup of vestigial ice-I-like structure in liquid water fortuitously compensates the increase in viscosity expected for normal liquids due to the loss of free volume. The absence of any marked dependence of D on the nature or concentration of the supporting electrolyte except for Ca^{2+} and Eu^{3+} (for which $D \sim 30\%$ lower than the average for the others) suggests that CoW_{12}–cation ion pairing is not very far advanced for the alkali metal cations, in accordance with the characterization of the polyoxometalate ion as interacting only weakly with other species in solution.[4,15] Ion pairing should increase the apparent hydrodynamic radius a of a polyoxometalate ion and so reduce D, but ion pair formation constants for polyoxometalates with alkali metal ions in aqueous–organic mixtures are known[18,19] to increase in the order $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$, and this is the opposite of the (albeit slight) trend in D seen in Table S1.

Reaction Volumes. The absence of significant variation of the $\Delta V_{Ag/AgCl}$ data for $CoW_{12}{}^{5-/6-}$ in Table 2 with supporting electrolyte concentration or type echoes the findings for cyanometalate couples,[13] and implies once again that ion pairing is not extensive in the media used here. We have demonstrated that $\Delta V_{Ag/AgCl}$ is the same for Ag/AgCl reference cells containing saturated NaCl (used in this work) as for 4.0 mol L^{-1} KCl,[13] so that $\Delta V_{Ag/AgCl}$ values in Tables 2 and 5 may be compared directly with those tabulated in ref 13. Tregloan et al.[13,27] have proposed, on the basis of the Born and Drude–Nernst solvation models, that $\Delta V_{Ag/AgCl}$ for one-electron reductions of a series of related couples such as $Fe(CN)_{6-2x}(phen)_x{}^{(2x-3)/(2x-4)}$ should be a linear function of $\Delta(z^2)/r$, where $\Delta(z^2)$ is the change in the square of the charge number of the electroactive species in a one-electron reduction and r is its effective radius:

$$\Delta V_{Ag/AgCl} = \Delta V_{ref} + B\Delta(z^2/r) \tag{1}$$

In eq 1, B is a positive constant at a given pressure ($=(N_Ae^2/8\pi\epsilon_0\epsilon)(\partial \ln \epsilon/\partial P)_T$, where ϵ is the relative permittivity of the medium), ΔV_{ref} is the contribution of the reference electrode to the reaction volume (inferred[13] to be -9 cm^3 mol^{-1} for Ag/AgCl/KCl(4.0 mol L^{-1}) in water), and the second term on the right represents the contribution of change in solvent electrostriction. Qualitatively, then, we would expect $\Delta V_{Ag/AgCl}$ for $PW_{12}{}^{4-/5-}$ ($\Delta(z^2) = -9$) to be more negative than that for $PW_{12}{}^{3-/4-}$ ($\Delta(z^2) = -7$), and this is correct (Table 5). However, $\Delta V_{Ag/AgCl}$ for $CoW_{12}{}^{5-/6-}$ ($\Delta(z^2) = -11$) should be more negative again, given that the effective radii of CoW_{12} and PW_{12} in water are both considered to be about 560 pm,[4] whereas its actual average value (-23 cm^3 mol^{-1}) lies between the two PW_{12} values. Moreover, taking the radius of $Fe(CN)_6{}^{3-}$ to be about 440 pm,[10] we would expect $\Delta V_{Ag/AgCl}$ for $CoW_{12}{}^{5-/6-}$ to be even more negative than that for $Fe(CN)_6{}^{3-/4-}$ (average about -36 cm^3 mol^{-1} [13]), but it is some 13 cm^3 mol^{-1} more positive. In any event, use of a theoretical value of B (which is pressure dependent) gives electrostrictive contributions that are too small. It may be concluded that the Born–Drude–Nernst concept of solvent electrostriction may account qualitatively for the trend in reaction volumes for successive reductions of a particular solute, but that eq 1 fails either because r is not a physically meaningful parameter or because, at the very least, additional terms are needed.

Electrode Reaction Kinetics. Bearing in mind the poor reproducibility of values of k_{el} between different runs because of the variability of the electrode surface, we can deduce from Table 3 that k_{el} is roughly the same, and not significantly dependent on cation concentration, for $NH_4{}^+$, Li^+, Na^+, and Ca^{2+}, and is somewhat higher for H^+ and Eu^{3+}. The data for $HClO_4$, with and without addition of $NaClO_4$ to maintain constant ionic strength I, imply that I is not a significant variable in this context (unfortunately, reliable data could not be obtained for 1.0 mol L^{-1} H^+). Comparison of the entries in Table 3 for Na^+, Ca^{2+}, and Eu^{3+} shows that variation of cationic charge at approximately constant crystallographic cation radius (106 pm[28]) is also unimportant; hence it seems unlikely that CoW_{12}–cation pairing affects k_{el} significantly in water (contrast the demonstrated importance of ion pairing of polyoxometalates with group 1 cations in aqueous–organic media[18,19]). However, k_{el} rises substantially with rising [KCl], and also in the sequence $Na^+ < K^+ < Rb^+ < Cs^+$, indicating a definite cation-specific enhancement of the electron-transfer rate for the heavier alkali metal ions. Enhancements of the rates of *electrode* reactions of

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[26] Sørensen, T. S.; Sloth, P.; Schrøder, M. *Acta Chem. Scand. A* **1984**, *38*, 735–756.

[27] Sachinidis, J. I.; Shalders, R. D.; Tregloan, P. A. *Inorg. Chem.* **1994**, *26*, 6180–6186.

[28] Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751–767.

cyanometalates by cations have been noted by several authors,[11,29−34] but this appears to be the first such report for polyoxometalates.

Taking the data of Table 3 as a whole, it seems unlikely that this rate enhancement could arise from simple Coulombic effects of the supporting electrolytes on the electrode surface or double layer. Instead, a specific catalytic effect of the partially (or possibly wholly) dehydrated heavier group 1 cations may be invoked, as in the case of various cyanometalates,[11−14,35] and may be linked to the ease of dehydration of these cations relative to the others in Table 3.[36] Dogonadze et al.[35] suggested that dehydration of the heavier group 1 cations aids their role as anion−anion bridges for electron transfer by exposing the more polarizable core ions. The lack of strong catalytic activity by the multiply charged cations (Table 3), which are more energetically hydrated than the alkali metal ions, supports the dehydration hypothesis and makes it clear that the catalysis is not due to simple CoW_{12}−cation pairing as such (indeed, as noted above, no signs of significant ion pairing emerged in this aqueous study—the ion pairing detected by Grigoriev et al.[18,19] occurred in aqueous *tert*-butyl alcohol). Further evidence for the dehydration mechanism comes from the strongly positive values of $\Delta V_{el}^{\ddagger}$ associated with the Na^+, K^+, Rb^+, and Cs^+ supporting electrolytes (Table 4), since dehydration, partial or otherwise, of aqueous cations results in a net expansion of the system.[37] Consistent with the dehydration concept, $\Delta V_{el}^{\ddagger}$ at constant $[M^+]$ declines slightly with the crystallographic cation radius in the sequence $Cs^+ > Rb^+ > K^+$.[37] In fact, *all* the $\Delta V_{el}^{\ddagger}$ values of Table 4 are positive to some degree, whereas for simple electrode reactions of cationic couples in water $\Delta V_{el}^{\ddagger}$ is invariably *negative* as theory predicts.[14,24] Thus, a cation-modulated mechanism of anion−anion electron transfer probably operates with greater or lesser effectiveness for all the supporting electrolytes studied here. The positive values of $\Delta V_{el}^{\ddagger}$ cannot be attributed to rate control by solvent dynamics, which would lead to $\Delta V_{el}^{\ddagger} \leq \Delta V_{diff}^{\ddagger}$,[24,38] i.e., to $\Delta V_{el}^{\ddagger}$ no more positive than -0.9 ± 1.1 cm^3 mol^{-1} for these aqueous systems.

Regardless of interpretation, the empirical observation emerges that, for electrode reactions of aqueous anionic couples such as cyanometalates and CoW_{12} alike, k_{el} is subject to counterion catalysis and $\Delta V_{el}^{\ddagger}$ is invariably positive, in the presence of necessary concentrations of supporting electrolytes and H^+. In contrast, for aqueous cationic couples, k_{el} shows little influence of the nature of the counterion and $\Delta V_{el}^{\ddagger}$ is always negative.[13,14,24] Unfortunately, because of the need to maintain acidities of at least 1 mmol L^{-1} to suppress hydrolysis of CoW_{12}, it may not be feasible to examine the CoW_{12} electrode kinetics in the absence of supporting electrolyte in the manner of Lee and Anson,[39] who found a "very pronounced inhibition" of the reduction of $Fe(CN)_6^{3-}$ at a microelectrode in the presence of little or no supporting electrolyte. In retrospect, the much less familiar $AlW_{12}O_{40}^{5-/6-}$ Keggin couple,[40−42] which is stable in neutral as well as acidic aqueous media, might have been a more appropriate choice for the present study than either CoW_{12} or PW_{12}, given the objectives stated above, and accordingly work on the 12-tungstoaluminate system is now under way in our laboratory.

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Supporting Information Available: Tables of diffusion coefficients and activation volumes for diffusion. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) Sohr, R.; Müller, L.; Landsberg, R. *Electroanal. Chem. Interfacial Electrochem.* **1974**, *50*, 55−63.

(30) Bindra, P.; Gerischer, H.; Peter, L. M. *Electroanal. Chem. Interfacial Electrochem.* **1974**, *57*, 435−438.

(31) Sohr, R.; Müller, L. *Electrochim. Acta* **1975**, *20*, 451−455.

(32) Peter, L. M.; Dürr, W.; Bindra, P.; Gerischer, H. *J. Electroanal. Chem.* **1976**, *71*, 31−50.

(33) Campbell, S. A.; Peter, L. M. *J. Electroanal. Chem.* **1994**, *364*, 257−260.

(34) Krulic, D.; Fatouros, N.; Khoshtariya, D. E. *J. Chim. Phys.* **1998**, *95*, 497−512.

(35) Dogonadze, R. R.; Ulstrup, J.; Kharkats, Yu. I. *Electroanal. Chem. Interfacial Electrochem.* **1972**, *39*, 47−61.

(36) Marcus, Y. *Ion Properties*; Marcel Dekker: New York, 1997; pp 120−129.

(37) Swaddle, T. W. *Inorg. Chem.* **1983**, *22*, 2663−2665.

(38) Zhou, J.; Swaddle, T. W. *Can. J. Chem.* **2001**, *79*, 841−847.

(39) Lee, C.; Anson, F. C. *J. Electroanal. Chem.* **1992**, *323*, 381−389.

(40) Cowan, J. J.; Hill, C. L.; Reiner, R. S.; Weinstock, I. A. *Inorg. Synth.* **2002**, *33*, 18.

(41) Cowan, J. J.; Bailey, A. J.; Heintz, R. A.; Do, B. T.; Hardcastle, K. I.; Hill, C. L.; Weinstock, I. A. *Inorg. Chem.* **2001**, *40*, 6666.

(42) Weinstock, I. A.; Cowan, J. J.; Barbuzzi, E. M. G.; Zeng, H.; Hill, C. L. *J. Am. Chem. Soc.* **1999**, *121*, 4608.