



Interactive voltammetric instrumentation for identification of chlorinated hydrocarbons and the determination of reduction pathways for selected aromatic chlorine compounds
by Sherry Owen Farwell

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemistry
Montana State University
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Abstract:

Two new electronic analytical instruments were constructed from integrated circuits for use in the voltammetric experiments. The first instrument was a programmable waveform generator that included analog derivatives of the current-voltage curves. The output capabilities of this versatile waveform generator are single and multiple triangular waves, sawtooth waves, ramps with variable holds, and combinations of these modes.

The second instrument was specifically designed to provide a voltage ramp that is controlled by the electrochemical behavior of the electroactive sample. This apparatus causes a temporary interruption in the voltage sweep being applied to the electrochemical cell when a reduction peak is detected. The interrupted-sweep instrumentation is particularly advantageous in obtaining reproducible voltammetric data for multi-reducible compounds that display overlapping reduction peaks. For example, the reduction potential reproducibility was typically ± 5 mV. This particular instrument has a theoretical resolution of 43 mV for overlapping reduction peaks, and experimentally, reduction peaks separated by less than 60 mV were resolved.

Characteristic voltammetric "fingerprints" were obtained for the aromatic chlorinated compounds including the 12 chlorinated benzenes (PC Φ), 32 chlorinated biphenyls (PCB), 38 chlorinated naphthalenes (PCN), and certain organochlorine pesticides. Over 100 chlorinated hydrocarbons were analyzed with the interrupted-sweep technique, and only six of these compounds could not be positively identified.

The electrochemical reduction behaviors of the 12 PC Φ and the 19 PCB with chlorine atoms on one ring were thoroughly examined with interrupted-sweep voltammetry, controlled-potential electrolysis, and controlled-potential coulometry. The results of these experiments were used to predict the cathodic reduction pathways for these PC Φ and PCB.

The organochlorine pesticides investigated were dieldrin, aldrin, endrin, heptachlor, lindane, cis- and trans-chlordane, oxychlordane, chlordene, dichlorochlordene, 2,4-D, and 10 members of the DDT family. The voltammetric reduction potentials for the DDT series of compounds were used to propose cathodic reduction pathways for these aromatic chloroethanes and chloroethylenes. The voltammetric "fingerprints" were even distinctive for dieldrin and its stereoisomer, endrin, and cis- and trans-chlordane.

A reduction mechanism was formulated for the voltammetric cleavage of the carbon-chlorine bond that differs from the currently accepted radical mechanism. The experimental and theoretical results suggest that the initial electron transfer step yields a radical anion (R $^{\cdot-}$ -Cl) which subsequently either adds a second electron to form the dianion (R $^{2-}$), or protonates to form a radical which then adds a second electron. The final reduction products, RH and Cl $^-$, are the same regardless of the intermediate pathways.

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by

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fulfillment of the requirements for the degree

of

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in

Chemistry

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The entire process would not have been possible without the help and encouragement of my wife, Judy.

To Judy, Gary and Jodey

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ABSTRACT

Two new electronic analytical instruments were constructed from integrated circuits for use in the voltammetric experiments. The first instrument was a programmable waveform generator that included analog derivatives of the current-voltage curves. The output capabilities of this versatile waveform generator are single and multiple triangular waves, sawtooth waves, ramps with variable holds, and combinations of these modes.

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INTRODUCTION

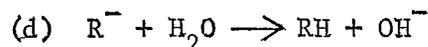
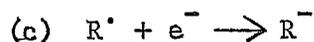
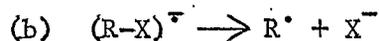
A considerable amount of work has been done on the electrochemistry of organic halogen compounds, however, little of this has been done systematically on individual groups of aromatic chlorine compounds. The results of the numerous isolated studies that have been reported do not always agree since each investigator performed the reduction experiments under different conditions. In addition, the polarographic behavior of polychloro-aromatic compounds with regard to the influence of one chlorine atom on the reduction of other chlorine atoms has been insufficiently examined. Since the voltammetric reduction of several groups of chloro-aromatic compounds was studied in this project, it is important to review the polarographic cleavage of carbon-halogen bonds, the reduction of the parent aromatic hydrocarbons, and the techniques for obtaining voltammetric information. The properties of the polychlorinated biphenyls, the polychlorinated benzenes, the polychlorinated naphthalenes, and certain chlorinated pesticides are also briefly reviewed.

Reduction of the Carbon-Halogen Bond

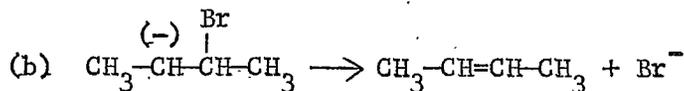
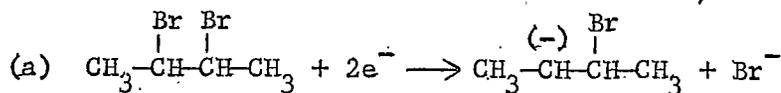
The electrochemical reduction of the carbon-halogen (C-X) bond has been rather extensively studied and a wide variety of organic halogen compounds has been examined polarographically. The only systematic investigation of halogenated aliphatic and aromatic hydrocarbons was reported by Von Stackelberg and Stracke (1). They made the following

generalizations from their study:

1. The ease of reduction is $I > Br > Cl > F$.
2. Polyhalogenation facilitates the reduction and increases the number of reduction waves.
3. Allylic halides undergo facile reduction, but vinyl and aryl halides are more difficult to reduce.
4. The ease of reduction of aliphatic halogen compounds increases as the size of the aliphatic portion decreases. For example, methylchloride was reduced but ethylchloride and propylchloride were not reducible in their system.
5. The ease of reduction of a halogen attached to an aromatic ring is similar to that of a halogen attached to a large alkyl group.
6. Controlled-potential electrolysis (Cpe) indicates that in almost all cases polarographic reduction replaces the halogen atom by hydrogen, except that vic-dihalides often lose two halide ions to give an olefin without hydrogen uptake. For example, the electrolysis of methyl iodide, ethyl bromide, α -bromonaphthalene, allyl bromide, and 2,3-dibromobutane produced methane, ethane, naphthalene, propylene, and 2-butene, respectively. The mechanisms proposed to account for these results were:



and



7. The reductions were irreversible and the half-wave ($E_{1/2}$) potentials were pH-independent in all cases.

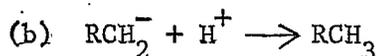
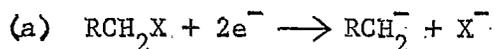
8. The relatively small slopes of the reduction waves for the halogen compounds were characteristic of irreversible electrode reactions and consequently, the individual reduction waves were quite broad.

9. The heights of the reduction waves for the halogens (especially the chlorides) were lower than the heights expected for diffusion-controlled processes.

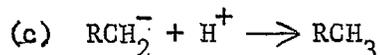
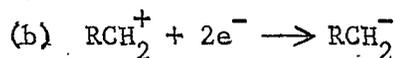
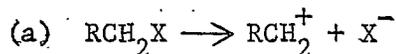
10. The wave heights were proportional to concentration and therefore, were useful for quantitative determinations. For example, CCl_4 and CHCl_3 were simultaneously determined in a mixture of CCl_4 , CHCl_3 , CH_2Cl_2 , and CH_3Cl . The work described by Von Stackelberg and Stracke (1) involved polarography and Cpe in 75% dioxane - 25% water and in 90% butanol - 10% water. The fact that halide reduction potentials are not pH-dependent indicates that hydrogen does not take part in the potential determining step and that the mechanism must involve at least two steps.

In addition to the radical anion scheme outlined above, Elving (2) has suggested two additional mechanisms: a) an $\text{S}_{\text{N}}2$ -like process, and

b) an S_N1 -like process. In the S_N2 mechanism the cathode acts like a nucleophile and attacks the carbon end of the carbon-halogen bond, then a pair of electrons effects a backside displacement of halide ion. The resulting carbanion is then protonated.



In the S_N1 process the carbon-halogen bond ionizes in the strong electrostatic field at the electrode/electrolyte interface and the resulting carbonium ion is subsequently reduced to the carbanion and protonated.



Thus, in this context, a difference between these two mechanisms is that one conceives the displacement to be effected by a pair of electrons, whereas the other conceives the displacement to be effected by the electric field.

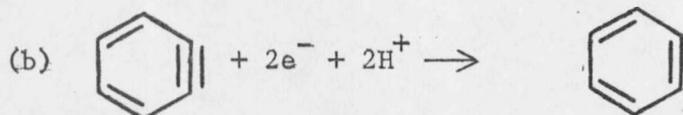
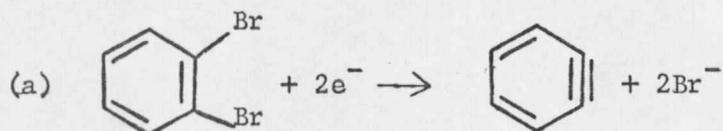
Of the three mechanisms proposed, the radical anion scheme has been widely accepted since it appears to be best supported by experimental evidence. With regard to the several reduction schemes which have been proposed, the S_N1 -like mechanism is the only one that requires the carbon to acquire a positive charge in the potential determining state. By contrast, the other two proposed mechanisms involve the uptake of one or two electrons in the potential determining step. The

studies by Sease and coworkers (3) have indicated a negatively-charged potential determining transition state, and this conclusion and similar results by others have ruled out the S_N1 -type mechanism. Further experimental evidence for this conclusion are reviewed by Mann and Barnes (4), by Perrin (5), and by Ebersson and Schafer (6). A discussion of the S_N2 -like mechanism for the electrochemical reduction of the carbon-halogen bond is difficult because considerable controversy has arisen over the interpretation of steric effects on halide reductions. Occurrence of an S_N2 -type mechanism should cause inversion of the configuration of a carbon atom bonded to a halogen whereas an S_N1 -type mechanism presumably would lead to racemization. Lambert and Kobayashi (7) have made a rather extensive study of the steric effects on polarographic half-wave potentials of alkyl bromides. They found that the ease of reduction parallels S_N2 reactivities, but that there were exceptions to this correlation. They concluded that the steric effects were less important than would be the case for normal S_N2 chemical reactions. For further discussion of this particular study and numerous others, three excellent reviews are recommended (4,5,6). The radical-anion scheme is supported by the following observation. It seems reasonable to expect that the addition of the second electron to the radical (R^\cdot) in the radical-anion scheme would in some cases occur at more negative potentials than the addition of the first electron to the original molecule (RX). If this process occurred, then two-step polarograms would be observed in these instances. That this is indeed

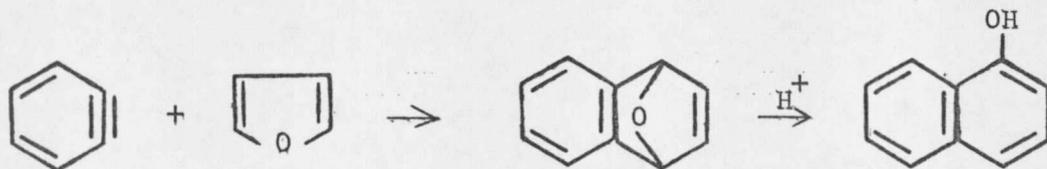
true in some cases, is demonstrated by the reports of dimers (R-R) in several reaction products and the corresponding occurrence of two-step polarograms (4,5,6). In many cases, the addition of the second electron is the predominant pathway, but there are some cases in which dimerization can also occur. For example, bromomaleic acid is reduced to a mixture of fumaric acid, maleic acid, and butadiene-1,2,3,4-tetracarboxylic acid (8). The data of Petrovich and Baizer (9) on the polarographic reduction of allyl chloride, allyl bromide, and their 2-carbethoxy derivatives in aqueous ethanol, dimethylsulfoxide, and dimethylformamide solutions also supports the radical anion mechanism. Allyl chloride showed only one reduction wave, but the other compounds showed two or more waves. These two-step reductions were interpreted to indicate a radical anion process. In the reduction of allyl bromide, the potential for addition of the second electron was more cathodic than for the first, causing two waves; for allyl chloride the potential required to add the first electron was at least equal to that for the second, hence, one wave.

Electrochemical reductions of polyhalogenated hydrocarbons have been investigated by several groups (10,12,13,14,15,16,17). When aliphatic molecules containing more than one halogen are considered, three types are encountered: those containing more than one halogen on a single carbon, those having halogens on adjacent carbons, and those having halogen atoms attached to carbons that are not adjacent. Both gem and vic halides reduce more readily than simple halides. Vic

halides are more easily reduced than comparable gem halides. Polyhalo-
aromatics usually undergo stepwise reduction. The first reported ex-
ception to this stepwise replacement of aromatic halogen atoms by hydro-
gen atoms was o-dibromobenzene (10). The o-dibromobenzene is reduced in
a single four-electron step to benzene and the suggested reduction mech-
anism involves formation of benzyne as an intermediate.



Controlled-potential electrolysis of o-dibromobenzene in the presence of
furan produced naphthalene-1,4-epoxide, which was converted by acid
hydrolysis to 1-naphthol. The electrolysis solution had to be vigor-
ously stirred to remove benzyne from the electrode surface before it
was reduced further. A similar electrolysis experiment with
o-dichlorobenzene produced a very small amount of 1-naphthol.

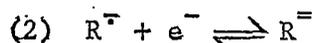
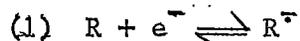


Yakobson and Petrov (11) also studied the electrochemical reduction of o-dibromobenzene and confirmed the above reduction scheme. In addition, they reported that o-bromiodobenzene and o-diiodobenzene showed three reduction waves instead of the two waves expected. The preparatory electrolysis of o-diiodobenzene at a potential corresponding to its first reduction wave indicated that both iodine atoms were lost in one two-electron reduction. They suggested that the reduction intermediate reacts with the mercury cathode to form diaryl mercury (R_2Hg) because organomercurials were identified in the electrolysis products. This explained why neither the second nor third half-wave potentials for the reduction of diiodobenzene corresponded to the half-wave potential of iodobenzene.

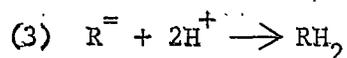
Reduction of Aromatic Hydrocarbons

It is fundamental to this work that any reduction peaks due to the reduction of the unsaturated hydrocarbon portions of the halogenated molecules are identified as such, and thereby, not confused with the reduction of the carbon-chlorine bonds. Peover (18) has reviewed the electrochemistry of aromatic hydrocarbons. While saturated hydrocarbons are not reducible at electrodes, nearly all unsaturated hydrocarbons can be reduced electrochemically. Exceptions are compounds containing isolated carbon-carbon double bonds or benzene rings (1). The reduction of aromatic hydrocarbons generally involves addition of two electrons

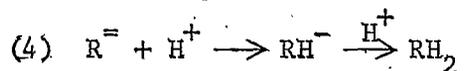
and of two protons to a pi-electron system to produce a dihydro compound. Hofjtkink and Van Schooten (19,20) have examined the polarographic reduction data of twenty aromatic compounds, and have predicted a reduction scheme based on these data and theory.



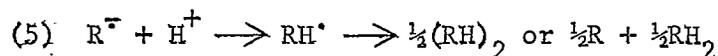
In bulk solution



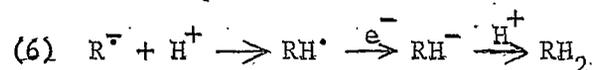
In double layer



In bulk solution



In double layer



The first step is reversible and potential-determining. If the solvent system is aprotic, the anion radical ($R^{\cdot-}$) may be stable (21). At a sufficiently cathodic potential, addition of a second electron occurs as in step 2. The polarogram corresponding to this scheme shows two one-electron waves.

At sufficiently high proton concentrations, the anion radical ($R^{\cdot-}$) may be protonated. If the rate of diffusion of ($R^{\cdot-}$) into the bulk of the solution is greater than the rate of protonation, the free radical (RH^{\cdot}) will react chemically and the polarogram will consequently show a single one-electron wave. If, however, the rate of protonation is

