ELECTROCHEMICAL DEHALOGENATION OF OPEN-CHAIN VICINAL DIHALIDES AT MERCURY CATHODES: THE EFFECT OF LEAVING GROUP IDENTITY ON $E_{1/2}$ VALUES AND ON STERIC COURSE

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The title problem has been investigated polarographically in the homologous series of *erythro* and *threo*-5,6-dihalodecanes (X = Br, Y = I; X = Cl, Y = I; X = F, Y = I; X = Br, Y = Br; X = Cl, Y = Br; X = F, Y = Br; X = Cl, Y = Cl; X = F, Y = Cl). Each dihalide from the series gave a single two-electron wave. A very pronounced dependence of half-wave potential on halogen group identity was found in the series, the $E_{1/2}$ values ranging from -0.3 V (X = Br, Y = I) to -2.8 V (X = F, Y = Cl). Controlled-potential electrolyses of the dihalides were accomplished at mercury pool electrode affording always *cis*- and/or *trans*-5-decene as the sole product, in almost quantitative (>90%) yields. Stereochemistry of the dehalogenation was deduced from the olefin-isomer distribution data determined by VPC. Very marked differences were found in the series, the elimination stereochemistry ranging between a clean *anti* and a prevalent *syn*, in dependence on the identity and configuration of the halogen groups.

Although electrochemical reduction of vicinal dihalides to olefins has been investigated at numerous occassions[1,2], only little is known about stereochemistry of the reaction. Moreover, the scantly stereochemical evidence[3,4] is restricted to the reduction of dibromides.

As a part of our general interest[5] in stereochemistry of olefin-forming reactions, we have recently[6] prepared a series of the configurationally uniform *erythro*- and *threo*-5,6-dihalodecanes $Ia-Ih$ and investigated steric course of several dehalogenation reactions. In this paper we report the results from the electrochemical dehalogenation at mercury cathodes.

$$C_4H_9.CH(X).CH(Y).C_4H_9$$

Ia: X = Br, Y = I	*Id*: X = Br, Y = Br	*Ig*: X = Cl, Y = Cl
Ib: X = Cl, Y = I	*Ie*: X = Cl, Y = Br	*Ih*: X = F, Y = Cl
Ic: X = F, Y = I	*If*: X = F, Y = Br	

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EXPERIMENTAL

Materials: The dihalides *Ia—Ih* as well as the corresponding monohalides (5-decyl halides) were available from the previous work[6,7].

Polarography: The conventional dc polarograms were obtained by using a multi-purpose polarographic analyzer GWP 673 (Akademie der Wissenschaften, DDR) with a three-electrode cell. The dropping electrode (capillary diameter 0·03 mm) had a fixed drop time ($t_1 = 2·5$ s). The reference electrode was a silver/silver chloride electrode in a saturated solution of potassium chloride. Stability and reproducibility of the reference electrode was tested by measuring the $E_{1/2}$ value of the potassium ion (KBr; $-2·006 \pm 0·008$ V). The 0·1 mol l^{-1} solution of tetra-n-butyl-ammonium perchlorate in dimethylformamide (0·1% H$_2$O) was used as the supporting electrolyte. The concentration of depolarizers was chosen in such a way that the wave-heights were practically constant (about 2·5 . 10^{-3} mol l^{-1}).

The evaluation of the polarograms has been accomplished in most instances by the logarithmic analysis described in detail elsewhere[8] (maximum deviation $\pm 0·005$ V). Extremely negative waves have been evaluated by a standard graphical procedure (maximum deviation $+0·01$ V).

Controlled-potential electrolyses: Performed with the polarographic analyzer GWP 673 equipped with a build-in potentiostat. The electrolytic cell consisted of a magnetically stirred mercury pool cathode (60 mm diameter), a platinum gauze counter electrode (separated from catholyte by a sintered-glass cylinder) and a reference silver/silver chloride electrode (separated from catholyte by a porous carbon) placed in a Heyrovský vessel.

The dihalide (about 0·3 mmol) was dissolved in 0·1 mol l^{-1} solution of tetra-n-butylammonium perchlorate in dimethylformamide (60 ml) and electrolyzed at a chosen potential under a nitrogen blanket. In appropriate time intervals the electrolysis has been interrupted and progress of the reduction has been tested by polarography and/or by VPC.

Product analysis: Polarographic determination of unreacted dihalides was carried out directly in the electrolytic vessel using an auxiliary dropping electrode. Reaction products were analyzed by VPC under the conditions described in the preceding paper[6]. Aliquots of the electrolyzed solutions containing an internal standard (n-nonane) were withdrawn by an injection syringe, transferred into a 50 ml volumetric flask containing water (48 ml) and pentane (1 ml), the contents were shaken and a sample of the pentane layer was injected into the gas-chromatograph.

RESULTS AND DISCUSSION

Polarographic Behaviour

5-Decyl halides were employed as the reference compounds in the polarographic study of the vicinal dihalides *Ia—Ih*. The polarographic behaviour of the monohalides is summarized in Table I. Only two of the four monohalides examined are reduced under the employed conditions. In analogy with the recent study of 1-decyl iodide and 1-decyl bromide[9], 5-decyl iodide exhibits two one-electron waves corresponding to the formation of 5-decyl radical and 5-decyl carbanion, respectively, and 5-decyl bromide exhibits one two-electron wave, corresponding to a direct formation of 5-decyl carbanion. The 5-decyl chloride and fluoride are polarographically inactive, up to the decomposition of the supporting electrolyte ($-2·9$ V).

Unlike the monohalides, Table II shows that all the dihalides *erythro-* and *threo-Ia—Ih* are reduced under the polarographic conditions, each exhibiting a single two-electron wave. The half-wave potentials are spread between the values -0.3 V and -2.8 V, depending on the configuration and identity of the halogen groups. Although both X and Y groups participate in control of the $E_{1/2}$ values, the effect

TABLE I

Polarographic behaviour of 5-decyl halides

Y	$E_{1/2}$, V	$I \cdot 10^3$	$\dfrac{2 \cdot 3RT}{n\alpha F}$
I	-1.86^a; -2.36^b	1.57^c	159^a; 111^b
Br	-2.56	1.67	155
Cl	$-\,^d$	$-\,^d$	$-\,^d$
F	$-\,^d$	$-\,^d$	$-\,^d$

[a] The first wave. [b] The second wave. [c] The total height. [d] Only decomposition of the supporting electrolyte is observed.

TABLE II

erythro- and *threo-5,6-Dihalodecanes*

Compound			erythro			threo		
No	X	Y	$E_{1/2}$, V	$I \cdot 10^3$	$\dfrac{2 \cdot 3RT}{n\alpha F}$	$E_{1/2}$, V	$I \cdot 10^3$	$\dfrac{2 \cdot 3RT}{n\alpha F}$
Ia	Br	I	-0.28	1.44	144	-0.32	1.46	132
Ib	Cl	I	-0.71	1.67	323	-0.90	1.58	270
Ic	F	I	-1.33	1.40^a	196	-1.42	1.40^a	176
Id	Br	Br	-1.48	1.52	274	-1.61	1.53	241
Ie	Cl	Br	-1.95	1.60	212	-2.04	1.61	212
If	F	Br	-2.29	1.45^a	175	-2.36	1.50^a	170
Ig	Cl	Cl	-2.60	1.78	179	-2.67	1.63	184
Ih	F	Cl	-2.81	1.40^a	$-\,^b$	-2.81	1.40^a	$-\,^b$

[a] Corrected on the impurities present in the depolarizator; *cf.* ref.[6]; [b] Not determined.

of the more polarisable of the two groups (designed Y in Table II) is stronger, as evidenced by the gradual shift to negative values observed on going from the iodo--halides $Ia-Ic$ (Y = I; X = Br, Cl, F) to the bromo-halides $Id-If$ (Y = Br; X = Br, Cl, F), and further still to the chloro-halides Ig and Ih (Y = Cl; X = Cl, F). Regardless of the $E_{1/2}$ variation, 5- decenes are always the sole products of the polarographic reduction.

Two alternative mechanism have to be considered[2] for the dehalogenation reaction (Scheme 1). In the former, two-step, mechanism (A), the polarographic reduction
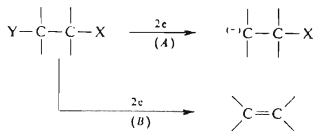
SCHEME 1

of the more easily reducible halogen group Y takes place first, yielding a carbanion intermediate which subsequently decomposes into olefin by a non-electrode displacement of the other halogen. In the latter mechanism (B), the reduction of the Y group

TABLE III
Differences in half-wave potentials between the corresponding monohalides ($E_{1/2}^{H,Y}$) and dihalides ($E_{1/2}^{X,Y}$)

	Halogen		*erythro*	*threo*
	X	Y	$E_{1/2}^{X,Y} - E_{1/2}^{X,Y}$	$E_{1/2}^{H,Y} - E_{1/2}^{X,Y}$
	Br	I	-1.55^a; -2.05^b	-1.51^a; -2.01^b
	Cl	I	-1.12^a; -1.62^b	-0.93^a; -1.43^b
	F	I	-0.50^a; -1.00^b	-0.41^a; -0.91^b
	Br	Br	-1.08	-0.95
	Cl	Br	-0.61	-0.52
	F	Br	-0.27	-0.20
	Cl	Cl	$\geqq -0.30$	$\geqq -0.23$
	F	Cl	$\geqq -0.09$	$\geqq -0.09$

^{a} Calculated from the first wave of 5-decyl iodide. ^{b} Calculated from the second wave of 5-decyl iodide.

is concerted with the displacement of the X group and with the incipient double bond formation.

A tentative distinction between the two mechanisms may be attained on examining the influence of the X group upon $E_{1/2}$ value in the polarographic reaction. As a measure of the influence we have taken the $\Delta E_{1/2}$ value expressing the difference between the half-wave potentials determined for the corresponding monohalide and dihalide $\left(E_{1/2}^{H,Y} \text{ and } E_{1/2}^{X,Y}, \text{ respectively}\right)$. The $\Delta E_{1/2}$ values are summarized in Table III.

As Table III shows, the $\Delta E_{1/2}$ values in the iodo-series $(Y = I; X = Br, Cl, F)$ and in the bromo-series $(Y = Br; X = Br, Cl, F)$ decrease in order $X = Br > X = Cl > X = F$. The overall spread of the $\Delta E_{1/2}$ values is impressively large in the two series ranging between -0.2 V and -2.0 (16 kJ and 160 kJ, respectively). Such results are in an apparent discord with the carbanion mechanism (A). An exactly opposite order of $\Delta E_{1/2}$ values would be expected for carbanion stabilization in the dihalide series on basis of the Taft σ^* values for —CH_2X group (—CH_2Br; $1.00 <$ < —CH_2Cl; $1.05 <$ —CH_2F; 1.10). Also the observed magnitude of $\Delta E_{1/2}$ values appears to be in respect to the carbanion mechanism unreasonably high.

On the other hand, the data in Table III agree well with the concept of the concerted mechanism (B) when possible variation between productlike and reactantlike transition state in the dihalide series is taken into account. In accord with the variable

TABLE IV

cis-trans 5-Decene composition (and steric course) in the electrochemical dehalogenation of *erythro*- and *threo*-5,6-dihalodecanes *Ia–Ih* at mercury pool cathode. The corresponding data from the zinc-protomited dehalogenation are included for comparison (figures in italics)

Compound			erythro				threo			
No	X	Y	% cis[a] (syn)		% trans[a] (anti)		% cis[a] (anti)		% trans[a] (syn)	
Ia	Br	I	0	*3*	100	*97*	>98	*96*	<2	*4*
Ib	Cl	I	0	*5*	100	*95*	>98	*86*	<2	*14*
Ic	F	I	32	*32*	68	*68*	48	*42*	52	*58*
Id	Br	Br	0	*6*	100	*94*	>98	*97*	<2	*3*
Ie	Cl	Br	0	*6*	100	*94*	96	*85*	4	*15*
If	F	Br	31	*32*	69	*68*	41	*42*	59	*58*
Ig	Cl	Cl	0	*10*	100	*90*	75	*66*	25	*34*
Ih	F	Cl	33	*32*	67	*68*	40	*42*	60	*58*

[a] Corrected values; for impurities present in some of the reactants *cf.* ref.[6].

transition state theory[10], we have suggested already in the preceding paper[6] that extent of double bond development in transition state of a concerted dehalogenation from $Ia - Ih$ depends inversely on the strength of the C—X bond. Since strength of the carbon-halogen bond increases in the order Br < Cl < F, the observed $\Delta E_{1/2}$ values Br > Cl > F (Table III) may be taken to indicate the diminishing energy bonus arising from a partial double bond development in the transition state of the polarographic reduction.

Controlled-Potential Electrolyses

In order to determine products of the polarographic reduction, a semimicro electrolysis of the individual dihalides was carried out at constant potential chosen at the beginning of the limiting current of the respective polarographic wave and the isolated products were analyzed by VPC. 5-Decenes (*trans-* and/or *cis-*) have been formed as the sole products, arising in all the experiments in practically quantitative yields (> 90%). The olefin-isomer composition data are listed in Table IV. *syn-anti* Stereochemistry of the dehalogenation has been deduced from these data on basis of the configurational correlation in Scheme 2.
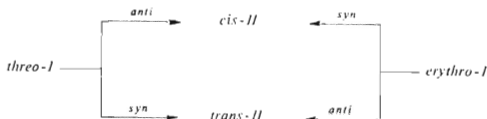
SCHEME 2

As Table IV shows, a gradual shift from a clean *anti*-elimination to a prevalent *syn*-elimination is induced on increasing strength of the C—X and C—Y bonds in the *threo*-dihalide series. In the *erythro*-series, the stereochemical changes are analogous but less pronounced.

In the preceding paper[6], we have found a similar pattern of *anti-syn* elimination in the zinc-promoted dehalogenation of the dihalides $Ia - Ih$ (Table IV, data in italics) and interpreted it as a consequence of a gradual shift from a productlike to a reactant-like transition state. In accord with the above analysis of the $\Delta E_{1/2}$ values in Table III, we are inclined to extend this interpretation also for the electrochemical dehalogenation at mercury cathodes.

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