Cyclic Voltammetry of Polyquinocycloalkanes

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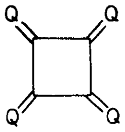
Summary Unusually high (positive) reduction potentials have been observed for the title compounds by cyclic voltammetry in CH_2Cl_2.

Recently we have synthesized and characterized a new class of cyclic polyquinoid compounds, the polyquinocycloalkanes [(**1**)—(**6**)].[1] These compounds have at least two π-conjugated quinoid groups and can therefore behave like



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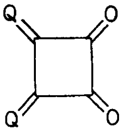

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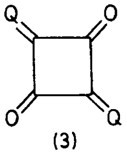

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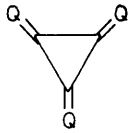

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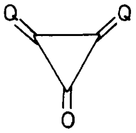

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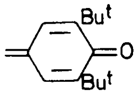


quinones in reduction–oxidation reactions. Here, we report the reduction potentials for this series of compounds as determined by cyclic voltammetry in CH_2Cl_2.

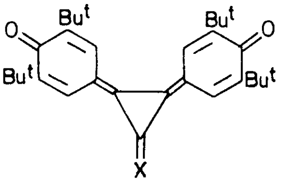
TABLE

Reduction potentials ($E_{1/2}$)[a] of polyquinones in dichloromethane[b]

Quinone	$E_{1/2}$ V *vs.* SCE 1st wave	2nd wave
(**1**)	$-0{\cdot}18$	$-0{\cdot}51$
(**2**)	$+0{\cdot}30$	$(-0{\cdot}14)$[c]
(**3**)	$+0{\cdot}20$	$-0{\cdot}45$
(**4**)	$+0{\cdot}05$	$-0{\cdot}33$
(**5**)	$+0{\cdot}13$	$-0{\cdot}34$
(**6a**)	$+0{\cdot}30$	$-0{\cdot}24$
(**6b**)	$+0{\cdot}17$	$-0{\cdot}32$
(**6c**)	$+0{\cdot}09$	$-0{\cdot}24$
(**6d**)	$+0{\cdot}25$	$-0{\cdot}14$
(**6e**)	$+0{\cdot}22$	$-0{\cdot}25$
(**6f**)	$+0{\cdot}16$	$-0{\cdot}26$
p-Benzoquinone	$-0{\cdot}56$[d]	$(-1{\cdot}38)$[c]
Chloranil	$+0{\cdot}00$[d]	$-0{\cdot}78$[d]
DDQ	$+0{\cdot}57$[d]	$-0{\cdot}32$[d]

[a] Average of cathodic and anodic peak potentials of cyclic voltammograms. [b] Quinones, 1×10^{-4}M. Supporting electrolyte: Bu_4NClO_4, 0·1M. [c] Irreversible waves. [d] These data agreed well with the polarographic $E_{1/2}$ in acetonitrile reported by M. E. Peover (*J. Chem. Soc.*, 1962, 4540) using Et_4NClO_4 as a supporting electrolyte, but not with those reported by R. M. Scribner (*J. Org. Chem.*, 1966, **31**, 3671) using $LiClO_4$ as supporting electrolyte.

The compounds [(**1**)—(**6**)] all exhibited a well defined two-wave pattern corresponding to two discrete one-electron transfer processes forming radical anions initially and then dianions. Each electron-transfer step was found to be reversible by detailed analysis of the F_p and i_p data. Compounds [(**2**)—(**6f**)] all show higher first reduction potentials than those for *p*-benzoquinone and chloranil, and compounds (**6a**—**f**) generally show second reduction potentials even higher than that for DDQ (2,3-dichloro-5,6-dicyano-*p*-benzoquinone) (Table). The unusually high (positive) values for $E_{1/2}$ indicate that these compounds have remarkably high electron affinities compared with other quinones, and may be useful as organic oxidizing agents.



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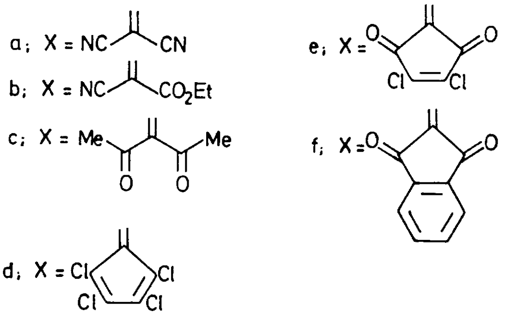

The experimental results are in accord with Hückel molecular orbital calculations which indicate a very low energy for the lowest unoccupied molecular orbitals of [(**1**)—(**6f**)]. The relatively low reduction potentials for (**1**) may be explained by the nonplanarity of this compound,[2] causing less effective π-conjugation in the anions.

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[1] S. K. Koster and R. West, *J. Org. Chem.*, 1975, **40**, 2300; R. West, D. C. Zecher, S. K. Koster, and D. Eggerding, *ibid.*, p. 2295; R. West and D. C. Zecher, *J. Amer. Chem. Soc.*, 1970, **92**, 155.

[2] Unpublished data by R. West, M. Rao, and J. Calabrese; also see S. K. Koster, Ph.D. Thesis, University of Wisconsin-Madison, 1974.