[CONTRIBUTION FROM THE RESEARCH LABORATORIES, ROHM & HAAS CO.]

A Systematic Polarographic Study of the Aromatic Chloroethanes[1]

BY ISADORE ROSENTHAL AND RENÉ J. LACOSTE

RECEIVED DECEMBER 15, 1958

A considerable amount of isolated work has been done on the polarography of the aromatic chloroethanes. Little of this, however, has been done systematically. Such a study is presented and establishes the nature of the various waves by large scale electrolysis. A new general rule governing the behavior of compounds of the type $C_6H_5CR{=}CCl_n$ has been found (where R = C_6H_5 or H). This rule is that, contrary to chemical reduction, vinyl halogen compounds of the type illustrated reduce at lower potentials than the corresponding saturated compounds and that all the vinyl halogens are removed before the double bond is reduced.

The polarography of the carbon–halogen bonds has been rather extensively studied[2] and a great deal is known about the reduction of compounds containing this linkage.

In the case of polyhalogenated alkyl compounds, two general types of reduction have been found. The reduction of carbon tetrachloride[3a] and of ethyl tribromoacetate[3b] are typical examples of one type, stepwise-reductions, which proceed as

$$\mathrm{CCl_4} \xrightarrow[\text{wave I}]{(-0.75\text{ v.})} \mathrm{CHCl_3} \xrightarrow[\text{wave II}]{(-1.67\text{ v.})} \mathrm{CH_2Cl_2}$$

The halogens are removed independently in a stepwise manner and the half-wave potentials are *p*H independent. If we designate the first reduction, wave I, and the second, wave II, then we find that wave I for chloroform corresponds to wave II for carbon tetrachloride. The second general type of reduction, which is not so well understood, is that for compounds similar to dibromosuccinic acid[4] or tetrabromoethane,[5] in which both halogens are removed simultaneously in a two-electron wave to yield a double bond. Obviously such a reduction must occur at a lower half-wave potential than that for either of the isolated halogens.

The authors have been interested in the polarography and large scale electroreduction of the aromatic chloroethanes both for theoretical and practical reasons. This class of compounds includes at least four insecticides now in commercial use; 1,1,1-trichloro-2,3-bis-(*p*-chlorophenyl)-ethane (DDT), 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)-ethane (Rhothane),[6] 1,1-dichloro-2,2-bis-(*p*-ethylphenyl)-ethane (Perthane)[6] and 1,1,1-trichloro-2,2-bis-(*p*-methoxyphenyl)-ethane (Methoxychlor),[7] and one miticide; 1,1,1-trichloro-2-hydroxy-2,2-bis-(*p*-chlorophenyl)-ethane (Kelthane).[6]

A considerable amount of isolated work has been done on this group of compounds but this has been largely limited to aspects concerning the analysis of DDT. Nothing has been done with respect to suspected impurities or degradation products such as the dehydrohalogenation products, of these materials.

This paper reports the results of a study of the reduction of these compounds polarographically and by macro-electrolysis at controlled potentials in an effort to systematize their behavior. On the whole, this effort has been successful and, in addition, has revealed that the behavior of vinyl halogens is of an unusual type.

Experimental

The current–voltage curves were obtained with a Leeds and Northrup Electrochemograph, type E, at a damping position of 1. All potential measurements were made with a saturated calomel electrode. Potassium ion was excluded from contacting the dropping electrode by filling both sides of an H-cell with the sample solution. The dropping electrode and the salt bridge from the reference electrode were inserted in opposite sides and were separated by a porous disk. The H-cell was thermostatically maintained at 25 ± 0.1°. The cell resistance, as measured with a Serfass conductivity bridge, was 9000 ohms. The half-wave potentials were corrected for *iR* drop in all cases where this was 0.01 volt or more.

The base electrolyte was 10% aqueous 1.0 *M* methyltri-*n*-butylammonium chloride (prepared by neutralizing a 1.0 *M* solution of the hydroxide to *p*H 8 with concentrated hydrochloric acid), and 90% 2B ethanol (Publicker Industries product). To obtain the current voltage curve for 1,1,1-trichloro-2-hydroxy-2,2-bis-(*p*-chlorophenyl)-ethane, 1.2%, 0.12 *N* hydrochloric acid was added to the base electrolyte to prevent a haloform-type reaction which occurs at higher *p*H values.

The capillary had a drop time of 7.7 sec. and a mercury flow rate of 0.588 mg./sec. at open circuit with a 60-cm. mercury head. These values were 3.4 sec. and 0.611 mg./sec., respectively, at −2.2 volts *vs.* the S.C.E. Polarographic constants reported are calculated from *m* and *t* values measured at the potential at which the diffusion current for the wave was measured.

The macro-reductions were done with a modified Lingane–Jones Potentiostat.[8,9] A one-pint mason jar served as the electrolysis vessel. About 40 ml. of mercury used in a pool served as the cathode. The anode was a 1/8 inch dia. silver wire formed into a closely wound flat spiral of about 2 inches dia. The jar screw-cap was punctured with suitable holes to admit: (1) the silver anode, (2) a mercury-filled glass tube with a platinum wire sealed in the tip for electrical contact with the cathode, (3) a degassing tube, (4) a motor-driven stirrer shaft and (5) the salt bridge from the reference cell. The surface of the pool was kept well agitated with a magnetic stirring bar. To avoid interference from potassium ions at control potentials above −2 volts, a 1.0 *M* tetramethylammonium chloride salt bridge was used between the electrolysis cell and the S.C.E. reference cell. The electrolysis solutions contained 2–4 g. of the reducible compound dissolved in 12.5% water and 87.5% 2B ethanol that was 0.5 *M* in tetramethylammonium chloride. Because of polarization of the anode from deposition of silver

---

(1) Presented at the 133rd A.C.S. National Meeting, San Francisco, Calif.

(2) (a) P. J. Elving, *Record Chem. Progr.*, **14**, 99 (1953); (b) S. Wawzonek, *Anal. Chem.*, **28**, 638 (1956); (c) **30**, 661 (1958).

(3) (a) I. M. Kolthoff, T. S. Lee, D. Stocesova and E. P. Parry, *ibid.*, **22**, 521 (1950); (b) I. Rosenthal, C. S. Tang and P. J. Elving, THIS JOURNAL, **74**, 6112 (1952).

(4) I. Rosenthal and P. J. Elving, *ibid.*, **73**, 1880 (1951).

(5) M. Von Stackelberg and M. Stracke, *Z. Elektrochem.*, **53**, 118 1949).

(6) Registered Trademark of the Rohm and Haas Co., Phila., Pa.

(7) Registered Trademark of the du Pont Chemical Co., Wilmington, Del.

(8) J. J. Lingane and S. L. Jones, *Anal. Chem.*, **22**, 1169 (1950).

(9) Private communication, J. J. Lingane to I. Rosenthal Dec. 5, 1956.

TABLE I

HALF-WAVE POTENTIALS AND DIFFUSION CURRENT CONSTANTS[a]

Compound	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV
Wave type[b]	$(ClC_6H_4\text{-}p)_2CHCCl_3$	$(ClC_6H_4\text{-}p)_2CHCHCl_2$	$(C_2H_5C_6H_4\text{-}p)_2CHCCl_3$	$(C_2H_5C_6H_4\text{-}p)_2CHCHCl_2$	$(CH_3OC_6H_4\text{-}p)_2CHCCl_3$	$(C_6H_4\text{-}p)_2CHCCl_3$	$(ClC_6H_4\text{-}p)_2COHCCl_3$	$(ClC_6H_4\text{-}p)_2COHCHCl_2$	$(ClC_6H_4\text{-}p)_2CClCCl_3$	$(ClC_6H_4\text{-}p)_2C{=}CCl_2$	$(ClC_6H_4\text{-}p)_2CClCHCl_2$	$(ClC_6H_4\text{-}p)_2C{=}CHCl$	$(ClC_6H_4\text{-}p)_2C{=}CH_2$	$ClC_6H_4\text{-}p\text{-}CHClCHCl_2$	$C_2H_5C_6H_4\text{-}p\ CHClCHCl_2$
A to B									(2.6) 0.00[e]						
B to C									↑	↑					
C to D									(8.0) 1.93	(7.7) 1.92	(4.7) 1.96	(5.2) 1.97		↑	↑
D to E									↓	↓[d]	↓[d]	↓[d]	(3.1) 2.05[d]	(6.2) 2.14	(6.4) 2.32
A′ to B′	(2.8) 0.93		(2.8) 1.09		(2.6) 0.98	(2.8) 1.09	(2.1) 0.93								
B′ to C′	(3.1) 2.32	(3.1) 2.31	(1.8) 2.40	(2.1) 2.41	(1.8) 2.40	(2.7) 2.42	(2.7) 2.16	(2.7) 2.21							
C′ to D′	(5.8) 2.64	(6.0) 2.65	[c]	[c]	[c]	[c]	(6.0) 2.64	(5.4) 2.66							
A″ to C											(2.0) +0.16[e]			(3.0) 1.61	(3.4) 1.70

[a] Potentials are negative and measured *vs.* the S.C.E. The numbers in parentheses are $i_d/Cm^{2/3}t^{1/6}$. [b] As shown in Fig. 1. [c] No wave before decomposition of supporting electrolyte. [d] Split wave probably due to reduction to free radical than to carbanion. [e] To avoid interference from mercury oxidation in chloride, this wave was measured in an electrolyte consisting of 7 parts alcohol, 2 parts water, 1 part 1.0 *M* KNO_3 adjusted to *p*H 1–1.5 with HNO_3.

chloride, this electrode was replaced with clean silver wire periodically during the electrolysis.

Reduction products were identified by infrared spectra obtained on a Perkin–Elmer model 21 spectrophotometer or on a Perkin–Elmer Infracord, elemental analysis and melting points.

With the exception of the du Pont product, Methoxychlor,[7] the compounds studied were prepared at the Rohm and Haas Co. Research Laboratories.

Results and Discussion

The results and interpretation of the experimental work are summarized in Fig. 1 and Table I and can be understood through the application of three principles: (1) The reduction of polyhalogenated compounds of the type $RCCl_3$ proceeds through the stepwise removal of halogens, ($RCCl_3 \rightarrow RCHCl_2 \rightarrow RCH_2Cl$), with the product of micro-reduction in the diffusion layer behaving at the dropping electrode as if the compound were present throughout the solution. (2) The reduction of vicinal halogens yields double bonds. (3) Contrary to chemical behavior, vinyl halogens of the type $C_6H_5CR{=}CCl_n$, (where R = C_6H_5 or H) are easier to reduce electrolytically than the corresponding saturated compounds and are reduced at lower potentials than those required for the reduction of the corresponding unsubstituted double bond. This is a new generalization yet to be tested on other series of compounds.

This last principle is the final link that enables us to tie together apparently unrelated data.

All the steps in Fig. 1 are treated as 2-electron steps. This has been done on the basis of the comparison of diffusion currents for the various steps or composite steps to that for DDT,[10] or on the identification of the products of macro-reduction at controlled potential.

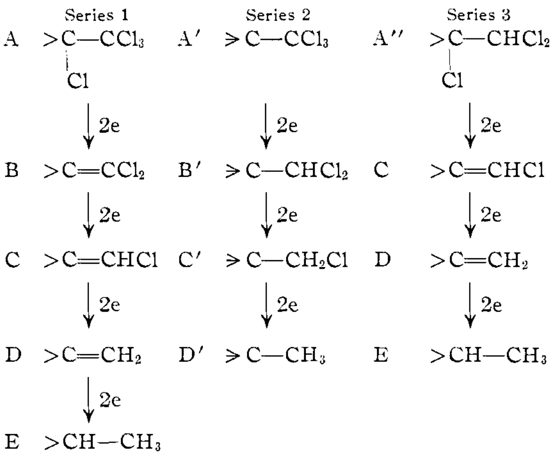

Fig. 1.—Reduction steps in aromatic chloroethanes.

In series 2, the reduction of A′ to B′, B′ to C′ and C′ to D′ are sufficiently separated on the potential scale so that relative wave heights are readily measured for each step. The ratio of the second wave to the first in DDT is essentially one. The first step has been identified as corresponding to the reduction of DDT to Rhothane.[10] The fact that the diffusion current constant for the third wave is almost twice as high as the first can be explained by the effect of the capillary characteristics on the diffusion current. The negative potential at which this wave is measured causes the drop time to fall to about one second. At this fast drop rate, sufficient stirring occurs at the drop to disturb the diffusion process. A few reduction waves in compounds related to DDT deviate more than expected from the 1:1 ratio with the corresponding DDT waves (Table I, *e.g.*, A′ to B′ in Kelthane, B′ to C′ in 1,1,1-trichloro-2,2-bis-(*p*-ethylphenyl)-ethane, Perthane and Methoxychlor).

Series 1 and 3, although similar in type to each other, are not superimposable and are treated separately. In series 1, wave A to B is separated

---

(10) I. Rosenthal, G. J. Frisone and R. J. Lacoste, *Anal. Chem.*, **29**, 1639 (1957).

from B to C. However, B to C is not clearly resolved from C to D and D to E. The ratio of currents for the composite wave B through E to that for A to B is 3 to 1 (Table I), which is consistent with the number of electrons involved in this reduction scheme. A similar situation also occurs in series 3 where the wave A″ to C is clearly resolved from wave C to D but C to D merges with D to E. In this case the ratio of currents is 2 to 1 for the second composite wave to the first wave A″ to C. In both series the composite waves show a slight splitting into component parts.

The evidence for this series of reduction steps is: (1) Macro-reduction at controlled potential of A yields B. (1,1,1,2-Tetrachloro-2,2-bis-(*p*-chlorophenyl)-ethane yields 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)-ethylene, 78% of theory isolated.) (2) Macro-reduction at controlled potential of B yields E. (1,1-Dichloro-2,2-bis-(*p*-chlorophenyl)-ethylene yields bis-(*p*-chlorophenyl)-ethane, 63% of theory isolated.) (3) Polarographic reduction of C yields a 4-electron composite wave. (4) Polarographic reduction of D gives a 2-electron wave. (5) Macro-reduction at controlled potential of A″ yields C. (1,1,2-Trichloro-2-(*p*-ethylphenyl)-ethane yields 1-chloro-2-(*p*-ethylphenyl)-ethylene, 75% of theory isolated.)

From macro-reduction at controlled potential it was demonstrated that A does not dimerize in the course of its reduction to E. The first two-electron step involves the formation of a double bond as shown by infrared examination and elemental analysis of the reduction product. The reduction of the unsaturated product, B, might proceed through: (1) the double bond and then the two chlorines, (2) both chlorines and then the double bond or (3) one chlorine, then the double bond followed by the last chlorine. In the first instance the intermediate product would be B′. This compound has its first wave (B′ to C′) close enough to that for the composite wave (B to E) so that one would not expect to be able to distinguish the alternatives purely on the basis of half-wave potentials. However, the next wave (C′ to D′)[11] is at a much more negative potential than the composite 6-electron wave experimentally observed for the reduction of B to E. Therefore, the reduction does not proceed through route (1). A similar type of reasoning excludes route (3) and, therefore, it is concluded that both chlorines must be reduced before the double bond. All of the compounds listed in Table I fit into one of the series listed in Fig. 1 and need no special discussion.

The mechanism of reduction for waves A to B and A′ to B′ has been considered in a series of papers by Elving and Rosenthal.[12] However, the reduction B to C presents a new situation for which there is not a great deal of data.

Stackelberg's[5] work on the reduction of vinyl bromide, −2.47 volts *vs.* S.C.E., and bromoethane, −2.08 volts *vs.* S.C.E., appears to be in contradiction to the postulated greater ease of reduction of vinyl halogens. Of course in the cases discussed in this paper the vinyl halogens are not of the simple type, but are conjugated with aromatic rings. Postulation of a mechanism of reduction must await the investigation of other vinyl halogens. However, it is of interest to point out that the carbon–halogen bond in vinyl compounds is a stronger bond than the corresponding saturated halogen and has considerable double bond character, with one resonance state involving a formally positively charged halogen.

It is interesting to note that in vicinal reduction, the lowering of the half-wave potential can be quite appreciable as compared to the corresponding stepwise reduction (note Table I compounds I and IX, and II and XI). This cannot be explained alone by the effect of the vicinal chlorine in reducing the electron density on the carbon in the 1-position of the ethylene, because the corresponding 2-substituted hydroxyl compounds VII and VIII have approximately the same reduction potentials as the parent compounds I and II. Vicinal reduction must then proceed by a mechanism that involves the removal of the vicinal halogens in the potential-determining step. This is additional evidence that the reduction of vicinal halogens involves the simultaneous removal of both halogens.

The influence of various structural changes on reduction potentials, such as replacing one of the phenyl groups by hydrogen, or a ring chlorine by an ethyl, methoxyl or hydrogen is apparent from the data given in Table I and needs no further elaboration. It should be pointed out, however, that only in the case of the *p,p′*-chlorine compounds can the wave for the step $-CH_2Cl \rightarrow -CH_3$ be observed since this wave is close to the base electrolyte discharge potential and, without the activation of the ring chlorine, it merges into the background.

Several analytical uses of practical importance can be developed based on the data presented here. An example is the analysis of DDT in Rhothane. The value of this type of general approach is that one can predict those mixtures which are susceptible to analysis by examination of the half-wave potential tables.

Acknowledgment.—The authors wish to acknowledge the work of various people who prepared these compounds with special thanks to H. F. Wilson and J. W. Nemec. Many of the experimental measurements were made by V. P. DeMarco.

PHILADELPHIA, PENNA.

---

[11] D′ is the same as E in this case.

[12] I. Rosenthal, J. R. Hayes, A. J. Martin and P. J. Elving, THIS JOURNAL, **80**, 3050 (1958) (see this paper for references to earlier work).