mol^{-1},[1] we calculate PA(ketene) = 825.4 ± 3.2 kJ mol.$^{-1}$ This is in excellent agreement with the original result of Ausloos and Lias[6] and lies in the middle of the range of values cited above. Any correction for excess energy at threshold based on the data of Haney and Franklin[3] results in a PA for ketene which is too high by more than 70 kJ mol^{-1}. We do not believe that translational-energy measurements made at energies significantly greater than threshold can be applied in a straightforward manner as thermochemical corrections for experimental appearance energies.

Conclusion

The general application of eq 1 for calculating 298 K cationic heats of formation from AE measurements has extended previous work[4,37] to include unimolecular decompositions in which the neutral fragment is not a monatomic species. The range of values for $\Delta H_f°_{298}(CH_3CO^+)$ obtained from photoionization data[1] has been shown to be due to a neglect of the necessary enthalpy corrections (ΔH_{corr}) and in some cases to an overestimation of the AE because of kinetic-shift effects. Except for the acetyl halides and acetic anhydride, there is no evidence to suggest any significant excess energy at the decomposition threshold for the acetyl compounds studied here. When the *stationary* electron convention for cationic heats of formation is used, the recommended value for $\Delta H_f°_{298}(CH_3CO^+)$ is 657.0 ± 1.5 kJ mol^{-1} which leads to PA(ketene) = 825.4 ± 3.2 kJ mol.$^{-1}$ An upper limit of ≤−227 kJ mol^{-1} can be placed on the heat of formation for the acetoxy radical.

Acknowledgment. We are pleased to acknowledge the financial support of the Australian Research Grants Committee and the assistance of Dr. J. B. Peel with the photoelectron spectroscopic measurements.

Registry No. Acetyl cation, 15762-07-9; acetaldehyde, 7507-0; acetone, 67-64-1; methyl ethyl ketone, 78-93-3; acetic acid, 64-19-7; methyl acetate, 79-20-9; biacetyl, 431-03-8; acetic anhydride, 108-24-7.

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Electrochemistry of Perfluorotetracyclobuta-1,3,5,7-cyclooctatetraene, a Powerful Neutral Organic Oxidant

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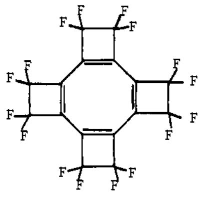
Received September 25, 1981

Abstract: The electrochemistry of perfluorotetracyclobuta-1,3,5,7-cyclooctatetraene (**1**) (a flat cyclooctatetraene) shows two reversible one-electron reductions at 0.79 and 0.14 V vs. SCE. The apparent electron-transfer rate constant for the first reduction is 0.07 ± 0.02 cm/s. The first reduction potential of **1** is more than 2.3 V positive of cyclooctatetraene (COT), and the apparent rate constant is more than an order of magnitude higher. It is suggested that the larger electron transfer rate constant for **1** compared with COT is due to the lower molecular reorganization energy required to reach the transition state for electron transfer. The unusually positive reduction potential of **1** is probably due at least in part to the 16 fluorine atoms.

We report our findings on the electrochemistry of perfluorotetracyclobuta-1,3,5,7-cyclooctatetraene,[1] **1**, which is one of the most powerful neutral organic oxidants known, reducing at positive 0.79 V vs. SCE.



1

Our initial interest in the electrochemistry of **1** was prompted because it is a flat cyclooctatetraene[2] (COT), and comparison of its electrochemistry with tub-shaped COT[3] and other COT derivatives of various conformations[4] could provide insight into the structural changes occurring prior to electron transfer. The COT molecule has been an important species for electrochemical studies because electron transfer awaits COT ring flattening to afford the planar anion radical.[3,4] Experimental data[3,4] suggest the activation energy for ring flattening is manifested by the slow electron transfer rate constant in support of Marcus' theory.[5] It was therefore anticipated that electron transfer to **1** would be faster than to COT, since **1** is already flat. We have confirmed this expectation by fundamental harmonic ac voltammetry measurements.[6]

Experimental Section

Chemicals. Baker HPLC grade acetonitrile was passed through a column of activated alumina (550 °C, ≥15 h; MCB chromatography grade) immediately before use. All electrochemical cell components, syringes, volumetric flasks, and electrolytes were dried in a vacuum oven at 120 °C for at least 8 h before use. Tetrabutylammonium hexafluorophosphate was dried for 24 h in a vacuum oven at 120 °C and

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0002-7863/82/1504-5322$01.25/0

Table I. Comparison of the Electrochemistry of 1 with COT, COTR, DBCOT and DBCOD

	wave 1			wave 2			
compd	α	$E_{1/2}$ vs. SCE	k_0, cm/s	α	$E_{1/2}$ vs. SCE[f]	k_0, cm/s	ref
1	0.42 ± 0.04	+0.79	$(7 \pm 2) \times 10^{-2}$ [a]	0.53 ± 0.03	0.14	$>7 \times 10^{-2}$ [b]	
COT[c]	0.4 ± 0.3		$(2 \pm 0.5) \times 10^{-3}$	0.5 ± 0.03		$(1.5 \pm 0.1) \times 10^{-1}$	3a
COT[d]		−1.61			−1.80		3b
DBCOT[e]	0.7 ± 0.05	−1.935 ± 0.003	$(4 \pm 1) \times 10^{-3}$		−2.02	$(2 \pm 1) \times 10^{-2}$	4
DBCOD[e]		−1.610 ± 0.003	$(5 \pm 1) \times 10^{-2}$		−2.1[f]		4
COTR[c]	0.5 ± 0.04		$(8.3 \pm 0.4) \times 10^{-2}$				3a

[a] Determined from the slope of Figure 3 and eq 2, where the error represents the 90% confidence interval for the slope. The diffusion coefficient was assumed to be 1×10^{-5} cm²/s.[10] [b] See ref 20. [c] 0.1 M tetrabutylammonium perchlorate in dimethylformamide at 25 °C, with a mercury cathode. [d] 0.1 M tetrabutylammonium perchlorate in dimethyl sulfoxide. [e] 0.5 M tetrabutylammonium perchlorate in dimethylformamide with a Pt cathode. The first and second waves are merged. The $E_{1/2}$ values for the waves are reversible potentials calculated via digital simulation. [f] Only compound 1 has a reversible reduction. The $E_{1/2}$ for the second wave of DBCOD is calculated from the irreversible potential.

redried (see above) immediately before use. All solutions contained a small amount, ca. 100 mg, of activated alumina and were degassed for 15 min with helium (99.998% min purity, <5 ppm water, <8 ppm O_2) before the cell was sealed. Compound **1**[1] was sublimed and approximately 1-mg samples were sealed in capillary tubes in a drybox under argon. The capillary tubes were kept in a screw-cap vial under argon until needed and then were dropped into the electrochemical cells, crushed with a dry glass rod under a helium atmosphere, and bubbled with helium to effect solution.

Apparatus. The electrochemical cell had a catholyte working volume of 1–2 mL, which was separated from the anode compartment by a 0.8-cm fine porosity glass frit. Degassing of the anolyte and catholyte was accomplished through a Teflon stopcock via a 6-in. stainless steel needle. The counter electrode was 1-cm² Pt foil, and the working electrode was 0.127-mm-diameter Pt wire sealed in glass and polished flat. Before each series of experiments the cathode was washed in boiling 2% detergent for 1 h, rinsed thoroughly with distilled water, boiled in distilled water for 1 h, soaked in 50% HNO_3 for 3 h, rinsed thoroughly in distilled water, and then dried with a heat gun. Potentials were measured vs. a pseudosilver reference electrode, which was separated from the catholyte via a $^1/_8$-in. long by $^1/_8$-in. diameter unfused Vycor rod sealed in heat shrink Teflon tubing and introduced into the cell through an Ace-Thred adapter. Potentials were converted to the SCE scale by measuring the half-wave potential for ferrocene[7] oxidation and the applying the following equation: $V_{\text{SCE}} = V_{\text{obsd}}(\text{ferrocene}) + 0.315$ V. Cyclic voltammograms were run with either PAR 173, 175, 176 instrumentation or a PAR 174, 174/50 (with manual switching) employing IR compensation in all cases. AC voltammetry employed the PAR 174, 174/50 interface, a Krohn-Hite Model 5200A function generator for the ac modulation (8 mv peak to peak), and a PAR 128A lock-in amplifier. Modulation amplitudes and frequencies were measured on a Hitachi Model V550B oscilloscope. Recordings of data were accomplished with a Houston Instruments Model 2000 X,Y recorder. The cot ϕ values were determined at the peak potential by taking the ratio of the in-phase and quadrature components of the ac current, after correcting each for backgrounds.

Results

Table I summarizes our experimental findings for **1** and compares these with four related systems, cyclooctatetraene (COT), *sym*-dibenzocyclooctatetraene (DBCOT), *sym*-dibenzo-1,5-cyclooctadiene-3,7-diyne (DBCOD), and 1,3,5-cyclooctatriene (COTR). Compound **1** and DBCOD are planar systems, while COT and DBCOT are tub-shaped molecules.

Compound **1** was examined by cyclic voltammetry and phase-sensitive fundamental harmonic ac cyclic voltammetry. Figure 1 displays cyclic voltammograms of **1** with and without ferrocene (used as an internal voltage standard). The most striking features are the unusually positive reduction potential for the first wave (see Table I) and the fact that the two reduction waves are the only electrochemical processes observed between 2.7 and −2.8 V vs. SCE in dry acetonitrile. Plots of the cyclic voltammetry peak currents vs. the square root of the voltage scan rate are linear for both waves, consistent with diffusion-controlled processes.[8] The anodic and cathodic peak separations for waves 1 and 2 are 70 and 60 mV, respectively, at 500 mV/s scan rate with peak current ratios of 1, indicating essentially reversible one-electron transfers.[8] Addition of 0.5 M water produced an increase in peak separation for the first wave, but qualitatively the voltammogram looked unchanged. This attests to the unusual stability of the anion

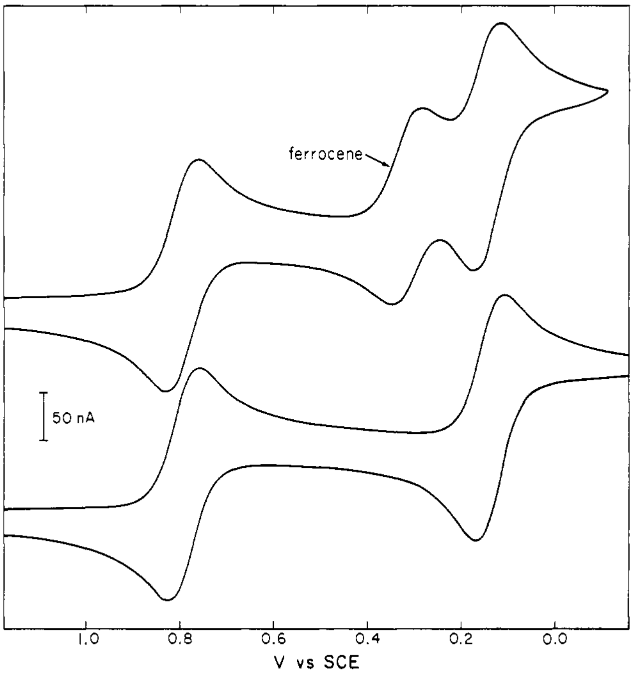

Figure 1. Cyclic voltammograms of **1** and ferrocene (ca 0.8 mM) in 0.2 M tetrabutylammonium hexafluorophosphate in acetonitrile. Scan rate is 200 mV/s.

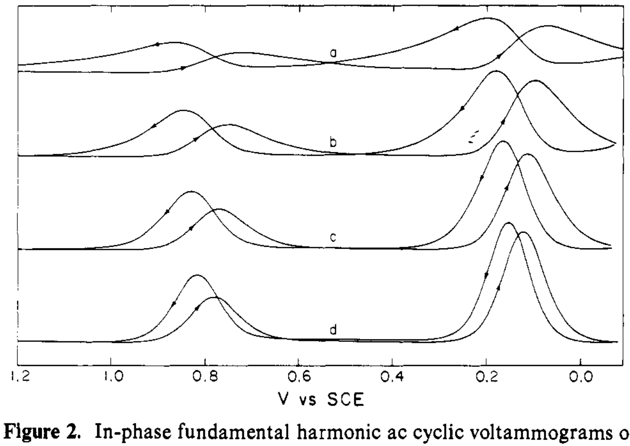

Figure 2. In-phase fundamental harmonic ac cyclic voltammograms of **1** at different dc scan rates: (a) 500 mV/s, (b) 200 mV/s, (c) mV/s, (d) 50 mV/s. The ac frequency is 700 Hz and the scan direction indicated by the arrows. Other conditions as described in the Experimental Section.

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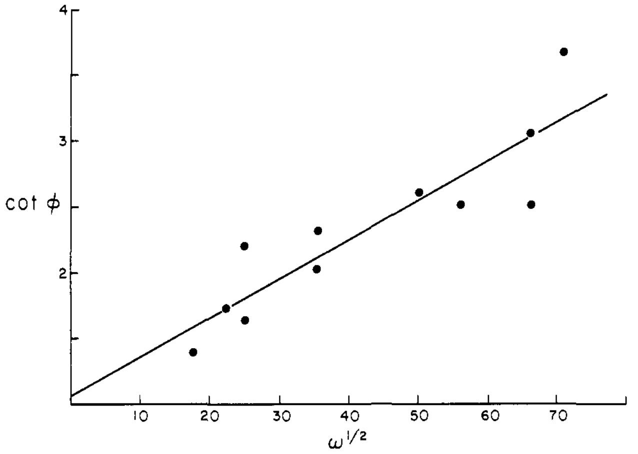

Figure 3. Cot ϕ vs. $\omega^{1/2}$ plot for **1**. This figure represents two separate experimental data sets. See footnote *a* of Table I and Experimental Section for details.

radical and dianion of **1**, in contrast with COT.[3c]

The in-phase fundamental harmonic ac cyclic voltammograms at different dc scan rates are shown in Figure 2. The sensitivity of this technique to dc reversibility is dramatically illustrated by the separation of the forward and reverse peaks, indicating dc quasi-reversibility.[9] The point where the forward and reverse scans intersect is called the crossover potential and is related to the transfer coefficient, α, by[9]

$$E_{co} = E_{1/2}{}^{r} + \frac{RT}{nF}\ln\left(\frac{\alpha}{1-\alpha}\right) \tag{1}$$

from which the transfer coefficients can be calculated (see Table I).

For ac and dc quasi-reversible systems, the phase angle (ϕ) between the applied ac modulation and the ac current is related to the apparent heterogeneous rate constant for electron transfer by[6]

$$\cot\phi = 1 + \frac{(2D_O{}^{\beta}D_R{}^{\alpha}\omega)^{1/2}}{k_0}\left[\frac{1}{e^{\beta a}(1+e^{-a})}\right] \tag{2}$$

where $a = (nF/RT)(E_{dc} - E_{1/2})$, ω = angular frequency, $2\pi f$, $\beta = 1 - \alpha$, and D_O, D_R = the diffusion coefficients of the oxidized and reduced forms, and k_0 = standard rate constants. A plot of this relation is shown in Figure 3, and the electron transfer rate constant determined from the slope is given in Table I.

Discussion

It is of interest to compare the electrochemistry of **1** with DBCOD[4] which also contains a flat conjugated eight-membered ring. Kojima, Bard, Wong, and Sondheimer[4] observe a reversible one-electron transfer at −1.61 V vs. SCE followed by an irreversible second wave, which when corrected for kinetics gave an $E_{1/2}{}^{r}$ of −2.1 V. The reduction potential and the first and second wave separation are typical for aromatic compounds[10] but distinctly different from those observed for **1**. The ΔE_p of 0.65 V for **1** is larger and about 150 mV greater than predicted by HMO theory when inclusion of electron repulsion, solvation, and ion pairing are taken into account.[10,11] It is known, however, that enhanced separations can occur when delocalization over a large molecular framework is not possible. For example, $\Delta E_{1/2}$ for tetracyanoethylene is 0.72 V compared to 0.42 V for tetracyanoquinodimethane.[12] In the case of **1**, there is no possible delocalization of charge (at least by resonance) beyond the eight-membered ring.

In contrast with the energetic differences between **1** and DBCOD, their apparent rate constants are in close agreement (0.07 ± 0.02 and 0.05 cm/s, respectively) and are comparable to that of COTR (0.08 cm/s). The electron-transfer rates for **1** and DBCOD are significantly larger than those for COT[3a] and DBCOT, supporting the premise that the energetics of ring flattening reduces the rate.[3,4] The free energy of activation for electron transfer can be deduced by application of Marcus' theory[5] from the relation

$$\Delta G^* = kT(\ln\kappa + \ln Z - \ln k_s) \tag{3}$$

where k is the Boltzmann constant, k_s is the electron-transfer rate constant, Z is the collision frequency of the reactant molecules at the reaction site, and κ is the transmission coefficient, taken as unity for an adiabatic reaction. The collision frequency is related to the reduced mass m by[13]

$$Z = (kT2/\pi m)^{1/2} \tag{4}$$

Substitution into eq 3 and 4 for **1** and COT gives values of 0.27 eV and 0.38 eV, respectively, for ΔG^*. This activation energy can be reduced further into[4,5,13]

$$\Delta G^* = w^* = \frac{[\lambda + w - w^*]^2}{4\lambda} \tag{5}$$

where $\lambda = \lambda_o + \lambda_i$, the outer and inner sphere reorganizational energies, w^* is the work required to transport the reactant from the bulk of solution to the reaction site, and w is the corresponding work term for the reactant. If we assume that the potential at the reaction site is equal to the bulk potential,[13] the work terms become zero and eq 5 becomes

$$\Delta G^* = \frac{\lambda_i + \lambda_o}{4} \tag{6}$$

Substitution of the ΔG^* values for **1** and COT into eq 6 gives 1.08 and 1.52 eV for their respective reorganization energies. Simple theory would predict that the solvent reorganization energy is similar for the two molecules because of the size of their π systems.[10] The difference between the free energies of activation for **1** and COT can then be taken as an approximate measure of the difference in inner-sphere reorganization energy. This calculation gives a difference of 10 kcal/mol, which is similar to 13.7 kcal/mol, the activation energy for flattening the COT ring,[14] and is consistent with the view that COT is flattened or partially flattened in the transition state of electron transfer.

The comparable electron-transfer rates to **1**, DBCOD, and COTR (see Table I) are not surpising, since the three molecules are of similar size and structure. This might suggest that Frumkin corrections[15,16] for the double layer either are not important or are similar for these three molecules. The latter possibility seems unlikely, since double-layer corrections depend upon the integral of the differential double-layer capacitance from the potential of zero charge (which is unknown)[17] to the reduction potential of the molecule. Since the reduction potentials for these three molecules vary widely, it would be fortuitous if these corrections were similar.

A point made earlier[4] about the low value of k_s for DBCOD compared with typical aromatic compounds also applies here. Why should electron-transfer rates for **1** and DBCOD be about

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2 orders of magnitude smaller than for perylene, for example? Work and double-layer corrections are unlikely to significantly alter these findings, and solvent reorganization energies should be similar. This suggests inner-sphere reorganizational energies for **1** and DBCOD are larger than for aromatic compounds. Calculations indicate that changes in geometry in going from benzene (a simple aromatic model system) to its anion radical are small,[18] while Dewar and co-workers[19] predict that bond alteration decreases in the anion radical of COT compared with the neutral molecule. Formation of such a symmetric anion radical would require considerable changes in bond lengths affording larger activation energies. This rationale is also consistent with our qualitative findings[20] that the second electron transfer to **1** is faster than the first. Since major structural changes occur at the first wave, little additional distortion is required to form the expected symmetric dianion.

A final comment regarding the origin of the oxidizing power of **1** is in order. Its reduction potential is almost the same as the reduction of the *cation radical* of tri-*tert*-butylpentalene, **2** (0.75 V), also a planar 8 π electron molecule.[21] Comparison of the reduction potential of **1** with **2** (−1.4 V) and DBCOD (−1.61 V) eliminates strain or antiaromaticity as major factors. Obviously the 16 fluorine atoms must play an important role here. While we are unaware of an appropriate model system that would allow evaluation of the substituent effect, it is worth noting that both decafluorobiphenyl[22] and tetrafluorotetracyanoquinodimethane[12] reduce more positive than the parent molecules by ca. 0.1 V per fluorine atom.

We are currently examining a series of fluorinated model compounds to gain better insight into the energetics for reduction of **1**.

Acknowledgment. We thank EG and G for the loan of a PAR 174/50 ac interface and Dr. Bob Glosser for use of his PAR 128A lock-in amplifier. This work was aided by Grants AT-748, AT-646, and AF-585 from the Robert A. Welch Foundation. Helpful discussions with Albert J. Fry, Donald E. Smith, and Ronald, H. Fleming are gratefully acknowledged.

Registry No. 1, 42858-85-5; ferrocene, 102-54-5.

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Dynamic Features of the Ethylenediaminetetraacetate Complexes in Aqueous Solutions Studied by the Ultrasonic Absorption Method. 2. Zn and Cd Complexes

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Abstract: Ultrasonic relaxation absorption was observed in aqueous solutions of zinc and cadmium ethylenediaminetetraacetate (EDTA) complexes. The absorption was ascribed to the rapid structural change of the EDTA complex, i.e., pentacoordinate structure $\rightleftharpoons$ hexacoordinate structure (k_f, k_b). The proportions of the two structures were evaluated from the absorption amplitude. In the case of the Cd complex, the stability of the hexacoordinate structure is much larger than those of the Zn and alkaline-earth complexes. The rate constant k_f was found to be closely related to the water-substitution rate constant of the metal ion. A reaction mechanism with a steady-state intermediate is proposed.

Metal chelates of EDTA have received much attention and have been studied by a variety of techniques. However, their structures and kinetic properties in solution are still ambiguous. Concerning them, one of the most fundamental and important problems might be that of how many coordinating groups of EDTA bind to the metal ion. To date, many conflicting results have been proposed for the problem.[1-12]

For the study of the dynamic features of the complex in solution, the ultrasonic absorption measurement is one of the most valuable techniques. As far as we are aware, few ultrasonic absorption studies have been made on either EDTA[13] or its metal complexes.[14,15] In a previous paper,[15] we have applied the ultrasonic absorption method to the Co(II)– and alkaline-earth–EDTA complex solutions, proposed a mechanism for the reaction of the pentacoordinate structure $\rightleftharpoons$ hexacoordinate structure, and given the kinetic parameters. An accumulation of much more information is required in order to establish the clear structure of the complex in solution. Along this line, the present work was undertaken to obtain the static and kinetic information for the Zn– and Cd–EDTA complexes on the basis of the results obtained in the previous work.

Experimental Section

Materials. Reagent Grade zinc and cadmium nitrates and K_2EDTA were used without further purification. Solutions were prepared by mixing the desired amounts of metal nitrates, K_2EDTA, and KOH in a mole ratio of 1:1:2, and the final pH was adjusted to 6.5 by dropwise addition of KOH or HNO_3 solution. The ionic strength was adjusted to

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