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AC CONDUCTIVITY OF ALKYLARENELITHIUM COMPLEXES IN AROMATIC SOLVENTS

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Summary

Polyamine chelates have been made of the lithium derivatives of a number of alkylaromatic hydrocarbons and the conductivities of their solutions measured. The dependence of the specific conductivity of toluene solutions of chelated benzyllithium on the nature of the amine, and the relation between the pK_a of the parent hydrocarbon and the specific conductivity in benzene solution of the chelates of its lithium derivative have been examined. The structures of the conducting species are discussed.

Introduction

Solvation with Lewis bases has made it possible to increase considerably the electrical conductivity of solutions of organolithium compounds [1,2]. It has even been proposed to use these types of solution as electrolytes in lithium batteries [3]. Forster and Langer [4] have demonstrated that chelating polyamines are particularly effective in increasing the conductivity, and they have studied the dependence of the conductivity on the nature of the amine, the concentration and temperature of the solution, and the frequency of the alternating current. Their studies were mainly with diphenylmethyllithium.

It was therefore of interest to study the variation of conductivity with the acidity of the hydrocarbon used to prepare the salt, i.e. with its pK; these measurements should also give information on the structure of the above compounds, i.e. on the nature of the dissolved ion pairs.

Results

Before studying the influence of the pK of the hydrocarbon on the conductivity of its lithium salt, it was thought useful to run a series of tests comparable to those carried out by Forster and Langer [2] with diphenylmethyllithium. This was done using a solution of benzyllithium in toluene, and by varying the concentration of the

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TABLE 1

DEPENDENCE OF THE SPECIFIC CONDUCTIVITY OF SOLUTIONS OF BENZYLLITHIUM IN TOLUENE AT 30°C ON THE CHELATE CONCENTRATION AND THE NATURE OF THE POLYAMINE

TMEDA [a]				TMCHDA [b]				HMTTA [c]			
c (mol/l)	log c	λ [d]	log λ	c (mol/l)	log c	λ	log λ	c (mol/l)	log c	λ	log λ
2.0	0.301	0.232×10^{-3}	−3.634	1.818	0.259	0.045×10^{-3}	−4.346	1.0	0	0.131×10^{-3}	−3.883
1.0	0	0.069×10^{-3}	−4.161	0.952	−0.021	0.276×10^{-4}	−4.558	0.5	−0.301	0.741×10^{-4}	−4.130
0.5	−0.301	0.105×10^{-4}	−4.979	0.499	−0.302	0.129×10^{-4}	−4.888	0.25	−0.602	1.778×10^{-5}	−4.7050
0.25	−0.602	0.263×10^{-5}	−5.580	0.261	−0.582	0.403×10^{-5}	−5.394	0.125	−0.903	3.077×10^{-5}	−5.512
0.125	−0.903	0.941×10^{-6}	−6.0264	0.137	−0.863	1.303×10^{-6}	−5.885	0.0625	−1.204	1.632×10^{-6}	−5.787
0.0625	−1.204	0.800×10^{-6}	−6.0969	0.0719	−1.143	0.632×10^{-6}	−6.199	0.03125	−1.505	1.524×10^{-6}	−5.817
0.03125	−1.505	0.865×10^{-6}	−6.063	0.0376	−1.424	0.700×10^{-6}	−6.155	0.0156	−1.806	1.600×10^{-6}	−5.796

[a] *N,N,N′,N′*-Tetramethylethylenediamine. [b] *N,N,N′,N′*-Tetramethylcyclohexane-1,4-diamine. [c] Hexamethyltriethylenetetramine(2,5,8,11′-tetramethyl-2,5,8,11-tetra-azadodecane). [d] Specific conductivity (ohm^{-1} cm^{-1} eq^{-1}).

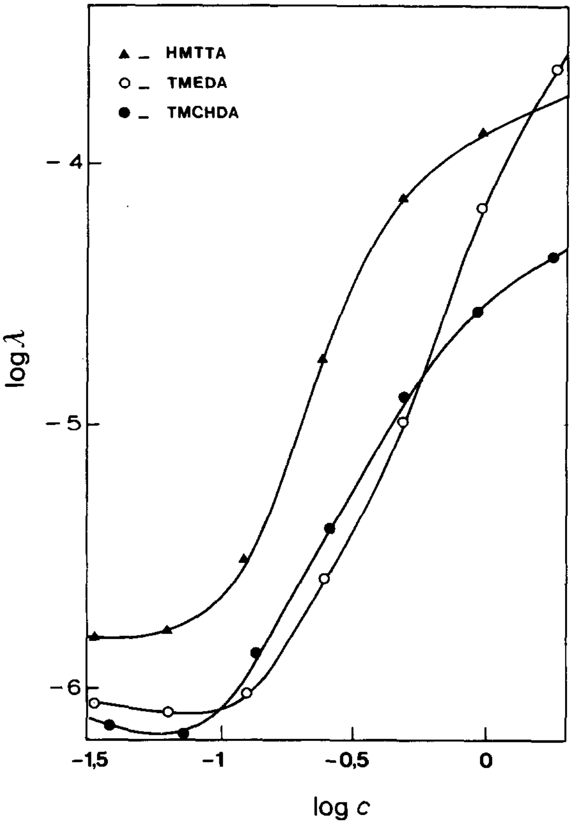


Fig. 1. Dependence of the specific conductivity of benzyllithium solutions in toluene at 30°C on the chelate concentration and the nature of the polyamine, tetramethylethylenediamine (TMEDA), tetramethylcyclohexanediamine (TMCHDA) and hexamethyltriethylenetetramine (HMTTA).

solution of the organolithium compound. As the acidity of the two corresponding hydrocarbons differed greatly, it could not be taken for granted, a priori, that Forster and Langer's conclusions would be valid for the salts of the less acid hydrocarbon. Indeed, we were only interested in hydrocarbons less acidic than diphenylmethane.

Influence of the amine and the chelate concentration

In all our tests we used a stoichiometric quantity of the chelating amine, i.e. 1 mol of amine per mol of metalate (RLi). The following amines were studied: tetramethylethylenediamine (TMEDA), tetramethylcyclohexanediamine (TMCHDA), and hexamethyltriethylenetetramine (HMTTA).

The solvent used in all these tests was toluene. The results obtained using the three amines are shown in Table 1 and Fig. 1. It can be observed (and these results do indeed confirm those of Forster and Langer) that there is a large increase in specific conductivity with increase in concentration. For example, with tetramethylethylenediamine the specific conductivity increases by a factor of 290 when the concentration increases from 0.0625 mol/l to 2 mol/l (the non-specific conductivity is multiplied by 9300).

TABLE 2

SPECIFIC CONDUCTIVITY OF SOLUTIONS OF THE LITHIUM SALTS IN BENZENE [a]

Hydrocarbon used for lithium salt formation	Log λ [b]		ΔpK [e]
	TMEDA [c]	HMTTA [d]	
p-Xylene	−5.87	−4.68	0.96
p-t-Butyltoluene	−5.79	−4.79	0.72
Mesitylene	−5.66	−4.29	0.43
m-Xylene	−5.54	−4.31	0.24
Toluene	−5.48	−4.37	0
1,4-Dimethylnaphthalene	−4.93	−3.64	−0.88
2,6-Dimethylnaphthalene	−5.63	−4.11	−1.05
2-Methylnaphthalene	−5.06	−3.57	−1.66
2-Ethylnaphthalene	−6.17	−4.70	−1.76
1-Methylnaphthalene	−4.81	−3.52	−1.91
1-Ethylnaphthalene	−6.22	−4.43	−2.01
Diphenylmethane	−4.14	−3.35	−3.75

[a] At 30°C, concentration 0.25 mol/l. [b] Specific conductivity: $\text{ohm}^{-1}\ \text{cm}^{-1}\ \text{eq}^{-1}$. [c] *N*,*N*,*N'*,*N'*-Tetramethylethylenediamine. [d] Hexamethyltriethylenetetramine. [e] Obtained from metalation equilibrium constants [8].

Figure 1 shows that the two diamines TMEDA and TMCHDA have a comparable effect at low concentrations; however, higher conductivity values can be reached at high concentration with TMEDA. But, at equal chelate concentrations, the tetramine generally makes it possible to increase markedly the conductivity of benzyllithium solutions: the conductivity is, for example, multiplied by 7 when the

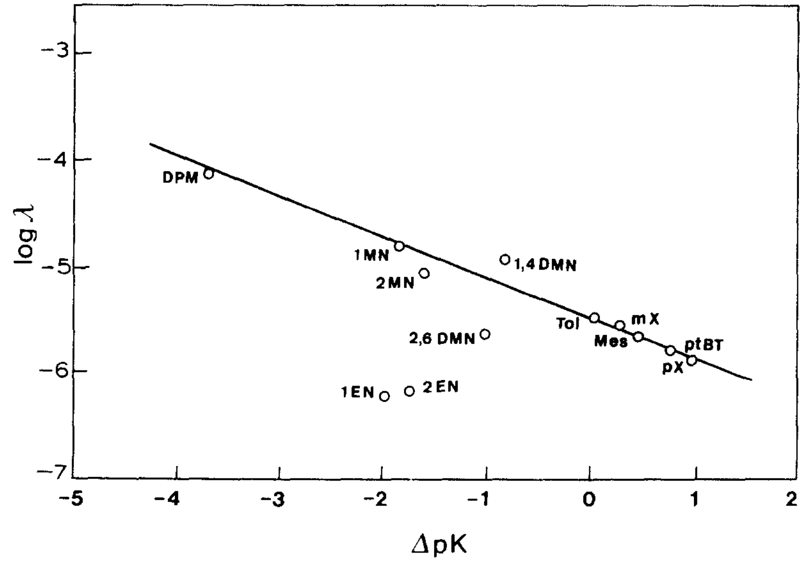


Fig. 2. Correlation between the specific conductivity of TMEDA-chelated lithium salts and ΔpK of the parent hydrocarbons. pX, *p*-xylene; ptBT, *p*-t-butyltoluene; Mes, mesitylene; mX, *m*-xylene; Tol, toluene; 1,4 DMN, 1,4-dimethylnaphthalene; 2,6 DMN, 2,6-dimethylnaphthalene; 2 MN, 2-methylnaphthalene; 2 EN, 2-ethylnaphthalene; 1 MN, 1-methylnaphthalene; 1 EN, 1-ethylnaphthalene; DPM, diphenylmethane).

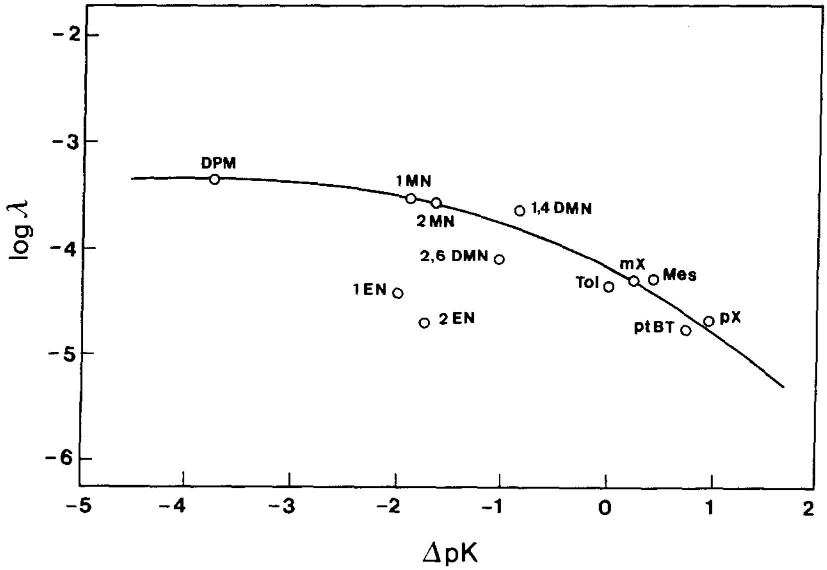


Fig. 3. Correlation between the specific conductivity of HMTTA-chelated lithium salts and ΔpK of the parent hydrocarbons. (Symbols as in Fig. 2.)

tetramine HMTTA replaces TMEDA in solutions where the concentration is lower than 0.5 mol/l.

Influence of the pK of the hydrocarbon

The pK values of the hydrocarbons used have been defined elsewhere [5]. In general, they are obtained by means of the proton–lithium exchange reaction [6–8]:

$$R^1H + R^2Li \overset{K_{12}}{\rightleftarrows} R^1Li + R^2H \qquad (1)$$

$$\Delta pK_{12} = -\log K_{12}$$

The values of the specific conductivity, at a given concentration in lithium salt (25×10^{-2} mol/l), were determined for a series of alkylaromatic hydrocarbons. These results are shown in Table 2 and Figs. 2 and 3.

Apart from the lithium salts of the ethylnaphthalenes and 2,6-dimethylnaphthalene, with the diamine TMEDA the values of the logarithm of the specific conductivity vary linearly with the pK of the hydrocarbon used to prepare the salt: the more acid the hydrocarbon, the stronger the ionization.

This does not apply to the complexes with the tetramine HMTTA and a levelling effect is clearly apparent in Fig. 3. Once again the conductivities of the ethylnaphthalene salts and the 2,6-dimethylnaphthalene salts are lower than those corresponding to the pKs of these hydrocarbons.

Discussion

It can therefore be observed that by chelating the lithium salts of alkylaromatic hydrocarbons with polyamines it is possible to prepare highly conducting solutions, especially at high concentrations. Obviously, this is not because free ions are present, since the dielectric constants of benzene and toluene are very low.

The considerable increase in conductivity with concentration is similar to that observed by Kenausis et al. [9,10] who used solutions of tetraamylammonium thiocyanate, $(\text{n-amyl})_4N^+(CNS)^-$, in *p*-xylene, and by Forster and Langer who used solutions of $(C_6H_5)_2CHLi(TMEDA)_2$ in toluene.

The most rational explanation [4] of these results is that at high concentration, ion aggregates which increased conductivity are formed. It can be observed (Fig. 1) that above a certain threshold ($c < 0.1$ mol/l) the conductivity of benzyllithium solutions chelated by the diamine TMEDA or the tetramine HMTTA increases in proportion to the cube of the concentration:

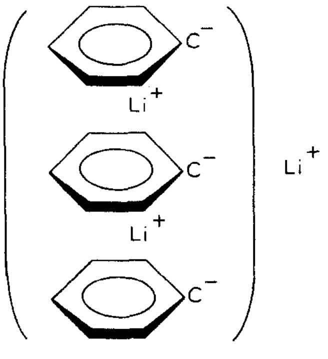
$$\lambda' = ac^3$$

This result can be interpreted readily using the following model:

$$3\,(\mathrm{RLi\cdot TMEDA}) \rightleftarrows \left[(\mathrm{R_3Li_2})^-(\mathrm{Li})^+\cdot(3\,\mathrm{TMEDA})\right] \qquad (2)$$

the complex formed being an "ate" complex, $(R_2Li)^-Li^+$ of the type described by Wittig [11].

If we assume that the equilibrium constant of this reaction is small, the solution indeed has a concentration of trimer and as a consequence, a conductivity proportional to the third power of the monomer concentration. As the electrostatic force between the soft anion of the "ate" complex and the highly solvated Li^+ cation is very low, this species can effectively conduct alternating current like a true ionic solution. It should be noted that the solvent (benzene or toluene) molecules can easily be included between the "ate" complex ions, as has been shown by an NMR study of the benzene protons in a solution of $[Al(CH_3)_4]^-Li^+$ [12]. This inclusion would be more difficult because of steric hindrance when the solvent is mesitylene, and Forster and Langer have found that the conductivity is 1.7 times lower when $(C_6H_5)_2CHLi\cdot(TMEDA)_2$ is dissolved in mesitylene than when it is dissolved in benzene.



This complex anion is in reality an agglomerate; we can consider that the Li cation is above the aromatic nucleus level and as a result the agglomerate would be of the "sandwich" type [13]. It is mainly the two Li atoms of this complex which are influenced by the ring currents of the aromatic rings of the anion; this phenomenon would therefore explain the enormous affects of the ring currents in the ^{7}Li NMR spectra mentioned in a previous publication [5]. If this is accepted, it is clear that all the factors which prevent the transfer of the cation onto the nucleus also prevent the agglomerate being formed. The steric effect of methyl groups on the α-carbon atoms, or the formation of the allylic complex of 2-methylnaphthalene would prevent this transfer, and as a result would also prevent the agglomerate being formed. The results shown in the curves (Figs. 2 and 3) indicate clearly that the conductivities of these hindered salts are abnormally low, especially those of the ethylnaphthalenes.

The increase in conductivity using the tetramine HMTTA is very great: this could be due to the greater charge delocalization towards the aromatic rings and consequently to the greater attraction between the rings and the cations, which favour formation of agglomerates. The ion pairs of the most acidic hydrocarbons are transformed completely into separated ion pairs and there is thus "levelling" at the 1-methylnaphthalene level [6]; in the same way, the conductivity no longer increases when the pK of the hydrocarbon decreases, the equilibrium 2 being completely displaced towards the right-hand side.

For all the series of hydrocarbons considered, the diamine shows a consistent behaviour which corresponds to contact ion pairs, with small but increasing quantities of aggregates as the hydrocarbon pK decreases.

In conclusion, the study of the conductivity of organolithium compounds has enabled us to show that the same relationships and the same anomalies apply here as already observed in the ^{7}Li NMR spectra. As far as the reactivity is concerned, it can be considered that the agglomeration of ions, i.e. the formation of "sandwich" Li complexes, is much more a result of delocalization than a cause, and that these agglomeration phenomena do not play any role whatsoever in the reactivity of salts.

Veracini and Gau [7] have shown that the kinetic equation is always first order in the organolithium compound; this order can be explained by assuming that the "sandwich" complex is not very reactive and that its concentration in the medium remains very low for all the series of salts considered. However, on the contrary, Hogen-Esch and Smid's results [13] show that for lithium and sodium salts of very acidic hydrocarbons, the kinetic order in the metalation reaction is fractional; this means that for these salts the majority of ions are associated in "sandwich" complexes.

Experimental

The organolithium salt solutions were prepared from n-butyllithium dissolved in hexane, according to the method which is described elsewhere [5]. The electrical conductivity was measured using a TACUSSEL type CD 6 N conductimeter, which generally operated at a frequency of 50 Hz. It has been verified that a change of frequency has an insignificant effect at the concentrations used. All of the measurements were taken at 30°C. The specific conductivities were obtained by dividing the conductivity by the concentration of the lithium salts.

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