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Reactions of Phenols with Lewis Acids: XX.* Tautomerism of Naphthols

A. V. Golounin, Yu. S. Shchedrin, and E. A. Ivanova

Siberian State Technological University

Institute of Chemistry and Chemical Technology, Siberian Division, Russian Academy of Sciences,
ul. K. Marksa 42, Krasnoyarsk, 660049 Russia
fax: (3912) 238 658

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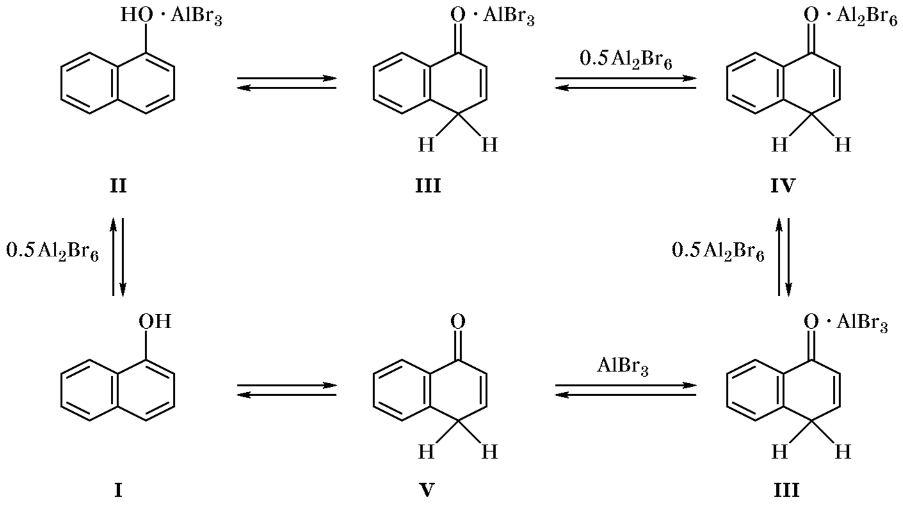
Abstract—Thermodynamic parameters of tautomeric transformations of naphthols and their derivatives were estimated on the basis of experimental data and quantum-chemical calculations.

In the preceding communication [1] we reported on the tautomerism of methylated phenols. Its quantitative parameters were determined on the assumption that both methylated phenols and methylated 2,5-cyclohexadienones form complexes with similar composition and structure. The calculated enthalpies of tautomeric transformations tend to decrease as the number of *ortho*- and *meta*-methyl groups in the ring increases.

It is known that in nonpolar solvents in the presence of aluminum halides naphthols and their derivatives are quantitatively converted into complexes of the corresponding keto tautomers [2–4]. Therefore, we can presume that the tautomeric constant of naphthols should be greater than the tautomeric constant of methylated phenols.

The state of tautomeric equilibrium of naphthols was determined using the procedure described in [1]. The heat effect of the reaction of 1-naphthol with $AlBr_3$ (Scheme 1) can be determined either by measurement of the heat effects of consecutive transformations **I** → **II** → **III** → **IV** or by summation of

Scheme 1.



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

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the enthalpies of the transitions **I** → **V** → **III** → **IV**. Equation (1) may be written:

$$\Delta H_{1,2} + \Delta H_{2,3} + \Delta H_{3,4} = \Delta H_{1,5} + \Delta H_{5,3} + \Delta H_{3,4}. \qquad (1)$$

The sum of the enthalpies of particular stages of the transition **I** → **II** → **III** → **IV** is equal to the overall heat of formation of complex **IV** starting from naphthol **I** and 2 equiv of $AlBr_3$ [Eq. (2)]:

$$\Delta H_{1,2} + \Delta H_{2,3} + \Delta H_{3,4} = \Delta H_{1,4}. \qquad (2)$$

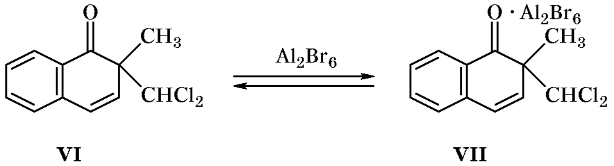
The right part of Eq. (1) can be represented as the sum of the enthalpy of tautomeric transformation of naphthol **I** into ketone **V** and the enthalpy of binding of ketone **V** into complex **IV** [Eq. (3)]. The quantity ΔH_T is given by Eq. (4):

$$\Delta H_{1,4} = \Delta H_T + \Delta H_{5,4}; \qquad (3)$$

$$\Delta H_T = \Delta H_{1,4} - \Delta H_{5,4}. \qquad (4)$$

Replacement of $\Delta H_{5,4}$ in Eq. (4) by the heat effect for binding of a stable analog of ketone **V** gives (in the first approximation) the enthalpy of tautomeric transformation of naphthol **I**. As a model of ketone **V** we used 2-dichloromethyl-2-methyl-1,2-dihydronaphthalen-1-one (**VI**) (Scheme 2). The heat of formation of triple complex **VII** $\Delta H_{6,7}$ is 130.2 kJ/mol.

Scheme 2.



The heats of formation of triple complexes derived from naphthol were reported previously [5]. The enthalpies of tautomeric transformations of naphthols, calculated by Eq. (4), are given in table. As expected, the ΔH_T value for 1-naphthol (27.6 kJ/mol) turned out to be much lower than ΔH_T for methylated phenols, including pentamethylphenol (34.8 kJ/mol [1]). The value of ΔH_T for 2-naphthol is 26.8 kJ/mol. The presence of methyl groups provides additional stabilization of the ketone tautomer by more than 4 kJ/mol.

We also performed quantum-chemical calculations of ΔH_T by the Meller–Plesset procedure (MP2) [6]. The calculated values were very consistent with those found experimentally. It should be noted that introduction of a methyl group into 2-naphthol produces much weaker stabilization than does methyl substitution of 1-naphthol: the resulting value is comparable with that calculated for unsubstituted 1-naphthol. A plausible explanation is as follows. Rearrangement of 2-methyl-1-naphthol involves proton migration from the hydroxy group to the C^4 atom, and the keto tautomer thus formed is stabilized by the *ortho*-methyl group (for stabilization of keto forms by *ortho*-CH_3 groups, see [1]). In the molecule of 1-methyl-2-naphthol proton migrates to the substituted C^1 atom (*ipso*-addition), which requires an additional energy. We did not succeed in revealing difference in the enthalpies of formation of the complexes by thermochemical methods.

Enthalpies (kJ/mol) and constants of tautomeric transformations of naphthols and their derivatives

Compound	ΔH_T		pK_T	
	exptl.	calcd.	exptl.	calcd.
1-Naphthol	27.6	24.2	4.9	4.3
2-Naphthol	26.8	22.9	4.8	4.0
2-Methyl-1-naphthol	23.0	16.5	4.1	3.0
1-Methyl-2-naphthol	22.2	24.6	4.0	4.4
1,4-Dihydroxy-naphthalene	16.3	16.1	2.9	2.9

Simultaneous influence of fusion with an aromatic ring and the presence of one more hydroxy group on the state of the phenol–dienone equilibrium in 1,4-dihydroxynaphthalene should be noted. The difference in the heats of formation of 1,4-dihydroxynaphthalene and its keto form is as small as 16.3 kJ/mol (pK_T 2.9). Therefore, it becomes possible to observe the equilibrium by physical methods. Pearson *et al.* showed by ^1H NMR spectroscopy [7] that melted 1,4-dihydroxynaphthalene (200°C) exists as a 1 : 2 mixture of the ketone and enol forms. The ketone fraction of 1,4,5-trihydroxynaphthalene in the melt increases to 3.5 : 1, and the fraction of the ketone form of melted 1,4,5,8-tetrahydroxynaphthalene exceeds that of the enol form by a factor of 20 [7].

Polycyclic phenols, such as anthranol and anthrahydroquinone, are prone to ketone–enol tautomerism even more strongly. According to Baba and Nakemura [8], in nonpolar solvents anthranol is completely converted into anthranone (K_T 476, ΔH_T –13.6 kJ/mol). Anthrahydroquinone in DMSO at 40°C exists mainly (95%) as anthraquinone [9].

Our results allowed us to estimate the contribution of different structural fragments to stabilization of the ketone tautomers of phenols. In particular, fusion of an aromatic ring (1- and 2-naphthols) provides a stabilization effect of 44–45 kJ/mol. The effect of fusion of two aromatic rings is 85 kJ/mol; in this case the ketone form becomes more stable than phenol. The constants of tautomeric equilibrium of naphthols are in the range $(1.2–1.6) \times 10^{-5}$; they increase to $(0.8–1.0) \times 10^{-4}$ on introduction of electron-donor substituents. Fusion with aromatic rings leads to displacement of the phenol–dienone equilibrium to the dienone, so that the ketone tautomers become thermodynamically more stable under usual conditions.

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