Electrochemical Reduction of Allyl Halides in Nonaqueous Solvents—a Reinvestigation

Allen J. Bard*[1a] and Andreas Merz[1b]

*Contribution from the Department of Chemistry,
The University of Texas at Austin, Austin, Texas 78712, and the
Fachbereich Chemie und Pharmazie der Universität, D-8400 Regensburg,
West Germany. Received September 28, 1978*

Abstract: The electrochemical reduction of allyl iodide (**1a**), allyl bromide (**1b**), (*E*)-3-bromo-1-phenyl-1-propene (**1c**), and (*E*)-5-bromo-2,2,6,6-tetramethyl-3-heptene (**1d**) was studied in dry acetonitrile with TBAP as supporting electrolyte by means of cyclic voltammetry and coulometry at mercury, platinum, and vitreous carbon electrodes. Compounds **1a–c** showed multiple waves on platinum and mercury because of halide surface effects. However on vitreous carbon **1a–d** gave single reduction waves, with half-peak potentials of -1.38, -1.64, -1.11, and -1.89 V (vs. SCE), respectively. Apparent coulometric n values of 1 for **1a–c** were shown to arise from rapid nucleophilic substitution of the allyl anion intermediates with starting halide to give electroinactive dimers. Sterically hindered **1d** showed an n_{app} of 2 and did not exhibit surface interactions with Hg and Pt. Thus allyl halides, contrary to previous statements in the literature, are reduced via a two-electron electrode reaction and the reduction of the allyl radical to the allyl anion cannot be seen as a separate step. Evidence was also obtained for the formation of the allyl anion by reduction of **1a** and **1b** with solvated electrons in liquid ammonia; the electrochemical oxidation of this species in this medium occurred at ca. -1.2 V.
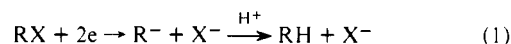
Introduction

The electrochemical reduction of organic halogen compounds has been widely investigated and several reviews are available.[2] As was first shown by von Stackelberg and Stracke,[3] the overall reaction involves cleavage of the carbon–halogen bond in a single two-electron polarographic wave to give a carbanion which is subsequently protonated (Scheme I). Among several more detailed mechanisms which were developed for this reaction,[4] the one outlined in Scheme II involving radical anions and free-radical intermediates is now the generally accepted one. Overall Scheme II corresponds to Scheme I as long as two assumptions are valid: (1) the decay of the radical anion (eq 3) is very fast (or even concerted in combination with eq 2) to prevent escape of $RX^-\cdot$ from the electrode surface by diffusion; (2) the reduction of the free radical (eq 4) is instantaneous at the potential required for eq 2 to occur.
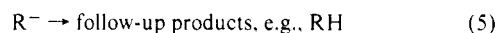
There is theoretical[5] and kinetic[6] evidence that the first assumption holds for most organic halides. Only when the parent (halogen-free) system is capable of stabilizing the radical anionic state will the lifetime of the radical anions of organic halides be greatly enhanced. Thus, some halogenated aromatic ketones, nitro and nitrile compounds, and some halogenated polynuclear aromatics can be reduced to fairly stable radical anions which could be characterized by electrochemical and ESR methods.[7] Because in these cases the radical anions can diffuse away from the electrode, cleavage into free radicals and halide ions (eq 3) occurs in the bulk solution and the final products result, at least partially, from free-radical reaction pathways.[8]

The second assumption is implicit in the two-electron character of the reduction waves of most halides. Unambiguous electrochemical characterization of the reduction of the radical (eq 4) would, however, be possible only if the radicals or carbanions were available for independent study (vide infra) or, in the case of organic halides, if the second electron transfer occurred at *more negative* potentials than the first one. The latter has been suggested to be true for allyl,[9] benzyl,[10] and tertiary alkyl[11] bromides and iodides, since these compounds show two reduction waves in dc polarography at the dropping mercury electrode. Using second harmonic ac voltammetry at platinum and gold electrodes, Breslow and co-workers found two distinct responses for allyl, benzyl, and *tert*-butyl iodides.[12]
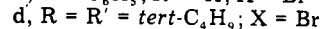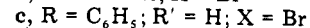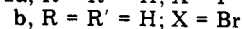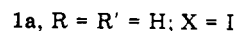
Scheme I

$$RX + 2e \rightarrow R^- + X^- \xrightarrow{H^+} RH + X^- \qquad (1)$$

Scheme II

$$RX + e \rightarrow RX^-\cdot \qquad (2)$$

$$RX^-\cdot \rightarrow R\cdot + X^- \qquad (3)$$

$$R\cdot + e \rightarrow R^- \qquad (4)$$
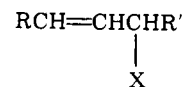
$$R^- \rightarrow \text{follow-up products, e.g., RH} \qquad (5)$$

The more negative ones were assigned to the reversible thermodynamic half-wave potentials of the corresponding radical-anion couples and the values were in turn used in a thermodynamic cycle to calculate the thermodynamic acidities of the carbon–hydrogen bonds. The pK_a values thus obtained for propene, toluene, and isobutane are strikingly different from those previously available in the literature.[13] On the other hand, no detailed mechanistic studies were carried out in the cited literature,[9–12] and attempts to detect the free radicals by direct ESR measurements[11] or spin trapping techniques[14] failed. We, therefore, felt the necessity of a careful reinvestigation and report, in this paper, the results of our studies on several allylic halides.

Results and Discussion

The electrochemical reduction of allyl iodide (**1a**), allyl bromide (**1b**), (*E*)-3-bromo-1-phenyl-1-propene (cinnamyl bromide) (**1c**), and (*E*)-5-bromo-2,2,6,6-tetramethyl-3-heptene (di-*tert*-butylallyl bromide) (**1d**) at mercury, platinum,

$$RCH{=}CHCHR'$$
$$|$$
$$X$$

1a, R = R' = H; X = I
b, R = R' = H; X = Br
c, R = C_6H_5; R' = H; X = Br
**d**, R = R' = *tert*-C_4H_9; X = Br

and vitreous carbon electrodes was studied by means of cyclic voltammetry and coulometry in water-free acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) as supporting electrolyte. The latter two compounds were included to obtain information on conjugative and steric effects.

Table I. Cyclic Voltammetric Data for Allyl Halides in Acetonitrile–TBAP

allyl halide	concn, mM	electrode material	first Wave,[a] E_p	second wave[a]			anodic wave,[a,b] E_p
				E_p	$E_{p/2}$	current function[c]	
1a	4.4	Hg[d]	−0.62	−2.26			
1b	6.1	Hg[d]	−1.62	−2.25			
1d	2.25	Hg[c]		−2.36	−2.22	constant with $v^{1/2}$	−0.66
1a	4.4	Pt	−1.3	−1.99	−1.80	870	
1a	3.3	Pt[e]	−1.3	−1.96	−1.82	1050	
1b	4.9	Pt	−1.4	−2.30	−2.12	not constant with $v^{1/2}$	
1b	4.9	Pt[f]		−2.25	−2.12	1380	
1c	5.0	Pt	ill defined	−1.92	−1.78	variable shape and height	
1d	2.25	Pt		−2.75[g]			
1a	5.5	vitr[h] C		−1.50	−1.38	1280	
1b	3.0	vitr[h] C		−1.78	−1.64	1260	
1c	5.25	vitr[h] C		−1.30	−1.11	930	
1d	2.25	vitr[h] C		−2.09	−1.89	1190	−0.26

[a] All potential values in volts vs. SCE for a scan rate of 0.2 V/s. [b] Except halide oxidation. [c] $i_p/v^{1/2}AC$ ($V^{-1/2}$ A cm s$^{-1/2}$ mol^{-1}). [d] Area of Hg drop not determined. [e] 0.1 M TBAI in acetonitrile. [f] Electrode potential pulsed between −0.5 and −2.5 V before scanning the voltammogram. [g] Shoulder on back-ground rise. [h] Vitreous.
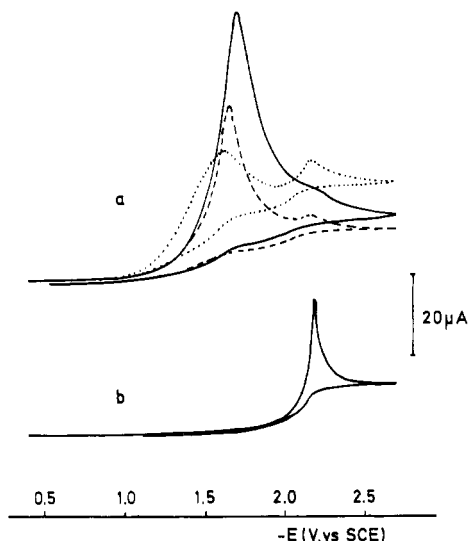
Figure 1. Cyclic voltammograms of allyl bromide (**1b**, 5.8 mM) in 0.1 M TBAP in acetonitrile at the hanging mercury drop electrode: (a) cyclic voltammograms of the original solution at 0.5 (—), 0.2 (- - -), and 0.1 V/s (· · ·); (b) after coulometric reduction at −1.7 V (0.2 V/s).

Table II. Coulometry of Allyl Halides in 0.1 M TBAP in Acetonitrile

allyl halide	electrode material	applied potential (V vs. SCE)	n_{app} (faradays mol^{-1})
1a	Hg	−0.7	0.86
1a	Hg	−2.8	0.91[a]
1a	Hg	−2.8	1.25
1a	Pt	−1.4	1.04
1a	Pt	−2.5	1.03
1a	C	−2.4	0.98
1b	Hg	−1.8	1.01
1b	Hg	−2.8	0.65[a]
1b	Hg	−2.8	1.28
1b	Pt	−1.5	no current
1b	Pt	−2.7	0.97
1b	C	−2.1	1.00
1c	Hg	−1.7	1.00
1c	Pt	−2.2	1.05
1c	C	−1.7	1.01
1d	Hg	−2.7	1.85
1d	C	−2.5	1.83
1d	C	0.0	−0.14[a,b]

[a] Coulometry following the preceding reduction in the same solution. [b] Negative sign signifies anodic process.

Cyclic voltammetric and coulometric data are presented in Tables I–III. Potential values are given with respect to the saturated aqueous calomel electrode (SCE).[15]

Results on Mercury. Most of the previous studies of allyl halides were performed at the dropping mercury electrode. Goodin reported that the reduction of allyl bromide (**1b**) at a hanging mercury drop electrode (HMDE) showed a very broad cathodic wave at −1.65 V.[14] We confirmed this result and obtained additional information about the process. The reduction peak of **1b** at the HMDE is indeed very broad, but the wave becomes sharp in the peak region. This behavior, together with a scan rate dependency of the peak current which lies between a $v^{1/2}$ and v proportionality, indicates the presence of some surface interaction. Furthermore, a second wave develops at *slow* scan rates (≤0.2 V/s), which suggests that a new electroactive species is *formed* following the first reduction wave (Figure 1a). This was confirmed by coulometry at a mercury pool electrode where reduction at −1.70 V consumed

0.98 faradays/mol (n_{app}). The resulting solution still showed the second voltammetric peak at −2.36 V (Figure 1b) and a second coulometric reduction carried out at −2.70 V showed n_{app} = 0.6 and produced a clean reductive background. The reduction behavior of allyl iodide (**1a**) followed a similar pattern; however, the first reduction wave occurred at a very positive potential (−0.62 V) and had a peculiar shape. The peak current of this wave depended on how long the mercury drop was exposed to the test solution before taking the voltammetric scan, thus indicating a preceding chemical reaction with the mercury surface. A second reduction wave appeared at −2.38 V, the same position as in the allyl bromide case. Again, two consecutive coulometric reductions carried out at −1.10 and −2.70 V showed n_{app} values of 0.90 and 0.91, respectively. If **1a** or **1b** were coulometrically reduced immediately at −2.70 V only 1.2–1.3 faraday/mol were consumed.

The second waves observed for **1a** and **1b** cannot be assigned to the reduction of the allyl radical to the allyl anion, since the
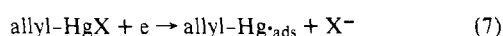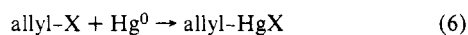
Table III. Voltammetry and Coulometry of Allyl Halides **1a–d** at Vitreous Carbon in the Presence of Acids

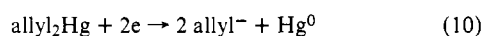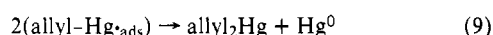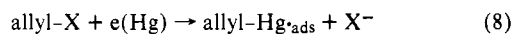| allyl halide | concn, mM | acid, mM | | | $i_d{}^a$ | $n_{app}{}^a$ | isolated product (%) |
		PhCOOH	Et₃NH⁺Br⁻	H₂O			
1a	2.75	1.4			1472	1.11	
1a	2.75	2.8			1680	1.18	
1a	2.33	17.0			1770	1.55	
1b	6.07		25		1740		
1c	5.25	7.8			1550		
1c	10.0	21.5			1550	1.61	
1c	170.0		none			0.96	**2** (80)
1c	152			700		1.15	**3** (55), **4** (45)

^{a} For comparison with values without acid, see Tables I and II.

former would not be expected to survive on the time scale of a coulometric experiment. It is thus necessary to assume that organomercury intermediates are involved in the reduction mechanism and we suggest the mechanistic scheme outlined in Scheme III.[16] Similar reaction schemes have been proposed by other authors.[17] The reduction potentials of dialkylmercury compounds seem to strongly depend on the nature of the solvent–supporting electrolyte system but our value ($E_{p/2}$ = −2.15 V) is in good agreement with the one given by Reutov et al. for the polarographic reduction of diallylmercury in nonaqueous DMF.[18] The voltammogram of di-*tert*-butylallyl bromide (**1d**) was entirely free from surface effects and showed only one, diffusion controlled, irreversible peak at −2.36 V. We interpret this to indicate the prevention of formation of organomercurials by the steric hindrance at the two tertiary butyl groups. We note also that an anodic peak is observed on the backward scan at −0.66 V which, on scan reversal, reveals a cathodic peak at −0.82 V. Since coulometry at −2.70 V showed n_{app} = 1.85, indicating a two-electron reduction to the carbanion, it is tempting to assign these peaks to the radical–carbanion couple as discussed below.

Scheme III

$$allyl\text{-}X + Hg^0 \rightarrow allyl\text{-}HgX \qquad (6)$$

$$allyl\text{-}HgX + e \rightarrow allyl\text{-}Hg\text{·}_{ads} + X^- \qquad (7)$$

or

$$allyl\text{-}X + e(Hg) \rightarrow allyl\text{-}Hg\text{·}_{ads} + X^- \qquad (8)$$

$$2(allyl\text{-}Hg\text{·}_{ads}) \rightarrow allyl_2Hg + Hg^0 \qquad (9)$$

$$allyl_2Hg + 2e \rightarrow 2\ allyl^- + Hg^0 \qquad (10)$$

Results on Platinum. Allyl iodide (**1a**), at a platinum disk electrode, showed two irreversible reduction waves with peak potentials at −1.3 (very broad) and −2.01 V; the ratio of the peak currents was strongly dependent on the condition of the platinum surface and the purity of the allyl iodide employed. Thus, the first wave was almost absent in the *very first* voltammetric scan in the clean test solution at a previously polished platinum electrode (Figure 2a). After a few consecutive sweeps, the first wave increased to yield about a 1:1 peak-current ratio for both waves at slow scan rates (≤0.2 V/s). At higher scan rates the peak current of the second wave increased in proportion to the square root of the scan rate while the first wave was almost independent of the scan rate (Figure 2b). Pure **1a** is a slightly greenish yellow liquid which upon storage assumes an orange color due to free iodine. If such a colored sample was studied, the first wave already appeared in the first scan and its peak current was sometimes even higher than that of the second one. Completely analogous results have been obtained by Bartak[19] with benzyl iodide. The obvious difference between an impure allyl iodide sample or a solution in which several reductive scans have been taken and a "clean"
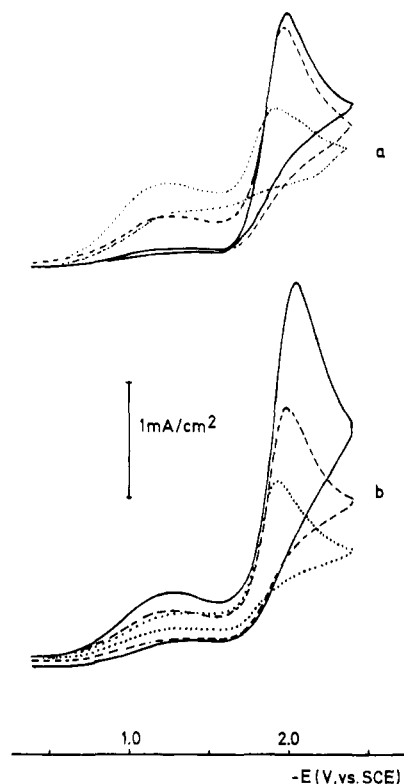
Figure 2. Cyclic voltammograms of allyl iodide (**1a**, 3.8 mM) in 0.1 M TBAP in acetonitrile at a platinum disk electrode: (a) consecutive scans at 0.2 V/s—1st scan (—), 7th scan (- - -), and 20th scan (· · ·); (b) scan rate dependency—0.5 (—), 0.2 (- - -), and 0.1 V/s (· · ·), 3rd to 5th scans in a fresh solution.

solution is the presence of *iodide ions* which are known to be strongly adsorbed on platinum in aqueous solution.[20] When the electrode potential was pulsed several times between −0.5 and −2.5 V (10-ms pulse duration) which may cause desorption of iodide, a voltammogram taken immediately afterward shows a marked decrease of the first reduction wave. Thus the first reduction wave of **1a** at platinum probably represents a reduction process assisted by adsorbed iodide ions, whereas the second wave represents the ordinary electron transfer through the metal solution interface to a molecule in solution. Allylic type species are also known to strongly interact with platinum in aqueous solutions and even produce modified platinum surfaces.[21] Thus, the simultaneous interaction of allyl iodide and adsorbed iodide ions with the Pt surface could lead to the formation of a surface complex which would lower the energy of the σ* orbital of the carbon–iodine bond and thus facilitate electron transfer. However, when the voltammetric reduction of **1a** was performed in acetonitrile containing 0.1 M tetra-*n*-butylammonium *iodide* (TBAI), the prewave was almost completely suppressed. In terms of our model this could mean
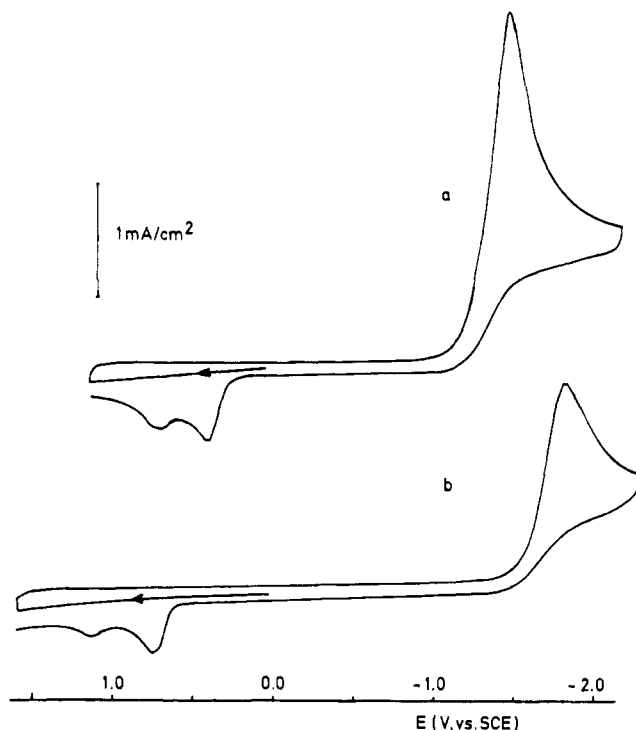
Figure 3. Cyclic voltammograms of (a) allyl iodide (**1a**, 5.5 mM) and (b) allyl bromide (**1b**, 3.0 mM) in 0.1 M TBAP in acetronitile at a vitreous carbon disk electrode, scan rate 0.2 V/s. The anodic peaks represent the oxidation of bromide and iodide ion, respectively.

Figure 4. Cyclic voltammogram of cinnamyl bromide (**1c**, 5.2 mM) in 0.1 M TBAP in acetonitrile at vitreous carbon, scan rate 0.2 V/s: pure (—) and in the presence of 7.8 mM of benzoic acid (- - -).

effective blocking of surface sites by excess iodide such as to prevent interaction of the allylic substrate with the surface.

Effects of halide ions, initially present or electrogenerated, have been noticed by Boto and Bard[22] in the electrochemical reduction of 9,10-dichloro-9,10-dihydro-9,10-diphenylanthracene in dry DMF or acetonitrile at platinum and gold electrodes. It thus seems that surface effects in the reduction of halo compounds at Pt electrodes are a frequent occurrence and deserve further study.

Similar but less pronounced effects were observed with allyl bromide (**1b**) and cinnamyl bromide (**1c**) at platinum (see Table I). Again no surface phenomena were detected with di-*tert*-butylallyl bromide (**1d**); in this case the reduction occurred only as a shoulder on the background current rise at ca. -2.75 V.

Results on Vitreous Carbon. In searching for an electrode material which would allow the study of the electrochemical reduction of allyl halides free of complications from surface interactions, we investigated vitreous ("glassy") carbon, which had already been shown by Lambert and Ingall to give improved results in the reduction of simple alkyl chlorides.[23] All four compounds (**1a–d**) gave well-resolved and highly reproducible cyclic voltammograms at a vitreous carbon disk electrode (Figures 3 and 4). The general features compared with those of the other electrode materials are as follows: (1) only a single diffusion-controlled reduction wave was observed for each compound; (2) the peak potentials were considerably less negative than those of the second peaks at platinum; and (3) the voltammetric peaks were sharper than at platinum but showed electrochemical irreversibility as documented by a scan rate dependent peak shift and a scan rate independent kinetic current at the foot of the waves for $i < 0.1$ i_{peak}. These voltammetric results clearly show that the electrochemical reduction at this electrode material is free of specific substrate and product surface interaction and thus represents pure diffusion-controlled electroreduction of a solution species. Again we note that similar behavior was found by Bartak for benzyl
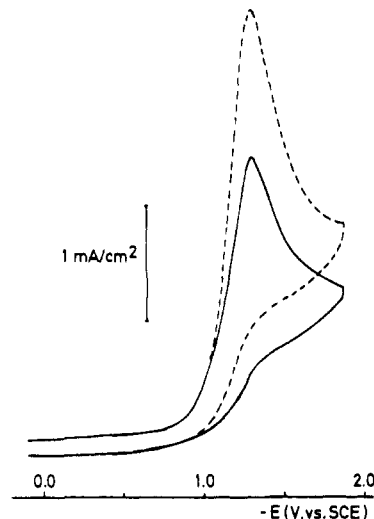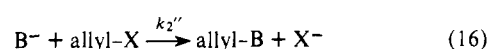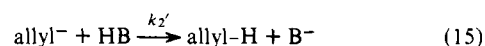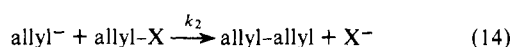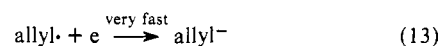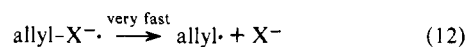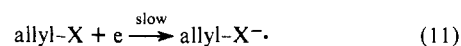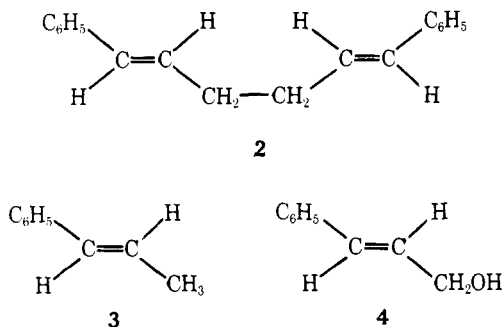
iodide.[19] With the exception of **1d**, no anodic peaks could be detected on reversal anodic scans, apart from the expected oxidation peaks for bromide or iodide ions (Figure 3). This was studied for scan rates up to 20 V/s, which was the experimental limit in our studies because of the relatively large double-layer capacity at vitreous carbon. Coulometric reductions were carried out at reticulated vitreous carbon (RVC), a recently described porous "glassy" carbon material. Compounds **1a–c** cleanly consumed 1 faraday/mol, while for **1d** n_{app} was 1.85.

Mechanistic Implications. According to Scheme II a two-electron coulometry is expected if the reduction proceeds to the carbanion (eq 2–4). The clean one-electron n_{app} values found for the halides **1a–c** might thus suggest reduction only to the free radicals which would dimerize. It has, however, been pointed out by other authors that dimer formation with the electrochemical reduction of organic halides may well be the result of a nucleophilic, Wurtz–Fittig-type attack of the carbanion intermediate on the starting halide, which would be even more likely with the highly reactive allylic species.[24] The observed n_{app} of 1.85 for the sterically hindered **1d** provides the first support that such a mechanism could be operative, as presented in Scheme IV. Assuming that the combined steps, eq 11–13, can be treated as essentially concerted, at least on the time scale of diffusional events, the overall resulting n_{app} should be dependent only on the relative rates of eq 14–15 (and 16; see below). In the absence of an appropriate proton donor, HB, eq 14 would be the predominant path, giving rise to an n_{app} value of 1, although the elementary electrode reaction is a two-electron process.

Scheme IV

$$\text{allyl–X} + \text{e} \xrightarrow{\text{slow}} \text{allyl–X}^{-}\cdot \tag{11}$$

$$\text{allyl–X}^{-}\cdot \xrightarrow{\text{very fast}} \text{allyl}\cdot + \text{X}^{-} \tag{12}$$

$$\text{allyl}\cdot + \text{e} \xrightarrow{\text{very fast}} \text{allyl}^{-} \tag{13}$$

$$\text{allyl}^{-} + \text{allyl–X} \xrightarrow{k_2} \text{allyl–allyl} + \text{X}^{-} \tag{14}$$

$$\text{allyl}^{-} + \text{HB} \xrightarrow{k_2'} \text{allyl–H} + \text{B}^{-} \tag{15}$$

$$\text{B}^{-} + \text{allyl–X} \xrightarrow{k_2''} \text{allyl–B} + \text{X}^{-} \tag{16}$$

We carried out voltammetric and coulometric experiments with the halides **1a–d** at vitreous carbon in dry acetonitrile containing benzoic acid, triethylammonium bromide, or water as Brønsted acids to increase the protonation rate over the substitution rate. In all experiments a substantial increase in the voltammetric peak currents (Figure 4), as well as in the coulometric n_{app} values, was found (Tables II and III). Furthermore, in the case of cinnamyl bromide (**1c**), the validity of the proposed mechanism (scheme IV) was tested by isolation of the products formed in preparative electrolyses. In dry acetonitrile, **1c** is reduced to a mixture of dimers in which (E,E)-1,6-diphenyl-1,5-hexadiene (**2**) is predominant to ~80%. In the presence of water, no dimer is formed and instead a 55% yield of 1-phenylpropene (**3**), the product of carbanion protonation, was obtained together with 45% cinnamyl alcohol (**4**). The latter product is obviously derived from the reaction

Figure 5. Cylic voltammogram of the solution obtained by reduction of allyl iodide (**1a**) or bromide (**1b**) with solvated electrons in 0.3 M KI in liquid ammonia at platinum at −75 °C.

of OH^- ion, the conjugate base liberated in the protonation process, with starting halide. This side reaction,[25a] which corresponds to eq 16, also explains why we could never observe pure two-electron coulometric reduction even in the presence of excess acid. Formation of bisallyls by dimerization of allyl radicals is thus clearly ruled out, since such a reaction type would not be affected by the presence of proton donors. Additionally, Figure 4 shows that the kinetic current at the foot of the wave does not change with the addition of acid; i.e., the electron-transfer rate-controlled part of the overall reaction does not change. Equation 14 is also in agreement with the coulometric results of **1a** and **1b** at the mercury pool electrode. Electrolyses at −2.7 V, beyond the reduction potential of diallylmercury, generates allyl anions in the presence of starting material and this gives n_{app} values close to 1. However, two subsequent electrolyses at −1.5 and −2.7 V consume a total amount of current close to 2 faradays/mol because all of the starting material is consumed in the first step forming diallylmercury which is unreactive toward the former.

The proposed mechanism implies that the potential for reduction of the allyl radicals occurs at potentials substantially more positive than the potential required for the first electron transfer to the allyl halide. Di-*tert*-butylallyl bromide (**1d**) exhibited an anodic wave at −0.26 V on the backward scan following the reduction of **1d**. This wave persisted to some extent even after coulometric reduction and was immediately quenched by addition of water. A similar oxidation wave was observed for the same compound at mercury at −0.65 V. These values seem too far positive to represent the oxidation wave of the 1,3-di-*tert*-butylallyl anion and might rather be due to reduction of an imidate ion formed by addition of the carbanion to the solvent, acetonitrile. Oxidation waves of carbanions in the range of −0.8 to −1.2 V have, however, been observed in other solvents.[25-29] The considerably more negative redox potentials of the cycloheptatrienyl (−1.63) and cyclopropenyl (−1.78) radical–anion couples have to be ascribed to the high degree of antiaromaticity of the anions.[28]

In a further attempt to obtain the oxidation potential of the allyl anion we studied the electrochemistry of **1a** and **1b** in liquid ammonia, a solvent which combines the advantages of
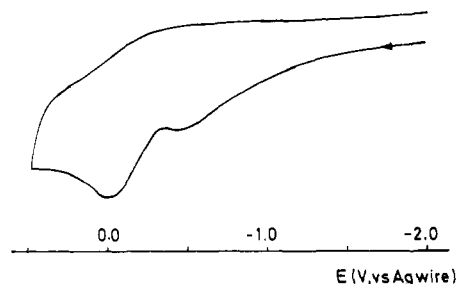
excellent conductivity at low temperature operation and low acidity.[29] Cyclic voltammetry and coulometry were carried out at −75 °C in a 0.3 M potassium iodide solution in liquid ammonia at platinum electrodes with potentials measured vs. a silver wire immersed in a separate fritted tube.[30] Allyl iodide (**1a**) and allyl bromide (**1b**) each showed a single irreversible reduction wave with peak potentials of −1.11 and −1.30 V, respectively. In the case of **1b**, a prewave at −1.11 V appeared after some time, indicating the formation of **1a** by a nucleophilic substitution reaction of **1b** with the supporting electrolyte anion. Coulometry of either species consumed 1 faraday/mol leaving a clean background. At scan rates higher than 20 V/s, a broad anodic wave appeared on the reverse scan in the cyclic voltammograms of **1a** and **1b** at ca. −0.5 V, which was enhanced when the cathodic sweep was extended to −2.4 V allowing excess solvated electrons to form.[31] If we assign the anodic wave to the oxidation of the allyl anion, these results suggest that nucleophilic substitution is still fast under these conditions but that two-electron reduction of the allyl halides by solvated electrons in homogeneous solution might be fast enough to overcome allyl dimerization. To test this assumption, **1a** or **1b** was added to a two- to fivefold excess of solvated electrons in liquid ammonia which were coulometrically generated at a large platinum cathode at −2.6 V. The number of solvated electrons that reacted was determined by coulometric back-oxidation at −2.0 V to be 1.9–2.4 faradays/mol of starting halide. The remaining solution was slightly yellow and showed the same voltammogram starting from either **1a** or **1b** (Figure 5), consisting of a broad anodic wave with two peaks at −0.35 and −0.04 V. Complete oxidation of this solution at +0.25 V consumed 0.8–0.9 faradays/mol of allyl halide, but the yellow color of the solution disappeared at some earlier stage of the electrolysis. Allyllithium, in THF, has an absorption maximum at 315 nm (log ϵ 3.66) and the solution is slightly yellow due to tailing of the absorption band into the visible region.[32] Thus, we ascribe the yellow color and the oxidation peak at −0.35 V to the allyl anion in liquid ammonia. The second peak can be assigned to the oxidation of the amide ion present in acid–base equilibrium.[33] The half-peak potential corresponds to ca. −1.2 V vs. SCE[30] and is in good agreement with the extrapolated scale of Lochert and Federlin[27] when a pK_a value of 35 is assumed for the α H of propene.

Kinetics. The rate-determining step of the overall reaction is probably the first electron transfer which can, however, be looked upon in two different ways: either taking eq 11 and 12 as two distinct steps (ec type) or as one, concerted step. Different thermodynamic half-wave potentials have to be considered for these processes, since the products of eq 11 and 12 are on different energy levels. The actual position of the wave in the cyclic voltammogram can thus be interpreted either as shifted *positive* from the E_0 of eq 11 by a fast chemical follow-up reaction or shifted *negative* from the E_0 of combined eq 11 and 12 by a sluggish (irreversible) electron transfer. In general, organic halides can behave, depending on their elec-
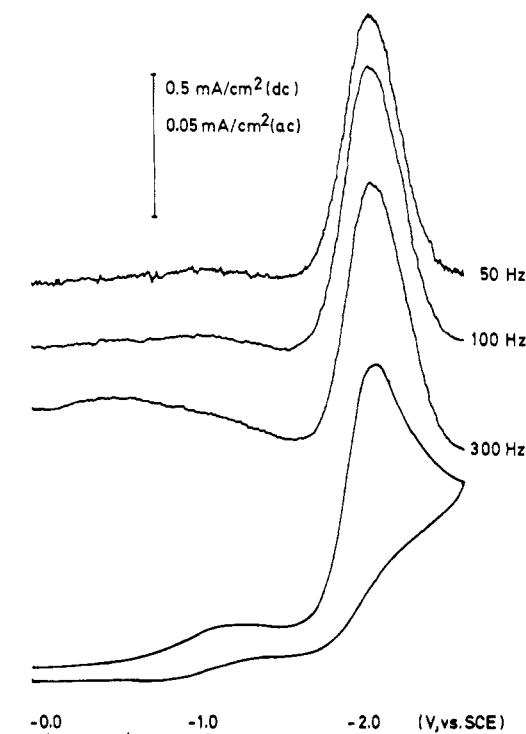
Figure 6. Cyclic voltammogram (bottom, 0.2 V/s) and ac voltammograms at a stationary platinum disk electrode of a 2.2 M solution of allyl iodide (**1a**) and 0.1 M TBAP in acetronitrile.

tronic structure, within the whole range given by these extremes.

Attempts to determine heterogeneous rate constants as well as the homogeneous kinetic rate constants of the following chemical reactions (eq 14–16) were not successful. Digital simulation using finite difference methods[34] showed that, over a wide range, the peak currents of the voltammetric waves depended simultaneously on several chemical rate constants and diffusion coefficients and it was difficult to simulate very large rate constants. Work on this problem is continuing. We should mention, however, the very interesting results of Savéant and co-workers[35] who have been able to extract homogeneous and heterogeneous rate constants for the reduction of aromatic and aliphatic halides by studies of homogeneous redox catalysis. They have also proposed an essentially simultaneous electron-transfer bond-breaking process for the reduction of aliphatic halides.

Alternating Current Voltammetry. Because of the inconsistency of our results with the previously mentioned second harmonic ac studies of Breslow and Grant,[12a] we also studied fundamental harmonic ac voltammetry of allyl iodide (**1a**) at platinum and vitreous carbon in 0.1 M TBAP in dry acetonitrile. Alternating current voltammetric peaks were indeed observed with both electrode materials. One single peak was observed at the carbon electrode close to the peak potential of the cyclic voltammogram. On platinum two peaks appeared; the relative height of these varied with the surface condition of the electrode as found in cyclic voltammetry. Figure 6 presents a comparison between cyclic voltammetry and ac voltammetry obtained from the sample sample. Maximum peak currents were seen at 90° phase angle and the signals did not appreciably change over the range of 10–800-Hz ac frequency. We should note that small ac responses result even from irreversible systems,[36] as well as with potential dependent adsorption–desorption processes or any potential dependent change in the double-layer capacity.[37]

The observed ac responses cannot be associated with thermodynamic half-wave potentials, since they appear, in the

same solution, at different potentials with different electrode materials. We feel that the second harmonic ac data cannot be used to find such reversible potentials until the electrochemical reaction mechanism is completely elucidated and the absence of double-layer effects established.[38]

Conclusions

In summary, our results of the electrochemical reduction of allyl iodide (**1a**) and bromide (**1b**) and two substituted allyl bromides at vitreous carbon electrodes show that the reduction of allyl halides, in principle, follows the classical reduction mechanism of von Stackelberg and Stracke;[3] i.e., the two-electron cleavage of the carbon–halogen bond cannot be resolved into single steps. The special situation with allylic bromides and iodides is characterized by rapid reaction of the electrogenerated carbanions with the starting halide to give bisallyl derivatives or, in the presence of proton donors, also by reaction of the conjugate base of the protonating acid with the starting material. Previous claims in the literature that the electrochemical reduction of allyl bromides and iodides proceeds in two distinct one-electron steps, the second one of which would represent the reduction of the allyl radical to the allyl anion, cannot be confirmed in our studies.[42] Those findings do in fact arise from specific surface interactions of the allyl halides with the electrode materials employed. The evidence also suggests that the standard potential of the allyl radical–anion couple is more positive than that of the reduction wave of allyl iodide (-1.4 V vs. SCE).

Experimental Section

Chemicals. Supporting electrolytes and solvents were purified as previously described.[41] Allyl iodide (Eastman Kodak) was stirred over powdered $Na_2S_2O_3$ for 15 min, followed by distillation onto K_2CO_3, and the mixture was again stirred for 15 min and finally flash vacuum distilled. Allyl bromide (Matheson Coleman and Bell) was passed over a short column of neutral alumina (Brockmann) prior to vacuum distillation. Cinnamyl bromide (Eastman Kodak) was twice sublimed at 10^{-5} Torr and ambient temperature yielding slightly yellow crystals, mp 35 °C. (E)-5-Bromo-2,2,6,6-tetramethyl-3-heptene (**1d**) was synthesized in two steps from (E)-2,2,6,6-tetramethyl-3-hepten-5-one.[39] The enone (0.05 mol) was reduced with $NaBH_4$ (0.025 mol) in 95% aqueous methanol containing 0.05 M sodium hydroxide (1 h) to give a quantitative yield of (E)-2,2,6,6-tetramethyl-3-hepten-5-ol which was isolated by hydrolyzing the reaction mixture with water and extraction with pentane: ^1H NMR ($CDCl_3$) 0.87 (s, 9 H), 1.02 (s, 9 H), 1.80 (s, 1 H), 3.6–3.7 (m, 1 H), 5.2–5.9 ppm (m, 2 H). The alcohol (0.04 mol) which appeared to be 95% pure from its NMR spectrum was used without further purification and converted into the bromide **1d** by treatment (30 min) at 25 °C with a mixture of 10 mL of 48% aqueous hydrobromic acid and 2 mL of concentrated H_2SO_4. The product was extracted with pentane, dried over $CaCl_2$ without previous washing, and distilled to give an 85% yield of **1d**, bp 70 °C (3 Torr). In the ^1H NMR spectrum (CCl_4), the two tertiary butyl groups show as one singlet at 0.92 ppm. The allyl system gives an ABX coupling pattern with δ_A 5.47, δ_B 5.48, δ_X 4.25 ppm (J_{AX} = 4.7, J_{BX} = 5.3, J_{AB} = 11.8 Hz).

Electrochemical Cell and Instrumentation. All experiments except preparative electrolyses were carried out in a glove box in a helium atmosphere. A conventional three-electrode three-compartment cell was used; additionally, the working electrode chamber held a large-area electrode to allow coulometric and voltammetric experiments as desired. The HMDE was a mercury drop attached to a small amalgamated platinum disk. The platinum disk electrode used for the studies on platinum was treated with hot nitric acid for 10 min, then stored in distilled water, and polished with 5-μm alumina powder prior to use. The vitreous carbon electrode was only polished with alumina preceding each use. The silver wire used as a quasi-reference electrode was likewise carefully polished immediately before use. Care was taken not to introduce any halide salts which would shift the reference potential. Potentials obtained with this reference electrode were highly reproducible.[15] The vitreous carbon electrode used in coulometric experiments was a sample of Reticulated vitreous carbon (RVC 2X1-45-5) obtained from Chemotronics Inc., Ann Arbor, Mich.

Electrical contact to platinum or stainless steel wires was made by means of a hardening graphite cement (Graphoxy, Dylon Industries, Cleveland, Ohio). Cyclic voltammetric and coulometric data were obtained with a PAR (Princeton Applied Research) 173 potentiostat in combination with a PAR 175 signal processor and a PAR 179 digital coulometer. Alternating current voltammetry was performed with a PAR 170 electrochemical system. Full iR compensation was employed in all experiments. The work in liquid ammonia was carried out using vacuum line techniques as described previously.[29]

Preparative Electrolysis. Electrolyses of (E)-3-bromo-1-phenyl-1-propene (**1c**) were conducted in 0.1 M TBAP–acetonitrile solutions with or without added water using the same equipment as described above. Upon completion of electrolysis, the catholyte was diluted with water (1:1 v/v) and twice extracted with carbon tetrachloride. After the CCl_4 solution was washed thoroughly with water and dried over Na_2SO_4, it was concentrated and analyzed by NMR spectroscopy. Yields were determined by adding an appropriate standard, e.g., CH_2Cl_2. When electrolysis of **1c** was conducted in dry acetonitrile, the NMR spectrum obtained was identical with the one of 1,6-diphenyl-1,5-hexadiene (**2**) prepared independently:[40] 2.25 (m, 4 H), 6.0–6.5 (m, 4 H), 7.3–7.5 ppm (m, 10 H). When electrolysis of **1c** was conducted in acetonitrile with a fourfold excess of water, the NMR spectrum consisted of two slightly broadened doublets at 1.70 and 3.90, a multiplet at 6.0–6.4, and a broad singlet at 7.0–7.5 ppm which is an exact superposition of the literature spectra of 1-phenyl-1-propene (**3**) and 1-phenyl-1-propen-3-ol (**3**) in a molar ratio of 55:45.

References and Notes

(1) (a) University of Texas at Austin; (b) Universitat Regensburg.
(2) (a) C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems", Marcel Dekker, New York, 1970, p 201; (b) A. J. Fry, "Synthetic Organic Electrochemistry", Harper and Row, New York, 1972, p 170; (c) M. R. Rifi in "Organic Electrochemistry", M. M. Baizer, Ed., Marcel Dekker, New York, 1973, p 279; (d) M. R. Rifi in "Technique of Electroorganic Synthesis", Part II, N. L. Weinberg, Ed., Wiley, New York, 1975, p 170; (e) M. D. Hawley in "Encyclopedia of Electrochemistry of the Elements", Vol. XIV, A. J. Bard and H. Lund, Eds., Marcel Dekker, New York, Chapter 2, in press.
(3) M. von Stackelberg and W. Stracke, *Z. Elektrochem.*, **53**, 118 (1949).
(4) P. J. Elving and B. Pullman, *Adv. Chem. Phys.*, **3**, 1 (1961).
(5) E. Canadell and L. Salem, private communcation.
(6) J. F. Garst, R. D. Roberts, and J. A. Pacifici, *J. Am. Chem. Soc.*, **99**, 3528 (1977).
(7) L. Nadjo and J. M. Savéant, *J. Electroanal. Chem.*, **30**, 41 (1971); J. G. Lawless and M. D. Hawley, *ibid.*, **21**, 365 (1969); D. E. Bartak, K. J. Houser, B. C. Rudy, and M. D. Hawley, *J. Am. Chem. Soc.*, **95**, 6033 (1973). Reversible reduction of 9,10-dichloroanthracene: T. Teherani, J. Leal, and A. J. Bard, unpublished work.
(8) J. Grimshaw, R. J. Haslett, and J. Trocha-Grimshaw, *J. Chem. Soc., Perkin Trans 1*, 2448 (1977), and previous papers cited there; W. J. M. van Tilborg, C. J. Smit, and J. J. Scheele, *Tetrahedron Lett.*, 2113, 3651 (1977).
(9) J. P. Petrovich and M. M. Baizer, *Electrochim. Acta*, **12**, 1249 (1967).
(10) L. W. Marple, L. E. I. Hummelstedt, and L. B. Rogers, *J. Electrochem. Soc.*, **107**, 437 (1960). See, however, L. B. Rogers, and A. J. Diefenderfer, *ibid.*, **114**, 942 (1967).
(11) A. K. Hoffmann, W. G. Hodgson, D. L. Maricle, and W. H. Jura, *J. Am. Chem. Soc.*, **86**, 631 (1964).

(12) (a) R. Breslow and J. L. Grant, *J. Am. Chem. Soc.*, **99**, 7745 (1977); (b) R. Breslow and R. Goodin, *ibid.*, **98**, 6077 (1976).
(13) D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, 1965, p 19.
(14) R. D. Goodin, Ph.D. Dissertation, The University of Texas at Austin, 1975.
(15) The silver wire in 0.1 M TBAP in acetonitrile used in the actual measurements has a stable potential of 0.1 ± 0.01 V positive of an aqueous SCE as obtained by direct measurements and examination of standard redox systems of known potential. In 0.1 M TBAI the potential of the silver wire was 0.69 V positive of the SCE.
(16) A. J. Fry and D. Herr, *Tetrahedron Lett.*, 1721 (1978), have recently shown that organic bromides can be reduced even nonelectrochemically by finely divided mercury.
(17) (a) N. S. Hush and K. B. Oldham, *J. Electroanal. Chem.*, **6**, 34 (1963); (b) G. M. McNamee, B. C. Willett, D. M. La Perriere, and D. G. Peters, *J. Am. Chem. Soc.*, **99**, 1831 (1977).
(18) K. P. Butin, I. P. Beletskaya, A. M. Kashin, and O. A. Reutov, *J. Organomet. Chem.*, **10**, 177 (1967).
(19) D. E. Bartak, University of North Dakota, private communication; the potential values were $E_{p/2} = -1.67$ at platinum and -1.36 V at carbon.
(20) A. T. Hubbard, R. A. Osteryoung, and F. C. Anson, *Anal. Chem.*, **38**, 692 (1966).
(21) R. F. Lane and A. T. Hubbard, *J. Phys. Chem.*, **77**, 1401–1411 (1973).
(22) K. G. Boto and A. J. Bard, *J. Electroanal. Chem.*, **65**, 945 (1975).
(23) F. L. Lambert and G. B. Ingall, *Tetrahedron Lett.*, 3231 (1974).
(24) (a) M. M. Baizer and J. L. Chruma, *J. Org. Chem.*, **37**, 1951 (1972); see also ref 9. (b) The cyclization of 1,3- and 1,4-dihalides can also be interpreted in this way: M. R. Rifi, *J. Am. Chem. Soc.*, **89**, 4442 (1967); *Tetrahedron Lett.*, 1043 (1969).
(25) (a) K. Itaya, M. Kawai, and S. Toshima, *Chem. Phys. Lett.*, **42**, 179 (1976); (b) K. Itaya, M. Sawai, and S. Toshima, *J. Am. Chem. Soc.*, **100**, 5996 (1978).
(26) R. Dietz and M. E. Peover, *Trans. Faraday Soc.*, **62**, 3535 (1966).
(27) P. Lochert and P. Federlin, *Tetrahedron Lett.*, 1109 (1973); potential values in this work are given vs. the ferrocene–ferrocinium couple and are adjusted in our text to the SCE scale by adding +0.45 V.
(28) M. R. Wasielewski and R. Breslow, *J. Am. Chem. Soc.*, **98**, 4222 (1976).
(29) W. H. Smith and A. J. Bard, *J. Am. Chem. Soc.*, **97**, 5203 (1975), and references therein.
(30) By comparison with the reduction of nitrobenzene in this solvent the silver wire quasi-reference electrode in 0.3 M KI in liquid ammonia has a potential of ∼0.6 V positive of an aqueous SCE; see also ref 29.
(31) K. Itaya, T. Teherani, and A. J. Bard, *Nouv. J. Chim.*, **2**, 481 (1978).
(32) R. Waack and M. A. Doran, *J. Am. Chem. Soc.*, **85**, 1651 (1963).
(33) G. A. Olah, G. Asensio, H. Mayr, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **100**, 4347 (1978), recently described the formation of allylic type carbanions by treatment of the corresponding hydrocarbons with potassium amide in liquid ammonia.
(34) S. W. Feldberg in "Electroanalytical Chemistry", Vol. 3, A. J. Bard, Ed., Marcel Dekker, New York, 1969, p 199.
(35) (a) J. M. Savéant, private communcation; (b) C. P. Andrieux, J. M. Duman-Bouchiat, and J. M. Savéant, *J. Electroanal. Chem.*, **87**, 55 (1978).
(36) B. Timmer, M. Sluyters-Rehbach, and J. H. Sluyters, *J. Electroanal. Chem.*, **14**, 169, 181 (1967); D. E. Smith and T. G. McCord, *Anal. Chem.*, **40**, 474 (1968).
(37) D. E. Smith in "Electroanalytical Chemistry", Vol. 1, A. J. Bard, Ed., Marcel Dekker, New York, 1966, p 77 ff.
(38) A. M. Bond and D. E. Smith, *Anal. Chem.*, **46**, 1946 (1974).
(39) W. Rundel, *Chem. Ber.*, **102**, 374 (1969).
(40) W. P. Koch, *J. Chem. Soc.*, 1111 (1948).
(41) S. N. Frank, A. J. Bard, and A. Ledwith, *J. Electrochem. Soc.*, **122**, 898 (1975).
(42) Professor R. Breslow, after reading this work, has written the following: "A reinvestigation of the electrochemistry of benzyl iodide[12a] by Dr. Bernhard Jaun in our laboratory has made it clear that reduction occurs by a single two-electron process. We believe that the reduction wave of a first reduction wave is also present in that same paper[12a] reporting work with allyl iodide, as the work of Bard and Merz shows, and with propargyl iodide. This means that our published pK_a's for toluene, propene, and propyne[12a] are simply upper limits. However, this technical problem was not present in our previous work on *tert*-butyl anion,[12b] cyclopropenyl anions,[28] etc.".