the β form, respectively, for the C_nE_m compounds.

The rigid conformation of a homologous series of the C_nE_m surfactants has now been substantially established. It has been demonstrated that vibrational spectroscopy (Raman and infrared) is one of the most powerful techniques to determine conformational details of the molecule, provided that pertinent analysis methods are effectually applied.

Implications of the Conformational Behavior in Other Properties. The conformational behavior of the C_nE_m surfactants in the solid state is likely to have implications in various physical properties of these substances. Examination of the thermodynamic properties of the $C_{12}E_m$ compounds (m = 2–8) in aqueous solution[59] indicates that the entropy of micellization changes much sharply between $m = 3$ and 4 as compared with the change at other m values. According to the study of the aggregation of the $C_{10}E_m$ homologues (m = 1–7) in heptane,[60] on the other hand, the behavior of their apparent molar heat capacities with decreasing molar fraction of the surfactant is quite different between those of $m \leq 3$ and those of $m \geq 4$. This leads to a break of the linear change, with increasing oxyethylene chain length, of the limiting molar heat capacity between $m = 3$ and 4. The distinct difference in the behavior of the two quantities mentioned above for the homologues of $m \leq 3$ and those of $m \geq 4$ is certainly associated with the difference of the conformational properties of these substances; the homologues with the shorter oxyethylene chain assume the extended form, whereas those with the longer oxyethylene chain assume the helical/extended diblock form in the solid state.

A study on the thermodynamic quantities of adsorption of $C_{12}E_m$ (m = 2–5)[61] has shown that the partial molar area of the surfactant at the saturated adsorption surface is very small for $C_{12}E_2$ in comparison with the values for the other homologues. The geometrical arrangement of the adsorbed molecules of $C_{12}E_2$ may be interpreted on the basis of the conformational state of this compound in the solid state.

Conclusions

Molecular conformations of a homologous series of 71 C_nE_m compounds in the solid state have been established by Raman spectroscopy (Table I). For the compounds with $n \leq 4$, the conformation is basically helical, though several different forms are found, with the predominating oxyethylene chain which intrinsically favors the helical structure. For $n \geq 5$, on the other hand, the molecular conformation greatly depends on the oxyethylene chain length. As the number of oxyethylene units (m) increases, a conformational transition takes place at m = 3–4 from the highly extended form to the helical/extended diblock form. This conformational behavior of the C_nE_m compounds is elucidated by the conformational competition between the alkyl and oxyethylene chains. The classical model of the meander conformation of the oxyethylene chain is thought to be very unstable owing to heavy steric hindrance and is therefore quite unlikely to exist.

The conformational properties in the solid state should be closely related to various structural aspects of the amphiphilic molecules. Although the structure of the amphiphiles in solvent media is expected to depend on the amphiphile–solvent interaction as well, the conformational properties in the solid state are fundamental in that these properties certainly contain the nature of the amphiphilic molecules themselves. The reported thermodynamic quantities of the C_nE_m surfactants are in fact indicative of strong correlations with the conformational behavior of these homologous compounds.

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Mixed-Dimer Formation between Dimeric Lithium 2,6-Dimethylphenolate and the Lithium Salts of Strong Acids

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Abstract: The ^{13}C, ^{7}Li, and ^{6}Li NMR spectra of lithium 2,6-dimethyl-, 4-bromo-2,6-dimethyl-, and 2,4,6-tribromophenolates in 1,3-dioxolane and THF and in the presence of $LiClO_4$, $LiBPh_4$, LiCl, and lithium p-toluenesulfonate are reported for a wide range of temperature and concentration. It is established that all systems give rise to mixed dimers. The extent of mixed-dimer formation is shown to depend on the basicity of the phenolate ion, the cation solvation power of the solvent, and the nature of the anion. ΔH (kcal mol^{-1}) and ΔS (cal mol^{-1} deg^{-1}) for lithium 2,6-dimethylphenolate are 0, 14 ($LiClO_4$/dioxolane); 0, 7 ($LiClO_4$/THF); and −1.2, −1.3 ($LiBPh_4$/dioxolane), respectively. The $^{13}C_{para}$ chemical shifts for mixed dimers of lithium 2,6-dimethylphenolate are strongly dependent on the nature of the anion. The structures of the mixed aggregates are postulated to be ion pairs of the type $[Li_2P]^+X^-$ that are contact, partially solvent separated, or fully solvent separated depending on the nature of X and the solvent. Exchange of X^- between Li_2PX and free salt is rapid on the ^{13}C NMR time scale at −100 °C. Exchange of phenolate between dimeric phenolate and mixed dimer is a slower process that appears to involve the intermediacy of monomeric lithium phenolate.

It is now well-established that organic lithium reagents (organolithium compounds, lithium amides, lithium enolates) form aggregates in weakly polar, aprotic solvents.[1,2] In some cases, at least, these aggregates have been shown to be the primary reactants[3-5] and may therefore be responsible for controlling reactivity as well as regio- and stereochemistry in their reactions with electrophiles. Furthermore, there is an increasing body of evidence to suggest the reactions of these aggregates can be

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dramatically modified by the formation of mixed aggregates derived from added salts or salts formed during the course of the reaction. This latter effect, for example, has been shown in the aldol reaction, in which the enantioselectivity is altered during the reaction, presumably by the formation of a mixed aggregate between the lithium enolate and aldolate, a process that has been termed "enantioselective autoinduction".[6] Similarly, the regiochemistry (C:O ratio) of the methylation of lithioisobutyrophenone has been observed to exhibit "regioselective autoinduction" and to be affected by the initial addition of a variety of lithium salts.[7]

There are a number of examples of mixed-aggregate formation by organolithium compounds.[8-19] Using low-temperature ^{1}H and ^{7}Li NMR, Brown and his co-workers demonstrated the existence of mixed tetramers of the structure $Li_4R_xX_{4-x}$ (where R = methyl and X = halide) in equilibrium with "pure" tetramers of methyllithium when either lithium bromide or iodide was added to ether solutions.[8] Similar structures involving alkyllithiums and lithium alkoxides were also identified in the gas phase[9] and in ether solutions.[10] More recently, McGarrity and Ogle[11] and Thomas, Clarke, Jensen, and Young[12] have shown, also by NMR, that such complexes occur in THF and cyclopentane, respectively. Crystal structures of mixed aggregates incorporating one and two molecules of lithium bromide with phenyllithium[13] and cyclopropyllithium,[14] respectively, have been reported. Both structures consist of distorted cubes. Fewer cases of organolithium mixed-dimer formation are known. Glaze and West crystallized a number of alkyllithium/lithium halide complexes from hydrocarbon solutions, some of which were shown by powder X-ray diffraction to have 1:1 stoichiometries.[15] Mixed dimers are also known to form between two different organolithium compounds in solution.[16]

A number of reactions utilizing organolithium reagents are known to be affected by the addition of lithium salts (alkoxides, halides, etc.),[3a,17] and in some cases, these "salt effects" have been attributed to the formation of mixed aggregates. However, the first conclusive evidence of direct mixed-aggregate participation in a chemical reaction was provided by McGarrity, Ogle, Brich, and Loosli[4] in their study of the addition of butyllithium to benzaldehyde. Using an elegant technique termed rapid-injection NMR (RINMR), they were able to observe individual butyllithium aggregates reacting with the aldehyde and to obtain relative rates of addition for each tetrameric species with the structure $Li_4R_xOR_{4-x}$ (where x = 1–4). The reactivity of these species was shown to increase with the number of alkoxide anions incorporated into the aggregate. Very recently, Lochmann[18] observed a similar change in reactivity in the alkylations of "complex bases" prepared from organolithium compounds and heavier alkali metal alkoxides. The rates of reaction with a number of alkyl bromides, as well as the types of products formed, were found to be directly dependent on the proportion of alkoxide ions present in the structure of the reagent.

Mixed-aggregate formation by lithium amides and their derivatives has also been documented.[20-23] DePue and Collum[20] showed, by NMR and colligative measurements, that mixed-dimer formation occurs when lithium bromide is added to THF/hydrocarbon solutions of lithium diphenylamide. In kinetic studies of N-alkylation, the mixed dimer was observed to be dramatically more reactive than the pure dimer, presumably due to the decrease in the steric demand of the bromide ion in the former.[5] Addition of salts to lithium amide solutions has also been demonstrated to accelerate the deprotonation of δ-hydroxy esters prior to alkylation with an alkyl halide.[21]

An example of mixed-aggregate formation by a lithium enolate was presented early in our studies with this class of reagents.[24] By use of a variety of NMR techniques, lithioisobutyrophenone was shown to form mixed tetramers with lithium chloride and bromide in ethereal solvents. Two X-ray structures of mixed aggregates of enolates have been published, both by Williard.[22,27] One is a lithium enolate/lithium amide tetrameric 2:2 complex having a ladder structure, and the other is a unique mixed alkali metal enolate/alkoxide aggregate.

Seebach[2] has provided compelling evidence for mixed-aggregate formation between lithiocyclohexanone and a chiral lithium secondary amide. Formation of this species resulted in significant asymmetric induction in both the aldol reaction and the Michael addition of the enolate. A ladder structure was postulated by Williard[22] to serve as a useful model for such reactions in which stereoselectivity is achieved by addition of chiral amide bases.[23] Ester enolate/amide mixed dimers are believed to play an important role in the alkylation reaction of the enolate when an excess amount of amide is added to the reaction.[26] As mentioned above, a variety of salts affect the alkylation of lithioisobutyrophenone, although the role of mixed aggregates as primary reactants, while highly plausible, has not been rigorously established. The addition of lithium chloride to this enolate also caused a slight increase in the half-life of the alkylation reaction with dimethyl sulfate.[25]

In the course of our kinetic studies of the alkylation of lithium phenolates in weakly polar, aprotic solvents, it emerged that mixed aggregates play a vital role in the mechanisms for the overall reaction, and it therefore became necessary to understand the structures of these entities and the factors that control the equilibria between them and the parent aggregates. In this paper, we will consider the specific case of mixed-dimer formation by some lithium 2,6-disubstituted phenolates that are themselves dimers in a number of weakly polar, aprotic solvents.

Experimental Section

Materials. Solvents were purified as previously described.[30-32] All phenols were obtained from Aldrich Chemical Co. and were purified by recrystallization from hexane immediately prior to use. Lithium chloride and lithium tetraphenylborate were obtained from Aldrich. Lithium perchlorate was obtained from J. T. Baker Chemical Co. Lithium *p*-

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toluenesulfonate was prepared by literature methods[33] and recrystallized from acetic acid. All other lithium salts were recrystallized twice from distilled H_2O. After purification, salts were heated to 160 °C under high vacuum for at least 8 h to remove recrystallization solvent. The anisoles were prepared by methylating the appropriate phenols,[30] and their ^{13}C NMR spectra were obtained under conditions similar to the spectra of the phenolates.

Sample Preparation. The preparations were carried out by use of previously described vacuum-line techniques for filling NMR tubes.[30-32] All salts were added to NMR tubes by syringing a known amount from a dry methanol solution and removing the solvent under vacuum. NMR tubes were then heated to 160 °C under high vacuum for at least 8 h immediately prior to addition of the phenolate solution to ensure complete removal of water and/or solvent. The absolute phenolate concentration of each sample was determined by quenching with standardized HCl and back-titrating with standardized NaOH.

NMR Spectroscopy. NMR spectra were obtained with Bruker WP-200, Bruker AM-300, Bruker WM-360, and Bruker AM-500 instruments. ^{13}C chemical shifts are reported relative to internal C_6D_{12} (26.40 ppm) or THF (26.50 ppm). ^7Li and ^6Li chemical shifts are reported relative to external 0.1 M $LiOH/D_2O$ (0.00 ppm) at 22 °C. For thermodynamic and kinetic measurements, the exact temperatures were determined with use of a methanol standard; otherwise, absolute temperatures were not determined, but the nominal values are known to be accurate within ±2 °C.

The ^7Li, ^6Li, and ^{13}C relaxation times were measured with the inversion-recovery method. The relaxation times were determined by use of the Bruker three-parameter nonlinear least-squares program. The $^{13}C_{para}$ and ^7Li measured T_1 values used in the determination of the ^7Li quadrupolar splitting constant (QSC) for lithium 2,6-dimethylphenolate (0.25 M) in THF at 22 °C are 1.183 and 0.815 s, respectively.

The low-temperature dimer/mixed-dimer equilibrium constants for the lithium 2,6-dimethylphenolate/lithium perchlorate and lithium 2,6-dimethylphenolate/lithium tetraphenylborate systems were determined by direct integration of the respective C(4) signals. The ^{13}C (90.56-MHz) spectra were obtained by use of a 90° pulse width and a relaxation delay of $>5T_1$. The ^6Li (73.6-MHz) integrals used in the determination of the mixed-dimer stoichiometry were obtained by direct integration of the signals in the natural-abundance ^6Li spectra. The ^6Li signals were found to have long T_1 values ($\sim$10 s), and therefore, in order to obtain spectra with high signal to noise ratios and accurate integrals in a reasonable period of time, the Ernst angle of 40° (acquisition time 4 s) was used for the data acquisition. In order to verify the accuracy of the integrations, some of the experiments were repeated with the incorporation of additional relaxation delays, and no change in the relative populations was observed.

The dimer/mixed-dimer exchange rates were determined by simulating the line shapes of the C(4) signals for the two exchanging species. The spectra obtained were treated as an unequally populated two-site exchange problem in which both populations and the exchange rate are a function of temperature. The simulations were done with DNMR3,[34] which requires input of limiting chemical shifts, relative populations, values for T_2^*, and a rate constant. The values of T_2^* at the various temperatures were assumed to be equal to those obtained for the lithium phenolate at similar concentrations but in the absence of added salts. The activation parameters were calculated by the method of nonlinear least squares.

The room-temperature equilibrium constants for the mixed-dimer/dimer equilibrium were determined from the room-temperature C(4) chemical shift data. A constrained simplex routine was used to fit the experimental data by varying the equilibrium constant and the difference ($\Delta\delta$) for the chemical shifts for the two species.

The ^{35}Cl (49.0-MHz) and ^{11}B (96.6-MHz) spectra were obtained with use of a 90° pulse width. The line width of the signals was determined with use of the Lorentzian fitting routine provided in the Bruker software.

Results

Empirical Formulas of the Mixed Aggregate. Lithium 2,6-dimethylphenolate is a tetrasolvated dimer in dioxolane (QSC = 147 kHz).[30] We have now determined the ^{13}C chemical shifts and ^7Li quadrupolar splitting constant[35] for the species in THF. The latter (169 kHz) is consistent with the dimeric, tetrasolvated species $Li_2P_2S_4$ (S = THF) as is the value of the chemical shift of the $^{13}C_{para}$ atom (111.2–112.0 ppm over the temperature range −90 to +22 °C).

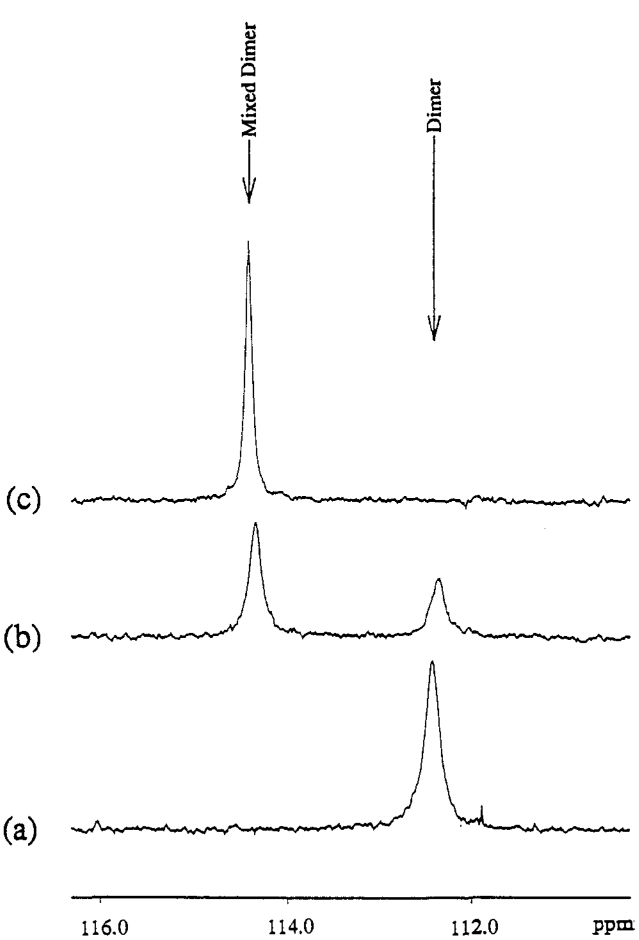

Figure 1. $^{13}C_{para}$ (90.56-MHz) resonance of lithium 2,6-dimethylphenolate (0.25 M) in dioxolane at −90 °C with (a) no added salt, (b) 0.70 equiv of $LiClO_4$, and (c) 2.50 equiv of $LiClO_4$.

The empirical formulas of the mixed aggregates formed by the additions of various salts to solutions of the dimeric phenolate can be determined by establishing the stoichiometries of the equilibrium between free salt plus dimer and the mixed aggregate. The concentrations of the species involved in these equilibria are available over a wide range of temperatures. At low temperatures, for which the rates of exchange are slow on the NMR time scale, the ^{13}C, ^7Li, and/or ^6Li signals are well-resolved (Figures 1 and 2) and the concentrations can be determined directly from integrations. At higher temperatures, it is necessary to perform line-shape analysis for the unequally populated two-site exchange systems. At temperatures for which exchange is fast on the NMR time scale, estimates of the concentrations can be made by analyzing $\Delta\delta(^{13}C_{para})$ vs salt concentration data to yield the equilibrium constant for the assumed stoichiometry and the limiting chemical shift of the mixed aggregate.

Because sample preparation involves vacuum-line techniques, it is difficult to make solutions of accurately known concentration, although that of the phenolate can be subsequently determined titrimetrically. Fortunately, in the low- and intermediate-temperature regimes, it is possible to establish the empirical formula without knowing the absolute concentrations of the phenolate and the added salt through the use of the relation (1) between the intensities of the $^{13}C_{para}$ and ^7Li (or ^6Li) signals that are characteristic of the dimer (I_C(d) and I_{Li}(d)) and mixed aggregate (I_C(ma) and I_{Li}(ma)), where y in the generalized empirical formula $Li_{y+1}P_y$ is given by $y = 1/(n - 1)$. This method was applied to

$$I_C(\mathrm{d})/I_C(\mathrm{ma}) = nI_{Li}(\mathrm{d})/I_{Li}(\mathrm{ma}) \qquad (1)$$

the mixed aggregate formed by lithium perchlorate in dioxolane, and the data are presented in Table I. The values of y firmly

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Table I. Values of *y* in $\mathrm{Li}_{y+1}\mathrm{P}_y\mathrm{X}$ Determined by Integration of ^{13}C, ^{7}Li, and ^{6}Li Signals for X = $\mathrm{ClO_4}$ and $\mathrm{BPh_4}$ in Dioxolane at −90 °C

[phenolate], M	LiX, equiv	*y*	
		^{6}Li	^{7}Li
	$\mathrm{LiClO_4}$		
0.25	0.30	1.04	0.91
0.25	0.40	0.97	1.25
0.25	0.50	1.00	1.23
0.25	0.60	0.83	1.26
0.40	0.30	1.02	1.07
0.40	0.50	0.92	1.19
0.40	0.70	1.06	
av		0.98	1.15
sd		0.08	0.14
	$\mathrm{LiBPh_4}$		
0.40	0.50	*a*	0.91[b]

[a] Signals not resolved. [b] −100 °C.

Table II. Values of K_{eq} Calculated for the Mixed Dimer ($\mathrm{Li_2PX}$) and Mixed Tetramer ($\mathrm{Li_4P_2X_2}$) of Lithium 2,6-Dimethylphenolate at −90 °C

X	[P], M	[S], M	% d	% ma	K_{eq}, M^{-1} ($\mathrm{Li_2PX}$)	K_{eq}, M^{-2} ($\mathrm{Li_4P_2X_2}$)
$\mathrm{LiClO_4}$/ dioxolane	0.25	0.125	55	45	1200	5200
	0.25	0.175	38	62	1300	4100
	0.24	0.216	23	77	1300	3400
	0.25	0.275	11	89	1300	2900
$\mathrm{LiClO_4}$/ THF	0.25	0.075	81	19	29	310
	0.25	0.125	71	29	21	150
	0.25	0.175	61	39	21	100
	0.25	0.225	48	52	31	120
	0.25	0.325	33	67	27	82
$\mathrm{LiBPh_4}$/ dioxolane	0.20	0.065	82	18	19	260
	0.24	0.128	70	30	20	137
	0.24	0.179	60	40	19	97
	0.24	0.223	55	45	13	62

Table III. Population (%) of Mixed Dimer for Lithium 2,6-Dimethylphenolate (0.25 M)/Lithium Perchlorate Solutions in Dioxolane as a Function of Temperature

	% mixed dimer		
$\mathrm{LiClO_4}$ equiv	22[a]	−48[b]	−90[c]
0.10	6		
0.30	28	29	25
0.50	47	49	45
0.70	63	65	62
0.90	78		77
1.10	84		88
1.30	90		
1.50	95		
2.50	100		100

[a] Chemical shift. [b] Line-shape analysis. [c] Integration.

Table IV. Equilibrium Constants for $\mathrm{Li_2P_2} + 2\mathrm{LiX} \rightleftharpoons 2\mathrm{Li_2PX}$ as a Function of Temperature for Lithium 2,6-Dimethylphenolate in Dioxolane

T, K	[P], M	[LiX], M	*I*(md)/*I*(d)	K_{eq}, mol^{-1}
		$\mathrm{LiClO_4}$		
203	0.40	0.20	0.85	1200
208	0.40	0.20	0.85	1200
213	0.40	0.20	0.85	1200
218	0.40	0.20	0.85	1200
223	0.40	0.20	0.85	1200
228	0.40	0.20	0.85	1200
230	0.40	0.20	0.85	1200
		$\mathrm{LiBPh_4}$		
183	0.24	0.22	0.81	13
193	0.24	0.22	0.76	11
203	0.24	0.22	0.71	10
213	0.24	0.22	0.68	8.0
295	0.24	0.22		3.0[a]

[a] Calculated by extrapolation on van't Hoff plot.

establish the empirical formula $\mathrm{Li_2PX}$ (X = $\mathrm{ClO_4}$). The method was also used to determine the empirical formula of the mixed aggregate formed by lithium tetraphenylborate in dioxolane with the same result. It cannot be applied, however, if any of the appropriate pairs of signals are unresolvable as is the case for the systems LiCl/dioxolane and LiOTs (OTs = *p*-toluenesulfonate)/dioxolane. The structures of the mixed aggregates in these systems are based on similarities between their NMR spectroscopic properties and those of the $\mathrm{LiClO_4}$/dioxolane system (see the following text).

Molecular Formulas and Equilibrium Constants. The preceding experiments do not distinguish between a mixed dimer and the mixed tetramer $\mathrm{Li_4P_2X_2}$. The latter could be either a cubic[14] or a ladder[22] array of anions and cations. In order to establish the molecular formulas, it is necessary to rely on the absolute concentrations of phenolate and salt. Measurement of intensities as functions of concentrations then affords the stoichiometry of the equilibrium between mixed aggregate and phenolate/free salt provided the degree of association of the free salt is known.

The solution structure of $\mathrm{LiClO_4}$ in both dioxolane and THF has been extensively studied. In particular, it has been shown that the perchlorate ion can be characterized as the free ion, solvent-separated and contact ion pairs, and ion-pair aggregates. James and Mayes[36] have studied the Raman-active A_1 stretching vibrational bands of the perchlorate ion in diethyl ether and have established that aggregation only occurs above approximately 0.3 M in $\mathrm{LiClO_4}$. Since diethyl ether strongly favors aggregation, the predominant species in the less hindered donor solvents dioxolane and THF are expected to be either solvent-separated or contact ion pairs. Measurements of molar conductivities indicate that dissociation to free ions is also extremely low ($K_{\mathrm{diss}} \approx 10^{-7}$) for dioxolane.[37] Other evidence from colligative measurements,[38] ^{35}Cl NMR line widths,[39] and dielectric relaxation[40] confirms this conclusion. We may therefore consider the equilibria to be of the form (2). It has also been established that $\mathrm{LiBPh_4}$ in dioxolane

$$n\mathrm{Li_2P_2} + 2n\mathrm{LiClO_4} \rightleftharpoons 2(\mathrm{Li_2PClO_4})_n \tag{2}$$

exists predominantly as solvent-separated ion pairs,[44] so that eq 2 is likewise appropriate for the $\mathrm{LiBPh_4}$ system. The data in Table II clearly show that $n = 1$; i.e., the mixed aggregates in both dioxolane and THF are mixed dimers $\mathrm{Li_2PX}$.

Thermodynamic Parameters for Mixed-Aggregate Formation. The temperature range over which the equilibrium constants can be determined can be extended by studying the $^{13}\mathrm{C}_{\mathrm{para}}$ resonance in the regions of intermediate and fast exchange. The extraction of exchange rates and populations of the dimer and mixed dimer from the $^{13}\mathrm{C}_{\mathrm{para}}$ resonance at temperatures for which the rates and chemical shift difference are of the same order was achieved by comparing the observed and simulated line shapes as described in the experimental section. Under fast-exchange conditions, the populations are related to the observed chemical shift of the $^{13}\mathrm{C}_{\mathrm{para}}$ by eq 3.

$$\delta_{\mathrm{obs}} = p_{\mathrm{d}}\delta_{\mathrm{d}} + (1 - p_{\mathrm{d}})\delta_{\mathrm{md}} \tag{3}$$

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(36) James, D. W.; Mayes, R. E. *Aust. J. Chem.* **1982**, *35*, 1785.

(37) Onishi, S.; Farber, H.; Petrucci, S. *J. Phys. Chem.* **1980**, *84*, 2922.

(38) Wong, M. K.; Popov, A. I. *J. Inorg. Nucl. Chem.* **1972**, *34*, 3615.

(39) Cahen, Y. M.; Handy, P. R.; Roach, E. T.; Popov, A. I. *J. Phys. Chem.* **1975**, *79*, 80.

(40) Xu, M.; Inoue, N.; Eyring, E. M.; Petrucci, S. *J. Phys. Chem.* **1988**, *92*, 2789.

(41) Fischer, A.; Leary, G. J.; Topsom, R. D.; Vaughan, J. *J. Chem. Soc. B* **1966**, 782.

(42) Pless, J. *Peptides, Proc. Eur. Symp. 5th*, Oxford, **1962**, 69.

(43) Pauling, L. In *The Nature of the Chemical Bond and the Structure of Molecules and Crystals*; Cornell University Press: Ithaca, NY, 1946; p 189.

(44) Olmstead[45] has determined that $K_{\mathrm{dis}} \approx 5 \times 10^{-5}$. Furthermore, since the conductivities of the $\mathrm{LiBPh_4}$/dioxolane solutions are only slightly enhanced by the addition of $\mathrm{Li^+}$ chelating reagents, it appears that the ion pair is a solvent-separated species.

(45) Olmstead, W. N. *Proceedings of the Symposium on Lithium Batteries*, Proc. Vol. 81-4; Battery Division, The Electrochemical Society: Pennington, NJ, 1980; p 144.

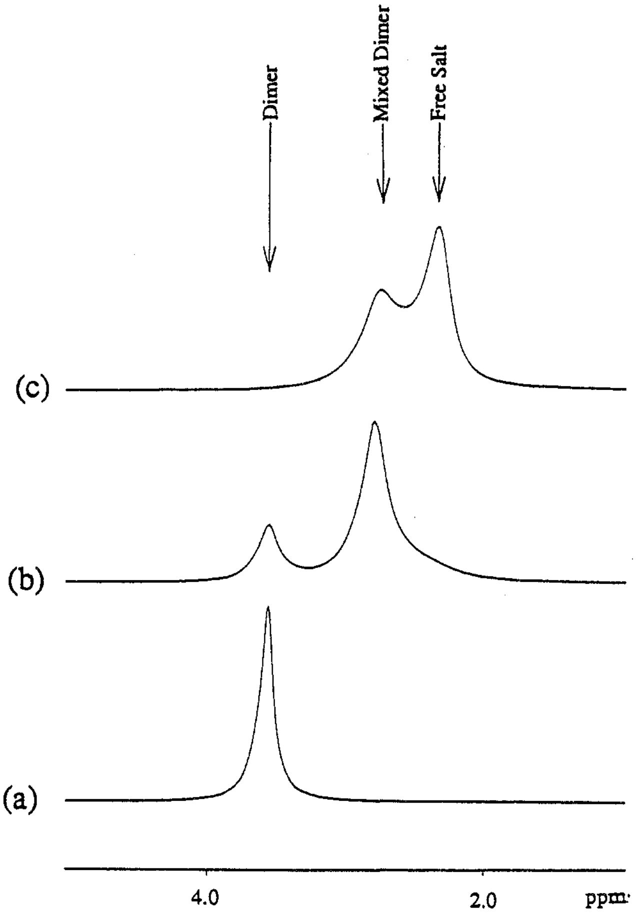


Figure 2. ^{7}Li (139.9-MHz) resonance of lithium 2,6-dimethylphenolate (0.25 M) in dioxolane at -90 °C with (a) no added salt, (b) 0.70 equiv of $LiClO_4$, and (c) 2.50 equiv of $LiClO_4$.

Table V. Equilibrium Constants and Thermodynamic Parameters for Mixed-Dimer Formation of Lithium 2,6-Dimethylphenolate with Lithium Salts

syst	t, °C	K_{eq}	ΔH, kcal mol^{-1}	ΔS, cal mol^{-1} deg^{-1}
$LiClO_4$/	22	1200	0	14.0
dioxolane	-90	1200		
$LiClO_4$/	22	30	0	6.7
THF	-90	30		
$LiBPh_4$/	22	3.0	-1.2	-1.3
dioxolane	-90	13		

The value of δ_d was obtained from salt-free samples. The fractional population of the mixed dimer (p_d) is a function of K_{eq} and the concentrations of the phenolate and the added salt. A constrained simplex search of data consisting of δ_{obs} vs [$LiClO_4$] at constant phenolate concentration was carried out to yield the values of K_{eq} and δ_{md} that minimized the squares of the residuals. The fit of the experimental data for three salts is shown in Figure 3.

The dimer/mixed-dimer equilibrium for $LiClO_4$ in dioxolane has been investigated as a function of $LiClO_4$ concentration (Table III) and temperatures (Tables III and IV). It is clear that the equilibrium is isothermal within experimental error. With THF as solvent, the equilibrium is also approximately isothermal but the dimer is more favored entropically (Table V). The thermodynamics of the mixed dimer of lithium tetraphenylborate in dioxolane have also been studied. The data for equilibrium constants are given in Table IV and ΔH and ΔS in Table V.

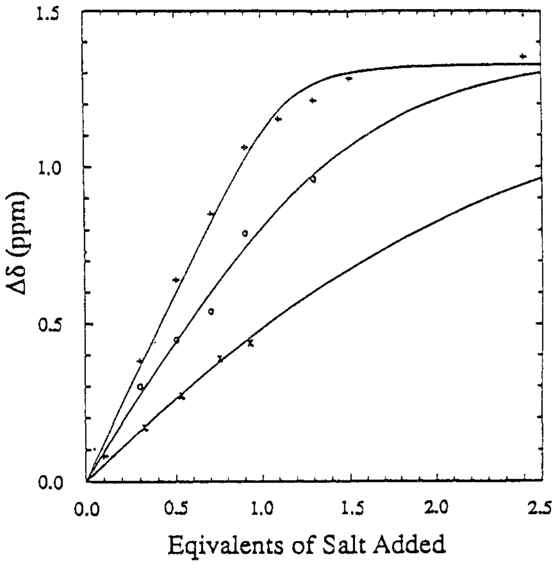


Figure 3. Change in ^{13}C (50.32-MHz) chemical shift $(\Delta\delta)_{para}$ vs equivalents of added salt for various lithium 2,6-dimethylphenolate (0.25 M)/added salt systems at 22 °C ("+" = $LiClO_4$/dioxolane, "O" = $LiClO_4$/THF, "×" = $LiBPh_4$/dioxolane). The solid lines correspond to the "best fit" for the dimer/mixed-dimer equilibrium.

Table VI. Extent of Mixed-Dimer Formation for Lithium 2,6-Dimethylphenolate with Added Lithium Tosylate and Lithium Chloride in Dioxolane

salt	T °C	[P], M	[S], M	% d	% ma
LiOTs	-90	0.23	0.042	82	18
	-90	0.22	0.077	65	35
	-90	0.21	0.097	54	46
	-90	0.23	0.160	36	64
LiCl	-103	0.25	0.125	63	37
	-103	0.40	0.200	60	40

Lithium chloride and tosylate also give rise to mixed aggregates in dioxolane (Table VI), although lower temperatures, particularly for the former, are required to slow interaggregate exchange sufficiently to allow observation of the two species. Because of the poorer solubilities of LiCl and LiOTs and of the uncertainties concerning their states of aggregation, it was not possible to establish, with certainty, the molecular formulas of their mixed aggregates, although chemical shift data (see the following text) suggest that they also are mixed dimers.

Mixed Aggregates of Other Lithium Phenolates. In order to establish a possible relationship between phenolate ion basicity and mixed-aggregate formation, we have investigated the 4-bromo-2,6-dimethyl and 2,4,6-tribromo derivatives, ^{13}C chemical shift data for which are presented in Table VII. 4-Bromo-2,6-dimethylphenolate appears to exist as the same single species in both dioxolane and THF. Although the differences for the $^{13}C_{para}$ chemical shifts relative to the corresponding anisole are somewhat more negative than that for lithium 2,6-dimethylphenolate, we believe the species to be the dimer $Li_2P_2S_n$ (n is unknown) because the monomer is expected to be even more shielded (3-4 ppm). This argument is supported by the observation that the 2,4,6-tribromo compound, at low concentrations in THF, exists as two species at -100 °C that are concentration dependent and must therefore be assigned to the dimer and monomer (this is the first observation of a monomeric lithium phenolate in a weakly polar, aprotic solvent). The $^{13}C_{para}$ of the monomer is shielded by 3.9 ppm relative to the dimer. Only the dimer is observed in dioxolane.

Both of these dimeric lithium phenolates form mixed aggregates with $LiClO_4$, the chemical shift differences between the dimer and the mixed aggregate, in both systems (Table VII) being similar to the corresponding value for the 2,6-dimethyl derivative. We conclude that these species are also mixed dimers.

As can be seen in Table VIII, the tendency for mixed-aggregate formation decreases with decreasing basicity of the anion. Bromine and $-CH_3$ have very similar van der Waals radii,[43] so steric effects in all three compounds are expected to be similar.

Kinetics of Interaggregate Exchange. Line-shape analysis of both the ^{6}Li and the $^{13}C_{para}$ resonances affords rate constants for

Table VII. Chemical Shifts of Various Substituted Phenolates in Dioxolane and THF

substit	concn, M	T, °C	$\delta(^{13}C)$ 1	2,6	3,5	4	$\Delta\delta(^{13}C_{para})$
			THF				
2,6-$(CH_3)_2$	0.25	−90	166.8	125.1	128.3	111.2	−12.8
4-Br-2,6-$(CH_3)_2$	0.50	−90	165.9	127.8	130.4	101.8	−15.0
2,4,6-Br_3	0.20	−100	160.9	115.9	133.9	101.9	−15.5 (d)
			161.3	115.6	133.5	98.0	−19.4 (m)[a]
			Dioxolane				
2,6-$(CH_3)_2$	0.70	−90	166.5	125.8	128.9	112.4	−12.0 (d)
			165.0	126.4	129.4	114.5	−9.9 (t)[b]
4-Br-2,6-$(CH_3)_2$	0.50	−90	165.6	128.6	130.9	102.7	−14.1
2,4,6-Br_3	0.50	−90	160.8	115.9	134.4	103.0	−14.4

[a] 8% monomer formation. [b] 5% tetramer formation.

Table VIII. Extent of Mixed-Dimer Formation (%) for Various Phenolates (0.5 M) with Added $LiClO_4$ (0.5 M) as a Function of Basicity and Solvent at −90 °C

phenolate	pK_a	solvent	$\Delta\delta$	% md
2,6-$(CH_3)_2$	10.6[b]	dioxolane	2.0	84
2,6-$(CH_3)_2$		THF	1.7	60
4-Br-2,6-$(CH_3)_2$	9.8[b]	dioxolane	1.8	68
4-Br-2,6-$(CH_3)_2$		THF	1.7	25
2,4,6-Br_3	8.3[c]	dioxolane	1.2	9
2,4,6-Br_3		THF		0[a]

[a] Solubility problems at low temperatures. [b] Reference 41. [c] Reference 42.

Table IX. Rates of Exchange as a Function of Temperature between Mixed Dimer and Dimer for 0.40 M Lithium 2,6-Dimethylphenolate with 0.20 M Added Salt in Dioxolane

$LiBPh_4$ T, K	k	$LiClO_4$ T, K	k
243	800	233	600
238	500	228	400
233	300	223	300
228	190	218	200
223	100	213	140
		208	100
		203	60

Table X. Rates of Exchange between Mixed Dimer and Dimer for Lithium 2,6-Dimethylphenolate and Various Salts in Dioxolane

concn, M	salt	concn, M	T, °C	pop. md	rates of exchange, τ^{-1} md → d	d → md
0.25	$LiClO_4$	0.075	−60	0.28	270	100
0.25	$LiClO_4$	0.125	−60	0.49	150	160
0.25	$LiClO_4$	0.175	−60	0.65	100	190
0.40	$LiClO_4$	0.12	−60	0.29	160	66
0.40	$LiClO_4$	0.20	−60	0.48	130	120
0.40	LiCl	0.20	−103	0.40	45	30
0.40	$LiClO_4$	0.20	−103[a]	0.48	2.3	2
0.40	$LiBPh_4$	0.20	−103[a]	0.27	0.005	0.002

[a] Estimated by extrapolating the Eyring plot.

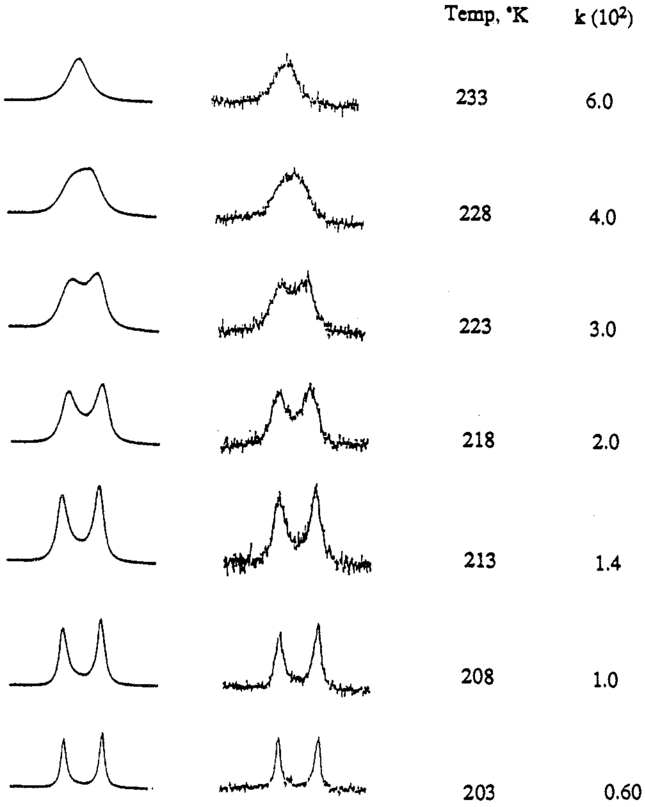


Figure 4. Observed and simulated $^{13}C_{para}$ (90.56-MHz) line shapes and the rates of exchange for the mixed dimer (δ 114.3)/dimer (δ 112.4) for the system lithium 2,6-dimethylphenolate (0.40 M)/lithium perchlorate (0.20 M) in dioxolane as a function of temperature.

Figure 5. Observed and simulated ^6Li (44.2-MHz) line shapes for the mixed dimer (δ 2.8)/dimer (δ 3.6) of lithium 2,6-dimethylphenolate (0.40 M)/lithium perchlorate (0.20 M) in dioxolane at −78 °C.

exchange over a limited temperature range as well as populations of species present. A typical example is shown in Figure 4, and k vs T data for $LiClO_4$ and $LiBPh_4$ are given in Table IX. The approximate values of $\Delta H^\ddagger$ are 7 and 11 kcal mol^{-1}, respectively. A value for $k_{d\rightarrow md}$ of 34 s^{-1} obtaind for ^6Li exchange (Figure 5) in the system $LiClO_4$/dioxolane at −78 °C is equal within experimental error to the value (35 s^{-1}) for ^{13}C exchange obtained by extrapolation of the k vs T data in Table IX for the same solution.

Data for the dependence of the rate constants ($1/\tau$) for exchange as functions of the concentrations of the phenolate and salt and of the nature of the salt anion are given in Table X.

The mixed dimer for each of the salts examined has a characteristic $^{13}C_{para}$ chemical shift at temperatures for which interaggregate exchange is slow. These are presented as the first four entries in Table XI. Solutions containing mixtures of two salts exhibit only *one* $^{13}C_{para}$ resonance for a mixed dimer, the shift of which is intermediate between those expected for the two pure mixed dimers. Since the differences in chemical shifts (in Hertz) that are to be averaged in the various exchange processes are very similar, we conclude that even at temperatures for which exchange of ^{13}C, ^6Li, and ^7Li is slow on the NMR time scale, the exchange of anions between mixed dimers is rapid. Indeed, even at −100 °C, solutions containing a mixture of $LiClO_4$ and $LiBPh_4$ exhibit only one mixed-dimer resonance (Figure 6a). Furthermore, for $LiClO_4$/$LiBPh_4$/dioxolane the observed chemical shifts agree well

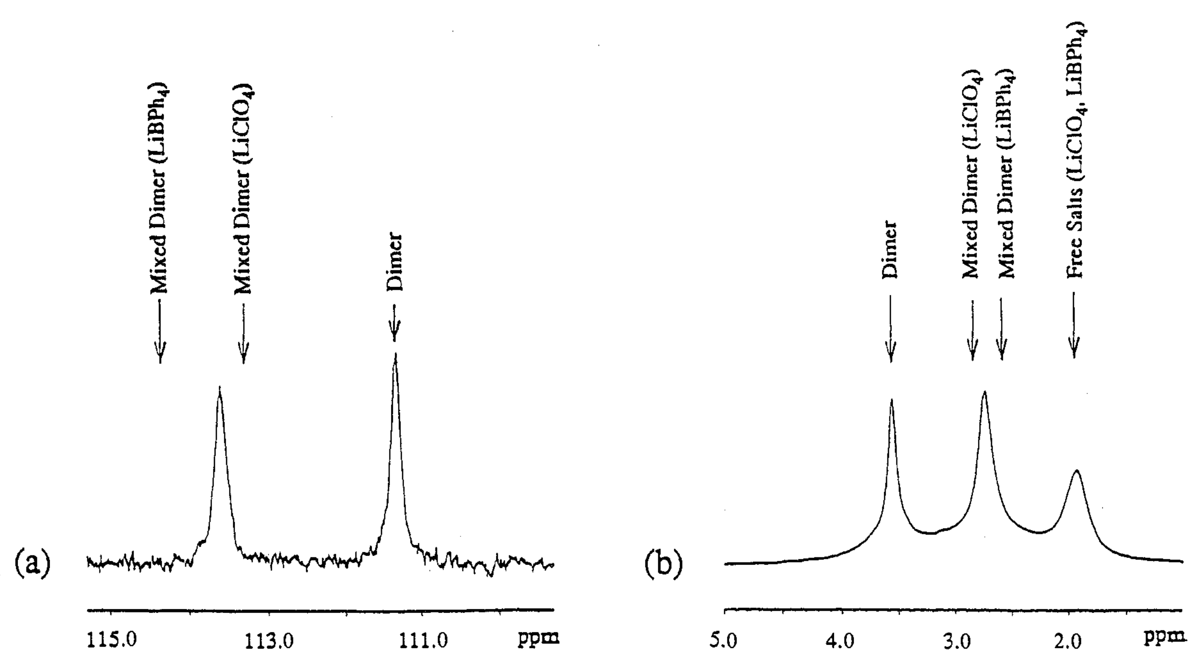


Figure 6. (a) $^{13}C_{para}$ (90.56-MHz) resonances of lithium 2,6-dimethylphenolate (0.25 M) with 0.50 equiv of $LiClO_4$/0.50 equiv of $LiBPh_4$ in dioxolane at −100 °C. (b) ^7Li (139.9-MHz) resonances of lithium 2,6-dimethylphenolate with 0.50 equiv of $LiClO_4$/0.50 equiv of $LiBPh_4$ in dioxolane at −100 °C.

Table XI. $^{13}C_{para}$ Chemical Shifts of Lithium 2,6-Dimethylphenolate (0.25 M) and Populations of Mixed Dimers with Two Added Salts in Dioxolane at −90 °C

salt(s)	equiv of salt	% md	$\delta(^{13}C)$ (md)	calcd[b] $\delta(^{13}C)$ (md)
$LiClO_4$	0.1–2.5		114.3	
$LiBPh_4$	0.3–1.0		115.4	
LiOTs	0.1–0.6		113.2	
LiCl	0.2–0.5		113.3	
$LiClO_4$ $LiBPh_4$	0.5 0.5	51	114.6	114.6
$LiClO_4$ $LiBPh_4$	0.2 0.6	33	114.9	114.9
$LiClO_4$ LiOTs	0.2 0.2	36	113.8	
$LiClO_4$ LiOTs	0.2 0.4	52	113.6	
$LiClO_4$ LiCl	0.4 0.4	51	113.8[a]	

[a] −100 °C. [b] Calculated by use of K_{eq}'s and by solving for populations.

with those calculated by use of the two equilibrium constants, the known chemical shifts of the pure mixed dimers, and the relative concentrations of the added salts (Table XI).

^{35}Cl and ^{11}B Line Widths. Table XII shows the effect of mixed-dimer formation on the ^{35}Cl line width of the perchlorate ion. It can be seen that $\nu_{1/2}$ reaches a maximum value at high phenolate to salt ratios of ~3.3, which presumably is characteristic of the mixed dimer. Further increase in this ratio results in a small decrease in $\nu_{1/2}$ that, if genuine, could indicate the formation of solvent-separated ion pairs or free ions. In THF, addition of the lithium phenolate to $LiClO_4$ also causes an increase in $\nu_{1/2}$, although not as great as in dioxolane because the equilibrium constant for the mixed-dimer formation is smaller in this solvent (Table V).

In contrast, the line width of ^{11}B in lithium tetraphenylborate in dioxolane is, within experimental error, unaffected by mixed-dimer formation, suggesting that the cations are well-removed from the BPh_4 anion in the mixed dimer.

Discussion

Factors Controlling Mixed-Dimer Formation. The determination of the empirical and molecular formulas of the mixed aggregates of lithium 2,6-dimethylphenolate and several lithium salts of strong acids provides unequivocal evidence for the formation of mixed dimers. The extent to which mixed dimers are formed appears to be the result of a complex interplay involving the electronic and steric properties of the phenolate, the second anion, and the solvent. We will first consider the properties of the phenolate ion.

Table XII. ^{35}Cl and ^{11}B Line Widths at Half-Height [$\nu_{1/2}$ (Hertz)] for $LiClO_4$ and $LiBPh_4$ with and without Added Lithium 2,6-Dimethylphenolate in Dioxolane and THF at 22 °C

no phenolate		0.25 M phenolate	
concn, M	^{35}Cl $\nu_{1/2}$	concn, M	^{35}Cl $\nu_{1/2}$
	$LiClO_4$/Dioxolane		
0.01	32.0	0.010	263
0.05	36.3	0.050	268
0.1	40.0	0.075	278
0.2	46.3	0.125	273
0.5	66.9	0.175	263
1.0	93.0	0.225	263
2.0	136.3	0.275	248
3.0	212.9	0.325	242
4.0	360.0	0.375	246
		0.625	206
	$LiClO_4$/THF		
0.26	44[a]	0.225	184
no phenolate		0.25 M phenolate	
concn, M	^{11}B $\nu_{1/2}$	concn, M	^{11}B $\nu_{1/2}$
	$LiBPh_4$/Dioxolane		
0.125	8.2	0.125	8.2

[a] Reference 39.

Mixed-dimer formation can be thought of as a competition between the phenolate and solvent for the solvated lithium cation of the added salt. This concept is formalized by either eq 4a or 4b, depending on whether the salt is a contact or solvent-separated ion pair. It follows that if steric factors remain constant, the

$$2LiXS_3 + Li_2P_2S_4 \rightleftharpoons 2Li_2PXS_4 + 2S \qquad (4a)$$

$$2LiS_4{}^{+}X^{-} + Li_2P_2S_4 \rightleftharpoons 2Li_2PXS_4 + 4S \qquad (4b)$$

tendency of a dimeric lithium phenolate toward mixed-dimer formation will increase with the Brønsted basicity of the phenolate anion. This is shown to be the case by the data presented in Table VIII. It is interesting to note that mixed-dimer formation between lithioisoburyrophenone and LiCl in dimethoxyethane does not occur.[24] In this solvent, the enolate coexists as dimer and tetramer and the addition of LiCl converts both species to a mixed tetramer. The steric factors for the enolate and 2,6-dimethylphenolate are rather similar, and the different behavior of the enolate may be due to its higher O-basicity.[46]

It might be expected that increasing solvent Lewis basicity would decrease the extent of mixed-dimer formation, and indeed, this trend is observed for $LiClO_4$ in dioxolane and THF (Table VIII). These two solvents presumably have very similar steric requirements, but the former is a substantially weaker Lewis base, its heat of reaction with BF_3 being some 5 kcal mol^{-1} less exothermic than that of THF.[48] However, the solvent effect is much less than expected and is essentially entropic in origin (Table VI). This must reflect the relative degree of solvation of the added salt and the mixed dimer since the dimer itself is tetrasolvated in both solvents. If, for the moment, we assume that $LiClO_4$ in both dioxolane and THF exists predominantly as solvent-separated ion pairs, we can write eq 5. Values of n = 1, 2 correspond to the

$$2LiX{\cdot}4S + Li_2P_2S_4 \rightleftharpoons 2Li_2PX{\cdot}(4 + n)S + (4 - 2n)S \quad (5)$$

formation of partially or fully solvent-separated ion pairs for the mixed dimer, a process that certainly will be favored by THF relative to dioxolane, thus accounting for the lower entropy in the former solvent. This picture nicely accommodates observation of the essentially zero entropy change for the formation of the mixed dimer with $LiBPh_4$ in dioxolane. Contact ion pairs with the tetraphenylborate ion, while not impossible,[49] are very unlikely, and in this case, they appear to be excluded by the absence of any perturbation of the ^{11}B QSC on mixed-dimer formation (Table XII) and by the evidence cited previously.[44] The value of n in this system is therefore 2; i.e., there is no change in the total number of solvent molecules associated with the formation of the mixed dimer.

The assumption that $LiClO_4$ in dioxolane exists entirely as the solvent-separated ion pair is not strictly correct. Xu, Inoue, Eyring, and Petrucci[40] have made a careful analysis of the degenerate bending mode, ν_4(e), of the perchlorate ion in the infrared spectrum of $LiClO_4$ in dioxolane. They assign bands at 624 and 639 cm^{-1} to the solvent-separated and contact ion pair, respectively, on the grounds that only the former is observed in the presence of crown ethers. The relative intensities of the two bands indicate that the solvent-separated ion pair is the major species (~4:1). Only the solvent-separated ion pair is expected in the better donor solvent, THF.

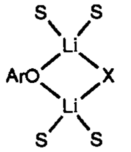
While we have not rigorously established the molecular formulas of the mixed aggregates formed by lithium tosylate and chloride, the ^{13}C chemical shifts leave little doubt that the species are also mixed dimers. Experimentally, the tendencies of these anions to form mixed dimers is more difficult to evaluate because of solubility problems and the possible propensities of these salts to form aggregates. There is, for example, evidence from colligative measurements[38] that indicates that LiCl in THF in the concentration range 0.04–0.14 M is extensively dimerized. As pointed out previously, the degree of aggregation of the sparingly soluble lithium tosylate is not known.

Table XIII. $\Delta\delta(^{13}C_{para})$ for the Mixed Dimer of Lithium 2,6-Dimethylphenolate As a Function of Added Salt Basicity in Dioxolane at -90 °C

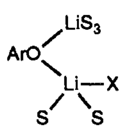
salt	pK_a(CA)	δ_{md}	$\delta_{md}-\delta_d$
Li-2,6-$(CH_3)_2$	10.6[b]	112.4	0.0
LiOTs	-6.5[c]	113.2	0.8
LiCl	-7.0[d]	113.3[a]	0.9
$LiClO_4$	-10.0[d]	114.3	1.9
$LiBPh_4$		115.4	3.0

[a] -108 °C. [b] Reference 41. [c] Reference 51. [d] Reference 52.

Structures of Mixed Dimers. The precise structures of the mixed aggregates does not follow directly from their molecular formula (Li_2PX) since this does not include solvent molecules in the primary coordination spheres of the lithium cations. Thus, three possibilities, **1**–**3**, must be considered, **1** and **2** may be regarded as contact ion pairs and **3** as a solvent-separated ion pair. The species **3** might also be in equilibrium with the fully dissociated ion. Several results presented previously throw some light on these structural problems.



1



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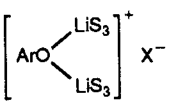

3

The structure **1** has been established for the parent dimer (X = OAr). At the other end of the scale, the mixed aggregate with $LiBPh_4$ in dioxolane has the structure **3** based on the consideration of essentially zero entropy of its formation from the dimeric phenolate (n = 2 in eq 5). Since the entropy of formation of the $LiClO_4$ mixed dimer in dioxolane is quite large, it presumably has either the structure **1** or **2**. This conclusion is consistent with the observation of a greatly increased ^{35}Cl line width for the mixed dimer.

Some further insight concerning the structures of the mixed dimers is obtained from a consideration of the $^{13}C_{para}$ chemical shifts (Table XIII). The value for the $LiBPh_4$ mixed dimer shows that there is increased localization of the charge on oxygen as expected for the triple ion $[Li_2OAr]^+$. In fact, the value $\delta(^{13}C_{para})$ is approximately 1.0 ppm less shielded than the tetramer in which the oxygen is attached to three lithium atoms. There is also a considerable deshielding for X = ClO_4, and it is tempting to assign the structure **2**. The corresponding shifts in the mixed dimers with X = Cl and OTs are much closer to that observed for the dimer itself, which, in the absence of values for the thermodynamic parameters for their formation, may be used as evidence that they have the structure **1**. The other possibility is that all three species (X = ClO_4, Cl, OTs) have the same structure, either **1** or **2**, and that the changes in charge delocalization are a manifestation of the basicities of the anions (see Table XIII). One argument favoring the first explanation is that a change of ~17 pK_a units in going from X = OAr to Cl results in the same change in $\delta(^{13}C_{para})$ (~1 ppm) as caused by a change of only 3 pK_a units in going from Cl to ClO_4. This is consistent with the formation of a new structural type, presumably **2**.

Kinetics of Dimer/Mixed-Dimer Exchange. We have not undertaken an in-depth study of the mechanism of the exchange process, but some tentative conclusions can be drawn from the data in Table X.

In an earlier study[24] of the exchange between tetrameric lithioisobutyrophenone (Li_4E_4) and the mixed tetramer (Li_4E_3Cl), it was shown that the rate constants for exchange $1/\tau_{mt\to t}$ are linearly dependent on the ratio of populations p_t/p_{mt} but independent of the absolute concentration of enolate and salt provided p_t/p_{mt} is held constant. The rate constant for the reverse process $1/\tau_{t\to mt}$ is relatively insensitive to both the concentration and the ratio of populations. These observations are consistent with a mechanism involving dissociation of the *mixed aggregate* to a lesser aggregation state with no contribution from dissociation of the

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[46] The pK_a for the enol of acetophenone has been estimated to be 10.3.[47] The effect of an *o*- or *p*-methyl substituent on the acidity of phenol is to raise the pK_a by ~0.3 unit. Assuming the same effect operates in enols, we estimate that the pK_a of the enol of isobutyrophenone is ~0.3 units higher than that of 2,6-dimethylphenol.

[47] Haspra, P.; Sutter, A.; Wirz, J. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 617.

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[49] Close contacts (2.21–2.44 Å) between lithium and the aromatic rings of VPh_6^{4-}, $CrPh_6^{3-}$,[50a] and $Mn_2Ph_6^{2-}$[50b] have been reported in crystal structures of the etherates.

[50] (a) Bartlett, R. A.; Olmstead, M. M.; Power, P. P.; Shoner, S. C. *Organometallics* **1988**, 1801. (b) Olmstead, M. M.; Power, P. P.; Shoner, S. C. *Organometallics* **1988**, 1380.

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tetramer itself. The $LiClO_4$ data in Table X correspond to a somewhat different behavior in that while $1/\tau_{md\to d}$ is directly proportional to p_d/p_{md} for constant phenolate concentration, it is also dependent on the absolute concentration of phenolate. Furthermore, the reverse reaction is inversely proportional to p_d/p_{md} and is dependent on phenolate concentration. We postulate that the exchange reaction involves the intermediacy of monomeric lithium phenolate and involves a trimer as an intermediate (or transition state). There are therefore two pathways, depending on whether the "trimer" is derived from the dimer or mixed dimer as shown in eqs 6a and 6b, respectively. If only pathway 6a is

$$Li_2P^*X \rightleftharpoons LiP^* + LiX \tag{6a}$$

$$Li_2P_2 + LiP^* \rightarrow [Li_3P_2P^*] \rightarrow Li_2PP^* + LiP$$

$$Li_2P_2^* \rightleftharpoons 2LiP^* \tag{6b}$$

$$Li_2PX + LiP^* \rightarrow [Li_3P^*PX] \rightarrow LiP + Li_2P^*X$$

involved, the observed behavior would be similar to that of the Li_4E_4/Li_4E_3Cl system. Pathway 6b would give exactly the opposite result. The few available data in Table X suggest that for the $Li_2P_2/Li_2P(ClO_4)$ system in dioxolane both pathways contribute.

The very pronounced dependence of the nature of the anion is noteworthy. These findings suggest that the chloride mixed dimer exchanges with the dimer through pathway 6a. This is reasonable because dissociation is favored due to the stronger interaction of the chloride ion in the product LiCl compared to the analogous salts of the ClO_4^- and BPh_4^-. It is possible that the $LiBPh_4$ system involves only pathway 6b.

A further point in favor of the monomer as an intermediate is that, as was shown previously, this species can be directly observed in the case of lithium 2,4,6-tribromophenolate in THF, although it undergoes rapid exchange with the dimer above −100 °C. Clearly, a much more extensive study will be needed in order to establish these postulated pathways, and the full mechanistic picture should also take into account the solvent's direct role, if any, in affecting the dissociation of the dimeric species.

The observation that, for mixed dimers, exchange of anions is much more rapid than exchange of phenolate or lithium cations between dimer and mixed dimer or of lithium cations between mixed dimer and the added salt clearly implicates the intermediacy of a relatively free anion, which could be either a free ion or solvent-separated ion pair. This is certainly readily understood in terms of the structures **2** and **3**. The anion may also be somewhat more free in **1** since the ^{13}C chemical shifts, in all mixed dimers, indicate increased binding of Li^+ to oxygen, presumably as a consequence of decreased binding to the less basic, foreign anion.

Summary

(i) Lithium phenolates that are dimeric in weakly polar, aprotic solvents form mixed dimers (Li_2PX) with a number of lithium salts of strong acids.

(ii) The extent of mixed-dimer formation increases with the basicity of the phenolate ion.

(iii) Mixed-dimer formation is favored by decreased cation solvating power of the solvent.

(iv) There is no simple relation between the basicity of the anion of the added salt and mixed-dimer formation.

(v) The structures of the dimers can be regarded as dimeric ion pairs ($Li_2P^+X^-$) that may be contact or partially or fully solvent separated.

(vi) Interaggregate exchange appears to involve the intermediacy of monomeric lithium phenolate derived from the mixed aggregate and/or the dimeric phenolate.

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Photochemistry of a μ-Alkylidene Piano-Stool Dimer[1]

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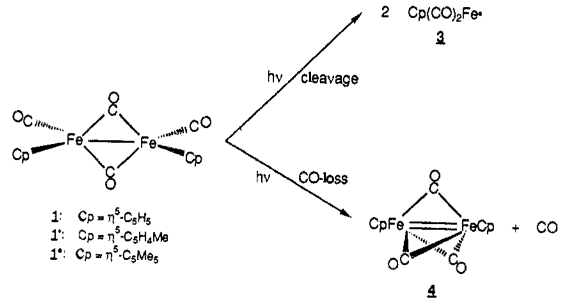
Abstract: Irradiation of the piano-stool dimer $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (**2**) results in the formation of a CO-loss intermediate as the only photochemical pathway available for this dimer. The CO-loss intermediate is proposed to have the structure $[CpFe]_2(\mu\text{-}CO)_2(\mu\text{-}CHCH_3)$ (**6a**). Thermal reactions of **6a** with a variety of species have been elucidated by laser flash photolysis (LFP) experiments. The kinetics and activation parameters for **6a** with a variety of reagents (CCl_4, CO, CH_3CN, and several phosphines) indicate that the reaction is an associative bimolecular process. Comparison of the reaction chemistry of **2** is discussed to that of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)_2$ (**1**).

The past decade has seen a tremendous growth in the studies of the fundamental photoprocesses of organometallic compounds.[2] Such systems offer the potential for a diverse class of photochemical reagents wherein changing the metal–ligand combinations could lead to selective photochemistry.[3] To achieve this goal requires a concise picture of the factors that control the photochemical channels available to the molecule. In the case

Scheme I



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