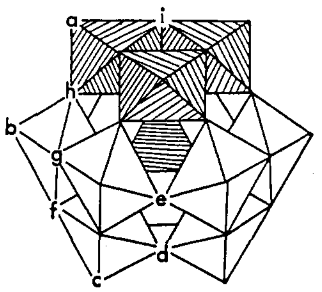

Figure 1. Polyhedral representation of the α-Keggin structure adopted by the heteropoly browns I, II, and III. The tungsten(IV) ions occupy the three octahedra shaded. Letters indicate positions of terminal water molecules (a) and oxygen atoms (b–i). A ninth type of oxygen atom occupies the corners of 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_3CN	95	90 m	Me_2SO	Me_2S (75)
II	toluene	110	400 m	Ph_2SO	Ph_2S (75)
I	toluene	110	10 m	Ph_3AsO	Ph_3As (>33)
I	CH_3CN	95	90 m	Ph_3AsO	Ph_3As (60)
I	toluene	25	10 m	PhNO	PhN(O)═NPh (~50)
I	CH_3CN	25	<1 s	PhNO	PhN(O)═NPh (70[c])

[a] Molar ratio polyanion:XO = 1:3. [b] Percent conversion of starting material to product. Yields have not been optimized. [c] No 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 ^{17}O-labeled Me_2SO with unenriched III in toluene leads to $SiW_{12}O_{40}^{4-}$ 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, Holm[17] has proposed a scale of reactivity based upon the enthalpy of the reaction $XO \rightarrow X + {}^1/_2O_2$. The results shown in Table I are broadly consistent with that scale, that is Me_2SO ($\Delta H = -27$ kcal) and Ph_3AsO (>−35 kcal) are reduced by I, but $(MeO)_2SO_2$ (−49), Me_2SO_2 (−52), PhNCO (−50), and Ph_3PO (−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 polyanion[19] 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.

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(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 experiments[9] 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 ^{17}O-enriched Me_2SO ($\delta_O = 15$ ppm) yielded a product that contained an impurity ($\delta_O = 320$ ppm) that we have been unable to identify. Although the latter chemical shift is identical with that of BrO_3^-, 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 Bu_4NBrO_3.[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 Toluenes[1]

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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-workers[3] 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

$$X\text{-}C_6H_4CH_3 \rightarrow X\text{-}C_6H_4\dot{C}H_2 + H^\bullet \tag{1}$$

$$X\text{-}C_6H_4\dot{C}H_2 \rightarrow X\text{-}C_6H_4CH_2^- \tag{2}$$

$$H^\bullet \rightarrow {}^1\!/_2H_2 \tag{3}$$

$$^1\!/_2H_2 \rightarrow H^+ \tag{4}$$

$$X\text{-}C_6H_4CH_3 \rightarrow X\text{-}C_6H_4CH_2^- + H^+ \tag{5}$$

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

$$t\text{-BuO-OBu-}t \xrightarrow{h\nu} 2t\text{-BuO}^\bullet \tag{6}$$

$$t\text{-BuO}^\bullet + X\text{-}C_6H_4CH_3 \rightarrow t\text{-BuOH} + X\text{-}C_6H_4\dot{C}H_2 \tag{7}$$

$$X\text{-}C_6H_4CH_2C(O)CH_3 \xrightarrow{h\nu} X\text{-}C_6H_4\dot{C}H_2 + CH_3\dot{C}O \tag{8}$$

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 minigrid working electrode in acetonitrile/di-*tert*-butyl-

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(1) Issued as NRCC Publication No. 29630.

(2) See, for example: (a) Streitweiser, 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.

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Table I. Reduction Potentials of Substituted Benzyl Radicals and Calculated pK_a Values for Substituted Toluenes

substituent	$E_{1/2}^{\text{red}}$ (V vs SCE)[a,b]	pK_a (X-$C_6H_4CH_3$)[c]	ΔpK_a[d]
4-OMe	−1.75[e]	55.2	4.1
4-Me	−1.62	53.8	2.7
3-Me	−1.50	52.2	1.1
4-F	−1.50	52.2	1.1
H	−1.43 (−1.45)[f]	51.1	0.0
4-Cl	−1.40	50.8	−0.3
3-CN	−1.11	46.8	−4.3
4-CN	−0.77	41.2	−9.9 (−11)[g]
4-C(O)Me	−0.71	39.8	−11.3

[a] Reduction potential of X-$C_6H_4\dot{C}H_2$ measured by PMV at 53 Hz modulation. All values have an experimental uncertainty of ±50 mV. [b] Radicals were generated by hydrogen atom abstraction, eq 6 and 7 in acetonitrile/di-*tert*-butyl peroxide (9:1) containing TBAP (0.1 M). [c] Calculated with eq 9, uncertainty ±2 pK_a units. Absolute pK_a of toluene is 51 in acetonitrile and 42 in DMSO. [d] Relative to toluene. [e] Radical generated by photolysis of 4-methoxyphenylacetone in acetonitrile/TBAP (0.1 M). [f] Reference 2e. [g] Reference 2d.

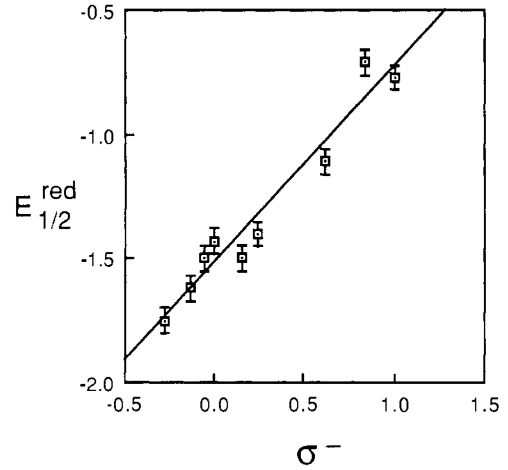

Figure 1. Hammett plot of $E_{1/2}^{\text{red}}$ (V vs SCE) versus σ^- for the reduction of substituted toluenes.

peroxide (9:1) solvent containing 0.1 M tetrabutylammonium perchlorate, TBAP) are reported in Table I. A Hammett plot, Figure 1, shows that they correlate with σ^-, and the slope (770 mV, $r = 0.97$) corresponds to a ρ value of 13. The correlation with σ^- implies that the redox potentials are dominated by the carbanion stability. Extended Hammett treatment of the data using σ^- and $\sigma_\alpha^\bullet$, which reflects the substituent effect on the radical stability,[5] does not improve the correlation.

The linearity of the Hammett plot suggests either that the measured potentials, $E_{1/2}$, are close to the standard potential, $E°$ (which is a thermodynamically significant value[6]), or that they are all irreversible and that the overpotentials vary monotonically with σ^-. In fact, it is easy to differentiate between these possibilities. The measured $E_{1/2}$ value for the reduction of the benzyl radical is indeed close to $E°$ since our value is within 20 mV of that for the reverse process, i.e., the oxidation of the benzyl anion.[3c] The linearity of the Hammett plot, therefore, implies that all of the $E_{1/2}$ values are close to $E°$. This conclusion is further supported by the good agreement between our calculated ΔpK_a value for 4-cyanotoluene and a literature value[2d] (vide infra, Table I).

The pK_a values were calculated, eq 9, by combining the measured reduction potentials, eq 2, with the free energy for homolytic bond dissociation, eq 1,[7-9] and by introducing the free energies for reactions 3 ($\Delta G_3° = 48.6$ kcal mol^{-1}) and 4 ($E_4° = 0.254$ V vs SCE).[12] The energies for the homolytic cleavages are barely affected by the substituents,[7,8] the maximum variation being 2–3 kcal mol^{-1}. In fact, the contributions from the reduction potentials dominate the changes in acidities and Δp$K_a \approx F\Delta E_2°/2.3RT$.

$$\mathrm{p}K_a = (\Delta G_1° - F(E_2° - E_4°) - \Delta G_3°)/2.3RT \qquad (9)$$

It is interesting to compare the pK_a's in acetonitrile with those reported by Bordwell with the titration method in dimethyl sulfoxide.[2d] For toluene and 4-cyanotoluene, $\mathrm{p}K_a^{\mathrm{CH_3CN}} - \mathrm{p}K_a^{\mathrm{DMSO}}$ is completely accounted for by only considering the change in solvation of the proton indicating that the free energy change for the transfer of the carbanion between the two solvents, $\Delta G_{\text{tr}}°(\mathrm{R}^-)$, is small.[4c] The implication of this result is that $\Delta G_{\text{tr}}°(R^-)$ for all of the substituted benzylic carbanions is small (i.e., less than 2 kcal mol^{-1}).

Acknowledgment. We thank Dr. Larkin Kerwin for a "President's Award" that made this work possible.

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(9) Pryor[7] originally reported a correlation with σ ($\rho = 2.8$). However, we have found that the BDE values for a series of substituted phenols correlated with σ^{+}[10] supporting a suggestion originally made by Zavitsas and Pinto.[11] Pryor's original data, in fact, give a somewhat better correlation with σ^+ ($\rho = 2.3$) ($r = 0.96$ for σ^+ versus $r = 0.89$ for σ). Therefore, we have used $\Delta G_3° = 80 + 2.3\sigma^+$ kcal mol^{-1} in the calculation of pK_a (eq 9) where $\Delta G_3° = 80$ for toluene.

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Structure and Binding for Rebek's Diacid in Chloroform. A Demure Host for Pyrazine

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A major, current activity in bioorganic chemistry is the development of synthetic receptors[1] that selectively bind neutral organic molecules in organic solvents[2] or water.[3] Rebek has actively studied a class of hosts that feature a binding cleft with convergent functional groups.[2a] Both binding and catalysis have been demonstrated for **1**.[4,5] In particular, this host is postulated to sequester pyrazine **2** via the "two-point binding" shown below.[4] However, it is not obvious that the ratio of observed[4] K_a's of only

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