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Polar Radicals. 15.[1] Interpretation of Substituent Effects on the Mechanism of Electrolytic Reduction of the Carbon–Halogen Bond in Series of Substituted Benzyl Halides

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The electrochemical polarographic reduction of a series of substituted benzyl chlorides and benzyl bromides showed half-wave potentials which gave excellent Hammett linear free-energy correlations for each series. These correlations were obtained using σ^- substituent constants. The correlation with σ^- suggests that the potential-determining electrochemical process involves carbon–halogen bond breaking or, alternatively, radical anion intermediate formation. The Hammett ρ values for each correlation were calculated; their magnitudes, Cl > Br, were in the inverse order of their reactivity toward chemical reduction. As in the case of trialkyltin hydride reduction, both ρ values were positive. The results of the polarographic electroreduction of benzyl iodide and benzylmercuric iodide confirmed the previously reported mechanism for reduction; namely, that the iodide underwent reaction with mercury to form benzylmercuric iodide, which was subsequently reduced, as was benzylmercuric iodide itself, by a process having two distinct polarographic waves. The half-wave potentials for the second wave (the wave at the most negative potential) for series of substituted benzyl iodides and benzylmercuric iodides were both found to give excellent Hammett correlation, having positive ρ values. The correlations were both obtained by using σ^- substituent constants. The success of the use of these substituent constants was taken as a confirmation of the suggestion, previously made, that the second step in the electroreduction was the reduction of the benzylmercuryl radical, and suggests that the process is concerted with carbon–mercury bond rupture.

Recently[2] the results of a mechanistic study of the reduction of benzyl halides by trialkyltin hydride led to the prediction that if the mechanism were to involve electron transfer from metal to halogen, a series of benzyl chlorides, benzyl bromides, and benzyl iodides should show Hammett linear free-energy correlations having positive ρ values. The transfer would be concerted with bond breaking, and the correlation should be obtained by using σ^- substituent constants. Further, the magnitude of the ρ values would be predicted to be in the order Cl > Br > I, the inverse order which would be observed for their relative rates of reduction. It was argued that a suitable model for the electron-transfer reactions in general might be the electrochemical reduction of the corresponding benzyl halides. Previous studies on the electrochemical reduction of alkyl and aryl halides indicated that the proposal had some validity; however, the data in the literature were incomplete, and further studies were necessary to substantiate this hypothesis.

Colichman[3] demonstrated a Hammett linear free-energy relationship for the half-wave potentials obtained in the reduction of a series of substituted iodobenzenes. Streitwieser and Perrin[4] subsequently reported that the half-wave potentials obtained from the polarographic reduction of a number of substituted benzyl chlorides in dimethylformamide containing tetraethylammonium chloride gave an extremely rough approximation to a straight line, although the slope of the plot of $E_{1/2}$ vs. σ was undoubtedly positive. The electrolytic reduction of series of chlorobenzenes,[5a] bromobenzenes,[5a] iodobenzenes,[5a] and benzyl bromides[5a,b] has more recently been reported to show Hammett correlations. The first two series showed better correlations with σ^- substituent constants, while the plots of the latter two series gave equally good fits with σ or σ^- substituent constants.[5a] In the case of the benzyl bromides,[5a] however, the differentiation between the choice of correlations was made on the basis of the reduction of only one compound, *p*-cyanobenzyl bromide.

The electrochemical reduction of benzyl iodide has previously been studied in aqueous ethanol[6] and in acetonitrile.[7] In aqueous ethanol, Hush and Oldham[6] have shown that the polarographic reduction of benzyl iodide gave two waves identical with those of benzylmercuric iodide and that electrolysis of benzyl iodide at mercury yields benzylmercuric iodide in quantities vastly in excess of those predicted by Faraday's law. These observations were interpreted as being due to a chain reaction of benzyl iodide with mercury to produce benzylmercuric iodide, in which only the initial step (formation of the benzyl radical) required electroreduction (see Scheme I).

Scheme I

$$C_6H_5CH_2I + e^- \rightarrow C_6H_5CH_2\cdot + I^-$$

$$C_6H_5CH_2\cdot + Hg \rightarrow C_6H_5CH_2Hg\cdot$$

$$C_6H_5CH_2Hg\cdot + C_6H_5CH_2I \rightarrow C_6H_5CH_2Hg^+ + C_6H_5CH_2\cdot + I^-$$

$$C_6H_5CH_2Hg^+ + I^- \rightarrow C_6H_5CH_2HgI$$

The reduction of benzylmercuric iodide in two waves was interpreted as reduction to the radical and halide anion (eq 1) followed by either further reduction of the benzylmercuric radical (eq 3) or disproportionation followed by reduction of the disproportionation product (eq 2; see Scheme II).

Scheme II

$$C_6H_5CH_2HgI + e^- \rightleftharpoons C_6H_5CH_2Hg\cdot + I^- \qquad (1)$$

$$2C_6H_5CH_2Hg\cdot \rightarrow (C_6H_5CH_2)_2Hg + Hg^0 \qquad (2)$$

$$(C_6H_5CH_2)_2Hg + e^- \rightarrow C_6H_5CH_2^- + \cdot HgCH_2C_6H_5$$

$$C_6H_5CH_2Hg\cdot + e^- + H^+ \rightarrow C_6H_5CH_3 + Hg \qquad (3)$$

The work of Wawzonek[7] using acetonitrile is consistent with the mechanism proposed by Hush and Oldham[6] and

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[1] For part 14, see ref 2.

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[6] Hush, N. S.; Oldham, K. B., *J. Electroanal. Chem.* **1963**, *6*, 34.

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Table I. Results of the Polarographic Behavior of Substituted Benzyl Chlorides and Benzyl Bromides in Solvent Acetonitrile at 25 °C

				benzyl chloride[b]		benzyl bromide[c]	
	substituent	σ^a	σ^-	$\Delta E_{1/2}$, V[d]	αn_a	$\Delta E_{1/2}$, V[d]	αn_a
1	H	0.0		0.0[e]	0.40	0.0[f]	0.43
2	*p*-Cl	0.24		0.16	0.36		
3	*p*-F	0.15		0.03	0.36		
4	*p*-*t*-Bu	−0.15		0.01	0.39		
5	*p*-C_6H_5	−0.01	0.08	0.35	0.38	0.11	0.28
6	*p*-CN	0.70	0.99	0.78	0.40	0.44	max
7	*p*-COC_6H_5	0.46	0.88	0.87	0.55	0.51	max
8	*p*-CHO	0.47	1.04	0.85	0.56	0.50	0.51
9	*p*-$CO_2C_2H_5$	0.44	0.74			0.34	0.50
10	*m*-Cl	0.37		0.23	0.36		
11	*m*-CH_3	−0.06		0.01	0.36	0.01	0.30
12	*m*-F	0.34		0.11	0.39	0.11	0.24
13	*p*-CH_3	−0.14				−0.04	0.22
14	*m*-CN	0.62				0.20	0.43
15	*m*-Br	0.37				0.11	max
16	*p*-Br	0.26				0.11	0.36

[a] Unless otherwise specified, values were taken from the recommended best values: Exner, O. "Correlation Analysis in Chemistry"; Chapman, N. B., Shorter, J., Eds.; Plenum: London, 1978. [b] Benzyl chlorides were determined by using a tetraethylammonium iodide (0.01 M) electrolyte and a AgI/Ag reference electrode. [c] Benzyl bromides were determined by using a tetraethylammonium bromide (0.01 M) electrolyte and a AgBr/Ag reference electrode. [d] Difference in $E_{1/2}$ of substituted and unsubstituted halides. [e] The average value determined for benzyl chloride was −2.23 ± 0.005 V. [f] The average value determined for benzyl bromide was −1.83 ± 0.02 V.

also suggested that the second wave corresponded to the reduction of the carbon–mercury bond.

The present study was undertaken to establish whether satisfactory Hammett correlations having positive ρ values could be obtained for both a series of benzyl chlorides and benzyl bromides, whether these ρ values would be obtained by using σ^- substituent constants, and whether the order of the magnitude of the ρ values could be established as Cl > Br. Related to this study, it was of further interest to investigate the possibility that the second wave observed in the reduction of benzyl iodide (i.e., benzylmercuric iodide) was indeed, as suggested,[6,7] the observation of the electrochemical reduction of the carbon–mercury bond. If this were in fact the case, a series of benzyl iodides or benzylmercuric iodides should show a positive Hammett correlation with σ^- substituent constants for the second wave observed in their polarographic reduction.

Results

Polarography. The differences in half-wave potentials between benzyl chloride and bromide and their corresponding substituted benzyl halides are shown in Table I. To eliminate the minor drift of the reference electrodes, the half-wave potential of the unsubstituted benzyl halide was frequently remeasured and used as the reference point, since the differences in potential rather than their absolute magnitudes are significant. The actual half-wave potentials are the values given in Table I less the half-wave potential of the unsubstituted benzyl halide (−2.230 ± 0.005 V for $C_6H_5CH_2Cl$ in $(C_2H_5)_4NI$ against AgI/Ag, −1.83 ± 0.02 V for $C_6H_5CH_2Br$ in $(C_2H_5)_4NBr$ against AgBr/Ag). In all cases only the expected single irreversible wave was obtained.

For all of the benzyl bromides in $(C_2H_5)_4NBr$, this wave was well-defined (for all compounds run, i_d = 1.9 ± 0.1 μA); measurements on a similar solution of benzylmercuric bromide gave waves of more erratic form but of the same total height. Attempts to study benzyl chlorides in $(C_2H_5)_4NCl$ against AgCl/Ag were not successful.

Polarographic reductions of substituted benzyl iodides were carried out in $(C_2H_5)_4NI$ as the supporting electrolyte against the AgI/Ag reference electrode. Two waves were obtained, as was previously reported,[6,7] and the half-wave potentials are given in Table II. A number of substituted benzylmercuric iodides were synthesized and their electroreductions studied. Since the complete series of benzylmercuric iodides or benzyl iodides were not easily attainable by the usual method of synthesis, the reductions of the corresponding benzyl bromides were carried out in acetonitrile with tetraethylammonium iodide as the supporting electrolyte and an Ag/AgI electrode. As expected[2] the exchange reaction between the organic bromide and the iodide anion of the electrolyte took place, and the reduction characteristics observed were those of the corresponding benzyl iodides (or benzylmercuric iodides; see Table II). Maxima of the first and second kind were again observed, and the half-wave potential of the second wave of $C_6H_5CH_2Br$ (i.e., $C_6H_5CH_2HgI$) was −1.47 ± 0.01 V (−1.44 ± 0.01 V), in reasonable agreement with the values obtained for benzyl iodide and benzylmercuric iodide (−1.49 ± 0.02 V) in the same supporting electrolyte.

Since the polarograms obtained for the reduction of the benzyl iodides were clearly different in appearance from those of the chlorides and bromides, additional studies of related compounds were undertaken. These included polarography of the parent compounds benzyl iodide, benzylmercuric iodide, and dibenzylmercury and, in addition, when possible, the substituted benzylmercuric iodides. The observed patterns for the parent compounds are shown in Figure 1. Solutions of benzyl iodide and benzylmercuric iodide gave identical curves only when the benzylmercuric iodide was examined immediately upon mixing (Figure 1A); when the sample was allowed to stand, the polaragram of benzylmercuric iodide (but not the benzyl iodide) altered; wave II decreased, while a third wave, III, appeared. Wave I appeared to be unchanged. The substituted benzyl iodides followed the two-wave pattern of benzyl iodide, while the substituted benzylmercuric iodides followed the behavior of their parent compound, benzylmercuric iodide. For the entire series of benzyl iodides and benzylmercuric iodides the ratio of the plateau currents of I to II was 1.20 ± 0.05:1 (20 curves, 10 compounds, mean plateau current of II 2.0 ± 0.1 μA).

Cyclic Voltammetry. Cyclic voltammetric studies of the benzyl halides indicated that significant variations in mechanism existed between the halogens. The simplest

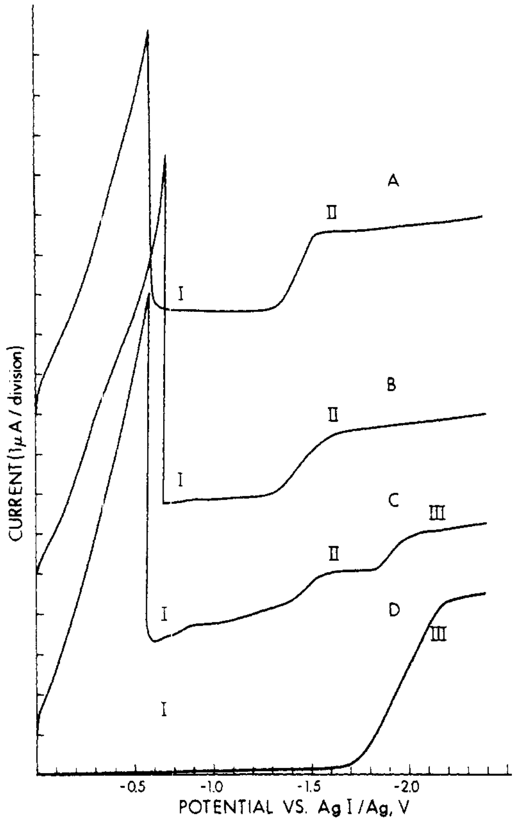


Figure 1. Polarography of benzyl iodide (A), benzylmercuric iodide (B), benzylmercuric iodide upon standing (C), and dibenzylmercury (D) in acetonitrile: tracings of actual maximum currents, drop time 2 s, scan rate 5 mV/s.

behavior was observed for the bromides and the most complex for the iodides. A solution of benzyl bromide run in $(C_2H_5)_4NBr$ against a AgBr/Ag reference exhibited a single, totally irreversible cathodic peak ($E_p = -1.11$ V at 100 mV/s) whose height was directly proportional to the square root of the scan rate. The peak was shifted to more negative potentials by about a 90 mV/decade change in scan rate. The supporting electrolyte gave a peak at −1.9 V, while mercury oxidation was observed at potentials more positive than −0.3 V. This behavior is that expected for a totally irreversible process without other complications.

Solutions of several substituted benzyl chlorides were studied, of necessity in $(C_2H_5)_4NI$ against a AgI/Ag reference. In all cases, two successive totally irreversible cathodic peaks were observed rather than the single peak observed for benzyl bromide. The peaks were well separated only at and above scan rates of 100 mV/s. At 100 mV/s the peak potentials were as follows: for the 4-chloro compound, −1.71 and −1.90 V; for the 4-phenyl compound, −1.56 and −1.86 V; for the 3-fluoro compound, −1.20 and −1.84 V. All of the peaks were roughly proportional in height to the square root of the scan rate and shifted negative with increasing scan rate by approximately 90 mV/decade. This behavior is that expected for two successive totally irreversible electron transfers; since the peaks merged below 100 mV/s, the wave seen in the slower technique of polarography must be due to the overall two-electron irreversible process.

Solutions of benzyl iodides show radically different behavior; benzyl iodide itself (in $(C_5H_5)_4NI$ against AgI/Ag) exhibited a low cathodic current at all potentials negative of −0.3 V, peaking slightly at −0.95 V. That is, a significant cathodic current was always present, even though solutions of the supporting electrolyte alone had no significant cathodic current at potentials less negative that −2.4 V. The main peak ($E_p = -1.84$ V at 100 mV/s) was totally irreversible, and its height was proportional to the square root of the scan rate. On the anodic return cycle a low cathodic current was observed at −0.8 V and continued to −0.3 V; no anodic current was ever observed (Figure 2). Solutions of benzylmercuric iodide or benzyl bromide in iodide electrolyte (which by exchange gives benzylmercuric iodide) gave curves indistinguishable from those of benzyl iodide itself.

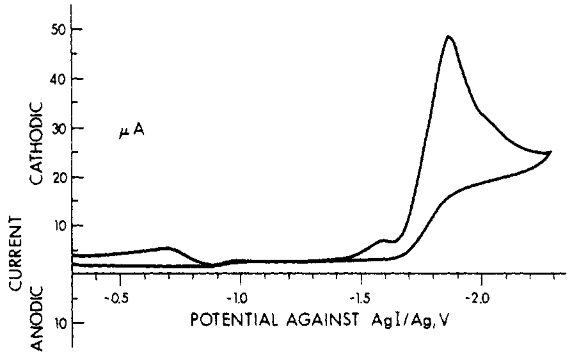


Figure 2. Cyclic voltammetry of benzyl iodide (10^{-3} M) in an acetonitrile solution containing tetraethylammonium iodide (10^{-2} M): scan rate 100 mV/s, HMDE.

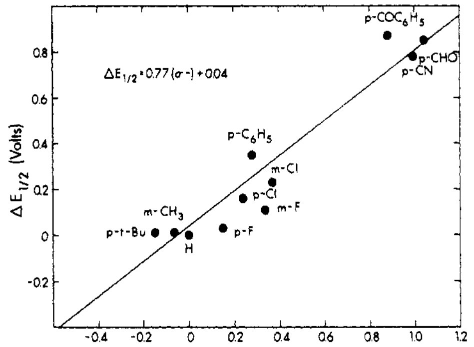


Figure 3. Comparison of the effect of substituents on the polarographic half-wave potential for reduction of benzyl chloride with Hammett σ^- substituent constants.

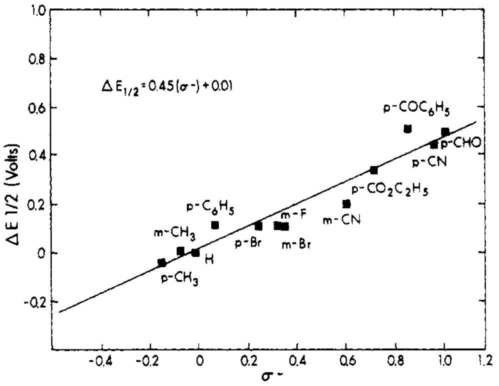


Figure 4. Comparison of the effect of substituents on the polarographic half-wave potential for reduction of benzyl bromide with Hammett σ^- substituent constants.

Discussion

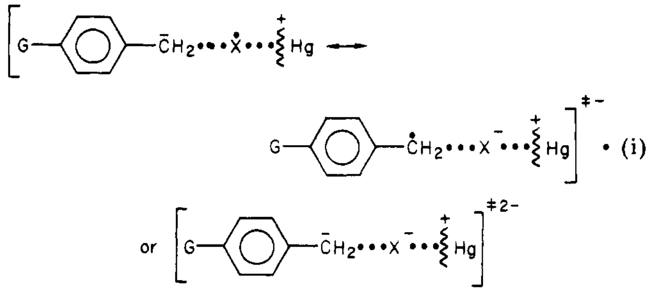
The half-wave potentials determined for the reduction of the series of benzyl chlorides in tetraethylammonium iodide against AgI/Ag and of the series of benzyl bromides determined in tetraethylammonium bromide vs. AgBr/Ag were found, as predicted from the tin hydride studies,[2] to show excellent ($r = 0.93$, $S_\rho = 0.10$; $r = 0.96$, $S_\rho = 0.04$)

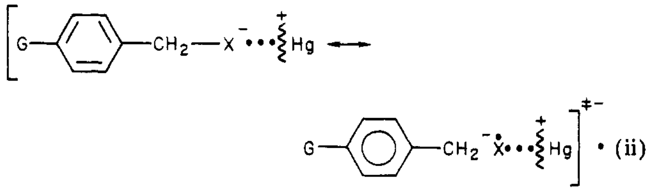
Table II. Results of the Polarographic Behavior of Substituted Benzyl Bromides, Benzyl Iodides, and Benzylmercuric Iodides with Tetraethylammonium Iodide in Acetonitrile at 25 °C

substituent	wave	$-E_{1/2}$V[c]	αn_a[b]	$\Delta E_{1/2}$ (sec wave), V[a]
	Benzyl Iodides			
H	first	0.16		
	second	1.44	1.83	0.0
p-CN	first	0.22		
	second	1.06	max	0.38
m-CN	first	0.32		
	second	1.30	2.28	0.14
p-Cl	first	0.32		
	second	1.41	2.06	0.03
p-$CO_2C_2H_5$	first	0.22		
	second	1.08	max	0.36
p-CH_3	first	0.32		
	second	1.56	2.03	−0.12
p-C_6H_5	first	0.40		
	second	1.36	1.58	0.08
	Benzylmercuric Iodides			
H	first	0.23		
	second	1.49	0.97	0.0
	third	(1.82)		
p-CN	first	0.25		
	second	1.08	max	0.41
	third	(~1.27)		
m-CN	first	0.31		
	second	1.32	2.28	0.17
	third	(~1.48)	2.31	
p-Cl	first	0.28		
	second	1.50	max	−0.01
	third	(1.80)		
p-CH_3	first	0.26		
	second	1.52	0.58	−0.03
	third	(2.03)	2.37	
	Benzyl Bromides			
H	first	0.20		
	second	1.47		0.0
p-CH_3	first	0.24		
	second	1.55		0.08
p-CN	first	0.26		
	second	1.05		0.42
p-COC_6H_5	first	0.27		
	second	0.97		0.50
p-Br	first	0.22		
	second	1.40		0.07
m-Br	first	0.18		
	second	1.32		0.15
m-F	first	0.26		
	second	1.35		0.12
p-CHO	first	0.25		
	second	1.01		0.46
m-CN	first	0.30		
	second	1.31		0.16
p-C_6H_5	first	0.25		
	second	1.40		0.07
p-$CO_2C_2H_5$	first	0.26		
	second	1.13		0.34

[a] Difference in half-wave potentials of substituted and unsubstituted halides and mercuric halides. [b] Entry labeled "max" means that the value could not be accurately obtained due to a polarographic maximum. [c] The values in parentheses are assigned to the two-electron reduction wave of dibenzylmercury and only appeared after the sample had aged. The approximate values indicate interfering maxima.

Hammett correlations when plotted against the corresponding σ^- substituent constants (Figures 3 and 4), while the attempted correlation with σ substituent constants gave no correlation ($r = 0.77$, $S_\rho = 0.28$; $r = 0.78$, $S_\rho = 0.14$; see Table I). The correlation with σ^- substituent constants militates that the potential determining electrochemical process associated with the reduction involves either the breaking of the carbon–halogen bond, be it a single or double electron-transfer process (i), or the less likely event, that the electron transfer forms a radical anion intermediate (ii).[8] Wawzonek[7] has shown that benzyl chloride undergoes two-electron reduction. In this work, since the heights of the polarographic plateaus observed for the reduction of the benzyl bromides were nearly identical with those of the corresponding chlorides, both reductions proceed by a two-electron process. In the report of Wawzonek on the electrolysis of benzyl chloride in tetrabutylammonium iodide electrolyte, it was noted that a relatively slow exchange takes place between the organic halide and the electrolyte iodide. It was possible, however, to carry out the polarographic analyses herein reported (see Table I) rapidly enough to avoid this complication.


(i)


(ii)

Polarographic reductions of organic halides are well-known[9,10] to be irreversible, and the overall two-electron process leads to a carbanion which is then protonated. In aprotic solvents, products may be formed from the carbanion, the radical anion produced by the first electron transfer, or the radical produced by the decay of the radical anion as shown in Scheme III.

Scheme III

$$RX + e^- \rightarrow RX^{-}\cdot \qquad (4)$$

$$RX^{-}\cdot \rightarrow R\cdot + X^- \qquad (5)$$

$$R\cdot + e^- \rightarrow R^- \rightarrow \text{products} \qquad (6)$$

The decomposition of the radical anion (eq 5) is very fast or even concerted in combination with electron transfer. With organic alkyl halides, RX, it has been proposed[11,12] that the structure of the alkyl group R will determine the relative timing of the processes depicted in Scheme III. In the case of the benzyl halide reductions, where R is potentially a resonance-stabilized substituted benzyl radical, the electrochemical process observed by the polarographic studies, in order to be consistent with a σ^- correlation, must

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(8) The lifetimes of alkyl halide radical anions generated by chemical reduction have been estimated to be near or less than 10^{-10} s.[11] Since it is not unreasonable that the lifetime of the benzyl halide anion radicals would be even less than the analogous aliphatic halides by several orders of magnitude, it is likely that the correlation of half-wave potential with σ^- reflects a dissociative electron-transfer pathway.

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(12) Bard, A. J.; Merz, A. *J. Am. Chem. Soc.* **1979**, *101*, 2959.

be either the more probable dissociative electron-transfer process followed by a fast nonpotential-determining second electron transfer or the formation of a transient intermediate radical cation.

For isoentropic processes which proceed by the same mechanism, the response of the reactions to substituents (i.e., the magnitude of the ρ values observed) should be proportional to the relative ease of the reaction. Since, regardless of the detailed timing of the bond breaking, the ease of acceptance of an electron by halogen and the bond dissociation energy of the carbon halogen bond would both predict that the most fascile reaction, I > Br > Cl, would have the smallest ρ values. In this case, the relative magnitude of the ρ values calculated from the half-wave potentials for the reduction of the benzyl chlorides and benzyl bromides could not be compared directly since the $E_{1/2}$ values for the two series of halides were determined in different electrolytes. The reduction of the benzyl chlorides occurred at a more negative potential than did the reduction of the other halides. The series of chlorides, because of their high negative reduction potentials, could not be reduced at potentials which were distinguishable from those of either the chloride (Ag/AgCl, $(C_2H_5)_4NCl$) or bromide (Ag/AgBr, $(C_2H_5)_4NBr$) electrolytes,[13] and their $E_{1/2}$ determinations were only successful when the reductions were carried out in the iodide electrolyte (see Table I). The ρ values for the bromides and the chlorides were calculated, following the suggestion of Streitwieser,[4] by the use of the differential form of an expression derived from the Hammett equation and the equation for irreversible polarographic waves given by Delahay.[14] Under our conditions of controlled drop time and with the assumption that all species have the same diffusion coefficient, the equation derived takes the form given in eq 7.

$$\rho = \frac{d(\log k^{0}_{f,h}/k^{00}_{f,h})}{d\sigma} = \left(\frac{\alpha n_a F}{2.303RT}\right)\left(\frac{d\Delta E_{1/2}}{d\sigma}\right) \qquad (7)$$

In this equation the symbols have their usual significance[4] except that $k^0_{f,h}$ is the forward (reduction) heterogeneous rate constant for the substituted benzyl halide at the reversible reduction potential of the unsubstituted benzyl halide while $k^{00}_{f,h}$ is the same constant for the unsubstituted (parent) benzyl halide. The values for αn_a, the product of the transfer coefficient and the number of electrons transferred in the rate-limiting electrode process, were found to be 0.42 ± 0.07 from an analysis of the current–voltage curves of the series of substituted benzyl chlorides and 0.39 ± 0.1 for the benzyl bromides.[15] The ρ values calculated from the least-squares slopes of the $\Delta E_{1/2}$ vs. σ^- plots (see Figures 3 and 4) were $\rho = 5.0$ for the series of chlorides and $\rho = 2.8$ for the series of bromides. Although a change in the supporting electrolyte will affect the magnitude of $E_{1/2}$ to a small extent, the ρ values obtained in the two series can qualitatively be compared directly.[16] The response of the electrochemical process to substituents, as measured by the magnitude of the ρ values observed, does increase in the order chlorides > bromides with any reasonable values for αn_a.

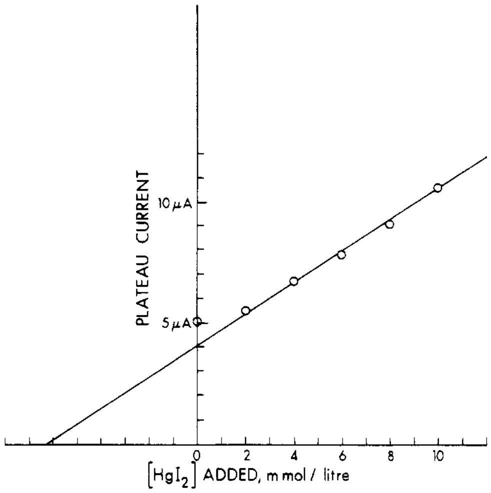

Figure 5. Response of the plateau current measured for wave I upon addition of mercuric iodide to benzylmercuric iodide solution.

Benzyl Iodides. The reduction of the benzyl iodides, as previously suggested,[6,7] proceeds by a more complex mechanism than does that of the other benzyl halides. This was confirmed, in this study, not only by the appearance of the polarographic and voltammetric curves obtained but also by the much higher calculated αn_a values (see Table II and Figures 1 and 2).

The nonelectrochemical mechanism proposed by Hush and Oldham[6] for the formation of benzylmercuric iodide (Scheme I) was sufficient to account for the identity of the polarographic curves obtained by using fresh solutions of benzyl iodide and of benzylmercuric iodide (see Figure 1, curves A and B). The appearance of the first wave of these polarograms can be ascribed, as previously suggested by Wawzonek,[7] to the reduction of the arylmercuric halide to a univalent mercury species (eq 8). The formation of

$$C_6H_5CH_2HgI + e^- \rightarrow I^- + C_6H_5CH_2Hg\cdot \qquad (8)$$

benzylmercuric iodide, although formed primarily by the electrochemically initiated mechanism proposed previously,[6] should be modified to some extent since the reaction of benzyl iodide with metallic mercury is a precedented reaction.[17] Under polarographic conditions (room temperature, acetonitrile, metallic mercury, 20–85 min) a small amount of benzylmercuric iodide appears to be formed without the passage of current. As indicated previously,[7] with time a disproportionation reaction of benzylmercuric iodide takes place which forms dibenzylmercury and mercuric iodide (eq 9). The resulting curve

$$2C_6H_5CH_2HgI \rightleftharpoons (C_6H_5CH_2)_2Hg + HgI_2 \qquad (9)$$

obtained for the reduction of this mixture is shown in Figure 1 (curve C). In an attempt to determine the position of the equilibrium, polarographic studies of solutions containing benzylmercuric iodide and different concentrations of mercuric iodide were carried out. A plot of the diffusion-limited current of wave I against the concentration of mercuric iodide added (Figure 5) did not extrapolate to zero, while the diffusion-limited current of wave II (when corrected for the increase in preceding wave I) was unchanged by addition of mercuric iodide. These results suggested that aged solutions of $C_6H_5CH_2HgI$ ex-

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(13) The chloride to bromide or chloride to iodide interchange reported by Wawzonek[7] was significant only at times greater than 20–30 min in our study and thus did not interfere.

(14) Delahay, P. "New Instrumental Methods in Electrochemistry"; Interscience: New York, 1954; p 74 ff.

(15) The αn_a values calculated in the present study range upward from the value $\alpha n_a = 0.22$ reported by Streitwieser[4] for the reduction of benzyl chloride in DMF using a chloride-supporting electrolyte.

(16) The values of the half-wave potentials are all significantly negative with respect to the ECM, which is 50 mV negative of the reference electrode potential in both bromide and iodide media (as noted from polarography of the supporting electrolyte above). Thus the ρ values may be affected by nonspecific salt effects (see, for example, Reinmuth et al.), but the effects should be similar in both media. Reinmuth, W. H.; Rogers, L. B.; Hummelstedt, L. E. I. *J. Am. Chem. Soc.* **1959**, *81*, 2947.

(17) Maynard, J. *J. Am. Chem. Soc.* **1932**, *54*, 2108.

Table III. Linear Free-Energy Correlations for the Reduction of Substituted Benzylmercuric Iodides[a]

correl employed	remarks[b]	slope	correl coeff	regression from mean
σ	all points	0.47	0.76	0.09
σ^-	all points	0.40	0.92	0.04
σ	benzyl iodides	0.46	0.83	0.14
σ^-	benzyl iodides	0.41	0.94	0.07
σ	benzylmercuric iodides	0.44	0.87	0.14
σ^-	benzylmercuric iodides	0.38	0.95	0.07
σ	benzyl bromides $(C_2H_5)_4N^+I^-$	0.47	0.70	0.16
σ^-	benzyl bromides $(C_2H_5)_4N^+I^-$	0.40	0.92	0.06

[a] Values of $\Delta E_{1/2}$ taken from Table II while the values of σ and σ^- were taken from Table I. [b] See Figure 6 for a plot of the data used.

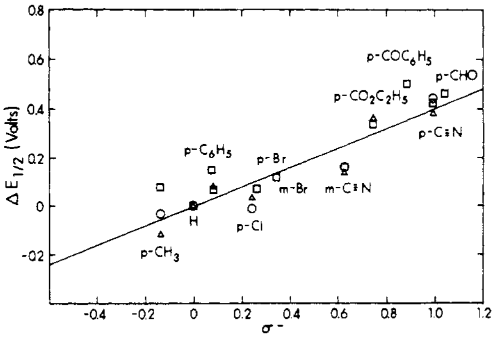

Figure 6. Comparison of the effect of substituents on the polarographic half-wave potential of the second wave for reduction of benzyl iodide (△), benzylmercuric iodide (○), and benzyl bromide with tetraethylammonium iodide electrolyte (□).

hibit a reduction wave, wave I, due to both $C_6H_5CH_2HgI$ itself and HgI_2 which is formed from its disproportionation. These reductions are indistinguishable; both species are probably present in adsorbed form or as the slightly soluble mercurous iodide (produced by reaction of HgI_2 at the electrode surface). The cyclic voltammetric observations of a low cathodic current which persists during the positive sweep at all potentials negative of mercury oxidation is consistent with a process which produces oxidized mercury at the electrode surface either by reduction of HgI_2 or $C_6H_5CH_2HgI$ or by the reduction of a benzyl cation formed ionically in acetonitrile (eq 10). A similar nonelectrochemical reaction of allyl iodide on mercury has recently been suggested by Bard and Merz.[12]

$$ArCH_2I \rightleftharpoons ArCH_2^+ + I^- \tag{10}$$

Polarography of a solution of dibenzylmercury[7] (Figure 1, curve D), which shows a single two-electron reduction wave at $E_{1/2} = -1.97$ V (wave III) in $(C_2H_5)_4NI$ against AgI/Ag, allows the assignment of the third wave in Figure 1C to dibenzylmercury. It is significant that waves I and II are absent in this curve, confirming both the assignment of waves I and II and the easier reduction of benzylmercuric radicals relative to dibenzylmercury.

Since wave II could be assigned to the reduction of the benzylmercuryl radical, polarographic study of the reduction of a series of substituted benzylmercuric iodides affords the opportunity for the establishment of the substituent effects associated with the reduction of an organometallic bond. A correlation for the $\Delta E_{1/2}$ values (wave II) was obtained for the reduction of the series of benzyl iodides, benzylmercuric iodides, and benzyl bromides in tetraethylammonium iodide electrolyte. The correlation for the individual series and for the combined series are listed in Table III. As predicted, the plot of $\Delta E_{1/2}$ (wave II) obtained for the three series, all equivalent to the reduction of substituted benzylmercuric iodides, showed a correlation with the corresponding Hammett substituent constant. The slope was positive in all three of the series. As can be seen in Table III, satisfactory correlation was only obtained in the individual series and with the combined series by using σ^- substituent constants (see Figure 6). The correlation with σ^- establishes that the mechanism for the potential-determining step in the reduction involves an electron transfer which is concerted with the rupture of the carbon–mercury bond.

Experimental Section

Materials. The acetonitrile was obtained electrochemically pure by subjecting commercial (MCIB Chemical Co.) acetonitrile to the purification method of O'Donnell, Ayrs, and Mann.[18] The tetramethylammonium halides (Eastman Kodak Co.) were recrystallized from acetone and dried in vacuo: mp 292–295 °C, chloride; mp 285–287 °C, bromide; mp 296–297 °C, iodide.

The substrates, benzyl chloride (Fisher Scientific Co.) and benzyl bromide and benzyl iodide (Eastman Kodak Co.), were fractionally distilled through a packed column and shown to be single compounds (>99%) by GLC (10 ft × $^1/_8$ in. column, 3% OV-101 on 100–120-mesh Chromosorb W/AW).

p-Cyanobenzyl chloride[19] (mp 79.5–80 °C) was prepared by the photochlorination[20] of the corresponding toluene. The purity was checked by elemental analysis and GLC (OV-101 column).

p-Benzoylbenzyl chloride was prepared by the free-radical chlorination[20] of *p*-methylbenzophenone, and the product was purified by repeated recrystallization from ethanol; mp 95–96 °C (lit.[21] mp 97–98 °C).

p-Carbethoxybenzyl bromide[22] and *p*-carbethoxybenzyl iodide[2] were prepared as previously described. Likewise, *p*-methylbenzyl iodide,[23] *p*-chlorobenzyl iodide,[23] *p*-cyanobenzyl iodide,[24] *p*-phenylbenzyl iodide,[25] benzylmercuric bromide,[26] benzylmercuric iodide,[27] and benzylmercuric chloride[28] were synthesized by using established procedures. The purities of the products were checked either by elemental analysis for new compounds and/or by a comparison of the physical properties with those reported in the literature for the compounds which had previously been reported.

Benzylmercuric chloride, mp 103.5–104.5 °C (lit.[28] mp 107 °C). Anal. Calcd for C_7H_7HgCl: C, 25.68; H, 2.16. Found: C, 25.59; H, 2.15.

p-Formylbenzyl chloride[29] was prepared by $SnCl_2$/HCl reduction of *p*-cyanobenzyl chloride. *p*-Formylbenzyl bromide (mp 92–93 °C) was prepared analogously by using $SnBr_2$, HBr, and *p*-cyanobenzyl bromide. Its structure was assigned by its NMR and IR spectra [NMR (CCl_4) τ 5.55 (s, 2 H), 2.0–2.6 (m, 4 H), 0.01 (s, 1 H); IR (C=O), 1710 cm^{-1}] and by its analogous method of preparation.

p-Benzoylbenzyl bromide was prepared by the photobromination[30] of *p*-methylbenzophenone to yield a solid, which was recrystallized from ethanol; mp 110–111 °C. Its structure

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[18] O'Donnell, J. F.; Ayrs, J. T.; Mann, C. K. *Anal. Chem.* **1963**, *37*, 1161.

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was assigned on the basis of its method of preparation and its NMR spectrum (CCl_4): τ 5.50 (s, 2 H), 2.1-2.7 (m, 9 H).

p-Phenylbenzyl bromide was prepared from *p*-biphenylmethanol by using potassium bromide and sulfuric acid;[31] mp 83-84 °C (lit.[25,32] mp 85 °C).

All of the remaining benzyl halides were commercially available (Aldrich Chemical Co.) Their purities were checked by GLC (OV-101) for the liquids or by recrystallization to a constant melting points (ethanol) for the solids. Compounds which contained the corresponding toluenes as impurities or were less than 99% pure were purified by low-temperature fractional crystallization or, as in the case of the solids, by recrystallization from ethanol.

The substituted benzylmercuric iodides were prepared analogously to the method used for the formation of benzylmercuric iodide. In all cases, an equivalent of zinc was allowed to react with the appropriate benzyl iodide in dry tetrahydrofuran. The resulting organozinc was then treated with 1 molar equiv of HgI_2 in THF to form the benzyl mercuric iodide which was then recrystallized from ethanol. The NMR spectra of all of the organomercuriles were consistent with their structures.

m-Cyanobenzylmercuric iodide: colorless crystals; mp 153–154 °C. Anal. Calcd for C_8H_6NHgI: C, 21.66; H, 1.37; N, 3.16. Found: C, 21.55; H, 1.35; N, 3.08.

p-Methylbenzylmercuric iodide: pale yellow crystals; mp 130–131 °C. Anal. Calcd for C_8H_9HgI: C, 22.21; H, 2.10. Found: C, 22.26; H, 2.11.

p-Chlorobenzylmercuric iodide: pale yellow crystals; mp 149.5 °C. Anal. Calcd for C_7H_6ClHgI: C, 18.56; H, 1.34. Found: C, 18.74; H, 1.41.

p-Cyanobenzylmercuric iodide: yellow crystals; mp 169–170 °C. Anal. Calcd for C_8H_6HgNI: C, 21.66; H, 1.37; N, 3.16. Found: C, 21.73; H, 1.41; N, 2.78.

Dibenzylmercury:[33] white crystals; mp 111–111.5 °C. Anal. Calcd for $C_{14}H_{14}Hg$: C, 43.90; H, 3.69. Found: C, 43.88; H, 3.73.

Procedures. Polarographic measurements were carried out with a Princeton Applied Research (PAR) Model 174A polarograph in a PAR 9300-9302 cell thermostated at 25 °C. Cyclic voltammetry was carried out with a PAR 9323 HMDE and a PAR Model 173-175-176 configuration; the resulting curves were recorded on an X-Y recorder. The cell in all cases used a three-electrode configuration in which the counterelectrode was platinum and the reference electrode was isolated by two glass frits. The reference electrode was AgCl/Ag, AgBr/Ag, or AgI/Ag prepared in each case by anodization of a clean Ag wire in the appropriate supporting electrolyte. The solutions were anhydrous acetonitrile prepared as described above and containing only the benzyl halide (1.0 mmol/L) and the appropriate tetraethylammonium halide supporting electrolyte (10.0 mmol/L).

Cyclic voltammetric curves were obtained by using 0.01 M $(C_2H_5)_4NI$ as the supporting electrolyte. The supporting electrolyte showed no processes between −0.3 V (mercury oxidation) and −2.3 V (electrolyte discharge). No anodic peaks were observed for any compound within this potential range.

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Registry No. Benzyl chloride, 100-44-7; *p*-chlorobenzyl chloride, 104-83-6; *p*-fluorobenzyl chloride, 352-11-4; *p-tert*-butylbenzyl chloride, 19692-45-6; *p*-phenylbenzyl chloride, 1667-11-4; *p*-cyanobenzyl chloride, 874-86-2; *p*-benzoylbenzyl chloride, 42728-62-1; *p*-formylbenzyl chloride, 73291-09-5; *m*-chlorobenzyl chloride, 620-20-2; *m*-methylbenzyl chloride, 620-19-9; *m*-fluorobenzyl chloride, 456-42-8; benzyl bromide, 100-39-0; *p*-phenylbenzyl bromide, 2567-29-5; *p*-cyanobenzyl bromide, 17201-43-3; *p*-benzoylbenzyl bromide, 32752-54-8; *p*-formylbenzyl bromide, 51359-78-5; *p*-carbethoxybenzyl bromide, 26496-94-6; *m*-methylbenzyl bromide, 620-13-3; *m*-fluorobenzyl bromide, 456-41-7; *p*-methylbenzyl bromide, 104-81-4; *m*-cyanobenzyl bromide, 28188-41-2; *m*-bromobenzyl bromide, 823-78-9; *p*-bromobenzyl bromide, 589-15-1; benzyl iodide, 620-05-3; *p*-cyanobenzyl iodide, 874-88-4; *m*-cyanobenzyl iodide, 69113-58-2; *p*-chlorobenzyl iodide, 35424-56-7; *p*-carbethoxybenzyl iodide, 73373-16-7; *p*-methylbenzyl iodide, 4484-74-6; *p*-phenylbenzyl iodide, 73373-17-8; benzylmercuric iodide, 20632-18-2; *p*-cyanobenzylmercuric iodide, 75101-80-3; *m*-cyanobenzylmercuric iodide, 75101-81-4; *p*-chlorobenzylmercuric iodide, 75101-82-5; *p*-methylbenzylmercuric iodide, 75101-83-6; benzylmercuric chloride, 2117-39-7; dibenzylmercury, 780-24-5.

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Polar Radicals. 16.[1] Comments on a Recently Published Mechanistic Study of Photobromination Using Bromotrichloromethane

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The mechanism of the photobromination reactions of a series of 10-substituted 9-methylanthracenes with bromotrichloromethane was reexamined. It was shown, contrary to the previous report, that the reaction proceeded by a mixed chain involving abstraction by both the bromine atom and the trichloromethyl radical. The kinetic results obtained from these reactions were shown to be dominated by reversible hydrogen transfer of the radicals formed in the reaction with the small amounts of hydrogen bromide produced from bromine atom abstraction. When the reactions were carried out in the presence of a hydrogen bromide scavenger, either ethylene oxide or powdered potassium carbonate, the kinetic results of photobromination were found to be almost insensitive to the effects of the changes in substituents. The reactivities of fluorene relative to the 10-substituted 9-methylanthracenes were found to be anomalously high, as was previously reported; however, when the reactions were carried out in the presence of ethylene oxide, the relative reactivities were shown to be predictably almost the same as those obtained when *tert*-butoxy radicals were the abstracting species.

The results of a reinvestigation of the mechanism of the photoinitiated bromotrichloromethane side-chain bromination of arenes has been published a number of years ago.[3-5] The reaction mechanism was found to be more complex than originally proposed[6] (see Scheme I). An

Scheme I

$$\cdot CCl_3 + ArCH_3 \rightarrow ArCH_2\cdot + HCCl_3 \tag{1}$$

$$ArCH_2\cdot + CCl_3Br \rightarrow BrCH_2Ar + \cdot CCl_3 \tag{2}$$

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[1] Part 15: D. D. Tanner, J. A. Plambeck, D. W. Reed, and T. W. Mojelsky, *J. Org. Chem.*, preceding paper in this issue.

[2] University of Alberta, Postdoctoral Fellow, 1980.

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