Electrolyte Effects upon the Polarographic Reduction of Alkyl Halides in Dimethyl Sulfoxide

Albert J. Fry* and Richard L. Krieger

Hall-Atwater Laboratory of Chemistry, Wesleyan University, Middletown, Connecticut 06457

Received August 8, 1975

The polarographic half-wave potentials of a variety of alkyl halides are shown to be sensitive to the nature of cation of the supporting electrolyte. As the size of the tetraalkylammonium cation increases, the polarographic wave moves to more negative potentials. Because this change can be very substantial, polarographic waves are not observable at all for some halides when large electrolyte cations are employed; it is suggested that this phenomenon may be of analytical and synthetic value. The phenomenon is due in part to a decrease in the rate constant for electron transfer as the electrolyte cation increases in size; this was shown by measurements of a number of such rate constants.

A number of studies have demonstrated that the polarographic behavior of alkyl halides is dependent upon the experimental conditions employed, and one of the significant variables is known to be the nature of the supporting electrolyte.[1] Our interest in this problem was aroused as a result of investigations into the polarographic behavior of *trans*-15,16-dimethyldihydropyrene (DMDHP) and other aromatic compounds,[2] and of cyclooctatetraene (COT).[3] We observed[2] that the spacing between the two polarographic waves of DMDHP, 9,10-diphenylanthracene, and pyrene was dependent upon the nature of the supporting electrolyte, and, with others, we interpreted[2,3] the observed changes as being associated with ion pairing between the electrolyte cation and the aromatic radical anion and dianion, particularly the latter. We observed, however, a different phenomenon with COT.[3] While the same ion-pairing effects appear to operate, and indeed even dominate the observed polarographic behavior of COT, we also noted, using ac polarography, that the relative *rates* of electron transfer to COT appear to depend upon the nature of the R group in the tetraalkylammonium ion $R_4N^+X^-$ used as electrolyte: as R increased from methyl through heptyl, electron transfer to COT became progressively slower as shown by increasingly irreversible appearance of the ac (and dc) polarograms. We theorized[3] that the same effect may be operating with aromatic hydrocarbons, but would be experimentally unobservable because of the intrinsically high rates of electron transfer to these substances. On the other hand, employing the same reasoning, electrolyte effects ought to be pronounced in the case of cathodic processes in which electron transfer is very slow. One prominent class of compounds for which the latter requirement is met is that of alkyl halides, for which electron transfer is totally irreversible by all of the common criteria.[4] With this in mind, we carried out a study of the dependence of the polarographic behavior of a number of alkyl halides (comprising a variety of structural types) on the nature of the supporting electrolyte. Of particular interest was the question whether rates of heterogeneous electron transfer to alkyl halides are affected by the electrolyte, and, if so, the magnitude of this effect. The results of that study, described herein, promise to be of synthetic and analytical interest.

Experimental Section

Polarograms were measured using an all-glass jacketed cell (J. R. Tacussel Co.) and a Princeton Applied Research Model 170 electrochemistry system. The reference electrode was a saturated calomel electrode with porous Vycor barrier to prevent solvent flow into the reference.

The solvent reagent grade dimethyl sulfoxide (Matheson Coleman and Bell) was used without further purification. Supporting electrolytes were dried, after the indicated purification, in an Abderhalden drying pistol for 6–10 hr at 100° and 2 mm pressure.

A. Tetramethylammonium Hexafluorophosphate (Me_4NPF_6 or TMAHP). Tetramethylammonium hexafluorophosphate (Ozark-Mahoning Co.) was used without further purification.

B. Tetraethylammonium Bromide (Et_4NBr or TEAB). Tetraethylammonium bromide (5.7 mmol, Aldrich Chemical Co.) was dissolved in 36 ml of ethanol and recrystallized by slow addition of 108 ml of anhydrous ethyl ether. The precipitate was filtered under vacuum and dried as indicated above.

C. Tetra-*n*-propylammonium Tetrafluoroborate (*n*-Pr_4NBF_4 or TPAFB). Tetra-*n*-propylammonium tetrafluoroborate (Ozark-Mahoning Co.) was used without further purification.

D. Tetra-*n*-butylammonium Perchlorate (Bu_4NClO_4 or TBAP). Tetra-*n*-butylammonium perchlorate (Matheson Coleman and Bell) was used as supplied.

E. Tetra-*n*-heptylammonium Iodide (THpAI or Hp_4NI). Tetra-*n*-heptylammonium iodide (Eastman Organic Chemicals) was purified by the same procedure used for TEAB.

The dried salts were stored in a vacuum desiccator over phosphorus pentoxide.

Except where noted, the electroactive substances to be examined by polarography were purchased from commercial sources and used without further purification. 1-Iodo-1-chloroneopentane (**2**) was prepared by a published procedure; 1-bromonorbornane (**1**) was supplied by Professor J. W. Sease, who had obtained it from Professor K. B. Wiberg; 1,1-dichloroneopentane (**3**) was prepared by the procedure below. Except for diphenylanthracene, used as a saturated solution in Me_2SO, and 1-iodo-1-chloroneopentane (used as a 0.5 stock solution in Me_2SO), stock solutions of all compounds were 1.0 *M* in decane. After the polarographic background had been recorded, a quantity of the stock solution sufficient to afford a final concentration of 0.001 *M* was injected into the polarographic cell, and the polarogram was then recorded.

Synthesis of 1,1-Dichloro-2,2-dimethylpropane (3). A finely powdered suspension of 69.4 g (0.33 mol) of phosphorus pentachloride in 200 ml of carbon tetrachloride was cooled to −10°C. A solution of 35 ml of freshly distilled pivalaldehyde in 15 ml of carbon tetrachloride was then added dropwise to the cold, vigorously stirred suspension. The system was maintained under nitrogen throughout. The reaction mixture was carefully poured onto crushed ice, washed several times with water, and finally neutralized with aqueous potassium carbonate and dried over anhydrous magnesium sulfate. After the carbon tetrachloride was removed by distillation, the crude product was obtained in 87% yield. NMR spectroscopy showed this material to contain a substantial quantity of rearranged dichloride (2,3-dichloro-2-methylbutane). Pure 1,1-dichloroneopentane was obtained by vacuum distillation (60–67°, 127 mm) and then preparative gas chromatography (20 ft × 0.25 in. column packed with 10% Carbowax 20M on Chromosorb Pat 135°). The NMR spectrum consisted of two singlets at τ 4.5 and 8.9, relative areas 1:9, respectively.

Results and Discussion

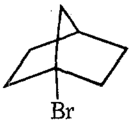
The polarographic reduction of the following 16 organic compounds, 14 of them organic halogen compounds, was studied in dimethyl sulfoxide (Me_2SO) in the presence of up to five different quaternary ammonium salts as supporting electrolytes: *n*-pentyl bromide; isobutyl bromide; neo-

Table I
Electrolyte Effects on the Polarographic Half-Wave Potentials of Some Organic Compounds

			$-E_{1/2}$, V[a]				
Registry no.	Electroactive substance	R (in R_4N^+)	Me[b]	Et[c]	*n*-Pr[d]	*n*-Bu[e]	$\Delta E_{1/2}$, V[f]
110-53-2	*n*-Pentyl bromide		2.09	2.21	2.34	2.56	0.47
78-77-3	Isobutyl bromide		2.14	2.28	2.51	2.65	0.51
630-17-1	Neopentyl bromide		2.23	*g*	2.58	>2.8[h]	≥0.6
39927-70-3	*sec*-Pentyl bromide		2.12	2.27	2.41	2.53	0.41
507-19-7	*tert*-Butyl bromide	E_1	1.91	1.94	1.99	2.08	0.17
		E_2	2.18	2.28	2.39	2.46	0.28
106-93-4	1,2-Dibromoethane		1.35	*g*	*g*	1.47	0.12
13474-70-9	1-Bromonorbornane		2.38	>2.6[h]	>2.7[h]	>2.8[h]	≥0.5
108-86-1	Bromobenzene		2.07	2.23	2.45	2.58	0.51
99-90-1	*p*-Bromoacetophenone	E_1	1.60	*g*	*g*	1.60	0
		E_2	1.95	*g*	*g*	1.94	0.01
		E_3	2.34	*g*	*g*	>2.8	≥0.47
108-90-7	Chlorobenzene		2.56	2.58	*h*	*h*	*g*
29559-54-4	1,1-Dichloroneopentane		2.31	*g*	*g*	~2.8[i]	~0.5
10199-24-3	1-Iodo-1-chloroneopentane	E_1	1.08	1.12	1.22	1.26	0.18
		E_2	1.37	1.32	1.43	1.45	0.08
591-50-4	Iodobenzene		1.59	1.64	1.74	1.82	0.23
589-87-7	*p*-Bromoiodobenzene	E_1	1.50	*g*	*g*	1.66	0.16
		E_2	2.06	*g*	*g*	2.54	0.48
98-86-2	Acetophenone	E_1	1.96	*g*	*g*	*g*	*g*
		E_2	2.34	*g*	*g*	*g*	*g*
1499-10-1	9,10-Diphenylanthracene	E_1	1.83	*g*	*g*	1.82	−0.01
		E_2	2.29	*g*	*g*	2.35	0.06

[a] Polarographic half-wave potential, vs. SCE. [b] Tetramethylammonium hexafluorophosphate. [c] Tetraethylammonium bromide. [d] Tetra-*n*-propylammonium tetrafluoroborate. [e] Tetra-*n*-butylammonium perchlorate. [f] ($E_{1/2}$, R = Me[b]) − ($E_{1/2}$, R = Bu[e]). [g] Not measured. [h] Polarographic wave not observed before the solvent decomposition potential. [i] $E_{1/2}$ coincides with the solvent decomposition potential.

pentyl bromide; 1,2-dibromoethane; 2-bromopentane; *tert*-butyl bromide; 1-bromonorbornane (**1**); 1-iodo-1-chloroneopentane (**2**); 1,1-dichloroneopentane (**3**); iodobenzene;



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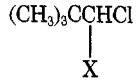

$$\underset{\displaystyle X}{(CH_3)_3C\overset{|}{C}HCl}$$

2, X = I

3, X = Cl

bromobenzene; chlorobenzene; *p*-bromoacetophenone; *p*-bromoiodobenzene; acetophenone; and 9,10-diphenylanthracene. The data are presented in Table I. A number of generalizations may be made based upon the data in Table I. First, the polarographic half-wave potentials of all alkyl halides studied underwent a progressive displacement to more negative potentials (and became more drawn out) as the cation of the supporting electrolyte was increased in size progressively from tetramethylammonium through tetrabutylammonium. This behavior is quite dissimilar from that exhibited by polycyclic aromatic compounds, where the potential of the first wave is essentially independent of the nature of the supporting electrolyte.[2,3] (The behavior of cyclooctatetraene is, as expected, intermediate, with $\Delta E_{1/2}$ = 0.05.)[3] The one apparent exception among the alkyl halides is *p*-bromoacetophenone, but reduction of this compound presumably follows a different mechanism involving electron injection into the π system followed by carbon–halogen bond breakage,[4,5] whereas the other halides are reduced by direct cleavage of the carbon–halogen bond.[4] The behavior of *p*-bromoacetophenone thus is similar to the aromatic hydrocarbons, which also undergo electron injection by the electrode into their π systems.

The range of potentials over which polarographic measurements can be made is limited by E_d, the decomposition potential of the supporting electrolyte. This potential moves slowly negative with increasing size of the electrolyte cation: Me_4N^+, −2.65 V;[5] Et_4N^+, −2.74 V; Pr_4N^+, −2.86 V; Bu_4N^+, −2.88 V; Hp_4N^+ (Hp = *n*-heptyl), −2.96 V.[6] This, along with the observed large shifts of half-wave potentials for the alkyl halides, gives rise to a striking effect: for a number of alkyl halides (neopentyl bromide, 1-bromonorbornane, and 1,1-dichloroneopentane) and also for the third wave of *p*-bromoacetophenone, the polarographic wave cannot be observed when electrolytes are used which have the most negative E_d's, yet can be seen clearly using electrolytes with more positive E_d's! This behavior, associated with the differential shifts of $E_{1/2}$ and E_d, is in contrast with intuition and the usual generalization that one selects large tetraalkylammonium ions, usually tetrabutylammonium, in order to obtain the widest accessible potential range for reduction processes. We suspect that this latter generalization is true only for substrates undergoing rapid electron transfer, and that the converse may often be true, as it clearly is here, with processes involving slow electron transfer. We believe that the phenomenon is of considerable potential utility in synthetic or analytical electrochemistry, since one may use it to shift reduction waves of carbon–halogen bonds in or out of accessible regions, or to separate closely spaced reduction waves. Dramatic examples are provided by 1,1-dichloroneopentane (**3**), whose reduction potential is cleanly resolved from background in the presence of tetramethylammonium ion, yet almost indistinguishable from background when the electrolyte cation is tetrabutylammonium,[8] and by 1-bromonorbornane, whose polarographic wave disappears merely upon changing the electrolyte cation from tetramethylammonium to tetraethylammonium!

Some other features of the data deserve comment. The progressively negative shift of the half-wave potential proceeding from *n*-pentyl to isobutyl to neopentyl bromide is an example of the known steric effect upon ease of alkyl halide reduction,[7] and presumably accounts for the difficulty with which 1,1-dichloroneopentane is reduced. Also, note that *tert*-butyl bromide and 1-iodo-1-chloroneopentane exhibit two polarographic waves, unlike the other alkyl halides studied. The wave heights show that both of these compounds undergo reduction by two one-electron

Table II
Relative Rates of Electron Transfer to Alkyl Halides as a Function of Supporting Electrolyte

Halide	$-E$, V[a]	$k_{f,h,Me} \times 10^4$, cm sec^{-1} [b,d]	Relative electron transfer rates[c,d]				
			Me	Et	Pr	Bu	Hp
Isobutyl bromide	2.14	7.8	1	0.16	0.025	0.015	0.0015
tert-Butyl bromide	1.91	6.8	1	0.73	0.44	0.19	0.018
Bromobenzene	2.07	6.6	1	0.062	0.046	0.024	0.015
Iodobenzene	1.59	3.9	1	0.24	0.026	0.010	0.0075

[a] Potential at which relative rates were measured. [b] Heterogeneous electron-transfer rate in the presence of tetramethylammonium ion. [c] Relative to the rate in presence of tetramethylammonium ion as unity. [d] For definition of Me, Et, Pr, and Bu, see footnotes *b–e* of Table I; Hp = tetra-*n*-heptylammonium iodide.

transfers, unlike most other halides, which are reduced in a single two-electron step. The cause of this split into two discrete steps is probably different for each halide. The mechanism of reduction of alkyl halides is now generally accepted as consisting of two one-electron steps, involving initial formation of a free radical R· and subsequent reduction of R· to a carbanion, i.e.,

$$RX \xrightarrow[E_1]{e,\ -X^-} R\cdot \xrightarrow[E_2]{e} R:^-$$

The potential E_2 at which R· is reduced is generally positive of that (E_1) necessary to effect the first electron transfer, hence normally one observes a single two-electron wave. With a few halides, the two waves have been resolved.[4] In the present examples, the observance of two waves for 1-iodo-1-chloroneopentane presumably arises because for this compound E_1 occurs at a very positive potential, owing to the fact that this compound is both an alkyl iodide and a geminal dihalide. With *tert*-butyl bromide, on the other hand, separation is achieved not because E_1 is exceptionally positive, but rather because E_2 is unusually *negative*, owing to the difficulty of reducing a *tert*-butyl radical to the corresponding carbanion. *tert*-Butyl iodide has in fact previously been observed to exhibit two polarographic waves.[10a] In that study *tert*-butyl bromide was found to exhibit a single two-electron wave in tetrahydrofuran. Apparently in Me_2SO one or both waves are shifted sufficiently to permit their resolution. The sensitivity of the second wave of *tert*-butyl bromide and the third wave of *p*-bromoacetophenone to the nature of the electrolyte is presumably because these waves, involving anionic species, reflect ion-pairing and solvation effects (see footnotes 9 and 11 in ref 3).

With the observation in hand that polarographic half-wave potentials are sensitive to the nature of the supporting electrolyte, we were next interested in establishing to what extent the observed changes are related to changes in the rate of heterogeneous electron transfer to the two substrates, as opposed to, e.g., a shift in the location of the outer Helmholtz plane (OHP) with changes in the size of the electrolyte. The latter effect is undoubtedly also involved, although the necessary electrocapillary data to assess its magnitude is not available. In order to measure relative electron-transfer rates, we turned to a method developed by Koutecky.[11] He showed that the polarographic current for a totally irreversible electrochemical process can be written in terms of two parameters, χ and $F(\chi)$

$$\frac{i_{irrev}}{i_{rev}} = F(\chi) \qquad (1)$$

$$\chi = \frac{a k_{f,h} t^{1/2}}{D_0^{1/2}} \qquad (2)$$

where $a = (12/7)^{1/2}$, $k_{f,h}$ = rate constant for heterogeneous electron transfer, t = polarographic drop time, D_0 = diffusion coefficient of the electroactive species, and $F(\chi)$ is the computed ratio of the polarographic current for the irreversible (slow) electron transfer to the corresponding current for a rapid reversible electron transfer at the same potential. Koutecky computed values of $F(\chi)$ for various values of χ and presented the results in tabular form. To obtain the heterogeneous electron-transfer rate constant, $k_{f,h}$, at any point on the rising portion of the polarographic wave, one measures the ratio of the current at that potential to the polarographic diffusion current, i_d; this ratio is numerically equal to $F(\chi)$.[12] From Koutecky's tabulation, one obtains the corresponding value of χ, and thence $k_{f,h}$, by substitution of the drop time at that potential and an estimated value of the diffusion coefficient into eq 2. The diffusion coefficient may be estimated from model compounds[13] with acceptable accuracy (e.g., for isobutyl bromide in Me_2SO we estimate $D_0 = 2.5 \times 10^{-6}$ cm^2 sec^{-1}). In practice, the most useful way to present the data is as *relative* rates of electron transfer to a given halide in the presence of different electrolytes, thus eliminating any error involved in the estimates of the diffusion coefficient. What was done was to measure $k_{f,h}$ for a given alkyl halide in the presence of various electrolytes, at a potential corresponding to the half-wave potential in the presence of tetramethylammonium ion, and to calculate relative rates referred to the rate in the presence of this ion as unity. The data are presented in Table II. The rates do clearly depend upon the nature of the electrolyte to a substantial degree. At least part of the difference is likely due to a shift in the location of the OHP with changes in the nature of the cation, but this cannot be the whole cause of the observed changes, because the log-plot slopes[14] also change substantially with electrolyte, indicating changes in the nature of the electron-transfer process.

Because of the clear differences in values of $\Delta E_{1/2}$ for different substrates (Table I), it was of interest to measure relative rates of electron transfer to the various substrates in the presence of a single electrolyte. To do this, a potential was selected for each electrolyte such that the polarographic waves for bromobenzene and isobutyl and *tert*-butyl bromides were rising at that potential. The value of

Table III
Relative Rates of Electron Transfer to
Alkyl Halides in the Presence of a Common Electrolyte

Alkyl halide	$-E$, V[a]	Relative electron transfer rate
Tetramethylammonium Hexafluorophosphate		
Isobutyl bromide	2.00	1
Bromobenzene	2.00	3.8
tert-Butyl bromide	2.00	46.7
Tetrabutylammonium Perchlorate		
Isobutyl bromide	2.04	1
Bromobenzene	2.04	4.2
tert-Butyl bromide	2.04	39.6

[a] Potential (vs. SCE) at which relative rates were measured.

$k_{\mathrm{f,h}}$ at this potential was measured for each bromide and divided by $k_{\mathrm{f,h}}$ for isobutyl bromide to obtain relative electron-transfer rates. The data are displayed in Table III. The high relative rate of cleavage of the carbon–bromine bond of *tert*-butyl bromide is probably associated with the stability of the resulting tertiary radical manifesting itself in the transition state for electron transfer.[10b] It is possible that reduction of bromobenzene involves initial electron injection into the π system of the aromatic ring,[4,5] rather than direct bond breakage in the electron-transfer step, but as one of us has argued previously,[4] we regard this as unlikely because of the very negative potential necessary to reduce benzene directly.

Conclusions

The changes in half-wave potential of alkyl halides as the supporting electrolyte is varied could in principle be taken advantage of in a variety of ways, both synthetic and analytical, because they offer a way to improve the resolution of closely spaced voltammetric waves. The caution must be repeated here again that when dealing with highly irreversible systems it is not necessarily true that the supporting electrolyte with the most negative reduction potential ought to be selected; on the contrary, the converse may be true.

Acknowledgment. Financial support was provided by the National Science Foundation. Professors Sease and Wiberg kindly provided the sample of 1-bromonorbornane.

Registry No.—TMAHP, 558-32-7; TEAB, 71-91-0; TPAFB, 15553-52-3; TBAP, 1923-70-2; THpAI, 3535-83-9; pivalaldehyde, 630-19-3.

References and Notes

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(12) Reference 4, p 44.
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(14) The log-plot slope is defined as the slope of a plot of E vs. log $i/(i_{d-i})$, where E is the potential, i is the polarographic current at that potential, and i_d is the diffusion current (see ref 4, pp 38 and 44). The log-plot slope of isobutyl bromide increases, e.g., from 110 to 222 mV when the electrolyte cation is changed from Me_4N^+ to Bu_4N^+.

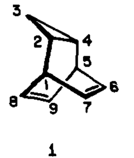
Response of Homo- and Benzhomobarrelenes to Uniparticulate Electrophilic Attack. Effect of a Lateral Cyclopropane Ring on the Direction and Stereochemistry of Chlorosulfonyl Isocyanate Addition[1]

William E. Volz and Leo A. Paquette*

The Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210

Received June 26, 1975

On reaction with chlorosulfonyl isocyanate, homobarrelene (1) afforded two isolable β-lactams, a γ-lactam, and a γ-lactone. All arise by electrophilic attack at the anti double bond with strong preference for endo approach. The site exclusivity was confirmed by ^{1}H NMR studies with unlabeled and 6,7-dideuterio-1. By way of contrast, the lone double bond in *syn*-benzohomobarrelene (2) experienced addition preferentially from the exo direction; two β-lactams and a γ-lactam were isolated in this instance. *anti*-Benzohomobarrelene (3) proved unreactive to chlorosulfonyl isocyanate under conditions where 1 and 2 reacted readily. Product structural assignments were made chiefly on the basis of spectral data, with extensive utilization of europium pseudocontact shifting. The mechanistic implications of these findings are discussed.



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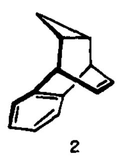

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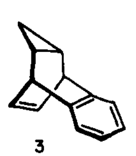

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The rigid geometry and special three-dimensional π-electron character of barrelene has prompted experimental scrutiny of its capability to enter into molecular rearrangements.[2,3] High levels of interaction between the adjacent olefinic bridges are seen, but the symmetry properties of barrelene are such that stereochemical tests cannot be applied. To gain such information, some structural perturbation becomes necessary. In this paper, we report the first examples of electrophilic addition to homobarrelene (tricyclo[3.2.2.0^{2,4}]nona-6,8-diene, 1) and its isomeric benzo derivatives 2 and 3. Molecules other than 1 can in principle be selected to address the stereochemical issue, but none of these share with homobarrelene the unique features imparted by the cylopropane ring. Brown's examination of the steric effect caused by 7,7-dimethyl substitution at the