

Electrochemistry of the C₆₀H₂ Fullerene

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The electrochemistry of fullerenes has been one of the most intensely studied aspects of fullerene chemistry. The electrochemical properties of C₆₀,¹⁻⁴ several higher fullerenes,^{5,6} and a number of fullerene derivatives have been reported.⁷⁻⁹

Recently, the preparation and purification of C₆₀H₂, C₆₀H₄, and other hydrogenated fullerenes have been described,^{10,11} but little is known of their chemical and electrochemical behavior. In this paper we report the electrochemical behavior of the simplest hydrocarbon derivative, C₆₀H₂.

Samples of C₆₀H₂ were prepared by zinc/acid reduction¹¹ and purified by gel permeation chromatography in toluene. The identity of each sample was confirmed by negative ion FABS mass spectrometry, and the purity was determined to be >90% by C₁₈ reversed-phase HPLC. This material is spectroscopically and chromatographically identical to samples we have made using the method of Cahill.¹⁰

In many respects, the electrochemical behavior of C₆₀H₂ is very similar to that of the parent fullerene, with C₆₀H₂ being only slightly more difficult to reduce than C₆₀ itself. For example, in benzonitrile/0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆), three reversible reductions are observed (at sweep rates > 1000 mV/s), and the half-wave potential for each of these processes is 120–170 mV more negative than that for the corresponding C₆₀ reduction. Similar results were obtained in CH₂Cl₂ (see Figure 1a) and in toluene/CH₃CN (80/20). An additional fourth reversible reduction, at -2.36 V vs Fc⁺/Fc, was noted in the case of toluene/CH₃CN; this couple is tentatively assigned to C₆₀H₂^{3-/4-}. These results are summarized in Table I.

Interestingly, the reduction of C₆₀H₂ at slower scan rates is accompanied by the appearance of a new set of reoxidation waves at potentials which closely match the anodic peak potentials of the C₆₀^{0/-}, C₆₀^{-/2-}, and C₆₀^{2-/3-} couples (see Figure 1b). These new waves become more prominent as the scan rate is decreased, suggesting that C₆₀H₂ reduction under such conditions is best described as an EC (or perhaps ECC) process leading to formation of the C₆₀ radical anion.

Evidence for the formation of C₆₀ during cyclic voltammetry of C₆₀H₂ is provided by the appearance of the full complement of C₆₀ reduction waves in samples that have been repeatedly cycled (or electrolyzed) at potentials sufficiently negative to cause C₆₀H₂

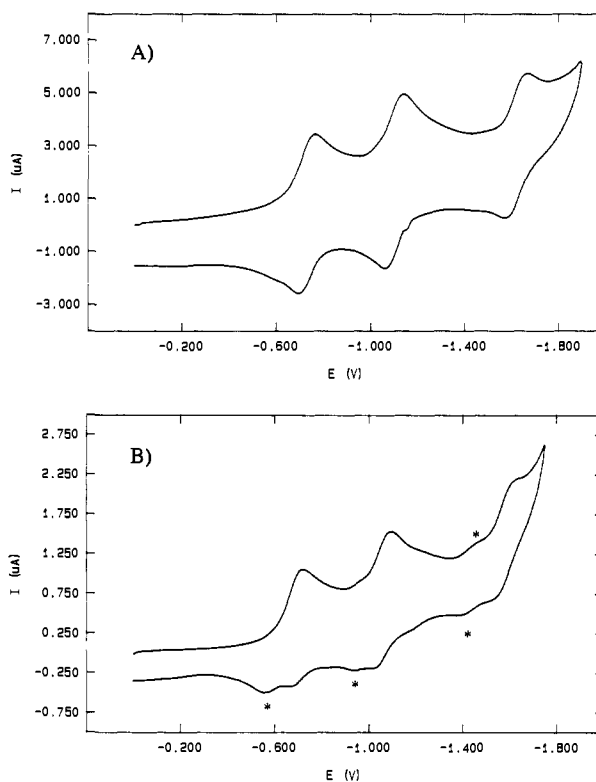


Figure 1. Cyclic voltammetry of C₆₀H₂ in CH₂Cl₂ solution with TBAPF₆ as supporting electrolyte. The working electrode was a 1 mm diameter Pt disk, and the counter electrode was a coiled Pt wire. An Ag wire functioned as a quasireference electrode. Ferrocene was included as an internal standard. (A) Scan rate = 2000 mV/s. (B) Scan rate = 200 mV/s; waves assigned to C₆₀ redox couples are labeled with an asterisk.

Table I. Half-Wave Potentials for Reduction of C₆₀H₂ in Various Solvents

solvent ^a	<i>E</i> _{1/2} ^b V vs Fc ⁺ /Fc			
	C ₆₀ H ₂ ^{0/1-}	C ₆₀ H ₂ ^{1-/2-}	C ₆₀ H ₂ ^{2-/3-}	C ₆₀ H ₂ ^{3-/4-}
toluene/CH ₃ CN	-1.05	-1.44	-1.99	-2.36
PhCN	-1.04	-1.43	-2.01	
CH ₂ Cl ₂	-1.11	-1.48	-1.99	

^a 0.1 M TBAPF₆ used as supporting electrolyte in all cases. ^b *E*_{1/2} taken as the average of the anodic and cathodic peak potentials. The working electrode was a Pt disk.

reduction. Analysis of the electrochemical reaction mixture by C₁₈ reversed-phase HPLC after repeated cycling or electrolysis also shows that C₆₀ is produced by C₆₀H₂ reduction. There is no evidence for the formation of C₆₀H₄ or other reduced fullerenes, thus ruling out disproportionation.

The addition of a single electron is sufficient to induce conversion of C₆₀H₂ to C₆₀, and the anodic wave corresponding to the reoxidation of C₆₀⁻ is readily observable whenever the potential is swept beyond the first reduction of C₆₀H₂ at slow scan rates (≤500 mV/s). Figure 2 shows a series of voltammograms in which the scan rate is decreased from 1000 mV/s to 200 mV/s. Using the method of Nicholson and Shain,¹² we calculate a rate constant of 0.4 (± 0.1) s⁻¹ for the decomposition of C₆₀H₂⁻ to C₆₀⁻.

It is fascinating that C₆₀H₂ undergoes a net oxidation under "reducing" conditions. Similar reactions have been observed using chemical reductants; specifically, 1,4 cyclohexadiene can be catalytically dehydrogenated to benzene with naphthalene radical anion.¹³ In that case, attempts to use electrochemical catalysis

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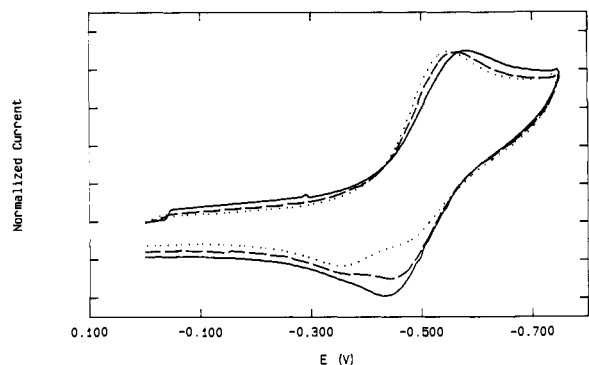


Figure 2. Cyclic voltammetry of $C_{60}H_2$ in toluene/ CH_3CN (80/20) containing 0.1 M TBAPF₆ as supporting electrolyte at scan rates of 1000 (solid line), 500 mV/s (dashed line), and 200 mV/s (dotted line). Other conditions are as in Figure 1. Cathodic peak currents are proportional to the square root of scan rate but have been normalized here for purposes of comparison.

failed, possibly due to the difficulty of reducing isolated alkenes. Electrochemically produced 9-substituted fluorene radical anions do undergo loss of an H-atom to produce the fluorenyl anion.¹⁴ Fullerenes are reduced much more easily, which makes the process observable at relatively low potentials. We believe that dissolving metal reductions using zinc¹¹ or lithium¹⁵ give reduction products because of proton sources available in the reaction mixtures. Bulk electrolysis of C_{60} in the presence of acid has been shown to lead to the formation of hydrogenated fullerenes.¹⁶

The electrochemical oxidation of $C_{60}H_2$ is most cleanly observed in benzonitrile. Two chemically irreversible multielectron steps ($E_p = +1.13$ and $+1.35$ V vs Fc^+/Fc ; see Figure 3) are detected, and no return waves are evident even at scan rates up to 8000 mV/s. Such behavior is consistent with the coupled loss of two protons and two electrons from $C_{60}H_2$ to yield C_{60} (first step),

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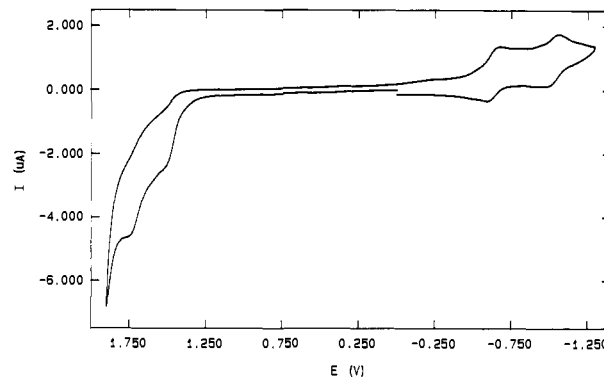


Figure 3. Cyclic voltammogram of $C_{60}H_2$ in benzonitrile/0.1 M TBAPF₆; other conditions are as in Figure 2. Scan rate = 2000 mV/s. Anodic wave at $+1.75$ V vs Ag is assigned to C_{60} oxidation.

followed by the oxidation of C_{60} (second step). Indeed, the peak potential for the latter process is in good agreement with literature values.^{2,17} As with the reductive electrochemistry, the familiar set of new reduction waves attributable to C_{60} grows in following $C_{60}H_2$ electrooxidation.

Ongoing investigations will include a quantitative study of the electrochemically induced dehydrogenation kinetics in various solvents. Since the nature and concentration of the electrolyte can exert a significant influence on fullerene redox thermodynamics, such effects will also be examined.¹⁸ These studies will be extended to the next member of the reduced fullerene series, $C_{60}H_4$, which has recently been isolated as a mixture of isomers.¹¹

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Supplementary Material Available: Chromatograms showing the appearance of C_{60} after repeated cycling of $C_{60}H_2$ (2 pages). Ordering information is given on any current masthead page.

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