



Instrumental design requirements for measurements of electrochemical reduction rates of haloorganics
by Richard Allen Hughes

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in
Chemistry

Montana State University

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Abstract:

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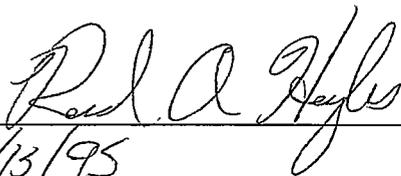
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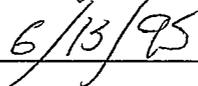
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To Tammy, Allyson, Dad and Mom

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TABLE OF CONSTANTS

A = area of electrode

α = transfer coefficient

C_o^* = Bulk concentration of oxidized species

D_o = diffusion coefficient

E = potential of an electrode vs a reference

E° = standard potential of an electrode

$E^{\circ'}$ = formal potential of an electrode

E_p = peak potential

E^* = potential at which reduction rate is to be measured

F = Faraday constant

i_p = peak current

k_f = heterogeneous rate constant for reduction

k_{homo} = rate constant for a homogenous reaction

k° = standard (intrinsic) heterogeneous rate constant

n = electrons per molecule oxidized or reduced

n_a = number of electrons involved in the rate determining step

R = gas constant

T = temperature

v = potential sweep rate

ABSTRACT

The degradation rates of environmental contaminants are of potential use in many fields. As such, a methodology for the rapid determination of the rates of degradation of electroactive species could prove valuable.

An attempt was put forth to construct a micro-computer controlled interface and electrochemical instrumentation. It was hoped that a highly flexible instrument capable of high speed, high resolution data transfer would aid in the investigation of the rates of degradation of selected haloorganics.

A commercial instrument (EG&G Par 273A) was utilized in a preliminary investigation of the degradation rates of carbon tetrachloride and carbon tetrabromide.

The instrumentation which was constructed was not utilized in this study due to difficulties with data transfer capabilities and other problems with the electronics. However, utilizing the information gathered with the commercial instrumentation, preliminary values for the rate constant of the aqueous degradation of carbon tetrachloride were determined.

INTRODUCTION

Degradation Pathways and Kinetics

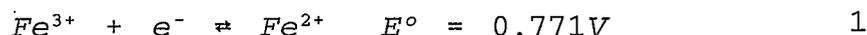
Since the advent of pesticides, herbicides and other chemicals used to control pests, there has been concern about the longevity of these compounds within the environment. Many of these compounds are halogenated organics¹ and as such may be susceptible to oxidative or reductive destruction. It is known that there are non-biological conditions in localized environments that can cause reduction or oxidation of electro-active organic substances. For instance in ground water or flooded soil systems the reduction or oxidation of an electro-active species may be governed by the presence of soluble, thermodynamically reversible redox couples. However, the potential at which these redox couples exist may be mediated by microbial or other biological systems and the contaminants themselves may be degraded by these biological systems.^{1,2,3}

Utilizing certain electrochemical techniques it may be possible to predict the fate and minimum rate of environmental degradation for many of these halogenated organic chemicals from their electrochemical redox kinetics and other measurable redox properties in the environment. These procedures could prove to be a viable method for predicting the environmental fate and minimal rate of

degradation of a variety of newly proposed pesticides, chemicals that may have intentional exposure to the environment and to provide quick and reasonable predictions of degradation rates in areas of environmental concern.

For the purposes of this investigation only those reduction processes which do not involve direct biological intervention will be considered. The rates for these processes are minimal rates, uncatalyzed by biological activity. The half life for these rates can range from minutes to centuries, depending upon the substrate and the concentration of the reversible redox couples in the environment. There are several underlying assumptions and principals which will support the use of electrochemical techniques for investigating the minimum rates of localized degradation of environmental contaminants.

The existence of an oxidation reduction potential (ORP) in the environment is confirmed by a simple potentiometric measurement, with an inert and reference electrode pair. From this measurement the ratio of the concentrations of reduced to oxidized species can be determined. This is according to the well known Nernst equation (Eq 2). So, for example, using iron species as the redox couple (Eq 1):

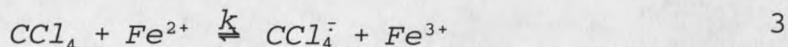


$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \quad 2$$

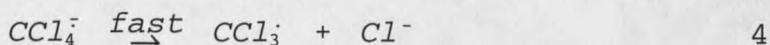
Therefore, the ratio of the species present sets the measured potential of the local environment. Again it is understood that certain biological systems can potentially alter the observed potential, but for the purpose of this study it is assumed that experimental steps will be taken to minimize this so that the desired information will be obtained.

Carbon tetrachloride is a common organic solvent and was widely used in the past. Although use has declined due to its carcinogenicity, it has been the source of isolated but serious environmental contamination problems.⁴ For this reason and for ease of explanation, the discussion of determining the degradation rates of electro-active halogenated organics will focus on carbon tetrachloride (CCl_4). The degradation rate of CCl_4 depends on three main factors. First, the concentrations of the reduced and oxidized species of the major reversible redox couple(s), and therefore the redox potential. Second, the concentration of CCl_4 , the electro-active species of interest. And third, the intrinsic homogeneous rate constant, k_{homo} , for the acceptance of an electron by CCl_4 at the measured redox potential.

The reaction to consider would then be

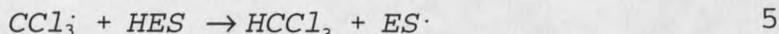


The radical anion produced is unstable and rapidly dissociates to form free chloride and the reactive radical $CCl_3\cdot$.

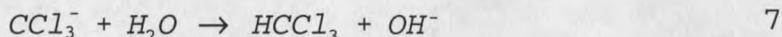
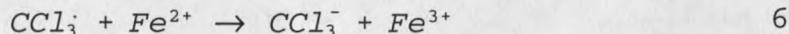


The radical will react via one of several possible reaction sequences, depending upon the relative concentrations of reactants.

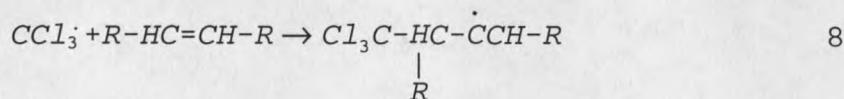
1. Abstract a hydrogen atom from an Environmental Source (HES) to give a more stable radical ($ES\cdot$) and a less halogenated compound. (Note, abstraction of a hydrogen atom from water is not likely as the hydroxy radical is more reactive and would reverse the process.)



2. Abstract an electron from the reduced form of a reversible redox couple to form a very basic anion that reacts with water.



3. Addition to a pi bond system, like $>C=C<$, $>C=O$, or $-N=O$, again giving rise to a new radical.



4. Coupling with relatively stable radicals in the environment, like triplet dioxygen or perhaps the

nitric oxide ($\cdot\text{NO}$) radical from the further reduction of nitrite.



It should be noted that sequences 1 and 2 would lead to the replacement of a halogen with hydrogen, a frequently observed anaerobic process.^{5,6} Sequences similar to 3 and 4, however, would lead to a variety of products with diverse chemistry that will not be considered in this study. Also note that sequences 1 and 3 would generate a free radical chain reactions in addition to their other pathway.

Since reaction 3 is rate limiting and the same for all these reaction sequences, the overall rate of disappearance of CCl_4 is controlled by its intrinsic rate constant, k_{homo} .

$$\frac{-d(\text{CCl}_4)}{dt} = k_{\text{homo}}[\text{CCl}_4][\text{Fe}^{2+}] \quad 10$$

Electrochemical reduction of organohalogen compounds, like CCl_4 , follow the sequence of Reactions 3, 4, 6 and 7 of the pathways discussed above with the electrode taking the place of the reversible redox couple and acting as an infinite source of electrons. However a key difference is that the rate constant is based on a heterogeneous reactions at the electrode surface.

A critical factor within this study will be the ability to directly relate heterogeneous and homogeneous rate constants for the reactions that are being investigated. One possible solution to this dilemma would be to consider

the homogeneous system at the molecular level and consider each interaction of analyte and reduced redox species as an independent heterogeneous reaction. It may be possible to derive a mathematical equation that will allow this comparison. To verify this, it would be necessary to obtain data via two independent experimental techniques^{7,8}.

Methodology for Determining the Heterogeneous and Homogeneous Degradation Rates of CCl_4

Investigating Homogeneous Degradation Kinetics

Consider the following system; where CCl_4 degradation in a sterile, sealed, reversible redox system is possible over a reasonable range of ORP values. Considering only redox systems that transfer a single electron it would be possible to determine the degradation kinetics and compare them to Equation 10. Such an experimental environment might be envisioned to consist of an inert electrolyte (perhaps 0.1 M potassium chloride) and a metal ion complex poised at the desired ORP, either by chemical or electrochemical titration. To ensure pseudo first order kinetics for the disappearance of CCl_4 , the reduced metal ion complex concentration would be >10 times that of CCl_4 initially. To maintain the ORP relatively constant during the experiment, the oxidized to reduced species ratio of the redox couple must not change significantly during the course of the reaction. This requirement limits the usefulness of the environmentally important iron(II)/(III) couple for this

study under simulated anaerobic experimental conditions since the ORP would tend to be quite positive under standard conditions. An ORP of less than ≈ -0.10 volts vs. SCE is much more practical. The cobalt(II/III) ammonia complex couple with a $E^\circ = -0.133$ volts⁹ could be a useful surrogate for these first tests. Working with a sealed system avoids loss of volatile CCl_4 or HCCl_3 during the course of the experiment.

The progress of the CCl_4 degradation could be followed both by *in situ* electrochemistry and by removing samples for analytical analysis. With the electrodes sealed into the system the ORP could be monitored continually by potentiometry to ensure a stable ORP. The concentrations of redox species and carbon tetrachloride could be measured periodically by cyclic voltammetry. Other electrochemically active products may be observed when concentrations reach detectable limits. These experiments would not appreciably perturb the system.

Results of these experiments should give insight into several aspects of the degradation system. It should show whether the degradation rate is first order in CCl_4 as predicted. The reduction capacity of the system could be determined if the degradation rate is first order with respect to the reduced species of the reversible redox couples. The log of the intrinsic homogeneous rate constant (k_{homo}) for the CCl_4 degradation could be compared to the

measured ORP value in order to investigate if they are in fact proportional. Lastly, the mass balance between observable products and CCl_4 disappearance could be monitored to verify its completeness and also allow a check on major routes of degradation.

Investigating Heterogeneous Degradation Kinetics

The previous example relied on indirect determination of the rate based on the change in concentration over time. The goal of this study is to demonstrate that by utilizing quality instrumentation and the known electrochemical technique of cyclic voltammetry it is possible to predict the degradation rates at virtually any potential within a short period of time. This method would allow the determination of the intrinsic heterogeneous rate constant (k°) for the reduction of CCl_4 at a metal electrode over a range of potentials.

To briefly review cyclic voltammetry, a compound of interest, in a solvent containing electrolyte, is subjected to a linear potential change. Then at the limiting voltage the potential sweep is reversed until the chosen end potential is reached. The resultant current which flows is recorded relative to this applied potential. Generally, the features of interest are the potential where the cell current peaks, E_p , and the value of the peak current, i_p . The equations which explain the relationship of peak current

and potential in irreversible systems are shown in equations 11 and 12 below.¹⁰

$$E_p = E^{o'} - \frac{RT}{\alpha n_a F} \left[0.780 + \ln \left(\frac{D_o^{1/2}}{k^o} \right) + \ln \left(\frac{\alpha n_a F v}{RT} \right)^{1/2} \right] \quad 11$$

$$i_p = 0.4958 n F A C_o^* D_o^{1/2} v^{1/2} \left(\frac{\alpha n_a F}{RT} \right)^{1/2} \quad 12$$

Equations 11 and 12 can be combined to give

$$i_p = 0.227 n F A C_o^* k^o \exp \left[- \left(\frac{\alpha n_a F}{RT} \right) (E_p - E^{o'}) \right] \quad 13$$

or, after rearrangement

$$\ln i_p - \ln n = \ln(0.227 F A C_o^*) + \ln k^o - \left[\left(\frac{\alpha n_a F}{RT} \right) (E_p - E^{o'}) \right] \quad 14$$

Thus a plot of $(\ln i_p - \ln n)$ vs $(E_p - E^{o'})$ for data collected over a wide range of sweep rates would give a slope of $-\alpha n_a F / RT$ and an intercept of $\ln(0.227 F A C_o^*) + \ln k^o$.¹⁰

In the above equations there are two terms that cannot actually be used as defined, the formal electrode potential, $E^{o'}$, and the standard rate constant, k^o .

The formal electrode potential, $E^{o'}$, is defined as the measured half-cell potential where the ratio of oxidized to reduced species is unity and the other solution conditions are in their standard state.¹⁰ For an irreversible reaction $E^{o'}$ cannot be defined. This is because if a reduction process is irreversible perhaps due to a subsequent chemical

reaction, then there is no reverse reaction and unity, even though it may exist, cannot be maintained. It is therefore impossible to determine the point of unity for a species in an irreversible reaction when the reactant can be transformed into product just by making a measurement on the system. Energy applied to the system in an attempt to force unity will ultimately cause either degradation of the species present or will cause the species present to find alternative pathways to new products not previously considered part of the reaction. A remedy to this dilemma will be discussed shortly.

The second term that must be considered is the standard rate constant k° . The standard rate is defined as the rate of the forward or reverse reaction rate at the formal potential.¹⁰ Considering this relationship and remembering that E°' cannot be defined for an irreversible reaction, k° is then, also not strictly definable.

There is a convenient solution to this problem. If E°' is redefined to be the potential at which the rate is to be determined, E^* , then the rate constant of the reaction under consideration, k_f , would be the rate constant at this potential. So if we reconsider equation 14 and substitute the new values, the following equation results,

$$\ln i_p - \ln n = \ln(0.227FAC_o^*) + \ln k_f - \left[\left(\frac{\alpha n_a F}{RT} \right) (E_p - E^*) \right] \quad 15$$

Cyclic voltammetry experiments on CCl_4 in a supporting electrolyte solution done over the widest possible range of sweep rates would give a set of peak currents, i_p , and potentials, E_p . Thus a plot of $(\ln i_p - \ln n)$ vs $(E_p - E^*)$ would give a slope of $-\alpha n_a F/RT$ and an intercept of $\ln(0.227FAC_o^*) + \ln k_f$.

Equation 15 shows how k_f can be determined at any desired E_{ORP} from these data by utilizing electrochemical techniques. These k_f values could be correlated with k_{homo} values determined using the methodology discussed earlier. This will permit an empirical correction factor between these two types of rate constants to be determined and enable rate data obtained by these two methods to be compared. However, the recordable range of values of E_p is limited by the instrumentation and determination of k_f at the desired potential, E_{ORP} , may require extensive extrapolation of the data collected. Thus it is imperative that the instrument provide very accurate and precise peak potential and current measurements.

Instrumental Considerations

Computer controlled electrochemical instrumentation has been in existence and use for more than 20 years.^{11,12}

Instrumentation for investigating electrochemical phenomena

are essentially available from three sources. First, a few complete commercial instruments are available that are capable of an array of electrochemical experiments. This equipment is usually capable of interfacing directly with a personal computer thus allowing computer control of the instrument and computerized data workup. Second, commercial data acquisition equipment is available that would allow conversion of analog data to digital data, which would be stored and retrieved by computer. Also possible with this data acquisition equipment is event timing and analog output for use in controlling remote circuitry. Information from separate electrochemical instrumentation could be digitized and transferred into a personal computer via the data acquisition system. The final option is to build an entire data conversion, storage and instrumentation system. This would allow for maximum flexibility, yielding a customized and upgradable system. It would be very similar to the second option but all components would be designed and constructed from scratch.

STATEMENT OF PROBLEM

The goal of this work was to develop improved microcomputer controlled electrochemical instrumentation that would be versatile for use in a wide variety of electrochemical experiments. Initially this instrumentation was to be used in the investigation of the reduction rates of various halogenated organics. A brief investigation was eventually performed using commercial instrumentation.

Funding for this work was limited and the possibility of purchasing commercial electrochemical instruments was not an option. At the initiation of this work the option of utilizing commercial data acquisition equipment was only a remote possibility for two reasons. First, at the inception of this project, the capabilities and availability of most of this equipment was limited. Second, if the desired equipment was available the purchase cost kept it from being a workable option. The final alternative for obtaining new and improved electrochemical instrumentation was to design and construct the desired system. It was felt that it was possible and practical to develop a system, which would be as good as, if not better than, that which was commercially available. This is the avenue that was initially pursued in this study.

There have been several other instruments designed and built by the Geer group since 1974 that were used in a variety of electrochemical investigations.^{7,13} The most

recent instrument was an Apple IIe based cyclic voltammeter. This instrument greatly improved the capabilities of the Geer group to record and store data but the instrument was cumbersome, data retrieval was time consuming and tedious and overall the instrument was inflexible with respect to its upgradeability.¹⁴ Also, the overall capabilities of this instrument would have been the limiting factor based on the quality of the data that is needed to estimate degradation rates. The proposed instrument is IBM PC based, and is designed to be capable of data acquisition from a variety of electrochemical instruments. It is designed such that upgrades are not only possible but expected with each major function existing as a separate module. These modules are largely independent and can be changed without significant effect to the rest of the system.

Brief studies into the nature of aqueous reductions of carbon tetrachloride and carbon tetrabromide are of interest in this thesis. The Geer group has done extensive reduction studies on haloorganics,^{5,6,7,8,15,16} but little has been done in aqueous systems concerning the rates of these reductions. It is felt that this information could eventually aid in the determination of degradation rates in the environment of a variety of halogenated organic molecules.

EXPERIMENTALComputer Interface and Instrumentation

For this study the instruments built by the Geer group not only lack the flexibility, but the precision and accuracy necessary. In this work, a modular computer interface was designed and built with instrumentation circuitry separate from the interface circuitry. This design however would enable future users to upgrade the system as better semiconductor devices and instrumentation designs become available. Separate instrumentation circuitry allows different instruments to be easily utilized and critical circuitry to be close to the electrochemical cell, which can aid in the reduction of noise. Also, if a new instrument or interface card is being developed the old card can still be used, minimizing the down time of the instrument. Within the interface there are currently three independent cards. These include an analog to digital converter card, a digital to analog converter card and an I/O and clock timer card. As previously mentioned the interface is connected to and controlled by an IBM PC clone computer. Within the computer, a decode card, which is essentially an extension of the computer bus, allows the computer software to communicate with the interface and acts as a buffer for incoming data. Explanation of each of the modules and instrumentation cards follow.

Decode Card

The decode card provides a means by which information can be sent to, or received from, the remote interface. Within that realm it serves 5 essential functions. It controls address and data lines, supplies timing and control signals to the interface, provides temporary data storage and shuttles data from the interface into computer for final storage. A schematic of the decode card is shown in Figure 1. Nomenclature for bus, card and chip assignments are shown in Appendix A. The basic circuitry for the decode(control) of address lines and data lines was predesigned by the manufacturer of the card. This board was purchased from and manufactured for JDR Microdevices, catalog number JDR-PR10. The circuitry supplied by the manufacturer can be divided into three specific areas. First, four bi-directional data bus buffers control 16 bits of I/O data lines and 16 bits of memory. Second, four uni-directional buffers drive the address bus and several other control bus signals. Third, two PAL16L8's programmable chips which are programmed by the manufacturer, are used to assign the decode card an address and allow the decode card to communicate with the computer and visa versa. This decode card is preprogrammed to communicate at the hex 300 base address of the computer.¹⁷

Design and construction of the remaining circuits on this card were done jointly with Mr. Mike Morrison. This

was necessary since Mr. Morrison wrote the software that allows the computer to communicate with the interface and instrumentation. Communication between the computer and the decode card is a critical link and joint design was of utmost importance here. The program for running the interface is provided in Appendix B.

The circuitry that was installed onto the decode card can be divided into 3 specific areas: Port Address Enable (PAEN), first in first out 2048 x 9 bit data input buffering (FIFO) and address line buffering.

The PAEN signal line is generated by utilizing a 74LS04 (quad inverter) to invert address line signals A5, A6 and A7 and to invert the computer bus signal Address Enable (AEN). These four inverted signals and address lines A8 and A9 are then input into a 74LS30 (8 input and gate) to create the final signal, PAEN. This signal is later used to give each interface card a specific address allowing each interface card to be communicated with independently and enabling data transfer to and from that card. This addressing scheme will be discussed later.^{18,19,20}

First in first out is a form of memory that allows data to be temporarily stored in such a manner that the first data stored is the first data removed when the computer retrieves the data from the chip.²¹ This configuration allows data generated by the interface and instrumentation, which is sent to the computer, to be temporarily stored by

