EFFECT OF NATURE OF THE NUCLEOPHILE ON THE MECHANISM OF NUCLEOPHILIC AROMATIC SUBSTITUTION REACTIONS INVOLVING FLUORENYL AND TRIMETHYLSTANNYL ANIONS

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We have previously studied the kinetics of nucleophilic substitution reactions of a series of perfluoroaromatic compounds with alkali metal salts of transition metal carbonyl anions [1, 2]. It was found that tight (contact) ion pairs of the carbonyl anions were more reactive than either solvent-separated ion pairs of free ions. In order to draw any conclusions concerning the similarity or difference in the kinetic principles of these types of reactions for carbon- and metal-containing nucleophiles it is necessary to carry out a comparative analysis of the kinetics of nucleophilic aromatic substitution reactions of analogous substrates with alkali metal salts of CH-acids.

The CH-acid salts selected for study were the K derivatives of 9-carbomethoxyfluorene (9-MeOCOF1) and 9-cyanofluorene (9-NCF1); the aromatic substrates were pentafluoropyridine and p-nitrofluorobenzene.

 $R^{-}K^{+} + ArF \rightarrow ArR + KF$ (I), (II)  $A_{\mathbf{r}} = N \xrightarrow{F}_{\mathbf{F}} F, \qquad R = 9-MeOCOFI$ (Ia) R = 9-NCF1(Ib)  $A_{\mathbf{r}} = p-O_{2}NC_{6}H_{4},$  R = 9-MeOCOF1(II).

The kinetic measurements were made at room temperature under an atmosphere of carefully purified Ar in the anion concentration range  $2.3 \cdot 10^{-3}$  to  $1.7 \cdot 10^{-2}$  M and at a substrate concentration range of  $7.0 \cdot 10^{-3}$  to  $2.3 \cdot 10^{-1}$  M in THF. The course of the reactions was monitored by potentiometric determination of the concentration of fluoride ion formed, and also spectrophotometrically. The agreement in the results measured by the two different methods was satisfactory. Graphs of the kinetic curves were linear up to ca. 60-70% degree of conversion based on the anions. All of the final reaction products were isolated preparatively in yields of 84-87% and were characterized by elemental analysis and IR and PMR spectroscopy.

The kinetic results are summarized in Table 1. In all cases the rates of nucleophilic substitution increased when the reactions were carried out in the presence of solvating additives (18-crown-6 ether or HMPA) (cf. experiments 1 and 3; 2 and 4; 8 and 9, 10; 12 and 13, 14), while the addition of NaBPh<sub>4</sub> (in order to suppress dissociation of the anion salts in solution) led to rate retardation (cf. experiments 2 and 6; 8 and 11; 12 and 15). 9-MeOCOF1<sup>-</sup> was found to be the more reactive anion, which is consistent with the acidity data for the corresponding CH-acids: 9-MeCO<sub>2</sub>FlH pK<sub>a</sub> = ca. 10, 9-NCF1H pK<sub>a</sub> = ca. 8 [3, 4]. Pentafluoro-pyridine was found to be more active substrate, as might be expected, since the reactivity of  $p-O_2NC_6H_4F$  is similar to that of  $C_6F_6$  [5, 6], while  $C_5F_5N$  is significantly more reactive than  $C_6F_6$  with respect to aromatic nucleophilic substitution reactions [1].

As the concentration of carbon salt in solution was reduced the reaction rates were found to increase slightly (experiments 1 and 2), apparently due to increased dissociation of the salts with dilution.

The observed results indicate that in these reactions the reactivity of solvent-separated ion pairs and free anions is greater than that of tight (contact) ion pairs. This is, of

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Experiment	C103 an	C <sub>sub</sub> 10 <sup>2</sup>	Additivo \$	
Laportmone	moles		Addicive	10 <sup>2</sup> , M * sec
		$9-MeOCOF1 + C_5F_5$	N	
1 **	3,28	20,0		1,40
2	5,05 6,50	7,34		1,42
	4,96 16 70	0,93		1,33
	31,30	22,80	1	1,10
3**	2,86 2.35	9,66 8,85	18-C-6,2 18-C-62	9,40 9,52
4	4,38	0,825	18- C-6,1	8,80
5	4,78	3,75	18-C-6,2 HMPA, 20	9,20
	3,46	2,90	HMPA, 20	9,50
6	3,72 4,09	2,10	NaBPh <sub>4</sub> , 10 NaBPh <sub>4</sub>	0,99 1,01
		$9-NCF1 + C_5F_5N$		
7 **	1,64	3,03		1,10
8	3,83 5.67	5,73 4.19		1,07
	7,20	2,13	10 - 01	0,94
9	6,00 3,35	5,05 2,84	18-C-6,1 18-C-6,1	6,70
		$9-NCF1 + C_5F_5N$		
10	4,10	3,24	HMPA, 20	6,80
11	6,05 6,60	4,14 5.14	MMPA, 20 NaBPh	0.57
	4,40	8,05	HMPA, 20	0,56
	9	-MeOCOF1 + p-FC <sub>6</sub> H	NO <sub>2</sub>	
12	4,90	3,48		0,089
13	0,80 3,20	5,24 1,65	18- <b>C-</b> 6,2	0,470
	4,05	2,10	18- 6-6,2	0,465
14	3,10 5,70	2,20 4, <b>2</b> 6	HMPA, 20 HMPA, 20	0,480
15	4,77	3,13	NaBPh <sub>4</sub>	0,049
1	0,24	3,31	NaBPh <sub>4</sub>	0,049

TABLE 1. Rate Constants for the Reactions of K Salts of Carbanions with Fluoroaromatic Substrates (20°C, THF)

\*Number of equivalents of additive per mole of anion. \*\*Spectrophotometric data.

course, the most widely observed type of reactivity pattern, which is seen, for example, in  $S_N2$ -type reactions [7, 8]. With respect to the  $S_NAr$  reaction, as far as we know only one study has appeared, in which it was shown that free cyanodimethylacetamide anion reacts 18-78 times faster than its ion pair with nitrochlorobenzenes [9].

From the point of view of the observed difference in the reactivity patterns of transition metal carbonyl anions and carbanions it would be interesting to compare the kinetic data for  $S_NAr$ -type reactions involving a trialkylstannyl anion  $R_3Sn^-$ , since these reactions would also result in the formation of compounds with C-metal bonds. The reaction chosen for study was that of the trimethylstannyl anion  $Me_3Sn^-$  with pentafluoropyridine

$$Me_3Sn^- + C_5F_5N \rightarrow 4-Me_3SnC_5F_4N + F^-$$

Due to the extremely fast rate of this reaction the kinetic measurements were made at -52 °C in the anion concentration range  $1.7 \cdot 10^{-3}$  to  $4.6 \cdot 10^{-3}$  M, and at a substrate concentration between  $8.7 \cdot 10^{-3}$  and  $1.22 \cdot 10^{-2}$  M in THF; a potentiometric method was used.

The kinetic results for this reaction are summarized in Table 2; they reveal that in this case an increase in the degree of cation solvation due to addition of HMPA (cf. experiments 1 and 3) or because of replacement of the K<sup>+</sup> counterion by Li<sup>+</sup> (cf. experiments 1 and 2) retards the nucleophilic substitution reaction:  $k_2$  decreases 8-10-fold (the data concerning the ionic state of Me<sub>3</sub>SnM salts, where M = Li, K, Cs, in ether solvents was obtained by <sup>1</sup>H and <sup>7</sup>Li NMR spectroscopy [10, 11]). In contrast, addition of a Li borate salt such as Ph<sub>4</sub>BLi

to the solution, which suppresses dissociation of  $LiSnMe_3$ , led to rate acceleration (cf. experiments 2 and 4); under these conditions the reaction rate was the same as that observed in the reaction with the K salt (experiments 1 and 4). It follows, therefore, that the Me<sub>3</sub>Sn<sup>-</sup> anion tight ion pairs are more reactive than either solvent-separated ion pairs or the free ion, just as was observed in the case of the reactions of transition metal carbonyl anions. The similarity in the kinetic principles of these two reactions suggests that their mechanisms are similar as well.

We have thus shown that, depending on the nature of the anion used, the degree of ionic association can affect the reaction rate in different ways. In the case of carbanions the general reactivity pattern or profile is followed: free ions are more active than ion pairs, while in the case of metal carbonyl anions and the trimethylstannyl anion, ion pairs are more reactive than the free anions. These results are consistent with the well-accepted two-stage mechanism for aromatic nucleophilic substitution reactions, namely, that a change in the nature of the anion leads to a change in the rate-limiting step for the reaction:



Thus, if the steady state principle is operating, such that  $k_{obs} = k_1 k_2 / (k_{-1} + k_2)$ , then we would expect that in the case of carbanions, where the C-Nu bond is stronger than the C-X bond (where Nu is the carbanion),  $k_2 >> k_{-1}$  and  $k_{obs} = k_1$ . Under these conditions the rate-determining step is formation of the anionic  $\sigma$ -complex, and free ions and solvent-separated ion pairs are therefore more reactive (than tight ion pairs).

In the case, however, where the C-Nu bond which is formed is not as strong as the C-X bond (such as is the case where Nu is a transition metal carbonyl anion or  $Me_3Sn$ ), the contribution of the reverse reaction becomes significant, i.e.,  $k_{-1} >> k_2$  and  $k_{obs} = K_{eq}k_2$ . Under these conditions the rate-limiting step is cleavage of the C-X bond ( $k_2$ ). If we assume, furthermore, that the counterion facilitates departure of the halide ion, then it is reasonable to expect to see increased reactivity of tight ion pairs of carbonyl anions relative to both solvent-separated ion pairs and free anions relative to both solvent-separated ion pairs and free anions: although  $K_{eq}$  is reduced, the increase in  $k_2$  is overriding.

In studying the effect of the leaving group one generally compares the relative reaction rates of nucleophiles with a series of different ArX substrates. We have carried out a similar type of study, using as an example the reaction of 9-MeOCOF1 anion and  $CpFe(CO)_2^-$  with one substrate, namely, pentachlorofluorobenzene, which contains both F and C1.



Nu equals carbanion (a) and transition metal carbonyl anion (b).

It was found that treatment of this substrate with the carbanion resulted primarily (75-100%) in substitution of the fluoride ion in the para-position relative to the chlorine atom. The extremely high degree of regioselectivity observed in this process is a persuasive argument in favor of a two-step, as opposed to a synchronous, reaction mechanism. The  $\sigma$ -complex formed with chlorine in the para-position is apparently the most stable. A synchronous

М	Can*103	C <sub>sub</sub> ·10 <sup>3</sup>		
	moles		Additive*	k-10-, liter/mole- sec
К	1.70 2.80	<b>12.2</b> 0 9.60		91,0
Li	2.20	10,60 9,80		12.3
. K	4,20 3,10	10,70 8,70	HMPA 20 Same	9,9
Li	$4.60 \\ 2,90$	8,20 9,60	Ph <sub>4</sub> BLi, 10 Same	999,0 97,5

TABLE 2. Rate Constants for the Reaction of  $Me_3SnM$  with  $C_5F_5N$  (-52°C, THF)

\*Number of equivalents per mole of anion.

mechanism would not explain the observed regioselectivity. The amount of chlorine substitution product in this case depended on the concentration of reagents and was ca. 25% at  $C_{an} = 9 \cdot 10^{-2}$  M and 0% at  $C_{an} = 5 \cdot 10^{-3}$  M, i.e., the process selectivity increased substantially with dilution of the reaction mixture.

In the case of the iron carbonyl anion as nucleophile, in contrast, selective substitution of the chloride ion in the substrate occurred, to give pure  $C_6H_5Fe(CO)_2Cp$  as the product; no traces of fluoride ion substitution products were observed in the reaction mixture, based on <sup>19</sup>F NMR spectral analysis.

These results are consistent with the data reported in [12], namely, that in reactions with carbanions fluoride ion is the preferred leaving group; this is most widely observed result in activated nucleophilic aromatic substitution [13, 14], and is a consequence of the fact that the rate-determining step is formation of the  $\sigma$ -complex ( $k_{obs} = k_1$ ) [13-16]. The reverse reactivity order is observed in the case of reaction with CpFe(CO)<sub>2</sub><sup>-</sup>: Cl >> F. A similar result was obtained in the case of the manganese carbonyl anion Mn(CO)<sub>5</sub><sup>-</sup>, which did not react with C<sub>6</sub>F<sub>6</sub>, but displaced bromine in C<sub>6</sub>F<sub>5</sub>Br [17]. Within the framework of the S<sub>N</sub>Ar mechanism for aromatic substitution this order of halogen reactivity is indicative of a change in the rate-determining step of this reaction, which in this case involves cleavage of the halide ion. Chloride ion is apparently more easily displaced (than fluoride).

Both of the results obtained in this study, namely, "inverse" order of halogen reactivity and increased reactivity of tight ion pairs in the case of metal carbonyl anions and  $Me_3SnM$ , could also be interpreted, however, in terms of a synchronous  $S_N2$ -type mechanism, involving assistance by the counterion in displacement of the halide ion.



It is not possible at the present time to draw a rigid distinction between these two possible mechanisms.

## EXPERIMENTAL

PMR spectra were recorded on a Tesla BS-467 spectrometer versus TMS as internal standard; electronic spectra were measured on a Hitachi-124 spectrophotometer using solutions in THF in 0.5-cm and 0.1-cm cuvettes. IR spectra were obtained on a UR-20 spectrophotometer using suspensions in vaseline oil. <sup>19</sup>F NMR spectra were recorded on a Varian XL-100 spectrometer (versus CFCl<sub>3</sub> as external standard).

THF and HMPA were purified using standard procedures. THF was stored under vacuum over benzophenone ketyl. 9-Cyanofluorene was separated from any impurities by TLC on  $SiO_2$  with a mixture of hexane and benzene (7:2) as eluent, and was then recrystallized twice from hexanebenzene (2:1), mp 150-151°C (cf. [18]). 9-Carbomethoxyfluorene was recrystallized twice from benzene, mp 64°C (cf. [19]). The carbanion starting material salts were generated from the corresponding CH-acids under vacuum ( $10^{-3}$  torr) immediately prior to their use in the reactions. K salts were obtained using either NaK alloy or K-mirror; Me<sub>3</sub>SnLi was prepared by treatment of Me<sub>6</sub>Sn<sub>2</sub> with lithium wire. After filtration of the anion solution the apparatus was charged with rigorously purified Ar, the substrate was added, and the concentration of fluoride ion was determined potentiometrically using a "Radelkis" (Hungary) fluoride selective electrode and an ÉV-74 potentiometer, according to the procedure reported in [1].

Kinetic measurements were also made spectrophotometrically in all-soldered vacuum cuvettes. The necessary amounts of substrate and any additives were added beforehand to the cuvettes in the form of evacuated beads, which were then crushed in turn. The course of the reaction was followed based on the loss in optical density D at a wavelength corresponding to one of the absorption maxima of the anion (9-NCF1<sup>-</sup> 409 nm; 9-MeOCOF1<sup>-</sup> 398.5 nm; 9-MeOCOF1 + 18-C-6 411.5 nm). The rate constants were calculated based on a second order kinetic equation. All of the reaction products were isolated preparatively and were characterized by elemental analysis and IR and PMR spectroscopy.

<u>General Procedure for Product Preparation.</u> A solution of anion, prepared in vacuo from 1 mmole of CH-acid or 0.5 mmole of  $Me_6Sn_2$  and 0.12 ml NaK in 10 ml THF was carefully filtered to remove any traces of alloy. The substrate (1 mmole) was either placed beforehand in a side-arm of the apparatus (in the case of  $p-FC_6H_4NO_2$ ), or was condensed (frozen) under vacuum ( $C_5F_5N$ ). The reaction mixture was stirred for 0.5-1.0 h. The solvent was evaporated and the residue chromatographed on SiO<sub>2</sub> plates with hexane as eluent in the case of  $4-Me_3SnC_5F_4N$ , and benzene as eluent in all the other cases. The product was crystallized twice from hexane and dried under vacuum ( $4-Me_3SnC_5F_4N$  was distilled under vacuum without recrystallization).

It should be noted that when the solutions of carbanion and substrate are layered together the reaction mixtures turn rose-colored ( $\lambda_{max}$  ca. 535 nm); the intensity and stability of this color change is directly proportional to the concentrations of components in solution. However, the color change does not affect either the overall rate of the reaction process or the linearity of the kinetic curves, which is consistent with the excellent agreement noted between the results obtained independently by spectrophotometric and potentiometric analysis. At the kinetic concentrations of reagents employed herein the optical density D of the solutions at  $\lambda_{535}$  nm was less than 0.1 (i.e., ~5% of the initial D value at the  $\lambda_{\max}$  value of the anion), and remained constant over the course of the reactions. The yields of substitution products were quantitative under these conditions. It is interesting that in the presence of solvating additives no color change developed. An analogous observation has been made in the case of reaction of Me<sub>3</sub>Sn<sup>-</sup> with  $C_5F_5N$ , in which the solution turned violet. This effect may be associated with the presence in solution of a preequilibrium involving formation of a charge transfer complex between the anion and the substrate; this is suggested, in part, by the fact that the color intensity is independent of the solvent. Complete charge separation accompanying the formation of a radical ion pair does not occur, as indicated by EPR spectroscopic data, and this charge transfer equilibrium apparently has no effect on either the rate or mechanism of the nucleophilic substitution process.

<u>9-Methoxycarbonyl-9-(2,3,5,6-tetrafluoropyrid-4-yl)fluorene (Ia)</u>. Yield, 86%, white crystals, mp 157-158°C. PMR spectrum (CD<sub>3</sub>CN,  $\delta$ , ppm): 7.35-8.2 m (8H), 3.8 s (3H). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1612 (C-C fluorene ring system), 1655 (C-C perfluoropyridine ring), 1742 (C=O), 1230 (C-O in CH<sub>3</sub>O). Found: C 64.56; H 3.29; N 3.73; F 20.67%. C<sub>20</sub>H<sub>11</sub>NF<sub>4</sub>O<sub>2</sub>. Calculated: C 64.35; H 2.97; N 3.75; F 20.36%.

 $\begin{array}{l} \underline{9\text{-}Cyano\text{-}9\text{-}(2,3,5,6\text{-}tetrafluoropyrid\text{-}4\text{-}y1)\text{fluorene (Ib).}}_{10} \quad \text{Yield, 87\%, white crystals,}\\ \text{mp 211°C. PMR spectrum (acetone-d_6, \delta, ppm): 7.5\text{-}8.4 m (8H).} \quad \text{IR spectrum } (\nu, \text{ cm}^{-1})\text{: 1657}\\ (C-C) \quad \text{perfluoropyridine ring, 2243 (C=N).} \quad \text{Found: C 66.76; H 2.45; N 8.09; F 22.41\%.}\\ C_{19}H_8N_2F_4. \quad \text{Calculated: C 67.06; H 2.37; N 8.23; F 22.33\%.} \end{array}$ 

 $\frac{9-\text{Methoxycarbonyl-9-(4-nitrophenyl)fluorene (II). Yield, 84%, white crystals, mp 162°C.} \text{PMR spectrum (acetone-d_6, $\delta$, ppm): 7.15-8.3 m (12H), 3.8 s (3H). IR spectrum ($\nu$, cm^{-1}$): 1343, 1519 (NO_2), 1592 (C-C fluorene ring), 1620 (C-C pefluoropyridine ring)* 1735 (C=O). Found: C 73.04; H 4.45; N 3.99%. C_{21}H_{15}O_4N. Calculated: C 73.03; H 4.38; N 4.06%.$ 

\*As in Russian original - Editor.

<u>Reaction of  $C_6F_5Cl$  with  $CpFe(CO)_2K$ .</u> The K-metal carbonyl salt (0.216 g, 1 mmole) and substrate (0.203 g, 1 mmole) were mixed in 10 ml THF under vacuum (10<sup>-3</sup> torr); the substrate had been placed beforehand in an evacuated side-arm with a heating or vibrating baffle. The solution turned dark red upon mixing and a small amount of inorganic precipitate was deposited. Control chromatograms (Silufol UV-254) after 10 and 30 min of mixing were completely identical and indicated the presence of a yellow product in the reaction mixture, with an  $R_f$  value equal to that of  $C_6F_5Fe(CO)_2Cp$ ; a small amount of the iron carbonyl dimer was also formed. After solvent evaporation the residue was chromatographed on a SiO<sub>2</sub> column with benzenehexane (1:1) as eluent. Yield 0.033 g of dimer [CpFe(CO)<sub>2</sub>]<sub>2</sub> (22 mole %) and 0.230 g of a yellow crystalline material, which was identified as pure  $C_6F_5Fe(CO)_2Cp$  (mp 143°C, <sup>19</sup>F NMR spectrum superimposable with an authentic sample [1], yield 78 mole %).

<u>Reaction of  $C_6F_5Cl$  with Potassium Carbomethoxyfluorenyl (MeOCOF1<sup>-</sup>K<sup>+</sup>).</u> a) Reagent concentration  $9 \cdot 10^{-2}$  M. After solutions of 0.236 g (0.09 mole) 9-MeOCOF1<sup>-</sup>K<sup>+</sup> and 0.180 g (0.09 mole)  $C_6F_5Cl$  in 10 ml THF were mixed under vacuum ( $10^{-3}$  torr), a gradual red coloration developed. A control chromatogram (Silufol UV-254) after 1 h revealed the absence in solution of the starting materials and the presence of one spot for product (or a mixture of products); the color disappeared upon chromatography. The solvent was evaporated and the residue was dissolved in benzene and passed through a layer of SiO<sub>2</sub> (3 cm). The resulting white crystalline product (0.354 g) exhibited a <sup>19</sup>F NMR spectrum with two signals, corresponding to two different substitution products ( $C_6D_6$ ,  $\delta$ , ppm): p-ClC<sub>6</sub>F<sub>4</sub>FlOCOMe-9 (AA'BB'): 106.5 (2) and 138.6 (2), yield, as determined based on the integrated intensity ratio ca. 75%, and  $C_6F_5FlOCOMe-9$ : 108.9(2), 142.4(1), 146.0(2), yield, based on relative integrated intensity, ca. 25%.

b) Reagent concentration ~5·10<sup>-3</sup> M. Upon mixing of 0.026 g (1·10<sup>-4</sup> mole) MeOCOFI<sup>-</sup>K<sup>+</sup> and 1d 0.020 g (1·10<sup>-4</sup> mole) substrate in 20 ml THF under vacuum (10<sup>-3</sup> torr) the solution turned red; the color disappeared after several minutes. The reaction was terminated after 30 min. After workup of the reaction mixture as described in the preceding experiment a white substance was isolated, which based on its <sup>19</sup>F NMR spectrum appeared to be pure fluorine substitution product, p-ClC<sub>6</sub>F<sub>4</sub>FlOCOMe-9 (AA'BB') (C<sub>6</sub>D<sub>6</sub>,  $\delta$ , ppm): 106.5(2), 138.6(2).

## CONCLUSIONS

1. The kinetics of reactions of alkali metal salts of 9-carbomethoxy- and 9-cyanofluorene with para-nitrofluorobenzene and of  $Me_3SnM$  with pentafluoropyridine have been studied.

2. In the case of carbanions the free anions are more reactive, while in the case of  $Me_3SnM$  the corresponding tight (contact) ion pairs are more reactive.

3. The effect of the leaving group (on reactivity) was investigated using the reactions of pentafluorochlorobenzene with the K salts of 9-carbomethoxyfluorene and cyclopentadienylirondicarbonyl anions as examples.

4. The reaction mechanism has been shown to depend on the nature of the nucleophile.

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