# Effect of the structure of complex-forming additives on radical exchange between phenyllithium and bromobenzene

**A. P. Batalov**

*Scientific-Research Institute of Chemistry, N. I. Lobachevsky Nizhnii Novgorod State University,
23 prosp. Gagarina, 603600 Nizhnii Novgorod, Russian Federation*

Analysis of kinetic data of the effect of alkali-metal and tetramethylammonium halides on radical exchange between phenyllithium and bromobenzene allows estimation of their induction and steric constants. The additive character of the effect on kinetic and activation parameters of the exchange reaction was established. An equation that describes well the relation between the reaction parameters and the structure constants of metal halides and ethers was derived.

**Key words:** phenyllithium, bromobenzene, exchange reaction, complex-forming agents.

The reactivity of organometallic compounds is mainly determined by their complexing ability.[1] Earlier it was shown that alkali-metal halides MX[2–5] and tetramethylammonium halides $Me_4NX$[6] affect radical exchange according to the reaction:

$$C_6H_5Li + {}^{14}C_6H_5Br \overset{k}{\rightleftharpoons} {}^{14}C_6H_5Li + C_6H_5Br. \qquad (1)$$

This effect is based on the formation of PhLi · LiX (**1**) complexes (see Ref. 7), which differ in their nucleophilicity *n* (see Refs. 8, 9) from PhLi. The parameter *n*, which determines the overall effect of MX on the rate constant *k* of reaction (1), says nothing about the role of other possible effects. Nonetheless, *k* depends on the structure of complexes **1** (see Refs. 4, 7) and the methods of their formation.[6,7]

The discussion of the effect of MX on the course of reaction (1) in the present work is aimed at differentiation and quantitative evaluation of their structural features.

## Experimental

PhLi was synthesized by the known procedure.[1] The concentration of PhLi and PhBr was 0.1 *M*. Dry MX were obtained by calcination in a quartz tube in a flow of the corresponding HX. In all of the cases, the mole ratio MX/PhLi was 1.5 In the present work $^{14}C_6H_5Br$ was used. The exchange rate was monitored by following the increase in radioactivity of $^{14}$PhCOOH isolated after treatment of a reaction mixture with excess $CO_2$. The experimental procedure has been described earlier.[4]

## Results and Discussion

The experimental results (see Table 1) show that MX differ significantly in the character of their effect on the kinetic and activation parameters of reaction (1). Thus, LiX inhibit the exchange, while other MX catalyze it. They also are divided into two groups according to the effect of the halogen on *k*.

The effect of Li, Na, and K halides on *k* decreases in the following series: MI > MBr > MCl. It can be hypothesized that complex **1** is formed because p-electrons of a halogen atom use vacant or partially filled 2p-orbitals of Li in organolithium compounds (OLC).[10,11] Therefore, the catalytic effect must increase with the decrease in the halogen ionization potential, which is the case for NaX and KX. In the case of LiX, together with the donor-acceptor bond a second coordination bond is formed with the transfer of charge from the potential phenyl anion in PhLi to the Li atom in LiX, resulting in the closed structure of complex **1**.[3,7] This fact agrees with the results of electronographic studies of the $(LiX)_2$ structure (see Ref. 12) and the existence of fast exchange of Li atoms between LiX and OLC[13] with the retention of configuration of the latter. Thus, the cyclic structure of PhLi · LiX not only lowers its *n*, but also creates steric hindrance to reaction (1).

The catalytic effect of Rb, Cs, and $Me_4N$ halides decreases in the series: MCl > MBr > MI, and the rate constant *k* of reaction (1) is inversely proportional to the halide-ion $X^-$ radius *r* (Fig. 1). This indicates that they include ionic structures. In this case, the ability of MX with the same charge of $X^-$ to form complexes **1**

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 246—249, February, 1994.

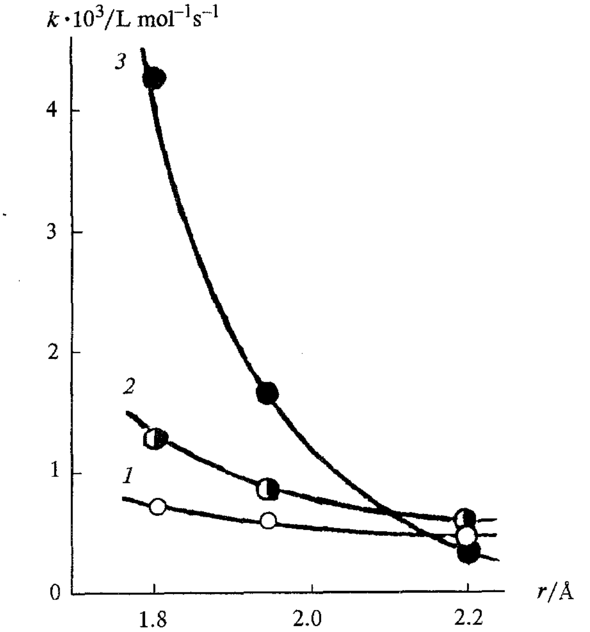

**Fig 1.** Dependence of rate constant of the radical exchange between PhLi and PhBr in diethyl ether in the presence of MX at 298 K on halogen ion radius. M = Rb (*1*); Cs (*2*); $Me_4N$ (*3*).

must increase with the decrease in $r$ (see Fig. 1). For $R_4N^+X^-$, $k$ is independent of the size of $R$ (see Ref. 6). The inverse proportionality coefficient increases in the series RbX < CsX ≪ $Me_4NX$. This suggests that RbX and CsX in ethereal solution exist as an equilibrium mixture of ionic and covalent structures.

Complex formation finally results in a change in Li—C bond polarity irrespective of its structure and the mode of its formation. Also, there is no complete separation of charge either in the complex or in the transition state[14] of reaction (1), and the Li—C bond retains its covalent nature. Consequently, the transmission of electron influence during complexing and the course of reaction (1) proceeds by an inductive mechanism. This altogether makes it necessary to evaluate the induction $\sigma^*$ and steric $E_s^0$ constants for MX.

Earlier the effect of $MX^{8,9}$ and ethers[9,15] on the reaction (1) rate constant $k$ was expressed by the parameter $n$. A linear dependence $\log k = f(n)$ was established for both kinds of complexing agents. Analysis of experimental data shows that this dependence is also observed quite well ($r$ = 0.998) when all of the data obtained are processed together (Fig. 2). This fact testifies in favor of a single complexation mechanism, allowing one to consider ethers and MX as Lewis bases with respect to PhLi as a Lewis acid.

**Table 1.** Kinetic and activation parameters of the radical exchange reaction between PhLi and PhBr in ethers in the presence of MX at 298 K

| Solvent | MX | $k\cdot10^5$/L·(mol·s)$^{-1}$ | $n$ | $\Delta G^{\neq}$/kJ·mol$^{-1}$ | $\Delta\Delta G_K$/kJ·mol$^{-1}$ | $-\sigma^*$ | $-E_s^0$ |
|---|---|---|---|---|---|---|---|
| *t*-BME | — | 0.1 | −1.621 | 102.3 | −9.3 | 0.278 | 3.738 |
| PT | — | 1.9 | −1.190 | 99.8 | −6.8 | −0.040 | 2.130 |
| AS | — | 3.0 | −0.990 | 98.6 | −5.6 | −0.110 | 1.700 |
| DBE | — | 9.3 | −0.496 | 95.8 | −2.8 | 0.250 | 2.794 |
| DPE | — | 20.4 | −0.157 | 93.9 | −0.9 | 0.241 | 2.507 |
| DO | — | 334.0 | 1.058 | 89.0 | 4.0 | 0.150 | 1.200 |
| THF | — | 1603.0 | 1.738 | 83.1 | 9.9 | 0.194 | 0.915 |
| DEE | — | 29.3 | 0.000 | 93.0 | 0.0 | 0.237 | 2.375 |
| The same | LiCl | 25.7 | −0.057 | 93.3 | −0.3 | 0.239 | 2.423 |
| » | LiBr | 16.0 | −0.263 | 94.5 | −1.5 | 0.244 | 2.596 |
| » | LiI | 13.4 | −0.340 | 95.0 | −2.0 | 0.246 | 2.660 |
| » | NaCl | 35.8 | 0.087 | 92.5 | 0.5 | 0.235 | 2.302 |
| » | NaBr | 40.8 | 0.144 | 92.2 | 0.8 | 0.234 | 2.254 |
| » | NaI | 51.0 | 0.240 | 91.6 | 1.4 | 0.231 | 2.173 |
| » | KCl | 39.0 | 0.133 | 92.2 | 0.8 | 0.234 | 2.263 |
| » | KBr | 50.9 | 0.240 | 91.6 | 1.4 | 0.231 | 2.173 |
| » | KI | 54.7 | 0.266 | 91.5 | 1.5 | 0.230 | 2.149 |
| » | RbCl | 75.5 | 0.411 | 90.7 | 2.3 | 0.227 | 2.030 |
| » | RbBr | 62.8 | 0.331 | 91.1 | 1.9 | 0.229 | 2.097 |
| » | RbI | 50.1 | 0.233 | 91.7 | 1.3 | 0.231 | 2.180 |
| » | CsCl | 95.8 | 0.513 | 90.1 | 2.9 | 0.224 | 1.943 |
| » | CsBr | 81.3 | 0.443 | 90.5 | 2.5 | 0.226 | 2.003 |
| » | CsI | 60.3 | 0.314 | 91.2 | 1.8 | 0.230 | 2.112 |
| » | $Me_4NCl$ | 431.0 | 1.168 | 86.3 | 6.7 | 0.208 | 1.394 |
| » | $Me_4NBr$ | 162.5 | 0.744 | 88.8 | 4.2 | 0.219 | 1.750 |
| » | $Me_4NI$ | 35.1 | 0.079 | 92.5 | 0.5 | 0.235 | 2.309 |

*Note.* *t*-BME, *tert*-butyl methyl ether; PT, phenetole; AS, anisole; DBE, dibutyl ether; DPE, dipropyl ether; DO, dioxane; THF, tetrahydrofuran; DEE, diethyl ether.

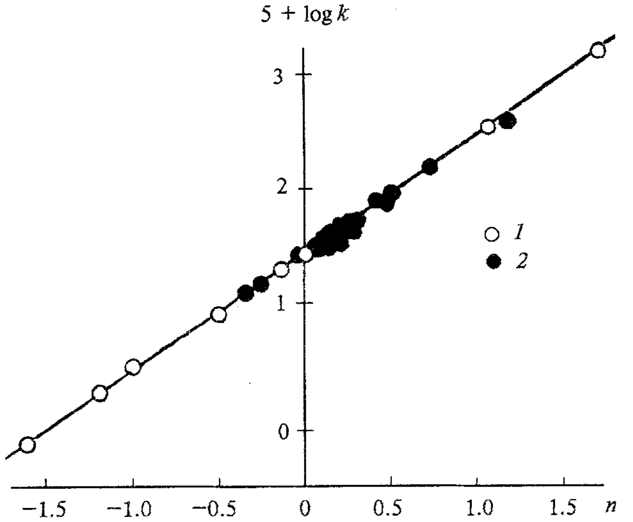

**Fig. 2.** Dependence of the logarithm of rate constant of the radical exchange between PhLi and PhBr at 298 K on the nucleophilicity of ethers (*1*) and MX (*2*).

It follows from Table 1 and Fig. 2 that the interval of variation of *k* and *n* for ethers is sufficiently large. The values of *k* and *n* for MX fall inside this interval. The effect of the structure of ethers on the parameters of reaction (1) has been established before.[15] Analysis of experimental data reveals that for some of the ethers monoparametric dependences are observed, which can be described by the equations

$$\log k = \left[\begin{array}{ll} \rightarrow 5.953 + 39.974\sigma^* & (2) \\ \rightarrow -0.707 + 1.19E_s^0, & (3) \end{array}\right.$$

$r = 0.999$.

A single mechanism of interaction of ethers and MX with PhLi, together with the existence of a linear dependence for all the experimental data (see Fig. 2) makes it possible to calculate the values of $\sigma^*$ and $E_s^0$ for MX using Eqs. (2) and (3) respectively (see Table 1).

The donor-acceptor nature of the bond in complexes **1** implies that the donor ability of MX must increase as $-\sigma^*$ increases, thus providing the increase in *k*. However, it follows from the table that the LiX with the highest $-\sigma^*$ constants have the lowest observed *k* values for all of the MX. This is associated with the steric effects in PhLi · LiX caused by their cyclic structure. For NaX and KX, the $\sigma^*$ values are virtually unchanged. The decrease in $E_s^0$ caused by the open structure of complexes **1** results in an increase in *k* on going from chlorides to iodides.

The values of $\sigma^*$ for RbX, CsX, and $Me_4NX$ have a tendency to increase on going from chlorides to iodides, which had to be accompanied by an increase in *k*. Nonetheless, the presence in their structure of the ionic component, whose donor ability depends on the radius of $X^-$ (see Fig. 1), stresses the role of steric effects in the formation of complex **1** and in its reactivity. It is

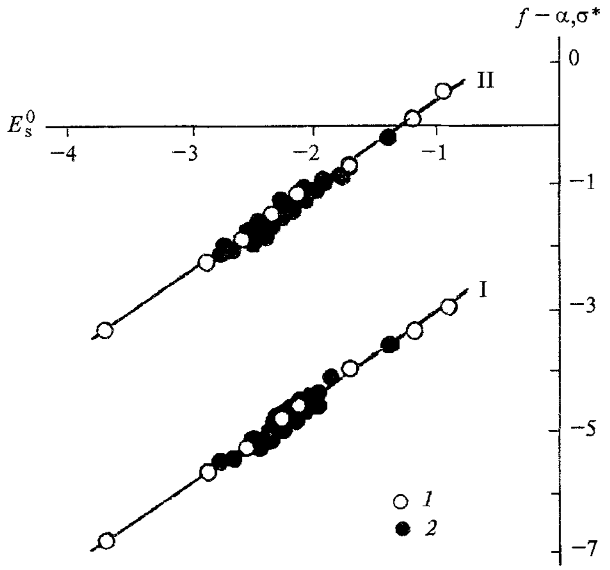

**Fig. 3.** Dependence of log $k-a_1\sigma^*$ (I) and $n-a_1\sigma^*$ (II) for the radical exchange reaction between PhLi and PhBr at 298 K on $E_s^0$-constants of ethers (*1*) and MX (*2*).

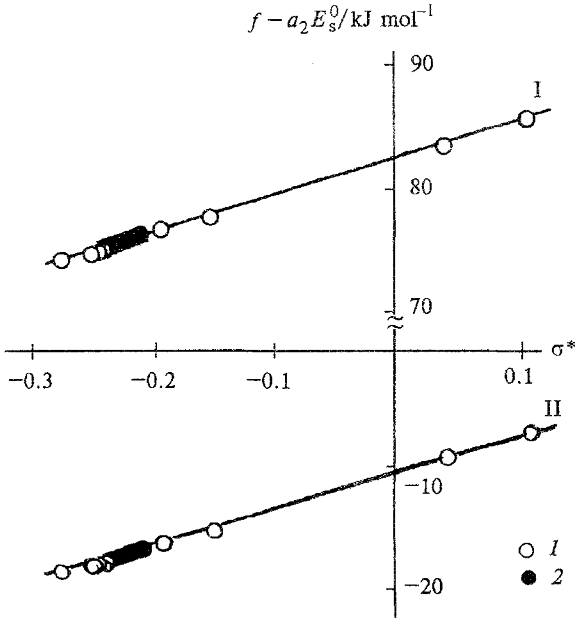

**Fig. 4.** Dependence of $\Delta G^{\neq}-a_2E_s^0$ (I) and $\Delta\Delta G_K-a_2E_s^0$ (II) for the radical exchange reaction between PhLi and PhBr at 298 K on $\sigma^*$-constants of ethers (*1*) and MX (*2*).

especially typical of $Me_4N^+X^-$ , which exist in ethereal solutions as ion pairs. The slight increase in $\sigma^*$ on going from chlorides to iodides is accompanied by a 1.7-fold increase of $E_s{}^0$, thus resulting in the decrease in $k$ by more than an order of magnitude.

Multiple correlation analysis[16] of the complete set of data (see Table 1) showed that the cooperative effect of steric and induction factors on the course of reaction (1) is described by equation

$$f = a_0 + a_1\sigma^* + a_2E_s{}^0 \qquad (4)$$

with the parameters shown below

| $f$ | $a_0$ | $s_{a_0}$ | $a_1$ | $s_{a_1}$ | $a_2$ | $s_{a_2}$ | $R$ |
|---|---|---|---|---|---|---|---|
| log $k$ | −1.637 | 0.01 | −5.481 | 0.026 | 1.346 | 0.006 | 0.999 |
| $n$ | 1.896 | 0.01 | −5.484 | 0.025 | 1.346 | 0.006 | 0.999 |
| $\Delta G^{\neq}$ /kJ · mol$^{-1}$ | 82.8 | 0.44 | 31.21 | 1.098 | −7.413 | 0.267 | 0.994 |
| $\Delta\Delta G_K$ /kJ · mol$^{-1}$ | −10.17 | 0.44 | 31.21 | 1.098 | −7.413 | 0.267 | 0.994 |

The coefficients $a_i$ practically do not differ from the respective values for ethers,[15] once more confirming the assumption that type (1) reactions in the presence of the ethers investigated and MX salts constitute a single reaction series.

The separate influence of the induction and steric effects of ethers and MX is clearly shown in Figs. 3 and 4. A monoparametric dependence of $f$—$a_1\sigma^*$ and $f$—$a_2E_s{}^0$ on $\sigma^*$ is observed. The pairwise correlation parameters have the same values as in the case of multiple correlation, thus confirming the additive nature of the effect of steric and induction factors on the course of reaction (1).

Thus the set of ethers and alkaline metal and tetramethylammonium halides made it possible to identify and quantitatively characterize the effect of their structural factors on the reactivity of phenyllithium in its radical exchange reaction with bromobenzene.

## References

1. T. V. Talalaeva and K. A. Kocheshkov, *Metody elementoorganicheskoi khimii* [*Methods of Organometallic Chemistry*], V. 1, Nauka, Moscow, 1971, 568 (in Russian).
2. H. J. S. Winkler and H. J. Winkler, *J. Am. Chem. Soc.*, 1966, **88**, 969.
3. A. P. Batalov, *Zh. Obshch. Khim.*, 1971, **41**, 158 [*J. Gen. Chem. USSR*, 1971, **41** (Engl. Transl.)].
4. A. P. Batalov and G. A. Rostokin, *Zh. Obshch. Khim.*, 1971, **41**, 1735 [*J. Gen. Chem. USSR*, 1971, **41** (Engl. Transl.)].
5. A. P. Batalov and I. G. Maleneva, *Zh. Obshch. Khim.*, 1984, **54**, 613 [*J. Gen. Chem. USSR*, 1984, **54** (Engl. Transl.)].
6. A. P. Batalov and G. A. Rostokin, *Zh. Obshch. Khim.*, 1971, **41**, 1738 [*J. Gen. Chem. USSR*, 1971, **41** (Engl. Transl.)].
7. A. P. Batalov and G. A. Rostokin, *Dokl. Akad. Nauk SSSR*, 1971, **198**, 1334 [*Dokl. Chem.*, 1971, **198** (Engl. Transl.)].
8. A. P. Batalov, *Dokl. Akad. Nauk SSSR*, 1986, **291**, 139 [*Dokl. Chem.*, 1986, **291** (Engl. Transl.)].
9. A. P. Batalov, *Metalloorg. Khim.*, 1988, **1**, 419 [*Organometal. Chem.*, 1988, **1** (Engl. Transl.)]
10. S. H. Bauer, T. Ino, and R. F. Ponter, *J. Chem. Phys.*, 1960, **33**, 685.
11. W. K. Klemperer and W. Norris, *J. Chem. Phys.*, 1961, **34**, 1071.
12. P. A. Akishin and N. G. Rambidi, *Vestnik MGU, Ser. Mat., Mekhan., Astr., Fiz., Khim.* [*Moscow State University Courier, Mathematics, Mechanics, Astronomy, Physics, Chemistry Series*], 1958, **6**, 223 (in Russian).
13. R. Waack, M. Doran, and E. B. Baker, *J. Chem. Soc., Chem. Commun.*, 1967, 1291.
14. A. P. Batalov and G. A. Rostokin, *Zh. Obshch. Khim.*, 1973, **43**, 1569 [*J. Gen. Chem. USSR*, 1973, **43** (Engl. Transl.)].
15. A. P. Batalov, *Metalloorg. Khim.*, 1992, **5**, 599 [*Organometal. Chem.*, 1992, **5** (Engl. Transl.)].
16. L. M. Batuner and M. E. Pozin, *Matematicheskiye metody v khimicheskoi tekhnike* [*Mathematical Methods in Chemical Engineering*], GNTI, Leningrad, 1963, 488 (in Russian).

*Received January 21, 1993*