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Structure of Potassium Carbonate Complexes with Phenols and Thiophenols in Aproyic Dipolar Solvents

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Abstract—By means of IR, ^{1}H, ^{13}C, and [39]K NMR spectroscopy the potassium carbonate was demonstrated to form complexes with phenols and thiophenols in aprotic dipolar solvents of the composition $(2ArXH)–K_2CO_3$.

A wide range of nucleophilic substitution reactions is carried out generating *in situ* a charged nucleophile by treatment of proton-donor compounds with a base [1]. The anhydrous potassium carbonate is known to be often applied as efficient base free of nucleophilic properties under conditions of systems liquid phase–solid phase [1–4]. A common procedure of charged nucleophile formation *in situ* involves three successive stages: (1) chemisorption of the nucleophile precursor on the deprotonating agent, (2) proton transfer from the former to the latter resulting in generation of a nucleophile salt adsorbed on the solid surface, and (3) the desorption of the salt into the solution [2]. It should be noted that with substrates capable to be sorbed on the surface of the potassium carbonate the nucleophilic substitution may occur on the phase boarder. Therewith the potassium carbonate surface governs the relative position of the nucleophilic and electrophilic centers of reagents providing an adsorption complex [4]. Thus interaction between proton-donor compounds with the potassium carbonate in a two-phase system results in formation either in solution or on the solid base surface of the corresponding salts which act as reagents in the nucleophilic substitution.

We studied formerly the substitution by phenoxy group of a nitro group in the 3,5-dinitrobenzotrifluoride and of a fluorine atom in the 5-nitro-3-fluorobenzotrifluoride in their reaction with phenols in the presence of K_2CO_3 in DMF [5]. It was established that in the two-phase system the nucleophilic substitution occurred in solution. It was also shown that the rate and selectivity of the nitro group and fluorine substitution were different at the use of the previously performed potassium phenolates or in the system K_2CO_3–ArOH. Therefore it was concluded that in these cases different types of nucleophiles

were operating. It was also demonstrated by IR and ^{19}F NMR spectroscopy that the spectra of phenols solutions prepared in the presence of K_2CO_3 are unlike spectra of authentic potassium phenolates in DMF [5]. Taking into account the results of concurrent reactions for 3-X-5-nitrobenzotrifluorides (X = NO_2, F) a scheme was suggested of diaryl ethers preparation involving a stage of phenol complex formation with potassium carbonate, $ArOH–K_2CO_3$, in DMF solution [5]. A common character of results of the concurrent substitution reactions of nitro group and fluorine in the 3-X-5-nitrobenzotrifluoride (X = NO_2, F) by treating it with phenol and thiophenols in the presence of K_2CO_3 in DMF suggested that the nucleophiles had a similar character [6].

The target of the present study is establishment of the nucleophiles state when they are generated *in situ* in a two-phase system by means of investigation of interaction between proton-donor compounds ArXH (X = O, S) with K_2CO_3 in aprotic dipolar solvent. We selected for the study a set of phenols (4-cresol, 4-cyano-, 5-bromo-3-nitro, 4-nitrophenols **Ia–d**) and thiophenols (2-thionaphthol, 4-nitrothiophenol **Ie, f**) of a wide acidity range (ΔpK_a 13.4) [7], therewith for all compounds **Ia–f** the authentic potassium salts ArX^-K^+ **IIa–f** were prepared (see EXPERIMENTAL).

It was shown for each one among the above mentioned compounds that its interaction in DMF with potassium carbonate at the molar ratio K_2CO_3–ArXH of 1.5 at 70°C within 3 h led to decrease in the weight of the solid phase by about 1/3 (see EXPERIMENTAL). Note that performing the reaction with thiophenols under argon flow diminished the yield of the corresponding diphenyl disulfides thus reducing the effect of oxidation on the reagents ratio (see EXPERIMENTAL) [8].

In solutions **IIIa, c** prepared by keeping the corresponding phenols **Ia, c** and K_2CO_3 in DMF at 70°C followed by filtration we detected potassium cation by means of ^{39}K NMR spectroscopy (Table 2). At increasing symmetry in the potassium surrounding the gradient of the electric field should decrease and consequently the mechanism of the quadrupole relaxation of ^{39}K nuclei should be suppressed [9]. In keeping with this rule the diminishing of the signal half width in the ^{39}K NMR spectra in going from solution of compound **II** to solution **III** for both substances indicates the increasing symmetry at least in the close neighborhood of the potassium cation [9]. Also in going from solution of **II** to solution **III** the potassium signal shifts upfield evidencing its greater shielding. The sum of results obtained suggests that in solutions **IIIa, c** the potassium atom is linked to more than one oxygen, and this is a sign of a coordination compound formation. It should be noted that the signal appearing in the ^{39}K NMR spectrum of the potassium solution in dimethyl ether in the presence of 15-crown-5 located at –9.9 ppm and with a half width of 50 Hz was attributed to potassium cation complex with the crown ether [10]. In going from solution **IIIa** to **IIIc** the gradient of the electric field in the place where the potassium nucleus is located that governs the degree of quadrupole line broadening is increased, and the shielding of the potassium nucleus decreases. Thus at growing acidity of phenol the symmetry of potassium surrounding diminished.

The comparison of ^1H NMR spectra (Table 1) revealed that the chemical shifts of proton signals from the aromatic system in solution **III'a** almost coincide with those in the solution of compound **Ia**, in solutions **III'c, e, f** are intermediate between those of solutions of compounds **Ic, e, f** and of compounds **IIc, e, f**, and in solution of compound **III'd** are close to those in solution of compound **IId** (Table 1). These data indicate the presence of a negative charge on the aromatic system in solutions **III'**, and its value grows with the acidity of the proton-donor reagent. A similar conclusion follows from the comparison of the ^{13}C NMR spectra, for the chemical shifts of the aromatic system of solutions **III'c, d** are close to those of solutions of compounds **IIc, d**, and in solution **III'a** the chemical shifts take an intermediate values between those of solutions of compounds **Ia** and **IIa** (the ^{13}C NMR spectra of solutions **IIIe, f** and of solutions **Ie, f, IIe, f** are complicated due to the presence of the corresponding diphenyl disulfides) (Table 1).

As seen from Table 1 in the ^1H NMR spectra of all the **III'** solutions alongside the protons of the aromatic system appears a proton signal with a chemical shift 3.4 ppm in solutions **III'd–f**, 11.2 ppm in solution **II'a**, and 6.2 ppm in solution **III'c**. In all cases the intensity ratio of all signals shows that to one ArO group corresponds one such proton (Table 1). Note that in the ^1H NMR spectra taken in DMSO-d_6 from solutions (**IIa, d**)* prepared from compounds **IIa, d** and water at the molar ratio 2:1 the chemical shift of the hydroxy group proton is equal to 3.5 ppm (Table 1).

In Table 2 are compiled the IR spectra of solutions **III'a, d** and solutions of compounds **Ia, d** and (**IIa, d**)* in DMSO-d_6. The comparison of vibration frequencies characteristic of the benzene ring, p-substituents, and the C–O bond shows that in every case the state of the ArO group in **III'** solution is unlike that in the solutions of compounds **I** and **II*** in agreement with the results of the study of these solutions by means of ^1H and ^{13}C NMR spectroscopy. The comparison of the IR spectra of solution **III'a** and solution of compound **IIa*** revealed that in the former solution water was present as indicated its characteristic absorption bands at 3450 (br.s) (stretching vibrations), 1663 (m) (bending vibrations), and 928 (w) cm^{-1} (pendulum vibrations) (Table 2) [11]. However a considerable downfield shift of the corresponding signal in the ^1H NMR spectrum in going from the solution of compound **IIa*** to solution **III'a** evidences the coordination bonding of water in the latter, and weak shielding of its protons is due to the influence of the partial positive charge generated on the oxygen as a result of the donor-acceptor interaction (the chemical shift of the hydroxonium ion in the diluted acid solutions is ~15 ppm [12]) (Table 1).

According to the general pattern of K_2CO_3 and proton-donor reagent interaction the presence of water in the solution should be accompanied with carbon dioxide formation. The latter has a characteristic absorption band in the IR spectrum at 2342 cm^{-1} belonging to the asymmetric stretching vibrations (the band of symmetrical stretching vibrations at 1337 cm^{-1} is not observed because of the linear structure of the carbon dioxide). It should be noted that in the IR spectrum of solution **III'a** alongside the absorption bands at 1663 and 928 cm^{-1} appear three additional bands at 3152 (m), 1490 (m0, and 1270 (m) cm^{-1} that are lacking in the spectra of solutions of compounds **Ia** and **IIa*** (Table 2). Assignment of the absorption bands at 3151 and 1490 cm^{-1} to perturbed stretching vibrations (asymmetric and symmetrical) of

Table 1. ^1H, ^{13}C, and ^{39}K NMR spectra of solutions **IIIa, c**,[a] **III'a, c–f**,[b] and solutions of compounds **Ia, c–f, IIa, c–f** and **II*a, c** in aprotic dipolar solvents[c]

Compound {Solution}	^1H NMR spectrum, δ, ppm (J, Hz)[b]	^{13}C NMR spectrum, δ, ppm[b,d]	^{39}K NMR spectrum, δ, ppm ($\Delta\nu_{1/2}$, Hz)[a]
4-$CH_3C_6H_4OH$ (**Ia**)	2.1 s (3H, CH_3), 6.6 d (2H, $H^{2,6}$, J 8.3), 6.8 d (2H, $H^{3,5}$, J 8.3), 10.77 br.s (1H, OH)	20.0 (CH_3), 115.0 (C^4), 127.1 ($C^{2,6}$), 129.6 ($C^{3,5}$), 155.0 (C^i)	–
4-$CH_3C_6H_4O^-K^+$ (**IIa**)	2.5 s (3H, CH_3), 6.7 d (2H, $H^{2,6}$, J 8.3), 7.1 d (2H, $H^{3,5}$, J 8.3)[e]	20.3 (CH_3), 116.7 (C^4), 117.6 ($C^{2,6}$), 129.2 ($C^{3,5}$), 166.4 (C^i)	–10.6 br.s (110)
4-$CH_3C_6H_4O^-K^+$ + H_2O (**IIa**)*	3.5 br.s (1H, H_2O), 6.7 d (2H, $H^{2,6}$, J 8.3), 7.0 d (2H, $H^{3,5}$, J 8.3)	20.2 (CH_3), 115.9 (C^4), 124.1 ($C^{2,6}$), 129.4 ($C^{3,5}$), 158.4 (C^i)	–12.1 br.s (55)
[2-(4-$CH_3C_6H_4OH$)]·K_2CO_3 (**IIIa**),[a] (**III'a**)[b]	2.2 s (3H, CH_3), 6.6 d (2H, $H^{2,6}$, J 8.3), 6.8 d (2H, $H^{3,5}$ J 8.3), 11.2 br.s (1H, OH)		
5-Br-3-$NO_2C_6H_3OH$ (**Ic**)	7.4 m (1H, H^4), 7.5 m (1H, H^6), 7.8 m (1H, H^2), 10.9 br.s (1H, OH)	109.3 (C^2), 116.3 (C^4), 122.0 (C^6), 124.5 (C^5), 149.2 (C^3), 159.0 (C^i)	–
5-Br-3-$NO_2C_6H_3O^-K^+$ (**IIc**)	6.5 m (1H, H^6), 6.6 m (1H, H^2), 6.7 m (1H, H^4)	102.6 (C^6), 111.4 (C^2), 121.6 (C^4), 128.0 (C^5), 150.0 (C^3), 172.7 (C^i)	–10.6 br.s (110)
[2-(5-Br-3-$NO_2C_6H_3OH$)]–K_2CO_3 (**IIIa**),[a] (**III'a**)[b]	6.2 very br.s (1H, OH), 6.7 m (1H, H^6), 6.8 m (2H, $H^{2,4}$)	101.6 (C^6), 111.1 (C^2), 121.4 (C^4), 127.7 (C^5), 150.0 (C^3), 172.5 (C^i)	–11.1 br.s (95)
4-$NO_2C_6H_4OH$ (**Id**)	6.9 d (2H, $H^{2,6}$, J 9.2), 8.1 d (2H, $H^{3,5}$, J 9.2), 10.5 br.s (1H, OH)	115.8 ($C^{2,6}$), 126.2 ($C^{3,5}$), 139.8 (C^4), 164.0 (C^i)	–
4-$NO_2C_6H_4O^-K^+$ (**IId**)	6.0 d (2H, $H^{2,6}$, J 9.5), 7.7 d (2H, $H^{3,5}$, J 9.5)	119.3 ($C^{2,6}$), 127.5 ($C^{3,5}$), 129.2 (C^4), 180.0 (C^i)	–
4-$NO_2C_6H_4O^-K^+$ + H_2O (**IId**)*	3.5 br.s (1H, H_2O), 6.0 d.d (2H, $H^{2,6}$, J 9.5), 7.7 d.d (2H, $H^{3,5}$, J 9.5)		–
[2-(4-$NO_2C_6H_4OH$)]–K_2CO_3 (**IIId'**)[b]	3.4 s (1H, OH), 5.9 d.d (2H, $H^{2,6}$, J 9.8), 7.7 d.d (2H, $H^{3,5}$, J 9.8)[e,g]; 6.0 d (2H, $H^{2,6}$, J 9.5), 7.7 d (2H, $H^{3,5}$, J 9.5), 8.9 s (0.3H, HCO_3H)[h]; 3.5 br.s (1H, H_2O), 6.0 d (2H, $H^{2,6}$, J 9.5), 7.7 d (2H, $H^{3,5}$, J 9.5)[i]	119.3 ($C^{2,6}$), 119.4 (CO_2), 127.5 ($C^{3,5}$), 127.9 (C^4), 180.5 (C^i)[f,g]; 119.3 ($C^{2,6}$), 127.5 ($C^{3,5}$), 173.7 (HCO_3H), 173.9 (H_2CO_3), 180.0 (C^i)[h]; 119.3 ($C^{2,6}$), 127.5 ($C^{3,5}$), 129.2 (C^4), 180.0 (C^i)[i]	–

Table 1 (Contd.)

Compound {Solution}	^{1}H NMR spectrum, δ, ppm (J, Hz)[b]	^{13}C NMR spectrum, δ, ppm[b,d]	^{39}K NMR spectrum, δ, ppm (Δν$_{1/2}$, Hz)[a]
2-C$_{10}$H$_7$SH (Ie)	5.7 br.s (1H, SH), 7.4–7.5 m (3H, H^{3,6,7}), 7.8 m (4H, H^{1,4,5,8})[j]	–	–
2-C$_{10}$H$_7$S$^-$K$^+$ (IIe)	6.9 d.m (1H, H^3), 7.1 t.m (1H, H^6), 7.1–7.3 m (4H, H^{4,5,7,8}), 7.4 m (1H, H^1), 7.7 d.m (1H, H^5)[j]	–	–
[2-(2-C$_{10}$H$_7$SH)]–K$_2$CO$_3$ (III'e)[b]	3.4 s (SH), 7.2 d.m (1H, H^3), 7.3 t.m (1H, H^6), 7.4 t.m (1H, H^7), 7.50–7.6 m (2H, H^{1,8}), 7.6–7.7 d.m (2H, H^{4,5})[j]	–	–
4-NO$_2$C$_6$H$_4$SH (If)	7.6–7.8 m (3H, SH, H^{2,6}, J 8.2), 8.1–8.2 d.m (2H, H^{3,5}, J 8.2)[j]	–	–
4-NO$_2$Cd6H$_4$S$^-$K$^+$ (IIf)	7.1 d (2H, H^{2,6}, J 9.0), 7.5 d (2H, H^{3,5}, J 9.0)[j]	–	–
[2-(4-NO$_2$C$_6$H$_4$SH)]·K$_2$CO$_3$ (III''')[b]	3.4 s (SH), 7.2–7.3 d.m (2H, H^{2,6}, J 8.3), 7.6–7.7 d.m (2H, H^{3,5}, J 8.3)[j]	–	–

a Solutions in DMF.
b Solutions in DMSO-d_6.
c The procedures for solutions preparation and spectra recording see in EXPERIMENTAL.
d Carbon signal of the carbonate group lacks in the spectrum of solution prepared by keeping K$_2$CO$_3$ for 3h at 70°C in anhydrous DMSO-d_6, in aqueous DMSO-d_6 (~10% H$_2$O) the signal appears at 174.1 ppm.
e The spectrum does not change at varying temperature and solution concentration. f In the ^{13}C NMR spectrum of solution prepared by keeping 4-nitrophenol (Id) in the presence of K$_2$CO$_3$ for 3 h at 70°C in moist DMSO-d_6 (~10% H$_2$O) carbon signals are observed appearing in the spectra of solution III'd and solution of compound Id.
g The solvent stored for 3 h.
h 7 days.
i 14 days.
j In the spectra of solutions III'e, f and solutions of compounds Ie, f and IIe, f are present signals of the corresponding disulfides (not given in the table).

Table 2. IR spectra of solutions **IIIb, e**[a], **III'a, d**[b], and solutions of compounds **Ia, b, d** and **II*a, b, d** in aprotic dipolar solvents[c]

Compound {Solution}	IR spectrum, cm^{-1}					
	H_2O	[H_2O–CO_2]	OH	Ar	4-R	C–O
4-CH$_3$C$_6$H$_4$OH[b] (**Ia**)	–	–	3294 br.s, 1349 m	3018 w, 1611 m, 1597 m, 1513 s, 1432 m, 1172 w, 1042 w	2920 w, 2864 w, 1460 m, 1354 m	1225 s
4-CH$_3$C$_6$H$_4$O$^-$K$^+$ + H$_2$O[b] (**IIa**)*	3180 br.s, 1631 m, 1001 w	–	–	3020 w, 1607 m, 1591 m, 1512 m, 1451 m, 1172 w, 1105 w	2920 w, 2867 w, 1476 m, 1378 m	1241 s
[2-(4-CH$_3$C$_6$H$_4$OH)]·K$_2$CO$_3$ (**III'a**)[b]	–	H$_2$O 3450 br.s, 1663 br.m, 928 w; CO$_2$ 3151 m, 1490 s; C–O 1270 s	–	3022 w, 1616 m, 1595 m, 1515 s, 1450 m, 1172 w, 1104 w	2931 w, 2868 w, 1470 m, 1370 m	1260 s
4-NO$_2$C$_6$H$_4$OH[b] (**Id**)	–	–	3356 br.s, 1210 m	3079 w, 1613 m, 1498 s, 1449 m, 1169 m, 1114 m	1593 s, 1289 m	1334 s
4-NO$_2$C$_6$H$_4$O$^-$K$^+$ + H$_2$O[b] (**IId**)*	3376 br.s, 1632 m, 1105 w	–	–	2828 w, 1557 m, 1502 m, 1458 m, 1170 m, 1118 m	1587 s, 1292 m	1310 s
[2-(4-NO$_2$C$_6$H$_4$OH)]·K$_2$CO$_3$ (**III'd**)[b]	–	H$_2$O 1619 m, 759 m; CO$_2$ 2980 cp, 1414 m; C–O 1386 m	–	2904 w, 1546 m, 1523 m, 1465 w, 1163 m, 1111 m	1585 s, 1291 m	1285 s
4-CNC$_6$H$_4$OH[a] (**Ib**)	–	–	3375 br.s, 1287 m	3070 w, 1607 m, 1585 m, 1508 m, 1170 m	2222 m	1254 s
4-CNC$_6$H$_4$O$^-$K$^+$ + H$_2$O[a] (**IIb**)*	3421 br.s, 1645 m, 984 w	–	–	3073 w, 1593 w, 1587 m, 1507 w, 1151 m	2185 m	1255 s
[2-(4-CNC$_6$H$_4$OH)]-K$_2$CO$_3$ (**IIIb**)[a]	–	H$_2$O 3500 br.s, 1690 m, 1012 w, 770 w; CO$_2$ 2948 m, 1440 m, 2914 w, 1453 w; C–O 1337 w, 1294 m; CO$_2$ 2920 m, 2850 w	–	3075 w, 1603 w, 1586 m, 1151 m	2206 m, 2189 w	1268 s, 1255 m
[2-(2-C$_{10}$H$_7$SH)]-K$_2$CO$_3$ (**IIIe**)[d]	–	–	3056 m		–	–

[a] Solutions in DMF. [b] Solutions in DMSO-d_6. [c] The procedures for solutions preparation and spectra recording see in EXPERIMENTAL. [d] For the range 3500–2500 cm^{-1}.

Table 3. Effects of temperature and concentration on chemical shifts of signals, δ, ppm (J, Hz), of protons from hydroxy group and aromatic ring in the ^{1}H NMR spectrum of solution **III'a** in DMSO-d_6

Run no.	25°C[a]			40°C			70°C		
	OH[b]	H^{2,6}	H^{3,5}	OH[b]	H^{2,6}	H^{3,5}	OH[b]	H^{2,6}	H^{3,5}
1^c	11.23 br.s	6.64 d (8.29)	6.84 d (8.29)	11.13 br.s	6.63 d (8.32)	6.84 d (8.32)	10.87 br.s	6.62 d.m (8.35)	6.84 d (8.35)
$2^{d,e}$	10.78 br.s	6.60 d (8.31)	6.84 d (8.31)	10.67 br.s	6.60 d.m (8.35)	6.84 d.m (8.35)	10.41 br.s	6.59 d.d^f (8.39)	6.84 d^f (8.39)

[a] The temperature changes reversibly.

[b] The signal width diminishes with growing temperature and decreasing concentration.

[c] Prepared from the 10% solution of compound **Ia**.

[d] Prepared from 7%-solution of compound **Ia.**

[e] ^{1}H NMR spectra of solution **III'a** from runs nos. (*1* and (*2*) after removing excess solvent coincide at 25°C.

[f] Chemical shifts of proton signals from aromatic ring of solution **III'a** coincide with those in the spectra of solution of compound **Ia**.

the $O=C=O$ structure, and of the band at 1270 cm^{-1} to the stretching vibration of a C–O bond permits identification in the **III'a** solution of a π-complex arising due to donor-acceptor interaction between p-orbital of the water oxygen and antibonding π-orbital of carbon dioxide acting as acceptor. As a result appears a moiety [H$_2$O–CO$_2$]. The partial negative charge on the carbon originating from the donor-acceptor interaction reduces the C=O bond polarity thus increasing the vibration frequencies of the CO$_2$ group [14].

Similarly to the moiety [H$_2$O–CO$_2$] may be assigned additional absorption bands in the IR spectrum of solution **III'd** (lacking in the spectra of solutions of compounds **Id** and **IId***) at 1386 (m), 1414(m), and 2980 (m) cm^{-1}. However in the spectrum of solution **III'd** lacked the absorption band of stretching vibrations in the coordinated water molecule, and this was apparently due to the significant effect of hydrogen bond on the state of the H$_2$O group (the frequency of bending vibration was equal to 1619 cm^{-1}) (Table 2). In this case the positive charge on the oxygen atom of the H$_2$O group and consequently the polarity of the donor-acceptor C–O bond in the moiety [H$_2$O–CO$_2$] would be smaller in solution **III'd** than in **III'a**. This fact probably caused the reduced frequency of the stretching vibrations of the CO$_2$ group and increased frequency of the stretching vibrations of the donor-acceptor C–O bond in the corresponding moiety in going from solution **III'a** to **III'd** (Table 2). The considerably stronger shielding of protons in the moiety [H$_2$O–CO$_2$] in solution **III'd** compared to **III'a** means that the corresponding protons form a hydrogen bond with a group capable to remote shield-

ing since with growing strength of these bonds its influence increases [15]. In the IR spectrum of solution **III'd** is also observed an absorption band at 759 cm^{-1} that can be regarded as belonging to out-of-plane bending vibrations of bound groups OH [16].

In the ^{13}C NMR spectrum of solution **III'd** besides the signals of benzene ring carbons appears at 119.4 ppm an additional signal of a carbon atom not linked to a hydrogen. This signal is in good agreement with the sp-hybridized state of the carbon in the moiety [H$_2$O–CO$_2$] (Table 1, Fig. 1) [17]. Since the carbon chemical shift in the ^{13}C NMR spectrum of carbon dioxide is 124.0 ppm [17], the stronger shielding of the carbon in the CO$_2$ group of [H$_2$O–CO$_2$] is apparently caused by a partial negative charge arising from the donor-acceptor interaction. In the ^{13}C NMR spectrum of solution **III'a** the respective carbon signal is lacking (Table 1).

As follows from the data of Table 3 and Fig. 2 in the ^{1}H NMR spectrum of solution **III'a** the chemical shift and signal width of protons belonging to the moiety [H$_2$O–CO$_2$] depend on the concentration and temperature. Thus at heating the solution from 25 to 40 and further to 70°C the half width of the corresponding signal decreased, and its position shifted upfield by 0.10 and 0.25 ppm respectively, and at cooling the solution from 70 to 25°C the initial pattern of the spectrum was recovered. On decreasing the concentration of solution **III'a** by about one third the signal reversibly shifted upfield by 0.45 ppm with simultaneous broadening; in the diluted solution was also observed a reversible upfield shift of the signal at increasing the temperature (Table 3, Fig. 2). The
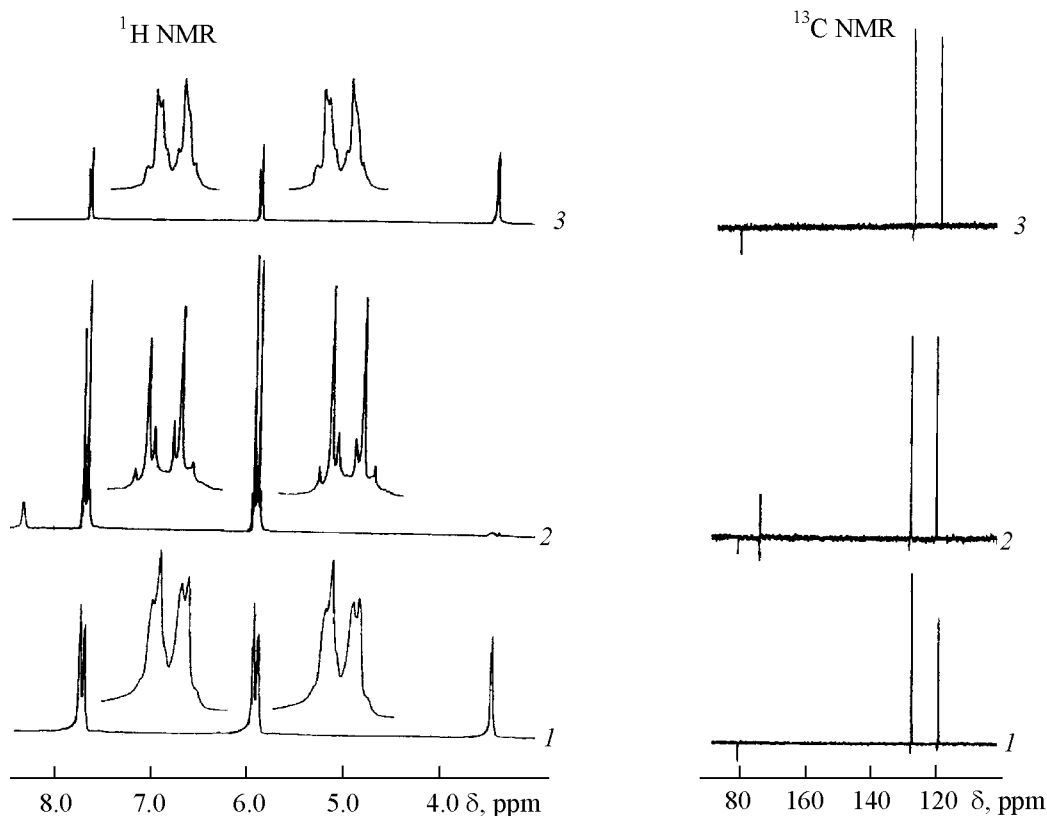
Fig. 1. ^{1}H and ^{13}C (JMOD) NMR spectra of solution **III'a** registered after different time of storage ((*1*) 3 h, (*2*) 7 days, (*3*) 14 days.

chemical shift of signals from the *ortho*-protons in the ^{1}H NMR spectrum of solution **III'a** also reversibly depends on temperature and concentration; therewith at growing temperature and decreasing concentr-

Table 4. Enthalpy of formation (ΔH_f^o) of compounds **Ia, d,** K_2CO_3, and complexes [2-(4-CH$_3$C$_6$H$_4$OH)]–K_2CO_3 and [2-(4-NO$_2$C$_6$H$_4$OH)]·K_2CO_3 (A and B structures) calculated by PM3 method, and heats of complexing (ΔH_c^o)

Compound	$-\Delta H_f^o$, kJ mol^{-1}	$-\Delta H_c^o$, kJ mol^{-1a}
4-CH$_3$C$_6$H$_4$OH	129.3	–
4-NO$_2$C$_6$H$_4$OH	132.6	–
K$_2$CO$_3$	1204.5	–
A	1600.9	137.8
[2-(4-CH$_3$C$_6$H$_4$OH)]–K$_2$CO$_3$		
B	1598.1	135.0
A	1661.2	191.5
[2-(4-NO$_2$C$_6$H$_4$OH)]–K$_2$CO$_3$		
B	1726.2	256.5

^{a} $\Delta H_c^o = \Delta H_f^o[(2\text{ArOH})–\text{K}_2\text{CO}_3]$ – [$\Delta H_f^o(\text{K}_2\text{CO}_3)$ + (H)2 – $\Delta H_f^o(\text{ArOH})$].

ation the shielding of these protons increases and in the limit attains the value of that in the solution of compound **Ia**, and the pattern of the corresponding signal starts to remind a doubled doublet (Table 3). It should be noted that the observed dependence of the proton chemical shifts on temperature and concentration is characteristic of intermolecular association [18]. The dependence of the coupling constants of the benzene ring protons in solution **III'a** on the temperature and concentration also points to this process (Table 3) [19].

Since in solution of compound **IIa** the position and pattern of signals from aromatic protons do not depend on the temperature and concentration (Table 1), it is presumable that in solution **III'a** the ArO group and the [H$_2$O–CO$_2$] moiety are included into a common complex capable of intermolecular association. It should be noted that the presence of [H$_2$O–CO$_2$] moiety in the structure of the complex shows that its formation involves the ratio ArOH : K$_2$CO$_3$ equal to 2 as confirmed by the above results. With the use of PM3 method we calculated the formation enthalpy (ΔH_f^o) of complexes (2ArOH)·K$_2$CO$_3$

(Ar = 4-$CH_3C_6H_4$, 4-$NO_4C_6H_4$) possessing A and B structures (Table 4). The comparison of heats of complexing ΔH_c^o shows that for the complex [2-(4-$CH_3C_6H_4OH$)]–K_2CO_3 the structure A is the most stable whereas for the complex [2-(4-$NO_4C_6H_4OH$)]–K_2CO_3 it is structure B (Table 4).

It should be emphasized that the fundamental characteristic of the assumed structure A is its amphiphilic nature (aryl group is lipophilic, and the inorganic part is hydrophilic). This character provides a possibility to form intermolecular associates in aprotic dipolar solvent due to polar interactions of hydrophilic ends (reversed micelles) [20]. Since the inorganic part of the A structure is virtually planar (carbonate group), the aggregation mechanism possible therewith may be based on stacking [21]. In this case the accumulation in the course of interaction between 4-cresol (**Ia**) and K_2CO_3 of a complex with the A structure till a concentration greater than the critical one for micelle formation would result in transition from a true (molecular) solution to a micellar solution that is characterized by equilibrium (1) [20].

$$nA \rightleftharpoons A_n \qquad (1)$$

The study of dependence of protons chemical shifts in the ^{1}H NMR spectrum of solution **III′a** on temperature and concentration permits a conclusion that this solution is micellar. Since at heating or dilution the difference in the shielding of the corresponding protons in solution **III′a** and in solution of compound **Ia** decreases, the structure of the monomeric form is in keeping with structure A, including a perturbed
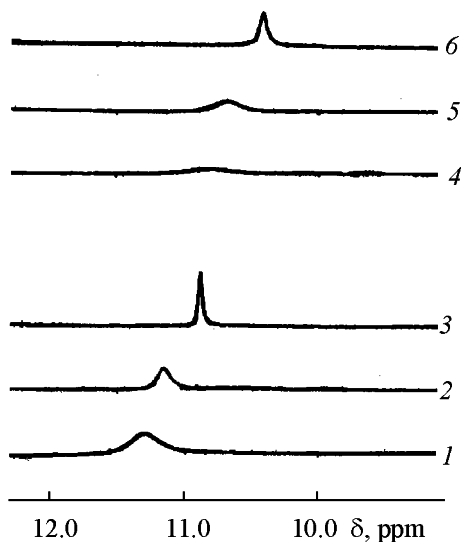
Fig. 2. ^{1}H NMR spectra of solution **III′a** at 25 °C (*1*), 40°C (*2*), 70°C (*)3*), and of diluted solution **III′a** at 25°C (*4*), 40°C (*5*), 70°C (*6*) in DMSO-*)d_6*.

form of the 4-cresol molecule. Although the character of the micelle structural unit as a whole is determined by the structure of the monomeric form the difference between these structures can be foreseen for the additional interactions in the core of micelle affect the state of the coordination and hydrogen bonds. From this viewpoint the results obtained by investigation of solution **III′a** with IR spectroscopy suggest that the structural units of the micelle include the moiety [H_2O–CO_2] and two ArO groups, and the equilibrium concentration of the micellar form A_n
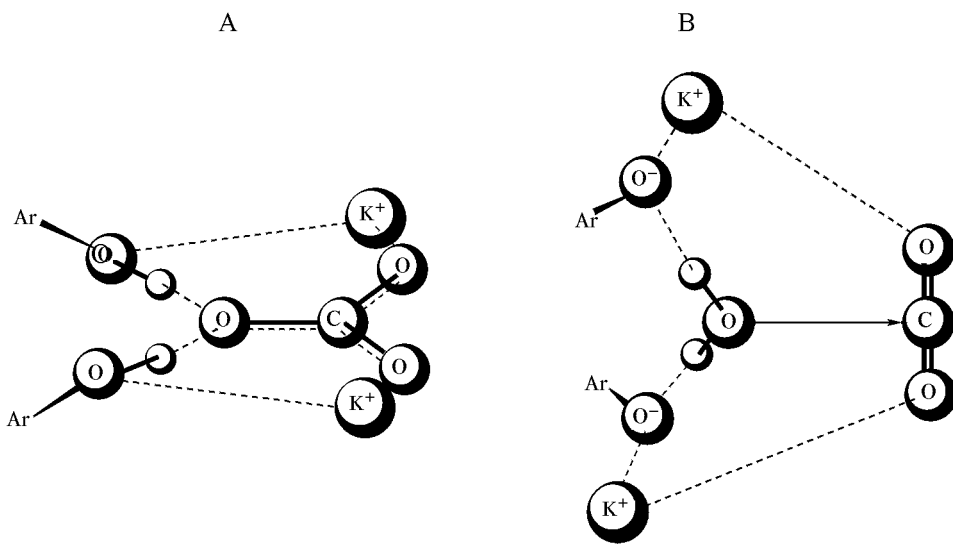
is significantly larger than that of the monomeric form A. The latter is apparently caused by greater stability of the micelle compared to monomer.

It should be noted that the prevalence in the solution **III'a** of the complex of A structure in the micellar form may be the reason why the signal of carbon atom from the $[H_2O-CO_2]$ moiety does not appear in its ^{13}C NMR spectrum: The regular structure of the micelle core may result in an unfavorable relation between spin-spin and spin-lattice relaxation $(T_2 < < T_1)$ existing in solid substances [22].

The B structure is well consistent with the results of studies of solution **III'd** by means of IR, ^1H and ^{13}C NMR spectroscopy. Since the position of proton signals in the ^1H NMR spectra of solution **III'd** is virtually insensitive to the temperature and concentration, and in the ^{13}C NMR spectrum appears the carbon signal from the $[H_2O-CO_2]$ moiety, it is presumable that solution **III'd** is a molecular one. The absence of micelles in solution **III'd** is apparently caused by the nonplanar hydrophilic part of the complex with the B structure and therefore the micelle formation by stacking process is hampered.

Evidently with the other proton-donor reagents from the set of phenols and thiophenols under study may presumably arise all three types of structures (A, A_n, and B) of the complex $(2ArXH)\cdot K_2CO_3$. It should be noted that a very broad signal from the hydroxy proton at 6.2 ppm in the ^1H NMR spectrum of solution **III'c** is probably due to the transitions between these structures [equation (2)].

$$A_n \rightleftarrows A \rightleftarrows B \qquad (2)$$

A similar state of the ArO group in solution **III'c** and in solution of compound **IIc** suggests that the equilibrium concentration of A structure is negligible (Table 1). The lack of the carbon signal belonging to the $[H_2O-CO_2]$ moiety in the ^{13}C NMR spectrum of solution **III'c** indicates that in solution **III'c** the equilibrium concentration of A_n structure is greater than that of B (Table 1). The identical position of proton signal from the $[H_2O-CO_2]$ moiety in the spectra of solutions **III'd–f** means that for thiophenols the equilibrium concentration of B structure is considerably higher than for 5-bromo-3-nitrophenol (Table 1). Thus in solutions **III'c, e, f** two types of structures of the complex $(2ArXH)\cdot K_2CO_3$ are present, A_n and B, and their equilibrium concentration depend on the acidity of ArXH.
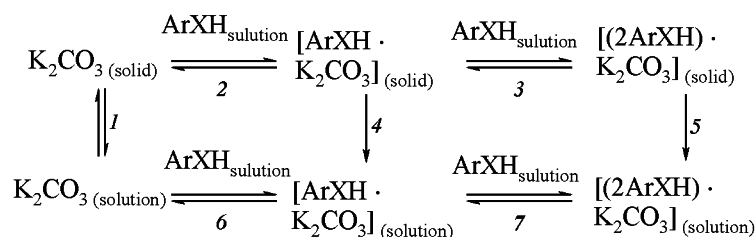
It was shown formerly that in the IR spectrum of solution **IIIb** obtained by keeping 4-cyanophenol (**Ib**)

and potassium carbonate in DMF at 70°C followed by filtration appeared two bands of similar intensity at 2206 and 2189 cm^{-1} which were assigned to the stretching vibration of the C≡N bond in the complex ArOH·K$_2$CO$_3$ [5]. It should be noted that in this spectrum are observed additional absorption bands (lacking in the spectra of solutions of compounds **Ib** and **IIb***) that may be attributed to the $[H_2O-CO_2]$ moiety $(3500, 2948, 1690, 1440, 1294,$ and $1012\,cm^{-1})$, and the state of ArO group is unlike that in solutions of compounds **Ib** and **IIb***. These spectral features are characteristic of the structure A_n (Table 2). But therewith in the IR spectrum of solution **IIIb** are present also additional weak absorption bands that may be assigned to the vibrations of C–O bond $(1255\ cm^{-1})$ and of $[H_2O-CO_2]$ moiety $(2914, 1453, 1337$ and $770\ cm^{-1})$ in a complex with B structure (Table 2). Thus the IR spectrum shows that in solution **IIIb** structures A_n and B are present, the former prevailing. If it is assumed that the high symmetry of the nearest surrounding of potassium atom is due to the regular structure of a micelle core then in going from solution **IIIa** to **IIIc** the equilibrium concentration of A_n structure decreases (see above). It should be noted that in the region 3500–2500 cm^{-1} of the IR spectrum of solution **IIIe** obtained by keeping 2-thionaphthol **Ie** and potassium carbonate in DMF at 70°C followed by filtration are observed the bands of stretching vibrations of C–H bonds of the aromatic system and two bands in the range 2923–2845 cm^{-1} that may be attributed to the antisymmetric stretching vibrations of CO$_2$ in structures A_n and B, and in DMF (as in DMSO-d_6) the equilibrium concentration of B is higher than that of A_n.

The agreement of results obtained by IR spectroscopy (2% solutions) and by ^1H, ^{13}C, and ^{39}K NMR spectroscopy (10% solutions) shows that the equilibrium concentrations of structures A, A_n, and B stronger depend on the acidity of ArXH than on the concentration of solutions. Comparison of results obtained in the studies of solutions of complexes between potassium carbonate and phenols prepared in DMF and DMSO-d_6 showed that state of nucleophiles generated *in situ* under conditions of a two-phase system is common for different aprotic dipolar solvents.

We formerly suggested a scheme of the complex ArOH·K$_2$CO$_3$ formation involving a stage of the corresponding phenol chemisorption on the potassium carbonate surface followed by irreversible desorption of the phenol bearing a K$_2$CO$_3$ molecule [5]. Within the framework of these scheme the complex of

Scheme 1.

$$K_2CO_3\text{ (solid)} \underset{2}{\overset{ArXH_{sulution}}{\rightleftarrows}} [ArXH \cdot K_2CO_3]\text{ (solid)} \underset{3}{\overset{ArXH_{sulution}}{\rightleftarrows}} [(2ArXH) \cdot K_2CO_3]\text{ (solid)}$$

$$\big\updownarrow 1 \qquad\qquad\qquad \big\downarrow 4 \qquad\qquad\qquad \big\downarrow 5$$

$$K_2CO_3\text{ (solution)} \underset{6}{\overset{ArXH_{sulution}}{\rightleftarrows}} [ArXH \cdot K_2CO_3]\text{ (solution)} \underset{7}{\overset{ArXH_{sulution}}{\rightleftarrows}} [(2ArXH) \cdot K_2CO_3]\text{ (solution)}$$

$(2ArXH)–K_2CO_3$ type having A and B structures may form in several ways.

For instance, the path $(2 \rightarrow 3 \rightarrow 5)$ includes two consecutive chemisorption stages of ArXH on the interphase surface of the solid phase followed by a stage of irreversible desorption, and the path $(2 \rightarrow 4 \rightarrow 7)$ consists of chemisorption of ArXH on the potassium carbonate surface, desorption of the intermediate complex, and of coordination of the latter with an additional phenol molecule in solution.
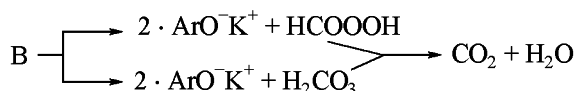
It is known that potassium carbonate is almost insoluble in aprotic dipolar solvents [23] as confirms the lack of a carbonate group signal in the ^{13}C NMR spectrum of DMSO-d_6 after keeping therein potassium carbonate followed by filtration (Table 1). Therefore the formation of the corresponding complex avoiding the stage of phenol chemisorption on the surface of the solid phase is improbable. However the ^{13}C NMR spectrum of a solution prepared by keeping potassium carbonate in a moist DMSO-d_6 with subsequent filtration appears a signal at 174.1 ppm (Table 1). Thus the presence of water in DMSO-d_6 increases the solubility of K_2CO_3, and in moist aprotic dipolar solvent may occur also a path $(1 \rightarrow 6 \rightarrow 7)$. It should be noted that in the ^{13}C NMR spectrum of solution prepared by keeping 4-nitrophenol (**Id**) and potassium carbonate in moist DMSO-d_6 for 3 h at 70°C appeared the signals of carbon atoms from the corresponding complex and from compound **IIg** (Table 1).

It is pertinent to note that the complex of B structure is less stable than that of A$_n$ structure for at keeping solutions **III'a, d** at room temperature for 14 days the changes were observed only in solution **III'd** (Table 1, Fig. 1). The comparison of two first ^1H NMR spectra (Fig. 1) reveals that in 7 days after preparation in solution **III'd** only decomposition products of the corresponding complex are present (one among them is potassium 4-nitrophenolate). This is seen from the disappearance of signals from the $[H_2O–CO_2]$ moiety; a proton signal is observed at 8.9 ppm, and the chemical shifts of the benzene ring

protons acquire the values common to those in the spectrum of solution of compound **IId** (Table 1, Fig. 1). The same conclusion follows from the comparison of the corresponding ^{13}C NMR spectra: The carbon signal of the $[H_2O–CO_2]$ moiety at 119.4 ppm disappears, new signals are observed from sp^2-hybridized carbons attached and not attached to proton at 173.9 and 173.7 ppm respectively, and the chemical shifts of the benzene ring carbons acquire the values common to those in the spectrum of solution of compound **IId** (Table 1, Fig. 1). The proton signal at 8.9 ppm and the signal of a carbon linked to proton at 173.9 ppm in the ^1H and ^{13}C NMR spectra respectively can be assigned to a formyl group [24]. Since the ^1H and ^{13}C NMR spectra of solution **III'd** after storage for 14 days and of solution of compound **IId**[*] are identical, it is clear that some products of complex decomposition revealed by ^1H and ^{13}C NMR spectra in solution **III'd** stored for 7 days are unstable, and their decomposition furnishes water and probably carbon dioxide (Table 1, Fig. 1). Evidently at decomposition of the complex of B structure its inorganic part built with a p-π bond between H_2O and CO_2 may rearrange providing carbonic acid to which belongs the protonless sp^2-hybridized carbon atom with a signal at 173.7 ppm in the corresponding ^{13}C NMR spectrum). However the decomposition of the inorganic part of the complex may proceed through a 1,2-anionic rearrangement for the "compatibility rule" permits an attack of the rear part of the oxygen atom orbital from the H_2O group on one of the oxygens of the CO_2 group providing another π-complex by a synchronous mechanism [25]. This process is apparently favored by the reduced contribution of the p-orbital of the carbon into the π-orbital because of diminished polarity of C=O bonds at the donor-acceptor interaction [25]. In this case further rearrangement results in performic acid (signals of a formyl group in the corresponding ^1H and ^{13}C NMR spectra). Obviously the carbonic and performic acids decompose further into water and carbon dioxide.

It might be well to point out that the complex decomposition processes observed in solution **III'd**

Scheme 2.

$$B \left\{ \begin{array}{l} \longrightarrow 2 \cdot ArO^-K^+ + HCOOOH \\ \longrightarrow 2 \cdot ArO^-K^+ + H_2CO_3 \end{array} \right\} \longrightarrow CO_2 + H_2O$$

indirectly support formation of complexes (2ArXH)·K_2CO_3 at the interaction of potassium carbonate with phenols and thiophenols in aprotic dipolar solvents.

EXPERIMENTAL

^{1}H NMR spectra of solutions in DMSO-d_6 were registered on spectrometers Bruker WP-200 SY and Bruker AM-400; ^{13}C NMR spectra were recorded on spectrometers Bruker WP-200 SY, Bruker AM-400, and Bruker DRX-500. ^{39}K NMR spectra were measured on spectrometer Bruker DRX-500 with a water solution of KBr as external reference. IR spectra were taken on Specord M-80 instrument from solutions in DMF and DMSO-d_6.

Table 5. Conditions of preparation of solvents (**IIIa–c,**) and (**III'a, c–f**)

Solution	ArXH, mmol	K_2CO_3, mmol	Solvent, ml
III'a	4-CH$_3$C$_6$H$_4$OH (0.6)	0.9	DMSO-d_6 (0.6)
	4-CH$_3$C$_6$H$_4$OH (0.1)	0.3	DMSO-d_6 (0.5)
IIIa	4-CH$_3$C$_6$H$_4$OH (0.6)	0.9	DMF (0.6)
IIIb	4-CNC$_6$H$_4$OH (0.5)	0.7	DMF (0.3)
III'c	3-Br-5-NO$_2$C$_6$H$_3$OH (0.3)	0.4	DMSO-d_6 (0.5)
IIIc	3-Br-5-NO$_2$C$_6$H$_3$OH (2.4)	3.5	DMF (4.5)
III'd	4-NO$_2$C$_6$H$_4$OH (0.5)	0.9	DMSO-d_6 (0.6)
	4-NO$_2$C$_6$H$_4$OH (0.1)	0.9	DMSO-d_6 (0.7)
III'e	2-C$_{10}$H$_7$SH (0.5)	0.7	DMSO-d_6 (0.7)
IIIe	2-C$_{10}$H$_7$SH (0.6)	0.9	DMF (4.7)
III'f	4-NO$_2$C$_6$H$_4$SH (0.4)	0.6	DMSO-d_6 (0.5)

A commercial DMF was dried with molecular sieves 4 A and distilled in a vacuum over CaH$_2$. A commercial DMSO-d_6 was dried with molecular sieves 4 A.

Commercial 4-cresol, 4-nitrophenol, 2-thionaphthol, and 4-nitrothionaphthol were purified by standard procedures. Before use a commercial K$_2$CO$_3$ of "pure for analysis" grade was calcined in a muffle furnace at 400°C for 3 h, then finely ground and additionally dried in a vacuum of an oil pump (~5 mm Hg) at 150°C for 2 h. 5-Bromo-3-nitrophenol was prepared from 3-bromo-3-nitroanisole by procedure from [5], mp 145°C [5]. The potassium phenolates and thiophenolates were synthesized as in [26].

Quantum-chemical calculations of the complexes (2–ArOH)–K$_2$CO$_3$ were carried out by semiempirical procedure PM3 with the use of software package MOPAC 6.0 [27]. Experimental conditions are given in Table 5.

Reaction of compounds Ia–f with K$_2$CO$_3$ in DMF. To a 19% solution of 0.02 mol of phenol or thiophenol in DMF was added 4.1 g (0.03 mol) of K$_2$CO$_3$, and the suspension was stirred for 3 h at 70°C (with thiophenols the reaction was carried out in a flow of dry argon). The solid K$_2$CO$_3$ was filtered off from the hot reaction mixture, washed on the filter with DMF, and dried for 3 h at 70°C in a vacuum of an oil pump (~5 mm Hg). The weight of the dry residue of K$_2$CO$_3$ was 2.8 g (0.02 mol) for phenols and 2.9 g (0.021 mol) for thiophenols.

Reaction of compounds Ia–d with K$_2$CO$_3$ in DMSO-d_6 and DMF. To a solution of phenol in DMSO-d_6 or DMF was added K$_2$CO$_3$, and the mixture was stirred for 3 h at 70°C; then the hot reaction mixture was filtered, and the filtrate was studied by spectral methods.

Reaction of compounds Ie, f with K$_2$CO$_3$ in DMSO-d_6 and DMF. To a solution of thiophenol in DMSO-d_6 or DMF was added K$_2$CO$_3$, and the mixture was stirred for 3 h at 70°C in a flow of dry argon; then the hot reaction mixture was filtered, and the filtrate was studied by spectral methods.

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