The Cycloheptatriene Radical Anion

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The reduction of cycloheptatriene (1) and some related trienes in aprotic solvents at a platinum electrode was studied by cyclic voltammetry and controlled-potential coulometry. A reversible wave at −2.5 eV for the production of the radical anion of 1 was observed in ammonia containing 0.1 M KI. Quasi-reversible or irreversible reduction was observed in acetonitrile and *N,N*-dimethylformamide. The radical anion was stable in ammonia on the voltammetric time scale but decayed slowly by disproportionation and coupling reaction pathways to give respectively 1,3- and 1,4-cycloheptadienes and $C_{14}H_{18}$ isomers which incorporate bitropyl carbon skeleta. The chemical fate of 1 radical anion is discussed, as is the difference in reaction course for electrochemical and dissolving-metal reductions in ammonia.

Our interest in the redox chemistry and the relative stabilities of highly basic carbanions has led us to examine the electrochemical reduction of 1,3,5-cycloheptatriene (**1**) in several aprotic solvents. We have found that the stability of radical anion $1^{-\cdot}$ in liquid ammonia is much greater than that in other aprotic solvents examined and that single-electron electrochemical reductions in this media can lead to product distributions which differ from those observed in related dissolving-metal reductions. We describe in this paper our cyclic voltammetric studies of the cycloheptatrienyl radical anion and our characterizations of the chemical reactions in which this radical anion participates.

Although the electrochemistry of cycloheptatrienylium ($C_7H_7^+$) and its derivatives has been described by several groups[1,2] and the two-electron oxidation of 1 to the tropylium ion has been reported,[3] little is known about the electrochemical reduction of the parent hydrocarbon. Levy and Myers have reported the electrochemical generation of $1^{-\cdot}$ in liquid ammonia in an ESR cavity.[4] These structural studies were suggestive of a boatlike conformation in the anion radical (as in the parent hydrocarbon) with negligible contribution from norcaradiene structures, but neither the required potentials nor the chemical fate of the radical anion was determined.

Results

The cyclic voltammogram of a solution containing 1 and 0.1 M KI in anhydrous NH_3 showed a reversible reduction wave at −2.5 eV (vs. SCE)[5] and a second, smaller quasi-reversible wave near the background reduction at −2.8 eV (Figure 1). A small oxidation wave at −1.4 eV was observed. Three controlled-potential reductions at −2.6 eV yielded an average value of 1.2 electrons/molecule. As the preparative electrolysis proceeded, the solution became intensely red-orange. This color faded immediately upon quenching with a proton source (H_2O or NH_4Cl).

Analogous voltammetric reductions in dry dimethylformamide (DMF) containing 0.1 M tetraalkylammonium perchlorate revealed a quasi-reversible wave at −2.6 eV.[5] The reverse oxidation was observable only at rapid scan rates (>200 mV/s), Figure 2. Similar results were obtained in acetonitrile (CH_3CN), where the first reduction wave (−2.6 eV) was nearly completely irreversible.

Similar results were obtained in the electrochemical reduction of bitropyl, the reversible reduction potential in ammonia being shifted to slightly more negative potentials (−2.6 eV vs. SCE) as was its irreversible reduction in acetonitrile (−2.7 eV). The reversible reduction of 1,3,5-heptatriene in ammonia was observable at −2.6 eV.

Table I. Product Yields in the Reduction of Cycloheptatriene in Ammonia

method	cation[a]	proton donor	product yields, % 2	3	$C_{14}H_{18}$
electrolysis[b]	Na	H_2O	18	16	58
electrolysis	K	H_2O	26	11	55
electrolysis	Na	NH_4Cl	14	25	55
electrolysis	K	NH_4Cl	18	18	57
chemical reduction[b]	Na	H_2O	58	18	17
chemical reduction	Na	NH_4Cl	28	45	19

[a] Inert electrolyte (NaI, KI) in electrolysis experiments, alkali metal in chemical reductions. [b] Values are the average of two experiments. Reproducibility ±3%. Yields are based on converted 1 with dodecane as internal standard.

Gas chromatographic/mass spectral (GC/MS) analysis of the products of preparative electrolysis in ammonia (1 equiv of electrons) showed the formation of 1,3- (**2**) and 1,4-cycloheptadiene (**3**) as well as reduced dimeric products of formula $C_{14}H_{18}$. At least ten isomeric dimers could be detected, but, of these, three were dominant. The mixture of these three isomers, which proved inseparable by high-pressure liquid chromatography, was exhaustively hydrogenated, giving a single compound by GC/MS (*m/e* 194) identical with that obtained by hydrogenation of bitropyl. The product of cyclodimerization of the tropyl anion (**4**) with cycloheptatriene[6] was specifically absent from the electrolysis mixture. If the red-orange electrolysis product was quenched by D_2O, the parent peak of the dimers shifted to *m/e* 188 from the parent *m/e* 186 formed with a H_2O quench. This deuterium incorporation is consistent with protonation of a dianion in the quenching step. The cycloheptadienes isolated in the D_2O-quenched experiment contained a single deuteron (*m/e* 95). Relative yields of these products depended on the associated cation (inert electrolyte) and on the identity of the quenching agent. Yields of products obtained by preparative electrolysis and by dissolving-metal (sodium) reduction of CHT in ammonia are listed in Table I.

Discussion

The greater stability of $1^{-\cdot}$ in liquid NH_3 than in CH_3CN or DMF speaks for the utility of this solvent as a useful medium for studying electron-transfer reactions. The

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[1] J. M. Leal, T. Teherani, and A. J. Bard, *J. Electroanal. Chem.*, **91**, 275 (1978), and references cited therein.

[2] A. Stasko and P. H. Plesch, *Z. Phys. Chem. (Leipzig)*, *256*, 418 (1975).

[3] D. H. Geske, *J. Am. Chem. Soc.*, 81, 4145 (1959).

[4] D. H. Levy and R. J. Myers, *J. Chem. Phys.*, 43, 3063 (1965).

[5] The reduction potentials observed were actually determined vs. a Ag pseudo-reference electrode. The values reported here were obtained by conversion to the more standard SCE reference.

[6] S. W. Staley and A. W. Orvedal, *J. Am. Chem. Soc.*, **96**, 1618 (1974).

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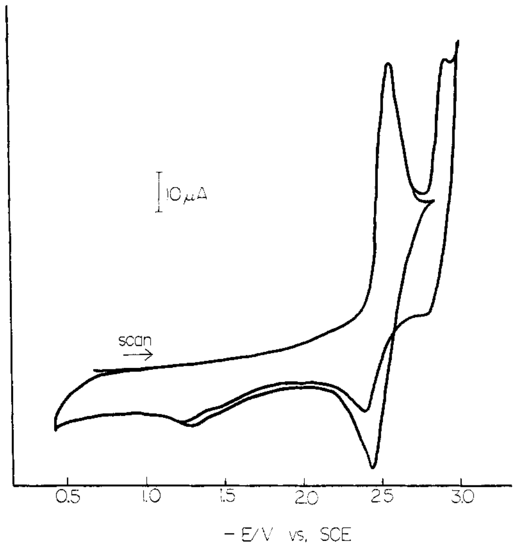


Figure 1. Cyclic voltammogram[5] of 1.0 mM 1 in 0.1 M KI/NH_3 solution at a scan rate of 200 mV/s^{-1}.

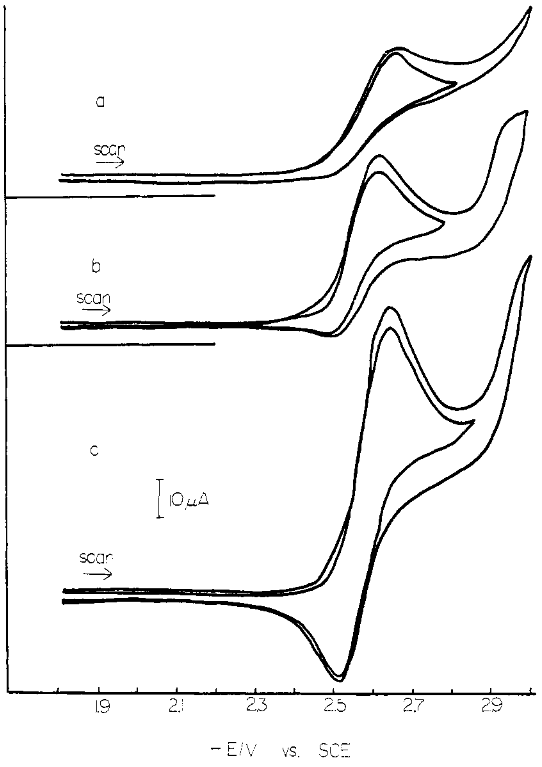
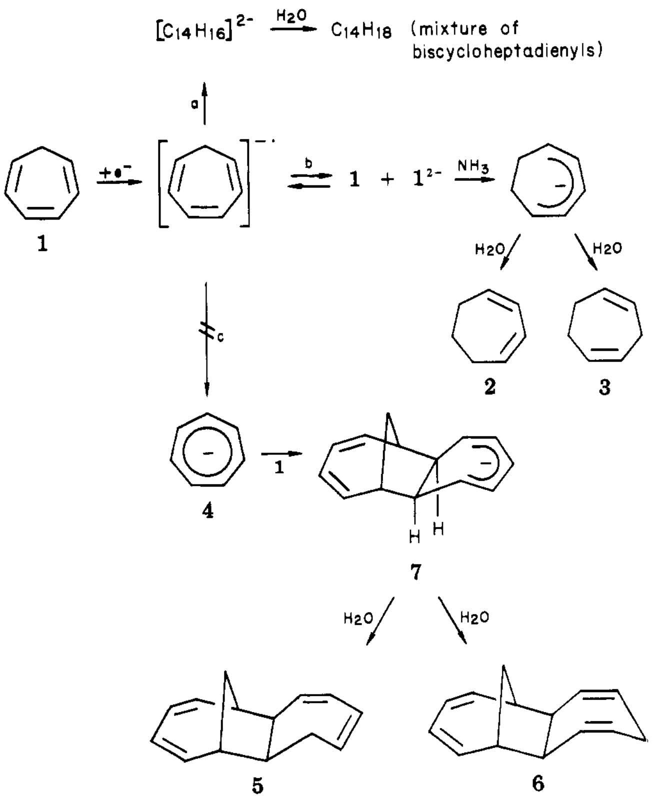


Figure 2. Cyclic voltammograms[5] of 1.0 mM 1 in 0.1 M TBAP/DMF solution at the following Scan rates: a, 50 mV s^{-1}; b, 200 mV s^{-1}; c, 500 mV s^{-1}.

superiority of NH_3 as solvent in such anion studies can be attributed to its low acidity, its high polarity, its large cathodic/anodic range, and the ease of its purification and drying. Application of the usual Nicholson-Shain criteria[7] to the cyclic voltammetric results in CH_3CN suggests that $1^{-}\cdot$ undergoes chemical reaction after the single electron transfer. Presumably, the irreversibility of the reduction in CH_3CN and in DMF can be attributed either to protonation by solvent, by inert electrolyte[8] or by acidic impurities which persist despite rigorous attempts at purification or to changes in the nature of solvation and/or ion pairing in these less polar aprotic media. These, in turn, will affect the stability of the anion and the rate of disproportionation to the more easily protonated dianion.[9]

Scheme I



Although the radical anion of 1 appears to be stable on a voltammetric time scale, it eventually reacts. Reasonable routes to the observed electrolysis products are thus shown in Scheme I. Coupling (path a) is apparently dominant over disproportionation (path b) since reduced dimeric products are formed in greater yield than are the simple reduction products which dominate in dissolving-metal reductions.[10,11] The absence of cyclodimerization product[6] in the electrolysis mixture suggests that H atom transfer (path c) to form the potentially antiaromatic 4 is not a significant decay mode for $1^{-}\cdot$.[12]

The possibility that the dianion product of path a arises from further reaction of cyclodimerization product from path c is unlikely. Anion 7 resists chemical attack by excess amide anion. In the absence of cycloheptatriene, an NH_3 solution of 7 containing KI fails to show any electrochemical reduction waves at potentials positive of −2.8 eV. Thus, the required reductive cleavage of 7 to dianion or its precursor seems difficult by chemical or electrochemical routes.

The formation of a dianion in path a is required by the deuterium-incorporation studies. While the characterization of the reduced dimeric products remains incomplete, the identity of the GLC relative retention times and mass spectral fragmentation patterns of the major products of hydrogenation of the electrolysis mixture and of bitropyl

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[7] R. S. Nicholson and I. Shain, *Anal. Chem.*, **37**, 178 (1965); R. S. Nicholson, *ibid.*, **37**, 1351 (1965).

[8] Tetrabutylammonium perchlorate cannot be the sole protonation source for $1^{-}\cdot$ in CH_3CN since the reduction wave remains quasi-reversible if tetramethylammonium perchlorate is employed as electrolyte.

[9] B. S. Jensen and V. D. Parker, *J. Am. Chem. Soc.*, **97**, 5211 (1975).

[10] A. P. terBorg and A. F. Bickel, *Recl. Trav. Chim. Pays-Bas*, **80**, 1229 (1961).

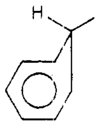
[11] H. Dirkzwager, Th. J. Nieuwstad, A. M. van Wijk, and H. van Bekkum, *Recl. Trav. Chim. Pays-Bas*, **92**, 35 (1973).

[12] The cyclodimerization product can be detected as a minor product in the Na/NH_3 reduction of 1. Presumably its absence here relates to the relative rates of reduction and of formation of potassium amide.

suggest that coupled C_7 fragments form the carbon skeleta of the reduced dimers and, perhaps, that dimerization may result from simple combination of a radical sites in two molecules of $1^{-}\cdot$. This view is also consistent with the dominance of three reduced dimers out of the 52 possible noncumulated $C_{14}H_{18}$ isomers with bitropyl skeleta.

The reduced reversibility of the more negative reduction wave (−2.8 eV) and the isolation of **2** and **3** containing one deuterium are consistent with rapid protonation of 1^{2-} by ammonia as in path b. This process has been established in the dissolving-metal reduction of **1**.[10,11] Apparently the lower yields of **2** and **3** in the electrolysis than in the reaction with alkalai metal reflect the slower rate of disproportionation of $1^{-}\cdot$ (electrolysis) than of capture of a solvated electron by $1^{-}\cdot$ (dissolving metal). As in the previous studies,[11] the relative proportions of **2** and **3** were found to depend on complexing cation and protonation source, the 1,3 isomer being favored in the presence of the heavier cation and weaker acid.

The similarity of the reduction potentials of **1**, of bitropyl, and of 1,3,5-heptatriene indicates that there is little difference in the importance of homoconjugative interaction in the neutral hydrocarbon **8** and in the anion radical **9** of **1**.



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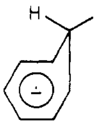

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Experimental Section

Electrochemical Reductions. The electrochemical cell used for cyclic voltammetric (CV) and coulometric studies was a standard three-compartment cell with a silver-wire quasi-reference electrode isolated from the test solution by a fine-porosity frit. The potential of the reference was determined following each series of experiments by adding benzoquinone and observing the behavior of this substance whose redox chemistry is known. The working electrode in the cyclic voltammetry was a platinum disk with an area of 0.05 cm^2. Ammonia was purified by a double distillation from sodium metal chunks (after storage overnight over Na). Acetonitrile and dimethylformamide were purified by standard procedures.[13] Electrolytes were dried by heating overnight under high vacuum. Solvents were rigorously degassed before each experiment. The electrochemical experiments in NH_3 were −40 ± 10 °C. CV studies in CH_3CN and DMF were conducted at room temperature and at −40 ± 10 °C. The electrochemical experiments were conducted with a PAR Model 173 potentiostat and a Model 179 digital coulometer equipped with positive feedback for IR compensation and a Model 175 universal programmer. An X-Y recorder (Houston Instruments) was used to record current-potential curves for scan rates below 500 mV/s.

Analytical Reduction of 1. Cycloheptatriene (Aldrich) (**1**) was purified by double distillation and was shown to be pure by gas chromatography (GLC) on a 6 ft × 0.25 in., 3% OV-1 on Chromosorb W column (column A; 50–150 °C, 10 °C/min). Typical conditions for CV are listed in Figure 1.

Analytical Reduction of Bitropyl. Bitropyl was prepared by the reduction of tropylium tetrafluoroborate[14] by the method of Doering and Knox.[15] Its CV behavior was obtained under conditions identical with those employed for **1**.

Analytical Reduction of 1,3,5-Heptatriene. 1,3,5-Heptatriene (Chemical Samples) was distilled before use. Its CV behavior was measured under identical conditions as described above.

Preparative Electrochemical Reduction of 1. Cycloheptatriene (250 μL) was reduced on a 2 × 2 cm platinum-foil electrode in 40 mL of 0.1 M KI in anhydrous NH_3 until 1 equiv of electrons had been taken up. Electrolysis conditions were otherwise identical with those of the analytical reductions. After electrolysis, 50 μL of dodecane was added as an internal standard, and the resulting mixture was quenched with 5 mL of H_2O, D_2O, or saturated aqueous NH_4Cl. (In the D_2O-quench experiments, 100 mL of anhydrous THF was added to the electrolysis mixture, and the ammonia was allowed to evaporate at 0 °C under a steady stream of nitrogen gas before the D_2O was added.) After the mixture was quenched 100 mL of pentane was added, and the ammonia was allowed to slowly boil off. The organic layer was removed, and the residue was taken up in water. After extraction (3×) with pentane, the combined organic layers were concentrated by careful distillation of the pentane and analyzed by GLC/MS (Finnegan 4023 automated GC/MS) on column A (50–150 °C, 10 °C/min) and by GLC [Antex 400 flame ionization detector gas chromatograph: 5 ft × $^1/_8$ in., SE-30 on Chromosorb W column (column B) (90–240 °C, 10 °C/min)]. Product distributions are listed in Table I.

The $C_{14}H_{18}$ fraction (50 mg), isolated by high-pressure liquid chromatography (Waters Associates Model 100) on coupled 2 ft × 0.25 in. Porasil A columns (50:50 Skelly B–ethyl acetate), was hydrogenated (1 atm of H_2, room temperature) in 25 mL of glacial acetic acid over activated PtO_2 until gas uptake ceased. A single major product peak detectable by GC/MS on column A (m/e 194) had a relative retention time identical with that of a standard sample of bicycloheptyl obtained by analogous hydrogenation of bitropyl.[15]

Dissolving-Metal Reduction of 1. Cycloheptatriene (**1**) was chemically reduced by the method of Dirkzwager et al.[11] Analysis of the resulting mixtures was conducted by GLC on column B (see Table I). Authentic samples of cyclodimerization products **5** and **6** were obtained by the method of Staley and Orvedal.[6] When a mixture of **5** and **6** was treated with 2 equiv of $NaNH_2$ in liquid ammonia (−33 °C), an intense red color developed. After 5 min the solution was treated with saturated ammonium chloride. Analysis by GLC (90–240 °C, 10 °C/min; column B) of the resulting hydrocarbons showed only **5** and **6** as major peaks. Specifically the $C_{14}H_{18}$ isomers obtained above were absent. The **5**–**6** mixture (30 mL) was taken up in an electrochemical cell containing 1 equiv of $NaNH_2$ in 20 mL of liquid ammonia. A red color developed. After the reaction mixture was held at −33 °C for 10 min, electrolyte was added from a side arm (0.1 M KI), and a cyclic scan of potential from 0 to −3.0 eV (vs. Ag quasi-reference electrode) was undertaken. No reduction peaks could be detected in this range.

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Registry No. 1, 544-25-2; **1** radical anion, 34473-56-8; **1** radical anion sodium, 70969-16-3; **1** radical anion potassium, 70969-17-4; **2**, 4054-38-0; **3**, 7161-35-5; **5**, 51736-90-4; **6**, 51777-81-2; $C_{14}H_{18}$, 70969-11-8; bitropyl, 831-18-5; bitropyl radical anion, 34473-37-5; 1,3,5-heptatriene, 2196-23-8; 1,3,5-heptatriene radical anion, 34548-47-5; bicycloheptyl, 23183-11-1.

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(13) S. N. Frank, A. J. Bard, and A. Ledwith, *J. Electrochem. Soc.*, **122**, 898 (1975); H. Kojima and A. J. Bard, *J. Electroanal. Chem. Interfacial Electrochem.*, **63**, 117 (1975).

(14) K. Conrow, *Org. Synth.* **43**, 101 (1963).

(15) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **79**, 352 (1957).