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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Complexes of *ortho*-Nitrophenols with Aluminum Bromide in Nonaqueous Solutions

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Abstract—The reactions of 2-nitro-, 2-nitro-4,6-dichloro-, 2,4-dinitro-, and 2,4,6-trinitrophenols with aluminum bromide in nitromethane solution were studied by calorimetry and by ^{1}H and ^{13}C NMR.

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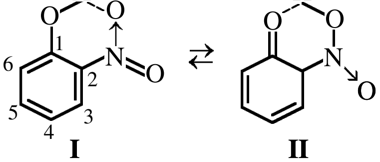
The reactions of methylated phenols, naphthols, and polyphenols with strong Lewis acids in nonaqueous solutions frequently result in tautomeric transformations [1–4]. Data on the reactions of nitrophenols with Lewis acids are searce. For example, it has been found that the reaction of 4-nitrophenol with $TiCl_4$ in benzene at room temperature yields the salt $NO_2–C_6H_4–O–TiCl_3$ [5]. In dry methanol, iron(III) chloride forms a coordination compound with 4-nitrophenol via OH group [6]. Complexes of 2-nitrophenol with gallium, aluminum, and boron halides in organic solutions were studied in [7, 8]. It was concluded that a coordination bond of metal halides with the nitro group is formed; however, in [9] this conclusion was to questioned.

The most complete data on the structure of complexes of nitrophenols with metal halides can be obtained by NMR spectroscopy. Therefore, we synthesized complexes of *o*-nitrophenols with aluminum bromide and recorded ^{1}H and ^{13}C NMR spectra of these complexes.

It is well known that metal halides are bonded in nonaqueous solutions with aromatic nitro compounds via nitro group [10, 11]. In the presence of other donor groups, such as hydroxy, carbonyl, or amino group, the coordination site may change. In the case of *o*-nitrophenol, nitro-aci tautomerism **I** : **II** is also possible Furthermore, formation of complexes of different compositions is possible; thus, the pattern becomes complicated.



I **II**

To determine the stoichiometry of complexes of *o*-nitrophenol **I** with aluminum bromide, we performed calorimetric measurements. First, an 0.01 M solution of *o*-nitrophenol in bromobenzene was titrated with an $AlBr_3$ solution at 100°C and then back-titration was performed. The experimental procedure has been repeatedly described in the literature [9, 10]. In the dependence of the enthalpy of reaction on the molar ratio of donor and acceptor $m_D : m_A$, there are two inflections: at the ratios of 1 : 1 and 1 : 2. The heat effects were evaluated by the procedure described in [9], assuming that the enthalpy of reaction is expressed by the equation

$$\Delta H_c = \Delta H_e + 0.5\Delta H Al_2Br_6 - \Delta H_{solv},$$

where ΔH_c is the heat of complexation; ΔH_e, enthalpy determined experimentally; $\Delta H Al_2Br_6$, enthalpy of dimer dissociation; and ΔH_{solv}, enthalpy of solvation [4].

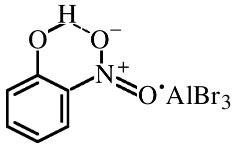
The first portion of the curve corresponds to ΔH_c = 31.5, and the second, to 20.1 kJ mol^{-1}. The total thermal effect is 51.6 1 kJ mol^{-1}.

To estimate the energy of *o*-nitrophenol transformation into an aci tautomer, we performed a quantum-chemical calculation. The molecular configurations of **I** and **II** were optimized using the restricted Hartree–Fock method. The energies were estimated by considering correlation effects in the framework of the Møller–Plesset method (MP-2) [13]. In the cal-

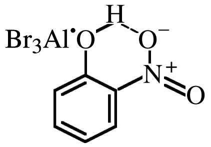
^{1}H Chemical shifts of nitrophenols and complexes in nitromethane

Nitrophenol	$AlBr_3$	H-2	H-3	H-4	H-5	H-6	OH
2-Nitrophenol	1 : 0		8.12	7.08	7.69	7.17	10.4
	1 : 1		7.89	6.92	7.75	6.92	8.37
	1 : 2		7.89	6.92	7.75	6.92	8.13
2-Nitro-4,6-dichlorophenol	1 : 0		8.14		7.84		10.7
	1 : 1		7.84		7.81 7.80		8.54
	1 : 2		7.84		7.81 7.80		8.28
2,4-Dinitrophenol	1 : 0		9.05		8.49	7.45	10.7
	1 : 1		8.79		8.55–8.62	7.29 7.24	8.98
	1 : 2		8.79		8.55–8.62	7.29 7.24	8.65
2,4,6-Trinitrophenol	1 : 0		9.10		9.10		11.0
	1 : 1		8.91		8.91		8.64
	1 : 2		8.91		8.91		8.40
Nitrobenzene	1 : 0	8.11	7.50	7.66	7.50	8.11	
	1 : 1	8.09	7.48	7.72	7.48	8.09	

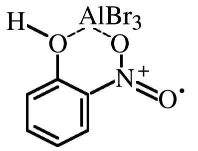
culations, we used the 6-31G* basis set. The calculated ΔH_t was 72.7 kJ mol^{-1}.



III



IV



V

To find the structure of the complexes, we recorded their ^{1}H and ^{13}C NMR spectra. The ^{1}H chemical shifts of the initial phenols and complexes are listed in the table. The specific feature of the spectra of free *o*-nitrophenols is that the signals of hydroxylic protons are shifted downfield (10–11 ppm) due to the presence of intramolecular hydrogen bond [10], contrary to phenols associated by intermolecular bonds (4–5 ppm) [2].

Attempts to obtain a complex of 2-nitrophenol with $AlBr_3$ in inert solvents at room temperature failed, since the reaction is complicated by the release of gaseous hydrogen bromide. The most suitable solvent was nitromethane.

The influence of $AlBr_3$ on the chemical shifts of nitro compounds bound into in a complex was demonstrated for nitrobenzene as an example. The ^{1}H NMR spectrum of its complex shows no differences from that of free nitrobenzene, except a certain broadening of the signals. This fact suggests that, in coordination with aluminum bromide, the charge on the nitrogen atom of the nitro group does not noticeably change [11].

In the spectrum of a solution of 2-nitrophenol with $AlBr_3$ the ^{1}H signals are noticeably shifted upfield (not downfield, as it is observed for complexes of methylated phenols and naphthols) relative to the signals of the initial phenol. Hence, it can be assumed that the coordination mode of 2-nitrophenol differs from that of nitrobenzene and phenols. The signals with chemical shifts of 8.37 and 8.13 ppm (approximately 3 : 1) were assigned to hydroxyl protons of complex compounds, since they have integral intensities corresponding to one hydrogen atom each. Accidentally, the chemical shifts of the 1 : 1 and 1 : 2 complexes almost coincide; as a result, all the signals in the spectrum are broadened. The ^{1}H signal of 3-H (8.12 ppm, $J_{3,4}$ 8.55; $J_{3,5}$ 1.64 Hz in the initial phenol) is a doublet at 7.89 ppm; in this case, no Moler remote coupling is observed. The split triplet of 5-H gives broadened signal at 7.75 ppm. The hydrogen atoms 4-H and 6-H appearing in the form of a split doublet at 7.17 and triplet at 7.08 in the initial *o*-nitrophenol in the complex give an unresolved multiplet in the range 6.8–7.1 ppm.

On heating, hydrogen bromide is released from the solution as a result of formation of $2\text{-}NO_2\text{–}C_6H_4\text{–}O\text{–}Al_nBr_{3n-1}$, and the intensities of the signals at 8.37 and 8.13 ppm decrease. All other signals remain unchanged. This fact indicates that the chemical shifts of the complexes and aluminum salts are close. A similar fact has been noted previously [14]. After recording the spectrum, hydrogen bromide was passed with cooling through the resulting solution until its saturation. As a result, the intensities of signals of hydroxyl protons increased to the initial value. The absence of any other changes in the ^1H NMR spectrum after saturation of the solution with HBr suggests that the complex compounds are protonated neither via the ring nor via the functional groups.

To elucidate whether the complexes obtained are actually complexes of aci form **II**, we recorded the ^{13}C NMR spectrum of a solution of 2-nitrophenol with $AlBr_3$. We did not find a signal at 170–190 ppm (coordinated carbonyl group [15]), which suggests the absence of a system of double bonds >C=O and >C=N–. This fact is in good agreement with calculations and calorimetric measurements.

The effect of substituents on the complexation of *o*-nitrophenols was determined in the reactions of 2-nitro-4,6-dichloro-, 2,4-dinitro-, and 2,4,6-trinitrophenols with $AlBr_3$ in nitromethane.

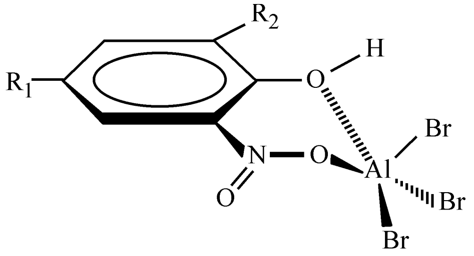
In the spectrum of a solution of 2-nitro-4,6-dichlorophenol with $AlBr_3$, the signal of 3-H protons is shifted upfield from 8.14 to 7.84 ppm, the signal of 5-H proton is split into two (7.81 and 7.80 ppm) but remains virtually at the same place. In addition, instead of the low-field (10.7 ppm) signal of the hydroxyl proton, two signals whose intensity corresponds to one proton appear in higher field at 8.54 and 8.28 ppm (ratio approximately 3 : 1).

The signal of 3-H in the spectrum of a solution of 2,4-dinitrophenol with $AlBr_3$ is shifted upfield from 9.05 to 8.79 ppm. The doublet of 6-H (7.45 ppm) is shifted to 7.25 ppm. The doublet of 5-H (8.49 ppm) transforms into a complex set of signals in the range 8.55–8.62 ppm, suggesting the existence of several complexes in the solution. Two signals of hydroxyl protons appear in the spectrum: at 8.86 ppm and in the range of the 5-H signal at 8.65 ppm. In the ^{13}C NMR spectrum of the 2,4-dinitrophenol complex, there are signals at 162.8 (C_1), 131.0 (C_2), 134.3 (C_3), 137.0 (C_4), 125.3 (C_5) and 125.3 ppm (C_6). As in the preceding case, the signals in the range 170–190 ppm corresponding to the coordinated C=O group [15] were not found.

A similar pattern is observed in the reaction of 2,4,6-trinitrophenol with $AlBr_3$. It is the common opinion that the yellow color of 2,4,6-trinitrophenol solution is caused by appearance of an aci structure (type **II**) [16]. However, both ^1H and ^{13}C NMR signals correspond to picric acid in the phenolic form. Upon addition of $AlBr_3$, the color of the solution becomes deeper and the signal of aromatic protons is insignificantly shifted upfield. In parallel, two signals appear at 8.65 and 8.40 ppm, whose intensity corresponds to one proton.

Thus, the NMR spectra show that, irrespective of the structure of *o*-nitrophenols, two complexes in which the aromaticity of the benzene ring is preserved are formed with $AlBr_3$.

The whole set of the results obtained is well accounted for by formation of chelate complexes. When considering a model of chelate complex 1 : 1 **V** (complex 1 : 2 has apparently the same structure excluding the fact that aluminum bromide is dimer), it is seen that $AlBr_3$ should be situated between OH and NO_2 groups. This arrangement of $AlBr_3$ will result in rupture of the intramolecular hydrogen bond. Due to the formation of a chelate, the fractional positive charge on the oxygen atom of the hydroxy group will be lower than that in the oxonium complex; therefore, the shift of hydroxyl proton in the NMR spectra will be intermediate between the shift in free phenols and oxonium complexes, which is actually observed. The upfield shift of aromatic protons in complexes is apparently caused by the anisotropic effect of aluminum atom in the resulting six-membered ring.



V

The model suggested is additionally confirmed by the ^{17}O NMR spectra obtained previously for the complex $2\text{-}NO_2\text{–}C_6H_4\text{–}OH \cdot BCl_3$ [8]. In the spectrum of the complex, two signals appear at 560 and 406 ppm, instead of one signal of two oxygen atoms of nitro group (569 ppm). The signal of oxygen atom of the hydroxy group is shifted after coordination from 94 to 144 ppm, i.e., one oxygen atom of nitro group and oxygen atom of hydroxy group are involved in the coordination. This fact can be explained by assuming that a chelate complex of *o*-nitrophenol with BCl_3 is formed.

EXPERIMENTAL

The phenols used had the following mp (°C): 2-nitrophenol 45.3–45.7, 4-nitrophenol 113–114, 2-nitro-4,6-dichlorophenol 124–125, and 2,4-dinitrophenol 115–116. Nitromethane was dried and distilled at bp 102–103°C. The complexes were prepared by dissolution of aluminum bromide in nitromethane with subsequent addition of nitrophenols in a molar ratio of 2 : 1 to the suspension cooled to –20°C. The enthalpy of the reaction of 2-nitrophenol with aluminum bromide was determined by the procedure described in [12]. The solutions of complexes were saturated with hydrogen bromide at 0°C. The ^{1}H NMR spectra were recorded on a Bruker Avance 200 spectrometer. In recording the spectra of free nitrophenols, TMS was used as an internal reference; the spectra of complexes were recorded using nitromethane as a reference (4.28 ppm).

CONCLUSIONS

(1) Calorimetric measurements show that *o*-nitrophenol forms 1 : 1 and 1 : 2 complexes with aluminum bromide, with the enthalpy of formation of 31.6 and 20.1 kJ mol^{-1}, respectively.

(2) Quantum-chemical calculation estimates the enthalpy of transition of *o*-nitrophenol into the aci form at 72.7 kJ mol^{-1}.

(3) The experimental data obtained indicate that *o*-nitrophenols in complexes with the chelate structure remains aromatic.

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