Quantitative evaluation of specific and nonspecific interactions in radical exchange between phenyllithium and bromobenzene

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The results of kinetic studies on the exchange of radicals between PhLi and PhBr in variuos binary pentane—ether mixtures in the presence of alkaline metal halides were discussed. The nucleophilicity of the ethers and metal halides, which is a quantitative measure of their influence on the exchange reaction, was determined. The specific and nonspecific components of coordination were identified and quantitatively evaluated for some parameters of the exchange reaction.

Key words: radical exchange, complex formation, solvation, nucleophilicity, specific and nonspecific interaction, free energy of coordination.

Radical exchange reactions are in common preparative use[1] and are typical of the chemistry of organometallic compounds (OMC). Proceeding easily under mild conditions, these reactions are sensitive to the action of disturbing factors,[2] including the ability of OMC to coordinate with various complex formating additives (CFA).[3—6] The properties of relatively stable OMC · CFA complexes differ from those of pure OMC to such an extent that one can say they are new reagents with unique parameters. In this case we deal with the of the specific effect of CFA on OMC reactivity.

The formation of OMC · CFA changes the polarity of the M—C bond[7] and, hence, the nucleophilicity of the potential OMC carbanions. As a result, additional molecular interactions between the complex reagents and the solvent arise without formation of covalent bonds.[8] This interaction, which is called nonspecific, exerts some effect on the reaction rate through the influence on the transition state.

The present work is aimed at the identification and quantitative evaluation of the influence of specific and nonspecific effects of CFA on OMC reactivity. For this purpose the radical exchange reaction between phenyllithium and bromobenzene

$$\mathrm{PhLi \cdot CFA} + {}^{14}\mathrm{PhBr} \rightleftharpoons {}^{14}\mathrm{PhBr \cdot CFA} + \mathrm{PhBr} \qquad (1)$$

in various *n*-pentane—ether (*S*) binary solvents (BS), where *S* is *tert*-butylmethyl ether (**1**), phenetole (**2**), anisole (**3**), dibutyl (**4**), dipropyl (**5**), diethyl (**6**) ether, and tetrahydrofuran (**7**), as well as in various pentane—ether **6** BS were studied in the presence of alkaline metal and tetramethyl ammonium halides (MX). *S* and MX are combined and designated as CFA.

Experimental

PhLi was prepared by a procedure similar to that described previously.[9] *S* were dehydrated and purified according to the reported procedures.[10] BS were characterized by dielectric constants, ε, calculated using the published procedure.[7] Anhydrous MX were obtained by calcination in a quartz tube in a flow of the appropriate HX. In all cases the molar ratio MX/PhLi = 1.5. The exchange rate was monitored by the increase in radioactivity of ^{14}PhCOOH isolated by excess CO_2. The experimental procedure was described previously.[11]

Results and Discussion

Reaction (1) proceeds with no complications as a bimolecular process in the studied BS both in the presence of MX, and in their absence. The second order rate constant (*k*) is invariant up to significant degrees of exchange. It increases by three orders of magnitude (Table 1) on going from compound **1** to **7** (Ref. 12). The MX also differ essentially in their effect on reaction (1) due to their structure[5] and the nature[11,13,14] of PhLi · MX complex formation.

Regardless of the structure and the nature of PhLi · CFA formated, the final result of the coordination is a change in the polarity of the Li—C bond. Hence, it is reasonable to suggest that a parameter should exist which quantitatively characterizes the abillity of the CFA to change the nucleophilicity of PhLi (*n*).

Reaction (1) may be presented as a series of reactions with constant electrophilic reagent PhBr and variable nucleophilic reagent PhLi · CFA, where the variable structural fragment is CFA. This approach allows one to consider a great number of the obtained results

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 272—275, February, 1995.

Table 1. Kinetic parameters of reaction (1) in various pentane—ether BS in the presence of MX at 298 K

Ethers	MX	$k \cdot 10^5$ /L mol^{-1} s^{-1}	n	b
1	—	0.7	−1.621	−2.38
2	—	1.9	−1.190	−1.09
3	—	3.0	−0.990	−0.51
4	—	9.3	−0.496	0.70
5	—	20.4	−0.157	1.93
	—	29.3	0.000	2.35
	LiCl	25.7	−0.057	2.18
	LiBr	16.0	−0.263	1.58
	LiI	13.4	−0.340	1.36
	NaCl	35.8	0.087	2.60
	NaBr	40.8	0.144	2.77
	NaI	51.0	0.240	3.05
	KCl	39.0	0.133	2.74
	KBr	50.9	0.240	3.05
6	KI	54.7	0.266	3.13
	RbCl	75.5	0.411	3.55
	RbBr	62.8	0.331	3.32
	RbI	50.1	0.233	3.03
	CsCl	95.8	0.513	3.85
	CsBr	81.3	0.443	3.64
	CsI	60.3	0.314	3.27
	Me_4NCl	431.0	1.168	5.76
	Me_4NBr	162.5	0.744	4.52
	Me_4NI	35.1	0.079	2.58
7	—	1603.0	1.738	6.39

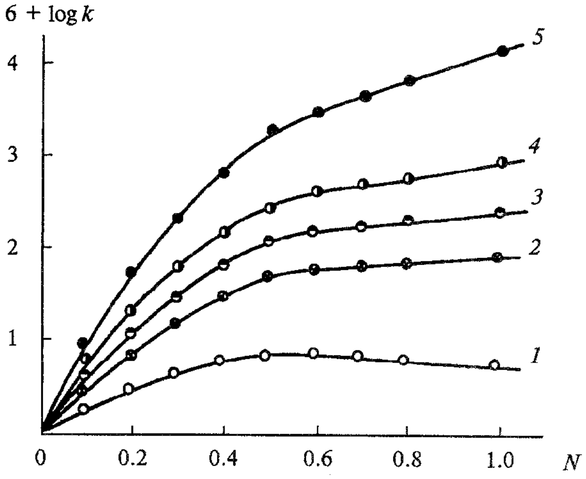

Fig. 1. The dependence of the exchange rate on the mol fraction of ethers in the mixture with pentane at 298 K: **1** (*1*), **4** (*2*), **6** (*3*), **6**+RbCl (*4*), **7** (*5*).

from a single viewpoint[15] and to quantitatively evaluate the value of n for various MX[6,16] and S[12] (see Table 1).

It is known that in pure pentane no exchange occurs because of the PhLi association.[17] The addition of compounds **1**—**7** to pentane gives impetus to reaction (1), and log k increases as the mol fraction N of **1**—**7** in BS increases.[18] However, the character of the change in log k is different for the BS studied (Fig. 1). In the region $N < 0.5$, log k increases with increasing N for all BS. At $N > 0.5$ the monotonic increase in log k continues for BS **4**—**7** (Fig. 1, curves *2*, *4*, *5*), while for BS **1**—**3** it decreases monotonically, with an extremum at $N = 0.5$ (curve *1*).

The character of the dependence obtained (see Fig. 1) points out that there are two types of solvation.[19] The increase in log k at $N < 0.5$ is caused by the influence of specific solvation, whereas at $N > 0.5$ log k is governed by nonspecific solvation. The decrease in log k at $N > 0.5$ for **1**—**3** indicates a drop in their electrodonating ability. The effect of p,π-conjugation in compounds **2** and **3** and the steric hindrances that arise when etherates PhLi · S with **1**—**3** form followed by interaction with PhBr[18] can explain this fact.

The dependence log $k = f(N)$ for BS **6** has the same character in the presence of MX as in their absence (see Fig. 1, curves *3*, *4*). For all CFA, log k changes in parallel with n (see Table 1, Fig. 1). Therefore, when carring out reaction (1) in BS **6** in the presence of MX, the combined coordination effect involves the effects of solvation and complex formation that are manifested over the whole range of N values.

The analysis of the results obtained suggests that the coordination effect be divided into specific (s) and nonspecific (n) components, which to be quantitatively evaluated. According to Fig. 1, the value of k for reaction (1) may be presented as follows:

$$\log k = \log k_s + \log k_n. \quad (2)$$

As a result of the standardization conditions[6,12,16]

$$\log k = \log k_0 + n, \quad (3)$$

$$\log k_s = \log k_{0s} + n_s, \quad (4)$$

$$\log k_n = \log k_{0n} + n_n, \quad (5)$$

k_0 is related to a standard reaction, where **6** is taken as the standard CFA.

The monotonic change in log k when $N > 0.5$ (see Fig. 1) is the result of electrostatic interaction between the reagents and the BS. It reflects the influence of the polarity of the BS, $Y = (\varepsilon - 1)/(2\varepsilon + 1)$,[20] on reaction (1) and is approximated as a polygonal curve in $\log k = f(Y)$ coordinates (Fig. 2). In pure pentane (Y_p) the exchange does not occur. When the polarity $Y = Y_e$, which corresponds to the inflection of the complicated curves at $N = 0.5$ (see Fig. 1), a singular point is observed. The increase in log k in the range Y_p—Y_e is caused by the fact that specific component of the coordination is faster, n for CFA is greater. Maximum log k_s value is achieved at $Y = Y_e$, when PhLi · CFA formation is over. Further changes in log k up to the value Y

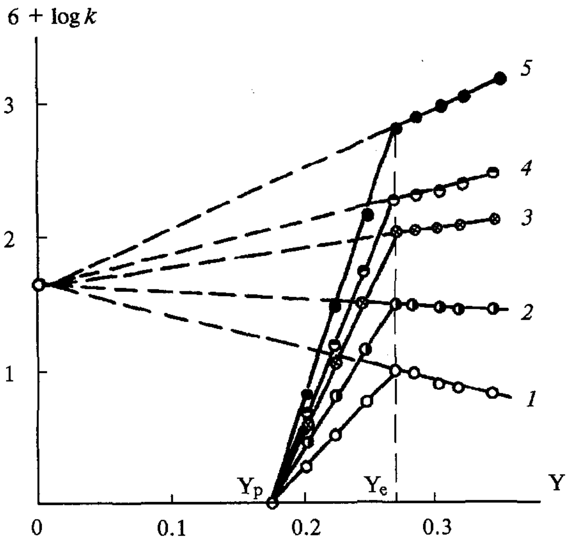

Fig. 2. The dependence of the exchange rate on the polarity of pentane—ether binary solvent at 298 K: **1** (*1*), **3** (*2*), **6**+LiI (*3*), **6** (*4*), **6**+Me$_4$NBr (*5*).

corresponding to pure **1**—**7** are caused by the nonspecific component of coordination.

Based on Fig. 2, the values k, k_s, and k_n may be calculated from the equations:

$$\log k = \log k_{00} + bY, \quad (6)$$

$$\log k_s = \log k_{00} + bY_e, \quad (7)$$

$$\log k_n = b(Y - Y_e), \quad (8)$$

where log k_{00} is the rate constant of hypothetical reaction (1) in the gase phase ($\varepsilon = 1$, $Y = 0$), $b = 1/(2.3RT)\Sigma\mu^2/r^3$ is the slope of the line (see Fig. 2) in the range Y_e — Y. Equation (6) in the terms of the accepted designations represents the Kirkwood equation[20] for dipole-dipolar interaction. It is fulfilled for all systems studied, differing only in the values of b (see Table 1), which also change in parallel with n.[18,22] For all systems the average value of $\log k_{00}$ is equal to 4.3378. This indicates that in the gas phase the hypothetical reaction (1) would occur at the same rate for all CFA studied. This is possible only in the absence of solvation and complex formation.

Combination of (3—5) with (6—8), respectively, results in the following expressions for n, n_s, and n_n:

$$n = (b - b_0)Y, \quad (9)$$

$$n_s = (b - b_0)Y_e, \quad (10)$$

$$n_n = (b - b_0)(Y - Y_e). \quad (11)$$

The values of n, n_s and n_n calculated by (9—11) show that Eq. (3—5) are fulfilled for all CFA studied:

$$\log k = n - 3.5331, \ r = 0.996,$$

$$\log k_s = n_s - 3.6958, \ r = 0.999,$$

$$\log k_n = n_n - 0.1636, \ r = 0.996.$$

Equations (9—11) allow one to estimate the contributions of the specific and nonspecific interactions to the total coordination effect. Dividing (10) and (11) by (9), one can obtain the expressions:

$$n_s = nY_e/Y, \quad (12)$$

$$n_n = n(Y - Y_e)/Y. \quad (13)$$

The influence of the coordination on the rate of reaction (1) is based on the change in the free energy of activation in going from the standard system to any CFA, which is denoted as the free energy of coordination ($\Delta\Delta G_c$). This postulate can be expressed *via* a rigorous mathematical formulation,[23] which is fulfilled both for combined k, n, and $\Delta\Delta G_c$ and for the specific and nonspecific components:

$$\log(k/k_0) = n = -\Delta\Delta G_c/2.3RT, \quad (14)$$

$$\log(k_s/k_{0s}) = n_s = -\Delta\Delta G_s/2.3RT, \quad (15)$$

$$\log(k_n/k_{0n}) = n_n = -\Delta\Delta G_n/2.3RT. \quad (16)$$

Equations (14—16) provide a thermodynamic basis for n, n_s and n_n and their energy equivalents $\Delta\Delta G_c$, $\Delta\Delta G_s$, and $\Delta\Delta G_n$, respectively. The linearity of the dependence $\Delta\Delta G_c = f(n)$[12] indicates the equivalence of these parameters in the quantitative evaluation of the influence of coordination on reaction (1). After insertion of the expressions for n and n_s from (14) and (15) into (12) and, respectively, n and n_n from (14) and (16) into (13), one can obtain the linear dependences (Fig. 3):

$$\Delta\Delta G_s = \Delta\Delta G_c Y_e/Y, \ r = 0.999,$$

$$\Delta\Delta G_n = \Delta\Delta G_c(Y - Y_e)/Y, \ r = 0.999.$$

For **1**—**7** $Y_e/Y = 0.796$, $(Y - Y_e)/Y = 0.204$.

The analysis of the data made it possible to identify and quantitatively evaluate the two components of the coordination and their influence on the reactivity of OMC. The donor-acceptor interaction is undoubtedly the most important in the change in OMC reactivity. However, even in the case of typical electron-deficient OMC (including lithium organyls), the nonspecific interaction is pronounced. About 80 % of the total coordination effect corresponds to the specific interaction and 20 % corresponds to the nonspecific interaction. The ratio of the two coordination components probably changes for different reactions and reagents.

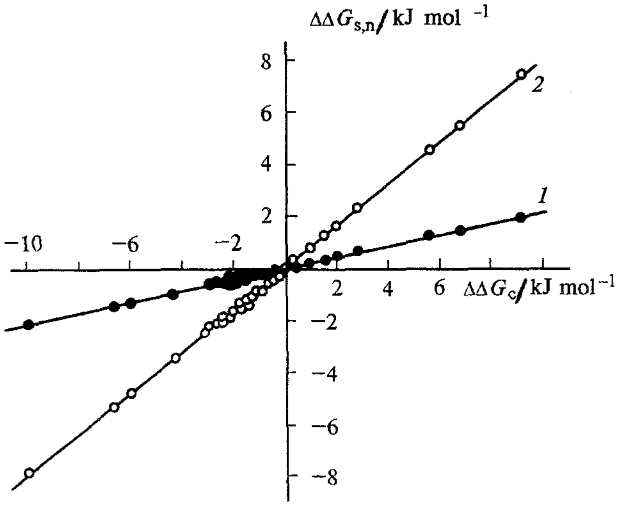

Fig. 3. The dependence of the specific (*2*) and nonspecific (*1*) components of the free energy of coordination on its total value.

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Received December 21, 1993;
in revised form March 15, 1994