The *n* Value for Electrochemical Reduction of 1-Iododecane Depends on Electrolysis Time

Sir:

In a recent publication[1] dealing with the electrochemistry of 1-iododecane and 1-bromodecane in dimethylformamide containing tetraalkylammonium salts, we determined the products resulting from controlled-potential electrolyses at mercury pool cathodes and we found that the coulometric *n* value for reduction of the carbon–halogen bond is unity. A polarogram for a 0.0025 M solution of 1-iododecane in dimethylformamide containing 0.1 F tetramethylammonium perchlorate was shown[1] to exhibit a single wave[2] with an anomalous maximum[3] near the middle of the limiting-current plateau; the *n* value obtained by measurement of the diffusion current at potentials more positive than the maximum is 1. These findings led us to propose that, regardless of potential, the electrolysis products are formed from radical intermediates. Although a similar conclusion was reached by Wagenknecht[4] in a study of the electrochemical reduction of 1-bromobutane, other workers have observed that reduction of a carbon–halogen bond is a two-electron reaction[5-7] or that, depending on the electrolysis potential, the process can involve either one or two electrons.[8-11] At present, there is no satisfactory explanation for these discrepancies. However, we report here that the number of electrons consumed in the reduction of 1-iododecane at mercury in dimethylformamide is dependent upon the time scale[12] of the experiment.

We first noticed the importance of the duration of the experiment on the reduction of 1-iododecane when chronocoulometric studies[13] were performed to determine if the starting material is adsorbed onto a mercury electrode in dimethylformamide containing 0.1 F tetramethylammonium perchlorate. In one experiment the potential[14] was stepped from −0.60 V at which no reduction of 1-iododecane occurs to −1.10 V which is on the limiting-current plateau of the polarographic wave and which is more positive than that of the current maximum. A second experiment entailed stepping from the same initial potential (−0.60 V) to a final value (−1.60 V) more negative than the potential of the polarographic maximum. In each experiment, data were collected for a period of approximately 50 ms before the potential was returned to its original value. When results from the two experiments were transformed[13] into a plot of Q vs. $t^{1/2}$, two straight lines were obtained having intercepts in good agreement with values of Q_{dl}, the quantity of electricity required to charge the double layer. Thus, there is little, if any, adsorption of 1-iododecane. However, the slopes of the two lines differed by a factor of 2. We interpret the latter observation as signifying that a two-electron transfer occurs at potentials negative of the polarographic maximum, whereas a one-electron process takes place at more positive potentials. This result is in sharp contrast to that obtained from large-scale controlled-potential electrolyses, for which the *n* value is 1 regardless of potential.

Additional proof that the reduction of 1-iododecane depends on the time scale of the experiment has emerged from a set of polarograms we recorded using controlled mercury drop times. As the drop time is made shorter, the polarographic maximum gradually diminishes and a definite second wave begins to appear at a potential just slightly negative of the maximum. At a drop time of 0.5 s, two waves of approximately equal height with half-wave potentials of −0.88 and −1.31 V are observed and only a small maximum remains.[15] Furthermore, when we recorded a pulse polarogram using a sampling period of 50 ms with a 2-s drop time, the polarographic maximum was gone and two waves with half-wave potentials of −0.93 and −1.36 V, each corresponding to a one-electron process, were seen.

Still more evidence that the reduction of 1-iododecane de-

pends on electrolysis time has been obtained from cyclic voltammetric experiments. For a scan rate of 100 mV/s in dimethylformamide containing 0.1 F tetramethylammonium perchlorate, a cyclic voltammogram shows a wave for reduction of the carbon-iodine bond with a peak potential of −0.96 V, followed by a current spike having a peak potential of −1.37 V. Upon reversal of the scan, an inverted wave[16,17] with a peak potential of −1.33 V appears. If the scan rate is changed to 500 mV/s, a pair of irreversible one-electron waves with peak potentials of −0.98 and −1.45 V is observed, but the current spike and inverted wave are absent.

Results obtained by means of chronocoulometry, polarography, cyclic voltammetry, and controlled-potential coulometry reveal that the relative time scale of the techniques is a parameter of great significance. For large-scale controlled-potential electrolyses performed with rapid stirring of the solution, the electrolysis time is ∼10 min and the *n* value is essentially unity throughout the entire potential region explored. However, the other three methods can be done with much shorter electrolysis times and an *n* value of 2 can be obtained at potentials negative of the polarographic maximum.

Controlled-potential electrolyses of 1-iododecane in the presence of a large excess of D_2O and at potentials negative of the polarographic maximum resulted in ∼35% incorporation of deuterium into decane, clear evidence for the intermediacy of decyl carbanions. However, the coulometric *n* value of 1 obtained in these experiments of relatively long duration suggests that 1-iododecane is consumed via a chemical pathway which competes with electrolytic cleavage of the carbon–halogen bond. We have verified that reaction of decyl carbanion with starting material is of little importance[18] and we propose that hydroxide ion, produced by deprotonation of water present in the solvent,[19] reacts with unreduced alkyl iodide to form 1-decene and 1-decanol.

Recent work in dry[20] dimethylformamide has yielded a coulometric *n* value of 1.28 for reduction of 1-iododecane at a potential of −1.7 V. Such a result is consistent with less consumption of starting material due to attack by hydroxide ion. Our research on the reduction of alkyl halides is continuing, and in a future report we will present representative data and mechanistic schemes in support of these observations. Nevertheless, it is clear that the electrolysis time, as well as the water content of the solvent, has a profound effect on the electrochemical behavior of 1-iododecane.

References and Notes

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(2) The polarogram shown in Figure 1B of ref 1 above for the reduction of 1-iododecane in the presence of 0.1 F tetramethylammonium perchlorate is, in fact, an anomaly due to fortuitous capillary constants; our most recent polarograms clearly show evidence of a second wave at potentials negative of the polarographic maximum.
(3) This polarographic maximum does not exhibit the usual response to added suppressors; the reason for its appearance is still under investigation.
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(12) The time scale of the experiment refers to the total elapsed time from the initiation of the voltage waveform to its termination.
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(14) All potentials are quoted with respect to a reference electrode consisting of a saturated cadmium amalgam in contact with dimethylformamide saturated with both cadmium chloride and sodium chloride; this electrode has a potential of −0.750 V vs. the aqueous saturated calomel electrode.

(15) A similar result is obtained in experiments with relatively long drop times if the concentration of tetramethylammonium perchlorate is decreased from 0.1 to 0.005 F. Work we are presently doing should help to explain this effect.

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(18) Electrolytic reduction of $C_8H_{17}CD_2CH_2Br$ produces only a small amount of 1,2,2-trideuteriodecane, which indicates that attack on starting material by decyl carbanion is not a favored process. In addition, none of the dimer (eicosane) is produced.

(19) The water content of typical solutions ready to be electrolyzed that are prepared from dimethylformamide redistilled from calcium hydride is ∼50 mM. Observations concerning the importance of water for the electrolytic reduction of 1-bromohexane at mercury have been discussed by Reed, R. C. Ph.D. Thesis, Wesleyan University, Middletown, Conn., 1971.

(20) Dry solvent was obtained by passage of the supporting electrolyte–dimethylformamide solution through a column containing activated neutral alumina. In addition, the electrolysis cell was charged with a small amount of the alumina. The water content of the solution to be electrolyzed was found to be ∼2 mM.

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Received May 12, 1978

Figure 1. Some elaboration products of cyclohexene via the nitro olefin **1b.** Reagents used for transformations A–L are indicated in the text.

A New Synthesis of Conjugated Nitro Cyclo Olefins, Unusually Versatile Synthetic Intermediates

Sir:

The position of the endocyclic carbon–carbon double bond as one of the most useful centers of reactivity for the elaboration of complex organic structures would be augmented by the availability of a *mild, position-selective* method for the replacement of a hydrogen on one of the olefinic carbons by a nitro group. Such conjugated cyclic nitro olefins are potentially both versatile and unique as synthetic intermediates, for example, for the stereoselective attachments of appendages and/or functional groups, for the extension of functionality to adjacent methylene groups, or for annulation reactions. Unfortunately the lack of general, selective, and suitably mild processes for the synthesis of cyclic nitro olefins has impeded the development of this whole domain of synthetic methodology.[1,2] We now describe a new and widely applicable route to cyclic (and noncyclic[3]) nitro olefins, and in addition we demonstrate some of the manifold ways in which these intermediates can be utilized in organic synthesis.

Our process for olefin nitration is typified by the conversion of cyclohexene (**1a**) to the 1-nitro derivative **1b.**[4] Reaction of
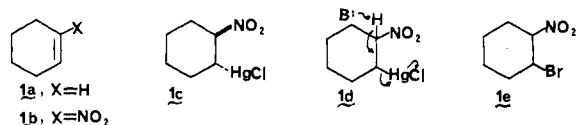
cyclohexene with 1 equiv of mercuric chloride and 2 equiv of sodium nitrite in aqueous solution at 25 °C for 30 h effected nitromercuration[5] and afforded after collection of the resulting precipitate the nitromercurial **1c** (80%). Treatment of **1c** in methylene chloride solution with 1.0 equiv of 2.5 N aqueous sodium hydroxide at 25 °C for 5 min with stirring followed by acidification (1 N hydrochloric acid), filtration through Celite (quantitative recovery of metallic mercury), extractive isolation, and distillation produced in >98% yield pure 1-nitrocyclohexene (**1b**).[6,7] The novel base-catalyzed elimination of mercury from **1c** can be formulated mechanistically as shown
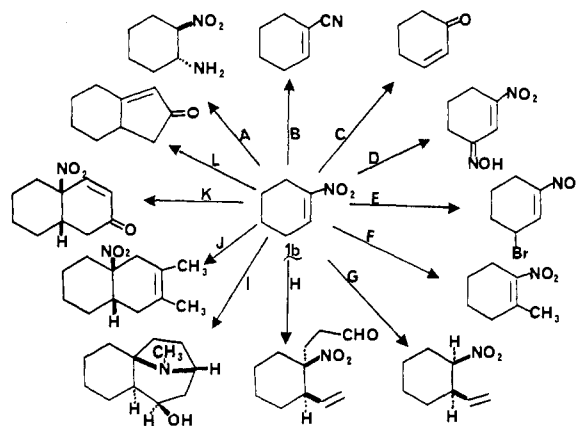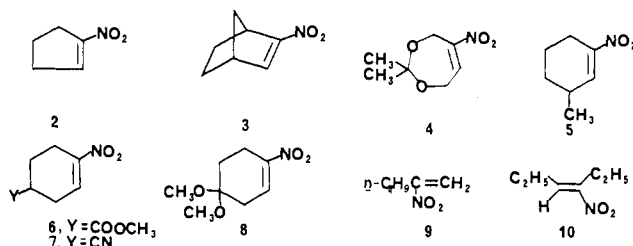
in expression **1d.**[8] An alternative, but less practical, and less general sequence for the conversion of **1c** to nitro olefin **1b** was also devised and consisted of the following steps: (1) bromination of **1c** by reaction with 1.6 equiv of bromine in a two-phase water-ether system at 0 °C for 10 min and 25 °C for 3.8 h to form **1e** and (2) reaction of **1e** with a small excess of triethylamine in tetrahydrofuran (THF) solution for 12 h at 25 °C to form **1b** (87% overall yield from **1c**).

The base-catalyzed conversion of nitromercurials to nitro olefins can also be effected by various tertiary amine bases, e.g., triethylamine or diazabicycloundecene (DBU), and these reagents are preferable to hydroxide ion in the case of base-sensitive nitro olefins. Studies with a range of substrates have led to a reasonably clear definition of the scope and selectivity of the new nitro olefin synthesis. In all cases investigated the demercuration step was rapid and remarkably clean (with hydroxide ion or tertiary amine as base) and uniformly gave essentially quantitative yield of the nitro olefin. As expected, the nitromercuration step was more variable with regard to rate and yield. In general this process was conducted at 25 °C in aqueous solution of pH 6.5 to 5.5 (phosphate buffer) until analysis of the reaction mixture (by GC or TLC) indicated complete or nearly complete consumption of starting olefin (45–60 h). The nitro olefins in the series **2–10** could be pre-

pared cleanly and selectively with overall isolated yields as follows: **2**, 61%; **3**,[9c] 77% (DBU as base); **4**, 67%; **5**, 80%; **6**, 78%; **7**, 75%; **8**, 80%; **9**,[9b,c] 71% (triethylamine as base); **10**, 65%. The clean formation of **3** indicates that carbonium ion rearrangement is not a problem, and the successful preparation of **4** and **8** shows the lack of interference by acid-sensitive functionality in the substrate. Cases **5**, **6**, **7**, and **8** for which complete position selectivity prevails (by chromatographic and spectroscopic analysis) illustrate the operation (and utility) of the remarkable directive effects (presumably involving bis coordination of mercuric ion) which Henbest and Nicholls first observed for olefinic acetoxymercuration,[10] and in the case of **5** the importance of steric effects. The structures of the nitro olefins **5–8** were proved by transformation of the nitrovinyl unit to methylenecarbonyl (-CH=C—NO_2 → -CH_2CO-) using