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GEOMETRICAL AND ELECTRONIC COOPERATIVITY IN CATION-MEDIATED ELECTROCHEMICAL REDUCTIONS OF ANTHRAQUINONE-SUBSTITUTED PODANDS

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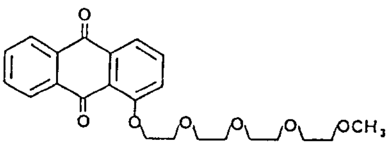
Summary Unlike their nitroaromatic counterparts, podands based upon the anthraquinone skeleton bind cations more strongly when reduced because of a combination of geometrical and electronic factors.

We wish to report the first example of an electrochemically switched anthraquinone podand, the success of which can be attributed to a combination of electronic and geometrical factors. The anthraquinone podands exhibit electrochemically-mediated binding enhancements whereas the nitroaromatic podands[1] previously studied did not. Moreover, the present species undergo electrochemical switching in two discrete steps involving first the formation of an anion and then of a dianion.

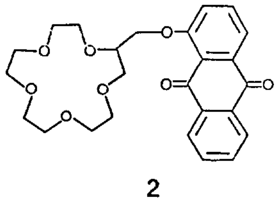
The cyclic voltammogram of compound 1[2] in MeCN containing 0.1M tetrabutylammonium perchlorate (Bu_4NClO_4, TBAP) is shown in Figure 1, voltammogram A. This compound shows a reversible redox couple at -0.90V (vs. SCE, see Table 1) corresponding to the formation of the anthraquinone anion-radical, and a quasi-reversible redox couple at -1.44V corresponding to the formation of the anthraquinone dianion. Addition of 0.5 equivalents of $LiClO_4$ (Figure 1B) to a millimolar solution of 1 in acetonitrile results in the observation of a new reversible redox couple at -0.58V, and the loss of the original couple which occurred at -1.44V. At 1.0 equivalents of $LiClO_4$ (Figure 1C) only the reversible redox couple at -0.58V remains. These results can be explained with the help of the electrochemical cycle shown in Scheme 1.

$$\begin{tikzcd}
 & L + M^+ \arrow[r, shift left, "K_1"] \arrow[dd, shift left] & LM^+ \arrow[l, shift left] \arrow[dd, shift left] & \\
1 & & & 1' \\
 & L^{\overline{\cdot}} + M^+ \arrow[uu, shift left, "e^-"] \arrow[r, shift left, "K_2"] \arrow[dd, shift left] & LM\cdot \arrow[l, shift left] \arrow[uu, shift left, "e^-"] \arrow[dd, shift left] & \\
2 & & & 2' \\
 & L^{=} + M^+ \arrow[uu, shift left, "e^-"] \arrow[r, shift left, "K_3"] & LM^- \arrow[l, shift left] \arrow[uu, shift left, "e^-"] &
\end{tikzcd}$$

Scheme 1



1



2

In the absence of any cation, the redox couples corresponding to steps 1 and 2 are observed. In the presence of 0.5 equivalents of Li^+ only steps 1 and 1' are observed. The absence of steps 2 and 2' is probably the result of rapid electron transfer between $L^{\dot{-}}$ and LM•. A similar observation has previously been reported[3] for the case where protons rather than metal cations were "complexed."

$$L^{\dot{-}} + LM\cdot \text{ -----> } L + LM^- \qquad \text{Equation 1}$$

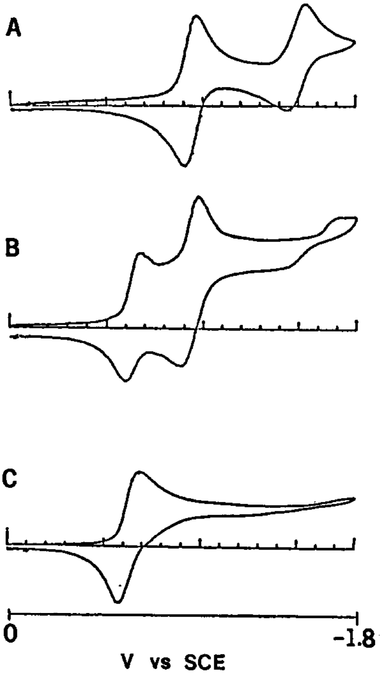
In the presence of 1.0 equivalent of Li^+, the equilibrium (K_1 in Scheme 1) lies to the right. As a result, the redox couple corresponding to step 1', but not that corresponding to step 1, is observed. The difference in the redox potentials ($\Delta E^{o\prime}$) between steps 1 and 1' is 0.32V which corresponds to a Li^+ binding enhancement (K_2/K_1) of 2.6×10^5.[4] The cation binding by reduced **1** is stronger than that of lariat ether **2** (see structure and reference 5) by more than 100. The Li^+ binding enhancement for the latter is 2.4×10^3.

We interpret these results in terms of the ligand geometry illustrated in Figure 2. Compounds **1** and **2** both possess rigid anthraquinone units and a polyether portion. In **1**, the polyether is attached directly to the 2-oxygen of anthraquinone but in **2**, the terminal hydroxymethyl portion of a glycerol unit connects the macroring to the reducible residue. An examination of CPK molecular models leads to the conclusion that podand **1** is more flexible than lariat ether **2**. As a result, the polyether portion of **1** can more effectively interact with the anthraquinone-bound cation. This improved interaction forms a stronger ion-pair between lithium cation and the anion-radical which, in turn, leads to a greater binding enhancement than that observed previously[5] for lariat ether **2**. The presence of a strong ion-pair also makes homogeneous electron transfer (Equation 1) a more facile process.

The results obtained from a study of **1** with Na^+ support the interpretation offered above. When 0.5 equivalents of $NaClO_4$ (Figure 1D) is added to a solution of **1**, four distinct redox couples are observed. These correspond to the original couples (steps 1 and 2 in Scheme 1) and two new couples (steps 1' and 2') which represent the first and second one-electron reductions of the anthraquinone•Na^+ complex. When 1.0 equivalent of $NaClO_4$ (Figure 1E) is added, only the redox couples corresponding to steps 1' and 2' are observed. Since Na^+ forms a weaker ion-pair than Li^+ with the anthraquinone anion-radical, homogeneous electron transfer is less favored. This leads to a species (LM) with a sufficiently long lifetime to observe steps 2 and 2' for the Na^+ case. The peak separations (Fig. 1E) indicate $\Delta E^{o\prime}$ values of 0.14V and 0.18V for the anion-radical and the dianion respectively. The sodium cation binding enhancements are therefore 2.3×10^2 for the anion-radical and 1.1×10^3 for the dianion (relative to the anion binding, K_3/K_2).

Electron spin resonance spectra of reduced **1** were obtained by electrolytic reduction of **1** in dry THF, under vacuum, and in the presence of 0.1 M TBAP as supporting electrolyte.[6] The spectrum of $\mathbf{1}^{\dot{-}}$ is shown in Figure 3A. A computer simulation of this spectrum was obtained using

Figure 1



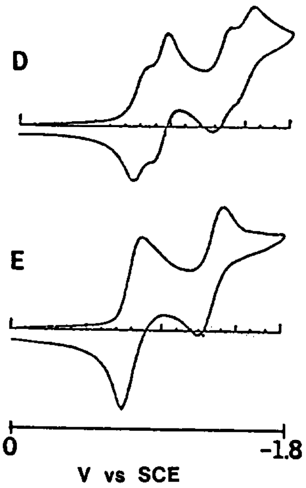


Figure 2

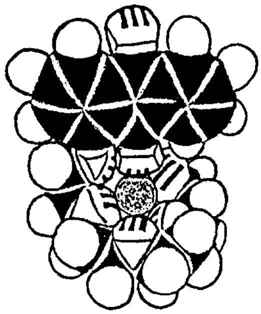


Table 1. Cation Dependence of Anthraquinone Podand Electrochemistry

Cation	Equivalent	Epc^1	Epa^1	E°^{1}	Epc^2	Epa^2	E°^{2}	Epc^3	Epa^3	E°^{3}	Epc^4	Epa^4	E°^{4}	ΔE^{1-2}	Enhancement	ΔE^{3-4}	Enhancement
None	—	-1.49	-1.39	-1.44	—	—	—	-0.93	-0.86	-0.90	—	—	—	—	—	—	—
Li$^+$	0.5	—	—	—	—	—	—	-0.93	-0.82	-0.88	-0.62	-0.54	-0.58	—	—	—	—
	1.0	—	—	—	—	—	—	—	—	—	-0.63	-0.52	-0.58	—	—	0.32	2.6×10^5
Na$^+$	0.5	-1.47	-1.39	-1.43	-1.32	-1.24	-1.28	-0.92	-0.86	-0.89	-0.79	-0.73	-0.76	—	—	—	—
	1.0	—	—	—	-1.32	-1.19	-1.26	—	—	—	-0.80	-0.72	-0.76	0.18	1.1×10^3	0.14	2.3×10^2

the following coupling constants: A_{2H} = 0.45 g, A_{1H} = 0.67 g, A_{2H} = 1.08 g, and A_{1H} = 1.34 g.[7] The linewidth was 0.11 g. In contrast, when the reduction was accomplished using alkali metals in THF, a drastic change in the spectrum was observed (Fig. 3B). A Li$^+$ splitting of 0.22 g was measured which confirmed formation of a strongly ion-paired complex. When Na$^+$ was used, a metal splitting of 0.17 g was observed.

The flexibility of podand **1** allows tighter ionic association upon reduction than does **2** or the nitroaromatic podands previously studied. As a result, large binding enhancements are observed for Li$^+$ and Na$^+$. In the case of Na$^+$, enhancements are observed for both the anion-radical and the dianion. The cooperation observed between geometrical and electronic factors are currently being studied in the hope of fine tuning these systems for selective binding enhancement.

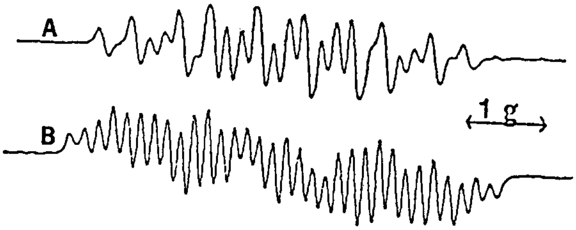


Figure 3 Electron Spin Resonance spectrum of **1** alone and in the presence of Li$^+$. The spectra were recorded in anhydrous THF solution.

Acknowledgment We warmly thank the National Institutes of Health and W. R. Grace & Co. for support of this work.

Notes and References

1. Morgan, C.R.; Gustowski, D.A.; Cleary, T.P.; Echegoyen, L.; Gokel, G.W.; J. Org. Chem. **1984**, 49, 5008-5010.

2. Compound **1**: mp = 70-72 °C; ^{1}H-NMR ($CDCl_3$) 3.35 (s, 3H), 3.58-4.09 (m, 14H), 4.34 (t, 2H), 7.30-8.26 (m, 7H); IR (KBr) 1670, 1590 cm^{-1}; Anal. Calcd. for $C_{23}H_{26}O_7$: C, 66.64; H, 6.34%. Found: C, 66.70; H, 6.38%.

3. For a general discussion on proton donor effects, see: Patai, S.; (Ed.), The Chemistry of the Quinonoid Compounds, Wiley, New York, 1974, p. 746.

4. These values were calculated as previously described: Gustowski, D.A.; Echegoyen, L.; Goli, D.M.; Kaifer, A.; Schultz, R.A.; Gokel, G.W.; J. Am. Chem. Soc., **1984**, 106, 1633-1635.

5. Echegoyen, L.; Gustowski, D.A.; Gatto, V.J.; Gokel, G.W.; J. Chem. Soc. Chem. Comm., **1986**, 220-223.

6. Delgado, M.; Echegoyen, L.; Gatto, V.J.; Gustowski, D.A.; Gokel, G.W.; J. Am. Chem. Soc. **1986**, 108, in press.

7. The subscripts refer to the number of equivalent hydrogens giving rise to the signal.

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