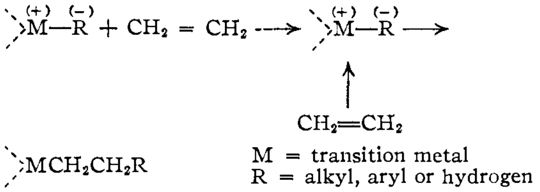
Although this reaction is written showing only one molecule of monomer coördinated to the transition metal, there may actually be two or more monomer molecules coördinated at one time. It is necessary



M = transition metal
R = alkyl, aryl or hydrogen

that the –R group be hydrogen or hydrocarbon rather than halogen, oxygen, etc., to provide a low energy initiation reaction (M–R bonds are weaker than metal–halogen bonds), for a low-temperature process. In this mechanism, transition metal valence plays an essential role. With all transition metals there is a decrease in the electronegativity of the metal center with a decrease in valence. For example, the electronegativity of vanadium changes from 1.8 for the pentavalent state to 1.2 for the divalent state,[30] and titanium changes from 1.6 for the tetravalent state to 1.1 for the divalent state.[31] With each unit reduction in valence one more orbital becomes half-filled by the addition of one electron. These two factors operate in opposite directions. The progressive filling of the transition metal orbitals with increasing reduction should decrease the electron-attracting power of the metal for olefins, but at the same time the decreasing electronegativity makes the C–M bond more polar so that any coördinated (polarized) monomer is more readily incorporated into the growing chain by the rearrangement reaction. Therefore, optimum catalytic activity would consist of a proper balance between these two features. Experimentally, the best catalytic activity is observed with the low transition metal valences, which suggests that a very polar C–M bond is essential. High valence transition metal compounds have electronegativities of 1.6–1.8 which is in the same range as aluminum; therefore, if these compounds are catalytic at all, the rate of propagation should be low, as it is with aluminum alkyls alone. In addition, the organic derivatives of transition metals in their higher valences are unstable and would readily decompose, thus causing molecular termination if the organic derivative were a growing polymer molecule. Higher transition metal valences, if active at all, should then give lower molecular weight polymer. The lowest valence transition metal compounds would be the most stable with little thermal decomposition and should make polymer of the highest molecular weight. This is in substantial agreement with experimental observations.[18]

There have been reports that traces of oxygen significantly accelerate the rate of ethylene polymerization with some of the organometallic mixed catalysts, and this fact has been interpreted by some investigators as suggesting that tetravalent titanium is necessary for catalytic activity in at least one case.[25] The authors also have observed that oxygen often increases the rate of polymerization and otherwise affects the behavior of soluble catalysts, such as those described in references 8 and 26; however, in the catalysts examined in this work there has been no indication that titanium or vanadium valences > 3 are catalytically active. Studies on oxygen cocatalysis are still in progress in this group, and the data will be reported later.

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(30) M. Haissinsky, *J. Phys. Radium*, **7**, 7 (1946).

(31) T. L. Allen, *J. Chem. Phys.*, **26**, 1644 (1957).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OCCIDENTAL COLLEGE, LOS ANGELES 41, CALIF.]

Polarography of Organic Halogen Compounds. I. Steric Hindrance and the Half-wave Potential in Alicyclic and Aliphatic Halides[1,2]

BY FRANK L. LAMBERT AND KUNIO KOBAYASHI

RECEIVED APRIL 25, 1960

Alkyl and cycloalkyl bromides yield well-defined waves at the dropping mercury electrode with tetraethylammonium bromide as the supporting electrolyte in N,N-dimethylformamide. Qualitative correlation of the half-wave potentials with S_N reactivity is present in the classic series of alkyl halides substituted at the carbon atoms alpha and beta to the halogen, as well as in the cyclic halides. Although the rate-determining step may involve transfer of a single electron, the results indicate that the reductive process can be likened to a nucleophilic substitution with noteworthy steric effects caused both by the bulk of the "attacking group" (the electrode) and by steric requirements of groups in the halide being reduced. The strong negative field of the electrode may be important both in orienting the halide as it approaches the electrode and in forcing an S_N1 type of electroreduction in *t*-butyl bromide.

Introduction

Most qualitative and semi-quantitative interpretations of the significance of the half-wave potential in organic polarography have been concerned with correlating electronic effects in a series of related organic molecules with the $\Delta E_{1/2}$ between members of the series.[3] The importance of steric factors in the reduction of organic substances at a dropping mercury electrode has been given relatively little attention.[2,4] Indeed, in the cases cited of steric influence on the half-wave potential, the majority

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[1] (a) This work was initiated by a Research Corporation grant. A portion is abstracted from the M.A. thesis of K. K. The Research was completed at the California Institute of Technology while F. L. L. was a Science Faculty Fellow of the National Science Foundation, 1957–1958.

[2] For a preliminary report of part of the work, see *Chemistry & Industry*, 949 (1958).

[3] (a) *Cf.* the review of P. Zuman, *Chem. Listy*, **48**, 94 (1954), especially pp. 97–114 and 124–135; (b) more modern work in ref. 2, footnote 1.

[4] P. Zuman, ref. 3a, pp. 115–121, and in *Chem. Listy*, **53**, 154 (1959), points out several examples of steric effects not explicitly stated, or overlooked by the original investigators.

involve steric interference with transmission of electronic effects from one portion of the molecule to the π-bond being reduced.

For example, in *o,o'*-disubstituted acetophenones or similarly disubstituted nitro compounds[5] the cause of the change in $E_{1/2}$ when the structure of the unhindered compound is altered by adding substituents lies in interference by the substituent with coplanarity, and thus with resonance or normal low energy molecular orbitals. Accordingly, the energy required to add an electron to the lowest unoccupied molecular orbital is greater for a substituted and sterically hindered compound than for the unsubstituted reducible substance, *i.e.*, $|E_{1/2}$ hindered$| > |E_{1/2}$ unsubstituted$|$.

Compounds such as the alkyl monohalides, in which a σ-bond is broken in the reduction process, frequently are reduced at more negative potentials than substances in which a π-bond is being reduced. Thus, research on the former class is more difficult experimentally and relatively few investigations have been made.[6]

Much of the pioneer work on reduction of halogenated aliphatic compounds has been concerned with the effect of *p*H on the $E_{1/2}$ in haloacids or with reduction of compounds containing groups capable of electronic interaction with the halogen being reduced or the electrode.[7] Because such electronic influences may cloud the picture of steric effects in the reduction potential, the simple alkyl and cycloalkyl halide compounds were chosen in this investigation as the key substances in investigating the possible relationship between $E_{1/2}$ and steric factors.

Experimental

General.—After extensive work with methanol- and ethanol-water solvent systems, anhydrous N,N-dimethylformamide (DMF) was proved to be a superior polarographic solvent for the reduction of organic halides.[8]

In DMF, tetrabutylammonium iodide gives polarographic waves of organic halides with extremely smooth envelopes due to regular current surges with each drop. Tetraethylammonium bromide (TEB) in DMF with halogen compounds yields polarographic records with slightly less regular current surges but steeper steps for the polarographic waves. After discovery of the reduction of chlorobenzene in TEB but not in tetrabutylammonium iodide,[9] all compounds were redetermined in TEB.

Materials.—Reagent N,N-dimethylformamide (Matheson, Coleman and Bell or Eastman Kodak Co.) was distilled through a glass-helix packed column and the mid-fraction used.

All halides were Eastman Kodak Co. white label products except decyl bromide (Sapon Laboratories), 3,5,5-trimethylhexyl bromide (Halogen Chemicals Co.), cyclopentyl bromide (Michigan Chemical Co.) and cycloheptyl bromide (Columbia Organic Chemicals). Neopentyl bromide was prepared according to Sommer and co-workers.[10] Cyclobutyl bromide was made by the procedure of Roberts and Chambers.[11] Cyclopropyl bromide was a generous gift of Professor John D. Roberts.[11]

Apparatus.—High purity nitrogen (Linde Air Products) was saturated with DMF and passed into the polarographic cell which was immersed in a water-bath controlled at a temperature of 25 ± 0.1°.

A most satisfactory cell design proved to be similar to that of Kolthoff and Coetzee[12] wherein a side tube was sealed into a simple cylindrical vessel of 35-cc. capacity made from a male 34/28 ₸ glass joint. The side tube was large enough to admit the leg of a conventional saturated calomel electrode (S.C.E.). The capillary characteristics were m = 1.20 mg. per second and t = 4.9 seconds for an open circuit with the electrode immersed in 0.01 M TEB in DMF at a pressure of 66.1 cm.

A Leeds and Northrup type E Electro-Chemograph was employed throughout. The resistance of the cell circuit was checked before and after each run with an Industrial Instruments model RC conductivity bridge. Resistances of the order of 10,000 ohms were encountered and all results were corrected for iR drop. (Concordant results were obtained by simple iR correction even in runs when the resistance was as high as 36,000 ohms.)

Procedure.—Twenty-five ml. of 0.01 M TEB in DMF was pipetted into the polarographic cell, the cell body was attached to the cap on the dropping mercury assembly, and the S.C.E. slipped into the side arm of the cell body. After the assembly had been lowered into the constant temperature bath, nitrogen was passed into the supporting electrolyte solution until oxygen had been removed. Approximately 0.1-ml. portions of a 0.04 M solution of the alkyl halide in DMF were added and the solution electrolyzed under a nitrogen atmosphere. The potentials reported are corrected for iR drop. Subsequent runs with the same solutions under the same conditions were reproducible to ±0.005 volt. Other workers using reagents and apparatus prepared by them obtained results ±0.01 volt of the values reported here. Because some reducible material diffused from the cell body to the side arm during a series of reductions, i_d/c values are not precise. However, they all were of the order of 5 to 6 μa./millimole.

In the non-aqueous solvent used, no pre- or post-waves or maxima were observed with low concentrations of organic halides, probably because of the absence of adsorption effects. The waves were highly irreversible, diffusion controlled and consisted of single steps.

Results

The results of reduction of some halides at the dropping mercury electrode are presented in Table I.

Summary

In the reductive process for alkyl halides it is generally accepted that the rate- and potential-determining step occurs in the first or the first two of the processes[13]

$$\text{R-X} + \text{e} \longrightarrow (\text{R}\dot{-}\text{X})^- \longrightarrow \text{R}^{\cdot} + \text{X}^- \qquad (1)$$

$$\text{R}^{\cdot} + \text{e} \longrightarrow \text{R}:^- \qquad (2)$$

$$\text{R}:^- + \text{H-solvent} \longrightarrow \text{RH} + \text{solvent}^- \qquad (3)$$

From Table I it can be seen clearly that steric hindrance to SN2 reaction in the classic β-substituted series of ethyl, propyl, isobutyl and neopentyl bromides is qualitatively reflected in the polarographic reduction potentials of −2.13, −2.20, −2.32 and −2.37 volts, respectively. The $E_{1/2}$'s of the compounds in the α-substituted series, ethyl (−2.13), isopropyl (−2.26) and *t*-butyl bromides (−2.19) are also in qualitative accord with well-

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(5) Ch. Prevost, P. Souchay and Ch. Malen, *Bull. soc. chim. France*. 78 (1953).

(6) (a) *Cf.* I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. II, 2nd ed., Interscience Publishers, Inc., New York, N. Y., 1952, Chap. 38; (b) other references in ref. 1 of P. J. Elving and C.-S. Tang, THIS JOURNAL, **74**, 6109 (1952).

(7) (a) E. Saito, *Bull. soc. chim. France*, 404 (1948); (b) P. J. Elving and C.-S. Tang, THIS JOURNAL, **72**, 3244 (1950), and later papers in the series by Elving and co-workers; especially pertinent to this paper are: (c) I. Rosenthal, C. H. Albright and P. J. Elving, *J. Electrochem. Soc.*, **99**, 227 (1952); (d) P. J. Elving, *Record Chem. Progr.* (*Kresge-Hooker Sci. Lib.*), **14**, 99 (1953); (e) P. J. Elving, J. M. Markowitz and I. Rosenthal, *J. Electrochem. Soc.*, **101**, 195 (1954); (f) P. J. Elving and J. T. Leone, THIS JOURNAL, **79**, 1546 (1957).

(8) F. L. Lambert, *Anal. Chem.*, **30**, 1018 (1958).

(9) F. L. Lambert and K. Kobayashi, *J. Org. Chem.*, **23**, 773 (1958).

(10) L. H. Sommer, H. D. Blankman and P. C. Miller, THIS JOURNAL, **73**, 3542 (1951).

(11) J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 3176 (1951).

(12) I. M. Kolthoff and J. F. Coetzee, *ibid.*, **79**, 870 (1957).

(13) N. S. Hush, *Z. Elektrochem.*, **61**, 734 (1957).

TABLE I

HALF-WAVE POTENTIALS OF ALKYL AND CYCLOALKYL BROMIDES

Bromide[a]	$E_{1/2}$[b]	Relative substitution rate constants[h] RBr + LiI in acetone	RBr + NaSCN in alcohol[g]
Ethyl	-2.13[c]	100[d]	100
Propyl	-2.20[c]	82[d]	69
Butyl	-2.23[c]		68
Amyl	-2.26[c]		72
Hexyl	-2.26[c]		73
Decyl	-2.28[c]		74
i-Butyl	-2.32	3.6[d]	3
Neopentyl	-2.37	0.0012[d]	
i-Propyl	-2.26[c]	0.78[d,f]	
t-Butyl	-2.19		
3,5,5-Trimethylhexyl	-2.31		
Cyclopropyl	-2.36	$<1 \times 10^{-5}$	
Cyclobutyl	-2.36	0.0059[f]	
Cyclopentyl	-2.19	1.25[f]	
Cyclohexyl	-2.29	0.0078[f]	
Cycloheptyl	-2.27	0.76[f]	

[a] Halide concentration of 1-2 × $10^{-4}M$ in anhydrous N,N-dimethylformamide with 0.01 M tetraethylammonium bromide as supporting electrolyte. [b] In volts *vs.* the S.C.E. and corrected for iR drop in the cell; results are reproducible to ±0.01 volt. [c] Ref. 2; these values are preferred to those of ref. 2. [d] L. Fowden, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 3187 (1955). [e] Ref. 11 states no reaction at 100°. [f] P. F. C. Fierens and P. Verschelden, *Bull. soc. chim. Belges*, 61, 427 (1952). [g] T. I. Crowell. THIS JOURNAL, **75**, 6046 (1953). [h] At 25° or adjusted to 25°.

known substitution studies where a change in mechanism and rate is found between isopropyl and *t*-butyl bromide. An unexpected variation of $E_{1/2}$ with chain length, which is not reflected in the rate of conventional substitution reactions, is disclosed in the unbranched alkyl halides.[14]

Good qualitative correlation between SN2 reactivity and the polarographic half-wave potential can be seen in the cycloalkyl halides. Certainly the alternating effect both in displacement reactivity and the $E_{1/2}$'s of the cyclic compounds in Table I is strong indication of the importance of steric effects in polarographic reductions.[15,16] (The $\Delta E_{1/2}$ between cyclohexyl and cycloheptyl bromides is small but significant because no value more negative than -2.27 has been obtained for cycloheptyl reduction and no value more positive than -2.29 for cyclohexyl reduction.)

Discussion

We believe that our results with these organic halides are best explained by emphasis on two aspects of the polarographic process: (1) The effect of the strong negative electrical field surrounding the mercury drop prior to and during the reduction; and (2) the great bulk of the portion of the mercury drop which is responsible for actual electron transfer to the new orbital being formed in the potential-determining step.

Considering these two aspects in some detail, we believe with Elving[7c,d,f] that the strong potential gradient near the surface of the mercury drop causes the organic halide to approach the mercury surface with the halogen atom away from the drop. Thus, the reactive site, the backside of the carbon holding the halogen, is in favorable position for accepting electrons unless sterically important groups are interposed. We would emphasize the latter factor in the analysis of our results. In addition, a large field effect should aid alkyl halide dissociation at all potentials.

The mercury drop, source of electrons for the reduction, is far more bulky than the usual nucleophilic attacking entities. This is true whether the portion of the drop which is acting in the electron transfer to the organic molecule is a major segment of the drop or a small group of mercury atoms with a high concentration of electrons, perhaps analogous in appearance to a solar flare on the sun, or a volume element of the charged double layer surrounding the drop. Because an essential step in electroreduction must be overlap of the bulky electron source with the anti-bonding sigma orbital of the carbon and because the alkyl halide approaches the mercury drop with the backside of its reaction-susceptible carbon, steric interference by substituents near the reaction site should be more prominent than in conventional displacement reactions.

Straight Chain Halides.—As has been noted briefly,[2] polarographic reduction of the simple straight chain alkyl halides is made more difficult by an increase in chain length. That the greater difficulty of reaction is not parallel to normal substitution rates is clear from Table I; SN2 rates decrease markedly in going from ethyl to propyl but remain approximately the same for higher homologs. In contrast, the increase in polarographic reduction potentials between ethyl and propyl bromides is continued to a lesser but very significant degree between propyl and butyl.

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(14) In their extensive exploratory work M. von Stackelberg and W. Stracke, *Z. Elektrochem.*, **53**, 118 (1949), chose only methyl, ethyl, butyl and octyl as straight chain bromides for investigation and therefore did not notice the details of $\Delta E_{1/2}$ revealed by propyl, amyl and hexyl bromides.

(15) E. L. Eliel in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. *121ff.*

(16) Admittedly, rates of cyclic free radical SH1[15] displacements would follow the same order [C. G. Overberger, H. Diletch, A. B. Finestone, J. Lilker and J. Herbert, THIS JOURNAL, **75**, 2078 (1953)]. However, the $E_{1/2}$'s of our acyclic halides bear no relationship to the SH1 rates determined by Overberger, *et al.*, on similar alkyl azo compounds [C. G. Overberger, W. F. Hale, M. B. Berenbaum and A. B. Finestone, THIS JOURNAL, **76**, 6185 (1954)]. In addition, the reactivities of alkyl chlorides toward sodium vapor in an SH1 type of reaction [N. Meer and M. Polanyi, *Z. physik. Chem.*, **19**, 164 (1932)] are not related to our $E_{1/2}$'s in chain lengthening, branching or substitution. Evans and Hush [(*J. chim. phys.*, **49**, 158 (1952)] describe a linear correlation between $E_{1/2}$ (from ref. 14) and the energy of activation for sodium flame reactions of polyhalides and methyl and ethyl bromides but no more complex monohalides. Accordingly, we conclude that polarographic reductions of alkyl monohalides in solution are not to be related to free radical reactions of the SH1 class.

Although an electroreduction may physically follow a path which is an SH2 free radical displacement wherein a single electron is transferred in the rate-determining step [(*Cf.* S. Wawzonek, E. W. Blaha, R. Berkey and M. E. Runner, *J. Electrochem. Soc.*, **102**, 235 (1955)], such organic halide reductions are most profitably compared with nucleophilic substitution processes and reactivites. There is no extensive body of work on SH2 reactions.

The dropping mercury electrode is a negatively charged attacker forming $(\mathrm{R} \mathbin{\dot{-}} \mathrm{X})^{-} \rightarrow \mathrm{R}^{\cdot} + \mathrm{X}^{-}$, and the $\mathrm{R}^{\cdot}$ immediately adds another electron to form a carbanion. The similarity to a nucleophilic substitution is great enough to commend the association-filled symbols of SN2- or SN1-electroreduction for purposes of discussion, although SH2 and SH1′ migbt be more nearly correct.

and butyl and amyl bromides.[17] This polarographic behavior can be understood on the basis of the two principles emphasized above. Lengthening the chain of an alkyl halide beyond propyl does not greatly interfere with the approach of a small nucleophile such as SCN$^-$ to the reaction site in ordinary displacements. Initial attack can be made from many angles and the nucleophile can force its way past the loose screen of methylene groups in several ways providing that the final approach is from the rear of the carbon holding the halogen. In polarographic reduction, on the other hand, interposition of methylene groups or a methyl group between the large mercury drop and the reactive site should cause increasingly difficult reduction until the reactive site is effectively covered by normal thermal agitation of the alkyl chain, *i.e.*, when the chain is 5 to 6 atoms long. From amyl or hexyl bromide to chains of many carbons no major change in $E_{1/2}$ should occur.

It might be proposed that the $\Delta E_{1/2}$ with increasing chain length can be explained better by stating that the principal effect of lengthening the alkyl chain is simply to keep the halogen of the RBr farther from the electrode, rather than to shield the reactive site on the carbon. Thus, the general field effect near the drop (as contrasted with the specific overlap of electrons from a portion of the mercury drop with the reactive backside) aiding dissociation of the carbon–halogen bond would be lessened and a greater negative potential would be required before the general negative field plus the specific "attacking mercury-drop site" are effective in causing electroreduction. However, the main cause of the chain length–$E_{1/2}$ relationship must be interference by the chain with specific overlap rather than decreased force by the general negative field on R–Br dissociation because otherwise an appreciable increase in $E_{1/2}$ should be detected in going from hexyl to decyl bromides. This conclusion does not deny the importance of the electrode's general electrical field in electroreduction, but merely defines its secondary role in these straight chain compounds. Where B-strain is present to weaken the R–Br bond (*cf.* S_N1 electroreductions such as *t*-butyl bromide and the α-bromoacids[7,c,d,e] or at extremely negative potentials (*cf.* neopentyl bromide), the effect of the general negative field of the electrode should be a dominant factor in reduction at the dropping mercury electrode.

β-Substituted Halides.—Excellent correlation between $E_{1/2}$ and S_N2 reactivity is seen in the well-known β-substituted alkyl halides. The $\Delta E_{1/2}$ between isobutyl and neopentyl bromides is somewhat smaller than might be expected on the basis of the enormous difference in S_N2 rates. It may be accounted for by the field effect of the electrons on the mercury drop at this very negative potential. Expulsion of the bromine atom as bromide should certainly be aided by the extremely strong field (at -2.37 volts) in the region of the bond under attack by electrons from the mercury drop. Proof that branching of the chain *per se* or adsorption related to such branching is not responsible for increasing the difficulty of polarographic reduction is given by the $E_{1/2}$ of 3,5,5-trimethylhexyl bromide, -2.31 volts. Here the large neopentyl group and a methyl group both on the β-carbon to the bromine are merely equivalent to two methyl groups on the β-carbon, as in isobutyl bromide ($E_{1/2}$ of -2.32 volts). However, when the neopentyl group is immediately adjacent to the bromine, *i.e.*, in neopentyl bromide itself, reduction does not occur until -2.37 volts.

α-Substituted Halides.—In the α-substituted series of ethyl, isopropyl and *t*-butyl bromides B-strain in the *t*-butyl bromide helps to effect the reduction at a less negative potential, again in qualitative accord with results from conventional displacement studies. We believe the change in displacement mechanism from S_N2 to S_N1 is amply indicated here in the polarographic reduction process. The tendency of *t*-butyl bromide to react by an S_N1 mechanism would be aided by the field of the mercury drop and by the change in potential between the layer of positive tetraethylammonium ions and the drop surface. Any quantitative discrepancy between $E_{1/2}$ series and substitution rates may lie in the relatively poor solvolytic power of N,N-dimethylformamide as compared to the usual solvents used in S_N1 displacement investigations.[18]

The compelling influence of steric factors on polarographic reduction is shown by the $E_{1/2}$ and S_N2 relationships of isopropyl and isobutyl bromides. In the conventional S_N2 displacement reaction, polar effects in isopropyl bromide contribute to the activation energy of such a reaction[19] and decrease its rate compared to isobutyl bromide in reaction with I$^-$ even though steric requirements may be somewhat greater for isobutyl bromide in the reaction.[20] The higher $E_{1/2}$ for isobutyl than for isopropyl bromide (-2.32 *vs.* -2.26) indicates that polar effects of this magnitude are overruled in electroreduction by steric requirements.

Cycloalkyl Halides.—Examination of the correlation of cycloalkyl halide $E_{1/2}$'s with substitution rates yields useful conclusions. The $E_{1/2}$ of cyclopentyl bromide is equal to propyl bromide whereas its S_N2 reactivity compares with isopropyl bromide, approximately 0.02 to 0.01 that of propyl bromide. On the other hand, both the $E_{1/2}$ and the S_N2 reactivity of cycloheptyl and isopropyl bromides are respectively comparable. The reason for the ready reduction of cyclopentyl bromide cannot lie simply in the openness of the backside of its reactive site if the bromine atom is in its normal position; isopropyl bromide is more open to a *large* attacking group. Polar effects are of the same order in isopropyl and cyclopentyl bromides. However, from consideration of the molecular models it can be deduced[21] that (1) the

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(17) It should be recalled that 0.10 volt is equivalent to 4.6 kcal. per mole for a two-electron reduction.

(18) E. M. Kosower, THIS JOURNAL, **80**, 3253 (1958).

(19) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 409..

(20) *Ibid.*, p. 405.

(21) The reactive backside of cycloheptyl bromide is completely blocked to access of a large attacking group when the bromine lies in an equatorial conformation. The polarographic reduction of cycloheptyl bromide, involving attack by the bulky electrode, could occur more readily than neopentyl bromide, for example, if the bromine is forced toward an axial position just prior to or during overlap of the effective

bromine in cyclopentyl bromide must be forced toward an axial position prior to or during overlap of the electrode electrons with the σ^* C–Br bond; and (2) the overlap is the potential-determining step in transition state attainment because of the cycloalkyl halides tested, only in cyclopentyl bromide with bromine forced by the negative electrode into an axial conformation is the backside of the reactive carbon as free as in propyl bromide.[22]

The potential-determining step in polarographic reductions of the S_N2 type can be ascribed to the steric requirements of initial overlap rather than steric requirements of a transition state with a planar central carbon atom coördinated with the mercury drop and a departing bromine. The latter state should certainly necessitate as stringent steric conditions as in S_N2 displacements. Yet, the $E_{1/2}$ of cyclopentyl bromide is markedly less negative than that of isopropyl bromide and of cycloheptyl bromide, although the S_N2 reactivity of the three compounds is of the same order, and cyclohexyl bromide is reduced strikingly more easily than cyclobutyl bromide, even though their S_N2 reactivity is quite similar.

The nearly equivalent ease of reduction of cyclopropyl bromide and neopentyl bromide mav be an example of anchimeric assistance in polarographic reduction. Overlap of the portion of mercury drop effective in reduction with the delocalized electrons of the cyclopropane ring could force cross-ring overlap with the reactive site. Displacement by an "S_Ni" process would be thereby aided.

Of course the cautions of Delahay[23] regarding facile correlation of the half-wave potentials of irreversible reduction processes with a polar or steric parameter must be borne in mind. This is especially true of the correlations which have been drawn in the last section of this discussion. However, the high degree of irreversibility of the reduction of RX compounds, and the striking correlation of half-wave potentials with steric factors in the classic series of substituted alkyl halides despite probable slight variation in α, the transfer coefficient, at least indicate that the interpretations given in the latter section may be worthy of consideration, although by no means constituting proof.

Polarographic investigation is continuing in the areas of sterically hindered halogen compounds and of anchimeric effects aided by the field of the dropping mercury electrode.

Acknowledgment.—We are indebted to Dr. Richard E. Robertson for helpful discussions of molecular orbital processes at the dropping mercury electrode.

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portion of the mercury drop with the σ^*-orbital of the halogen compound. Then steric interference of neighboring hydrogens with σ^*-overlap would be comparable to that present in the isopropyl bromide. Movement of bromine to an axial conformation can occur relatively readily in cyclopentyl bromide. Forcing the bromine to an axial position by the electrode process would take place only with much greater difficulty in the other cyclic halides of this work.

(22) Flanking methyl groups with closely contiguous hydrogens are present in isopropyl bromide. Hydrogen atoms on β- and γ-methylene groups obscure the backside of the C–Br in cycloheptyl bromide even when the bromine is axial. I-strain and other conformation and polar effects should affect the $E_{1/2}$ of cyclopentyl and cycloheptyl bromides equally.

(23) T. Berzins and P. Delahay, THIS JOURNAL, **75**, 5716 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN 1, N. Y.]

Intramolecular Carboxylate Attack on Ester Groups. The Hydrolysis of Substituted Phenyl Acid Succinates and Phenyl Acid Glutarates[1]

BY ERICK GAETJENS[2] AND HERBERT MORAWETZ

RECEIVED APRIL 6, 1960

The anions of phenyl acid succinate and phenyl acid glutarate are hydrolyzed by a unimolecular mechanism involving an attack of the neighboring carboxylate on the ester function. This reaction is very fast compared to the acetate ion catalyzed hydrolysis of phenyl esters. Reaction rates of these compounds and of 20 substituted phenyl esters were determined. The rate was found to be unusually sensitive to electron-withdrawing *para* substituents. Thus, *p*-nitrophenyl glutarate reacted 540 times as fast as phenyl glutarate, while the analogous intermolecular reactions, the acetate-catalyzed hydrolysis of nitrophenyl acetate and phenyl acetate, had rates differing by a factor of only 15. The high substituent sensitivity of the intramolecular reaction is due almost entirely to variations in the *entropy* of activation. The ionization constants of substituted phenols behave in a strikingly similar manner. The observations are interpreted by assuming that the intermolecular carboxylate attack on phenyl esters leads to a tetrahedrally bonded reaction intermediate, while the intramolecular reaction involves a direct displacement of the phenoxide by the attacking carboxylate. The reaction is 120–200 times as fast with succinates than with the corresponding glutarates. Chloro, bromo, methoxy and acetamido substitution leads to higher rates when the substituent is *ortho* rather than *para*, while methyl and carbomethoxy substituents in the *ortho* position give lower rates. The substituent sensitivies of hydrolytic reactions of substituted phenol derivatives are compared for inter- and intramolecular attack of the nucleophile and for a number of related enzymatic reactions.

Introduction

Phenyl esters carrying carboxyl groups at a suitable spacing to the ester function may be hydrolyzed at an unusually rapid rate because of a nucleophilic attack of the ionized carboxyl on the ester carbon.[3–7] Since under favorable conditions the effect of the carboxylate attack is very much

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[1] We are indebted for financial support of this investigation to the Upjohn Co., the Eli Lilly Co. and the National Institutes of Health.

[2] Abstracted from a Ph.D. thesis to be submitted by E. Gaetjens to the Graduate School, Polytechnic Institute of Brooklyn, in June, 1961.

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