



The use of molecular orbital calculations and electrochemistry to predict the reduction pathways of organochlorine compounds  
by Frederick Arthur Beland

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

The CNDO/2 molecular orbital method was used to investigate the electrochemical reduction of organochlorine compounds of environmental interest. As the degree of chlorination increased in chlorinated benzenes and biphenyls, the LUMO- $\zeta$  and LUMO- $\pi$  both decreased in energy. The HOMO of the radical anions for each of these species was always a  $\zeta$  orbital. The location of highest electron density in the LUMO- $\zeta$  for all of the chlorobenzenes, DDT, lindane and heptachlor predicted which chlorine was lost during electrochemical reduction. The electron density distribution in higher unoccupied  $\zeta$  orbitals of DDT and heptachlor predicted the order of carbon-chlorine bond scission in succeeding reductions.

Electrochemical reduction pathways correctly predicted the observed anaerobic degradation pathways for DDT, DTE, lindane and hexachlorobenzene. 2,3,4,5,6-Pentachlorobiphenyl and decachlorobiphenyl were resistant to anaerobic reduction. The first electrochemical reduction product of decachlorobiphenyl did undergo anaerobic reduction. During anaerobic degradation heptachlor lost the allylic chlorine first as opposed to the "anti" methylene bridge chlorine observed electrochemically. These results indicate that if a compound has an  $E_{2d}$  more cathodic than -1.75 V (vs. SCE) in a DMSO-TEABr solvent system, it will not reduce in an anaerobic environment. Compounds with an  $E_{2d}$  more anodic than this value may be reduced in the environment. Whether they do or not seems to depend on their actual structure which indicates that these compounds may have to fit into some type of an "active site."

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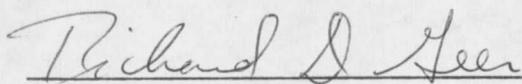
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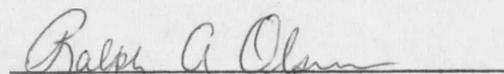
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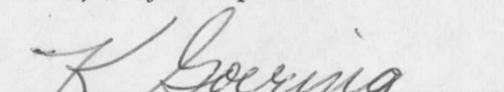
in

Chemistry

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MONTANA STATE UNIVERSITY  
Bozeman, Montana

August, 1974

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## ABSTRACT

The CNDO/2 molecular orbital method was used to investigate the electrochemical reduction of organochlorine compounds of environmental interest. As the degree of chlorination increased in chlorinated benzenes and biphenyls, the LUMO- $\sigma$  and LUMO- $\pi$  both decreased in energy. The HOMO of the radical anions for each of these species was always a  $\sigma$  orbital. The location of highest electron density in the LUMO- $\sigma$  for all of the chlorobenzenes, DDT, lindane and heptachlor predicted which chlorine was lost during electrochemical reduction. The electron density distribution in higher unoccupied  $\sigma$  orbitals of DDT and heptachlor predicted the order of carbon-chlorine bond scission in succeeding reductions.

Electrochemical reduction pathways correctly predicted the observed anaerobic degradation pathways for DDT, DTE, lindane and hexachlorobenzene. 2,3,4,5,6-Pentachlorobiphenyl and decachlorobiphenyl were resistant to anaerobic reduction. The first electrochemical reduction product of decachlorobiphenyl did undergo anaerobic reduction. During anaerobic degradation heptachlor lost the allylic chlorine first as opposed to the "anti" methylene bridge chlorine observed electrochemically. These results indicate that if a compound has an  $E_{2d}$  more cathodic than  $-1.75$  V (vs. SCE) in a DMSO-TEABr solvent system, it will not reduce in an anaerobic environment. Compounds with an  $E_{2d}$  more anodic than this value may be reduced in the environment. Whether they do or not seems to depend on their actual structure which indicates that these compounds may have to fit into some type of an "active site."

## INTRODUCTION

Organochlorine compounds have been used in agriculture and industry for the last thirty years. Their extensive use has been in part due to their chemical stability which has resulted in their becoming widespread pollutants. Great effort has been expended in developing the techniques to monitor the amount and presence of these residues. Considerable work has also been devoted to the chemistry of these compounds to better understand their mode of action and degradative pathways. We embarked on a project originally aimed at providing a technique for the specific identification of chlorinated hydrocarbon pollutants through the use of voltammetric identification. The results of this work have been reported by Farwell.<sup>1</sup> This investigation led us to the belief that perhaps reductive voltammetry could also be used to provide insight into the degradative pathways of these compounds. Furthermore since electrochemical reduction has provided a good test for quantum mechanics, we felt that molecular orbital calculations could provide insight into the breakdown pathways observed electrochemically and ultimately to those observed environmentally. The following sections in the introduction are offered to the reader so that the nature of the problem will be better understood.

### Electrochemical Reduction of Carbon Halogen Bonds

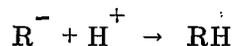
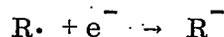
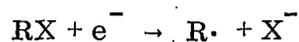
The history of the reduction of carbon halogen bonds is centered around the now classical work of Von Stackelberg and Stracke.<sup>2</sup> They systematically investigated a large number of alkyl halides and polyhalides and made the following observations (as modified by Fry<sup>3</sup>).

1. The ease of reduction of carbon halogen bonds decreases in the following order: allylic  $\approx$  benzylic  $>$  saturated  $\approx$  aryl  $>$  vinyl. Thus allylbromide has an  $E_{1/2}$  (half-wave potential) = -1.29 V (vs. SCE), n-butylbromide, -2.27 V, bromobenzene, -2.27 V, and vinylbromide, -2.47 V. (Solvent: 75% dioxane containing tetraethylammonium bromide (TEABr)).
2. The double bond in unsaturated halides is not electrochemically reducible.
3. Comparing different halides, the ease of reduction decreases as follows: I  $>$  Br  $>$  Cl  $>$  F.
4. Geminal and vicinal halides reduce more easily than simple halides. Thus:  $CX_4 > CHX_3 > CH_2X_2 > CH_3X$  and  $X-CH_2-CH_2-X > CH_3-CH-X_2 > CH_3-CH_2-X$ , where X = I, Br or Cl.
5. Increasing the chain length of a saturated aliphatic hydrocarbon increases the reduction potential. For example, the

$E_{1/2}$  increases as follows (i.e., the reduction becomes more difficult):

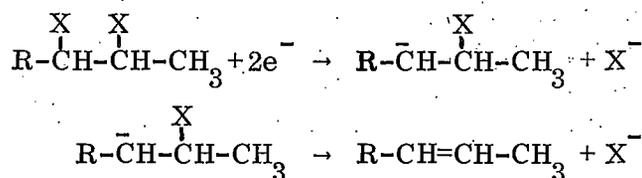
methylbromide < n-butylbromide < n-octylbromide.

6. The half-wave potentials are pH independent and the reductions are irreversible.
7. Except for vicinal dihalides, two electrons are gained for every halogen lost with concomitant gain of a proton. They suggested the following mechanism to account for this observation.

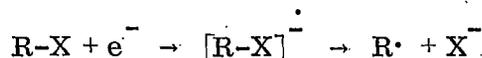


The initial addition of an electron was proposed to be the rate determining step.

8. For vicinal dihalides the proposed mechanism was:

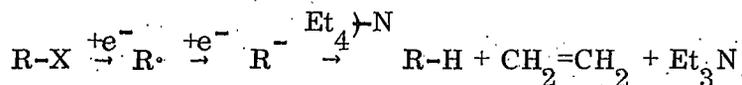


Building on the foundation established by Von Strackelberg and Stracke, others have continued the investigation of the reduction of the carbon halogen bond. C. K. Mann<sup>4</sup> has suggested that the first step in the reduction involves the formation of a radical anion which rapidly decomposes to the free radical.



This step should be reversible (the formation of the radical anion), but when employing cyclic voltammetry there has been no evidence of reversibility at even very high scan rates.<sup>5</sup> Fry argues that while the radical anion may represent a transition state, it is not a true intermediate.<sup>3</sup> His argument is based on the fact that while the reduction of alkyl chlorides by hydrated electrons (which generates radical anions) is independent of alkyl chain length, this is not what is observed under electrochemical reduction.

Von Stackelberg and Stracke's<sup>2</sup> mechanism for alkyl halide reduction invokes the formation of a radical (R·) and a carbanion (R<sup>-</sup>). Both of these species have been demonstrated, although through indirect evidence. Thus dimeric products,<sup>5</sup> organomercurial compounds,<sup>4</sup> and rearranged products,<sup>3</sup> have been detected which indicates the formation of free radicals. When the reduction solvent is aprotic, the Hoffman elimination product of the quaternary ammonium salt used as the supporting electrolyte was detected, which provides evidence for carbanion formation.<sup>4</sup>

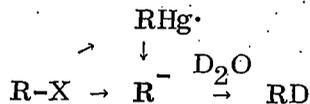


It is generally assumed that the radical (R·) will be able to gain an electron more easily (at a more anodic potential) than the parent alkyl halide. Thus only one polarographic wave is observed which represents a 2-electron transfer. However, there are exceptions; for instance two waves are observed

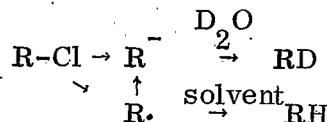
during the reduction of t-butyliodide, whereas only one was observed for t-butylobromide.<sup>6</sup> This again lends support for the formation of a radical (R·) followed by a carbanion (R<sup>-</sup>).

As previously mentioned, vinyl and aryl halides are reduced at potentials equal to or slightly greater than saturated halides. While the two former types of halides have not been studied as extensively as the corresponding saturated compounds, some interesting observations have been made. The most thorough study on aryl halides has been made by Farwell.<sup>1</sup> He performed polarographic studies on chlorinated benzenes, biphenyls, naphthalenes, diphenylethanes and -ethylenes. When the chlorine was substituted on the aryl moiety, the carbon-halogen bond was reduced by a 2-electron pH independent irreversible process. He furthermore performed controlled potential electrolysis on the benzene and biphenyl series and determined the reductive pathways for these series. The results of his work will be dealt with more extensively in later sections of this dissertation. Campbell<sup>7</sup> has studied the electrochemical reduction of a limited number of fluorinated benzenes, biphenyls, and naphthalenes. His results are consistent with previous observations that the halogens are lost in a 2-electron per halogen process, the fluoride being replaced by a hydrogen. Renaud<sup>8</sup> investigated the reduction of 1-halonaphthalenes in the presence of deuterated water. He postulated that bromo- and iodo-naphthalenes are reduced via an organometallic radical

intermediate or by the simultaneous addition of two electrons to form a carbanion.



However, since the amount of deuterium incorporated is much lower during the reduction of 1-chloronaphthalene, he proposes that it goes by either a simultaneous addition of two electrons or by a discrete radical pathway if a radical is formed. This could strip a hydrogen atom from the solvent thus giving an unlabeled product.



A number of investigators have postulated that during the reduction of aryl and vinyl halides the electron is initially transferred to the pi ( $\pi$ ) system followed by cleavage of the sigma ( $\sigma$ ) carbon halogen bond. This supposedly occurs with nitrophenyl,<sup>9</sup> nitrobenzyl,<sup>10</sup> polyphenylethylenic and vinyl halides,<sup>11</sup> and with halobenzophenones.<sup>12</sup> Finally, in comparison with alkyl halides the formation of dimers and alkyl mercury compounds during the reduction of aryl and vinyl halides is negligible.<sup>3</sup>

Polyhalogenation generally facilitates the ease of reduction and also usually increases the number of waves observed. For instance, in aqueous solvents, three 2-electron waves are observed during the reduction of carbon tetrachloride. These represent the formation (at each successive reduction)

of chloroform, methylene chloride and finally methylchloride.<sup>13</sup> [It should be mentioned that the situation changes drastically in aprotic solvents (in this case acetonitrile). Here carbon tetrachloride exhibits only two 2-electron waves resulting in the formation of methylene chloride. The interesting point is that a carbene intermediate is invoked.]<sup>13</sup>

In contrast to geminal dihalides, vicinal dihalides are reduced by the transfer of one electron per halogen. This results in the formation of olefins in what is thought to be a concerted process. The main evidence for this is that olefins are always found even in protic solvents, which should trap out a carbanion if one was formed. Since vicinal dihalides are reduced more easily than simple halides, they must possess a pathway not available to simple halides, such as a concerted pathway. This mechanism is supported by the results of Zavada et al.<sup>14</sup> Using rigid cyclic vicinal dihalides, they found the reduction to proceed most easily when the halogen-halogen dihedral angle was near  $0^\circ$  or  $180^\circ$ , while the most cathodic potentials occurred when the dihedral angle between the chlorines is  $90^\circ$ . This coplanarity would tend to facilitate a concerted reduction.

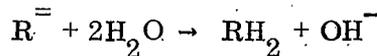
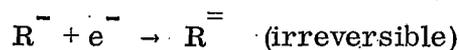
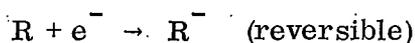
This review, while hopefully an aid to the reader, is not intended to be extensive. For a more eloquent presentation, the texts by Fry<sup>3</sup> and Mann and Barnes<sup>15</sup> are suggested.

Molecular Orbital Studies on Electrochemical Reductions

The rate determining step in the electrochemical reduction of a compound is the addition of the first electron. This appears to be the case in both reversible and irreversible systems. Thus if one can determine the level of the lowest unoccupied molecular orbital (LUMO), i. e., the orbital into which this electron will go, one should be able to develop a linear relationship between reduction potential and the energy level of the LUMO.

Maccoll<sup>16</sup> was the first to attempt this relationship, and applied it to a series of aromatic hydrocarbons. Since the LUMO for compounds of this type will be a  $\pi$  orbital he used a simple Huckel molecular orbital (HMO) approach, which only treats the  $\pi$  system, and was able to obtain a linear relationship.

Hoijtink and Van Schooten extended this concept.<sup>17</sup> The reduction pathway for aromatic hydrocarbons was considered to be:



In their treatment they assumed that the  $\log K_1/K_2$  (where  $K_1$  and  $K_2$  are the diffusion coefficients of R and  $R^-$  respectively) and the  $\Delta G_{\text{solvation}}$  are nearly the same for related molecules. If this is the case, then the electron affinity will be approximately equal to the energy of the LUMO. This is

Maccoll's original conclusion.<sup>16</sup> Hoijtink's and Van Schooten's real contribution was to predict reaction products based on the results of the molecular orbital calculations. Thus the location of greatest electron density in the highest occupied molecular orbital (HOMO) in  $R^{\ominus}$  will be the site of proton attack to give  $RH^{\ominus}$ . Furthermore, the location of highest electron density in the HOMO of  $RH^{\ominus}$  will predict where the second proton attacks to give  $RH_2^{\ominus}$ . They predicted that 1,4-dihydronaphthalene will be the 2-electron reduction product of naphthalene, which has since been proven experimentally.<sup>18</sup>

Our discussion on theoretical studies until now has only dealt with the  $\pi$  electron system. This has been based on the Huckel approximation that the  $\pi$  electrons will act independently of the  $\sigma$  system. While this is a rather simplistic approximation, it does lead to rather good predictions of chemical behavior.

Certain molecules, such as carbon tetrachloride, do not possess  $\pi$  systems and yet are electrochemically reducible. If a molecular orbital method could be developed to treat  $\sigma$  systems (even to the exclusion of the  $\pi$  electrons), insight could be gained into the reduction of compounds of this type. Theories of this type have been developed independently by Sandorfy<sup>19</sup> and Fukui et al.<sup>20-24</sup> When Fukui and coworkers applied their system to the reduction of organic halides, they made the following observations:<sup>23</sup>

1. Increasing the degree of halogen substitution does not seriously

affect the energy levels of the occupied  $\sigma$  molecular orbitals, but markedly lowers the  $\sigma$  LUMO.

2. There is a linear relationship between the  $\sigma$  LUMO and  $E_{\frac{1}{2}}$  for halomethanes.
3. The potential determining step is the addition of the first electron.
4. The electron distribution of the LUMO is greatly localized in the carbon halogen bond and the bond order is negative and large in absolute magnitude. This should cause the carbon halogen bond to break quite easily when the LUMO becomes occupied by an electron.
5. The  $\pi$  LUMO energy levels (obtained from HMO calculations) for chloroethylenes and chlorobenzenes do not significantly change upon increasing halogen substitution.
6. Finally, it was suggested that the LUMO for conjugated halides might be a  $\sigma$  rather than  $\pi$  orbital.

The next level of approximation would be to use a method that would allow calculation of  $\sigma$  and  $\pi$  energy levels simultaneously. The inherent advantages of this type of calculation will be discussed in a later section. For the present it should be mentioned that Dewar et al. have applied a theory of this type to study the electrochemical reduction of aromatic hydrocarbons. <sup>25</sup>

Instead of using the energy of the LUMO to estimate the electron affinity (EA) of the hydrocarbon, they calculated the EA by taking the difference between the heats of atomization of the radical anion and the parent hydrocarbon. One distinct advantage of their method is that it allows EA to be calculated in absolute energy terms instead of in units of  $\beta$ . This allows direct comparison of the energies obtained from calculations and experiments. When EA is plotted against  $E_{\frac{1}{2}}$ , a linear correlation was observed with the slope of the line equal to 0.99. They suggested that this implies that the differences in solvation energy between the parent hydrocarbons and the corresponding radical anions are constant. (This tends to confirm Hoijtink's and Van Schooten's original approximation).<sup>17</sup> This is because the reductions were performed in aprotic solvents which should not solvate the radical anions very efficiently. Dewar et al. offered as further evidence the fact that the slope of the line for the reduction of quinones was 0.39 (versus 0.50 theoretical value). In this latter case the reductions were performed in a protic solvent which should solvate the anions quite strongly.<sup>26</sup> Finally, they were able to predict reduction products in a manner quite analogous to Hoijtink and Van Schooten.

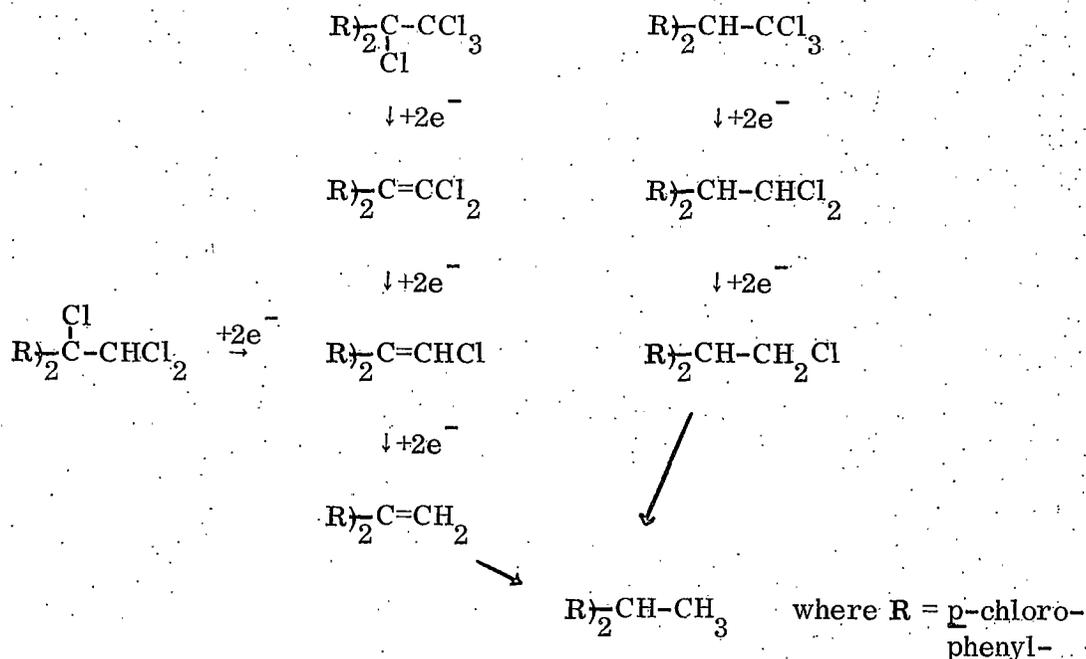
#### Electrochemical Reduction of Chlorinated Insecticides and Chlorinated Hydrocarbon Pollutants

There have been a number of studies on the electrochemical reduction of compounds of environmental interest. These have been primarily twofold in

nature: first to develop the analytical methodology to detect these contaminants and second to understand the nature of the carbon-chlorine reduction.

By far the most extensive study has been that of Farwell<sup>1</sup> and Farwell et al.<sup>27-29</sup> Besides establishing the reductive pathways for chlorinated benzenes and chlorinated biphenyls with chlorines on one ring he investigated the voltammetric behavior of chloronaphthalenes, DDT (1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl)ethane) and its various chlorinated analogues and other chlorinated insecticides including lindane ( $\gamma$ -1,2,3,4,5,6-hexachlorocyclohexane), dieldrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-endo-exo-1,4:5,8-dimethanonaphthalene), aldrin (1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-endo-exo-1,4:5,8-dimethanonaphthalene), and heptachlor (1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene).

Rosenthal et al.<sup>31</sup> conducted a systematic study on the polarographic behavior of the diphenylethanes and ethylenes found in the DDT series. Their work included controlled potential electrolysis and they were able to demonstrate the following reduction pathways.



Farwell<sup>1</sup> was able to reduce the last compound, 2,2-bis(p-chlorophenyl)-ethane (DDMS), presumably to 2,2-diphenylethane.

The electrochemical reduction of dieldrin and aldrin has been investigated by Swanepoel et al.<sup>32</sup> Using a solvent system of 75% aqueous methanol containing 0.1 M tetramethylammonium bromide (TEABr) they performed controlled potential electrolysis at potentials between -1.0 and -2.0 V (vs. silver/silver chloride electrode). Two products, representing successive reductions, were found from dieldrin, while only one from aldrin. These compounds were isolated and their identity established by nmr spectroscopy. Figure 1 shows the reduction pathways they determined.







































































































































































































































































































































































