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ELECTRONIC EFFECT OF THE CYCLOPENTADIENYL ANION AS A SUBSTITUENT. THE EFFECT OF THE ALKALI METAL CATION, SOLVENT AND COMPLEXING AGENTS ON ^{19}F CHEMICAL SHIFTS OF *m*- AND *p*-FLUOROPHENYLCYCLOPENTADIENYL ANIONS

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Summary

Salts of the carbanions $M^+[C_5H_4C_6H_4F\text{-}m(\text{-}p)]^-$, where M = Li, Na, and K, have been investigated by ^{19}F NMR spectroscopy. The effect of the alkali metal cation, the coordinating ability of the solvent, complexing agents (TMEDA, crown-ethers), and concentration on the ^{19}F chemical shifts has been studied. The results are discussed in terms of an equilibrium between tight and solvent-separated ion pairs. On the basis of ^{19}F chemical shift data for Li^+-$[C_5H_4C_6H_4F\text{-}m(\text{-}p)]^-$ in HMPA solution, the electronic effect of the $C_5H_4^-$ substituent as a "free ion" has been determined.

Introduction

^{19}F chemical shifts have been measured for the lithium salts of the *m*- and *p*-fluorophenylcyclopentadienyl anions, FC^-, in acetonitrile solution, and on the basis of these data the constants σ_I and σ_R^0, characterizing the electronic effect of the $C_5H_4^-$ group as a substituent, have been calculated [1].

It is well known that even 1 : 1 electrolytes can exist in several distinguishable forms, and the solvent sphere may include several solvent layers. The solution may contain various (two or more) types of ion pairs in a dynamic equilibrium [2].

In the case of salts of FC^- anions, as well as those of other aromatic carbanions, the equilibrium between tight (M^+, FC^-) and solvent-separated ion pairs ($M^+\|FC^-$) will depend on the cation size, the solvent coordinating ability, temperature, and also on how strongly solvating the cation complexing agents are. An increase in the solvent coordinating ability, lowering of temperature, and decrease in the cation size will favour the formation of solvent-separated pairs. It is evident that the carbanion can be assumed as being a "free ion" in a system where the perturbing effect of the cation is minimized.

Therefore, we undertook an investigation of the effect of the alkali metal cation, the solvent coordinating ability, the solvating ability of the cation complexing agents, and of the carbanion salt concentration on ^{19}F chemical shifts in salts of *m*- and *p*-fluorophenylcyclopentadienyl anions. Our interest in ionic cyclopentadienyl compounds was caused by the fact that cyclopentadienyl derivatives of transition metals form a large group of organometallic compounds, and the knowledge of the way the electronic properties of a cyclopentadienyl anion change upon coordination with a metal may allow us to gain a better insight into the nature of the metal—ligand bond. This refers also to the polar cyclopentadienyl compounds of some non-transition metals, InC_5H_5, TlC_5H_5, $Mg(C_5H_5)_2$ and others in which there is no agreement concerning the nature of the metal—ligand bond *.

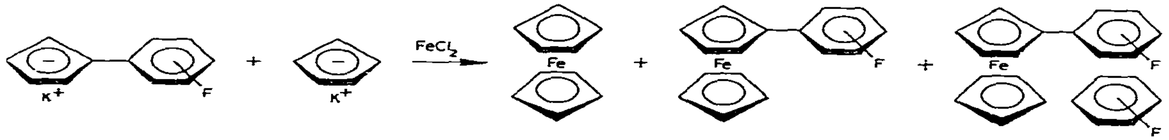
Several works [4—9] have been devoted to studying ion pairs of aromatic carbanions by ^1H NMR spectroscopy. Recently, it has been shown that ^7Li NMR is a useful method to investigate various types of ion pairs [4,10,11].

As will be shown in this paper, the proposed approach to the study of ion pairs by ^{19}F NMR has a number of advantages and can be successfully applied along with other methods. The ^{19}F chemical shift is more sensitive to electronic changes than is the ^1H one, and the significant distance to the nucleus studied in a *m*- or *p*-fluorophenyl-substituted carbanion makes it possible to eliminate the effect of the magnetic anisotropy of an aromatic carbanion on the ^{19}F chemical shift; finally, the shielding of ^{19}F nuclei reflects the electron density in the carbanion and can be used for calculating Taft's σ constants characterizing the inductive and resonance effects of a given carbanion as a substituent.

Results and discussion

We have measured the ^{19}F chemical shifts of lithium, sodium and potassium salts of *m*- and *p*-fluorophenylcyclopentadienyl anions in acetonitrile, tetrahydrofuran (THF), and hexamethylphosphoric triamide (HMPA) solutions at different concentrations. Tetramethylethylenediamine (TMEDA) and macrocyclic polyethers (18-crown-6 and dibenzo-18-crown-6) have been used as complexing agents which strongly solvate the alkaline cation.

Salts of *m*- and *p*-fluorophenylcyclopentadienyl anions were obtained by treatment of a mixture of the appropriate 1- and 2-fluorophenyl-substituted cyclopentadienes with n-BuLi, sodium hydride, and the potassium-sodium alloy, $NaK_{2.8}$. We had earlier confirmed the formation of *m*- and *p*-fluorophenylcyclopentadienyl anions by ^1H NMR and by converting them into the respective ferrocene derivatives upon treatment with ferrous chloride [1].



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* Recently, in studies of $TlC_5H_4CH(CH_3)C_6H_5$ by ^{13}C NMR spectroscopy (stereochemical approach) and of $TlC_5H_4C_6H_4F$-*m*(-*p*) by ^{19}F NMR, it has been shown that thallous cyclopentadienyls exist in THF solution predominantly in the form of tight ion pairs [3].

Concentration effect

The effect of concentration on the screening of carbanion protons has been previously studied in detail for a triphenylmethanide ion [8]. It was found that the chemical shift was only slightly dependent on concentration in the range from 0.02 to 0.8 *M*. Concentration effects for planar ions (such as fluorenide, indenide, and cyclopentadienide) were not studied so thoroughly; however, they showed a greater dependence on concentration than the triphenylmethanide ion. Generally, an upfield shift of the proton signal with increasing concentration was observed, greater changes being observed when ions existed as contact ion pairs. It has been proposed that the changes are due to intermolecular ring current effects [8,12].

We have studied the concentration dependence for lithium, sodium, and potassium salts of carbanions FC^- in solvents of different coordinating ability. While for lithium salts in acetonitrile and THF the ^{19}F chemical shift is only slightly dependent on concentration in the range studied (0.1—0.5 *M*), the sodium and potassium salts show a noticeable dependence on concentration. In all the cases studied the ^{19}F resonance shifts downfield with increasing concentration, whereas the signals of α- and β-protons in the substituted cyclopentadienyl ring shift upfield. This is clearly seen from the data given in Table 1: as the concentration of $K^+[FC\text{-}p]^-$ in acetonitrile increases from 0.05 to 1.00 *M*, the cyclopentadienyl proton screening increases by 0.16 ppm, whereas the ^{19}F nucleus resonance shifts downfield by 1.3 ppm.

The observed divergence in the screening of ^1H and ^{19}F nuclei with changing carbanion salt concentration can be reasonably accounted for by the formation of sandwich-like aggregates in solution. The formation of these aggregates was suggested previously for fluorenide ions [13—16].

In triple ions or higher sandwich-like aggregates cyclopentadienyl protons will be shielded due to the intermolecular ring current effect (there is experimental evidence for the presence of the ring current effect in a cyclopentadienide ion [17]), and the increasing concentration will lead to an increase in the upfield shift of cyclopentadienyl protons due to increased aggregation. At the same time, the increased aggregation will lead to an enhanced perturbing effect of alkali metal cations on the charge in the carbanions due to increased

TABLE 1

THE EFFECT OF $K^+[C_5H_4C_6H_4F\text{-}p]^-$ CONCENTRATION IN ACETONITRILE ON THE SCREENING OF THE CYCLOPENTADIENYL PROTONS AND OF THE FLUORINE NUCLEUS

Concentration (*M*)	Chemical shifts (ppm)		
	H_α [a]	H_β [a]	^{19}F [b]
1.00	5.80	5.47	12.1
0.50	5.87	5.51	12.4
0.40	5.87	5.51	12.4
0.20	5.91	5.56	13.0
0.10	5.94	5.60	13.2
0.05	5.96	5.63	13.4

[a] Downfield with respect to TMS. [b] Upfield with respect to fluorobenzene.

polarization. In other words, aggregation should lead to a decrease in ionic character of the cation—cyclopentadienide bond. This is actually the case: the ^{19}F resonance shifts downfield with increasing carbanion concentration.

Thus, the data obtained support the idea that planar aromatic carbanions can form sandwich-like aggregates in solution.

Cation effect

It is well known that there is a relationship between the size of the cation and the position of the equilibrium between tight and solvent-separated ion pairs. A smaller cation favours the formation of solvent-separated pairs and vice versa. on the other hand, within ion pairs the smaller the cation size the greater the charge perturbation it causes in the carbanion.

As can be seen from the data of Table 2, for solutions of $M^+[FC\text{-}p]^-$ salts in THF the fluorine atom screening increases with increasing size of the cation, $Li < Na \leq K$. Both in THF and in acetonitrile solutions the chemical shifts of sodium and potassium derivatives are very similar and are noticeably dependent on carbanion concentration. The latter indicates that in the solvents mentioned above the $M^+, FC^- \rightleftharpoons M^+\|FC^-$ equilibrium provides a considerable proportion of tight ion pairs in solution. So, the *para*-fluorine chemical shifts of carbanions in acetonitrile and THF (10.4—13.4 ppm) are considerably smaller than the value of 17.9 ppm found for a solvent-separated ion pair in HMPA (see below).

The observed effect of the cation ($K \geq Na > Li$) on ^{19}F chemical shifts can be explained by Fajan's rule [18]. Namely, the smaller the cation the greater the charge perturbation it causes in the adjacent anion, i.e. the smaller the ionic character of the cation—anion bond.

Solvent and complexing agent effects

As follows from the data given in Table 2, the formation of solvent-separated ion pairs is dependent on the coordinating ability of the solvent. Thus, for Li^+-

TABLE 2

THE EFFECT OF CATION, SOLVENT AND CONCENTRATION ON ^{19}F CHEMICAL SHIFTS (ppm) OF *m*- AND *p*-FLUOROPHENYLCYCLOPENTADIENYL ANIONS WITH RESPECT TO C_6H_5F

Cation	Concentration (*M*)	CH_3CN		THF		HMPA	
		(*m*-F)	(*p*-F)	(*m*-F)	(*p*-F)	(*m*-F)	(*p*-F)
Li	0.5	2.0	10.4	2.6	11.2	4.0	17.8
	0.25	2.0	10.4	2.5	11.1	4.1	17.9
	0.12	2.0	10.6	2.5	11.1	4.2	17.9
Na	1.0		12.4				
	0.4	2.5	12.5		12.2		17.7
	0.2	2.7	12.8		12.3		17.8
	0.1	2.9	13.0		12.3		17.8
	0.05		13.4				17.9
K	1.0		12.1				
	0.5		12.4				
	0.4		12.4	3.0	12.2		
	0.2		13.0	3.0	12.5		
	0.1		13.2	3.2	12.7		
	0.05		13.4		12.9		

$[FC\text{-}p]^-$ the ^{19}F chemical shift in acetonitrile, THF, and HMPA is 10.6, 11.1, and 17.9 ppm, respectively. In the same series the Gutmann donor number [19] of the indicated solvents increases: 14.1, 20.1, and 38.8. The dramatic upfield shift of the ^{19}F signal in HMPA, when the chemical shifts of lithium and sodium derivatives in this solvent coincide, indicates that in HMPA the studied salts exist completely (or predominantly) in the form of solvent-separated ion pairs. This conclusion is in agreement with the data of Cox and Terry [11], who have noted a considerable change in the ^7Li chemical shift (by approximately 8 ppm), depending on the nature of the solvent and carbanion, whereas in HMPA solution the ^7Li chemical shift variation for organolithium compounds was less than 0.6 ppm.

On comparing the data obtained for solutions both of sodium and potassium derivatives in acetonitrile and THF, it can be noted that the ^{19}F chemical shifts in acetonitrile are somewhat greater than those in THF. This variance with the donor number of acetonitrile and THF must be due to the formation of aggregates in solution of the sodium and potassium salts. Steric effects of a solvent may also be a determining factor.

Solvents consisting of polydentate compounds, such as dimethyl ethers of ethyleneglycols or ethylenediamine, are known to be effective solvating agents for alkali cations [20]. Macrocyclic polyethers, or crown-ethers, developed by Pedersen [21,22], are especially effective in the complexation of spherical cations. We have investigated the effect of TMEDA and of two polyethers, 18-crown-6 and dibenzo-18-crown-6, on the ionic character of the metal—cyclopentadienyl anion bond (Table 3). The investigation of Li^+, FC^- in acetonitrile and THF with addition of TMEDA in different proportions has shown that the ^{19}F screening of carbanion decreases when diamine is added. Evidently, adding TMEDA to solutions of Li^+, FC^- leads to a small shift of the equilibrium towards the formation of a contact ion pair:

$$[LiTMEDA]^+, FC^- + n\,S \rightleftharpoons [LiTMEDA]^+ \| FC^-$$

The result is somewhat unexpected, since it is well known that TMEDA strongly chelates the lithium cation, leading to a sharp increase in the reactivity of n-butyllithium in metallation reactions. The increased reactivity of the complex $[n\text{-Bu}]^-[LiTMEDA]^+$ is explained by the increased ionic nature of the lithium—carbon bond due to a decreased aggregation of alkyllithium reagents [23].

In our case, the decreased ionic character of the lithium—cyclopentadienyl anion bond can be explained in the following way. It is well known that the preferred coordination number of lithium is 4. In the ion $[LiTMEDA]^+$ substituents at the nitrogen atoms will hamper aggregation. It should be noted that there are no steric hindrances to complexation of lithium with two TMEDA molecules. Thus, in the complex $[(CH_3)Ni(C_2H_4)_2]^-[Li(TMEDA)_2]^+$ two diamine ligands tetrahedrally surround the lithium atom [24]. (However, in the case of lithium alkyls a strong basic carbanion will displace the "odd" molecule of a complexing agent or solvent from lithium coordination sphere.) In aromatic carbanions, the coordination number of the ion in $[LiTMEDA]^+$ is saturated due to favourably located π-orbitals of the carbanion. The possibility of the formation of a multicentre covalent bond by a bissolvated lithium atom

TABLE 3

THE EFFECT OF COMPLEXING AGENTS ON ^{19}F CHEMICAL SHIFTS OF *m*- AND *p*-FLUOROPHENYLCYCLOPENTADIENYL ANIONS [a]

Cation	Solvent and complexing agent in percentage ratio to carbanion salt	^{19}F chemical shift (ppm)	
		m-F	*p*-F
Li	CH_3CN	2.0	10.4
	CH_3CN + 100% TMEDA	1.7	9.9
	THF	2.6	11.2
	THF + 50% TMEDA	2.2	10.4
	THF + 100% TMEDA	2.1	10.3
	THF + 200% TMEDA	1.9	10.1
Na	THF		12.3
	THF + 25% 18-crown-6		13.6
	THF + 50% 18-crown-6		14.9
	THF + 100% 18-crown-6		16.2
	THF + 200% 18-crown-6		16.3
K	THF	3.2	12.7
	THF + 25% 18-crown-6	3.5	13.6
	THF + 50% 18-crown-6	3.5	14.2
	THF + 100% 18-crown-6	4.1	15.1
	THF + 200% 18-crown-6	4.1	15.1
	THF + 100% dibenzo-18-crown-6		14.6

[a] Measured for 0.1 *M* solutions of carbanion salts.

with aromatic carbanions follows from the X-ray data on indenyllithium tetramethylethylenediamine, [C$_9$H$_7$]$^-$[LiTMEDA]$^+$ [25], and lithium salts of other aromatic carbanions [26]. In a simple valence bond approach the lithium atom in [LiTMEDA]$^+$ is considered as sp^2 hybridized with two nitrogen atoms occupying two coordination sites and a delocalized carbanion in the third position (the N—Li—N plane is perpendicular to the carbanion plane). In this situation, the unhybridized *p*-orbital is parallel to the aromatic ring plane and forms a bond with the carbanion π-cloud [26]. Thus, the lithium ion chelation stabilizes this hybridization, thereby leading to decreased ionic nature of the lithium—cyclopentadienyl ion bond, as a result of electron density transfer to the empty *p*-orbital of lithium via the multi-centre covalent bond in Li$^+$, FC$^-$. An alternative explanation is that during complexation of Li$^+$ with TMEDA the cation size increases and the equilibrium shifts to the formation of a tight ion pair.

When 18-crown-6 is added to sodium and potassium salts of FC$^-$ anions in THF solution, an upfield shift of the ^{19}F signal occurs. As seen from the data given in Table 3, adding a complexing agent to Na$^+$, FC$^-$ or K$^+$, FC$^-$ leads to the formation of 1 : 1 complexes. Judging by the ^{19}F chemical shifts, in THF solution the sodium cation is more strongly solvated with the crown-ether than the potassium cation. The selectivity of crown-ether complexing is known to be influenced not only by the size of the cation and the cavity of the cyclic polyether, but also by the solvent nature. In methanol and in water a different complexing order has been observed, K > Na, which is explained by the competition between the solvent and the complexing agent [20].

Dibenzo-18-crown-6 turned out to be a less effective complexing agent than 18-crown-6: the ^{19}F chemical shifts for $K^+[FC\text{-}p]^-$ in the presence of these polyethers are 14.6 and 15.1 ppm, respectively. The electron-withdrawing effect of the benzene rings in dibenzo-18-crown-6 must lead to a reduction in the basicity of polyether oxygen atoms.

As can be seen from the comparison between ^{19}F chemical shifts of carbanion salts in HMPA and in THF with added crown-ether (E), complexing with the latter does not lead to such a drastic effect as that of HMPA. Possibly, this is partly due to the formation of an external complex of a polyether with a contact ion pair, E, M^+, FC^-, in equilibrium with a crown-separated ion pair M^+, E, FC^- [16].

The electronic effect of a cyclopentadienyl anion as a substituent

The values of ^{19}F chemical shifts obtained for lithium salts of *p*- and *m*-fluorophenylcyclopentadienyl anions in HMPA (4.2 and 17.9 ppm, respectively) have been used to calculate inductive and resonance constants by the Taft equations [27]:

$$\delta^F_M = -7.1\sigma_I + 0.6$$

$$\delta^F_p = -7.1\sigma_I - 29.5\sigma^0_R + 0.6$$

Results are given in Table 4, where, for comparison, the appropriate data are given characterizing the electronic effect of some groups as substituents in a benzene ring [27]. As can be seen, the $C_5H_4^-$ substituent, by its resonance effect, is similar to such substituents as methoxy, amino, and *N,N*-dimethylamino groups. At the same time, by its inductive effect it considerably exceeds the organic groups studied to date. According to the calculations carried out by Del Bene and Jaffé [28], in the cyclopentadienide ion the total electron density on each carbon atom is 4.15 electrons, and this decrease of charge on the carbons is accompanied by a corresponding increase in the electron density on the hydrogen atoms (1.05 electrons on each). As a result, one quater of the anionic charge is delocalized from the ring onto the hydrogens by the σ mechanism.

Our data on the electronic effect of the $C_5H_4^-$ substituent in a benzene ring constitute experimental evidence for the conclusion made on the basis of cal-

TABLE 4

COMPARISON OF ^{19}F CHEMICAL SHIFTS AND TAFT EQUATION PARAMETERS FOR C_5H_4-SUBSTITUENT AND OTHER GROUPS

Substituent	$\delta(m\text{-}F)$	$\delta(p\text{-}F)$	σ_I	σ^0_R
C_5H_4	4.20	17.90	−0.51	−0.50
C_6H_5	0.00	2.75	0.08	−0.09
CH_3	1.15	5.45	−0.08	−0.15
NH_2	0.50	14.30	0.01	−0.48
$N(CH_3)_2$	−0.08	15.78	0.10	−0.54
OCH_3	−1.18	11.45	0.25	−0.34
O	1.77	19.40	−0.16	−0.60

culations [28] that in a cyclopentadienide anion part of the negative charge is delocalized onto the σ framework.

Experimental

Syntheses of carbanion salts and subsequent operations with them were carried out under argon. The solvents were dried by standard methods and distilled under inert gas immediately before use. Lithium, sodium, and potassium salts of *m*- and *p*-fluorophenylcyclopentadienyl anions were obtained by adding n-butyllithium, sodium hydride suspension in paraffin, and potassium-sodium alloy, $NaK_{2.8}$, to the respective dienes. Lithium and potassium salts of carbanions were prepared in ether, precipitated by adding n-hexane to the solution, collected on a glass filter, washed with an n-hexane/ether mixture (1/3) and dried in vacuo. Samples to be investigated by NMR spectroscopy were prepared by dissolving carbanion salts in the appropriate solvent. Sodium salts of carbanions were not isolated dry, but prepared in the solvent in which they were intended to be studied. Salts of *m*- and *p*-fluorophenylcyclopentadienyl anions are white (or cream-coloured) crystalline substances stable on storage under inert gas.

18-crown-6 was synthesized by the known method [29], and dibenzo-18-crown-6 was kindly provided by A.L. Kurts of the M.V. Lomonosov Moscow State University.

^{19}F and ^{1}H NMR spectra were obtained on a Perkin-Elmer R-20 spectrometer with operating frequencies of 56.4 and 60.0 MHz, respectively.

m- and p-Fluorophenylcyclopentadienes

A solution of 10 g (0.12 mol) cyclopentenol [30] in 50 ml of ether was added over 1.5 h at —5°C to an stirred solution of the Grignard reagent obtained from 4.9 (0.2 g atom) of *m*- or *p*-fluorobromobenzene in 100 ml of ether. The stirring was continued for another hour and a half, after which the contents of the flask was carefully poured into a mixture of ice and 300 ml of concentrated aqueous ammonia saturated with ammonium chloride. The organic layer was separated, the aqueous one was extracted with ether. The oily residue obtained after evaporation of the solvent from the combined ether solutions was vacuum distilled under inert gas. To remove the water forming during thermal dehydration of cyclopentenols, the distillation was repeated. Fluorophenylcyclopentadienes are easily dimerized, and the reverse reaction occurs at high temperature. The bath temperature was slowly raised from 120 up to 210°C. The distillation temperature increases for an *m*-isomer from 52 up to 110°C (0.1 mmHg), and for a *p*-isomer from 66 to 160°C (0.1 mmHg), yield 10—14 g (50—70%). According to ^{1}H and ^{13}C NMR spectra *m*- and *p*-fluorophenylcyclopentadienes are obtained as a mixture of 1- and 2-isomers. *m*-Fluorophenylcyclopentadiene is a viscous substance at room temperature; the *p*-isomer is a solid.

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