ditions: 35–260 °C at 3°/min). The GC-MS experiments were performed on a Finnigan 4023 quadrupole instrument with a 30 m by 0.3 mm DB-5 (J&W) capillary column. Reconstructed ion chromatograms were accomplished with the INCOS data system.

Relative Rate Procedure for Compounds 1–17 with K/18-Crown-6/THF as the Electron-Transfer Reagent. The relative rates for compounds **2–17** were obtained in competitive reactions with compound 1, diphenyl ether, which was assigned a relative rate of 1.0. The following procedure was used for all the relative rates shown in Table I: to a 50-mL Schlenk flask were added 0.07 g (1.79 mmol) of potassium metal, 0.43 g (1.79 mmol) 18-crown-6, and 10 mL of dry, degassed THF along with a stirring bar and a septum for substrate addition. These transformations were carried out in a single-stage Vacuum Atmospheres glovebox under argon and provided a deep blue solution of solvated electrons. In another Schlenk flask were added 28 μL (0.18 mmol) of diphenyl ether (1) and an equimolar amount of compounds **2–17** in 10 mL of THF along with 40 μL of undecane as an internal standard for GC analysis [experiments with added *tert*-butyl alcohol (0.36 mmol) or hydroquinone (0.36 mmol) were done with compounds **1** and **3**]. After this mixture was degassed, it was cannulated under argon into the blue THF solution of K/18-crown-6 at 0 °C. This caused the blue color to dissipate to provide, depending upon the substrate, a yellow-red clear solution. At intervals of ~1–5 min, 0.5-mL aliquots were removed via a syringe and quenched with a drop of glacial acetic acid (neutral to pH paper) prior to GC analysis. A control experiment with esters **8–15** showed no hydrolysis products during the glacial acetic acid workup. The products were identified by comparison to known standards and confirmed by GC-MS analysis. The quantitation was obtained with standard solutions, response factors, and concentration/area plots using the HP data station for digital integration of peaks. We also ran individual reductive cleavage reactions for **2–17** under similar conditions to insure product identification by standards, response factors, and GC-MS analysis.

The relative rates ($k_{\mathrm{rel}} = k_{\mathrm{unk}}/k_{\mathrm{compd1}}$) were calculated by using percent conversion of substrate vs time plots and a similar plot for 1 and obtaining the slope of these linear plots by a least-squares regression analysis. The slopes of substrates **2–17** were simply divided by that of **1** to obtain the relative rate. Aromatic esters **10–14** were too fast to measure accurately by our GC method, since they totally reacted upon mixing at 0 °C, and we defined these relative rates as being >2.0. The esters **8** and **9** and the ethers **1–3** and **5–7** had conversions in the range of 70–100% after 20 min, while ether **4** was ~5% converted after 20 min.

Deuterium Incorporation Experiments with Compound 13. In a similar reaction procedure to what was mentioned above, we reacted **13** with K metal/18-crown-6 in THF at 0 °C. The reaction mixture was quenched with glacial acetic acid-d_4 and was analyzed by GC-MS to clearly show no significant deuterium incorporation in the benzene present ($C_6H_6/C_6H_5D = 17$). The ratio of acetic acid-d_4/acetic acid-d_3 was found to be >2. The only other product, 2-methoxyphenol, was also verified by GC-MS. This signifies that benzene radicals are formed rather than phenyl anions and that radical anions are the important intermediates.

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Registry No. 1, 101-84-8; 2, 103-50-4; 3, 946-80-5; 4, 831-82-3; 5, 1655-69-2; 6, 1695-04-1; 7, 40515-89-7; 8, 93-99-2; 9, 120-51-4; 10, 118-55-8; 11, 65853-67-0; 12, 4181-97-9; 13, 531-37-3; 14, 1523-19-9; 15, 2444-19-1.

Electrochemical Reduction of Vicinal Dinitro Compounds[1]

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Six vicinal dinitro compounds and 1,1-dinitrocyclohexane have been studied by cyclic voltammetry, chronoamperometry, and controlled potential coulometry. For dinitro compounds **1–3**, the electrochemical reduction at mercury electrodes in DMF was shown to proceed by an ECE scheme comprising initial reduction to a radical anion, which expels nitrite, forming a β-nitroalkyl radical that is more easily reduced than the original dinitro compound. The rate constants for expulsion of nitrite from the anion radical were determined at 0 °C. Compounds **4** and **5** behaved similarly to **1–3** though additional reactions occur. The radical anion of *trans*-1,2-dinitrocyclopropane, **6**, reacts quickly and could not be detected. 1,1-Dinitrocyclohexane is reduced in an initial two-electron step forming nitrite and the anion of nitrocyclohexane. The latter reacts rapidly with starting material to form 1,1′-dinitrobicyclohexyl, **2**, which was detected by voltammetry.

The importance of electron transfer in a variety of organic reactions is now widely recognized. Of particular interest is the $S_{RN}1$ mechanism[2–17] depicted in eq 1–4, where group L is replaced by nucleophile Nu$^-$. A number of substitutions at both aromatic and aliphatic centers have been shown to occur via the $S_{RN}1$ mechanism. These reactions normally proceed under mild conditions, good

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yields are obtained, they are relatively insensitive to steric hindrance, and some normally inert functional groups can be replaced.

$$RL + e \rightleftharpoons RL^{\bullet -} \quad (1)$$

$$RL^{\bullet -} \overset{k_2}{\rightleftharpoons} R^{\bullet} + L^{-} \quad (2)$$

$$R^{\bullet} + Nu^{-} \rightleftharpoons RNu^{\bullet -} \quad (3)$$

$$RNu^{\bullet -} \rightleftharpoons RNu + e \quad (4)$$

The nitro group, because of its high electronegativity, favors electron transfer and so it has been an important substituent in $S_{RN}1$ reactions, especially at aliphatic centers.[4,7-10] In many instances the nitro group is displaced in the overall process, demonstrating the importance of eq 2 (L = NO_2) in those cases. Reactions 1 and 2 have been investigated for a few aliphatic mononitro compounds by using electrochemical techniques,[18-20] and the rate of cleavage of nitrite from the radical anion is relatively slow, e.g., k_2 is about 1 s^{-1} for the radical anion of 2-methyl-2-nitropropane at room temperature.[19,20]

By contrast, the radical anions of α-substituted nitro compounds, $R_1R_2C(X)NO_2$ (where X is electron withdrawing), are exceedingly unstable,[16,17] rapidly giving NO_2^- or X^-, depending on the nature of X. Substitution of such groups at the β carbon, $R_1R_2C(X)C(NO_2)R_3R_4$, should give radical anions of intermediate stability, an expectation confirmed by Petsom and Lund[21] who were able to detect radical anions by cyclic voltammetry at room temperature for three compounds with X = benzoxy or acetoxy. The rate of loss of nitrite from the radical anion exceeds that seen with simple nitro alkanes, RNO_2, and both X and NO_2 are lost in the overall process, producing reasonable yields of olefin by electrolysis.

Interesting examples of β-substituted nitro compounds are those with X = NO_2, i.e., vicinal dinitro compounds. Electrochemical reduction of these compounds has been scarcely studied,[22] but the chemical reduction has been investigated as a synthetic route to olefins,[23-24] and their preparation via reaction of a 1,1-dinitro compound with the anion of a nitroalkane is an often cited example of a radical chain reaction.[7,8,9b,25,26]

We have investigated the electrochemical reduction of a number of vicinal dinitro compounds and have established the reaction pathway for the overall process, including an evaluation of the rate constants for cleavage of nitrite from the radical anion.

Results and Discussion

The electrochemical reduction of six aliphatic vicinal dinitro compounds (1–6) was studied by cyclic voltammetry (CV), chronoamperometry, and controlled potential electrolysis. Except where otherwise specified, measurements were made in *N,N*-dimethylformamide (DMF) with 0.30 M tetra-*n*-butylammonium hexafluorophosphate (TBAHFP) at a mercury film electrode on a 12.5 μm radius platinum disk substrate.

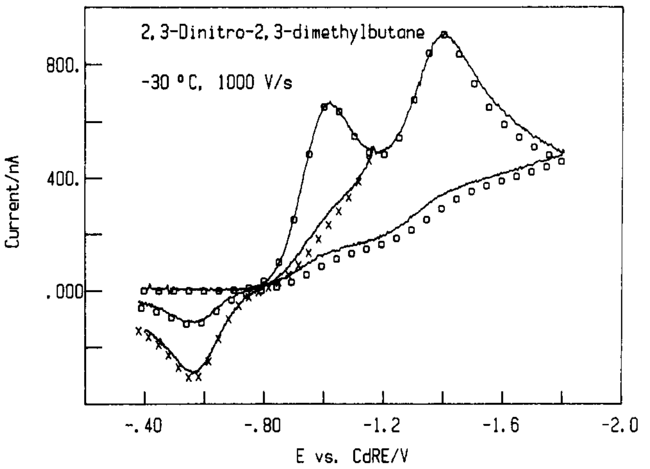
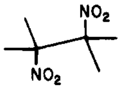


Figure 1. Cyclic voltammogram of 4.5 mM 1 in DMF/0.30 M TBAHFP at a 25 μm diameter mercury electrode. Curves: experimental voltammograms after subtraction of background current. Points: digital simulations. Parameters (subscripts refer to eq 6–10): $E°_6 = -0.80$ V; $k_{s,6}/D^{1/2} = 2.3$ $s^{-1/2}$; $\alpha_6 = 0.49$; $k_7 = 0$ (no cleavage of nitrite); $\alpha_{10} = 0.34$; eq 10 treated as a totally irreversible electrode reaction with potential and rate constant adjusted to cause simulated peak position to match experimental. Equations 8 and 9 are assumed to be fast.



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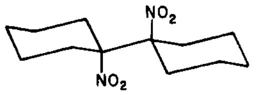

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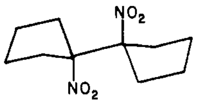

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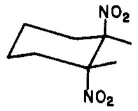

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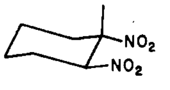

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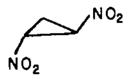

6

Compound 1 was studied in greatest detail and will be discussed first. The behavior of **2–5** was similar to that of **1**, but important differences were observed.

2,3-Dinitro-2,3-dimethylbutane, 1. The reduction of 1 was first investigated briefly by CV by using a hanging mercury drop electrode of conventional size (0.05-cm diameter). At scan rates up to 100 V/s, the only feature seen on the negative-going scan is a single, irreversible reduction peak at −1.0 V vs the cadmium amalgam reference electrode (CdRE) whose height corresponds to an overall two-electron process. On the return scan, an irreversible oxidation peak is seen at +1.2 V, coincident with the oxidation peak obtained with a sodium nitrite solution. These data provided little information about the reaction other than to suggest that nitrite was being formed during the reduction of 1. Faster experiments are required to reveal intermediates in the reduction process.

Microelectrodes permit the use of very high scan rates with only minor distortion due to solution resistance.[27-30]

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The 12.5 μm radius disk, which was used in this work, allowed meaningful results to be obtained at scan rates as large as 10000 V/s at −50 °C. At scan rates less than about 100 V/s, the effects of edge diffusion become apparent in the voltammograms so the electrode was used for the scan rate range of 100–10000 V/s, where the results could be analyzed by semiinfinite linear diffusion to account for mass transport.

CV of **1** at the microelectrode produced the same irreversible reduction peak at 100 V/s, but, as the scan rate was increased, a new reduction peak appeared about 0.4 V negative of the first. This new peak grew at the expense of the first until the two peaks were of almost equal height at the fastest scan rates. Coupled to the appearance and growth of the new peak was the detection of the product of the first reduction process through its oxidation at about −0.6 V. These new features are illustrated in the voltammograms of Figure 1, which were obtained at −30 °C and 1000 V/s. The two reduction peaks are of almost equal height, and the magnitude of the oxidation peak (in both voltammograms) equals that expected for the case where the product of the first reduction process is stable on the time scale of the experiment. Under these conditions, nitrite is not detected on the return sweep when the scan is reversed after the first reduction peak (−1.1 V) but is clearly evident when the scan is reversed after the second reduction (−1.8 V). No evidence for an oxidation process associated with the second reduction could be obtained even at 10000 V/s and −50 °C.

The curves in Figure 1 are the experimental current–potential data corrected for background current, while the points are examples of the fit of digital simulations to experiment based on quasireversible reduction of **1** to its radical anion (stable on the time scale of the experiment) followed by totally irreversible one-electron reduction of the radical anion at the second reduction peak.

Additional information was afforded by chronoamperometry. At 0 °C, a step to a potential (−1.8 V) negative of the second reduction peak produced a diffusion-controlled current–time curve as indicated by constant $it^{1/2}$ (0.5–5 ms at 50 μm electrode) at a level corresponding to an overall two-electron reduction (n = 1.8 by comparison to nitrocyclohexane as internal standard). However, the current obtained after a step to a potential between the two reduction peaks (−1.15 V) exhibited kinetic character. The values of $it^{1/2}$ increased with time approaching the two-electron level at long times, >10 ms.

Controlled potential electrolysis of **1** at a potential negative of the first peak with either a platinum gauze (−1.4 V) or a mercury pool electrode (−1.2 V) passes 2 equiv of electrons per mole (n = 2.2, three trials, 1.1–11.2 mM, room temperature). After electrolysis, the reduction peaks are absent, but peaks corresponding to oxidation of nitrite are present. Spectrophotometric determination of nitrite indicated an 87% yield (average of four trials) based on eq 5. Similarly, the olefinic product, 2,3-dimethyl-2-butene, was found in 80% yield by gas chromatography (average of two trials).

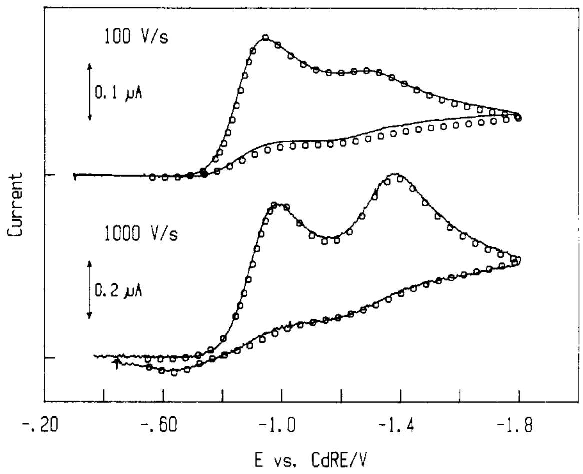
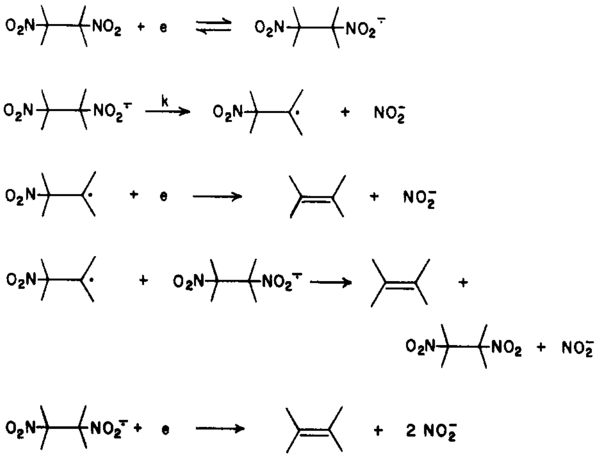


Figure 2. Cyclic voltammograms of 4.5 mM **1** in DMF/0.30 M TBAHFP at a 25 μm diameter mercury electrode at 0 °C. Curves: experimental. Points: digital simulations. Parameter values: $E^\circ_6 = -0.78$ V; $k_{s,6}/D^{1/2} = 7.4$ s$^{-1/2}$; $\alpha_6 = 0.50$ (100 V/s), 0.44 (1000 V/s); $k_7 = 850$ s^{-1}; $\alpha_{10} = 0.33$; other conditions as in Figure 1.

$$1 + 2\,e = (CH_3)_2C{=}C(CH_3)_2 + 2\,NO_2^- \qquad (5)$$

All of these data are consistent with the ECE reaction sequence proposed in eq 6–10. The first four steps comprise the processes that produce the single irreversible, two-electron reduction seen at low scan rates. No peak due to electrode reaction 10 (reduction of the anion radical of **1**) is seen because the anion radical loses nitrite (eq 7), and the resulting β-nitroalkyl radical is reduced at the electrode (eq 8) or, mainly, in solution (eq 9). At higher scan rates or lower temperatures, the rate of loss of nitrite (eq 7) is not sufficiently large to affect the voltammograms, and the two reduction peaks correspond to eq 6 and 10. Loss of the second nitrite (associated with the second stage of reduction, eq 8–10) is considered to be extremely rapid. At intermediate temperatures and time scales, the voltammograms are affected by eq 7 and it is possible to measure the rate constant, k, and to confirm that the response changes with the time scale of the experiment in the manner predicted by this reaction scheme.



(6) (7) (8) (9) (10)

We have made these measurements by chronoamperometry and by digital simulation of the cyclic voltammograms. Examples of the agreement between simulated and experimental voltammograms are given in Figure 2, and the numerical results are summarized in Table I. In the digital simulations, eq 6–10 were included in the model with the solution electron transfer (eq 9) treated as fast

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(31) (a) In this system of terminology, E designates an electron transfer reaction occurring at the electrode surface and C indicates a chemical reaction occurring in solution near the electrode. An ECE scheme is composed of an electron transfer reaction giving an intermediate, which undergoes a chemical reaction producing another intermediate, which reacts at the electrode. These correspond to eq 6–8. In addition to reacting at the electrode, the intermediate can be reduced by a solution electron transfer reaction (eq 9). This reaction is formally a disproportionation, and when it is fast so that eq 7 is rate-limiting, the reaction sequence is designated as DISP1, i.e., disproportionation with first-order kinetics.[31b] (b) Amatore, C.; Savéant, J.-M. *J. Electroanal. Chem.* **1977**, *85*, 27–46.

Table I. Rate Constants for Loss of NO_2^- from the Anion Radical of 1 (eq 7) as Measured by CV and Chronoamperometry at 0 °C[a]

cyclic voltammetry		chronoamperometry	
scan rate, V/s	$k \times 10^{-2}$, s^{-1}	time, ms	$k \times 10^{-2}$, s^{-1}
100	8.5	0.15	9.3
200	10.2	0.2	9.4
500	8.1	0.3	9.2
1000	8.5^b	0.4	9.5
2000	8.5^b	0.5	9.8
av	9.1	0.6	9.7
		0.7	9.4
		0.8	9.6
		0.9	9.0
		1.0	8.7
		av	9.4

[a] 0.30 M tetra-*n*-butylammonium hexafluorophosphate in DMF. For cyclic voltammetry: 12.5 micron radius electrode, 2.2 mM 1. For chronoamperometry: 25 micron radius electrode, 2.3 mM 1, potential step −0.3 to −1.2 V. [b] Approximate values because the kinetic effect is small at these scan rates. These results are not included in the average.

Table II. Parameters Measured for the Reduction of Nitro Compounds in DMF/0.30 M Tetra-*n*-butylammonium Hexafluorophosphate at 0°C

compound	$k \times 10^{-3}$, s^{-1}	$E°_1$, V	E_{p2},[a] V	k_s,[b] cm/s	n^c
1	$0.93^{d,e}$	−0.81	−1.38	0.1	1.8
2	1.3^d	−0.81	−1.35		1.8
3	$12.^e$	−0.80	−1.33		1.7
4	$2.8^{d,f}$	−0.85	−1.65		1.6
5	$0.075^{d,f}$	−0.80	−1.37	0.1	1.8
2-methyl-2-nitropropane	0.0001^d	−1.02		0.02	
nitrocyclohexane		−1.01		0.05	

[a] v = 1000 V/s. [b] Measured in DMF/0.30 M tetraethylammonium perchlorate at 0 °C. [c] Measured by chronoamperometry at −1.8 V with comparison to the currents of an internal standard of nitrocyclohexane or nitromesitylene. [d] Determined by chronoamperometry. [e] Determined by cyclic voltammetry. [f] Apparent rate constant. Data were fit by ECE scheme of eq 6–10 though it is not an adequate description of the reduction of 4 or 5.

and irreversible. For chronoamperometry, the working curve for the simple ECE mechanism[32] was modified to include the effects of eq 9 as developed originally by Hawley and Feldberg.[33]

The rate constant was found to be independent of the concentration of 1 from 1 to 5 mM and was not affected by the presence of 10 mM nitrite (which supports the view that eq 7 is irreversible). Also, the addition of 1% water had no effect. When benzonitrile or acetonitrile was used as solvent, the rate constant was about one-third that found in DMF, a change that is within the expected range of solvent effects on reaction rates.[20b] Results qualitatively similar to those obtained with mercury electrodes were obtained when glassy carbon was employed, supporting the view that the material of the electrode is not participating in the overall reaction.

1,1′-Dinitrobicyclohexyl, 2. The electrochemical behavior of 2 was nearly identical to that of 1 (Table II). The radical anion of 2 is an important intermediate in the radical chain reaction of 1,1-dinitrocyclohexane with the anion of nitrocyclohexane,[23,25,26] and the reversible potential for the $2/2^{\bullet-}$ couple, first reported here, provides needed information to evaluate the energetics of the key chain-propagating reaction.

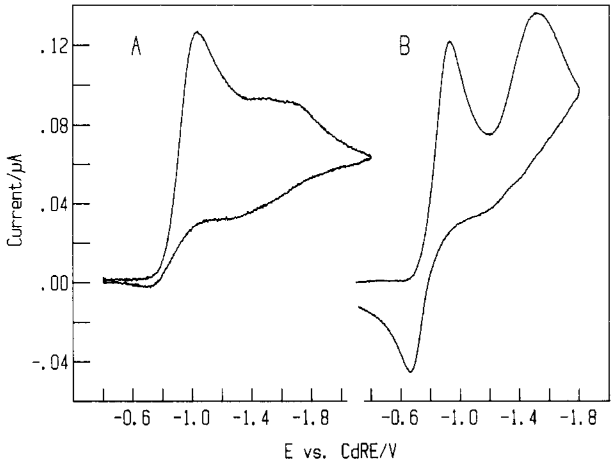

Figure 3. Cyclic voltammograms of (A) 1.7 mM *trans*-1,2-dimethyl-1,2-dinitrocyclohexane, 4, and (B) 2.4 mM *trans*-1-methyl-1,2-dinitrocyclohexane, 5, in DMF/0.30 M TBAHFP at a 25 μm diameter mercury electrode at 0 °C. (A) 500 V/s. (B) 200 V/s.

1,1′-Dinitrobicyclopentyl, 3. Again, the electrochemical behavior of 3 is very similar to that of 2. Surprisingly, the rate constant for cleavage of nitrite from the radical anion of 3 ($1.2 \times 10^4\ s^{-1}$) is about 10 times greater than that for 1 or 2.

***trans*-1,2-Dimethyl-1,2-dinitrocyclohexane, 4.** The reduction of this compound was also studied by cyclic voltammetry and chronoamperometry, giving the results summarized in Table II. Controlled potential electrolysis negative of the first reduction peak required 2.1 equiv per mole (−1.4 V, mercury pool cathode, room temperature). After electrolysis, the only electroactive compound in solution was nitrite, and the yield of 1,2-dimethylcyclohexene was quantitative within experimental error.

The only difference noted with 4 was that, under conditions where the loss of nitrite was limited (low temperatures and/or high sweep rate) and the reduction of the radical anion could be detected, there appeared to be two new reduction peaks rather than a single peak as seen with 1–3 (Figure 3).

***trans*-1-Methyl-1,2-dinitrocyclohexane, 5.** The reduction of 5 is not fully described by eq 6–10. At low temperatures and high scan rates, two reduction peaks are seen just as with 1–4. The chronoamperometric data were successfully treated by the ECE scheme of eq 6–10, giving the rate constant for loss of nitrite shown in Table II. However, in addition to the two reduction peaks seen at −0.9 and −1.5 V in the cyclic voltammogram (Figure 3), a third irreversible reduction peak appears at about −2.2 V. Its height corresponds approximately to a one-electron process, and its peak current function is constant at scan rates of 5–100 V/s (at a 100-μm electrode). However, at higher scan rates and lower temperatures the peak decreases and almost vanishes at 8000 V/s and 0 °C.

As with 4, the second reduction peak at −1.5 V is broad and may be a composite of more than one process. Multiple cycles between −0.3 and −1.8 V (not encompassing the third reduction peak) produce a new reduction process growing in as a shoulder just positive of the first reduction peak. No such behavior was ever detected with multiple scans on 1–4.

Controlled potential electrolysis at a potential between the first two reduction peaks (mercury pool cathode, room temperature) required 1.55 equiv per mole, and the only electroactive product was nitrite. Nitrite was produced in 80% yield (spectrophotometry), but 1-methylcyclo-

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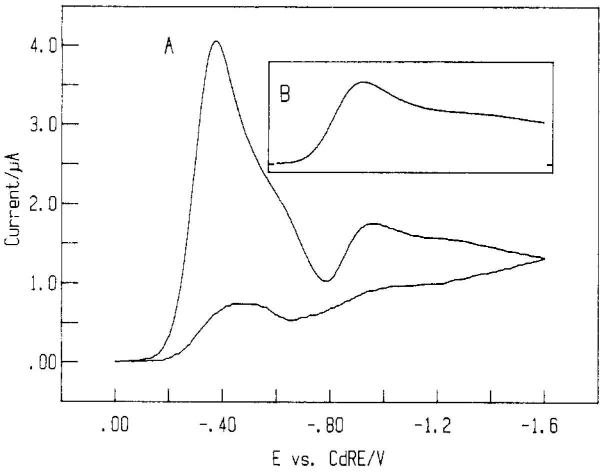


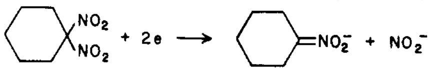
Figure 4. (A) Cyclic voltammogram of 3.2 mM 1,1-dinitrocyclohexane, 7, in DMF/0.30 M TBAHFP at an array of nine 25 μm diameter mercury electrodes at 160 V/s and 23 °C. (B) 2.77 mM 1,1′-dinitrobicyclohexyl, 2, at 200 V/s at a single 25 μm diameter mercury electrode. Currents have been multiplied by 5.

hexene was generated in only 50% yield and is the only volatile product detected by GC. It appears that reactions not included in eq 6–10 are occurring during reduction of 5.

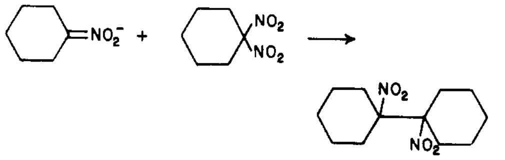
***trans*-1,2-Dinitrocyclopropane, 6.** This compound produces an irreversible reduction peak at −0.65 V (22 °C and 1000 V/s). No peak for oxidation of the anion radical could be unambiguously detected even at 8000 V/s and −47 °C due to its short half-life. Chronoamperometry (step from −0.1 to −1.7 V, 5-ms duration) produced diffusion-controlled currents with $n = 2.0$ by comparison to nitrocyclohexane as internal standard. We were not able to interpret the voltammograms quantitatively and conclude that reaction pathways other than eq 6–10 are operative. This vicinal dinitro compound is base-sensitive,[34b] so its reduction may be affected by the somewhat basic anions present in the diffusion layer during the voltammetric experiment.

1,1-Dinitrocyclohexane, 7. Though not a vicinal dinitro compound, 7 is of interest because its reaction with the anion of nitrocyclohexane produces 2 by a radical chain reaction in which the $2/2^{\bullet-}$ couple plays a central role. The voltammetry of 7 is affected by this radical chain reaction in an intriguing and informative manner. The principal reduction peak (Figure 4) appears at about −0.4 V. No oxidation peak associated with this reduction could be unequivocally identified even at 2000 V/s and −50 °C. In addition, at potentials just negative of the reduction peak, the current drops precipitously, much faster than a normal diffusion-controlled descent. The reduction peaks seen at about −0.95 and −1.3 V are due to 1,1′-dinitrobicyclohexyl, 2, an assertion supported by the voltammogram of 2 included in Figure 4. Chronoamperometry at the first peak (−0.6 V, 5 ms step duration) indicated a diffusion-controlled current (relatively constant $it^{1/2}$), but an n value of only 1.5 compared to nitromesitylene as an internal standard. Controlled potential electrolysis at −0.35 V required 1.1 equiv per mole of 7. Nitrite and 2 were found by voltammetry in the electrolysis solution, the latter in 95% yield.

These observations are best accounted for by eq 11 and 12. The reduction of 7 proceeds in an overall two-electron process, producing nitrite and the anion of nitrocyclohexane (eq 11). This reaction probably occurs by an ECE process in which the cleavage of nitrite from the radical anion of 7 is extremely rapid.[17] As the concentration of the anion of nitrocyclohexane builds up near the electrode, the rate of eq 12 increases, resulting in the consumption of starting material and the production of 2. Reaction 12 is known to proceed by a radical chain process.[23,25,26] The combination of eq 11 and 12 is net reaction 13, which requires one electron per molecule of 7. The voltammetric experiment can easily be carried out on a time scale that prohibits significant occurrence of eq 12. At 2000 V/s and 0 °C, no peaks for reduction of 2 are seen. The reaction pathway postulated for the reduction of 7 is very similar to the self-protonation reactions of anions reported by Amatore et al.[35]



(11)



(12)

(13)

Comparison of Results. Electrochemical data for two mononitro compounds, 2-methyl-2-nitropropane and nitrocyclohexane, were also obtained under the same conditions employed for the dinitro compounds (Table II). The reversible potentials for the neutral/anion radical couples of the mononitro compounds are about 0.2 V more negative than those of the *vic*-dinitro compounds due to the electron-withdrawing properties of the second nitro group.

The standard heterogeneous electron transfer rate constant, k_s, for the neutral/anion radical couple of mononitro aliphatics has long been known to be relatively small,[36] an observation usually attributed to the fact that the negative charge is localized on the nitro group in the anion leading to a relatively large solvent reorganization contribution to the activation energy for electron transfer. The values of k_s at a mercury microelectrode for four compounds were determined by cyclic voltammetry under identical solution conditions, 0.30 M tetraethylammonium perchlorate in DMF at 0 °C (Table II). The results are similar for all four compounds, with the mononitro compounds exhibiting slightly slower electron transfer kinetics.

In contrast, the rate constants for cleavage of the $C{-}NO_2$ bond of the anion radicals are much larger for the *vic*-dinitro compounds than for the mononitro analogues.[20] For example, the rate constant for 2 is about 10^4 times that for 2-methyl-2-nitropropane. Thus, the second nitro group has a strong activating effect for the expulsion of nitrite.

Experimental Section

Instrumentation and Procedures. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WM 250 spectrometer. Infrared

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spectra were recorded in chloroform solution by using a Bomem FT-IR. Melting points were obtained with a Büchi 510 melting point apparatus and were uncorrected. Gas chromatographic analysis of olefins was carried out with a Varian Model 3700 Gas Chromatograph with a 15% XF 1150 ChromW 60/80 6 ft × $^3/_8$ in. SS column. The column temperature was 90 °C for 5–8 min followed by a 10 °C/min increase to 200 °C. A thermal conductivity detector was used at 260 °C.

Nitrite was determined by diluting 1–2 mL of electrolysis solution (100–500 dilution factor, depending on concentration of nitrite) with distilled water. Two-milliliter aliquots of the diluted solutions were added to 4.00 mL of NEDA-Sulfa solution (10 g of sulfanilamide, 0.5 g of *N*-(1-naphthyl)ethylenediamine dihydrochloride, and 25 mL of 85% phosphoric acid diluted to 500 mL with distilled water). The mixture was allowed to react for 10 min, and the absorbance was obtained at 530 nm on a Bausch and Lomb Spectronic 20. The working curve was prepared from solutions of known concentrations of $NaNO_2$ with 0.5–1% DMF/0.1 M TBAHFP in distilled water.

Electrochemical instrumentation and methods for low-temperature voltammetry have been reported previously.[37] A Princeton Applied Research (EG & G Princeton Applied Research, Princeton, NJ) PAR Model 173 potentiostat, PAR Model 176 current-to-voltage converter and PAR Model 175 signal generator were used in conjunction with a Nicolet Model 4094 high-speed digital oscilloscope for data acquisition. To obtain adequate response time, the current-to-voltage converter was not operated at its most sensitive setting. Instead, the gain was limited to 10 μA/V for scan rates up to 500 V/s and to 100 μA/V for 1000–2000 V/s. The data were transferred to an IBM Instruments Model 9000 computer for storage on floppy disks and subtraction of background signals. Background signals were obtained with solvent and electrolyte alone for later subtraction from data obtained in the presence of the electroactive substrate. All voltammograms that were compared with digital simulations were corrected in this way. Current–time curves from potential step chronoamperometry were corrected manually.

Nitrocyclohexane was used as an internal standard for estimation of the number of electrons consumed per molecule of reactant (*n* value) by chronoamperometry. A current–time curve was obtained for the substance under study, a known concentration of nitrocyclohexane was then added, and a new current–time curve was recorded. Nitrocyclohexane undergoes a one-electron reduction on the time scale used, so the increase in current along with the original current can be used to determine the *n* value for the substance being studied. The diffusion coefficient of nitrocyclohexane is similar to those of the compounds studied, so the procedure is reasonably accurate.

The reference electrode was cadmium amalgam in contact with saturated $CdCl_2$ in DMF/0.10 M TBAHFP.[38] The potential of this cadmium reference electrode (CdRE) was found to be −0.64 V vs aqueous SCE.

The working electrodes were nominally 25 μm (for $v > 80$ V/s), 50 μm (v = 20–75 V/s), 100 μm (v = 5–15 V/s), and 200 μm (v = 1–5 V/s) diameter platinum disks prepared as described earlier.[30] Mercury was electrodeposited on the disks from 50 mM aqueous $Hg(NO_3)_2$ for 2–10 min at −0.2 V vs a Hg pool. The amount of charge passed upon anodic stripping of the mercury confirmed that the deposited mercury was just sufficient to form a hemisphere on the platinum disk support. In one experiment (the reduction of **7**) an array of nine 25 μm diameter platinum disks sealed in glass was used to produce larger currents.

The digital simulations employed the explicit finite difference technique[39] and included eq 6–10.

Chemicals. DMF (Burdick and Jackson) was purified by passage through a column of activated alumina just prior to use. TBAHFP was prepared by metathesis of ammonium hexafluorophosphate (Aldrich) and tetra-*n*-butylammonium bromide (Aldrich) in acetone/water followed by three recrystallizations from 95% ethanol and drying under vacuum at 100 °C for 18 h. The preparation of tetraethylammonium perchlorate has been described.[40] Compound **1**, 2-methyl-2-nitropropane, and nitrocyclohexane were purchased from Aldrich, and **2**,[41] **3**,[42] and **5**[43] were prepared according to the literature and identified by melting point and/or NMR. A sample of **6** was supplied by Professor Peter A. Wade (Drexel University, Philadelphia) and **7** by Professor F. G. Bordwell (Northwestern University, Evanston, IL).

Preparation of *trans*-1,2-Dimethyl-1,2-dinitrocyclohexane, 4. Approximately 0.5 mL of N_2O_4 (Aldrich, *caution*: corrosive, toxic) was condensed into a 25-mL one-necked flask at 0 °C. To this was added 10 mL of cold diethyl ether; 1.07 g of 1,2-dimethylcyclohexene (K + K Labs, purified by passing through a 4 mm × 5 cm column of activated alumina) was slowly added. This solution was stirred at 0 °C for 1.5 h, the volume was reduced 50% by warming to 30 °C under a stream of air, and 0.5 mL of methanol was added after cooling to 0 °C. This caused 170 mg of pure **4** to precipitate. The filtrate was poured into ice water, extracted with chloroform, and dried over $MgSO_4$. Evaporation left a blue oil, to which was added 3–4 mL of pentane and sufficient methanol to allow dissolution of the oil, and the solution was cooled to −20 °C overnight and filtered. The solid was washed with warm hexane and recrystallized from chloroform/pentane to give 270 mg of pure **4**. Total yield was 440 mg, 23%. MP: 203–205 °C. ^{1}H NMR: 1.4–2.6 (complex), 1.76 (s) ppm vs TMS. ^{13}C NMR: 91.78 (s), 35.18 (t), 21.91 (t), 21.02 (q) ppm vs TMS. IR: 1545 (s), 1350 (s) cm^{-1}. Anal. Calcd for $C_8H_{14}N_2O_4$: C, 47.52; H, 6.98; N, 13.85. Found: C, 47.35; H, 7.00; N, 13.65.

The ^{13}C NMR spectra of **4** show only four kinds of carbon, and the spectra do not change from room temperature to −50 °C in deuteriochloroform. For other cyclohexanes, interconversion of conformers is typically frozen out by −50 °C. Thus, **4** is the trans isomer as opposed to the cis, whose low-temperature spectrum should show eight different carbon nuclei. Additionally, **4** exists as predominantly one conformer.

More information was obtained from the NMR spectra of **5**, which has previously been identified as the trans isomer.[43] ^{1}H NMR spectra recorded in DMF-d_7 showed no significant change between 90 and −50 °C. The resonance that is farthest downfield (5.66 ppm) is due to the only proton that is α to a nitro group. It was coupled to the two adjacent methylene protons, giving a doublet of doublets with J = 12.1 and 4.3 Hz. J = 12.1 Hz corresponds closely to that expected for axial–axial coupling while 4.3 Hz is reasonable for axial–equatorial interactions.[44] Thus the proton α to nitro must be in the axial position, and the nitro groups are equatorial. Of course, this is likely to be the favored conformation on the basis of the A and G parameters of the nitro and methyl groups.[45]

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