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Dissociative Electron Transfer to Dihaloalkanes. Electrochemical Reduction of 1,3-Dihaloadamantanes, 1,4-Dihalobicyclo[2.2.2]octanes, and 1,3-Dihalobicyclo[1.1.1]pentanes

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Abstract: The electrochemical reductive cleavage of the title compounds was investigated by means of cyclic voltammetry and electrolysis. The reaction is a two-electron process that yields competitively ring closure (or fragmentation) products and the monohalide resulting from the expulsion of the best leaving halide ion. Product selection occurs at the level of the carbanion resulting from the reduction of the one-electron reductive cleavage radical. In the formation of the latter, electron transfer and bond breaking are concerted; thus, the anion radical is not involved as an intermediate. The variations in the reduction potential observed in the three series of compounds can be rationalized, by application of the dissociative electron-transfer theory, as related variations of the bond dissociation energy of the first carbon–halogen bond to be cleaved. In the adamantane and bicyclopentane series, these are mainly the result of through-space-bonded interactions in the one-electron reductive cleavage radical and, to a lesser extent, in the starting dihalide itself, while through-bond interactions appear to prevail in the bicyclooctane series.

Since the early days of polarography, the electrochemical reduction of alkyl halides has been the object of numerous studies.[2] Many of these have used mercury or other active metals as electrode material. In such cases, the electrode material may be suspected to be chemically involved in the electrochemical reaction and therefore to interfere in the product selectivity and in the reaction mechanism and dynamics as investigated by electrochemical kinetic techniques such as cyclic voltammetry. Among the various electrode materials that have been used so far, glassy carbon appears to be the best approximation of an outer-sphere heterogeneous electron donor, allowing the investigation of the intrinsic properties of alkyl halides toward single electron-transfer reduction.

Under these conditions, the electrochemical reduction of aliphatic monohalides in aprotic polar solvents, such as *N,N'*-dimethylformamide, gives rise to a series of products that can be rationalized on the basis of a one-electron reductive cleavage of the carbon–halogen bond,[3]

$$RX + e^- \rightarrow R^\bullet + X^- \qquad [1]$$

followed by the reduction of the alkyl radical to the carbanion,

$$R^\bullet + e^- \rightarrow R^- \qquad [2]$$

in competition with the formation of radical products through dimerization and H-atom disproportionation that depends on the respective reduction potentials of the starting halide and the radical. The carbanion may then react with the starting compound, with residual water, with solvent, or with the supporting electrolyte cation.

An important issue in the reduction of alkyl halides is whether the reductive cleavage reaction 1 is an elementary step in which electron transfer and bond breaking are concerted or a succession of two steps involving the transient formation of the anion radical as an intermediate:

$$RX + e^- \rightarrow RX^{\bullet -} \qquad [3]$$

$$RX^{\bullet -} \rightarrow R^\bullet + X^- \qquad [4]$$

It has been shown that the reduction of aliphatic monohalides follows the concerted mechanism, whereas that of aromatic and heteroaromatic monohalides goes through the intermediacy of an anion radical.[4a,b] Benzyl halides are an example of a family of compounds in which the nature of the reductive cleavage mechanism is a function of the π^* orbital energy as varied by the presence of substituents on the phenyl ring.[4c] The electrochemical reduction of butyl and benzyl halides has offered an opportunity to check the validity of a recently developed model of dissociative electron transfer leading to a quadratic activation–driving force relationship:[2d,4b,c,5]

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$$\Delta G^{\ddagger} = w_R + \Delta G_0{}^{\ddagger}\left(1 + \frac{\Delta G^{\circ} - w_R + w_P}{4\Delta G_0{}^{\ddagger}}\right)^2 \qquad \text{(i)}$$

where $\Delta G^{\ddagger}$ and ΔG° are the activation free energy and the standard free energy, respectively, of the forward electron transfer, and w_R and w_P represent the work required to bring the reactants and products, respectively, from infinite separation to reacting distance, i.e.,

$$\Delta G^{\ddagger} = \Delta G^{\ddagger}\left(1 + \frac{E - E^{\circ} - \phi_r}{4\Delta G_0^{\ddagger}}\right)^2 \qquad \text{(ii)}$$

in its electrochemical version (expressing the potential in volts and the free energies in electronvolts and where E is the electrode potential, ϕ_r is the potential difference between the reaction site and the solution, and E° is the standard potential of the $RX/R^{\bullet} + X^-$ couple). The intrinsic barrier free energy, $\Delta G_0{}^{\ddagger}$, is the sum of a solvent reorganization factor, λ_0, and a contribution of bond breaking equal to one-fourth of the bond dissociation energy, $D_{RX \rightarrow R^{\bullet} + X^{\bullet}}$:

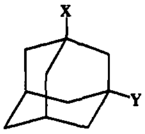
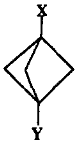
$$\Delta G_0{}^{\ddagger} = \frac{D_{RX \rightarrow R^{\bullet} + X^{\bullet}}}{4} + \frac{\lambda_0}{4} \qquad \text{(iii)}$$

Concerning aliphatic dihalides, a systematic investigation of the reduction of vicinal dibromides at a glassy carbon electrode,[6] following previous studies at mercury, platinum, and gold electrodes,[7] has shown that the first step of the reaction is a one-electron concerted reductive cleavage, yielding a β-bromo radical that is further reduced to the corresponding olefin with expulsion of the second bromide ion. Application of the above-mentioned model of dissociative electron-transfer dynamics revealed that the β-bromo radical is stabilized by delocalization of the unpaired electron over the C–C–Br framework to an extent of ca. 7 kcal/mol.[6b]

The electrochemical reduction of γ-dihaloalkanes has also been actively investigated. At mercury, good yields of the 1,3 reductive elimination cyclopropanes are obtained.[8–10] The fact that the reduction potential of 1,3-dibromopropane is significantly positive to that of 1-bromopropane has been taken as an indication that the ring closure might be concerted with the electron transfer.[8] However, the complete lack of stereoselectivity observed in the reduction of *meso*- and *dl*-2,4-dibromopentane led to the conclusion that the reaction proceeds via an intramolecular S_N2 reaction in the γ-bromo carbanion formed upon reduction of the γ-bromo radical resulting from the one-electron reductive cleavage of the starting dihalide.[10] A very recent work confirmed that the cyclopropanes are also formed in good yield and that the mechanism is the same when glassy carbon is used as the electrode material.[11a]

Particularly relevant to the present study is the observation that the electrolysis of 1,3-dibromo-1,3-dimethylcyclobutane in *N,N'*-dimethylformamide at a mercury electrode procedures 1,3-dimethylbicyclobutane in excellent yield.[8]

Chart 1

X-(1)-Y :	I-(1)-I	X-(2)-Y :	I-(2)-I	X-(3)-Y :	I-(3)-I
	I-(1)-Br		I-(2)-Br		I-(3)-Br
	I-(1)-Cl		I-(2)-Cl		I-(3)-Cl
	I-(1)-F		I-(2)-F		I-(3)-F
	I-(1)-H		I-(2)-H		I-(3)-H
	Br-(1)-Br		Br-(2)-Br		Br-(3)-Br
	Br-(1)-Cl		Br-(2)-Cl		Br-(3)-Cl
	Br-(1)-F		Br-(2)-F		Br-(3)-F
	Br-(1)-H		Br-(2)-H		Br-(3)-H

In the work reported below, the electrochemical reduction of the 1,3-dihaloadamantanes (X-(**1**)-Y), 1,4-dihalobicyclo[2.2.2]-octanes (X-(**2**)-Y), and 1,3-dihalobicyclo[1.1.1]pentanes (X-(**3**)-Y) shown in Chart 1 was investigated by means of cyclic voltammetry and electrolysis.

Besides determining the reaction products and the nature of the overall mechanism, particular attention was paid to establishing whether the initial one-electron reductive cleavage of the first carbon–halogen bond follows the concerted pathway depicted by reaction 1 or the stepwise pathway depicted by reactions 3 and 4. This question has important implications in the analysis of the possible role of single electron transfer in nucleophilic substitution reactions involving this type of compound, particularly trimethylstannylation.[12] A second important objective of the present study was to unravel the type and magnitude of the intramolecular interactions that make the reduction potentials of the dihalides vary between themselves and be different from the reduction potentials of the parent monohalides.

Results and Discussion

Figure 1 represents a typical example, that of the reduction of I-(**1**)-I and I-(**1**)-H, of the cyclic voltammograms obtained in the two series of dihalides and monohalides in acetonitrile at a glassy carbon electrode. In both cases, a single irreversible cathodic peak is observed, the height of which corresponds to the exchange of two electrons per molecule by comparison with thepeak height of the reversible wave of ferrocene recorded under the same conditions.

We note that the peak of I-(**1**)-I is positive to that of I-(**1**)-H and that the peak of I-(**1**)-H does not appear on the voltammogram of I-(**1**)-I, as it would if the monohalide were a product of the reduction of the dihalide.

The same cyclic voltammetric behavior was observed with all members of the three series. Their peak characteristics, numbers of electrons per molecule, peak potentials at 0.1 V/s, variations of the peak potentials with scan rate (in the range 0.1–20 V/s) under the form $\alpha = (RT/2F)/(\partial E_p/\partial \log v)$, and peak widths under the form $\alpha = (1.85RT/F)/(E_{p/2} - E_p)$ are summarized in Tables 1–3.

The observation of a two-electron per molecule stoichiometry and the fact that no second peak is present in the cyclic voltammetry of the dihalides indicates that, for I-( )-I, I-( )-Br, and Br-( )-Br, the reduction peak involves the uptake of two electrons and the ejection of two halides ions:

$$\text{X-( )-Y} + 2e^- \rightarrow (-) + X^- + Y^- \qquad [5]$$

If the more easily reduced carbon–halogen bond were converted

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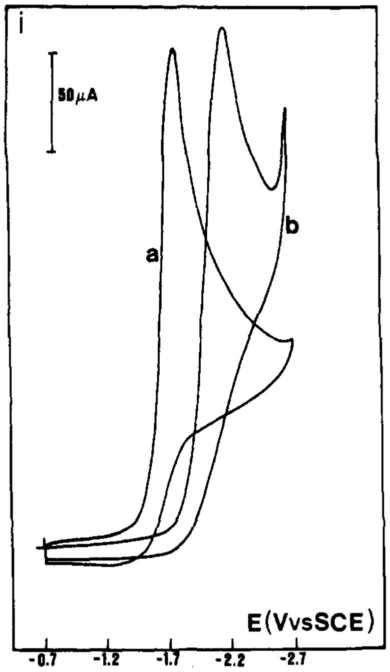


Figure 1. Cyclic voltammetry of (a) 1,3-diiodoadamantane, I-(**1**)-I (4.84 mM), and (b) 1-iodoadamandane, I-(**1**)-H (5 mM), in acetonitrile and 0.1 M *n*-Bu_4NBF_4 at a glassy carbon electrode. Scan rate, 0.2 V/s; *t*., 20 °C.

into a carbon–hydrogen bond either by a $2e^- + H^+$ reduction

$$\text{X-( )-Y} + 2e^- + H^+ \rightarrow \text{Y-( )-H} + X^- \qquad [6]$$

or by a one-electron reduction and an H-atom abstraction from the solvent (SH)

$$\text{X-( )-Y} + e^- + SH \rightarrow \text{Y-( )-H} + X^- + S^{\bullet} \qquad [6']$$

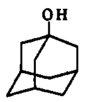
then the peak of I-( )-H or Br-( )-H, which can be observed before the discharge of the supporting electrolyte, would have appeared in the voltammogram of these compounds. A similar conclusion cannot be ascertained for the compounds containing at least one chlorine or one fluorine atom since the monohalides, Cl-( )-H and F-( )-H, do not exhibit any reduction peak before the current rise due to the supporting electrolyte discharge.

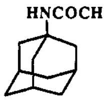
The products obtained in the electrolysis, also at a carbon electrode, of the compounds in the adamantane series were as follows. The reduction of the monohaloadamantanes I-(**1**)-H and Br-(**1**)-H was found to produce in both cases a 100% yield of adamantane:[11b]

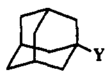
$$\text{Y-(1)-H} + 2e^- + H_2O \rightarrow \text{H-(1)-H} + Y^- + OH^- \qquad [7]$$

This observation indicates that both starting compounds are stable toward the bases, particularly OH^- from residual water, that are produced stoichiometrically with their disappearance. The four following products were found in variable proportions in the electrolysis of the various dihaloadamantanes as summarized in Table 4.


(—)


HO-(1)-H


CH$_3$CO(H)N-(1)-H


Y-(1)-H

HO-(**1**)-H, the formation of which is observed with I-(**1**)-I, I-(**1**)-Br, and Br-(**1**)-Br, derives from (—) by opening of the cyclopropane ring[12d] and not from the displacement of I and Br by OH^- or H_2O since I-(**1**)-H and Br-(**1**)-H are, as noted earlier, stable under similar conditions. The formation of $CH_3CO(H)N$-(**1**)-H from (—) in acetonitrile is described in the Experimental Section.

Table 1. Cyclic Voltammetric Characteristics of the Reduction of 1,3-Dihaloadamantanes[a]

	X-(1)-Y				
	I-(1)-I	I-(1)-Br	I-(1)-Cl	I-(1)-F	I-(1)-H
no. electrons/molecule	2.1	2.0	2.0	2.0	2.1
E_p (V vs SCE)[b]	−1.80	−1.98	−2.00	−2.15	−2.20
ϕ_r (mV)[c]	−0.072	−0.074	−0.074	−0.076	−0.076
$A \times 10^{-4}$ (cm/s)[d]	3.14	3.34	3.58	3.68	3.81
a (Å)[e], C (eV)[f], λ_0 (eV)[g]	3.06, 1.26, 1.029				
$\Delta G^{\neq}$ (eV)[h]	0.384	0.386	0.388	0.390	0.391
$D_{X\text{-}(1)\text{-}Y \rightarrow Y\text{-}(1)^- + X^{\bullet}}$ (eV)	2.07	2.18	2.20	2.29	2.32
ΔD (meV)[i]	25_1	14_0	12_5	3_1	0
$E^0_{X\text{-}(1)\text{-}Y/Y\text{-}(1)^{\bullet}+X^-}$ (V vs SCE)	−0.81	−0.92	−0.94	−1.03	−1.06
$\Delta G^{\neq}_{0,X\text{-}(1)\text{-}Y/Y\text{-}(1)^{\bullet}+X^-}$ (eV)	0.78	0.80	0.81	0.83	0.84
α_{exptl} (from $E_{p/2} - E_p$)	0.33	0.33	0.33	0.29	0.29
α_{exptl} (from E_p vs log ν)	0.33	0.30	0.30	0.29	0.30
α_{theor}	0.35	0.35	0.35	0.34	0.34

	X-(1)-Y			
	Br-(1)-Br	Br-(1)-Cl	Br-(1)-F	Br-(1)-H
no. electrons/molecule	2.2	2.2	2.0	2.1
E_p (V vs SCE)[h]	−2.30	−2.50	−2.65	−2.70
ϕ_r (mV)[c]	−0.077	−0.080	−0.081	−0.082
$A \times 10^{-4}$ (cm/s)[d]	3.60	3.90	4.04	4.20
a (Å)[e], C (eV)[f], λ_0 (eV)[g]	2.83, 1.85, 1.113			
$\Delta G^{\neq}$ (eV)[h]	0.388	0.393	0.393	0.393
$D_{X\text{-}(1)\text{-}Y \rightarrow Y\text{-}(1)^{\bullet} + X^{\bullet}}$ (eV)	2.70	2.82	2.91	2.94
ΔD (meV)[i]	24_5	12_4	3_1	0
$E^0_{X\text{-}(1)\text{-}Y/Y\text{-}(1)^{\bullet}+X^-}$ (V vs SCE)	−0.85	−0.97	−1.06	−1.09
$\Delta G^{\neq}_{0,X\text{-}(1)\text{-}Y/Y\text{-}(1)^{\bullet}+X^-}$ (eV)	0.95	0.98	1.01	1.01
α_{exptl} (from $E_{p/2} - E_p$)	0.33	0.33	0.29	0.29
α_{exptl} (from E_p vs log v)	0.33			
α_{theor}	0.32	0.32	0.31	0.31

[a] In acetonitrile and 0.1 M *n*-Bu_4NBF_4 at a glassy carbon electrode at 20 °C. [b] Peak potential at 0.1 V/s. [c] Potential difference between the reaction site and the solution. [d] Preexponential factor. [e] Equivalent hard-sphere radius. [f] $C = E^0_{X\text{-}(1)\text{-}Y/Y\text{-}(1)^{\bullet}+X^-} + D_{X\text{-}(1)\text{-}Y \rightarrow Y\text{-}(1)^{\bullet} + X^{\bullet}}$. [g] Solvent reorganization energy. [h] Activation free energy. [i] $\Delta D = D_{X\text{-}(1)\text{-}H \rightarrow H\text{-}(1)^{\bullet} + X^{\bullet}} - D_{X\text{-}(1)\text{-}Y \rightarrow Y\text{-}(1)^{\bullet} + X^{\bullet}}$.

Although there is some irreproducibility in the exact distribution of products, presumably due to the irreproducibility of the water content and of acidic impurities in the solution, the following trends clearly appear in the results summarized in Table 4.

In the absence of purposely added acids, the competition between reactions 5 and 6 varies considerably, from much in favor of [5] to completely in favor of [6], upon changing the second halogen, Y, from I to Br, to Cl, and to F.

In the case of I-(**1**)-I, the addition of 10 mM phenol to the solution makes the relative contribution of reaction 6 to go from almost 0 to about 0.5. We may therefore conclude that the ring closure reaction is not concerted with any of the two-electron-transfer steps but involves, at the level of the monohalogenated carbanion, in competition with proton abstraction, an intramolecular S_N2-type substitution according to the set of steps represented in Scheme 1.

Thus, whatever the ensuing fate of the carbanion, ring closure or protonation, the rate-controlling process is the irreversible formation of the 3-halo radical, Y-(**1**)$^{\bullet}$, whether it is produced or not through the intermediacy of the anion radical. The same should be true in the 1,4-dihalobicyclo[2.2.2]octane and 1,3-dihalobicyclo[1.1.1]pentane series. For the former, 1,4-dimeth-

Table 2. Cyclic Voltammetric Characteristics of the Reduction of 1,4-Dihalobicyclo[2.2.2]octanes[a]

	X-(2)-Y				
	I-(2)-I	I-(2)-Br	I-(2)-Cl	I-(2)-F	I-(2)-H
no. electrons/molecule	1.9	1.9	2.0	1.9	1.9
E_p (V vs SCE)[b]	-2.22_5	-2.22_5	−2.30	−2.30	-2.37_5
ϕ_r (mV)[c]	−0.076	−0.076	−0.077	−0.077	−0.078
$A \times 10^{-4}$ (cm/s)[d]	3.25	3.48	3.75	3.87	4.01
a (Å),[e] C (eV),[f] λ_0 (eV)[g]	3.06, 1.26, 1.029				
$\Delta G^{\neq}$ (eV)[h]	0.387	0.388	0.388	0.389	0.391
$D_{X\text{-}(2)\text{-}Y \rightarrow Y\text{-}(2)^{\bullet} + X^{\bullet}}$ (eV)	2.33	2.33	2.38	2.38	2.43
ΔD (meV)[i]	9_8	9_6	5_2	5_0	0
$E^0_{X\text{-}(2)\text{-}Y/Y\text{-}(2)^{\bullet} + X^-}$ (V vs SCE)	−1.07	−1.07	−1.12	−1.12	−1.17
$\Delta G^{\neq}_{0,X\text{-}(2)\text{-}Y/Y\text{-}(2)^{\bullet} + X^-}$ (eV)	0.84	0.84	0.85	0.85	0.86
α_{exptl} (from $E_{p/2} - E_p$)	0.33	0.33	0.33	0.29	0.29
α_{exptl} (from E_p vs log v)	0.33	0.30	0.30	0.29	0.30
α_{theor}	0.34	0.34	0.34	0.34	0.34

	X-(2)-Y			
	Br-(2)-Br	Br-(2)-Cl	Br-(2)-F	Br-(2)-H
no. electrons/molecule	2.2	2.0	2.2	2.1
E_p (V vs SCE)[b]	−2.70	−2.73	−2.75	−2.80
ϕ_r (mV)[c]	−0.082	−0.082	−0.083	−0.083
$A \times 10^{-4}$ (cm/s)[d]	3.77	4.12	4.28	4.78
a (Å),[e] C (eV),[f] λ_0 (eV)[g]	2.83, 1.85, 1.113			
$\Delta G^{\neq}$ (eV)[h]	0.390	0.392	0.393	0.396
$D_{X\text{-}(2)\text{-}Y \rightarrow Y\text{-}(2)^{\bullet} + X^{\bullet}}$ (eV)	2.93	2.96	2.97	3.00
ΔD (meV)[i]	7_0	4_8	3_5	0
$E^0_{X\text{-}(2)\text{-}Y/Y\text{-}(2)^{\bullet} + X^-}$ (V vs SCE)	−1.08	−1.11	−1.12	−1.15
$\Delta G^{\neq}_{0,X\text{-}(2)\text{-}Y/Y\text{-}(2)^{\bullet} + X^-}$ (eV)	1.01	1.02	1.02	1.03
α_{exptl} (from $E_{p/2} - E_p$)	0.31	0.31	0.31	0.31
α_{exptl} (from E_p vs log v)				
α_{theor}	0.31	0.31	0.31	0.31

[a] In acetonitrile and 0.1 M n-Bu_4NBF_4 at a glassy carbon electrode at 20 °C. [b] Peak potential at 0.1 V/s. [c] Potential difference between the reaction site and the solution. [d] Preexponential factor. [e] Equivalent hard-sphere radius. [f] $C = E^0_{X\text{-}(2)\text{-}Y/Y\text{-}(2)^{\bullet} + X^-} + D_{X\text{-}(2)\text{-}Y \rightarrow Y\text{-}(2)^{\bullet} + X^{\bullet}}$. [g] Solvent reorganization energy. [h] Activation free energy. [i] $\Delta D = D_{X\text{-}(2)\text{-}H \rightarrow H\text{-}(2)^{\bullet} + X^{\bullet}} - D_{X\text{-}(2)\text{-}Y \rightarrow Y\text{-}(2)^{\bullet} + X^{\bullet}}$.

ylenecyclohexane and [2.2.2]propellane are expected.[13a,b] While it is possible that the former predominant product arises from ring opening of a fleeting [2.2.2]propellane,[13c–f] trapping experiments for 4-halobicyclo[2.2.2]oct-1-yllithium derivatives, which readily yield 1,4-dimethylenecyclohexane, failed to indicate the intermediacy of [2.2.2]propellane.[12b,13g–i] For the latter series, [1.1.1]propellane is the expected product.[13j]

In all series, the values of the transfer coefficient, α_{expl}, derived from either the peak width or from the slope of the E_p – log v plots, are of the order of 0.3 (Tables 1 and 2), i.e., much lower than 0.5. In the framework of a quadratic activation–driving force relationshp, which is valid for both the stepwise and the concerted reductive cleavage mechanisms, this observation means that the peak potential is much negative to the standard potential of the rate-determining reaction. This is perfectly compatible with the concerted mechanism but not with the stepwise mechanism. In the first case (reaction 1), the intrinsic barrier is high because, besides solvent reorganization, there is a large contribution of bond breaking, thus making the effective reduction potential much negative to the standard potential. In the second case, solvent reorganization is less, and internal reorganization (changes in bond lengths and/or angles) in the electron-transfer step (reaction 3) is much less than the contribution of bond breaking, making the intrinsic barrier much lower. In addition,

Table 3. Cyclic Voltammetric Characteristics of the Reduction of 1,3-Dihalobicyclo[1.1.1]pentanes[a]

	X-(3)-Y				
	I-(3)-I	I-(3)-Br	I-(3)-Cl	I-(3)-F	I-(3)-H
no. electrons/molecule	2.0	1.9	2.0	2.1	2.0
E_p (V vs SCE)[b]	−1.50	−1.66	−1.84	-2.37_5	-2.22_5
ϕ_r (mV)[c]	−0.069	−0.070	−0.072	−0.078	−0.076
$A \times 10^{-4}$ (cm/s)[d]	3.44	3.73	4.08	4.21	4.42
a (Å),[e] C (eV),[f] λ_0 (eV)[g]	3.06, 1.26, 1.029				
$\Delta G^{\neq}$ (eV)[h]	0.388	0.390	0.390	0.394	0.396
$D_{X\text{-}(3)\text{-}Y \rightarrow Y\text{-}(3)^{\bullet} + X^{\bullet}}$ (eV)	1.89	1.99	2.11	2.43	2.35
ΔD (meV)[i]	45_5	35_1	23_1	-8_6	0
$E^0_{X\text{-}(3)\text{-}Y/Y\text{-}(3)^{\bullet} + X^-}$ (V vs SCE)	−0.64	−0.74	−0.84	−1.17	−1.09
$G^{\neq}_{0_{\text{exptl}}X\text{-}(3)\text{-}Y/Y\text{-}(3)^{\bullet} + X^-}$ (eV)	0.73	0.76	0.78	0.87	0.84
α_{exptl} (from $E_{p/2} - E_p$)	0.39	0.33	0.23	0.27	0.26
α_{exptl} (from E_p vs log v)	0.32	0.30	0.23		
α_{theor}	0.36	0.36	0.35	0.34	0.34

	X-(3)-Y			
	Br-(3)-Br	Br-(3)-Cl	Br-(3)-F	Br-(3)-H
no. electrons/molecule	2.0	2.2	2.1	
E_p (V vs SCE)[b]	−2.04	−2.36	-2.79_5	-2.73_5
ϕ_r (mV)[c]	−0.074	−0.078	−0.083	−0.082
$A \times 10^{-4}$ (cm/s)[d]	4.10	4.57	4.82	5.07
a(Å),[e] C(eV),[f] λ_0(eV)[g]	2.83, 1.85, 1.113			
ΔG^{*} (eV)[h]	0.388	0.393	0.393	0.393
$D_{X\text{-}(3)\text{-}Y \rightarrow Y\text{-}(3)^{\bullet} + X^{\bullet}}$ (eV)	2.55	2.74	3.00	2.97
ΔD (meV)[i]	41_9	22_5	-2_6	0
$E^0_{X\text{-}(3)\text{-}Y/Y\text{-}(3)^{\bullet} + X^-}$ (V vs SCE)	−0.70	−0.89	−1.15	−1.12
$\Delta G^{\neq}_{0_{\text{exptl}}X\text{-}(3)\text{-}Y/Y\text{-}(3)^{\bullet} + X^-}$ (eV)	0.92	0.96	1.03	1.02
$\alpha_{\text{ex tl}}$ (from $E_{p/2} - E_p$)	0.29	0.29	0.39	0.29
α_{exptl} (from E_p vs log v)	0.33	0.27		
α_{theor}	0.33	0.32	0.31	0.31

[a] In acetonitrile and 0.1 M n-Bu_4NBF_4 at a glassy carbon electrode at 20 °C. [b] Peak potential at 0.1 V/s. [c] Potential difference between the reaction site and the solution. [d] Preexponential factor. [e] Equivalent hard-sphere radius. [f] $C = E^0_{X\text{-}(3)\text{-}Y/Y\text{-}(3)^{\bullet} + X^-} + D_{X\text{-}(3)\text{-}Y \rightarrow Y\text{-}(3)^{\bullet} + X^{\bullet}}$. [g] Solvent reorganization energy. [h] Activation free energy. [i] $\Delta D = D_{X\text{-}(3)\text{-}H \rightarrow H\text{-}(1)^{\bullet} + X^{\bullet}} - D_{X\text{-}(3)\text{-}Y \rightarrow Y\text{-}(3)^{\bullet} + X^{\bullet}}$.

Table 4. Product Yields in the Electrolysis of 1,3-Dihaloadamantanes[a,b]

	X-(1)-Y			
	I-(1)-I	I-(1)-Br	I-(1)-Cl	I-(1)-F
electrolysis potential[c]	−1.90	−2.00	−2.20	−2.30
no. electrons/molecule[d]	2.0_0	2.0_0	2.0_0	2.0_0
(—)	0.90	0.34	0.40	0.00
$CH_3CO(H)N$-(1)-H	0.02	0.20	0.00	0.00
HO-(1)-H	0.05	0.21	0.04	0.00
total of products from reaction 5	0.97	0.75	0.44	0.00
Y-(1)-H[e]	0.03	0.08	0.56	1.00

	X-(1)-Y			
	I-(1)-I + 10 mM PhOH	Br-(1)-Br	Br-(1)-Cl	Br-(1)-F
electrolysis potential[b]	−1.90	−2.45	−2.55	−2.65
no. electrons/molecule[c]	2.0_0	2.0_0	2.0_5	2.0_5
(—)	0.00	0.79	0.70	0.00
$CH_3CO(H)N$-(1)-H	0.28	0.06	0.00	0.00
HO-(1)-H	0.25	0.08	0.00	0.00
total of products from reaction 5	0.53	0.93	0.70	0.00
Y-(1)-H[e]	0.46	0.03	0.30	1.00

[a] Setting the starting material to 1. [b] In acetonitrile and 0.1 M n-Bu_4NBF_4 at a carbon electrode at 20 °C. [c] In V vs SCE. [d] From coulometry. [e] Sole product from reaction 6.

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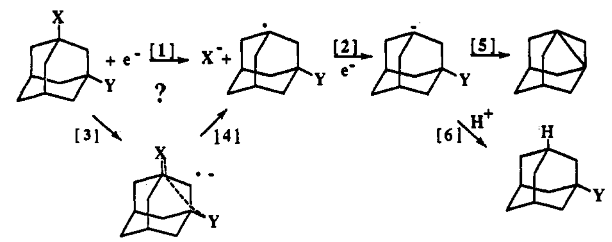
(13) (a) Wiberg, K. B.; Epling, G. A.; Jason, M. *J. Am. Chem. Soc.* **1974**, *96*, 912. (b) Dannenberg, J. J.; Prociv, T. M.; Hutt, C. *J. Am. Chem. Soc.* **1974**, *96*, 913. (c) Eaton, P. E.; Temme, G. H. *J. Am. Chem. Soc.* **1973**, *95*, 7504. (d) Stohrer, W. D.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 779. (e) Newton, M. D.; Schulman, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 4391. (f) The best theoretical calculations predict that [2.2.2]propellane should not exist: Feller, D.; Davidson, E. R. *J. Am. Chem. Soc.* **1987**, *109*, 4133. (g) Wiberg, K. B.; Pratt, W. E.; Bailey, W. F. *J. Am. Chem. Soc.* **1977**, *99*, 2297. (h) Wiberg, K. B.; Pratt, W. E.; Maturro, M. G. *J. Org. Chem.* **1982**, *547*, 2720. (i) Adcock, W.; Iyer, V. S. *J. Org. Chem.* **1985**, *50*, 1538. (j) Treatment of 1,3-dibromobicyclo[1.1.1]pentane with *tert*-butyllithium gives [1.1.1]propellane: Wiberg, K. B.; Walker, F. H. *J. Am. Chem. Soc.* **1982**, *104*, 5239.

Scheme 1



the reduction potential is driven toward positive potentials by the kinetic effect of the follow-up bond-breaking reaction 4,[14] which would result, on the whole, in transfer coefficient values larger than or close to 0.5. As discussed in more detail later on, the values of the transfer coefficient that are predicted theoretically by using the dissociative electron-transfer model are remarkably close, in most cases, to the experimental values (last rows in Tables 1–3).

We may therefore conclude that, in all series, the cleavage of the first leaving halogen follows the concerted mechanism, i.e., that the reaction does not proceed via the anion radical. In other words, the anion radical has so high an energy that the concerted pathway is energetically more advantageous in spite of the contribution of bond breaking to the intrinsic barrier.

Perusal of Tables 1–3 reveals that, with the exception of I-(**3**)-F, there is a clear positive shift of the peak potential in the 1-iodides of all series upon changing the 3- and 4-substituents respectively from H to F, to Cl, to Br, and to I.[15] The same is true for the bromides from H to F, to Cl, and to Br, again with the exception of Br-(**3**)-F. This effect is much larger in the adamantane and 1,3-dihalobicyclo[1.1.1]pentane series than in the 1,4-dihalobicyclo[2.2.2]octane series, which falls in line with the expectation that through-space intrabridgehead interactions should decrease as the distance between the two functional carbons increases. Significantly, electron transmission spectroscopic studies reveal 1,3-through-space interactions in 1,4-dichloro- and 1,4-dibromobicyclo[2.2.1]heptanes but no similar 1,4-intrabridgehead interactions in Cl-(**2**)-Cl and Br-(**2**)-Br.[16] Simple PMO considerations[17] suggest that "back-lobe" σ^*_{CX}–σ^*_{CY} orbital overlap interactions should be larger in X-(**1**)-Y than in the corresponding 1,4-disubstituted bicyclo[2.2.1]heptanes.

In the framework of the concerted mechanism, given the first leaving halogen, the variation of the peak potential with the nature of the 3- or 4-substituent results from the effect of these molecular interactions on the bond dissociation energy, $D_{\text{X-( )-Y}\rightarrow\text{Y-( )}^\bullet+\text{X}^\bullet}$. There is, in the first place, a driving force effect since the standard potential of the concerted reaction, $E^\circ_{\text{X-( )-Y/Y-( )}^\bullet+\text{X}^-}$, is related to the bond dissociation energy through the following equation:

$$E^\circ_{\text{X-( )-Y/Y-( )}^\bullet+\text{X}^-} = D_{\text{X-( )-Y}\rightarrow\text{Y-( )}^\bullet+\text{X}^\bullet} - T(\bar{S}_{\text{X-( )-Y}} - \bar{S}_{\text{Y-( )}^\bullet} - \bar{S}_{\text{X}^\bullet}) + E^\circ_{\text{X}^\bullet/\text{X}^-} \quad \text{(iv)}$$

where the entropic term (the $\bar{S}$ terms are the partial molar entropies of the subscript species) does not vary much from one compound to the other in each series. There is also an intrinsic barrier effect since the predominant factor in this quantity is one-fourth of the bond dissociation energy (eq iii). These two effects combine as described by eq ii. A rough estimation of their relative magnitude can be obtained by linearizing eq ii:

$$\Delta G^\ddagger_{\text{X-( )-Y/Y-( )}^\bullet+\text{X}^-} \approx \Delta G_0{}^\ddagger_{\text{X-( )-Y/Y-( )}^\bullet+\text{X}^-} + \frac{E_p - E^\circ_{\text{X-( )-Y/Y-( )}^\bullet+\text{X}^-} - \phi_r}{2\cdot} \quad \text{(v)}$$

Since, at a given scan rate, $\Delta G^\ddagger_{\text{X-( )-Y/Y-( )}^\bullet+\text{X}^-}$ is about constant in each series of compounds, approximately two-thirds of the variations of the peak potential with the bond dissociation energy comes from the driving force effect and one-third from the intrinsic barrier effect.

The dissociative electron-transfer model, as summarized by eq ii and iii, may be used more rigorously to derive from the values of the peak potential (Tables 1–3) the bond dissociation energies, $D_{\text{X-( )-Y}\rightarrow\text{Y-( )}^\bullet+\text{X}^\bullet}$, as well as the standard potentials, $E^\circ_{\text{X-( )-Y/Y-( )}^\bullet+\text{X}^-}$, and intrinsic barriers, $\Delta G_0{}^\ddagger_{\text{X-( )-Y/Y-( )}^\bullet+\text{X}^-}$, for all the dihalides and monohalides that we have investigated. These derivations are based on the application of the following set of equations (see particularly refs 4c and 5b).

At the peak, the activation free energy, $\Delta G^\ddagger$ (in eV), is related to the preexponential factor, A, the scan rate, v, the transfer coefficient, α, and the diffusion coefficient, D, through eq vi:

$$\Delta G^\ddagger = \frac{RT}{F}\ln\left[A\left(\frac{RT}{\alpha F v D}\right)^{1/2}\right] - 0.780\frac{RT}{F} \quad \text{(vi)}$$

D is taken as equal to 10^{-5} cm²/s in the whole series, and A has the values listed in Tables 1–3. From eq iv and from the analysis of previous systems where the pertinent thermochemical data were independently known, it appears that, given the halogen,

$$C = E^\circ_{\text{RX}\rightarrow\text{R}^\bullet+\text{X}^-} + D_{\text{RX}\rightarrow\text{R}^\bullet+\text{X}^\bullet} \quad \text{(vii)}$$

is approximately constant and so should be

$$C = E^\circ_{\text{X-( )-Y/Y-( )}^\bullet+\text{X}^-} + D_{\text{X-( )-Y}\rightarrow\text{Y-( )}^\bullet+\text{X}^\bullet} \quad \text{(viii)}$$

with those values of C listed in Tables 1–3. The solvent reorganization energy, λ_0, is obtained from the equivalent sphere radius, a, as previously defined in ref 5b by means of:

$$\lambda_0\,(\text{eV}) = \frac{3.15}{a\,(\text{Å})} \quad \text{(ix)}$$

Since a represents the solvation of the halogen atom, partially masked by the adjacent alkyl moiety of the molecule, we may assume that it is approximately the same as in the corresponding *tert*-butyl halides (Tables 1 and 2).[5b] For the potential at the reaction site, ϕ_r, we have taken:

$$\phi_r\,(\text{V}) = 0.111E_p\,(\text{V}) - 0.052 \quad \text{(x)}$$

as discussed earlier.[5b] We may then derive the bond dissociation energy from:

$$D_{\text{X-( )-Y}\rightarrow\text{Y-( )}^\bullet+\text{X}^\bullet} = {}^1/_2\{[(\lambda_0 + E_p - C - \phi_r - \Delta G^\ddagger)^2 + 4\lambda_0\Delta G^\ddagger - (\lambda_0 + E_p - C - \phi_r)^2]^{1/2} - (\lambda_0 + E_p - C - \phi_r - \Delta G^\ddagger)\} \quad \text{(xi)}$$

along with the standard potential from eq viii and the intrinsic

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[14] (a) Andrieux, C. P.; Savéant, J.-M. In *Electrochemical Reactions in Investigation of Rates and Mechanisms of Reactions, Techniques of Chemistry*; Bernasconi, C. F., Ed.; Wiley: New York, 1986; Vol. VI/4E, Part 2, pp 305–390. (b) Nadjo, L.; Savéant, J.-M. *J. Electroanal. Chem.* **1973**, *48*, 113.

[15] (a) It is worth noting in this connection that the polarographic half-wave reduction potentials (on mercury) of 3-haloadamantyl iodides[12d] and 4-halobicyclo[2.2.2]oct-1-yl iodides[15b] shift positively in the order H < F < Cl < Br < I. On the same electrode material, $E_{1/2}$ and E_p at 0.1 V/s should differ by only a small constant: with a transfer coefficient of 0.3, E_p should be not more than 50–100 mV negative to $E_{1/2}$. However, the $E_{1/2}$ values on Hg for the iodides[12d,15b] are too positive to the E_p values on glassy carbon (Tables 1 and 2), and, in addition, the effect increases upon changing the substituent from H to F, to Cl, and to I, pointing to an inner-sphere character of the electrochemical reduction on mercury (Hg chemically catalyzes the reductive cleavage reaction). It is thus difficult to relate the variations of the $E_{1/2}$ values on Hg to intrinsic properties of the molecules. (b) Adcock, W.; Kok, G. B.; Iyer, V. S.; Peters, D. G.; Lundy, K. M. *J. Org. Chem.* **1986**, *51*, 564.

[16] Huda, E.; Martin, H.-D.; Mayer, B.; Somnitz, K.-H.; Steigel, A.; Haddad, H.; Distefano, G.; Modelli, A. *Chem. Ber.* **1991**, *124*, 2879.

[17] Dewar, M. J. S.; Dougherty, R. C. *The PMO Theory of Organic Chemistry*; Plenum Press: New York, 1975.

barrier from eq iii. One may also derive the values of the transfer coefficient, α, predicted by the application of the model using eq xii:

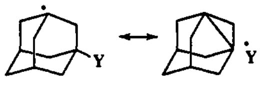
$$\alpha = {}^{1}/_{2}\left(1 + \frac{E_{\mathrm{p}} - E^{\circ}{}_{\mathrm{X\text{-}()\text{-}Y/Y\text{-}()^{\bullet} + X^{-}}} - \phi_{\mathrm{r}}}{4\Delta G_{0}{}^{\ddagger}{}_{\mathrm{X\text{-}()\text{-}Y/Y\text{-}()^{\bullet} + X^{-}}}}\right) \qquad \text{(xii)}$$

The ensuing values of the various quantities thus obtained are listed in Tables 1 and 2.

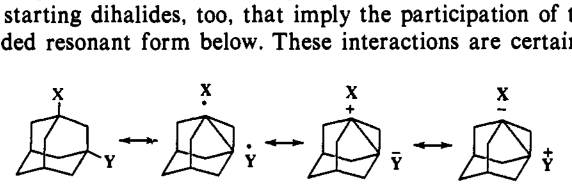
As noted earlier, there is, in most cases, a very good agreement between the theoretical and experimental values of α, which confirms that the reductive cleavage does follows the concerted mechanism.

The intramolecular interactions that affect the reduction potential may now be rationalized through the effect they have on the bond dissociation energy. In this respect, it is interesting to observe the variations of the weakening of the bond dissociation energy, ΔD, upon passing from the monohalide H-( )-Y to the dihalide X-( )-Y, which are listed in Tables 1–3. The experimental precision on the bond dissociation energies is of the order of ±5 meV. Additional errors may, however, result from the inaccuracy of the dissociative electron-transfer model itself and from inaccuracies in the estimation of the various numerical parameters used in its application.

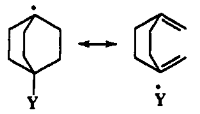
In the adamantane series, a first remark is that the dissociation energies of the carbon–halogen bond in the monoiodo and monobromo derivatives are 12_0 and 7_0 meV stronger than those in the corresponding iodo and bromobutanes ($D_{t\text{-BuI} \rightarrow t\text{-Bu}^{\bullet} + \mathrm{I}^{\bullet}}$ = 2.20 eV, $D_{t\text{-BuBr} \rightarrow t\text{-Bu}^{\bullet} + \mathrm{Br}^{\bullet}}$ = 2.87 eV[5b]), respectively. This difference can be rationalized as resulting from the strain energy that destabilizes the adamantyl radical by preventing, unlike the *tert*-butyl radical, the achievement of a planar structure. This corroborates a similar deduction made from the respective C–H bond dissociation energies in adamantane and isobutane.[18] In the I-(**1**)-Y series, the even weakening of the bond from Y = H to F, to Cl, to Br, and to I may be attributed to a "back-lobe" orbital overlap between the 1-carbon bearing the unpaired electron and the 3-carbon bearing the second halogen atom (σ^{*}_{CY}–$\sigma_{\mathrm{C}^{\bullet}}$), i.e., to the participation of the bonded resonant form depicted below. In accord with orbital energy level considerations,[17] the weaker the C–Y bond, the stronger the bonded interaction, as is in fact observed when going from H to F, to Cl, to Br, and to I.



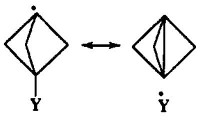
The same analysis also applies to the Br-(**1**)-Y series. However, one notices that ΔD is smaller for I-(**1**)-Br than for Br-(**1**)-Br (ΔD for the latter compound is in fact as large as that for I-(**1**)-I), pointing to the existence of through-space-bonded interactions in the starting dihalides, too, that imply the participation of the bonded resonant form below. These interactions are certainly weaker than those in the monohalo radical, leading only to a partial compensation. Given Y, they are expected to increase when the C–X dissociation energy decreases, as upon passing from Br to I. Combination of the effects of the through-space-bonded interactions at the level of the monohalo radical and at that of the starting dihalide thus allows the rationalization of the observed variations of the bond dissociation energies and therefore of the reduction potentials in the adamantane series.



In the 1,4-dihalobicyclo[2.2.2]octane series, the observed variations ΔD are smaller, as expected from the larger distance between the two functional carbon atoms and the ensuing weakening of the "back-lobe" orbital interactions. However, it is important to note that through-three-bond interactions[12b,19] also contribute to the variations of ΔD in this system and are most probably the dominant interactions (depicted by the following resonance structures). Note that, in contrast to the adamantane series, ΔD for I-(**2**)-Br is close to ΔD for Br-(**2**)-Br (it is even somewhat larger).



The case of 1,3-dihalobicyclo[1.1.1]pentanes is similar to that of 1,3-dihaloadamantanes. Several facts are, however, worth noting. (1) From the data pertaining to I-(**3**)-H and Br-(**3**)-H, it appears, from the comparison with *t*-BuI and *t*-BuBr, that the strain energy in H-(**3**)$^{\bullet}$ (100–150 meV) is somewhat larger than that in the adamantane series.[18b,20] (2) With the exception of I-(**3**)-F and Br-(**3**)-F, the values of ΔD are much larger in the former series than in the latter, as expected from a better σ^{*}_{CY}–$\sigma_{\mathrm{C}^{\bullet}}$ orbital overlap (depicted by the following resonance structures) due to the collinearity and proximity of the C–X and C–Y bonds in the starting dihalides. (3) The peak potentials of I-(**3**)-F and Br-(**3**)-F are more negative than those of I-(**3**)-H and Br-(**3**)-H, respectively, which translates into a strengthening of the C–I and C–Br bonds instead of the weakening observed with the other Y halogens. This observation may be a manifestation of a decrease in strain energy of the fluorohalides relative to the monohalides due to the effectiveness of the very electronegative fluorine removing electron density from the carbon bridgehead orbital and, thus, significantly reducing 1,3 nonbonded repulsion.[20a] In addition, there may be an electrostatic stabilization of the starting dihalide through $\mathrm{F}^{\delta-}$–$\mathrm{C}^{\delta+}$ dipole—$\mathrm{C}^{\delta-}$–I(or Br)$^{\delta+}$ induced dipole interaction, favored, as compared to the adamantane series, by the proximity and collinearity of the C–X and C–Y bonds. The overall stabilization of the starting molecule overcompensates the through-space-bonding stabilization in the radical, which is relatively small in the case where Y = F.



In all series, the values of ΔD provide a minimal estimate of the order of magnitude of the through-space-bonded interactions in the monohalo radical. We note that interaction energies reach very large values in the 1,3-dihalobicyclo[1.1.1]pentane series, where they are close to 0.5 V (>10 kcal/mol) in I-(**3**)-I and Br-(**3**)-Br. The ready decomposition of the 3-bromo- and 3-iodobicyclo[1.1.1]pent-1-yl radicals to give [1.1.1]propellane,[21] even in the presence of efficient trapping agents, graphically illustrates the importance of through-space interactions in these systems.

It is worth noting that the same kind of variations of the peak potential with the molecular structure are found in the electrochemical reduction of 1,3-dihalopropanes (see Table 1 in ref 11a).

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[18] (a) Kruppa, G. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 2162. (b) Walton, J. C. *Chem. Soc. Rev.* **1992**, 105.

[19] (a) Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499. (b) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1. (c) Adcock, W.; Krstic, A. R.; Duggan, P. J.; Shiner, V. J., Jr.; Coope, J.; Ensinger, M. N. *J. Am. Chem. Soc.* **1990**, *112*, 3140 and references cited therin.

[20] (a) Wiberg, K. B. *Tetrahedron Lett.* **1985**, *26*, 599. (b) Wiberg, K. B.; Hadad, C. M.; Sieber, S.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, *114*, 5820 and references cited therin.

[21] (a) Kaszynski, P.; McMurdie, N. D.; Michl, J. *J. Org. Chem.* **1991**, *56*, 307. (b) Adcock, W.; Krstic, A. R., unpublished work. (c) Della, E. W.; Taylor, D. K., unpublished work.

Their magnitude is between what was observed here for the adamantane and 1,4-dihalobicyclo[2.2.2]octane series, respectively. It has been argued that these variations are caused by through-bond inductive effects.[10b] However, as emphasized recently,[11a] inductive effects should produce opposite variations. We thus propose that the same through-space-bonded interactions as in the X-(**1**)-Y and X-(**3**)-Y compounds investigated here are responsible for the observed variations of the reduction potential.[22]

Conclusions

The main conclusions to emerge from the preceding results and discussion are as follows.

The electrochemical reduction of 1,3-dihaloadamantanes in acetonitrile at a carbon electrode is a two-electron reaction that yields competitively ring closure products and the monohalo derivative resulting from the expulsion of the best leaving halide ion. Product selection takes place at the level of the carbanion produced by reduction of the one-electron reductive cleavage radical as the result of a competition between an intramolecular S_N2 reaction and protonation. The relative yield of the first product accordingly varies from almost 1 to 0 as the second halogen varies from I to Br, to Cl, and to F.

In the initial formation of the one-electron reductive cleavage radical, electron transfer and bond breaking are concerted, i.e., the reaction does not involve the intermediacy of the anion radical. The same situation holds for the bicyclooctane and bicyclopentane series, where the carbanion for the former largely fragments and that the latter undergoes exclusive ring closure.

The variations in the reduction potential observed in all series of compounds can thus be rationalized, by application of the dissociative electron-transfer theory, as related variations of the bond dissociation energy of the first carbon–halogen bond to be cleaved which result from through-space-bonded interactions (adamantanes and bicyclopentanes) and through-bond (bicyclooctanes) interactions in the one-electron reductive cleavage radical and, to a lesser extent, in the starting dihalide.

Experimental Section

Cyclic Voltammetry. The working electrode was a 3-mm-diameter glassy carbon (Tokai) disk. It was carefully polished and ultrasonically rinsed with ethanol before each run. The counter electrode was a platinum wire and the reference electrode an aqueous SCE electrode. The reversible oxidation wave of ferrocene was used as an internal potential standard to avoid errors in the determination of the peak potential that might be caused by possible potential drift of the SCE reference electrode.

The potentiostat, equipped with a positive feedback compensation and current measurer, was the same as previously described.[23]

Electrolyses. The electrolyses were carried out in 8–10-cm^3 solution cells with a glassy carbon (Tokai) rectangular plate working electrode of 2-cm^2 surface area. The counter electrode was a platinum wire and the reference electrode an aqueous SCE. They were separated from the cathodic compartment by means of glass frits. The cell was thermostated at 20 °C, and the solution was kept under a nitrogen stream during the whole electrolysis. The disappearance of the starting material and the formation of the products were followed by in situ cyclic voltammetry and by chromatographic analysis of samples with the same column as described below (by comparison with authentic samples of the products). A home-built potentiostat was used, and the quantity of electricity passed was monitored with a Taccussel IG4-1100 coulometer. The quantities of electricity passed were typically 4–6 Coulombs, with 3–4 mM substrate concentrations.

Chemicals. Acetonitrile (Merck Uvasol) and the supporting electrolyte, n-Bu_4NBF_4 (Fluka, puriss), were used as received.

Adamantane Derivatives. Adamantane, 1-adamantanol, and 1-bromoadamantane were purchased from the Aldrich Chemical Co., Inc. The latter two compounds were also prepared according to literature procedures,[24,25] as was 1-fluoro-,[26] 1-chloro-,[24] 1-iodo-,[27] and 1,3-dibromoadamantane.[28] The remaining 1,3-dihaloadamantanes and 1,3-dehydroadamantane (tetracyclo[3.3.1.1^{3,7}.0^{1,3}]decane) were prepared as described elsewhere.[12d]

Bicyclo[1.1.1]pentane Derivatives. Literature procedures were followed in the preparation of 1-chloro-,[29a] 1-bromo-,[29b] 1-iodo-,[29a] and 1,3-diiodobicyclo[1.1.1]pentane.[30] The synthesis of 1-bromo-3-fluoro-, 1-fluoro-3-iodo-, 1-bromo-3-chloro-, 1-chloro-3-iodo-, 1-bromo-3-iodo-, and 1,3-dibromobicyclo[1.1.1]pentanes will be presented elsewhere in connection with other studies.[31]

Bicyclo[2.2.2]octane Derivatives. Literature procedures were followed in the preparation of 1-fluoro-,[32] 1-chloro-,[33] 1-bromo-,[34] 1-iodo-,[35] and 1,4-diiodobicyclo[2.2.2]octane.[35] Except for 1-fluoro-4-iodobicyclo[2.2.2]octane,[32] which was obtained in excellent yield (94%) by treatment of 4-fluorobicyclo[2.2.2]octane-1-carboxylic acid[32] with lead tetraacetate and iodine following a procedure outlined by Moriarty et al.,[36] all the remaining 1,4-dihalobicyclo[2.2.2]octanes (fluorobromo,[32] chlorobromo,[12b] chloroiodo,[35] dibromo,[13h] and bromoiodo[35] derivatives) were obtained from the respective 4-fluoro-,[32] 4-chloro-,[33] and 4-bromobicyclo[2.2.2]octane-1-carboxylic acids[34] by use of the procedures of Barton et al.,[37] as recently described for the preparation of 1,3-dihaloadamantanes.[12d]

HO-(**1**)-H and $CH_3CO(H)N$-(**1**)-H were found to be the products of the reaction of 1,3-dehydroadamantane with 0.5 M H_2SO_4 in acetonitrile. HO-(**1**)-H was identified by gas chromatography (3-m 5% OV17 column with a 5 deg/min, 100 °C to 280 °C temperature program and a flame ionization detection) by comparison with an authentic sample. After addition of water to the solution and ether extraction, $CH_3CO(H)N$-(**1**)-H was identified by its mass spectrum, MS (CI, NH_3) m/z 211 (100, M + 18), 194 (72, M + 1), 136 (25, M − 57), and IR amide bands at 1685 (CO) and 3440 cm^{-1} (NH). HO-(**1**)-H derives from protonation of 1,3-dehydroadamantane and subsequent trapping of the 1-adamantyl cation by water.[12d] Similarly, the carbocation may be trapped by acetonitrile to give $CH_3C{\equiv}N^+$-(**1**)-H, which reacts with water to form $CH_3CO(H)N$-(**1**)-H.

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(22) (a) The observed absence of stereoselectivity in the reduction of *meso*- and *dl*-2,4-dibromopentane implies that internal S_N2 ring closure in the carbanion is not fast enough to compete with bond rotation at the functional carbons. (b) "Back-lobe" orbital overlap $\sigma^*_{C-Br} - \sigma^*_{C-Br}$, which can occur only in a W-conformation for 1,3-dibromo acyclic alkanes, has recently been proposed in a mechanistic route for cyclopropane formation induced by electron transfer.[22c] (c) Liu, Y.; Sorensen, T. S.; Sun, F. *Can. J. Chem.* **1993**, *71*, 258.

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