

rotation. The calculated barriers for the benzyl anion, the 4-methylbenzyl anion, and the 4-silylbenzyl anion are 19.2, 18.2, and 21.3 kcal/mol, respectively. The trend in these calculated barriers is in good qualitative agreement with our results for anions 1 and 2 above. Indeed, a perusal of the Hückel electron-density distribution for the 4-silylbenzyl anion reveals a significant increase in negative charge in the silicon atom of the *planar* anion as compared with the transition state for aryl rotation. Since the extended Hückel method may not reflect accurately the relative importance of different types of orbitals in bonding for these anionic systems, such calculations do not provide an incisive picture of the specific orbital involvement in anion stabilization by silicon. Thus, while our experimental NMR data and the Hückel calculations reveal a clear-cut stabilization of the diphenylmethyl anion by a para trimethylsilyl group, an unequivocal theoretical description of such stabilization remains undefined.

**Acknowledgment.** C.H.B. is grateful to the National Science Foundation for support (Grant No. CHE78-21161). We acknowledge the support of the Southern New England High Field NMR Facility made possible by a grant from Biotechnology Resources Program of the National Institutes of Health (RR-798).

#### references and Notes

- (1) (a) Peterson, P. J. *Organomet. Chem. Rev. Sect. A* **1972**, *7*, 295. (b) Seyferth, D., Mammarella, R. E. *J. Organomet. Chem.* **1978**, *156*, 279.
- (2) Adcock, W.; Aldous, G. L. *Tetrahedron Lett.* **1978**, 3387, and references therein.
- (3) Solutions of 1 were prepared by the slow addition of tetrahydrofuran to a mixture of hexane-free butyllithium and 4-methyl-4'-trimethylsilyldiphenylmethane at  $-25^{\circ}\text{C}$  in an argon atmosphere. Satisfactory elemental analysis and spectral characterization were obtained for 4-methyl-4'-trimethylsilyldiphenylmethane.
- (4) Bushweller, C. H.; Sturges, J. S.; Cipullo, M.; Hoogasian, S.; Gabriel, M. W.; Bank, S. *Tetrahedron Lett.* **1978**, 1359.
- (5) The  $^1\text{H}$  NMR chemical shifts of the *static* 4-methylphenyl group of the 4-deuterio-4'-methylidiphenylmethyl anion [ $\delta$  6.63, 6.43, 6.30, 6.08, ( $^3J_{\text{H-H}} = 8.0$  Hz)] correlate almost exactly with those for the 4-methylphenyl group of 1.
- (6) Bank, S.; Sturges, J.; Bushweller, C. H. In "Stereochemistry of Molecular Systems", Sarma, R. H., Ed.; Pergamon Press: New York, 1979; p 147.
- (7) Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1.
- (8) Reynolds, W. F.; Hamer, G. K.; Bassindale, A. R. *J. Chem. Soc., Perkin Trans. 2* **1977**, 971.
- (9) Hoffmann, R.; Bissell, R.; Farnum, D. G. *J. Phys. Chem.* **1969**, *73*, 1789.
- (10) Alfred P. Sloan Research Fellow; Camille and Henry Dreyfus Teacher-Scholar.

Shelton Bank,\* John S. Sturges, Dennis Heyer  
Department of Chemistry, State University of New York  
Albany, New York 12222

C. Hackett Bushweller\*<sup>10</sup>  
Department of Chemistry, University of Vermont  
Burlington, Vermont 05405  
January 14, 1980

#### Isotopic Oxygen Studies on Aqueous Molybdenum(IV)

Sir:

The composition and structure of  $\text{Mo(IV)}_{\text{aq}}$  in acidic aqueous solution has been the subject of several studies,<sup>1-5</sup> but none define the ionic species present unambiguously. Several recent crystal structures of solid complexes<sup>6</sup> have shown a common trimeric core ion, but the extension from the solid state to solution is, as always, open to serious question. The studies reported here, a combination of  $^{18}\text{O}$  transfer experiments and an X-ray structure, strongly suggest the basic structure of this ion in acidic solution and allow definitive studies on the kinetic behavior of the bridged oxygens.

When  $\text{Mo(IV)}_{\text{aq}}$ <sup>7</sup> in 1-3 M HCl or  $\text{CH}_3\text{SO}_3\text{H}$  (obtained by

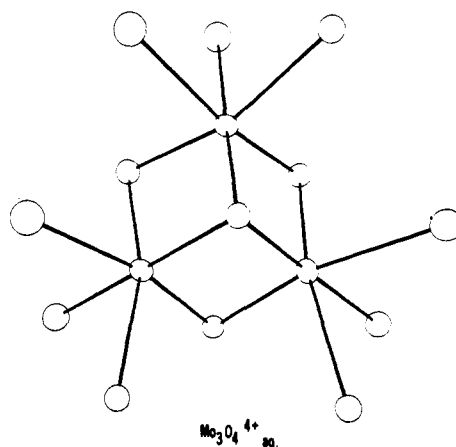


Figure 1.

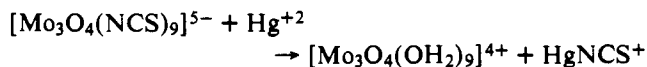
reaction of  $\text{MoO}_4^{2-}$  with  $\text{MoCl}_6^{3-}$  followed by ionic exchange separation)<sup>1</sup> is treated for extended periods of time with  $^{18}\text{O}$ -enriched water, some of the oxygens in the first coordination sphere of molybdenum are not exchanged with the solvent. This has been established unambiguously by converting  $\text{Mo(IV)}_{\text{aq}}$  into a crystalline solid by the addition of  $\text{NaSCN}$  and  $(\text{CH}_3)_4\text{N}^+\text{SCN}^-$  at  $0^{\circ}\text{C}$  and measuring its  $^{18}\text{O}$  content. The solid product which begins to precipitate within 1 min and is almost completely precipitated in  $\sim 20$  min has a constant composition with all coordinated waters replaced by  $\text{SCN}^-$  and no water of hydration in the vacuum-dried material (IR). A representative of about thirty experiments to determine what fraction of the oxygen in the solid  $\text{SCN}^-$  complex comes from the inner coordination sphere of the  $\text{Mo(IV)}_{\text{aq}}$  is given below. The experiment involved making  $\text{Mo(IV)}_{\text{aq}}$  in normal or  $^{18}\text{O}$ -enriched water, separating it on an ion-exchange column, eluting it with 3 M HCl or  $\text{CH}_3\text{SO}_3\text{H}$  in water differing in isotopic oxygen content from the original preparation, precipitating the  $(\text{CH}_3)_4\text{N}^+\text{SCN}^-$  salt, recrystallization, and determining the  $^{18}\text{O}$  content of all the oxygen in the solid complex by conversion into  $\text{CO}_2$  by the usual methods. The time of contact at  $25^{\circ}\text{C}$  between the ion and the solvent at differing  $^{18}\text{O}$  enrichments varied between 15 and 45 min in these experiments. The results clearly show that *all* of the oxygens ( $\pm 3\%$ ) in the solid complex come from the inner coordination sphere of  $\text{Mo(IV)}_{\text{aq}}$ . If the  $[\text{SCN}^-]$  is low or the  $(\text{CH}_3)_4\text{N}^+$  added too early, the products contain more unreplaced  $\text{H}_2\text{O}$  and the "apparent exchange" rises to 10-15%. Other experiments allowing extended time periods for exchange between the  $\text{Mo(IV)}_{\text{aq}}$  ( $^{18}\text{O}$  enriched) and  $\text{H}_2\text{O}$  (normal) showed no more than 10% exchange of these oxygens in 100 h at  $25^{\circ}\text{C}$ .

	$10^3 R_n$ (solvent) <sup>10</sup>	$10^3 R_n$ [Mo(IV)]	$10^3 R_n(\text{SCN}^-$ complex)
A. enriched solvent	9.800	3.920	3.914
B. enriched $\text{Mo(IV)}_{\text{aq}}$	3.980	8.302	8.179

Analysis of the  $\text{SCN}^-$  complex was not adequate to establish the O/Mo ratio or the structure of the complex ion. Attempts to produce single crystals met with only marginal success, but from  $\text{CH}_3\text{CN}-\text{H}_2\text{O}$  mixtures thin plates could easily be obtained in bulk and a few small ( $V = 8 \times 10^{-4} \text{ mm}^3$ ) semi-spherical crystals were prepared. A single-crystal X-ray study<sup>8</sup> showed the complex to be  $[(\text{CH}_3)_4\text{N}]_4[\text{Mo}_3\text{O}_4(\text{NCS})_8\text{OH}_2] \cdot 3\text{H}_2\text{O}$ , a trimeric structure very similar in nature to the oxalate or EDTA<sup>6</sup> complexes. This compound was the same as the bulk plates (film X-ray data) and reversibly forms by aequation of the  $(\text{SCN})_9$  complex when a large excess of  $\text{SCN}^-$  is not present in solution.

Since the complex ion is reversibly formed under mild con-

ditions and has the  $\text{Mo}_3\text{O}_4$  structure, the results suggest that the parent aqueous ion also contains the  $\text{Mo}_3\text{O}_4$  entity. To establish that no oxidation-reduction or reversible Mo-O-Mo bond breaking occurs during the formation of the  $\text{SCN}^-$  complex, we carried out the following reaction



and showed that the starting  $\text{Mo(IV)}_{\text{aq}}$  was obtained as the sole product (ion exchange) and that it had the proper ion-exchange properties, the correct spectrum, and extinction coefficients  $\epsilon$  62.8 at 505 nm. Further, conversion of the enriched  $\text{Mo(IV)}_{\text{aq}}$ , prepared in this manner, back into  $[\text{Mo}_3\text{O}_4(\text{NCS})_9]^{5-}$  was accomplished with <2%  $^{18}\text{O}$  exchange of the Mo oxygens with the solvent.

Similar behavior is shown by a (rapid forming) oxalate complex ion, prepared by eluting  $\text{Mo(IV)}_{\text{aq}}$  from Dowex 50W  $\times 2$  with 0.13 M  $\text{H}_2\text{C}_2\text{O}_4$ . When crystallized from solution by  $\text{Co(en)}_3^{3+}$ ,  $\text{Pt(en)}_2^{2+}$ , or  $\text{Pt(en)}_3^{4+}$ , it retains the Mo-O oxygens without exchange and all three complexes give a Mo-O/(Mo-O + O<sub>x</sub>-O) ratio of 4/(23  $\pm$  2). Further, the  $\text{C}_2\text{O}_4^{2-}$  may be reversibly removed by  $\text{Pb}^{2+}$  precipitation and the  $\text{Mo(IV)}_{\text{aq}}$  generated may be converted into  $[\text{Mo}_3\text{O}_4(\text{NCS})_9]^{5-}$  with complete ( $\pm 2\%$ ) retention of  $^{18}\text{O}$  in the Mo-O oxygens. This oxalate complex ion is similar to but not identical with that in the structure determined by Cotton et al.<sup>6</sup>

It is not difficult to conceive of reactions which reversibly form the  $\text{SCN}^-$  trimer from  $\text{Mo(IV)}_{\text{aq}}$  in some other state of oligomerization, thus negating the structural relationship between the  $\text{SCN}^-$  complex and  $\text{Mo(IV)}_{\text{aq}}$ . However, it seems impossible to accomplish this reversibility without simultaneously causing considerable, if not complete, bridging oxygen exchange. Since oxygen exchange does not occur, the  $\text{Mo}_3\text{O}_4$  entity found in the  $\text{SCN}^-$  complex is also present in  $\text{Mo(IV)}_{\text{aq}}$ .

We conclude that the structure of  $\text{Mo(IV)}_{\text{aq}}$  in acidic media consists of a trimer with three bridging oxygens and a capping oxygen (Figure 1). These oxygens are very slow to exchange.<sup>9</sup>

Each molybdenum probably has three additional waters (more labile) in its primary solvation sphere, two of one type (on capping-O side) and one on the bridging-O side, completing the distorted octahedral configuration around each molybdenum. There is some evidence that all of these oxygens (four types) are slow enough to exchange isotopically to be kinetically studied by conventional methods. Studies with these goals are in progress. A complete description of this work with a discussion of its relationship to previous investigations will be presented with the  $^{18}\text{O}$  kinetic studies.

**Acknowledgment.** We express our appreciation to Dr. E. O. Schlemper and Dr. M. S. Hussain for the cooperative effort on the X-ray studies, to M. Johnson for some of the  $^{18}\text{O}$  analyses, and to the University of Missouri Research Council for partial support.

#### References and Notes

- (1) J. Folorunso Ojo, Y. Sasaki, R. Taylor, and A. G. Sykes, *Inorg. Chem.*, **15**, 1006 (1976).
- (2) P. Souchay, M. Cadlot, and M. Duhamiaux, *C. R. Acad. Sci.* **262**, 1524 (1966).
- (3) S. Cramer, H. Gray, Z. Dori, and A. Blino, *J. Am. Chem. Soc.*, **101**, 2770 (1979).
- (4) M. Ardon and A. Pernick, *J. Less-Common Metals*, **54**, 233 (1977).
- (5) M. Ardon, A. Blino, and G. Yahaw, *J. Am. Chem. Soc.*, **98**, 2338 (1976).
- (6) Avi Blino, F. A. Cotton, and Z. Dori, *J. Am. Chem. Soc.*, **100**, 5252 (1978); *Inorg. Chim. Acta*, **33**, L133 (1979); *J. Am. Chem. Soc.*, **101**, 3842 (1979).
- (7)  $\text{Mo(IV)}_{\text{aq}}$  refers to the reddish ion ( $\epsilon$  63 at 505 nm) present in acidic solutions containing only weakly complexing acids such as HCl,  $\text{CH}_3\text{SO}_3\text{H}$ , or PTSA.
- (8) R. K. Murmann, M. S. Hussain, and E. O. Schlemper, *Acta Crystallogr.*, in press.
- (9) It has been demonstrated that nonbridging oxygens in  $[\text{Mo}(\text{CN})_4\text{O}_2]^{4-}$  and  $[\text{Mo}(\text{CN})_4\text{O}(\text{OH})]^{3-}$  exchange very rapidly, and with  $\text{Mo}_2\text{O}_7^{2+}$  the bridging oxygens are very slow compared with the  $\nu$  oxygens: P. Robinson and R. K. Murmann, *Inorg. Chem.*, **14**, 203 (1975); R. K. Murmann, *Inorg. Chem.*, in press.
- (10)  $F_n$  is the normalized ratio of  $^{18}\text{O}$  in the measured sample compared with a normal standard which are arbitrarily given the value  $4 \times 10^{-3}$  ( $4 \times 10^{-3}$  is the mole fraction of  $^{18}\text{O}$  found in nature).

R. Kent Murmann,\* Marc E. Shelton

University of Missouri, Department of Chemistry  
Columbia, Missouri 65211  
Received February 2, 1980

## Book Reviews

**Polymer Surfaces.** By D. T. CLARK and W. J. FEAST. xiv + 441 pp. John Wiley & Sons, Inc., Somerset, N.J. 1978. \$63.50.

The first six chapters of the book cover the fundamental aspects of the mechanical, physical, and electrical properties of the surfaces. These chapters assume a lot of fundamental knowledge. There is not enough detail for a novice to the field of polymer surfaces, and probably these chapters are of limited use to the expert. However, the rest of the book (Chapters 7-19) is well written, cohesive, and flows smoothly from chapter to chapter even though each chapter is written by a different author. Overall, the book provides an up-to-date discussion of the techniques that are used for making polymer films and/or for modifying the surfaces of synthetic polymers. The book also presents state-of-the-art methods that are being used to characterize these surfaces.

In particular, Chapter 8 contains an excellent description of the experiments that have been done for the preparation of films under controlled conditions. In addition, it includes a fairly extensive survey of the types of films that have been synthesized. Chapters 9 and 10 provide useful information on how surfaces can be modified, particularly through the application of plasma techniques. Also, the latter chapter contains a good discussion of the various theories of adhesion.

The major methods of probing polymer surfaces such as IR, ESCA, and SEM are well represented. Chapter 15 and sections in a few other

chapters give a good overview of the kinds of information that can be obtained about polymer surfaces through the use of infrared spectroscopy. For example, the multiple internal reflectance (MIR) infrared spectra of various polyethylene samples clearly show the effects of oxidation and/or etching.

The book provides a good combination of technical review and historical perspective. Many of the chapters are interesting and readable even by a novice in the field.

Adrian J. Vanderwielen, Steven J. Borchert, *The Upjohn Company*

**Conservation of Resources.** The Chemical Society, London. 1977. ix + 245 pp. \$12.00.

This is a collection of papers presented at the Annual Chemical Congress in Glasgow in April 1976, and is a broad overview of the problems of conservation of material and energy resources, both in the United Kingdom and worldwide. Topics are widely varied, ranging from the effect of human activity on climate to the role of photosynthesis and oxidative phosphorylation in biological energy consumption.

The papers are written by specialists to convey to specialists in other fields the problems, both technical and philosophical, that they are trying to solve, and some of the proposed solutions. As such, in addition to succinct prose, the well-referenced articles include numerous informative charts, graphs, and tables, with only a few simple equations.