Dissociation Behavior of Benzylalkali Compounds in Tetrahydrofuran: Effect of Countercation, Aromatic Methoxy Substitution, and α -Alkyl Substitution

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Conductometric measurements are carried out on different benzylalkali compounds (benzylcesium, -potassium, -sodium, and -lithium, and their o-CH₃O and p-CH₃O derivatives) in tetrahydrofuran at various temperatures, in order to get information on their dissociative behavior and on the influence of the alkali cation, aromatic methoxy substitution, and α -alkyl substitution on the carbon-metal bond strength. The dissociation constants of the organometallic compounds are determined by using the Kraus and Bray equation, the Fuoss equation, the Wooster equation, or by curve fitting depending on which species are involved in the solution conductance. Temperature variation of K_d is used to determine the enthalpy and entropy of dissociation. The information previously acquired by quantum chemical calculations and NMR measurements on the electronic structure of benzyl-type carbanions and the corresponding organometallic compounds appears to be of great value in interpreting the dissociation behavior of the benzyl- and styrylalkali compounds (which are also included in the study). The resonance saturation phenomenon encountered in the quantum chemical and NMR study turns out to be an important factor in the dissociative behavior of p-CH₃O compounds, as compared to the unsubstituted cases. The smaller dissociation constants of the o-CH₃O compounds also parallel the results of the quantum chemical calculations, showing an additional interaction between the cation and the CH₃O group. The weakening of the carbon-metal bond upon α -alkyl substitution parallels the increase of dissociation capability when alkyl or polymer chain substituents are present on the α -carbon atom.

Introduction

In anionic polymerization processes the rate of initiation and propagation and the microstructure of the obtained polymers is related to the polarity of the carbon-metal bond in the carbanionic species.¹⁻³ The polarity of the carbon-metal bond itself is influenced by the solvent polarity, the type of metal counterion, and the structure of the organic moiety. With regard to polystyrene systems we reported in previous papers the results of a quantum mechanical and NMR investigation on the effect of the methoxy substituent, the α -alkyl substituent, and the alkali cation on the electronic structure of the benzylcarbanion, which can be considered as a model compound for the polystyrene reactive chain end.⁴ The methoxy group was shown to have lost a part of its



 π -electron-donor capability in the anionic species, as compared to the situation in a neutral system, e.g., anisole. The extent to which this resonance saturation phenomenon⁵ occurs is less in case of ortho substitution. In the presence of the alkali countercations, particularly the smaller ones, the π -electron-donor capability is partly restored, due to polarization and eventually charge-transfer effects, by which less excess charge is delocalized from the CH₂⁻ group to the aromatic ring. The theoretical calculations show that an extra cation-anion stabilization energy must be attributed to the o-methoxybenzylalkali compounds. In these compounds the cation also interacts with the lone pair orbitals of the o-methoxysubstituent, a phenomenon which will be referred to as "intramolecular solvation". The methoxy group has an overall electron-withdrawing character; i.e., the number of electrons withdrawn along the σ -skeleton is larger than the number of electrons transfered to the aromatic ring by the π -orbitals. As shown previously, this results, in comparison with the unsubstituted benzylcarbanion, in a smaller electrostatic interaction energy⁶ between the p-methoxybenzyl carbanion and a positive unit charge, if the assumption is made that this charge does not perturb the electron distribution of the anion.

If the α -hydrogen of the benzyl carbanion is replaced by an alkyl group (methyl, ethyl, propyl) a σ -inductive electron flow, occurring from the α -carbon to the alkyl group, can be deduced from the theoretical calculations, the π -system being hardly changed. However, NMR results of the benzylic alkali compounds showed that an increase of the aromatic π -electron density occurs with increasing α -carbon substitution, the electron density of the α -carbon being reduced. As the difference in the number of delocalized excess electrons between the benzylalkali compound and the α -alkylbenzylalkali compound was cation-dependent and larger with decreasing cation radius, steric repulsion by the α -alkyl group was believed to obstruct the cation to approach as close by to the energetic minimum—situated in the proximity of the α carbon-as in the unsubstituted benzyl case. This results in a reduction of polarizing effects and, consequently, in an enhancement of the number of delocalized electrons. For the larger cations the energetic minimum is further away from the α -carbon and polarizing effects are less pronounced; so the α -alkyl group has a much smaller effect on the total electron density of the aromatic ring.

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In the present paper a report is made on the conductometric measurements carried out on different benzylalkali compounds in THF in order to get information on the dissociative behavior of those compounds and on the influence of the type of alkali cation, the aromatic methoxy substitution, and the α -alkyl substituent on the carbon-metal bond strength. The above-mentioned results concerning the electronic structure of the benzyl-type compounds will be used to explain the conductometric data.

Experimental Section

Benzylcesium, benzylpotassium, and benzylsodium were prepared by the reaction of dibenzylmercury with the corresponding metal mirror in tetrahydrofuran (THF) at -70 °C. 100% conversion was obtained after 24 h, except for the cesium compound for which the reaction time was limited to 4 h in order to avoid side reactions with the cesium mirror. Benzyllithium was synthesized by the reaction of dibenzylmercury with an equivalent amount of ethyllithium in cyclohexane at room temperature. The methoxy-substituted benzylcesium and benzylpotassium compounds were obtained by ether cleavage of the corresponding benzyl methyl ethers on a metal mirror in THF at -70 °C. The lithium compounds were prepared by stirring the benzyl methyl ethers with lithium powder in a 50/50 benzene-diethyl ether mixture for 48 h at room temperature. All preparations were carried out under high vacuum and with thoroughly dried solvents and reactants.

The conductances at different concentrations of benzylalkali compounds in THF were recorded with a Wayne Kerr-B905 universal bridge. Conductances were measured from -70 °C to a particular temperature determined by the stability of the product in THF. The concentrations of the solutions were determined spectrophotometrically with the aid of a Cary 17 spectrophotometer.

 λ_{max} (nm) and ϵ_{max} (M⁻¹ cm⁻¹) values are as follows: BenzCs: 368, 14 300; -K: 362, 15 600; -Na: 352, 15 800; -Li: 330, 13 600; pMeOBenzCs: 373, 8500; -K: 368, 13 600; -Li: 323, 11 100; oMeOBenzCs: 355, 8300; -K: 352, 13 100; -Li: 327, 10 800).

Method of Calculation

For the determination of the dissociation constants K_d use was made of the Kraus and Bray expression,⁷ the Fuoss expression,⁸ the Wooster expression,⁹ or curve fitting, depending on which species are involved in the solution conductance. These equations can be written as follows

Kraus and Bray: $1/\Lambda = 1/\Lambda_0 + \Lambda C/K_d \Lambda_0^2$ (1)

Fuoss:
$$\Lambda C^{1/2} = \Lambda_0 K_d^{1/2} + \lambda_0 K_d^{1/2} K_t C$$
 (2)

Wooster: $\Lambda^2 C = \Lambda_0^2 K_d + (2\Lambda_0\lambda_0' - \Lambda_0^2) K_d K_t' C$ (3)

curve fitting:
$$\Lambda = \sum \Lambda_{0i} \alpha_i, \quad \alpha_i = f(K_i, C)$$
 (4)

with Λ = the equivalent conductance at the analytical concentration C, Λ_0 = the sum of the equivalent conductances of the cation and the anion at infinite dilution, K_t = the triple-ion formation equilibrium constant, with the assumption that both kinds of triple ions are formed in an equimolar amount, λ_0 = the sum of the equivalent conductances of both kinds of triple ions at infinite dilution, K_t' = the equilibrium constant for the formation of one kind of triple ion, λ_0' = the sum of the equivalent conductances of the triple ion and the counterion at infinite dilution, and α_i = the mole fraction of the species i. Plotting $1/\Lambda$ as a function of ΛC will reveal linearity only if the simple dissociation equilibrium takes place. If also triple ions, positive as well as negative, are present, linearity will be obtained in the $\Lambda C^{1/2} - C$ plot. If only one type of triple ion is involved the $\Lambda^2 C - C$ plot will give a straight line. If association, i.e., dimerization, occurs, the



Figure 1. Kraus and Bray plot for benzylsodium in THF. Straight lines are obtained by least-squares fits.



Figure 2. Kraus and Bray plot for *p*-methoxybenzyllithium in THF. The curves drawn are obtained by fitting the experimentally obtained points.

equilibrium constants need to be determined by curve fitting.

For the estimation of the Λ_0^- values use was made of the Stokes relation $R^- = 0.219/\Lambda_0^-\eta$ (η being the viscosity of the solution), comparing the volume of the different anions relative to that of the fluorenyl anion, for which Λ_0^- is given in the literature.¹⁰ Combined with the Λ_0^+ -values from literature^{11,12} Λ_0^- values are obtained. The same procedure was followed for the determination of the λ_0^- values, the volume of the triple ions being taken twice that of the free anion in the case of the Li⁺-salts and 3 times that of the free anion in the case of the Cs⁺ salts, in view of the nonnegligible size of the Cs⁺ ion as compared to that of the Li⁺ ion.

Taking as an extreme error in volume for the negative ion a factor of 2, its Λ_0^- -value would change only by a factor of 0.79 if the volume would be twice bigger. The overall Λ_0 for the benzyl salts would then change by a factor of 0.85 in the case of the Li⁺ salt and a factor of 0.90 in the case of the Cs⁺ salt. This would lead to a change in K_d by a factor of 1.37 for the Li⁺ salt and a factor of 1.23 for the Cs⁺ salt.

Since the smallest difference discussed in this paper is by a factor of 1.9 between oMeOBenzLi and pMeOBenzLi and since the Λ_0^- -values of the oMeOBenz and pMeOBenz salts would have to be adjusted as well for the change in volume considered, the possible errors introduced by the choice of Λ_0^- hardly affect the relative values of the dissociation constants discussed and those of the ΔH_d and ΔS_d values derived from them via the study of the temperature variation of K_d .

Results and Discussion

I. Conductance Plots. Figure 1 shows a typical plot where the Kraus and Bray treatment could be used, whereas Figure 2 shows

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TABLE I: K_d Values for Benzylalkali Compounds in THF at Various Temperatures^a

| | Benzyl | | | pMeOBenzyl | | | oMeOBenzyl | | | | |
|---------------|--------------------------------------|---------------------------------------|-----------------------------------|---|---|---------------------------------------|--|--|---------------------------------------|---|--|
| <i>T</i> , °C | $\frac{Cs (3)}{K_{d} \times 10^{9}}$ | $\frac{K (1)}{K_{\rm d} \times 10^8}$ | Na (1) $K_{\rm d} \times 10^7$ | $\begin{array}{c} \text{Li (4)} \\ K_{\rm d} \times 10^9 \end{array}$ | $\frac{\text{Cs (1)}}{K_{\rm d} \times 10^9}$ | $\frac{K (1)}{K_{\rm d} \times 10^8}$ | $\begin{array}{c} \text{Li (4)} \\ K_{\rm d} \times 10^{10} \end{array}$ | $\frac{\text{Cs (1)}}{K_{\rm d} \times 10^{10}}$ | $\frac{K (1)}{K_{\rm d} \times 10^8}$ | $\frac{\text{Li } (4)}{K_{\rm d} \times 10^{10}}$ | |
| -70 | 1.48 | 4.66 | 4.35 | 5.68 | 2.77 | 4.43 | 5.03 | 7.69 | 1.05 | 2.66 | |
| -65 | 1.44 | 4.28 | 3.10 | 6.33 | 2.66 | 4.26 | 4.46 | 7.50 | 1.03 | 2.58 | |
| -60 | 1.44 | 4.16 | 2.25 | 4.90 | 2.55 | 4.06 | 4.24 | | 1.01 | 2.66 | |
| -55 | 1.43 | 3.76 | 1.60 | 5.11 | 2.46 | 3.93 | 4.00 | | 0.97 | 2.59 | |
| -50 | 1.41 | 3.51 | 1.15 | 7.07 | 2.40 | 3.76 | 3.90 | | 0.95 | 2.63 | |
| -45 | | 3.36 | 0.85 | 6.32 | | 3.53 | 3.95 | | | 2.89 | |
| -40 | | 3.10 | 0.63 | 6.55 | | 3.26 | 4.03 | | | 3.17 | |
| -35 | | | | 6.68 | | | 4.21 | | | | |
| -30 | | | | 5.68 | | | 4.30 | | | | |
| -25 | | | | 5.78 | | | 4.73 | | | | |
| -20 | | | | 5.76 | | | 5.10 | | | | |

^a The equation used in the calculation is indicated in parentheses: Kraus and Bray (1), Fuoss (2), Wooster (3), curve-fitting (4).



Figure 3. van't Hoff plot for various lithium salts in THF.

a case where use was made of the above-mentioned fitting procedure. They represent respectively the case of BenzNa in THF at -50 and -70 °C, and that of pMeOBenzLi also in THF at -30, -50, and -70 °C (complete list of plots can be obtained from the authors upon request).

The corresponding dissociation constants of the benzylalkali compounds are given in Table I. As can be deduced from the method of calculation mentioned in Table I, the potassium and sodium compounds only show the simple equilibrium of dissociation of ion pairs into free ions. Lithium compounds also form negative triple ions and dimers (the standard deviation is the smallest if the formation of positive triple ions is excluded in the curve fitting). For benzylcesium formation of triple ions is also observed. The methoxy-substituted benzylcesium compounds only show the dissociation equilibrium.

A typical van't Hoff plot for the lithium salts is shown in Figure 3. For comparison, the dissociation constants of fluorenyllithium (FlLi) and polystyryllithium (PStLi) are also shown. It should be emphasized that the ΔH_d and ΔS_d values for the benzyl and the methoxy-substituted benzyl salts are virtually independent of temperature at least in the temperature range where conductance measurements could be carried out.

II. Dissociation Constants of the Benzylalkali Compounds. 1. Influence of the Countercation for the Unsubstituted Benzyl Salts. The magnitude of the dissociation constant is determined

TABLE II: K_d , ΔH_d , and ΔS_d Values for Benzyl and Styrylalkali Compounds^a in THF at -60 °C

| | | | ΔS_{d} , |
|--------------------------|---------------------------|---------------------------------|------------------|
| | <i>K</i> _d , M | $\Delta H_{\rm d}, \rm kJ/mol$ | J/(mol K) |
| BenzCs | 1.44 × 10 ⁻⁹ | -1.0 | -174 |
| K | 4.16×10^{-8} | -4.9 | -164 |
| Na | 2.25×10^{-7} | -25.5 | -247 |
| Li | 4.90 × 10 ⁻⁹ | 0 | -159 |
| pMeOBenzCs | 2.55×10^{-9} | -2.8 | -177 |
| K | 4.06×10^{-8} | -3.8 | -159 |
| Li | 4.24×10^{-10} | 0. | -179 |
| oMeOBenzCs | 7.50×10^{-10} | | |
| K | 1.00×10^{-8} | -1.4 | -160 |
| Li | 2.66×10^{-10} | 0 | -183 |
| PhHLi ^{14a} | 9.1×10^{-8} | -5.5 | -160 |
| 2MeOPhPLi ^{14a} | 6.4×10^{-8} | -4.6 | -159 |
| 4MeOPhPCs ^{14a} | 4.3 × 10 ⁻⁹ | 0 | -160 |
| 2MeOPhPCs ^{14a} | 1.1 × 10 ⁻⁹ | 0 | -172 |
| 2PhPLi ¹⁵ | 6.55 × 10 ⁻⁶ | 0 | -100 |
| PStCs ^{14b} | 2.59 × 10 ⁻⁹ | -2.9 | -178 |
| K ^{14b} | 6.20×10^{-8} | -5.5 | -164 |
| Na ^{14c} | 8.55 × 10 ⁻⁶ | -27.0 | -223 |
| Li ^{14d} | 2.26×10^{-7} | -5.5 | -150 |
| PpMeOStCs ^{14e} | 5.8×10^{-9} | | |
| K ^{14b} | 1.2×10^{-7} | | |
| Na ^{14c} | 1.5 × 10 ⁻⁵ | -27.6 | -222 |
| Li ^{14e} | 8.7×10^{-8} | | |
| PoMeOStCs ^{14c} | 3.4×10^{-10} | | |
| Na ^{14c} | 6.7×10^{-7} | -21.2 | -217 |
| Li ^{14e} | 1.4×10^{-8} | | |
| FlCs ¹⁶ | 4.90 × 10 ⁻⁹ | -4.9 | -163 |
| K ¹⁶ | 2.01×10^{-6} | -12.7 | -167 |
| Na ¹⁶ | 4.05×10^{-5} | -7.9 | -121 |
| Li ¹⁶ | 1.50×10^{-5} | -3.0 | -106 |

^aPhH = 1-phenylhexyl, xMeOPhP = 1-(x-methoxyphenyl)pentyl, 2PhP = 2-phenylpentyl, PSt = polystyryl, Fl = fluorenyl.

by the following factors: the energy needed to separate the opposite charges (ΔH_{sep}), the energy change resulting from a change in solvent arrangement upon dissociation (ΔH_{solv}), and the entropy change associated with the change in solvent arrangement (ΔS_d) . From an analysis of the Stokes radii of the different alkali cations in THF (Cs⁺, 2.5 Å; K⁺, 3.5 Å; Na⁺ \simeq Li⁺, 4.5 Å)¹³ we can expect the entropy change to be the largest for the smallest cation; i.e., the smallest cation is surrounded by the largest cloud of solvent molecules. However, despite the similarity in Stokes radius for Na⁺ and Li⁺, ΔS_d for benzyllithium is smaller than for benzylsodium, as indicated in Table II. Recent results¹⁷ on the conductances and polymerization rates of polystyryllithium could indeed only be rationalized if it is assumed that the Li⁺ cation

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in the ion pair is more strongly solvated than the Na^+ ion in the corresponding pair. Less solvent molecules are thus involved in the coordination of the dissociating lithium cation than is the case for the benzylsodium compound.

Considering the K_d values of benzylcesium, benzylpotassium, and benzylsodium, the order of the dissociation constants is that of the cation capacity to coordinate with solvent molecules. For the smaller cation, for which the cation-anion bond is stronger, the gain of enthalpy upon dissociation is larger, due to an energetically more favorable cation-solvent coordination, and the gain of enthalpy compensates the loss of entropy to a larger extent; in other words, $\Delta H_{sep} + \Delta H_{sol} - T\Delta S_d$ is minimal for the sodium compound. Benzyllithium on the other hand is so tightly bonded, probably largely in a covalent way, that no gain of enthalpy results from dissociation, the energy gain by further coordination of the partly solvated lithium cation only being able to compensate the energy needed for the charge separation.

2. Influence of the Methoxy Substituent. 2.1. Cesium Compounds: The Importance of Electrostatic Interactions. Considering the K_d values of the various benzylcesium compounds, the following order of decreasing dissociation capability can be given: pMeOBenzCs > BenzCs > oMeOBenzCs. The differences in dissociation constants are rather small and only amount to a factor of 2. The fact that pMeOBenzCs dissociates better than BenzCs may be surprising at first sight. However, the carbonmetal bond in the cesium compounds can be thought to be purely electrostatic in nature. Furthermore it has been deduced from our theoretical calculations on the anions⁴ that there is an overall electron flow from the benzyl moiety to the methoxy group, thus reducing the electrostatic interaction energy between pMeOBenzand a positive charge, compared with the unsubstituted benzyl case. oMeOBenzCs appears with the smallest dissociation constant, which can be attributed to an additional specific interaction between the cesium cation and the o-methoxy substituent.

2.2. Potassium Compounds: The Importance of Polarization and Resonance Saturation Effects. For the benzylpotassium compounds the following sequence of dissociation constants is found: BenzK \simeq pMeOBenzK > oMeOBenzK. Again the ortho-substituted derivative is the least dissociated, this time more pronounced than in the case of the cesium compounds, the ratio between the dissociation constants being four. The intramolecular solvation by the o-methoxy group is becoming more important. If we consider the entropies of dissociation (ΔS_d) of the potassium salts to be largely due to the change in solvent arrangement and assuming therefore also that the part of ΔH_d which results from this change in solvent arrangement, and which we could call ΔH_{solv} , is nearly the same for the three potassium salts, the differences in $\Delta H_{\rm d}$ could then be ascribed to the specific interaction between the o-methoxy group and the K⁺ ion. In this approach the specific interaction between o-methoxy group and the potassium ion would lead to an additional stabilization by about 2.4 kJ/mol, as can be derived from the ΔH_d values for the pMeO- and oMeOBenzK salts.

The fact that, in contrast with the cesium compounds, BenzK and pMeOBenzK show the same dissociation constant can only be clarified by ascribing a small polarizing effect to the potassium cation. The total bond energy ($\simeq -\Delta H_{sep}$) between the carbanion and the potassium cation can be partitioned into an electrostatic term and a polarization term (no charge transfer from the anion to the cation is assumed). The first term stands for the energy the system gains when the potassium cation is brought into the energetic minimum of the electrostatic field surrounding the carbanion, without producing a change in the electron distribution of the anion, the electron distribution in the ion pair being the same as that of the free carbanion. The second term stands for the change in energy due to the redistribution of the electrons in the field of the cation (electrons are attracted toward the cation position) and for the concomitant enhancement of electrostatic interaction energy. As has been mentioned above, the electrostatic interaction energy in the case of the interaction with a proton (the molecular electrostatic potential) is less negative for pMeOBenzthan for Benz⁻. The total bond energy is about the same for both

potassium compounds (same $\Delta S_d \rightarrow \text{same } \Delta H_{\text{solv}} \rightarrow \text{same } \Delta H_{\text{sop}}$) so that the polarization term has to be more negative for pMeOBenzK than for BenzK. The latter must be related to the resonance saturation, occurring to a lesser extent in the pMeO-BenzK ion pair than in the free pMeOBenz⁻ carbanion. Polarization by the potassium cation, located at the proximity of the α -carbon, reduces the excess charge density in the aromatic ring, making the π -donor effect of the methoxy group less destabilizing, compared with the free carbanion case. The restoring of a part of the "normal" π -donor effect of the methoxy group may in turn lead to an extra enhancement of electrostatic interaction energy. It is also most likely that in order to reduce resonance saturation electrons are polarized to a larger extent in pMeOBenzK than in BenzK, again leading to an extra enhancement of electrostatic interaction energy.

2.3. Lithium Compounds: Increasing Importance of Polarization and Resonance Saturation. The Role of Solvation. It is clear that for the closer contact benzyllithium compounds the polarization term (and maybe the charge-transfer term) is becoming significantly more important. The K_d values can be arranged in decreasing order as follows: $BenzLi \gg pMeOBenzLi$ > oMeOBenzLi. Here the pMeOBenz derivative dissociates less easily by a factor of 10 than the Benz derivative, which is an indication for a considerable decrease of resonance saturation in the pMeOBenzLi compound. From the K_d values one can derive that, if the change in solvent arrangement upon dissociation were the same for both compounds (ΔS_d and ΔH_{solv} the same) about 4 kJ/mol more would be needed to separate the ions of pMeO-BenzLi compared with BenzLi. However, as far as the thermodynamic parameters can be regarded with confidence, ΔH_d for both compounds is zero, while for pMeOBenzLi ΔS_d is about 20 J/(mol K) more negative than for BenzLi. This can signify that the lithium cation in the pMeOBenzLi ion pair is externally solvated to a lesser amount than is the case in the BenzLi ion pair. Again the resonance saturation can be thought to be responsible for this. External solvation reduces the polarization capability of the lithium cation, by dispersing the positive charge and by enhancing the cation-anion distance, leading to an increase of the electron density in the aromatic nucleus and thus making the methoxy group more destabilizing. Also, if between the lithium ion and the anion a covalent interaction exists, external solvation would make the interaction between the cation and anion less favorable, the cation being already surrounded by the oxygen lone pair electrons of the THF molecules. oMeOBenzLi displays the smallest dissociation capacity, which once more can be ascribed to an additional stabilization by intramolecular solvation.

III. Comparison with Styrylalkali Compounds. 1. Unsubstituted Compounds. The K_d values of the benzylalkali compounds are, as can be deduced from Table II, always smaller than those of the corresponding polystyryl derivatives. For the larger cations, cesium and potassium, the ratio of the dissociation constants amounts maximum to a factor of 2. The ΔS_d values of polystyrylcesium and -potassium are about the same as those of the benzyl derivatives. If we accept the similar ΔS_d values for both type of compounds to be an indication for a similar change in solvation energy upon dissociation, the difference between the ΔH_d values and in consequence between the K_d values can be thought to result from a less stronger cation-anion bond in the polystyryl derivatives compared with the benzyl compounds. For polystyrylsodium and polystyryllithium the loss of entropy is slightly reduced with regard to the entropy loss for benzylsodium and benzyllithium; the ΔH_d values on the other hand are more negative. This results in a thirtyfold and fiftyfold increase of the dissociation constant for polystyrylsodium and polystyryllithium, respectively. Obviously the cations are more weakly bonded in the polystyrylalkali compounds, the carbon-metal bond being more polar than in the benzyl analogues. The same increase of the ionic character of the carbon-metal bond applies for the α -alkyl-substituted benzylalkali compounds, for which the K_d values are larger than those of the corresponding benzylalkali compounds, but, with the exception of the o-methoxy-substituted compounds, somewhat smaller than those of the polystyryl analogues. As shown by the

 K_d value of 2-phenylpentyllithium, substitution at the α -carbon with a second alkyl group leads to a further increase of the ionic character. The dissociation entropy ΔS_d is considerably less negative and the dissociation enthalpy ΔH_d is nearly zero, in conformity with the thermodynamic parameters of fluorenyllithium and fluorenylsodium, for which the carbon-metal bond at the given temperature is solvent-separated. Their ΔS_d values are strongly reduced and, although the cations are more weakly bonded than in the corresponding polystyryl salts, there is a smaller gain of solvation energy when the already highly solvated cations dissociate, resulting in a less negative ΔH_d value.

The higher ionic character of the carbon-metal bond in α alkyl-substituted compounds has been demonstrated in our previous papers⁴ by means of NMR and spectrophotometric data. We ascribed the higher bond polarity to a repulsion effect existing between the α -alkyl group and the cation, making the approach of the cation into the energetic minimum less favorable. The steric repulsion can be considered to be most pronounced for the more closely bonded and more externally solvated smaller cations, so that for them the most drastic effect on the dissociation behavior is to be expected. However, it should be noted that quantum mechanical calculations showed the α -alkyl group to be an inductive electron acceptor. As a consequence the α -alkyl effect on the dissociation behavior can also be explained as arising from a reduced electrostatic cation-anion interaction and, for the smaller cations, additionally from reduced polarization and charge transfer.

2. Methoxy-Substituted Compounds. Comparing now the K_d values of the polystyrylalkali compounds with those of the *p*-methoxy substituted analogues, it appears that only in the case of the lithium salt *p*-methoxy substitution gives rise to a smaller dissociation constant, whereas for the larger cations an effect is found similar to the above-mentioned methoxy group effect in BenzCs, namely a nearly twofold increase of the dissociation constant for the methoxy-substituted compound. Thus, in contrast with the benzylalkali compounds, in which even the potassium cation displayed a polarizing character, the carbon-metal bond in the polystyrylalkali compounds is, with the exception of the lithium salt, electrostatic in nature, a reduction of the electrostatic interaction energy occurring upon the introduction of the *p*-methoxy substituent.

Finally we wish to report that the K_d values of the o-methoxy-substituted polystyrylalkali compounds are not only smaller than those of the corresponding polystyrylalkali compounds but even smaller than those of the corresponding α -alkyl-o-methoxy-substituted benzylalkali compounds. This can be attributed to additional intramolecular solvation occurring by methoxy groups of foregoing units of the polymer chain.

Conclusion

The information, acquired by theoretical calculations and NMR measurements, on the electronic structure of benzyl-type carbanions and metal compounds appeared to be of great value for the interpretation of the dissociation behavior of benzyl and styryl alkali compounds. Both the overall electron-withdrawing effect of the methoxy group and the resonance saturation showing up in the theoretical calculations turn out to be important factors in the dissociation capability of the *p*-methoxy-substituted compounds. Depending on to what extent the cation perturbs the electron distribution of the anion, the dissociation capability of the p-methoxy-substituted compounds may be greater or smaller than that of the unsubstituted compound. Theoretical calculations showed that an additional interaction exists between the cation and the o-methoxy group in the o-methoxy-substituted compounds. For those compounds smaller dissociation constants are indeed found. The weakening of the carbon-metal bond upon α -alkyl substitution, as previously rationalized on the basis of NMR and theoretical results, parallels the increase of dissociation capability when alkyl or polymer chain substituents are present on the α carbon.

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Registry No. BenzCs, 19104-13-3; BenzK, 2785-29-7; BenzNa, 1121-53-5; BenzLi, 766-04-1; *p*MeOBenzCs, 99232-38-9; *p*MeOBenzK, 99232-39-0; *p*MeOBenzLi, 17179-20-3; *o*-MeOBenzCs, 99232-40-3; *o*MeOBenzK, 99232-41-4; *o*MeOBenzLi, 99232-42-5; EtLi, 811-49-4; CS, 7440-46-2; K, 7440-09-7; Na, 7440-23-5; Li, 7439-93-2; dibenzyl-mercury, 780-24-5; 1-methoxy-2-(methoxymethyl)benzene, 21998-86-7; 1-methoxy-4-(methoxymethyl)benzene, 1515-81-7.

Flash Photolysis of 1,3-Dichlorotetrafluoroacetone in the Presence of Oxygen. Kinetics and Mechanism of the Oxidation of the Chlorodifluoromethyl Radicals

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Flash photolysis of 1,3-dichlorotetrafluoroacetone through Suprasil and in Ar diluent gave transient spectra due to the 250-nm band system of CF₂. With O₂ present, ClO bands in the 265-292-nm region were observed, and the CF₂ bands were reduced in intensity. Evidence was found that Cl atoms are the precursor to ClO and that CF₂ClCOCF₂ is the precursor to CF₂. In the absence of O₂, CF₂ decayed by the bimolecular association reaction, $2CF_2 \rightarrow C_2F_4$. Formation of CF₂ occurs in 25-50 μ s, while ClO rises to a maximum in about 200 μ s. Both decay over periods of milliseconds. In the presence of O₂, CF₂ decay was greatly accelerated, and the ClO decay was faster than could be accounted for by known reactions and reported rate constants. A bimolecular reaction of CF₂ with ClO was suggested to explain this observation. Evidence that reaction of Cl with CF₂ClO₂ is the most important source of ClO was obtained. Two primary photochemical processes, yielding CF₂Cl radicals and CO, and CF₂ClCOCF₃ + Cl, were necessary to adequately explain the results. A detailed mechanism was developed, and numerical simulation employed to fit ClO profiles. The simulation required $\phi_{Cl}/\phi_{CO} \sim 0.33$. Sensitivity analysis was used to reduce the mechanism to the minimum number of reactions necessary for faithful reproduction of CF₂ and ClO profiles.

Introduction

In 1935, Lyons and Dickinson¹ reported the formation of phosgene in the photooxidation of liquid CCl₄. They suggested

case the reaction products were CF₂O, CO₂, and SiF₄, the last (2) W. C. Francis and R. N. Haszeldine, J. Chem. Soc., 2151 (1955).

that the CCl_3O_2 radical was an intermediate in the reaction. Later, Francis and Haszeldine² investigated the vapor-phase photo-

oxidation of CHF₃, CF₃Br, CF₂ClBr, CF₂Br₂, and CF₃I. In each

⁽¹⁾ E. H. Lyons, Jr., and R. G. Dickinson, J. Am. Chem. Soc., 57, 443 (1935).