

Further work will be needed to establish whether 2c owes its persistence to a thermal barrier against S → T intersystem crossing or cyclization of the singlet diradical.

It is our contention that by delocalization of the radical sites and by introduction of appropriate molecular constraints still more persistent triplet diradicals can be taylor-made.

Acknowledgment. We are grateful to the Ciba Stiftung, the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the National Science Foundation, the Schweizerischer Nationalfonds, and the Stiftung Volkswagenwerk for generous financial support.

Oxygen Atom Transfer Chemistry of Heteropolytungstate "Browns" in Nonaqueous Solvents

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Received July 1, 1988

The current increased interest in polyoxometalates¹ is fueled to a large extent by potential and realized applications as acid-base or redox catalysts and photocatalysts.² Hitherto, polyanion redox chemistry has been dominated by electron-transfer processes, either centered at the heteroatom (see, for example, the use of Co^{III}W₁₂O₄₀⁵⁻ as an oxidant in organic chemistry³) or at the addenda Mo or W atoms in the heteropoly blues.⁴ Atom transfer chemistry involving polyanions is much less common, although we have recently shown that lacunary polyanion fragments can mimic macrocyclic ligands and support oxygen transfer from iodobenzene in the conversion of SiMo₁₁O₃₉Cr^{III}(OH)₂⁵⁻ to SiMo₁₁O₃₉Cr^VO⁵⁻,⁵ and Hill has reported oxygen transfer from

oxygen donors to alkenes and alkanes that is catalyzed by PW₁₁(M)O₃₉⁵⁻ (M = divalent Mn, Fe, Co, Cu).^{2b,6} We now report the first general oxygen atom abstraction reactivity of reduced heteropolytungstates in nonaqueous solutions and incidentally the first examples of oxygen atom transfer to tungsten(IV). This reactivity suggests that new applications for unsubstituted heteropolyanions in synthetic and catalytic chemistry might be found.

The reduced anions in question are the heteropoly "browns" that were recently shown to contain trigonal groups of edge-shared W^{IV}O₅(OH₂) octahedra, XW^{VI}₉O₃₇W^{IV}₃(OH₂)₃ⁿ⁻ (X = H₂ (I), B (II), Si (III); n = 6, 5, 4, respectively,⁷ see Figure 1. Natural abundance ¹⁷O NMR spectra of these anions in aqueous solution show clearly resolved lines for most of the 11 different types of oxygen atoms in the C_{3v} structure.⁸ Resonances for the terminal water molecules occur at chemical shifts of -12 (I) and -10 ppm (II and III). Addition of ¹⁷O-enriched water to these solutions results in a slow enhancement of these resonances⁹ thereby demonstrating ligand exchange on W^{IV}. Approximate half-lives for exchange at ambient temperature range from 4.5 to 30 days, i.e.; 3.6 × 10⁵ s (I); 1.1 × 10⁶ s (II); 3.0 × 10⁶ s (III). These rates are comparable with that for the corresponding water molecules in the structurally related cation, W^{VI}₃O₄(OH₂)₉⁴⁺.¹⁰

Anions I-III are readily transferred into toluene or benzene solution by the phase transfer method that we have described earlier.¹¹ Excess noncoordinated water is removed by solvent-stripping, and the resulting salts are redissolved in fresh dry toluene or acetonitrile.¹² Treatment of such solutions with appropriate oxidants, XO, leads to regeneration of the oxidized heteropolyanion (identified by ¹⁸³W, ¹H, and ¹⁷O NMR, and by isolation of the tetrapropylammonium salt) and the formation of X or a successor species (¹H, ¹³C NMR, isolation). Yields of the oxidized heteropolyanion are quantitative based upon NMR.¹³ Representative yields of the organic products, based on NMR integration of unreacted substrate and product signals, are given in Table I. These yields, which are not optimized, demonstrate that on average more than one oxygen atom has been transferred per heteropolyanion.¹⁴ The overall rates of the reactions summarized in Table I are not inconsistent with the water exchange rates, except for the case of nitrosobenzene.¹⁵ That the reaction proceeds by

(1) (a) Pope, M. T. *Isopolyanions and Heteropolyanions. In Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: New York, 1987; Vol. 3, Chapter 38. (b) Day, V. W.; Klemperer, W. G. *Science* **1985**, *228*, 533. (c) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer Verlag: New York, 1983.

(2) Research activity is high in this area and has not been comprehensively reviewed recently. The following lists recent papers from some different research groups (alphabetically by first author) that are currently active and provides an entree to the literature. (a) Akid, R.; Darwent, J. R. *J. Chem. Soc., Dalton Trans.* **1986**, 395. (b) Ai, M. *Polyhedron* **1986**, *5*, 103. (c) Aoshima, A.; Yamaguchi, T. *Nippon Kagaku Kaishi* **1986**, 1161. (d) Baba, T.; Ono, Y. *J. Mol. Catal.* **1986**, *37*, 317. (e) Dun, J. W.; Gulari, E.; Streusand, B. *Appl. Catal.* **1986**, *21*, 61. (f) Finke, R. G.; Rapko, B.; Domaille, P. J. *Organometallics* **1986**, *5*, 175. (g) Fox, M. A.; Cardona, R.; Gaillard, E. *J. Am. Chem. Soc.* **1987**, *109*, 6347. (h) Hill, C. L.; Brown, R. B., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 536. (i) Kulikov, S. M.; Kozhevnikov, I. I.; Fomina, M. N.; Krysin, A. P. *Izv. Acad. Nauk SSSR, Ser. Khim.* **1987**, 752. (j) Misono, M.; Okahara, T.; Ichiki, T.; Arai, T.; Kanda, Y. *J. Am. Chem. Soc.* **1987**, *109*, 5535. (k) Moffat, J. B. *Stud. Surf. Sci. Catal.* **1987**, *31*, 241. (l) Nomiya, K.; Sugie, Y.; Miyazaki, T.; Miwa, M. *Polyhedron* **1986**, *5*, 1267. (m) Papaconstantinou, E.; Argitis, P.; Dimotikali, D.; Hiskia, A.; Ionnidis, A. *NATO ASI Ser., Ser. C* **1986**, *174*, 415. (n) Siedle, A. R.; Markell, C. G.; Lyon, P. A.; Hodgson, K. O.; Roe, A. L. *Inorg. Chem.* **1987**, *26*, 219. (o) Urabe, K.; Tanaka, Y.; Izumi, Y. *Chem. Lett.* **1985**, 1595. (p) Vasilevskis, J.; De Deken, J. C.; Saxton, R. J.; Wentreck, P. R.; Fellmann, J. R.; Kipnis, L. S. PCT Int. App. WO 87 01,615 [*Chem. Abst.* **1987**, *107*, 178602p]. (q) Venturello, C.; D'Aloisio, R.; Bart, J. C. J.; Ricci, M. *J. Mol. Catal.* **1985**, *32*, 107. (r) Yamase, T.; Watanabe, R. *J. Chem. Soc., Dalton Trans* **1986**, 1669.

(3) (a) Chester, A. W. *J. Org. Chem.* **1970**, *35*, 1997. (b) Ebersson, L.; Wistrand, L. G. *Acta. Chem. Scand.* **1980**, *B34*, 349. (c) Jönsson, L. *Acta. Chem. Scand.* **1983**, *B37*, 761. (d) Ebersson, L. *J. Am. Chem. Soc.* **1983**, *105*, 3192. (e) Ayoko, M. A.; Olatunji, G. A. *Polyhedron* **1983**, *2*, 577. (f) Olatunji, G. A.; Ayoko, M. A. *Bull. Soc. Chim. Fr.* **1985**, *5*, 705. (g) Saha, S. K.; Ghosh, M. C.; Banerjee, P. *J. Chem. Soc., Dalton Trans.* **1986**, 1301. (h) Saha, S. K.; Ghosh, M. C.; Banerjee, P. *Inorg. Chim. Acta* **1986**, *126*, 29.

(4) (a) Pope, M. T. In *Mixed-Valence Compounds*; Brown, D. B., Ed.; Reidel Publishing Company: Dordrecht, 1980; p 365. (b) Kozik, M.; Baker, L. C. W. *J. Am. Chem. Soc.* **1987**, *109*, 3160. (c) Kozik, M.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1986**, *108*, 7627.

(5) Katsoulis, D. E.; Pope, M. T. *J. Chem. Soc., Chem. Commun.* **1986**, 1186.

(6) Faraj, M.; Hill, C. L. *J. Chem. Soc., Chem. Commun.* **1987**, 1487.

(7) Piepgrass, K. W.; Pope, M. T. *J. Am. Chem. Soc.* **1987**, *109*, 1586.

(8) Spectra were recorded on ca. 0.15 M solutions in 0.5 M DCl/D₂O by using a Bruker AM-300WB spectrometer at 40.688 MHz with 10-mm tubes. Sweep widths were 62 000 or 83 000 Hz (acquisition times of 33 and 25 ms, respectively) with an acquisition delay of 150 μs to allow probe ringing to die out. The number of scans varied from 200 000 to 600 000. Chemical shifts are reported relative to external H₂O. Addition of Mn²⁺ at concentrations of 10⁻³ M was sufficient to remove the large solvent peak [Drago, R. S. *Physical Methods in Chemistry*; W. B. Saunders, Co.: Philadelphia, PA, 1977; p 205. Merbach, A. E. *Pure Appl. Chem.* **1987**, *59*, 161] and permitted observation of terminal H₂O resonances that were otherwise obscured. The presence of Mn²⁺ did affect resonances of some of the anions' terminal oxygen atoms as we discuss elsewhere [Piepgrass, K.; Barrows, J. N.; Pope, M. T. *J. Chem. Soc., Chem. Commun.*, in press] so that the complete spectra were obtained both with and without Mn²⁺.

(9) In the cases of I and II one other resonance also was enriched at about the same rate. We tentatively attribute this resonance (at ca. 400 ppm) to the oxygens (h in Figure 1) that bridge W^{IV} and W^{VI} atoms.

(10) (a) Merbach, A. E., private communication. (b) Richens, D. T.; Helm, L.; Pittet, P.-A.; Merbach, A. E. *Inorg. Chim. Acta* **1987**, *132*, 85.

(11) Katsoulis, D. E.; Pope, M. T. *J. Am. Chem. Soc.* **1984**, *106*, 2737.

(12) Extended reflux in acetonitrile results in replacement of terminal H₂O ligands by CH₃CN.

(13) Isolated yields of the oxidized heteropolyanion salts varied from 30 to 80% depending upon solubility.

(14) With inorganic oxygen donor Bu₄NBrO₃ 1 mol was sufficient to oxidize 1 mol of I completely.

(15) In this case the product solution contained no starting material a mixture of azoxybenzene (70%) and another unidentified product (30%). The rate of this reaction excludes a mechanism in which nitrosobenzene displaces a terminal ligand on tungsten(IV), and we are investigating this further.

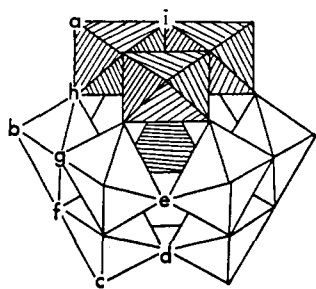


Figure 1. Polyhedral representation of the α -Keggin structure adopted by the heteropoly browns I, II, and III. The tungsten(IV) ions occupy the three octahedra shaded. Letters indicate positions of terminal water molecules (a) and oxygen atoms (b-i). A ninth type of oxygen atom occupies the corners of the central tetrahedron.

Table I. Reactions of Heteropoly Browns with Oxygen Donors, XO^a

anion	solvent	temp/°C	time	XO	product (yield ^b)
I	CH ₃ CN	95	90 m	Me ₂ SO	Me ₂ S (75)
II	toluene	110	400 m	Ph ₂ SO	Ph ₂ S (75)
I	toluene	110	10 m	Ph ₃ AsO	Ph ₃ As (>33)
I	CH ₃ CN	95	90 m	Ph ₃ AsO	Ph ₃ As (60)
I	toluene	25	10 m	PhNO	PhN(O)=NPh (~50)
I	CH ₃ CN	25	<1 s	PhNO	PhN(O)=NPh (70 ^c)

^aMolar ratio polyanion:XO = 1:3. ^bPercent conversion of starting material to product. Yields have not been optimized. ^cNo starting material remained, and a second unidentified product accounted for the material balance.

a true oxygen atom transfer is supported in one case by isotopic labeling. Reaction of ¹⁷O-labeled Me₂SO with unenriched III in toluene leads to SiW₁₂O₄₀⁴⁻ with the label appearing at the chemical shift of the terminal oxygen (765 ± 5 ppm).¹⁶ In his recent comprehensive and masterly review of oxygen atom transfer reactions in inorganic and bioinorganic chemistry, Holm¹⁷ has proposed a scale of reactivity based upon the enthalpy of the reaction XO → X + 1/2O₂. The results shown in Table I are broadly consistent with that scale, that is Me₂SO (ΔH = -27 kcal) and Ph₃AsO (>-35 kcal) are reduced by I, but (MeO)₂SO₂ (-49), Me₂SO₂ (-52), PhNCO (-50), and Ph₃PO (-67) are not affected, even after prolonged reaction times.¹⁸

The facile generation of heteropoly browns by electrochemical and photochemical^{2r} processes, their high thermal stabilities, and further potentialities for multiatom transfer per polyanion¹⁹ suggest numerous possibilities for stoichiometric and perhaps catalytic reactions. We are currently exploring these and other atom- and group-transfer reactions.

Acknowledgment. We thank Professors Merbach and Holm for helpful discussions. The research has been supported by grants from NSF and ARCO, and the NMR spectrometer was purchased with assistance from NSF and the Keck Foundation.

(16) With I and II the analogous experiment shows enrichment at one of the two μ_2 oxygens as well as at the terminal oxygens. Recall that the water exchange experiments⁹ also indicated a second site of exchange on these reduced anions. Synthesis [Fenselau, A. H.; Moffatt, J. G. *J. Am. Chem. Soc.* **1966**, *88*, 1762] of ¹⁷O-enriched Me₂SO ($\delta_0 = 15$ ppm) yielded a product that contained an impurity ($\delta_0 = 320$ ppm) that we have been unable to identify. Although the latter chemical shift is identical with that of BrO₃⁻, which is a plausible candidate for the impurity, the 320-ppm resonance was unaffected during the sulfoxide-polytungstate reaction, which resulted in the disappearance of the line at 15 ppm and the formation of a line at 765 ppm (terminal oxygen of the oxidized polytungstate). In separate experiments however, I was found to be rapidly oxidized by authentic Bu₄NBrO₃.¹⁴

(17) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401.

(18) Epoxides would, on the basis of the Holm criterion, be expected to be deoxygenated [see, for example, Moloy, K. G. *Inorg. Chem.* **1988**, *27*, 677]. Reactions of I with norbornene oxide and cyclohexene oxide in toluene at 115 °C resulted in partial oxidation to heteropoly blues, suggesting that proton- and electron-transfer processes had occurred. We are investigating this further.

(19) More extensively reduced "browns" with six, nine, and 12 W(IV) atoms are accessible, see, for example: Launay, J. P. *J. Inorg. Nucl. Chem.* **1976**, *38*, 807. Kazansky, L. P.; Launay, J. P. *Chem. Phys. Lett.* **1977**, *51*, 242.

Reduction Potentials for Substituted Benzyl Radicals: pK_a Values for the Corresponding Toluenes¹

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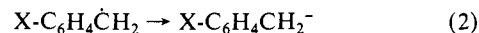
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Received September 19, 1988

Revised Manuscript Received November 23, 1988

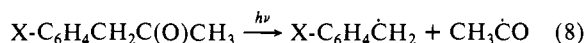
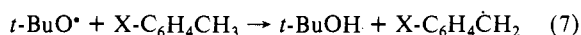
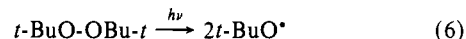
The acidities of carbon acids in aprotic solvents are of fundamental importance in physical-organic chemistry and have been the subject of extensive research.² Bordwell and his colleagues^{2e} developed a titration method to determine such pK_a values in dimethyl sulfoxide as solvent that made use of colored organic anions as indicators. However, the method was unsuitable for very weak acids such as toluene. Breslow and his co-workers³ took a different approach and calculated pK_a values relative to that for triphenylmethane by combining homolytic bond dissociation energies with the oxidation potentials of carbanions in a thermochemical cycle. Again, many weak acids were beyond the scope of this method because it was difficult to obtain stable solutions of the necessary carbanions for the electrochemical measurements.

In this work, we have quantified the pK_a values in acetonitrile for substituted toluenes by using the thermochemical cycle shown in eq 1-5. This approach is unique since the pK_a values are



calculated directly and do not rely upon relative measurements. The necessary reduction potentials were obtained by direct electrochemical measurements on the benzyl radicals by using the technique of photomodulation voltammetry (PMV) that we have described in detail elsewhere.⁴

In this approach radicals are generated by modulated photolysis, eq 6 and 7 or 8, so that the radical concentration oscillates at a



fixed frequency. Phase-sensitive detection at that frequency is then used to detect the electrochemical behavior of the radicals. This discrimination in favor of the radicals allows the reduction potential to be measured even when radical concentrations are ca. 10⁻⁷-10⁻⁸ M and lifetimes are 1 ms.

The reduction potentials of several substituted benzyl radicals (gold minigrad working electrode in acetonitrile/di-*tert*-butyl-

(1) Issued as NRCC Publication No. 29630.

(2) See, for example: (a) Streitwieser, A., Jr.; Murdoch, J. R.; Häfelinger, G.; Chang, C. J. *J. Am. Chem. Soc.* **1973**, *95*, 4248. (b) Streitwieser, A., Jr.; Granger, M. R.; Marcs, F.; Wolf, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 4257. (c) Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006. (d) Bordwell, F. G.; Algrin, D.; Vanier, N. R. *J. Org. Chem.* **1977**, *42*, 1817. (e) Bordwell, F. G. *Acc. Chem. Res.* **1988**, in press and references cited therein.

(3) (a) Breslow, R.; Balasubramanian, K. *J. Am. Chem. Soc.* **1969**, *91*, 5182. (b) Breslow, R.; Chu, W. *Ibid.* **1973**, *95*, 411. (c) Breslow, R.; Mazur, S. *Ibid.* **1973**, *95*, 584. (d) Wasielewski, M. R.; Breslow, R. *Ibid.* **1976**, *98*, 4222. (e) Breslow, R.; Grant, J. L. *Ibid.* **1977**, *99*, 7745. (f) Jaun, B.; Schwarz, J.; Breslow, R. *Ibid.* **1980**, *102*, 5741.

(4) (a) Wayner, D. D. M.; Griller, D. *J. Am. Chem. Soc.* **1985**, *107*, 7764. (b) Wayner, D. D. M.; Dannenberg, J. J.; Griller, D. *Chem. Phys. Lett.* **1986**, *131*, 189. (c) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132.