Electrochemical Behaviour of Halogenoamides. The Role of Additional Functional Groups on the Reduction Pattern and the Nature of the Products

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The electrochemical reduction of halogenoamides (**II**)—(**V**) in dimethylformamide solutions containing Et_4NClO_4 as supporting electrolyte, was investigated both at mercury and at vitreous carbon electrodes. Bromoamides (**II**) and (**III**) undergo one-electron reduction yielding the debrominated amides $CH_3CONHC_6H_{11}$ (**I**) and $CH_3CONHCH{=}CCl_2$ (**VI**) respectively, together with polymeric material. The nature and yield of these products account for a reduction pathway involving both electrochemically generated (e.g.c.; $\bar{C}H_2CONHR$) and derived (d.c.; $\bar{C}HBrCONHR$) carbanions. The presence of other functional groups causes a marked alteration of the reaction pathway as shown in the reduction of the amides (**IV**) and (**V**), where only products derived from e.g.c. are formed. The formation of amide (**VII**) together with (**VI**) from the macroscale electrolysis of bromoacetoxyamide (**V**) is regarded as an example of electrode-assisted nucleophilic substitution.

Recently, the electrochemical reduction of the carbon–halogen bond has been the subject of many papers, aimed at elucidating its mechanism[1] and at suggesting several synthetic applications.[2] In aprotic dipolar media, and at a mercury or vitreous carbon cathode, molecules such as $R(CH_2)_nCH_2X$ ($R = CO_2Et$, C_6H_5, CN; X = Cl, Br; $n = 0$—3)[3] undergo a first monoelectronic reduction (1) followed by a fast elimination (2) of the halide ion. The subsequent reduction (3) of the radical takes place at a potential ($E_2 > E_1$) more positive than that of the 'parent' molecule $R(CH_2)_nCH_2X$.

The nature of the reduction products, therefore, depends on the reactivity of the electrochemically generated carbanion (e.g.c.) $[R(CH_2)_nCH_2]^-$ towards the species present in the solution during the electrolysis (that is, the solvent HS and the unreduced halogenated compound).

The following reaction pathways can be considered. (a) Acid–base reactions: in this case dehalogenated products [reaction (4)] or/and halogenated derived carbanions (d.c.) are formed [reactions (5) and (6)]. The nature of the latter depends on the position of the acidic hydrogen atom in the 'parent' molecule.

(b) Intermolecular substitution reactions: in this case, formation of dimers [reaction (7)] and polymers has been proven [reactions (8) and (9)]. The formation of dimers is to be ascribed to the substitution reaction of the non-halogenated e.g.c. on the 'parent' molecule; the formation of polymers is operated by the halogenated d.c. The polymeric chain described in reaction (9) is interrupted when a further substitution is performed by a non-halogenated e.g.c. instead of a halogenated d.c.

(c) Elimination and intramolecular substitution reactions: in this case, unsaturated ($n = 1$) or cyclic ($n > 1$) products are formed [reaction (10)].

In the general context of our research, aimed at synthesizing nitrogen-containing cyclic compounds by electrochemical reduction, this paper reports the electrochemical behaviour of halogenoamides in connection with the presence of other functional groups in the molecule. In fact, some of the halogenoamides described in this paper contain, in addition to the amide group and the carbon–halogen bond, a third functional group that can be reduced at a potential more negative than that of the carbon–halogen bond. The presence of the third functional group is useful in acquiring the maximum information concerning the reactivity of the carbanionic intermediates formed during the reduction process.

$$R(CH_2)_nCH_2X + e \xrightarrow{E_1} [R(CH_2)_nCH_2X]^{\bullet-} \qquad (1)$$

$$[R(CH_2)_nCH_2X]^{\bullet-} \longrightarrow [R(CH_2)_nCH_2]^{\bullet} + X^- \qquad (2)$$

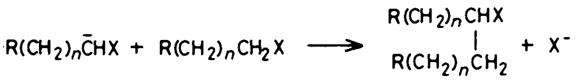
$$[R(CH_2)_nCH_2]^{\bullet} + e \xrightarrow{E_2} [R(CH_2)_nCH_2]^- \qquad (3)$$

$$R(CH_2)_n\bar{C}H_2 + HS \longrightarrow R(CH_2)_nCH_3 + S^- \qquad (4)$$

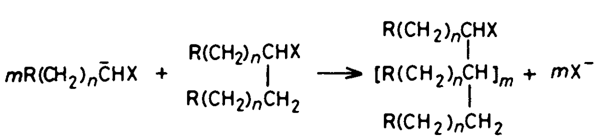
$$R(CH_2)_n\bar{C}H_2 + R(CH_2)_nCH_2X \longrightarrow R(CH_2)_nCH_3 + R\bar{C}H(CH_2)_{n-1}CH_2X \qquad (5)$$

$$R(CH_2)_n\bar{C}H_2 + R(CH_2)_nCH_2X \longrightarrow R(CH_2)_nCH_3 + R(CH_2)_n\bar{C}HX \qquad (6)$$

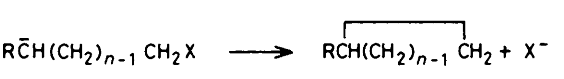
$$R(CH_2)_n\bar{C}H_2 + R(CH_2)_nCH_2X \longrightarrow [R(CH_2)_nCH_2]_2 + X^- \qquad (7)$$



$$R(CH_2)_n\bar{C}HX + R(CH_2)_nCH_2X \longrightarrow \begin{array}{c} R(CH_2)_nCHX \\ | \\ R(CH_2)_nCH_2 \end{array} + X^- \qquad (8)$$



$$mR(CH_2)_n\bar{C}HX + \begin{array}{c} R(CH_2)_nCHX \\ | \\ R(CH_2)_nCH_2 \end{array} \longrightarrow \begin{array}{c} R(CH_2)_nCHX \\ | \\ [R(CH_2)_nCH]_m \\ | \\ R(CH_2)_nCH_2 \end{array} + mX^- \qquad (9)$$



$$R\bar{C}H(CH_2)_{n-1}CH_2X \longrightarrow \overbrace{RCH(CH_2)_{n-1}CH_2} + X^- \qquad (10)$$

Experimental

To the aforesaid purposes, compounds **(I)**—**(VII)** were synthesized.

Electrochemical behaviour was investigated for *NN*-dimethylformamide (DMF) solutions containing tetraethylammonium perchlorate (TEAP) as supporting electrolyte, by means of polarography, cyclic voltammetry, coulometry, and preparative controlled-potential electrolysis, both at a mercury and at a vitreous carbon electrode. At the end of the electrolyses, products were isolated and characterized.

Polarographic and voltammetric measurements were performed by means of an Amel model 471 multipolarograph. The controlled-potential electrolyses and coulometry were carried out by means of an Amel model 552 potentiostat equipped with an Amel model 721 integrator. The cells used for all these kinds of techniques have already been described.[4] The reference electrode was a calomel type, as described by Fujinaga;[5] its potential was -0.029 V *versus* s.c.e., and did not vary during the time of our experiments; all the potential values are referred to this electrode. For the polarographic measurements, the dropping mercury electrode had a dropping time of 3.55 s and a mercury flux $m = 1.63$ mg s^{-1} at E -1.50 V and $h = 70$ cm. The cyclic voltammetry measurements were carried out at a dropping mercury electrode (Beckman) and at a glassy carbon microelectrode (Amel). All the electrochemical measurements were performed at 20.0 ± 0.1 °C. DMF (Riedel-DeHaen; spectranal) and TEAP (Carlo Erba) were purified as previously described;[4] the water content of DMF (<0.01%) was ascertained by titration according to the Karl Fischer method.

Preparative layer chromatography (p.l.c.) was performed on Merck silica gel 60 pre-coated plates (layer thickness 2 mm). Column chromatography was carried out on Merck silica gel 70—230 mesh. Gas chromatography was carried out on a Perkin-Elmer Sigma 3 gas chromatograph equipped with a Sigma 10B gas chromatography data station on a 50 m fused quartz capillary column, coated with Carbowax 20M-deactivated methyl silicone (SP-2100) fluid, operating at 160 °C. Quantitative g.c. determinations were carried out by using benzamide as internal standard. M.p.s were taken upon a Tottoli apparatus, and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 177 grating spectrophotometer; n.m.r. spectra were recorded on a Varian EM-390 spectrometer and the chemical shifts are reported relative to Me_4Si used as internal standard. Mass spectra were determined with a Hewlett-Packard 5980A low-resolution spectrometer.

$\mathrm{CH_3CONHC_6H_{11}}$

(I)

$\mathrm{BrCH_2CONHC_6H_{11}}$

(II)

$\mathrm{BrCH_2CONHCH{=}CCl_2}$

(III)

$\mathrm{CH_3CONHCH(OCOCH_3)CCl_3}$

(IV)

$\mathrm{BrCH_2CONHCH(OCOCH_3)CCl_3}$

(V)

$\mathrm{CH_3CONHCH{=}CCl_2}$

(VI)

$\mathrm{CH_3COOCH_2CONHCH{=}CCl_2}$

(VII)

Compound **(I)**, m.p. 102—104 °C (EtOH), was prepared from cyclohexylamine and acetic anhydride according to ref. 6.

Compound **(II)**, m.p. 107—108 °C (Et_2O–propan-2-ol), was prepared from cyclohexylamine and bromoacetyl chloride, according to ref. 7.

Compound **(III)**.—A solution of 2-bromoacetamide[8] (3 g, 0.022 mol) and anhydrous trichloroacetaldehyde (3.7 g, 0.025 mol) in dichloromethane (50 ml) was stirred at room temperature for 24 h. The precipitate formed was collected by suction and crystallized from benzene to give 2-bromo-*N*-(2,2,2-trichloro-1-hydroxyethyl)acetamide (4.5 g), m.p. 135—136 °C (lit.,[9] 133.5—134 °C). To a solution of the latter compound (0.45 g, 1.6 mmol) in anhydrous tetrahydrofuran (30 ml) was added PBr_3 (0.57 g, 2.1 mmol), the mixture was refluxed under stirring for 3 h, and maintained at room temperature for 20 h. The solvent was removed under reduced pressure, CH_2Cl_2 and aqueous $NaHCO_3$ were added to the residue, the organic layer was separated, dried (Na_2SO_4), and the solvent was removed under reduced pressure. Column chromatography of the residue (benzene–ethyl acetate 9:1 as eluant) gave, as the first eluted fraction, 2-bromo-*N*-(2,2-dichlorovinyl)acetamide **(III)** (0.15 g), m.p. 78—80 °C (cyclohexane); $\bar{\nu}$(Nujol) 3 260, 1 675, 1 660, and 1 500 cm^{-1}; δ([$^2H_6$]DMSO) 10.4—10.1 (1 H, d, NH, *J* 10 Hz, exchanges with D_2O), 7.26 (1 H, d, CH, *J* 10 Hz, reduces to s with D_2O), and 4.10 (2 H, s, CH_2); *m/e* (25 eV) 231 ($^{35}Cl^{79}Br$, M^+) and correct pattern of isotopic abundances.

Compound **(IV)**.—*N*-(2,2,2-Trichloro-1-hydroxyethyl)-acetamide, m.p. 164—166 °C (benzene) (lit.,[10] 170 °C), was prepared from acetamide and anhydrous trichloroacetaldehyde according to the above procedure. To a solution of the *N*-substituted acetamide (1 g, 5 mmol) and triethylamine (0.6 g, 6 mmol) in dichloromethane (20 ml), maintained under stirring at room temperature, was added dropwise a solution of acetyl chloride (0.45 g, 5.6 mmol) in dichloromethane (10 ml). After 1 h, the mixture was extracted with H_2O, the organic layer was separated, dried (Na_2SO_4), and the solvent was removed under reduced pressure. Crystallization of the residue from cyclohexane gave compound **(IV)** (0.75 g), m.p. 112—113 °C; $\bar{\nu}$(Nujol) 3 300, 1 770, 1 680, and 1 530 cm^{-1}; δ([$^2H_6$]DMSO), 9.30 (1 H, d, NH, *J* 10 Hz, exchanges with D_2O), 7.00 (1 H, d, CH, *J* 10 Hz, reduces to s with D_2O), 2.13 (3 H, s, $OCOCH_3$), and 1.93 (3 H, s, $COCH_3$); *m/e* (70 eV) 188 (^{35}Cl, $M^+ - CH_3COO$) and correct pattern of isotopic abundances.

Compound **(V)**.—This compound (1.0 g) was obtained from 2-bromo-*N*-(2,2,2-trichloro-1-hydroxyethyl)acetamide (1.6 g), triethylamine (0.6 g), and acetyl chloride (0.45 g) according to the procedure described for compound **(IV)**, m.p. 92—93 °C (cyclohexane); $\bar{\nu}$(Nujol) 3 300, 1 760, 1 680, and 1 530 cm^{-1}; $\delta(CD_3COCD_3)$ 8.8—8.4 (1 H, br s, NH, exchanges with D_2O), 7.10 (1 H, d, CH, reduces to s with D_2O), 4.00 (2 H, s, $COCH_2Br$), and 2.13 (3 H, s, $OCOCH_3$); *m/e* (70 eV) 266 ($^{35}Cl^{79}Br$, $M^+ - CH_3COO$) and correct pattern of isotopic abundances.

For the preparation of compounds **(VI)** and **(VII)**, see the controlled-potential electrolyses of **(III)**—**(V)**.

The controlled-potential electrolyses were carried out by stepwise addition of portions of halogenoamide, up to the total amount reported for the various runs, to 75 ml of DMF–0.1M-TEAP. The electrolyses were stopped when the current, from its initial values of 0.4 and 0.04 A (mercury and vitreous carbon cathode, respectively), had dropped to 10 and 3 mA, respectively.

The polarograms (mercury cathode) or the voltammograms (vitreous carbon cathode) carried out on the electrolysed solution showed the absence of any species reducible at the potentials of the electrolyses, and gave information on the nature and concentration of species, present in the solution, reducible at potentials more negative than that of the electrolysis potential.

At the end of the electrolysis, the DMF solution was separated, and the solvent removed at 40—45 °C under reduced pressure. The residue was extracted with Et_2O (5 × 50 ml), the precipitate filtered off, and the filtrate evaporated to constant weight under vacuum. Alternatively, the DMF solution was diluted with H_2O (300 ml) and extracted with $CHCl_3$ (6 × 50 ml). The combined organic layers were further extracted with H_2O (3 × 50 ml), the organic phase dried (Na_2SO_4), and the solvent removed under vacuum to constant weight. The residue was purified by p.l.c. or column chromatography.

Parameters of the various electrolyses, and analytical data of the electrolysed solutions, are given below.

$BrCH_2CONHC_6H_{11}$ **(II)** (0.77 g, 3.5 mmol) was reduced at a mercury cathode at -1.8 V. At the end of the electrolysis, the polarogram shows the absence of any species reducible at potential more positive than the discharge potential of the supporting electrolyte. Gas chromatographic analysis of the electrolysed DMF solution shows the presence of the dehalogenated amide **(I)** in *ca.* 40% yield. Work-up of the same solution by addition of H_2O and extraction with $CHCl_3$ gives a crude residue (0.5 g), whose gas chromatographic analysis shows that the dehalogenated amide **(I)** accounts for *ca.* 35% of the total amount. Column chromatography ($CHCl_3$–ethyl acetate 9:1 as eluant) of the same residue allows the separation of pure **(I)** (0.15 g, 30% isolated yield). The above results, together with n.m.r. spectrum of the crude residue, indicate that unidentified, polymeric material arises from the reduction, and accounts for *ca.* 50% of the total amount.

$BrCH_2CONHCH{=}CCl_2$ **(III)** (0.35 g) was reduced at a Hg cathode at -1.2 V. The polarogram recorded at the end of the electrolysis shows a reduction wave whose potential ($E_{\frac{1}{2}}$ -2.32 V) coincides with the half-wave potential of **(VI)**. The comparison between the diffusion current measured on this polarogram, and the diffusion current measured on polarograms of standard solution of **(VI)**, allowed the yield of the reduction of **(III)** into **(VI)** to be evaluated (ρ 0.5). The presence of the dehalogenated amide **(VI)** in the crude reduction mixture was confirmed on the basis of the i.r. spectrum recorded on the residue obtained after work-up of the electrolysed DMF solution, by evaporation of the solvent and extraction with Et_2O.

$CH_3CONHCH(OCOCH_3)CCl_3$ **(IV)** (0.30 g) was reduced at the mercury cathode at -1.5 V. At the end of the reduction, the polarographic analysis shows (see above) that 94% of the initial amount of **(IV)** was reduced to **(VI)**. The presence of **(VI)** in the crude reduction mixture was confirmed by the i.r. spectrum (see above).

The reduction of $BrCH_2CONHCH(OCOCH_3)CCl_3$ **(V)** (0.9 g) was carried out at both a mercury and a vitreous carbon cathode (E -1.8 V). The polarographic and voltammetric analyses, performed at the end of the electrolyses, show the presence of only one reduction process (wave). Its half-wave potential ($E_{\frac{1}{2}}$ -2.3 V) and peak potentials (E_{pHg} -2.35, E_{pC} -2.4 V) are close to the values for **(VI)** and/or **(VII)**. The diffusion current value shows the presence of **(VI)** and/or **(VII)** in such a concentration that 75% of the initial amount of **(V)** can be regarded as having turned into these compounds. Work-up of the electrolysed DMF solution by evaporation of the solvent and extraction with Et_2O, followed by p.l.c. of the crude residue, allows the isolation of two products. The first one, having the higher R_F value, was identified as 2-acetoxy-*N*-(2,2-dichlorovinyl)acetamide **(VII)**, m.p. 73—74 °C (cyclohexane); $\bar{\nu}$(Nujol) 3 300, 1 740, 1 710, 1 650, and 1 490 cm^{-1}; $\delta(CD_3COCD_3)$ 9.2—8.7 (1 H, br s, NH, exchanges with D_2O), 7.32 (1 H, d, CH, reduces to s with D_2O), 4.70 (2 H, s, CH_2), and 2.10 (3 H, s, CH_3); *m/e* (70 eV) 211 (^{35}Cl, M^{-+}) and correct pattern of isotopic abundances. The other product, having the lower R_F value, was identified as *N*-(2,2-dichlorovinyl)acetamide **(VI)**, m.p. 83—84 °C (cyclohexane) (lit.,[11] 86—87 °C); $\bar{\nu}$(Nujol) 3 230, 1 670, 1 650, and 1 510 cm^{-1}; $\delta(CD_3COCD_3)$ 9.3—8.7 (1 H, br s, NH, exchanges with D_2O), 7.34 (1 H, d, CH, reduces to s with D_2O), and 2.05 (3 H, s, CH_3); *m/e* (70 eV) 153 (^{35}Cl, M^+) and correct pattern of isotopic abundances.

In order to ascertain the possibility that, in the absence of applied potential as well, an acetate ion could effect the substitution of the bromine atom, we have treated the 2-bromoamides under study with acetate ion under the same experimental conditions as those employed in the macroscale electrolyses, except for the potential: in either case, the 2-bromoamide was recovered unchanged from the reaction mixture. In a typical run, a solution of **(II)** (0.135 g) and anhydrous ammonium acetate (0.046 g) in DMF containing 0.1M-TEAP (50 ml) was stirred under nitrogen at room temperature and in the presence of mercury for 1.5 h. Work-up of the reaction mixture as for the electrolysed solutions (see above) gives quantitatively unchanged **(II)**.

Results and Discussion

The polarographic and voltammetric analyses of all amides under study, with exception of **(I)**, show reduction processes at potentials less negative than that of the supporting electrolyte. Table 1 reports the half-wave and peak potentials both at mercury and at vitreous carbon. The comparison between the peak potentials using mercury electrode (E_{pHg}) and vitreous carbon electrode (E_{pC}), shows that the reduction of carbon–halogen bond occurs on mercury at potential values considerably more positive (0.3—0.6 V) than on vitreous carbon electrode.

These differences (also found in the reduction of α-halogenoesters[12]) are consistent with the hypothesis that the reduction potential on the mercury electrode can be affected by the formation of adducts between halogenoamides and the electrode material.

The usual polarographic checks show that all the waves that occur at potentials less negative than -2.0 V are irreversible and diffusion controlled. For compounds **(II)**—**(V)** the current function $I^* = i_{lim}/m^{2/3}t^{1/6}C$ was evaluated both in the absence and in the presence of a proton donor (3,4-xylenol) at various concentrations (Table 2).

The corresponding n_{app} values were evaluated both by using the first monoelectronic wave of pyrene as a standard (Table 2), and by means of coulometries run at a mercury or at a vitreous carbon cathode (Table 3). Electrochemical and chemical analyses were performed on the solutions at the end of the

Table 1. Half-wave potentials ($E_{\frac{1}{2}}$) and peak potentials values, V *versus* s.c.e. (both on mercury E_{pHg} and on glassy carbon E_{pC}) for **(II)**—**(VII)**, all at 1.0×10^{-3}M concentration, in DMF–0.1M-TEAP solutions

Compound	$E'_{\frac{1}{2}}$	$E''_{\frac{1}{2}}$	E'_{pHg}	E''_{pHg}	E'_{pC}	E''_{pC}
(II)	−1.25		−1.40		−1.95	
(III)	−0.8	−2.30	−0.94	−2.35	−1.50	−2.41
(IV)	−1.35	−2.35	−1.47	−2.38	−1.75	−2.40
(V)	−0.8	−2.3	−1.15	−2.4	−1.75	−2.4
(VI)		−2.32		−2.40		−2.45
(VII)		−2.27		−2.34		−2.36

Table 2. Polarographic data for halogenoamides RX: **(II)**, **(III)** (first wave), **(IV)** (first wave), **(V)** (first wave) in DMF–0.1M-TEAP in the absence and presence of 3,4-xylenol (HS)

		Amide (II)		Amide (III)		Amide (IV)		Amide (V)	
[RX]/mM	[HS]/mM	I^{*a}	$n_{app}{}^{b}$	I^{*a}	$n_{app}{}^{b}$	I^{*a}	$n_{app}{}^{b}$	I^{*a}	$n_{app}{}^{b}$
1.0		2.30	0.95	2.02	0.85	4.18	1.75	6.35	2.65
1.0	1.0	2.40	0.99	2.09	0.88	4.18	1.75	6.35	2.65

[a] Current function $I^* = i_{lim}/m^{\frac{2}{3}}t^{\frac{1}{6}}C$(μA mM^{-1} mg$^{-\frac{2}{3}}$ s$^{\frac{1}{2}}$), where C is the concentration of amide in mmol l^{-1}. [b] Values determined by comparison of the polarographic limiting current with the first monoelectronic wave of pyrene as a standard.

Table 3. Coulometric data and yields of the products for the electrochemical reduction on a mercury pool (cathode) and a vitreous carbon cathode for **(II)**—**(V)** in DMF–0.1M-TEAP

Compound	Cathode	Potential (V)	Products	$n_{app}{}^{a}$	Yield (%)
(II)	Hg	−1.8	**(I)**	1.0	40
(III)	Hg	−1.2	**(VI)**	0.9	50
(IV)	Hg	−1.5	**(VI)**	1.9	94
(V)	Hg	−1.8	**(VI)** + **(VII)**	2.8	75
(V)	C	−1.8	**(VI)** + **(VII)**	2.8	75

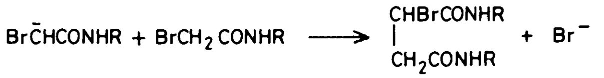
[a] Number of Faraday × mol^{-1} obtained by coulometry.

$$\mathrm{BrCH_2CONHR} + 2e \longrightarrow \mathrm{\bar{C}H_2CONHR} + \mathrm{Br^-} \qquad (11)$$

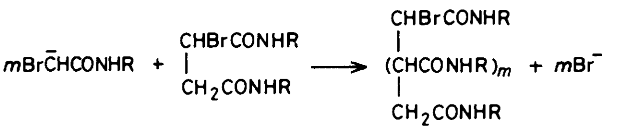
(R = cyclohexyl, CH=CCl$_2$)

$$\mathrm{\bar{C}H_2CONHR} + \mathrm{BrCH_2CONHR} \not\longrightarrow \mathrm{(CH_2CONHR)_2} + \mathrm{Br^-} \qquad (12)$$

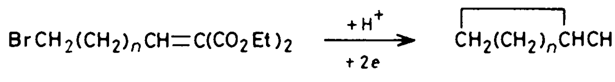
$$\mathrm{\bar{C}H_2CONHR} + \mathrm{BrCH_2CONHR} \longrightarrow \mathrm{CH_3CONHR} + \mathrm{Br\bar{C}HCONHR} \qquad (13)$$



$$\mathrm{Br\bar{C}HCONHR} + \mathrm{BrCH_2CONHR} \longrightarrow \begin{matrix}\mathrm{CHBrCONHR}\\ |\\ \mathrm{CH_2CONHR}\end{matrix} + \mathrm{Br^-} \qquad (14)$$



$$m\mathrm{Br\bar{C}HCONHR} + \begin{matrix}\mathrm{CHBrCONHR}\\ |\\ \mathrm{CH_2CONHR}\end{matrix} \longrightarrow \begin{matrix}\mathrm{CHBrCONHR}\\ |\\ \mathrm{(CHCONHR)}_m\\ |\\ \mathrm{CH_2CONHR}\end{matrix} + m\mathrm{Br^-} \qquad (15)$$



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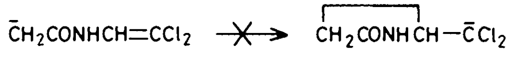
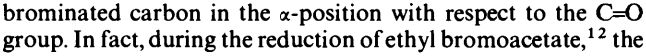


(17)

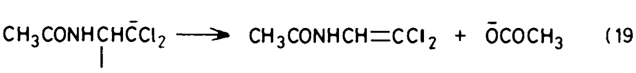
controlled-potential electrolyses, to ascertain the nature and the yield of the reduction products (Table 3). For the reduction of **(V)**, a more detailed picture of the electrochemical behaviour was obtained by changing the chemical nature of the cathode (vitreous carbon instead of mercury).

In fact, mercury might affect the nature and yield of the products of the electrochemical process by forming addition compounds with the reaction intermediates.[13] The electrochemical data and the results of the analyses performed on the reduced solutions suggest some considerations about the reduction mechanism of the halogenoamides and the reactivity of the carbanionic intermediates. These considerations can be summarized as follows.

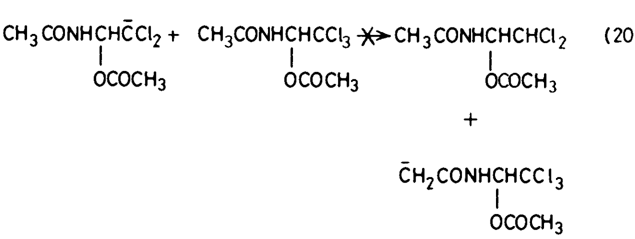
(a) *Reduction of* 2*-Bromoamides* **(II)** *and* **(III)**.—The value of n_{app} ($n_{app} = 1$), the nature of the reduction products, and their relative yields (hydrogenated monomer *ca.* 50%, polymer *ca.* 50%), suggest for this type of 2-bromoamides the same reduction scheme as already proposed for 2-bromoesters.[3a]. The e.g.c. $\mathrm{\bar{C}H_2CONHR}$, by the interaction with the brominated carbon atom of the 'parent' molecules could give rise both to the substitution reaction (12), and to the acid–base reaction (13). However, owing to the high acidity of the hydrogen on the brominated carbon in the α-position with respect to the carbonyl group, reaction (12) is not competitive with (13); therefore, among the reduction products, the presence of dimeric compounds could not be proved. This result agrees with our previous finding on the reduction of bromoesters; also in that case, the yield of monomeric and dimeric products was dependent on the presence of an acidic hydrogen atom on the brominated carbon in the α-position with respect to the C=O group. In fact, during the reduction of ethyl bromoacetate,[12] the dimer was obtained in 6% yield and the monomer in 82% yield, whereas in the reduction of ethyl 2-bromoisobutyrate[3a] the dimer was the only product formed. Furthermore, it should be noted that the current function values I^* are almost identical in the absence and presence of proton donors (3,4-xylenol) (Table 2), showing that the e.g.c., even in the presence of 3,4-xylenol, is protonated by the 'parent' molecule. As regards compound (**III**), no cyclic products were formed in the reduction process. Therefore, in this case, unlike that (16) for other unsaturated brominated compounds,[14] the intramolecular addition reaction (17) as well seems not to be competitive with the protonation reaction.



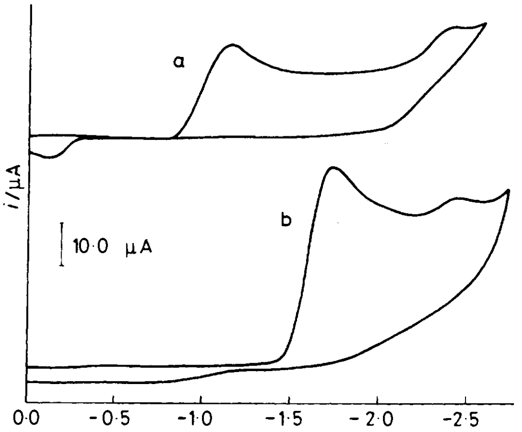
$$CH_3CONH\underset{\displaystyle OCOCH_3}{\underset{|}{C}}HCCl_3 + 2e \longrightarrow CH_3CONH\underset{\displaystyle OCOCH_3}{\underset{|}{C}}H\bar{C}Cl_2 + Cl^- \quad (18)$$



$$CH_3CONH\underset{\displaystyle OCOCH_3}{\underset{|}{C}}H\bar{C}Cl_2 \longrightarrow CH_3CONHCH{=}CCl_2 + \bar{O}COCH_3 \quad (19)$$



$$CH_3CONH\underset{\displaystyle OCOCH_3}{\underset{|}{C}}H\bar{C}Cl_2 + CH_3CONH\underset{\displaystyle OCOCH_3}{\underset{|}{C}}HCCl_3 \not\longrightarrow CH_3CONH\underset{\displaystyle OCOCH_3}{\underset{|}{C}}HCHCl_2 + \bar{C}H_2CONH\underset{\displaystyle OCOCH_3}{\underset{|}{C}}HCCl_3 \quad (20)$$



Cyclic voltammetry at mercury (a) and at glassy carbon (b) electrode of 2-bromo-*N*-(1-acetoxy-2,2,2-trichloroethyl)acetamide (1.0×10^{-3}M) in DMF–0.1M-TEAP (v 200 mV s^{-1})

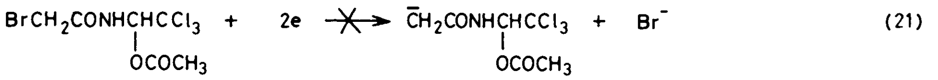
(b) *Reduction of* N-(1-*Acetoxy*-2,2,2-*trichloroethyl*)*acetamide* (**IV**).—The most remarkable features of this reduction are the value of $n_{app} = 1.9$, the formation of the unsaturated amide $CH_3CONHCH{=}CCl_2$ in an almost quantitative yield, and the absence, among the products, both of the amide $CH_3CONHCH(OCOCH_3)CHCl_2$ and of polymeric substances. This means that the α-elimination reaction (19) is the only reaction occurring for this kind of α-acetoxy-substituted e.g.c.

As no sufficiently acidic hydrogen atoms are present in the 'parent' molecule, the occurrence of an acid–base reaction (20) and, consequently, the formation both of the d.c. and of the monomer $CH_3CONHCH(OCOCH_3)CHCl_2$ is hindered. These results are in agreement with the hypothesis that the polymeric products, so frequently found in the reduction of halogeno-compounds, are formed through d.c. *via* reactions (8) and (9).

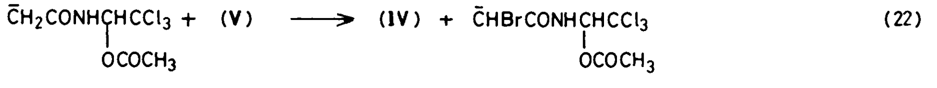
(c) *Reduction of* 2-*Bromo*-N-(1-*acetoxy*-2,2,2-*trichloroethyl*)-*acetamide* (**V**).—The reduction of (**V**) at −1.15 V could be connected to the initial uptake of an electron either at the C–Br bond or at the C–Cl bond (strongly activated by the presence of other two chlorine atoms on the same carbon atom). However, in the voltammograms at mercury cathode, the reduction peak at −1.47 V, corresponding to the reduction of the C–Cl bond of $CH_3CONHCH(OCOCH_3)CCl_3$ (**IV**), is not present (Figure). The initial uptake of an electron at −1.15 V in compound (**V**) cannot, therefore, take place at the C–Br bond. In fact, in this event, compound (**V**) should turn into (**IV**). In the voltammograms of (**V**), the reduction peak at −1.47 V, typical of (**IV**), should be present besides that at −1.15 V. This suggests that the initial reduction involves the C–Cl bond [reaction (23)] rather than the C–Br bond.

In the subsequent reduction (24) of the C–Br bond, the unsaturated 2-bromoamide $BrCH_2CONHCH{=}CCl_2$, formed through reaction (23), is involved (E_p −0.95 V). Therefore, this reduction can take place at the potential of reaction (23) (E_p −1.15 V).

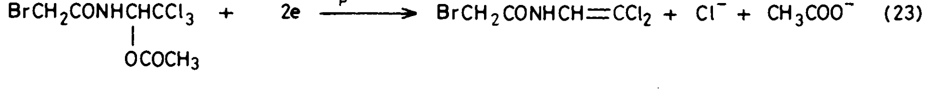
In the course of preparative electrolyses at a mercury cathode, run at −1.8 V, two products are formed: $CH_3CONHCH{=}CCl_2$ (n_{app} 4) and $CH_3COOCH_2CONHCH{=}CCl_2$ (n_{app} 2) and a value of $n_{app} = 2.8$ is measured. This suggests that two competitive processes are possible at the C–Br bond. The first process (24) involves the uptake of two



$$BrCH_2CONH\underset{\displaystyle OCOCH_3}{\underset{|}{C}}HCCl_3 + 2e \not\longrightarrow \bar{C}H_2CONH\underset{\displaystyle OCOCH_3}{\underset{|}{C}}HCCl_3 + Br^- \quad (21)$$

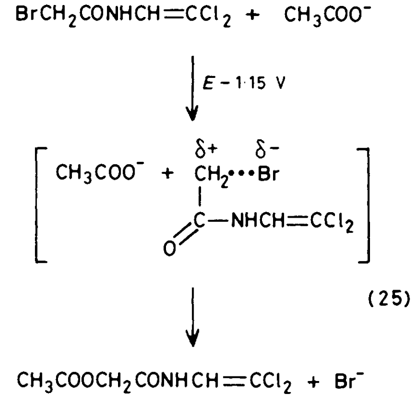


$$\bar{C}H_2CONH\underset{\displaystyle OCOCH_3}{\underset{|}{C}}HCCl_3 + (\mathbf{V}) \longrightarrow (\mathbf{IV}) + \bar{C}HBrCONH\underset{\displaystyle OCOCH_3}{\underset{|}{C}}HCCl_3 \quad (22)$$

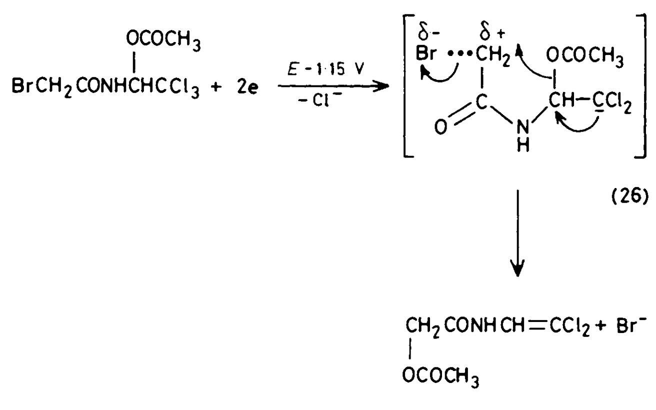


$$BrCH_2CONH\underset{\displaystyle OCOCH_3}{\underset{|}{C}}HCCl_3 + 2e \xrightarrow{E_p\,-1{\cdot}15\ V} BrCH_2CONHCH{=}CCl_2 + Cl^- + CH_3COO^- \quad (23)$$

$$BrCH_2CONHCH{=}CCl_2 + HS + 2e \xrightarrow{E_p\,-1{\cdot}15\ V} CH_3CONHCH{=}CCl_2 + Br^- + S^- \quad (24)$$



(25)



(26)

electrons by the electrode, and the participation of the solvent or of the same 'parent' molecule as proton donors (HS). The second process, on the other hand, may be ascribed to a nucleophilic displacement of a bromine atom by an acetoxy group. Whether the substitution occurs by an intermolecular S_N2 reaction (25), carried out by an acetate ion produced according to reaction (23), or by an intramolecular concerted [1,4] migration (26) of the acetoxy group, could not at present be ascertained.

However, some conclusions could be drawn from the experimental data. As preparative electrolyses carried out at vitreous carbon cathode give results comparable with that obtained using the mercury cathode, we can exclude the possibility that participation of the electrode material in the formation of the reduction intermediates might have affected the nature of the electrolysis products. On the other hand, in reactions (25) and (26) the electrode plays a role that cannot be overlooked; in fact, this substitution reaction cannot take place outside the electrode-solution double layer (see Experimental section). Therefore, the role that the electrode plays in the reaction is neither to supply electrons to the depolarizer, nor to take part in the formation of reaction intermediates, but probably to promote the incipient ionization of the C–Br bond, thus supporting easier attack of the nucleophilic agent (heterogeneous electrode-assisted ionization[15]). Processes (23)—(26), as a whole, can be regarded as an example of an electrode-assisted nucleophilic substitution. We are, at present, investigating how far this example can be generalized, and which might be the limiting conditions.

Acknowledgements

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