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Interactions of Phenols with Lewis Acids: XVII.[*] Thermodynamics of Naphthols Complexing with Aluminum Bromide

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Abstract—Enthalpy and formation constants of 1:1 and 1:2 complexes, constants and enthalpy of naphthols isomerization into tautomeric ketones at interaction of $AlBr_3$ and naphthols and dihydroxynaphthalenes were measured.

In preceding communications [1, 2] we reported on thermodynamics of complexing between substituted phenols and aluminum bromide. We established a relation between enthalpy ($\Delta Æ_c$), formation constants ($\log K$) of complexes and Hammett's σ-constants. It was demonstrated that the formation enthalpy of triple complexes ($\Delta Æ_c$) of polyalkylphenols may be sufficient for reconstruction of the aromatic π-system into a cross-conjugated one. As a result arise complexes of a tautomeric keto form.

The phenol-dienone tautomerism initiated by complexing was first discovered in the study of interaction between 1- and 2-naphthols with $AlCl_3$ and $AlBr_3$ [3]. It turned out that methyl-, phenyl-, halo-, and hydroxyderivatives of naphthols with $AlCl_3$ and $AlBr_3$ at concentration of the substrate up to 1 mol l^{-1} also were quantitatively converted into complexes of keto form [4, 5].

The ease of naphthols isomerization into ketone complexes suggests that the enthalpy of complex formation (ΔH_c) is higher with naphthols than with phenols, and it considerably surpasses the energy of the tautomeric transformation (ΔH_t) into the corresponding ketones.

In order to test this assumption we carried out thermochemical measurements of the heat evolution in reaction of naphthols and their derivatives with $AlBr_3$ in bromobenzene. The heat evolution was measured by temperature growth (ΔT) during calorimetric titration of naphthols **IV** solutions with $AlBr_3$

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[*] For communication XVI, see [1].

solutions and vice versa. The calculations were done along equation (1).
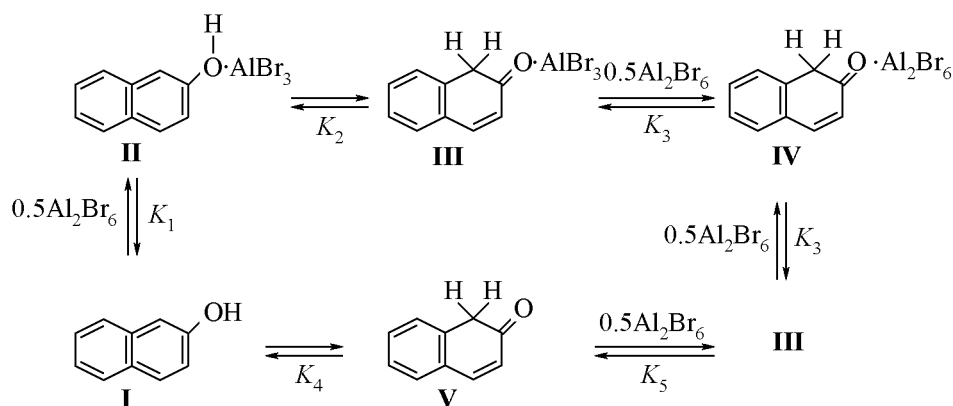
$$\Delta H_c = \Delta H_e + 0.5 \Delta H(Al_2Br_6) - \Delta H_{solv} \qquad (1)$$

where $\Delta H_{k(1:1)}$ and $\Delta H_{k(1:2)}$ are respectively formation enthalpies of 1:1 and 1:2 complexes (kJ mol^{-1}), $\Delta H(Al_2Br_6)$ is dissociation energy into monomer of Al_2Br_6, ΔH_e is experimentally measured heat evolution of reaction, ΔH_{solv} is solvation effect.

In a scheme below are presented two possible complexing paths for 2-naphthol (**I**): First possibility includes conversion into a complex of hydroxy form **II** followed by isomerization into keto form complex **III** and then transition into triple complex **IV**; the second way consists in fixing of the tautomeric keto form of 2-naphthol **V** with formation of the same complexes **III, IV**.

As expected, the heat evolution in reaction of naphthols with Al_2Br_6 was higher than that of phenol, 2-, 3-methyl-, 2,3-, 3,5-dimethyl-, and 2,3,5-trimethylphenols. The character of relation $\Delta T = f(n_a/n_d)$ (n_a and n_d are molar fractions of acceptor and donor respectively) suggests that in the solution arise two types of complexes, of 1:1 and 1:2 composition. Taking into account the spectral data [6] we presume that first forms an adduct of 1:1 composition ($\Delta H_{c(1:1)}$ 77.5 kJ mol^{-1}) that is a complex of **II** type whereas the 1:2 adduct ($\Delta H_{c(1:2)}$ 102.6 kJ mol^{-1}) is a complex of **IV** type. The methylated naphthols, 2-methyl-1- naphthol and 1-methyl-2-naphthol, give stronger complexes with $AlBr_3$ than those described above ($\Delta H_{c(1:2)}$ 107.2, 108.1 kJ mol^{-1}).

At measuring the heat evolution in reaction of 1,2- and 1,4-dihydroxynaphthalenes with $AlBr_3$ was observed HBr liberation, and we were obliged to reduce the initial temperature of solution to 5°C. 2,3- and 1,7-dihydroxynaphthalenes were sparingly soluble in bromobenzene and dibromomethane, and their complexes form a separate phase. Therefore the thermal effects given in the table for these compounds are of approximate character.

Higher values of formation enthalpy for the 1:2 complexes with $AlBr_3$ of 1,3- and 1,4-dihydroxy-naphthalenes as compared to those of naphthols is due apparently both to the higher basicity of the compounds and by the tendency of the complexes to transform into diketo form [4, 5].

The ability of 1,3- and 1,4-dihydronaphthalenes to form diketocomplexes (there is no such data with respect to 1,2-isomer) is due to the fact that the hydroxy group in complexes **VI** and **VIII** is enol in essence. The rearrangement of enols into the corresponding ketones does not require much energy. In particular, 3-hydroxy-5,5-dimethyl-2-cyclohexen-1-one in solution just under common conditions converts into 5,5-dimethylcyclohexa-1,3-dione [7]. Therefore it is presumable that under the experimental conditions the 1:2 complexes of 1,4- and 1,3-dihydroxynaphthalenes exist as diketo tautomers **VII** and **IX**.
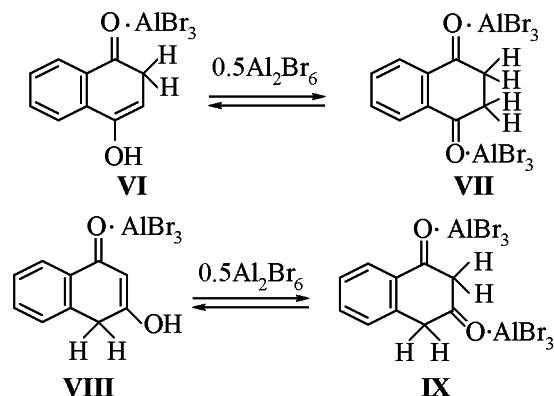
Thermodynamic characteristics of complexes of naphthols and their derivatives with $AlBr_3$ (bromobenzene, 16°C)

Compound	$-\Delta H_{1,2}$, kJ mol^{-1}	$-\Delta H_{1,4}$, kJ mol^{-1}	$-\Delta H_{2,3}$, kJ mol^{-1}	$-\Delta H_{3,4}$, kJ mol^{-1}	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_{1,3}$
1-Naphthol	77.5	102.6	−2.5	27.6	8.9	−0.4	4.8	13.3
2-Naphthol	77.9	103.4	−2.1	27.6	9.0	−0.3	4.8	13.5
2-Methyl-1-naphthol	78.7	107.2	0.9	27.6	9.1	0.2	4.8	14.1
1-Methyl-2-naphthol	78.8	108.0	1.6	27.6	9.1	0.3	4.8	14.2
1,4-Dihydroxynaphthalene	86.3	113.9 [a]	0	27.6	10.5	0	4.8	15.3
1,2-Dihydroxynaphthalene		114.7 [a]						
1,6-Dihydroxynaphthalene	87.5	102.6 [b]						
1,7-Dihydroxynaphthalene	84.2	101.7 [b]						
2,3-Dihydroxynaphthalene	87.9	103.8 [b]						
2-Methyl-2-dichloromethyl-dehydrotetralone		130.2						

[a] Titration at 5°C, solvent CH_2Br_2. [b] 2,3-, 1,6- and 1,7-dihydroxynaphthalenes as suspension, complexes form a second liquid phase.

It is not impossible that the complex of 1,2-di-hydroxynaphthalene possesses a chelate structure as those of pyrocatechol or 1,2-naphthoquinone.

The fact that no diketo complexes were detected even in the presence of a significant excess of $AlBr_3$ with dihydroxynaphthalenes having the hydroxy groups in different rings [6] is caused first of all by the necessity of transforming two aromatic rings in the unsaturated cross-conjugated systems. Since the distortion of aromaticity of one naphthalene ring requires ~56.3 kJ mol^{-1}, and of the second ring ~71.4 kJ mol^{-1} [9] then the enthalpy of transformation into complexes of diketo form for 1,6- and 1,7-dihydroxynaphthalenes should amount to no less than 127.7 kJ mol^{-1}. However the measured thermal effects of complexing of 1,6- and 1,7-dihydroxy-naphthalenes are not so large.

Taking in the first approximation for the entropy of interaction of naphthols and dienones with $AlBr_3$ the same value as measured for phenols (ΔS 88 J K^{-1} [3]) we calculated the constants of complex formation [equation (2)].

$$\log K_1 + \log K_2 + \log K_3 = \log K_{1,3} \qquad (2)$$

The $\log K_{1,3}$ value was estimated from the principal equation of thermodynamics. In the table are given both the values of constants of separate complexing stages and overall constants. In particular, the equilibrium constants of the first stage of reaction between 1- and 2-naphthols and $AlBr_3$ are equal to 2.5×10^9 and 3.1×10^9 respectively, the constants of the second stage are 2.5 and 2.0, and those of the third stage 6.3×10^4. Since the constant of the third stage is significantly greater than that of the first stage, the presence of excess of $AlBr_3$ over the equimolar quantity shifts the equilibrium to the triple complex.

In conclusion we state that in this study was investigated the thermodynamics of $AlBr_3$ reaction with naphthols and their derivatives, and complex formation constants were estimated. It was established that in solutions of 1×10^{-3} mol l^{-1} concentration the equilibrium is shifted to keto form complexes. The stability of keto complexes from naphthols is higher than those from mono- and dimethylphenols. Thus was confirmed the previously established rule that joining of phenol to an aromatic system stabilized ketotautomers [12].

EXPERIMENTAL

The calorimetric titration was carried out under dry atmosphere at 16°C. As recommended in [10] we used for calorimetric fluid the dry bromobenzene. The direct titration was carried out by addition of naphthol solutions to 10^{-3} mol l^{-1} solution of $AlBr_3$, at reversed titration procedure vice versa to a 10^{-3} mol l^{-1} solution of naphthol was added a solution of $AlBr_3$. The 1,7- and 2,3-dihydroxynaphthalenes were present in suspension, and their complexes separated into a special layer. Reaction of 1,2- and 1,4-dihydroxynaphthalenes with $AlBr_3$ was performed in CH_2Br_2 at 5°C. As calorimeter was used a Dewar flask with its proper heat capacity of 200 J. A Beckmann thermometer served as zero reader. The temperature control was within ±0.01°C, the dilution heat was taken into account in the calculation. The accuracy of measurements was ±2 kJ mol^{-1}. Enthalpy of dimer Al_2Br_6 dissociation was taken as 55.7 kJ mol^{-1} [11]. 2-Methyl-2-dichloromethyl-1,2-dihydronaphthalen-1-one (mp 67–68°C) was synthesized by chloromethylation of 2-methyl-1-naphthol [12].

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