

ELECTROCHEMICAL REDUCTION OF 1, 3- AND 1, 4-DIBROMIDES:
EVIDENCE FOR A TWO-STEP PROCESS¹

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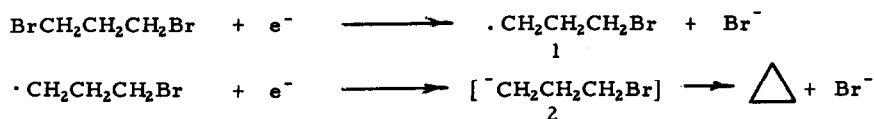
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The reduction of 1, 3-dihalides is a common procedure for the preparation of cyclopropanes,² and the reduction of 1, 4-dihalides has found some use in the preparation of cyclobutanes.³ In the latter case, the nature of the reducing agent has a major effect on the course of the reaction. Since this might be related to the half-cell potential of the reducing agents employed, we have examined the electrochemical reduction of 1, 3- and 1, 4-dihalides. It has been reported⁴ that the electrochemical reduction of the 1, 3-dibromopropane and 1, 4-dibromobutane proceeds in a manner similar to chemical reducing agents, and produces cyclopropane and cyclobutane, respectively.

The electrochemical reduction of 1, 3-dibromopropane was studied by cyclic voltammetry in dimethylformamide solution using a mercury coated platinum electrode, a mercury pool reference electrode, and a mercury counterelectrode. At a moderately slow sweep rate (0.3 v/sec) a surprising result is obtained--two irreversible waves are observed.⁵ As the sweep rate is increased, both waves move to a more negative potential, and begin to merge. Irreversible behavior was observed at even the fastest sweep rates (50 v/sec).

The observation of two waves at slow sweep rates suggested that there may be two successive irreversible one electron transfers, such as:⁶



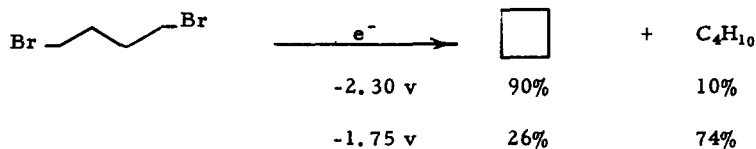
An alternative mechanism, involving formation of an organomercurial at the electrode surface, was ruled out by observing similar behavior when cyclic voltammetry was carried out using a platinum electrode in place of the mercury working electrode.

In order to test the hypothesis of the two successive one electron transfers, the reaction

was studied on a preparative scale at different electrode potentials. The reactions were performed on dilute solutions (ca. 0.25%) of 1,3-dibromopropane in dimethylformamide using a platinum electrode. Tetraethylammonium bromide was used as the supporting electrolyte, and small amounts (ca. 1%) of benzyl methyl ether were added to serve as a potential source of hydrogen atoms and thus act as a radical scavenger. The electrolytic cell was continuously swept with helium, and the exiting gas was passed through a liquid nitrogen trap to capture the gaseous products. The products obtained in this manner were analyzed by mass spectrometry. At a relatively high potential, (-2.65 v) the major product obtained was cyclopropane (91% cyclopropane, 9% propane). As the potential was made less negative, propane began to be formed, and at -1.45 v (where the current was only 0.0018 amp) the ratio of propane to cyclopropane had increased to 86% propane and 14% cyclopropane). When the reaction was not carried to completion, small amounts of 1-bromopropane could be detected by gas chromatography.

The above experiment did not indicate whether the propane was formed by removal of a proton from the solvent by an anionic intermediate (such as 2) or by removal of a hydrogen atom by a radical species (such as 1). Therefore, the reaction was carried out in a solution of 1% benzyl- α - d_2 -methyl ether⁷ and 99% dimethylformamide. The propane which was formed from this electrolysis contained 8.8% deuterium, indicating that the hydrogen was probably transferred as a hydrogen atom. This is in accord with the mechanistic hypothesis presented above.

The electrochemical reduction of 1,4-dibromobutane proceeded in a similar fashion. At a high negative potential, -2.30 v, the product consisted of 10% butane and 90% cyclobutane. No other products were observed in the mass spectrum. A measured amount of pentane, added as an internal standard to one run, indicated that the C_4 hydrocarbons were formed in 78% yield. When the potential was made less negative, the ratio of butane to cyclobutane increased, and at -1.75 v (with added benzyl methyl ether and a current of 0.023 amp) 74% butane and 26% of cyclobutane was formed.



The data presented above indicate that the dibromides may be reduced via a one electron process leading to a free radical. It is not unreasonable to suppose that the formation of cyclopropane or cyclobutane involves reduction of the initially formed radical followed by ring closure. However, it is not possible to rule out a change in mechanism at the more negative potentials and a direct two electron reduction forming the ring in one step.

Some care must be made in attempting to generalize these results to the reduction of all 1, 3-dihalo compounds. Our studies on related compounds⁸ indicate that structural changes can drastically change the cyclic voltammetric behavior of the reduction. Thus, for example, one does not obtain a resolution of two waves in the reduction of 2, 5-dibromopentane, contrasting sharply to the closely related 1, 3-dibromopropane. This may reflect changes in the mechanism of reduction, which could explain the current controversy over the mechanism of reduction of organic halides and dihalides.^{4,9}

References

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5. At a scan rate of 0.3 v/sec, the peak potentials were -1.75 and -2.0 v. When the scan rate was increased to 20 v/sec, one wave was found with a peak potential of -2.2 v.
6. These equations are illustrative of the type of process required to explain the following observations. It is unlikely that the free bromotrimethylene radical is formed at the first wave and survives long enough to be reduced at the second wave using a slow sweep rate.
7. Prepared by the reduction of ethyl benzoate with lithium aluminum deuteride, followed by alkylation of the anion of the deuterated benzyl alcohol with methyl iodide.
8. To be published.
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