A Correlation of ^{13}C NMR and Electrochemical Data for Benzyllithium

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Abstract: The effect of hexamethylphosphoramide on the ^{13}C NMR shift of the α carbon of benzyllithium in tetrahydrofuran parallels its effect on the one-electron electrochemical oxidation potential of benzyllithium. Thus the electrochemistry reflects the thermodynamics of a normally solvated species. Previous work on carbon cations is also consistent with the conclusion that the results of the electrochemical–thermodynamic method for determining hydrocarbon acidities, and the stabilities of carbon cations and radicals, are not being distorted by thermodynamic effects of a special solvent-free medium near the electrode.

We have described a technique that combines electrochemical and thermodynamic information (the E.T. method) to determine pK_a's of hydrocarbons. In the earliest version[1-5] the thermodynamic data were pK_{R^+}'s of carbon cations, combined with electrochemical potentials for two-electron reduction of the cations to anions. The pK_{R^+}'s were determined in aqueous acid, while the electrochemical reductions were performed in organic solvents. A standard system, triphenylmethyl, was used to calibrate the thermodynamic cycle since the pK_{R^+} of the triphenylmethyl cation (in aqueous acid) and the pK_a for conversion of triphenylmethane to the triphenylmethyl anion (in organic solvents) are both known. More recently[6,7] we have combined bond dissociation energies with electrochemical potentials for interconversion of radicals and anions. In this case, gas-phase bond dissociation energies are combined with solution-phase reduction potentials, determined either in the reductive direction (*tert*-butyl[6]) or in the oxidative direction (alkyllithiums oxidized to alkyl radicals[7]).

By the combination of known pK_a's of hydrocarbons with the two-electron reduction potentials for conversion of carbanions to carbocations we have also used the E.T. method to determine the stabilities of some carbon cations.[8] Furthermore, the one-electron potentials for reduction of cations to radicals have been combined with the pK_{R^+}'s of those cations to determine the bond dissociation energies of carbon radicals.[5] In all these applications, the E.T. method was able to duplicate known values of pK_a's, pK_{R^+}'s, or bond dissociation energies.

We have found that some carbanions produced by electrochemical reduction are poorly trapped by solvent, but can be protonated by acidic electrolytes.[9] In particular, highly reactive carbanions were not trapped by 50% acetic acid in the solvent, but were protonated by 0.4 M guanidinium cation in the electrolyte. Apparently the cationic acid is present at the cathode at which the carbanions are produced, but neutral acetic acid is excluded. The medium in which the electrochemistry occurs, at the electrode, is not a normal solvent but resembles a fused electrolyte salt. Thus one might wonder whether our E.T. data reflect the stabilities of normally solvated species; indeed, Streitwieser[10] has raised this question. What does electrochemistry in the unusual environment near an electrode tell us about the energies of carbanions, radicals, or carbocations in normal solution?

Such a concern could affect all electrochemistry, but it is not a general problem. For reversible processes the species involved at equilibrating, so thermodynamic activities of entities at the electrodes are equal to those of the fully solvated species.[11] However, many of the processes we have examined are only quasireversible. In such cases one could wonder whether the normal arguments still apply. We now wish to describe direct experimental evidence that at least with benzyllithium the E.T. method for pK_a determination indeed furnishes information about a normally solvated substance.

We had shown[7] that the electrochemical potentials for oxidation of benzyllithium, allyllithium, cyclopentadienyllithium, and (*tert*-butylpropargyl)lithium shift cathodically, and by different amounts, as HMPA is added to the THF solvent. The data are shown in Figure 1. At the same time, benzhydryllithium and (triphenylmethyl)lithium showed *anodic* shifts with added HMPA. Thus it seemed clear that the cathodic shifts were due to specific solvation of the substrate species by added HMPA, rather than some generalized solvation of electrodes, for instance. In particular, it seemed likely that in benzyllithium the HMPA was specifically solvating the lithium, replacing the THF in the coordination sphere.

As we noted previously,[7] the effect of HMPA may be to break up an organolithium cluster, to turn a THF-solvated intimate ion pair into an HMPA-solvated intimate ion pair, or to produce an HMPA-solvated solvent-separated ion pair. Any of these processes would destabilize benzyl anion and shift its peak cathodically, as observed. In any case, it seemed that we were observing a bulk solvation effect whose existence showed that the electrochemical potentials did not reflect the properties of some unusual unsolvated species at the electrode. To confirm this, we have used CMR to observe this solvation in bulk solution and find that the effects indeed parallel those for electrochemical oxidation.

In Figure 2 we have replotted the benzyllithium data of Figure 1, and we have also plotted our observed CMR shift[12] at −30 °C for the α-carbon of benzyllithium vs. the HMPA/Li^+ ratio. Since the HPMA is an excellent ligand, this seemed a better parameter than the simple percent HMPA in the solvent. In the NMR experiment the only lithium is that of benzyllithium itself, but in the electrochemical experiment the 5 mM organolithium concentration is greatly exceeded by the 200 mM $LiClO_4$ electrolyte, which is included in the calculation. As expected, HMPA had no significant effect on the CMR of (triphenylmethyl)lithium (see Experimental), which is not strongly associated even in THF. It is apparent that the bulk solution titration which the CMR shift reflects runs parallel to the electrochemical effects. If the electrochemistry had reflected special thermodynamics of oxidation of a *desolvated* species at the electrode, no such parallel should have been seen. Thus the normal thermodynamic equilibrium between species in solution and at the electrode holds here. It

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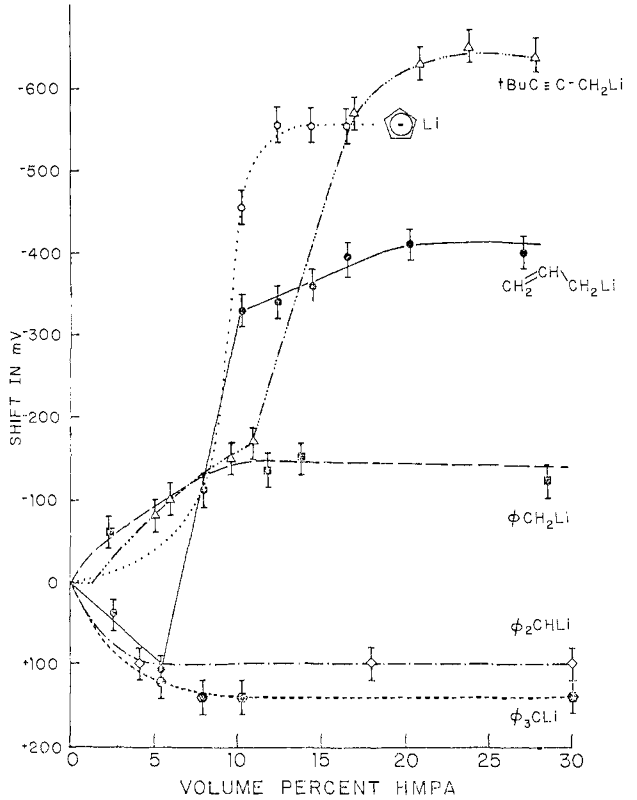

Figure 1. The shift in peak potential E_p in THF as a function of HMPA concentration in the cyclic voltammograms of organolithium compounds. The sweep rate was 200 mV/s and the temperature was −25 °C (except for cyclopentadienyllithium and (*tert*-butylpropargyl)lithium, which were at −60 °C). In the steep portions of the curves for allyllithium and for (*tert*-butylpropargyl)lithium two species were seen (cf. ref 7 for a discussion).

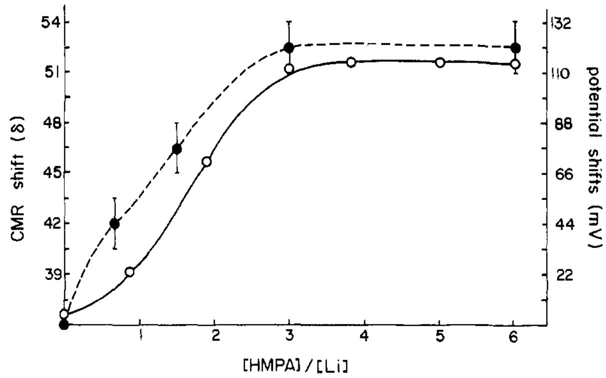

Figure 2. Shift of the CMR resonance for the α-carbon (○) and cathodic shift of the voltammetric peak potential (●) for benzyllithium as a function of equivalents of HMPA added per lithium cation in the THF solution.

presumably also holds for the other lithium derivatives[7] that showed anodic or cathodic HMPA effects (Figure 1) on their electrochemical potentials.

The anodic shifts of (triphenylmethyl)lithium and of benzhydryllithium probably reflect generalized solvation effects such as a shift in the reference electrode potential. If so, one might wonder whether it would be better to correct for this by plotting the *difference* between benzyllithium and (triphenylmethyl)lithium in Figure 2, rather than just the benzyllithium electrochemical data. When this is done, with an appropriate scale change, the fit to the CMR curve is even better than that shown in Figure 2.

The product of oxidation of benzyllithium is a benzyl radical, whose stability would not be strongly affected by solvent. Thus one might still worry about quasireversible electrochemical processes which produce *ions* in an unusual environment at an electrode, as in the two-electron reduction of carbon cations to carbon anions.[1-5] If the starting materials are in equilibrium with the bulk solvated species but the products produced at the electrode are not normally solvated, and not in equilibrium with solvated species, there could be a problem. However, some years ago we described[8] the two-electron oxidation of (9-phenylfluorenyl)lithium to the 9-phenylfluorenyl cation and of (triphenylindenyl)lithium to its cation. As Table I shows, in both cases the E.T. method gave the same pK_{R^+} for these cations as that obtained by normal equilibrium methods. The calibration compound was triphenylmethane, and the data were the known pK_a's of triphenylmethane, of 9-phenylfluorene, and of triphenylindene (in organic solvents), the known pK_{R^+} of triphenylmethyl cation (in H_2O/H_2SO_4), and the two one-electron electrochemical oxidation potentials for each species.

Table I. pK_{R^+} Values Derived by the E.T. Method and by Normal Procedures[8]

	pK_{R^+}	
compound	by titration	from E.T. method
triphenylmethyl cation	−6.63	taken as −6.63
9-phenylfluorenyl cation	−10.5	−10.8
1,2,3-triphenylindenyl cation	−12.6	−12.6

The predictions of electrochemical theory that these potentials should not be perturbed because of the unusual medium near the electrode are confirmed by both the CMR data on benzyllithium and the agreement with known values of data such as that[8] in Table I and in our previous studies.[1-7] Thus we conclude that the E.T. method does indeed give thermodynamic information about normally solvated species and is the method of choice for determining the stabilities of most very reactive cations, anions, and radicals.

Experimental

Benzyllithium was prepared as described previously,[7] as were the pure solvents. The electrochemical data of Figures 1 and 2 are from our previous work[7] and were determined with 5 mM substrate and 0.2 M $LiClO_4$ in purified THF/HMPA at −25 °C. The data for cyclopentadienyllithium and *tert*-butyllithium are at −60 °C. In contrast to allyllithium and *tert*-butyllithium, which show two species in the transitional region between THF and the HMPA plateau, benzyllithium shows only one species whose peak potential is plotted in Figures 1 and 2.

Carbon magnetic resonance spectra were obtained at −30 °C on a Bruker WM-300 MHz spectrometer equipped with a variable temperature probe. A 0.4-mL solution of benzyllithium (2.0 M) in THF was added to 0.6 mL of varying amounts of HMPA in THF at −30 °C in an evacuated glass vessel with stopcock, vacuum joint carrying a serum cap, and 5-mm NMR tube sidearm. After several freeze–thaw cycles the contents were tipped into the NMR tube sidearm with liquid N_2 cooling and freeze–thaw again, and the tube was then sealed off and removed. It was then placed into a 10-mm NMR tube containing acetone-d_6 by the use of Teflon spacers while maintaining low temperature. The CMR spectrum was then taken in the standard fasion[12] with the THF as internal standard and the chemical shift of all carbons recorded. The chemical shift of the meta carbons was constant at 127 ± 0.5, that of the ipso carbon shifted from 158.7 to 152.2 as HMPA was added, that of the ortho carbons went from 114.5 to 110.9 when 3–4 equiv HMPA/Li was present, that of the para carbon went from 102.0 to 91.6 over the same range, and that of the α-carbon went from 36.4 to 51.6 ppm. The values for the α-carbon are plotted in Figure 2.

For (triphenylmethyl)lithium at −30 °C, the chemical shifts are 148.78 (ipso), 126.98 (meta), 122.90 (ortho), 112.00 (para), and 89.64 ppm (α) in THF alone, and almost unchanged at 149.30, 126.84, 123.35, 111.61, and 90.03 ppm with 4.2 equiv of HMPA per lithium added.

Acknowledgment. This work was supported by the National Science Foundation.

Registry No. Benzyllithium, 766-04-1; (triphenylmethyl)lithium, 733-90-4.