

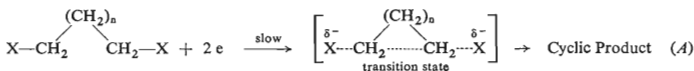
MECHANISM OF CARBON-HALOGEN
BOND CLEAVAGE. III.*
ELECTROCHEMICAL PREPARATION
OF HIGHLY STRAINED HYDROCARBONS

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Previously¹, we reported our investigation on the electrochemical behavior of vicinal and 1,3-dihalides and proposed a concerted mechanism (A), with the transition state shown below, for their cleavage. It was our contention that how well developed the central bond is in the transition state will be reflected in the half-wave potential of the dihalide. As an extension of this work, we have investigated the behavior of the dihalides in Table I and obtained data which is consistent with the above mechanism.



In the paracyclophane series, the *cis*-isomer (compound I in Table I) reduces at a more positive potential than its *trans* analogue, although both exhibited a diffusion current equal to that of 1,3-dibromopropane (the latter compound reduces in a two-electron step to afford high yield of cyclopropane even in the presence of water)¹. This indicates that both isomers afford the same product (olefin) and that the *cis*-isomer reduces *via* a concerted manner not favorable for the *trans*-isomer. 1,3-Dibromopropane (III) and 1,3-dibromo-2-propanol (V) reduce at a more positive potential than 1-bromo-3-chloropropane. Since the electronegativity of chlorine is greater than that of bromine, inductive effect cannot be operative, instead it is the ease of displacement of bromine as compared to that of chlorine that is responsible for the ease of reduction in a concerted manner. Furthermore, the detection of cyclopropanol from the reduction of 1,3-dibromo-2-propanol and the lack of detection of propane or chloropropane from the reduction of 1-bromo-3-chloropropane are strong indications that the reduction of these compounds do not proceed through anionic intermediates.

The reduction of 1,3-dibromoadamantane (VI) in hexamethylphosphoramide/tetrabutylammonium perchlorate afforded good yield of adamantane. There was no evidence for the formation of 1,3-dehydroadamantane. This may mean that the reduction of the dihalide proceeds in a stepwise manner with anionic intermediates or that the 1,3-dehydroadamantane was formed but was reduced (because it is unstable²) under the reaction condition to adamantane. The observation that 1,3-dibromoadamantane exhibits one polarographic wave is inconsistent with a stepwise mechanism as the monohalide would be expected to reduce at a more negative potential than the dihalide.**

* Part II: J. Am. Chem. Soc. 91, 4953 (1969).

** Compare for example the reduction of bromoadamantane to that of 1,3-dibromopropane in the work³.

Bicyclic compounds of the general formula shown below are of theoretical significance and may be prepared from the corresponding dihalides. It can be seen from Table I that the ease of reduction of the dihalide is related to its ring size. This is consistent with the ease of reduction of the corresponding monohalides⁴. The only dihalides that afforded the desired bicyclic compound is that of [3.2.1] bicyclooctane⁵ which also reduced at the most positive potential. That the reduction of this compound may proceed *via* the transition state described above is indicated from the half-wave potential and diffusion current of its chloro-bromo analogue. Again, based on inductive

TABLE I
Electrochemical Behavior of Dihalides in the System Dimethylformamide-Tetrabutylammonium Perchlorate

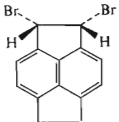
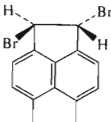
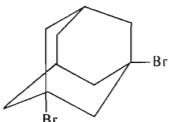
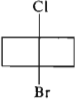
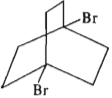

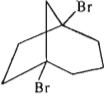
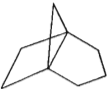
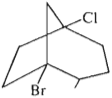
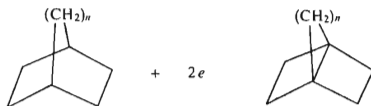
Dihalide	$-E_{vs}$ (S.C.E.)	Products
 (I) ^a	1.12	<i>b</i>
 (II) ^a	1.4	—
BrCH ₂ CH ₂ CH ₂ Br	1.91	Cyclopropane
BrCH ₂ CH ₂ CH ₂ Cl (IV)	2.04	Cyclopropane
BrCH ₂ CH(OH)CH ₂ Br (V)	1.90	Cyclopropanol (poor yield)
 (VI) ^c	1.97	Adamantane

TABLE I
(Continued)

Dihalide	$-E, V$ (s.c.e.)	Products
 <chem>ClC(Br)CCl</chem>	(VII) ^c 2-47	—
 <chem>BrC1(Br)CCCCC1</chem>	(VIII) ^c 2-2	 <chem>C=CC=CC=C</chem> ^d
 <chem>BrC1(Br)C2(Br)CCCC21</chem>	(IX) ^c 1-99	 <chem>C1CC2CCC12</chem> ^{c,d}
 <chem>ClC1(Br)C2(Br)CCCC21</chem>	(X) 2-28	—

^aKindly supplied by Dr D. J. Cram, University of California, Los Angeles. ^bSame I_d as 1,3-dibromopropane (III). ^cKindly supplied by Dr K. B. Wiberg, Yale University. ^dAccording to P. G. Gassman⁵, Hydrocarbon Division, Kolbe College, New Hampshire.

effects, compound X in Table I, would be expected to reduce at a more positive potential than compound IX. Instead it appears that the displacement of both halogens is involved in the transition state which is consistent with the above proposed mechanism.



REFERENCES

1. Rifi M. R.: *Tetrahedron Letters* 1969, 1043.
2. Peacock R. E., Torupka E. J.: *J. Am. Chem. Soc.* 91, 4953 (1969).
3. Závada J., Krupička J., Sicher J.: *This Journal* 28, 1664 (1963).
4. Sease J. W., Chang P., Groth J.: *J. Am. Chem. Soc.* 86, 3164 (1964).
5. Gassman P. G.: *Gordon Research Conference* (1969).

**BEHAVIOUR OF URANYL ION UPON REDUCTION
FROM THE ETHYLENEDISULPHURDIACETIC ACID SOLUTION
AT THE DROPPING MERCURY ELECTRODE**

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Chelate forming reactions between metal ions and S-containing organic ligands do not attract enough attention in the field of coordination chemistry. This probably is due to the low stability of some of the resulting compounds; also the data on polarographic behaviour of those reaction products are insufficient.

It was interesting, therefore, to investigate the stability, as well as the polarographic behaviour of the formed metal compounds from ethylenedisulphurdiacetic acid (H_2L) solution, because, on the other side, similar aminoacetic acids are well known as complex forming reagents.

Previous work of the author included investigations of some bivalent elements-chelates¹⁻³ as well as slightly soluble silver, mercury and copper salts with H_2L ⁴.

The aim of the present work was to study the polarographic behaviour of uranyl ion from H_2L as supporting electrolyte.

It was observed that the waves produced during UO_2^{2+} ion reduction at the D.M.E. from acidic perchlorate medium diminished on progressive addition of H_2L . The molar ratio $UO_2^{2+} : H_2L = 1 : 2$ having been reached the wave, asymmetrical to the half-wave potential, does not change on further addition of H_2L . The $E_{1/2}$ of this wave is somewhat more positive than that of the first wave obtained at the reduction of the uranyl ion from the perchlorate medium. It was noticed also that other two waves, ill-defined, exist at somewhat negative potentials. A similar picture was observed with the amperometric titration of UO_2^{2+} ion with H_2L in ascorbic acid solution.

It was assumed that the first wave was due either to phenomena caused by adsorption of the reduction form of the depolarizer or to the blocking of its slightly soluble form. However, the electrode reaction behaves in the same way in both cases.