792 *Inorg. Chem.* **1989**, *28*, 792-797

Contribution from the Departments of Chemistry, University of Victoria,
Victoria, BC V8W 2Y2, Canada, and University of Oregon, Eugene, Oregon 97403

Rapid, High-Resolution, Reversed-Phase HPLC Separation of Highly Charged Polyoxometalates Using Ion-Interaction Reagents and Competing Ions

A. D. Kirk,*,† W. Riske,† D. K. Lyon,‡ B. Rapko,‡ and R. G. Finke*,‡

Received July 22, 1988

Reversed-phase liquid chromatography, using ion-interaction reagents to promote retention and citrate ion as a competing ion to avoid tailing, is shown to result in excellent and rapid separations of highly charged polyoxometalate ions such as $PW_{11}VO_{40}^{4-}$, $PW_{10}V_2O_{40}^{5-}$, $PW_9V_3O_{40}^{6-}$, or $P_2W_{18}Zn_4(OH_2)_2O_{68}^{10-}$. Until now, HPLC has been a much needed but unavailable tool in polyoxometalate chemistry. Separation of a mixture of polyoxometalates, such as the above with charges ranging from 4– to 10–, can be achieved within 15 min by using a water/methanol gradient; for all components, the eluted peaks were close to Gaussian shape with little evidence of tailing. The present method has the major advantage of considerable flexibility. For example, the number of alkyl chains and the alkyl chain length of the ion-interaction reagent, $R_{4-x}NH_x^+$, as well as the solvent composition, can be, and have been, varied to increase or decrease retention times. Furthermore, the pH and the nature and concentration of the competing ion are also flexible parameters, providing the method with considerable potential for further development.

Introduction

Polyoxometalate chemistry[1] is an important subarea of modern inorganic chemistry with applications ranging from those in catalysis,[2] oxidation chemistry,[2] photochemistry,[3] and electron microscopy[4] to those involving polyoxometalates as inorganic drugs.[5] Crucial to the rapid development of polyoxometalate chemistry has been the concurrent development and application of modern methods of identification and characterization, notably 1- and 2-D ^{183}W NMR[6] or FAB mass spectroscopy.[7] However, work in polyoxometalate chemistry has been greatly frustrated by the lack of more generally applicable chromatographic tools, such as high-pressure liquid chromatography (HPLC). A few scattered reports of chromatography of certain subclasses of polyoxometalates have appeared,[8] but general chromatographic methods,[8c,9] and specifically HPLC, were essentially unavailable previously, as either analytical or preparative tools. Without these, one is left with crystallization as the sole method to ensure sample homogeneity. This in turn has tended to restrict the development of polyoxometalate polyanion chemistries (and presumably some other polyanion and polycation chemistries) to only those cases that readily crystallize, a debilitating and intolerable restriction.

Herein we report the results of our successful reversed-phase HPLC separation of polyoxometalates by charge type, including successful HPLC separation of the 10– ion $P_2W_{18}Zn_4(OH_2)_2O_{68}^{10-}$, thereby opening the door for further development of this much needed tool. None of these results have been reported elsewhere, and full details are reported herein to assist others who wish to use this valuable tool. These results extend significantly our recent findings where triply charged anions, $Co(CN)_5X^{3-}$ (X = I, Br, Cl, CN), were successfully separated.[10]

Results and Discussion

The structures of $PW_{12-x}V_xO_{40}^{-3-x}$, and the numbering system used for the 1,2- and 1,4-$PW_{10}V_2O_{40}^{5-}$ isomers and for the 1,2,3- and 1,4,9-$PW_9V_3O_{40}^{6-}$ isomers, are shown in Figure 1.[1c] The structures of $P_2W_{18}Zn_4(OH_2)_2O_{68}^{10-}$ and $P_4W_{30}Zn_4(OH_2)_2O_{112}^{16-}$, displayed as their coordination polyhedral models composed of edge- and corner-sharing octahedra, are shown in Figure 2. The important feature for the present work is that they form a series of heteropoly oxometalates of overall polyanionic charge ranging from 3– to 16–. However, it is important to realize that the overall charges shown overemphasize the surface charge density present. For example, writing $PW_{12}O_{40}^{3-}$ in a way that *under*emphasizes the surface charge density (and which illustrates the central PO_4^{3-} group shown in Figure 1) yields $(PO_4)^{3-}(W_{12}O_{36})^0$, a formulation that explains why the surface charge density of "$PW_{12}O_{40}^{3-}$" in fact approaches that of ClO_4^-.[11] Similarly, $PW_{11}VO_{40}^{4-}$, $PW_{10}V_2O_{40}^{5-}$, $PW_9V_3O_{40}^{6-}$, $P_2W_{18}Zn_4(OH_2)_2O_{68}^{10-}$, and $P_4W_{30}Zn_4(OH_2)_2O_{112}^{16-}$ can be rewritten respectively as

---

† University of Victoria.

‡ University of Oregon.

(1) (a) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: New York, 1983. (b) Day, V. W.; Klemperer, W. G. *Science* (*Washington, D.C.*) **1985**, *228*, 533. (c) The numbering system used herein for the $PW_{12-x}V_xO_{40}^{-x-3}$ isomers (as shown in Figure 1) is that employed in the recent literature.[20] It differs from recent IUPAC recommendations[1d] (see also the Appendix, pp 142–146, of ref 1a) but was chosen here to minimize confusion. (d) Jeannin, Y.; Fournier, M. *Pure Appl. Chem.* **1987**, *59*, 1529.

(2) For a few lead references using polyoxometalates in catalysis as soluble metal oxide (catalyst support) analogues,[2a] in Wacker-type chemistry,[2b] in oxygenation or other oxidation chemistries,[2c] and in the solid state,[2d] see: (a) Finke, R. G.; Edlund, D. J.; Lyon, D. K.; Nomiya, K. Submitted for publication in *J. Am. Chem. Soc.* Finke, R. G.; Rapko, B.; Domaille, P. J. *Organometallics* **1986**, *5*, 175. Finke, R. G.; Droege, M. W. *J. Am. Chem. Soc.* **1984**, *106*, 7274. (b) Ogawa, H.; Fujinami, H.; Taya, K. *J. Chem. Soc., Chem. Commun.* **1981**, 1274. Taraban'ko, V. E.; Kozhevenikov, I. V.; Matreev, K. I. *Kinet. Katal.* **1978**, *19*, 1160. Kozhevenikov, I. V.; Matreev, K. I. *Appl. Catal.* **1983**, *5*, 135; *Russ. Chem. Rev.* (*Engl. Trans.*) **1982**, *51*, 1075. (c) Katsoulis, D. E.; Pope, M. T. *J. Am. Chem. Soc.* **1984**, *106*, 2737. Katsoulis, D. E.; Pope, M. T. *J. Chem. Soc., Chem. Commun.* **1986**, 1186. Hill, C. L.; Brown, R. B., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 536. Faraj, M.; Hill, C. L. *J. Chem. Soc., Chem. Commun.* **1987**, 1487. Venturello, C.; Alneri, E.; Ricci, M. *J. Org. Chem.* **1983**, *48*, 3831. Venturello, C.; D'Aloisio, R.; Bart, J. C. J.; Ricci, M. *J. Mol. Catal.* **1985**, *32*, 107. Venturello, C.; D'Aloisio, R. *J. Org. Chem.* **1988**, *53*, 1553. (d) Moffat, J. B. In *Preparation of Catalysts IV*; Delmon, P., Grange, P., Jacobs, P. A.; Poncelet, G., Eds.; Elsevier: Amsterdam, 1987; p 241. Moffat, J. B. In *Catalysis on the Energy Scene*; Kaliaguine, S., Mahay, A., Eds.; Elsevier: Amsterdam, 1984; p 165. Misono, M.; Okuhara, T.; Ichiki, T.; Arai, T.; Kanda, Y. *J. Am. Chem. Soc.* **1987**, *109*, 5535. Misono, M.; Mizuno, N.; Katamura, K.; Kasai, A.; Konishi, Y.; Sakata, K.; Okuhara, T.; Yoneda, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 400. Saito, Y.; Niiyama, H. *J. Catal.* **1987**, *106*, 329. Black, J. B.; Scott, J. D.; Serwicka, E. M.; Goodenough, J. B. *J. Catal.* **1987**, *106*, 16.

(3) For lead references, see: (a) Papaconstantinou, E. *J. Chem. Soc., Chem. Commun.* **1982**, 12. (b) Yamase, T. *Inorg. Chim. Acta* **1983**, *76*, L25; **1981**, *54*, L207. Yamase, T.; Sasaki, R.; Ikawa, T. *J. Chem. Soc., Dalton Trans.* **1981**, 628. Yamase, T. *J. Chem. Soc., Dalton Trans.* **1987**, 1597. (c) Akid, R.; Darwent, J. R. *J. Chem. Soc., Dalton Trans.* **1985**, 395. (d) Hill, C. L.; Bouchard, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 5148. Renneke, R. F.; Hill, C. L. *J. Am. Chem. Soc.* **1986**, *108*, 3528. Prosser-McCartha, C. M.; Kadkhodayan, M.; Williamson, M. W.; Bouchard, D. A.; Hill, C. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1747. Renneke, R. F.; Hill, C. L. *J. Am. Chem. Soc.* **1988**, *110*, 5646. Hill, C. L.; Bouchard, D. A.; Kadkhodayan, M.; Williamson, M. W.; Schmidt, J. A.; Hilinski, E. F. *J. Am. Chem. Soc.* **1988**, *110*, 5471. Williamson, M. W.; Bouchard, D. A.; Hill, C. L. *Inorg. Chem.* **1987**, *26*, 1436 and references therein. (e) Fox, M. A.; Cardona, R.; Gaillard, G. *J. Am. Chem. Soc.* **1987**, *109*, 6347. (f) Ballardini, R.; Mulazzani, Q. G.; Venturi, M.; Bolletta, F.; Balzani, V. *Inorg. Chem.* **1984**, *23*, 300.

(4) (a) Zonnevijlle, F.; Pope, M. T. *J. Am. Chem. Soc.* **1979**, *101*, 2731. Mann, S.; Williams, R. J. P.; Sethuraman, P. R.; Pope, M. T. *J. Chem. Soc., Chem. Commun.* **1981**, 1083. (b) Keana, J. F. W.; Ogan, M. D.; Lü, Y.; Beer, M.; Varkey, J. *J. Am. Chem. Soc.* **1985**, *107*, 6714. Keana, J. F. W.; Ogan, M. D. *J. Am. Chem. Soc.* **1986**, *108*, 7951. Keana, J. F. W.; Ogan, M. D.; Lü, Y.; Beer, M.; Varkey, J. *J. Am. Chem. Soc.* **1986**, *108*, 7956.

0020-1669/89/1328-0792$01.50/0

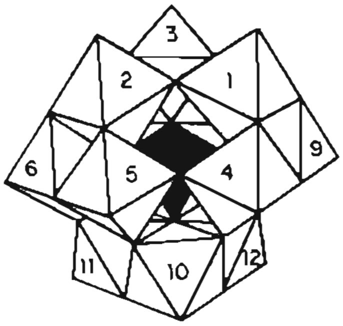


Figure 1. Coordination polyhedral representation of the Keggin polyoxometalate polyanion $PW_{12}O_{40}^{3-}$ ($=(PO_4)^{3-}(W_3O_9)_4{}^0$) showing the central PO_4^{3-} tetrahedron in black and the four W_3O_9 triads composed of edge-sharing WO_6 octahedra. The $PW_{12-x}V_xO_{40}^{-3-x}$ derivatives are formed by replacement of the indicated W (e.g. in 1,2-$PW_{10}V_2O_{40}^{5-}$ the 1-W and 2-W) by V.

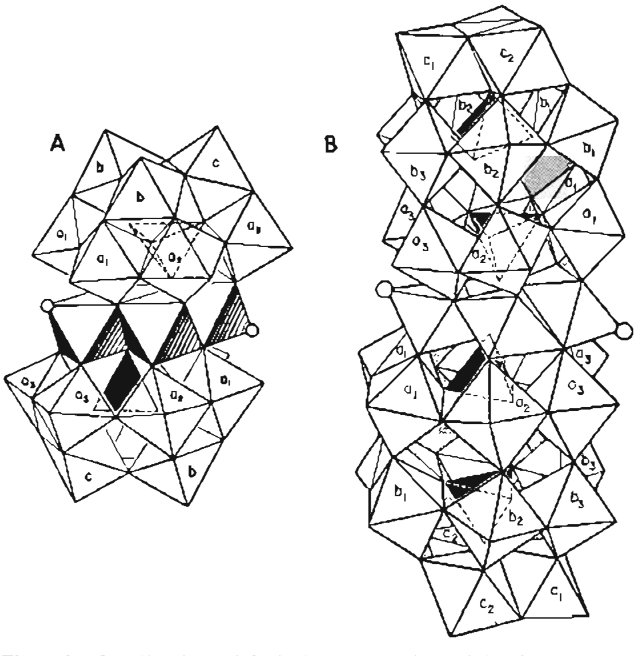


Figure 2. Coordination polyhedral representations of the C_{2h} symmetry structures of (A) $P_2W_{18}Zn_4(OH_2)_2O_{68}^{10-}$ with its two "PW_9" halves and four central ZnO_6 octahedra and (B) $P_4W_{30}Zn_4(OH_2)_2O_{112}^{16-}$ with its two "P_2W_{15}" halves and four central ZnO_6 octahedra. The circles on two of the ZnO_6 octahedra indicate the positions of the two constitutional waters. The a, a_1, a_2, b, b_1, b_2, c (and so on) labels indicate the C_{2h} symmetry equivalent and inequivalent types of W atoms.

$(PO_4)^{3-}(W_{11}VO_{36})^-$, $(PO_4)^{3-}(W_{10}V_2O_{36})^{2-}$, $(PO_4)^{3-}(W_9V_3O_{36})^{3-}$, $(PO_4{}^{3-})_2{}^{6-}(W_{18}Zn_4(OH_2)_2O_{60})^{4-}$, and $(PO_4{}^{3-})_4{}^{12-}(W_{30}Zn_4(OH_2)_2O_{96})^{4-}$. This is one reason why we anticipated the HPLC separation methods developed for $Co(CN)_5X^{3-}$ would extend to many polyoxometalates. We note that because the previous $Co(CN)_5X^{3-}$ studies were worked out at pH = 6.5,[10] this pH was chosen for this initial work aimed at demonstrating whether or not polyoxometalate separations by reversed-phase HPLC were possible. Eventually, one would like HPLC columns and conditions (e.g. competing ions) that would allow the use of a wide range of pH (e.g. pH ~ 1 to pH ≥ 10).

It is also useful to briefly mention here, before we describe our own results, how reversed-phase HPLC with ion-interaction reagents is thought to work. A dynamic, double layer[12] [analogous to the electrical "double layer" (or more exactly *multilayer*[12c,d]) found at electrode surfaces] is thought to be formed when hy-

---

(5) Rozenbaum, W.; Dormont, D.; Spire, B.; Vilmer, E.; Gentelini, M.; Griscelli, C.; Montagnier, L.; Barre-Sinoussi, F.; Chermann, J. C. *Lancet* **1985**, *1* (Feb 23), 450 and ref 4–10 therein.

(6) (a) Acerete, R.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1979**, *101*, 267. Acerete, R.; Harmalker, S.; Hammer, C. F.; Pope, M. T.; Baker, L. C. W. *J. Chem. Soc., Chem. Commun.* **1979**, 777. Acerete, R.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1982**, *104*, 5384. (b) LeFebvre, J.; Chauveau, F.; Doppelt, P.; Brevard, C. *J. Am. Chem. Soc.* **1981**, *103*, 4589. Brevard, C.; Schimpf, R.; Tourné, G.; Tourné, C. M. *J. Am. Chem. Soc.* **1983**, *105*, 7059. (c) Knoth, W. H.; Domaille, P. J.; Roe, D. C. *Inorg. Chem.* **1983**, *22*, 198. Domaille, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 7677. (d) Finke, R. G.; Rapko, B.; Saxton, R. J.; Domaille, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 2947.

(7) (a) Finke, R. G.; Droege, M. W.; Cook, J. C.; Suslick, K. S. *J. Am. Chem. Soc.* **1984**, *106*, 5750. (b) Suslick, K. S.; Cook, J. C.; Rapko, B.; Droege, M. W.; Finke, R. G. *Inorg. Chem.* **1986**, *25*, 241.

(8) (a) Sakurai, N.; Kadohata, K.; Ichinose, N. *Fresenius' Z. Anal. Chem.* **1983**, *314*, 634. (b) Braungart, M.; Rüssel, H. *Chromatographia* **1984**, *19*, 185. (c) Zeng, Q.; Zhu, M.; Xu, Y. *Huaxue Xuebao* **1987**, *45*, 96 and ref 1–8 therein. This paper examines the separation of $K_8SiW_{11}O_{39}$, "$K_4SiW_{12}O_{40}$ and $H_3PW_{12}O_{40}$" (or probably their decomposition products, vide infra), and $K_5SiW_{11}Fe^{II}(OH_2)O_{39}$ by reversed-phase HPLC with a MeOH/phosphate buffer eluent. Several aspects of this report are puzzling or worrisome: An optimum operating pH of 3.7–4.7 is reported, yet $PW_{12}O_{40}^{3-}$ decomposes initially *at diffusion-controlled rates*[14c] to $PW_{11}O_{39}^{7-}$ and then in seconds[14c] to $PW_9O_{34}^{9-}$ at pH > 1.5. The complex $SiW_{12}O_{40}^{4-}$ decomposes similarly but at pH > 4[1] and at a ca. 10^8 slower (though still rapid) rate constant for reaction with OH^- of $k_2 = 2.0 \times 10^3\ M^{-1}\ s^{-1}$ (25 °C, 1.0 M KCl).[14a] Also, $SiW_{11}O_{39}^{8}$ and $SiW_{11}Fe^{II}O_{39}^{5}$ showed identical retention times and thus are apparently not retained on the column, while the *less charged* "$PW_{12}O_{40}^{3-}$ and $SiW_{12}O_{40}^{4-}$" show *longer* retention times. In any event, the reported method cannot separate polyoxoanions by charge type, is not general or readily understood, and would seem to be eluting primarily polyoxoanion decomposition products (or, possibly, $MeOH/H^+$ derivatives).[12a] (d) We confirmed the expected, rapid decomposition of $PW_{12}O_{40}^{3-}$ at pH = 4.5 in a simple control experiment. Initially, 1.0 g of $H_3PW_{12}O_{40}\cdot 10H_2O$ was dissolved in 4.0 mL of 1:1 D_2O/H_2O (0.08 M) and then a ^{31}P NMR spectrum, $\delta = -15.3$ ppm (relative to an external 1% H_3PO_4 standard), was obtained as previously described[6d] on an NT 360-MHz NMR spectrometer for this pH(apparent) ≃ 1.1 solution, indicating the presence of intact $PW_{12}O_{40}^{3-}$ [δ(lit., ^{31}P) = −14.9 ppm].[1] Next, a separate sample containing 1.0 g $H_3PW_{12}O_{40}\cdot 10H_2O$ in 1.0 mL of 1:1 D_2O/H_2O was prepared, the pH was adjusted to 4.5 by the addition of 1.75 mL of 1 M $NaHCO_3$, and the solution was brought to a total volume of 4.0 mL with 1:1 D_2O/H_2O. The ^{31}P NMR spectrum was obtained within ca. 20 min with only a single $\delta = -10.8$ ppm resonance characteristic of $PW_{11}O_{34}^{7-}$ [δ(lit.) = −10.4 ppm].[1] (e) Papers involving the extraction of polyoxometalates into organic solvents are available: Ait, F.; Umland, F. *Z. Anal. Chem.* **1975**, *274*, 103. Ivanov, N. A.; Todorova, N. G. *Anal. Chim. Acta* **1977**, *91*, 389.

(9) A few scattered reports of other types of chromatography of polyoxometalates exist.[8c,9a-c] The literature on HPLC separations of polyphosphate polyanions should also be noted:[9d] (a) Harmalker, S. P.; Leparulo, M. A.; Pope, M. T. *J. Am. Chem. Soc.* **1983**, *105*, 4286. (b) Ogan, M. D. Ph.D. Dissertation, University of Oregon, Dec 1984, pp 51, 52, 59. See also the publications resulting from this work.[4b] (c) A valuable report describing reversed-phase HPLC separation of cationic metal carbonyl cluster compounds of up to 3+ charge has recently appeared. Significantly, and consistent with the literature[8c,9] and the present work, these workers find that the reversed-phase HPLC/C_{18} column conditions provide "by far, the best results for the separation of (cationic) gold cluster compounds". The value of using transparent, glass cartridge columns, preparative HPLC work, and other experimental tips are detailed in: Bos, W.; Steggerda, J. J.; Yan, S.; Casalnuovo, J. A.; Mueting, A. M.; Pignolet, L. H. *Inorg. Chem.* **1988**, *27*, 948. (d) A reviewer brought to our attention work on the *ion-exchange* HPLC of polyphosphates, $P_nO_{3n+1}{}^{(n+2)}$. Noteworthy is recent work showing the *apparent* separation of a series of species up to and including the claim of $n = 35$ ($P_{35}O_{106}^{37-}$) using pH = 10 KCl eluent (Baba, Y.; Yoza, N.; Ohashi, S. *J. Chromatogr.* **1985**, *348*, 27; **1985**, *350*, 119; and references cited in these two papers). It is difficult to reconcile the claimed $P_nO_{3n+1}{}^{(n+2)-}$ peak assignments in these papers, where very highly charged anions are claimed to be chromatographable, with the general lack of well-established HPLC methods for anions of ≥3− charge. (Indeed, and as noted elsewhere by A. D. K., discrete anions of ≥3− charge are typically very difficult to recover (elute) from anion-exchange columns.[10]) We note the $P_nO_{3n+1}{}^{(n+2)-}$ species claimed in the above work were not directly detected. Instead, an indirect detection method is used where an ill-defined, reduced molybdenum mixture (prepared from $(NH_4)_6Mo_7O_{24}$, H_2O, H_2SO_4, and Zn) at 140 °C is used to produce, apparently, heteropolymolybdate blue(s) that are detected at 830 nm. It is unclear from this work how many heteropolymolybdates are produced from a given "$P_nO_{3n+1}{}^{(n+2)-}$" and whether or not this affects the validity of the detection method. Furthermore, the literature indicates that, at least for the polycations, ion-exchange HPLC methods are inferior to reversed-phase HPLC methods.[13a-c] Additional work is obviously needed, including studies to determine whether or not ion-exchange HPLC methods can match or exceed the rapid and flexible reversed-phase HPLC methods developed herein. (Note that the pH = 10 conditions employed in the Baba et al. ion-exchange work are incompatible with most polyoxometalates.)

(10) Kirk, A. D.; Hewavitharana, A. K. *Anal. Chem.* **1988**, *60*, 797.

(11) For a study comparing the *molybdates* $PMo_{12}O_{40}^{3-}$ and $SiMo_{12}O_{40}^{4-}$ to ClO_4^-, see: Barcza, L.; Pope, M. T. *J. Phys. Chem.* **1973**, *77*, 1795.

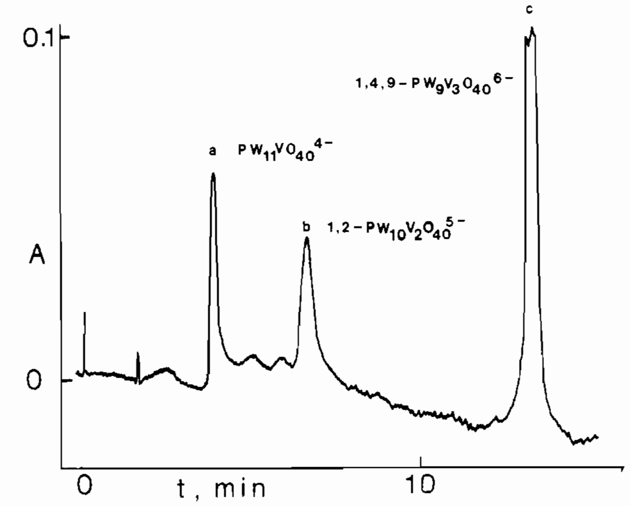


Figure 3. Separation of polyoxometalates of up to 6− charge (reversed-phase C_{18} column, λ_{ana} = 370 nm, 0–0.2 absorbance). The separate H_2O and 90% methanol solutions for gradient elution both contained 25 mM n-$C_6H_{13}NH_3^+$, 20 mM citrate, and added aqueous NH_3 (4 M) to attain pH = 6.5. Elution was part isocratic and part gradient according to the following program [time in minutes (percent of 90% methanolic eluent)]: 0 (70), 7 (70), 9 (80), 15 (80), 20 (70). Peaks, with retention times, are as follows: (a) $PW_{11}VO_{40}^{4-}$, 3.7 min; (b) 1,2-$PW_{10}V_2O_{40}^{5-}$, 6.5 min; (c) 1,4,9-$PW_9V_3O_{40}^{6-}$, 13.0 min. (1,4,9-$PW_9V_3O_{40}^{6-}$ has a greater absorbance at 370 nm, hence its off-scale reading.) The base line is noisy because this chromatogram is obtained in the 0.2 absorbance range, although some of the minor peaks are probably due to the impurities also seen by ^{51}V NMR spectroscopy.

drophobic ion-interaction reagents such as RNH_3^+ (and thus also anionic counterions or polyoxoanions) interact with the C_{18} phase. It is clear from this how a dynamic, ion-pairing[12c] and anion-exchange[12c] environment is set up and how a competing ion such as citrate, $^-O_2CCH_2$–$C(OH)(CO_2^-)CH_2CO_2^-$, is needed to displace a strongly ion-paired polyoxoanion. Details of the retention mechanism and the phenomenon of induced (system) peak formation have been published.[12d] The interested reader is also referred to important previous work by Buckingham[13a–d] and others[9c,13e–h] that discusses separating cations and anions by reversed-phase HPLC, work that shows the greater speed and efficiency of the method compared to those of ion-exchange HPLC methods (the latter may deserve additional investigation, however).[9d]

For the present studies, initial experiments showed that, in the absence of an ion-interaction reagent such as the hexylammonium ion that is partitioned into the C_{18} phase, each polyoxometalate ion eluted from the column without retention; this was so even for $P_4W_{30}Zn_4(OH_2)_2O_{112}^{16-}$. With the hexyl- or butylammonium ion and citrate both present in the eluent, sample retention was obtained for the whole range of polyoxometalates with charges ranging from 4− to 10− with either isocratic or gradient elution.

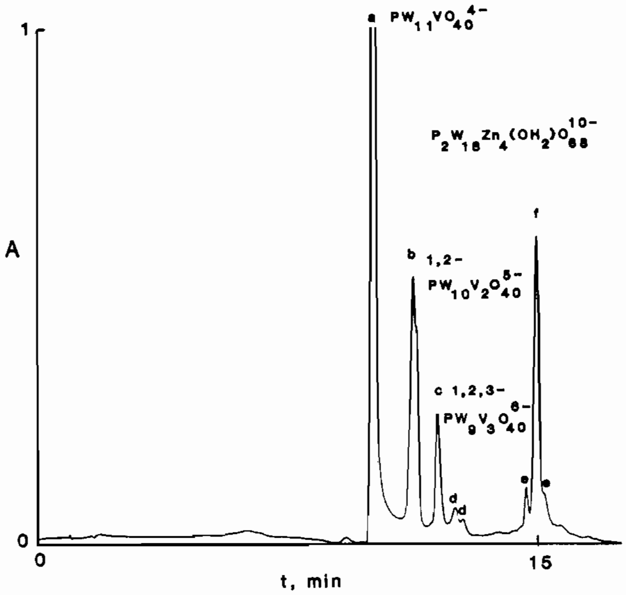


Figure 4. Separation of polyoxometalate ions of differeing charge. (reversed-phase C_{18} column, λ_{anal} = 240 nm, 0–1 absorbance). The separate H_2O and 90% methanol solutions for gradient elution both contained 60 mM n-$BuNH_3^+$ and 20 mM citrate at pH = 6.5. Gradient elution was according to the following program [time in minutes (percent of 90% methanolic eluent)]: 0 (10), 4 (15), 8 (50), 12 (90), 16 (90), 20 (10). Peaks, with retention times, are as follows: (a) $PW_{11}VO_{40}^{4-}$, 10 min; (b) 1,2-$PW_{10}V_2O_{40}^{5-}$, 11.2 min; (c) 1,2,3-$PW_9V_3O_{40}^{6-}$, 12 min; (d) impurity ions or decomposition peaks [*not* $PW_{11}O_{40}^{7-}$ on the basis of separate injections (but *possibly* $PW_{10}VO_{39}^{8-}$ (?))]; (e) the pre-(F) peak, which is an artifact,[12d] and the post-(F) peak, which is an impurity or decomposition peak; (f) $P_2W_{18}Zn_4(OH_2)_2O_{68}^{10-}$, 15 min.

Attempts to include the simple ion $PW_{12}O_{40}^{3-}$ failed as anticipated because of solubility problems under the HPLC conditions and due to the degradation of $PW_{12}O_{40}^{3-}$ at pH $\gg$ 1.5 by the following overall reaction[1] (at pH $\simeq$ 5); $PW_{12}O_{40}^{3-} + 6OH^- \rightarrow PW_{11}O_{39}^{7-} + WO_4^{2-} + 3H_2O$. The rate of the first step of this reaction, $PW_{12}O_{40}^{3-} + 6OH^- \rightarrow PW_{11}O_{39}^{7-} + WO_4^{2-} + 3H_2O$, is known to be instantaneous at pH = 7–9 in 0.1 M ionic strength aqueous solution on a stopped-flow-mixing time scale of 2 ms.[14] The next step, the formation of $PW_9O_{34}^{9-}$, occurs in seconds, and then $PW_9O_{34}^{9-}$ degrades to PO_4^{3-} and WO_4^{2-} in minutes to hours, depending primarily on the pH and temperature.[14c]

Figure 3 shows the chromatogram of a mixture of $PW_{11}VO_{40}^{4-}$, 1,2-$PW_{10}V_2O_{40}^{5-}$, and 1,4,9-$PW_9V_3O_{40}^{6-}$ obtained by using gradient elution with the hexylammonium ion and, again, a reversed-phase C_{18} column with the citrate trianion as a competing ion. Although each polyoxoanion component could be eluted isocratically, the range of retention times present in the mixture made the gradient given in the caption to Figure 3 far more time efficient. Encouraged by this result, we explored the separation of these same 4−, 5−, and 6− ions from the species $P_2W_{18}Zn_4(OH_2)_2O_{68}^{10-}$. Since the retention of the 6− ion was already very strong, requiring 80% of the methanolic (90% methanol) eluent to elute it, the ion-interaction reagent was changed for this separation to the less powerfully retaining butylammonium ion (a change that demonstrates the flexibility of the present HPLC method). After some trial and error the chromatogram shown in Figure 4 was reproducibly achieved by using initial isocratic conditions followed by a gradient that ran from 10 to 90% of the methanolic eluent. *Clearly, there is excellent separation of the polyoxometalates of different charge, up to and including those of 10− charge.* There is also a hint of separation of two species of 5− charge (Figure 4, top of peak b), one of which is also present as a very minor peak in a separate chromatogram of just the 4− ion, $PW_{11}VO_{40}^{4-}$. No impurity was detectable by ^{51}V NMR

---

(12) (a) Iskandarani, Z.; Pietrzyk, D. J. *Anal. Chem.* **1982**, *54*, 1065. (b) Bidlingmeyer, B. A.; Deming, S. N.; Price, W. P., Jr.; Sachok, B.; Petrusek, M. *J. Chromatogr.* **1979**, *186*, 419. (c) However, explanations based solely on ion-pairing or ion-exchange mechanisms do not explain all of the observables, so that a dynamic, double-layer model is currently preferred.[12a,b] In this regard, studies from electrochemistry[12e] showing that the "double layer" is really more correctly a "multilayer" are worth noting: (d) Hammers, W. E.; Aussems, C. N. M.; Janssen, M. *J. Chromatogr.* **1986**, *360*, 1. (e) Mohilner, P. M. In *Electroanalytical Chemistry*; Bard, A., Ed.; Marcel Dekker: New York, 1966; Vol. 1.

(13) (a) Buckingham, D. A.; Clark, C. R.; Deva, M. M.; Tasker, R. F. *J. Chromatogr.* **1983**, *262*, 219. (b) Buckingham, D. A.; Clark, C. R.; Deva, M. M.; Tasker, R. F. *Inorg. Chem.* **1983**, *22*, 2754. (c) Isied, S. S.; Lyon, J. M.; Vassilian, A.; Worosila, G. *J. Liq. Chromatogr.* **1982**, *5*, 537. (d) Gaudin, M. J.; Clark, C. R.; Buckingham, D. A. *Inorg. Chem.* **1986**, *25*, 2569. (e) Buckingham, D. A. *J. Chromatogr.* **1984**, *313*, 93. (f) Abou-El-Wafa, M. H. M.; Mansour, H.; Noubi, G. A. *Can. J. Chem.* **1986**, *64*, 1953. (g) Abou-El-Wafa, M. H. M.; Burnett, M. G.; McCullagh, J. F. *J. Chem. Soc., Dalton Trans.* **1986**, 2083. (h) Lethbridge, J. W.; Reeve, R. N. *J. Chromatogr.* **1984**, *314*, 387.

(14) (a) Kepert, D. L.; Kyle, J. H. *J. Chem. Soc., Dalton Trans.* **1978**, *137*; **1978**, 1781. (b) Tsigdnow, G. *Top. Curr. Chem.* **1978**, *76*, 1. (c) Kyle, J. H. *J. Chem. Soc., Dalton Trans.* **1983**, 2609.

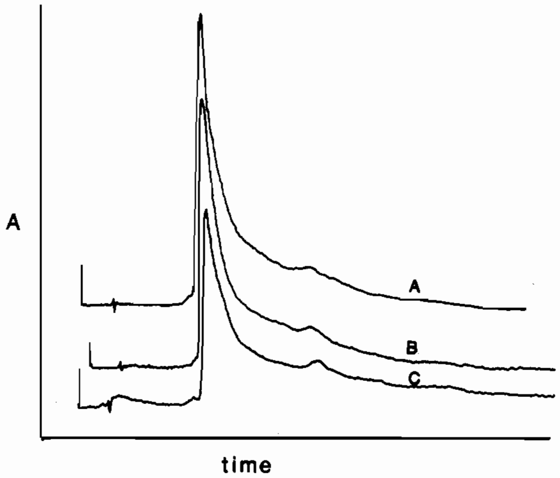


Figure 5. Time dependence of the chromatogram of $PW_{11}VO_{40}^{4-}$ (reversed-phase C_{18} column, λ_{anal} = 250 nm, 0–2.0 absorbance): (A) partially decomposed solution; (B) same solution after ca. 1 h at room temperature; (C) solution after a further 2 h at room temperature (these times are approximate). Peak a of Figures 3 and 4 for the same compound but kept on ice shows only slight tailing. The separate H_2O and *pure* methanol solutions for isocratic elution (at 50% CH_3OH) both contained 60 mM n-$BuNH_3^+$ and 20 mM citrate at pH = 6.5.

spectroscopy (see Experimental Section) even at a very high (203 to 1) signal to noise ratio, so that this peak may be due to a small amount of decomposition.[15] Alternatively, it seems more likely that we are detecting impurities at a level below the detection limit of ^{51}V NMR spectroscopy. We also note that the 5– ion (which contains impurities) gave rise to a peak that elutes just prior to the 6– ion, again on the basis of separate runs.[15b] Regardless of the exact origins of the small peaks seen in the separate chromatograms of the 4– and 5– ions (peaks of ca. 2–4% relative integrated absorbance), the important point is that even polyoxoanions such as $PW_{11}VO_{40}^{4-}$ and $PW_{10}V_2O_{40}^{5-}$, which are prepared and recrystallized at pH < 2.0, showed relatively little basic hydrolysis or degradation under our conditions. The data and Figure 4 also suggest that the method has considerable potential for detecting minor components and thus for analytical and kinetic studies on these compounds.

Further experiments that included $P_4W_{30}Zn_4(OH_2)_2O_{112}^{16-}$ in this separation scheme have been unsuccessful to date. In an initial control experiment, $P_4W_{30}Zn_4(OH_2)_2O_{112}^{16-}$ was not retained on the column in the absence of an ion-interaction reagent. This is an important and encouraging observation, as it indicates that some weak ion-interaction reagent will work. However, as soon as a small concentration of even butylammonium was present in the eluent, the polyoxoanion strongly adsorbed on the column (a second control experiment showed that it did not precipitates when mixed with the eluent). In subsequent experiments it or its decomposition products would elute, ruining several days work in this and other projects, so this compound was set aside for future studies. We are confident, however, that going to even higher methanol percentages or using a different ion-interaction reagent such as the propyl- or ethylammonium ion is likely to allow chromatography of this species as well as even more highly charged polyanions.

Some further observations on the basic-pH hydrolytic and thermal stability of the less negatively charged and thus greater base-sensitive ions, especially $PW_{11}VO_{40}^{4-}$, and the effect of this stability or instability on the chromatography are worth recording. In early work it was observed that a solution of 1,2-$PW_{11}VO_{40}^{4-}$ showed progressively worsening chromatographic peak tailing when the unbuffered sample was kept at room temperature and its natural pH (Figure 5). However, if the sample was kept on ice, this phenomenon disappeared and a good Gaussian peak was obtained over many hours even at low percentages of methanol, where tailing is often most pronounced with this technique. This suggests that any serious chromatographic tailing observed for these species may frequently be the result of decomposition of the sample and not a defect of the chromatography.

Nevertheless, an important feature of this technique is the presence of the competing ion, which serves to avoid peak tailing in fully stable samples; we have shown in our $Co(CN)_5X^{3-}$ studies[10,16] that the citrate ion does this by competing with the analyte ions for strong adsorption sites on the column, thereby linearizing the isotherm.

Next, experiments were undertaken to explore the possibility of separating isomeric polyoxometalates. The isomer pairs 1,2- and 1,4-$PW_{10}V_2O_{40}^{5-}$ and 1,2,3- and 1,4,9-$PW_9V_3O_{40}^{6-}$ were investigated. We will present only representative results for the latter. Separate injections of the 1,2,3- and 1,4,9-species using isocratic 65% methanol/25 mM hexylammonium and 20 mM citrate gave peaks with slightly different corrected retention times (and peak widths) of 16.6 (3.3) and 17.2 min (2.1), respectively. However, when a mixture of the compounds was injected, no separation was achieved and only a single peak was eluted.

Our efforts to accomplish separation of the 1,2,3- and 1,4,9-isomers by variations of flow rate and percentage composition of solvent were not successful. In an attempt to differentiate between the two ions, ethylenediamine was incorporated in the eluent at a concentration of 25 mM; the hope was that it might differentiate between the two ions on the basis of its potentially different interactions with the anionic 1,2- vs 1,4-vanadium–oxygen sites. However, its addition had a deleterious effect, as it seemed to interact more strongly with the citrate (at high concentrations a precipitate formed) than with the polyoxometalate ions. The net result was that the efficiency of the citrate in improving the peak shape was impaired, the chromatographic peaks became very badly tailed, and peak splitting[13c] became a problem even with moderate-size sample injections. Separation of such isomers will therefore have to await further development of the technique.

We have also begun experiments aimed at reversed-phase HPLC of organometallics supported on polyoxometalates such as $(C_5Me_5)Rh{\cdot}SiW_9Nb_3O_{40}^{5-}$ and lacunary polyoxoanions such as $PW_{11}O_{39}^{7-}$. The results so far are encouraging and will be described elsewhere in due course.

Conclusions and Future Directions

The results described above demonstrate that excellent separations of differently charged polyoxoanions, up to and including 10– ions, are now possible in ≤15 min, using reversed-phase HPLC with ion-interaction reagents and a competing-ion reagent. We believe that there is an enormous potential for future development of this method; moreover, there is little reason to see why the

---

(15) (a) The dilute concentrations on the column (inherent when UV/visible detection is used for this class of compounds) as well as the 0 °C temperatures used to prepare solutions for HPLC analysis should help inhibit both bimolecular and unimolecular polyoxoanion decomposition pathways.[14] (b) While we expected, given the literature,[1,20] that some degradation would occur for the 4– and 5– ions at the present operating pH of 6.5, no evidence for this was obtained in the ^{51}V NMR experiments (see Experimental Section, pH stabilities). Furthermore, added alkylammonium ions, $R_{4-x}NH_x^+$, and organic cosolvents such as MeOH are known to afford polyoxoanions with kinetic stabilization toward degradation,[14] so that stabilization, not accelerated degradation, is expected on the column.

(16) Some evidence that supports this, and proves the utility of the 3– citrate ion, is provided by the pH effects shown in Figure B, supplementary material, for some trianionic Co(III) complexes, $Co(CN)_5X^{3-}$. (These complexes were chosen to sidestep questions of the hydrolytic stability of the polyoxometalates as a function of pH.) At pH = 6.5 a significant proportion of the citrate in the eluent is in the 3– form; for the $Co(CN)_5X^{3-}$ sample shown in Figure B, excellent separations are achieved with Gaussian peak shapes. Lowering the pH to 3.5, at which there is virtually no 3– citrate present, leads to increased retention and a very poor peak shape and base linef returning to pH = 6.5 gives an immediate recovery of the chromatographic performance.

(17) (a) Since $MeOH/H^+$ can react with certain polyoxometalates such as[6d] $H_xP_2W_{15}V_3O_{62}^{x-9}$, other solvents like CH_3CN/H_2O, rather than the often superior HPLC solvent mixture[17c] $MeOH/H_2O$, may be needed. (Species like $PW_{12}O_{39}(OMe)^{2-}$ are known,[17d] but their formation and stability conditions are much different from the present HPLC conditions.) (b) Gloor, R.; Johnson, E. L. *J. Chromatogr. Sci.* **1977**, *15*, 413. (c) Knoth, W. H.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 4265. Knoth, W. H.; Farlee, R. D. *Inorg. Chem.* **1984**, *23*, 4765.

method should not extend in principle to other classes of inorganic polyanions (and polycations[13]). There is certainly a highly flexible and versatile range of ion-interaction reagents (1°, 2°, 3°, and 4° alkylammonium) and other column materials that one can try (and solvents other than MeOH if needed[17]). It is possible that column materials such as DVBPS (divinylbenzene/styrene copolymer) may be even better, as they are likely not to require competing ions and do not have the pH = 2–8 limitations of C_{18} columns that in turn limit the possible ranges of pH and of competing ions. The separation of isomers and finding a versatile preparative HPLC method (with its attendant problem of separation of the product from the eluent components) are worthy future goals. Also, the recovery of the more highly charged polyoxometalates from the eluent components should be possible by the proper choice of pH, countercation, and solvents. An important feature of the present HPLC method is that, with UV detection, it can significantly extend (to $\sim 10^{-5}$ M) the analytical concentration window to below that of other methods currently available in polyoxometalate chemistry (e.g. NMR, $\sim 10^{-3}$ M), thereby easily exposing minor impurities. The method also provides a fast, relatively low-cost monitoring technique for use in conjunction with preparative reaction chemistry.

We anticipate that the ability to include HPLC in the arsenal of available methods will have a significant impact upon polyoxometalates and related areas of inorganic and other chemistries involving polycharged ions. This follows since the ability to separate mixtures into their components has long been known to be a very important and fundamental aspect of all areas of chemical science. Other developments, such as HPLC/mass spectroscopy,[18] are also possible now that their individual components of HPLC and mass spectroscopy[7] are available.

Experimental Section

Materials. The polyoxometalates used in this work were obtained by the following published methods, except for $H_3PW_{12}O_{40}\cdot xH_2O$ which was obtained commercially [Sigma; 5.5% H_2O ($x \simeq 9$)], and have the indicated purities. $K_{10}P_2W_{18}Zn_4(OH_2)_2O_{68}\cdot xH_2O$ and $Na_{16}P_4W_{30}Zn_4(OH_2)_2O_{112}\cdot xH_2O$ (dried at 80 °C under vacuum so that $x < 10$) were prepared as part of our previous studies;[19] they are pure by ^{31}P and ^{183}W NMR and elemental analysis.[19] The following samples were a gift from Dr. Peter Domaille (Du Pont); their synthesis, characterization, and purity have been reported previously:[1c,20] $Li_4PW_{11}VO_{40}$, 1,2-$K_5PW_{10}V_2O_{40}$, 1,4-$K_5PW_{10}V_2O_{40}$, 1,2,3-$K_6PW_9V_3O_{40}$, and 1,4,9-$K_6PW_9V_3O_{40}$. In the specific case of the samples provided for this work, ^{51}V NMR spectroscopy at Du Pont in D_2O at pH(apparent) = 2.0 and comparison of measured spectra to published spectra for other samples[20] showed that 1,4-$PW_{10}V_2O_{40}^{5-}$ contained a minor amount of the 1,2-$PW_{10}V_2O_{40}^{5-}$ isomer and an even smaller amount of $PW_{11}VO_{40}^{4-}$ and other impurities [other isomers of $PW_{10}V_2$ (?)], while 1,2-$PW_{10}V_2O_{40}^{5-}$ showed very minor amounts of 1,4-$PW_{10}V_2O_{40}^{5-}$, $PW_{11}VO_{40}^{4-}$, and other impurities [other isomers of $PW_{10}V_2$ (?)]. (Such impurities indicate, incidentally, how even multiple fractional crystallizations (with their attendant loss in yields) often provide polyoxometalates of less than 100% purity.) The impurities in the $PW_{12-x}V_xO_{40}^{-x-3}$ heteropolyanions, visible by ^{51}V NMR spectroscopy under conditions closer to those of the HPLC runs, are reported as part of the next section.

Polyoxometalate Stabilities as a Function of pH. Because the HPLC methods used herein were previously worked out at pH = 6.5,[10] this pH was chosen for initial studies. In general, polyoxoanions have a range of stability as a function of pH, decomposing at high (as well as at very low) pH, with the more anionic polyoxometalates being more stable at higher pH values, such as pH $\sim$ 6.5, as one might expect. Of the present complexes, $P_2W_{18}Zn_4(OH_2)_2O_{68}^{10-}$ and $P_4W_{30}Zn_4(OH_2)_2O_{112}^{16-}$ are known to be relatively stable at pH $\sim$ 7.[19] The 1,2,3- and 1,4,9-isomers of $PW_9V_3O_{40}^{7-}$ have had their ^{31}P and ^{51}V NMR spectra recorded at pH = 5,[20] so that they were expected to be stable (and are, vide infra) in the dilute, 0 °C solutions used herein and especially on the column in the presence of $MeOH/H_2O$ mixtures and RNH_3^+ ions. (Organic cosolvents, e.g. MeOH with H_2O, and $R_{4-x}NH_x^+$ ions are known to kinetically stabilize polyoxometalates against degradation.[14]) On the other hand, the isomers of $PW_{10}V_2O_{40}^{5-}$ are prepared and recrystallized, and their NMR spectra are recorded, at pH < 2.0 (at 30 °C), while $PW_{11}VO_{40}^{4-}$ should be thermodynamically unstable at pH > 4 (if one uses $SiW_{12}O_{40}^{4-}$ as a model because of its similar charge).[1] $PW_{12}O_{40}^{3-}$ is known to degrade at pH > 1.5.[1]

To determine the solution stabilities of the $PW_{12-x}V_xO_{40}^{-3-x}$ polyoxometalates under conditions close to those present *prior to injection* on the HPLC instrument, ^{51}V NMR control experiments were done. Separate 100 mg/5.0 mL D_2O solutions (roughly 0.01 M) of $Li_4PW_{11}VO_{40}$, 1,2-$K_5PW_{10}V_2O_{40}$, 1,4-$K_5PW_{10}V_2O_{40}$, 1,2,3-$K_6PW_9V_3O_{40}$, and 1,4,9-$K_6PW_9V_3O_{40}$ were prepared at the same time by using 0 °C, unbuffered D_2O and were then kept in an ice bath. ^{51}V NMR spectra (at 94.94 MHz) were then recorded on a Nicolet NT 360 NMR spectrometer in 12-mm-o.d. sample tubes referenced to external neat $VOCl_3$ by using the substitution method and the following parameters: pulse width = 45 μs, delay = 262 ms, and acquisition time = 40.9 ms so that the recycle time = 302 ms, line broadening = 10 Hz, and sweep width = ±5000 Hz. The ^{51}V spectrum of each of the five samples was then taken (at 7 °C probe temperature) as rapidly as possible (and until the S/N ratio was ≥50 to 1) at times equal to "0", 2.5, 5, and 8 h. (t = "0" was actually ca. 30 min at 0 °C for the first sample and ca. 110 min for the last sample, since each spectrum took roughly 20 min.) This efficient procedure proved fully satisfactory, since in each case the $t = 0$ and $t = 8$ h ^{51}V NMR spectra *were identical*, indicating no decomposition at reduced temperatures (0–7 °C) in unbuffered D_2O for these dilute ($\simeq$0.01 M) polyoxoanion solutions (see Figure A, supplementary material). Under the above conditions and by ^{51}V NMR spectroscopy, $PW_{11}VO_{40}^{4-}$ and 1,2-$PW_{10}V_2O_{40}^{5-}$ appeared essentially pure, 1,4-$PW_{10}V_2O_{40}^{5-}$ and 1,4,9-$PW_9V_3O_{40}^{6-}$ showed minor impurities centered at −550 ppm and in the −520 to −560 ppm range, respectively, and 1,2,3-$PW_9V_3O_{40}^{6-}$ showed several impurities at ca. −550 ppm and between −490 and −520 ppm (Figure A, supplementary material). The pH(apparent) values of these solutions (100 mg of polyoxometalate in 5 mL of H_2O) were as follows: $Li_4PW_{11}VO_{40}$, 4.8; 1,2-$K_5PW_{10}V_2O_{40}$, 5.5; 1,4-$K_5PW_{10}V_2O_{40}$, 5.5; 1,2,3-$K_6PW_9V_3O_{40}$, 6.9; 1,4,9-$K_{6-x}H_xPW_9V_3O_{40}$, 3.4. This last value of 3.4 (which was repeated several times) is lower than that of the 1,2,3-isomer of 6.9, presumably because $x \simeq 0.3$ on the basis of Domaille's analytical data (see ref 20, p 1240). Alternatively, this pH value may reflect a greatly decreased basicity of the 1,4,9-isomer (relative to that of the 1,2,3-isomer) or the presence of impurities that consume OH^- (i.e. generate H^+ from H_2O) as they decompose.

The second type of control experiment one would ideally do, especially because it involves the higher pH (=6.5) where polyoxometalate decomposition is more likely, is to check (independently of the HPLC results, e.g. by ^{51}V NMR spectroscopy) the stabilities of the $PW_{12-x}V_xO_{40}^{-x-3}$ polyoxometalates under the *column conditions* ($\sim 10^{-2}$ mM polyoxoanion, 25–60 mM RNH_3^+, 20 mM citrate trianion, $MeOH/H_2O$). Unfortunately, the column and UV/visible detection conditions of $\sim 10^{-5}$ M are considerably lower than the required ^{51}V NMR concentrations ($\sim 10^{-2}$ M), and the $RNH_3^+/MeOH/H_2O$ conditions precipitate the polyoxovanadates at concentrations $<10^{-2}$ M. Fortunately, however, the HPLC results given later argue strongly against decomposition on the column except perhaps in the most base-sensitive case, $PW_{11}VO_{40}^{4-}$. In addition, a control experiment for $PW_{11}VO_{40}^{4-}$ at pH = 6.5 was done by ^{51}V NMR spectroscopy (21 °C, 0.036 M compound in pH = 6.5 60 mM butylamine/20 mM citrate buffer, 10% D_2O added as a lock solvent). The resulting spectrum was within experimental error identical with that seen in the 0 °C ^{51}V NMR experiments (Figure A, $PW_{11}VO_{40}^{4-}$ spectrum, supplementary material), clearly indicating that no decomposition had occurred under these (pH = 6.5) conditions.

Eluents. Eluents were prepared with butylamine (BD) or hexylamine (Aldrich) by using either organo-pure water (SYBRON/Barnstead Nanopure-A system) or HPLC grade methanol (Fisher) throughout. Concentrations of the alkylammonium species ranged from 25 to 60 mM during the work, with citrate concentrations in the range 20–25 mM.

As an example, the 60 mM alkylammonium/20 mM citrate solutions were made as follows. To 30 mmol of the amine in a 500-mL graduated flask were added 100 mL of water and then 2.10 g (10 mmol) of citric acid (Anachem). The clear solution that resulted was made up to 500 mL of solvent and the pH adjusted to 6.5 with 3 M HCl (no more than 3 mL was necessary). Both the aqueous and the 90% methanol (10% H_2O) eluents were filtered through a Whatman No. 1 filter to remove dust or other coarse materials and then through a Millipore 0.45-μm filter. In later work equivalent results were obtained by the less laborious preparation of 500 mL of a 600 mM alkylammonium/200 mM citrate stock solution containing 0.5 mL of chloroform as a stabilizer; this was adjusted to pH = 6.5, filtered, and stored. It was then used as required

---

(18) Elucidation of the components of catalytically interesting species such as "$PW_6V_6O_{40}^{9-n}$" and "$PW_8V_4O_{40}^{7-n}$", which are really a complex mixture of different charge types $PW_{12-x}V_xO_{40}^{-3-x}$ and their positional isomers, would be greatly aided by such a method.

(19) (a) Finke, R. G.; Droege, M.; Hutchinson, J. R.; Gansow, O. *J. Am. Chem. Soc.* **1981**, *103*, 1587. (b) Finke, R. G.; Droege, M. W. *Inorg. Chem.* **1983**, *22*, 1006. (c) Finke, R. G.; Droege, M. W.; Domaille, P. J. *Inorg. Chem.* **1987**, *26*, 3886.

(20) Domaille, P. J.; Watunya, G. *Inorg. Chem.* **1986**, *25*, 1239.

to prepare the appropriate concentration by dilution with pure methanol or water followed by a small pH readjustment.

The 25 mM alkylammonium/20 mM citrate solutions were made similarly, except that the pH was adjusted to 6.5 by using a 4 M $NH_4^+OH^-$ solution.

Instrumentation. A Varian 5000 chromatograph was used throughout this work. Samples were injected with a 10-μL loop injector, and sample detection employed a Varian VARI-CHROM variable-wavelength detector, 0.005–2 absorbance units, with a 1.0 mm diameter, 10 mm path length flow cell, volume 7.9 μL. A 4.6 mm diameter and 25 cm length C18 (10-μm particle size) reversed-phase column (Scientific Products and Equipment Ltd.) was used and was protected by an Upchurch Scientifics guard column packed with Perisorb RP-18 30–40-μm particles. The eluent flow rate read a nominal 2 mL min^{-1}, but calibration showed that this was closer to 1.4 mL min^{-1} and somewhat variable. Similarly, it was found that the proportioning pump on the instrument was inaccurate. For this reason, and also because of column variability, the nominal percentages of methanol and flow rates given in the following should be used only as a guide to establishing the conditions on other systems. *In general, the retention times were found to be quite sensitive to the exact percentage of MeOH. They will also likely vary significantly from column to column.*

Chromatographic Procedure. Before each set of injections, the column was prepared by washing with pure HPLC grade methanol, followed by equilibration for 15 min with the appropriate eluent composition. Eluent concentrations were always changed by using a gradient, to avoid column shock and to allow time for reequilibration. When not in use, the column was thoroughly cleaned and stored filled with pure methanol. Experiments were carried out with either isocratic or gradient elution, depending on the range of analyte retentivities present in the sample. Peaks were detected by their UV absorbance at appropriate wavelengths, given in the figure captions.

Samples (0.01–1.0 mM) for injection were dissolved in unbuffered water. Early experiments (prior to the ^{51}V NMR control experiments) gave evidence of thermal decomposition for some of the species on standing over periods of a few hours *at room temperature*, so that in the later work all samples were kept on ice, a procedure that seemd to completely eliminate the problem (as subsequently verified via the ^{51}V NMR control experiments). [For samples that degrade at higher pH values (at or above the present operating pH = 6.5) or samples of unknown pH stability, the literature[14] suggests that dissolving them *initially* in organic cosolvents (e.g. $MeOH/H_2O$) and in the presence of the ion-interaction reagent ($R_{4-x}NH_x^+$) could be used to inhibit their degradation, although this was not necessary and thus was not confirmed as part of the present studies.]

Acknowledgment. Work at Victoria was supported by NSERC Grant A1291 and by the University of Victoria Faculty Research Fund, while work at Oregon was supported by NSF Grant CHE-861924. We are indebted to Dr. Peter Domaille for his generous gift of the $PW_{12-x}V_xO_{40}^{-3-x}$ samples.

Supplementary Material Available: Figure A, spectra for the ^{51}V NMR control experiments, and Figure B, chromatogram of the effect of pH on chromatographic efficiencies and the efficiency of the competing ion citrate (3 pages). Ordering information is given on any current masthead page.

Notes

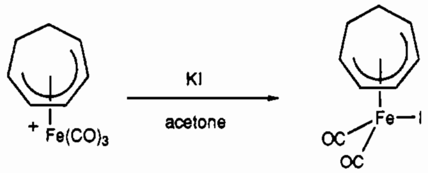
Contribution from the Department of Chemistry
and Biochemistry, California State University,
Fullerton, California 92634, and Department of Chemistry,
University of California, Irvine, California 92717

Synthesis and Chemistry of (η^3-Pentadienyl)iron Tricarbonyl Halides

Gregory M. Williams*,[1a,b] and Duane E. Rudisill[1b]

Received May 3, 1988

There are now many compounds of the general form $(ped)_xML_y$ ($x = 1, 2; y = 0$–4; ped = pentadienyl), where L is a neutral donor ligand and M may be any of a number of transition or rare-earth elements.[2-4] In contrast, there are few pentadienyl complexes that also contain ligands such as halogen or hydrocarbyl.[5,6] Insofar as the significance of pentadienyl complexes will depend upon the degree to which chemistry can be carried out at the metal center, the synthesis of metal-functionalized pentadienyl complexes becomes important. In this regard, we are studying the chemistry of $(\eta^5\text{-chp})Fe(CO)_2I$[6] (chp = cycloheptadienyl), a species prepared by reaction of $(\eta^5\text{-}C_7H_9)Fe(CO)_3^+$ with KI:[5a,b]



Similar results were reported for $(\eta^5\text{-chx})Fe(CO)_3^+$ and $(\eta^5\text{-coc})Fe(CO)_3^+$[5a,b,d] (chx = cyclohexadienyl; coc = cyclooctadienyl). Recently, Ernst used this synthesis to prepare $(\eta^5\text{-2,4-Me}_2\text{-ped})Fe(CO)_2I$.[5e] In contrast, we find that halide addition to other acyclic cationic iron dienyl complexes follows a different path. In these cases, halide ion induces an isomerization of the pentadienyl ligand in preference to displacement of carbon monoxide.

---

* To whom correspondence should be addressed at California State University.

(1) (a) California State University. (b) University of California.

(2) (a) Ernst, R. D. *Acc. Chem. Res.* **1985**, *18*, 56 and references therein. (b) Stahl, L.; Hutchinson, J. P.; Wilson, D. R.; Ernst, R. D. *J. Am. Chem. Soc.* **1985**, *107*, 5016. (c) Kowaleski, R. M.; Basolo, F.; Trogler, W. C.; Ernst, R. D. *Ibid.* **1986**, *108*, 6046. (d) Kowaleski, R. M.; Basolo, F.; Trogler, W. C.; Gedrige, R. W.; Newbound, T. D.; Ernst, R. D. *Ibid.* **1987**, *109*, 4860. (e) Stahl, L.; Ernst, R. D. *Ibid.* **1987**, *109*, 5673. (f) Ma, H.; Weber, P.; Ziegler, M. L.; Ernst, R. D. *Organometallics* **1986**, *5*, 2009. (g) Ma, H.; Sergeson, G.; Zahn, T.; Ziegler, M. L. *Ibid.* **1987**, *6*, 848. (h) Kralik, M. S.; Rheingold, A. L.; Ernst, R. D. *Ibid.* **1987**, *6*, 2612.

(3) (a) Bleeke, J. R.; Kotyk, J. J. *Organometallics* **1983**, *2*, 1263. (b) Bleeke, J. R.; Hays, M. K. *Ibid.* **1984**, *3*, 506. (c) Bleeke, J. R.; Peng, W. J. *Ibid.* **1984**, *3*, 1422. (d) Bleeke, J. R.; Kotyk, J. J. *Ibid.* **1985**, *4*, 194. (e) Bleeke, J. R.; Donaldson, A. J. *Ibid.* **1986**, *5*, 2401. (f) Bleeke, J. R.; Stanley, G. G.; Kotyk, J. J. *Ibid.* **1986**, *5*, 1642. (g) Bleeke, J. R.; Hays, M. K. *Ibid.* **1987**, *6*, 486. (h) Bleeke, J. R.; Hays, M. K. *Ibid.* **1987**, *6*, 1367. (i) Bleeke, J. R.; Peng, W. J. *Ibid.* **1987**, *6*, 1576. (j) Bleeke, J. R.; Rauscher, D. J.; Moore, D. A. *Ibid.* **1987**, *6*, 2614. (k) Bleeke, J. R.; Kotyk, J. J.; Moore, D. A.; Rauscher, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 417. (l) Bleeke, J. R.; Moore, D. A. *Inorg. Chem.* **1986**, *25*, 3522.

(4) (a) Paz-Sandoval, M. A.; Powell, P.; Drew, M. G. B.; Perutz, R. N. *Organometallics* **1984**, *3*, 1026. (b) Lush, S. F.; Liu, R. S. *Ibid.* **1986**, *5*, 1909. (c) Lee, G. H.; Peng, S. M.; Lee, T. W.; Liu, R. S. *Ibid.* **1986**, *5*, 2378. (d) Lee, G. H.; Peng, S. M.; Lush, S. F.; Liao, M. Y.; Liu, R. S. *Ibid.* **1987**, *6*, 2094. (e) Cheng, C. H.; Liu, R. S. *J. Organomet. Chem.* **1986**, *308*, 237. (f) Lee, G. H.; Peng, S. M.; Liao, M. Y.; Liu, R. S. *Ibid.* **1986**, *312*, 113. (g) Seyferth, D.; Goldman, E. W.; Pornet, J. *Ibid.* **1981**, *208*, 189. (h) Lehmkuhl, H.; Naydowski, C. *Ibid.* **1982**, *240*, C30. Rinze, P. V. *Ibid.* **1974**, *77*, 259.

(5) (a) Dauben, H. J.; Bertelli, D. J. *J. Am. Chem. Soc.* **1961**, *83*, 5049. (b) Hashmi, M. A.; Munro, D. J.; Pauson, P. L. *J. Chem. Soc. A* **1967**, 240. (c) Edwards, R.; Howell, J. A. S.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1974**, 2105. (d) Schiavon, G.; Paradisi, C. *J. Organomet. Chem.* **1981**, *210*, 247. (e) Ma, H.; Weber, P.; Ziegler, M. L.; Ernst, R. D. *Organometallics* **1987**, *6*, 854. (f) Newbound, T. D.; Freeman, J. W.; Wilson, D. R.; Kralik, M. S.; Patton, A. T.; Campana, C. F.; Ernst, R. D. *Ibid.* **1987**, *6*, 2432. (g) Hegedus, L. S.; Varaprath, S. *Ibid.* **1982**, *1*, 259. (h) Paz-Sandoval, M. A.; Powell, P. *Ibid.* **1983**, *252*, 205. (i) Bleeke, J. R.; Peng, W. J. *Ibid.* **1986**, *5*, 635.

(6) (a) Williams, G. M.; Rudisill, D. E. *J. Am. Chem. Soc.* **1985**, *107*, 5357. (b) Williams, G. M.; Fisher, R. A.; Heyn, R. H. *Organometallics* **1986**, *5*, 818.

0020-1669/89/1328-0797$01.50/0