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ELECTROCHEMICAL OXIDATION AND REDUCTION OF A TETRAALKYLATED CYCLOBUTADIENE

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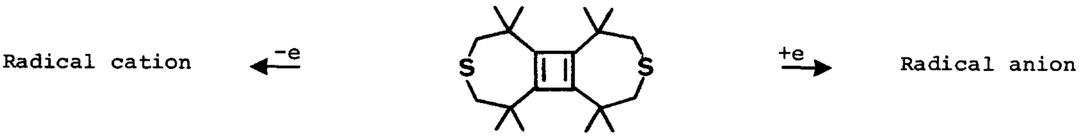
All quantum-mechanical treatments of cyclobutadiene indicate that it should have a relatively high energy HOMO and low energy LUMO. It should thus be easily oxidizable electrochemically, and also easily reducible, compared with simple reference compounds. The availability and stability of 1,[1] a cyclobutadiene perturbed only by simple bulky alkyl substitution, permitted us to examine its electrochemistry.



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Sealed ampoules of 1 were introduced into an electrochemical cell under an argon atmosphere. Cyclic voltammetry at platinum gave an oxidation wave near +0.6 V (vs. s.c.e.), and a reduction wave near -2.7 V.[2] Both waves disappeared when O_2 was admitted, which is known to destroy 1.[1] Even on the fast time-scale of cyclic voltammetry the cation radical and the anion radical of 1 were chemically unstable; in neither case could a reverse wave be detected on reversing the scan direction. The two waves were correlated, since electrolysis at a potential at or beyond either wave, without stirring, reduced the cylic voltammetric amplitude of the other wave by exhausting the material at the electrode; the original amplitude returned on stirring. This novel technique demonstrates that both the oxidation and the reduction involve the same species, presumably 1, rather than some impurity. The assignment of the oxidation wave to 1 is confirmed by the correlation with gas-phase ionization potentials described below. Polarography at a dropping mercury electrode gave a reduction wave with $E_{1/2}$ = -2.5 V, with a wave shape indicating a nearly reversible process.[3] Second

Table 1

ELECTROCHEMICAL POTENTIALS (V)[a]

Compound		Acetonitrile	Dimethoxyethane	Dimethylformamide
Cyclobutadiene Derivative (1)	-e	f	+.65[b]	+.53[b]
	+e	f	-2.70[b] -2.50[d] -2.57[e]	g
1,3-Butadiene (2)	-e	+2.27[b,12] +2.36[c]	g	g
	+e	-2.80[d]	-2.75[d] -2.73[e]	-2.94[b] -2.80[c] -2.61[d,13]
1,3-Cyclohexadiene (3)	-e	+1.50[b] +1.58[c]	g	g
	+e	-2.95[c]	-2.90[d]	-3.1[b] -3.0[c] -2.75[d]
Cyclooctatetraene (4)	-e	+1.43[b,14]	g	+1.57[b]
	+e	-2.30[b] -1.90[d]	-1.98[b] -1.78[d] -1.68, -1.88[e]	-2.01[b] -1.75, -1.95[d,15]

a) Potentials in volts vs. s.c.e., reproducible within .05 V for 1, .01 V for 2, 3, 4. Tetrabutylammonium perchlorate (TBAP) as supporting electrolyte at 0.1 M.

b) Peak potential from cyclic voltammetry at a Pt disc electrode.

c) Peak potential from cyclic voltammetry at an Au disc electrode.

d) $E_{1/2}$ from polarography at a dropping mercury electrode.

e) Crossing potentials from second harmonic a.c. polarography at Hg, at 100 Hz (1) and 45 Hz (2, 4). Similar data for 4 are reported in ref. 4b.

f) Material insoluble.

g) Potential beyond the solvent cutoff.

harmonic a.c. polarography, which yields $E_{1/2}$'s unshifted by subsequent kinetic processes,[4] gave a symmetric wave (at 100 Hz) with crossing point -2.57 ± .03 V. The potentials by all these techniques were thus in good agreement. The data on 1 and several reference compounds, using various electrodes and solvents, are listed in Table 1.

The data show minor solvent effects on the potentials, and small systematic effects related to the nature of the electrode. Pt can influence these potentials by selective adsorption of the olefins, but Hg and Au are more inert. Taking these effects into account, it is seen that the cyclobutadiene 1 is more easily oxidized than is 1,3-butadiene (2), 1,3-cyclohexadiene (3), or 1,3,5,7-cyclooctatetraene (4). Gas phase ionization potentials are known for 1: 6.89 V,[6] 2: 9.06 V,[7] 3: 8.25 V,[8] and 4: 8.04 V.[9] A plot[10] of these ionization potentials vs. our oxidation potentials at Pt fits equation (1) with a correlation coefficient of 0.991. Compound 1 is also more easily reduced than is 2 or 3, but not 4.

$$E_{peak}(V) = .75(IP) - 4.55 \qquad (1)$$

Of course 1 is a tetraalkylated cyclobutadiene, and alkyl groups are known to shift both oxidation and reduction waves of dienes cathodically.[11] From the magnitude of such effects in other systems,[11] we estimate that unsubstituted cyclobutadiene would oxidize near +1.0 V, and reduce near -2.2 V. Thus the qualitative prediction that cyclobutadiene should be more easily oxidized or reduced than are simple reference compounds such as 2 or 3 is supported by our data. The relationship of this data to that for cyclooctatetraene (4) is more complex, involving not only the substituent effects but also the conformational change in 4 and the different electron repulsion terms in the two ring systems.

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3. A plot of E vs. $\log(i/i_d - 1)$ gave slope 0.070 V (for a reversible one electron process, expected 0.059 V) and intercept -2.50 V with correlation coefficient 0.997. (cont'd)

$E_{1/4} - E_{3/4}$ was 0.070 V (for a reversible one electron process, expected 0.056 V). By contrast, the polarographic reduction of 4 gave a curve with slope 0.107 V, and $E_{1/4} - E_{3/4}$ 0.110 V. This irreversibility reflects the conformational change associated with reduction of 4.[5]

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