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VOLTAMMETRY OF ORGANIC HALOGEN COMPOUNDS. IV. THE REDUCTION OF ORGANIC CHLORIDES AT THE VITREOUS (GLASSY) CARBON ELECTRODE[1]

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We wish to report the general reduction of alkyl monochlorides at the vitreous (glassy) carbon electrode (GCE), a process which has not been effected at the dropping mercury electrode (DME).[2,3] (Aromatic chlorides are also readily reduced at this carbon electrode.) In view of the increasing interest in electrochemical techniques in organic synthesis, our reduction of chloroalkanes may be of greater import than simply an example of a novel electroreduction with a comparatively unused electrode system.

In their pioneering investigation of the polarography of organic halides, von Stackelberg and Stracke found that alkyl bromides of all types were readily reduced at the DME.[2] However, they showed that the only monochlorides reducible at the DME were methyl chloride and compounds such as allyl or benzyl chloride in which the chlorine is activated. Subsequently, we succeeded in reducing chlorobenzene using tetraethylammonium bromide as the supporting electrolyte in N,N-dimethylformamide (DMF)[4] but despite many variations in conditions using the DME system, neither other investigators[3] nor we have been able to reduce non-activated alkyl monochlorides other than methyl chloride.

In our current research on the electrochemistry of bromoalkanes at the glassy carbon electrode,[5] we noted a second very negative wave following the reduction of bromine in 1-bromo-5-chloropentane. Subsequent work with 1-chloropentane and other non-activated alkyl monochlorides indicated that this wave was due to the reduction of the chlorine in such molecules and that the process was general. Half-wave potentials for a number of chlorides are given in Table I. Voltammetric curves for typical compounds are reproduced on the next page to show the characteristics of the electrode response.

Coulometric studies at these very negative potentials were experimentally more difficult than conventional coulometry at controlled potentials but still clearly indicate that the reduction mechanism cannot

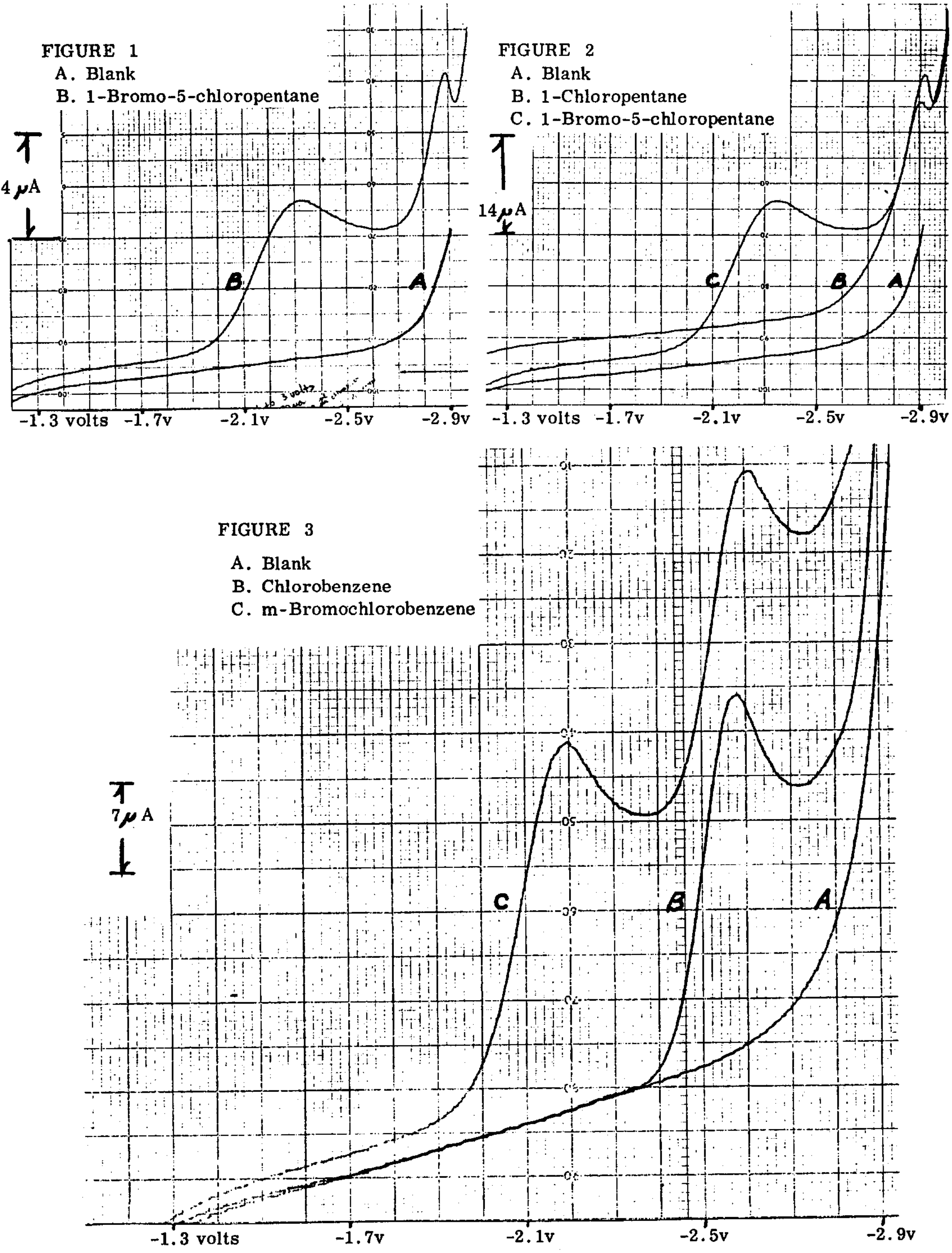

FIGURE 1
A. Blank
B. 1-Bromo-5-chloropentane

FIGURE 2
A. Blank
B. 1-Chloropentane
C. 1-Bromo-5-chloropentane

FIGURE 3
A. Blank
B. Chlorobenzene
C. m-Bromochlorobenzene

Voltammetric Reduction of Organic Chloro Compounds at the Glassy Carbon Electrode

TABLE I

Electrochemical Characteristics of Organic Chloro Compounds at the Glassy Carbon Electrode (GCE)[a]

Class	Compound	Half-Wave Potential[b]		i_d/C[c]
Simple Primary	Methyl chloride	-2.76		....
	Ethyl chloride	-2.79		....
	Propyl chloride	-2.80		1.7
	Pentyl chloride	-2.79		1.7
	Hexyl chloride	-2.80		1.7
	Neopentyl chloride	-2.83		1.7
Secondary	Isopropyl chloride	-2.63		1.0
	sec-Butyl chloride	-2.66		1.3
	2-Chloropentane	-2.66		1.3
	3-Chloropentane	-2.66		1.4
Tertiary	tert-Butyl chloride	-2.60		1.1
	tert-Pentyl chloride	-2.64		1.1
Mixed Function Primary	β-Phenylethyl chloride	-2.44		1.3
	γ-Phenylpropyl chloride	-2.79		1.6
	3-Chloropropanenitrile	-2.09		1.0
	4-Chlorobutanenitrile	-2.58		1.3
	1-Bromo-5-chloropentane	-2.80	(-2.15)[d]	1.2
Aromatic	Chlorobenzene	-2.57		1.9
	m-Bromochlorobenzene	-2.57	(-2.16)[d]	1.9

[a] Halide concentrations of 1-3 x 10^{-3} M in purified anhydrous N, N-dimethylformamide (ref. 1) with 0.01 M tetraethylammonium perchlorate as supporting electrolyte. Curves recorded on a Beckman Electroscan 30 with saturated calomel electrode (SCE) as reference, platinum wire as auxiliary, and glassy carbon disk of 7.9 sq. mm. area (Tokai Electrode Mfg. Co., Tokyo, Japan) as working electrode at 25° C. Light polishing of the working electrode surface with Linde 0.05 micron alumina, wet with DMF, between runs was essential for reproducibility of (typically) 3 mv standard deviation. [b] In volts vs. SCE. [c] In microamperes per 10^{-4} M. [d] Half-wave potential for the bromo group.

be the simple traditional[2] two-electron stepwise process. 1-Chlorohexane required only 1.7 electrons for its reduction at -2.90 volts and gave hexane as the principal product with less than one per cent of hexene or dodecane. 3-Chloropentane, a secondary chloride, under coulometry at -2.80 volts required only 1.2 electrons per molecule but also formed less than one per cent of pentene or 3,4-diethylhexane, the possible dimer. 2-Chloro-2-methylbutane, tertiary amyl chloride, at -2.80 volts required 1.7 electrons for reduction but formed 34 per cent of 2-methylbutenes and 66 per cent of 2-methylbutane.

Quite obviously from the coulometric data, a one-electron process is an important, but not exclusive, pathway for the reduction of alkyl chlorides at glassy carbon in DMF. Any free radical which might be formed by such a one-electron reduction of primary or secondary chlorides does not subsequently disproportionate nor dimerize under our experimental conditions.

In addition to the general importance of this process for the controlled reduction of any alkyl monochloride, several qualitative deductions can be drawn from the results shown in Table I. At the GCE tertiary chlorides are only somewhat easier to reduce than comparable secondary chlorides, but both of these classes have markedly less negative reduction potentials than simple primary chloro compounds. Some steric hindrance may be contributing to the reduction potentials of chloro compounds at the GCE (viz., methyl (-2.76), pentyl (-2.80) and neopentyl (-2.83) chloride half-wave potentials, as well as the increase of ca. 0.03 volts in going from the simplest secondary or tertiary chloride to the more complex members of their respective classes) but it is far less than in the reduction of bromo compounds at the dropping mercury electrode.[1]

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