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Reactions of Phenols with Lewis Acids:
XIX.* Complexes of *ortho*-Quinones and Benzenediols with Aluminum Bromide

A. V. Golounin, Yu. S. Shchedrin, and V. A. Fedorov

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

Abstract—Enthalpies of the reactions of Al_2Br_6 with 3,5-di-*tert*-butyl-1,2-benzoquinone, 1,2-naphthoquinone, 9,10-phenanthrenequinone, dimedone, isomeric benzenediols, and 4-methoxyphenol have been determined.

Unlike common ketones, complex formation of *ortho*-quinones with most multivalent metal halides is complicated by electron transfer from the acceptor to donor [2–4]. It may appear that the nature of donor–acceptor interaction changes. In fact, there is no conflict provided that the formation of paramagnetic complexes is considered to be the result of secondary processes involving electron density redistribution inside the complex. As was shown in [2–4], paramagnetic complexes of *ortho*-quinones are formed in polar solvents with 2 equiv of metal halide. A scheme was proposed which explains the reaction between *ortho*-quinones and Al_2Br_6 (Scheme 1). According to Scheme 1, aluminum halide dimer first dissociates into $[AlBr_2]^+$ cation and $[AlBr_4]^-$ anion. The latter acts as a source of electron, i.e., it is a donor. *ortho*-Quinone oxidizes $[AlBr_4]^-$ anion, thus being converted into semiquinone radical which then reacts with $[AlBr_2]^+$. Free monomeric $AlBr_3$ and atomic or molecular bromine remain in the solution.

In the framework of our studies on the phenol complexes with aluminum halides it was interesting to examine the thermochemistry of the above process, taking into account that relevant published data are absent. In addition, we expected to obtain new information which could clarify the mechanism of reactions with polyatomic phenols differing by arrangement of the hydroxy groups. As follows from Scheme 1, the complex formation with *ortho*-quinones is an intricate process, and it is impossible to distinguish a stage responsible for the formation of only dative bond. Therefore, we measured the overall heat effect ΔH:

$$\Delta H = \Delta H_{exp} + 0.5\Delta H_{Al_2Br_6} - \Delta H_{solv} + \Delta H_{Hlg}.$$

Here, ΔH_{exp} is the enthalpy of reaction determined experimentally, $0.5\Delta H_{Al_2Br_6}$ is the enthalpy of dissociation of alumine bromide dimer, ΔH_{solv} is the enthalpy of solvation, and ΔH_{Hlg} is the heat effect of bromination.

According to the data of calorimetric titration of a solution of aluminum bromide with quinones, a 1:2 adduct is formed initially. Provided that the amount

Scheme 1.

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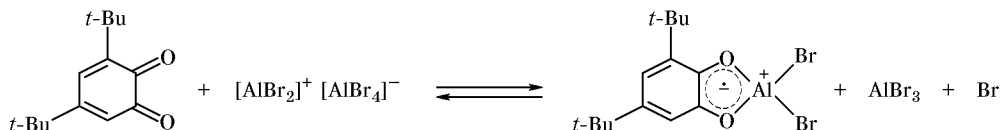
* For communication XVIII, see [1].

of quinone is sufficient, the 1:2 adduct is converted into 1:1 adduct. The enthalpy of the reaction with quinones turned out to be much greater than that found for β-diketones. In particular, the ΔH_{exp} value for 3,5-di-*tert*-butyl-1,2-benzoquinone exceeds the corresponding value for dimedone by 66.1 kJ/mol. A sharp increase of the heat effect in the titration of *ortho*-quinones as compared to diketones is explained by the facts that (1) *ortho*-quinones form more stable chelates, (2), the coordinated organic ligand acquires an aromatic character, and (3) the complex formation process is accompanied by side bromination.

It was recommended to generate semiquinone radicals from *ortho*-quinones with the aid of Al_2Br_6 in acetone or other polar solvents [4, 5]. However, aluminum bromide was shown to irreversibly form a 1:1 strong complex with acetone ($\Delta H_c = 102.6$ kJ × mol^{-1} [5]). Therefore, the formation of semiquinolates in acetone should involve concurrent coordination of *ortho*-quinones to the AlBr$_3$–acetone complex. The absence of [AlBr$_4$]$^-$ ions in acetone and other aprotic polar solvents allows us to rule out Scheme 1.

The initial formation of a triple complex including *ortho*-quinone does not fit the above-discussed scheme. Obviously, in inert solvents the dimer Al$_2$Br$_6$ coordinates at one carbonyl oxygen atom of *ortho*-quinone **I**, yielding 1:2 complex **II**. Electron density is transferred from the coordinated oxygen atom to the benzene ring to give dipolar ion **III**. The latter is then converted into chelate **IV**. The positively charged oxygen atom in **IV** acts as oxidant. Its positive charge is compensated by electron transfer from the nearest bromine atom of aluminum bromide. A three-center four-electron bond is formed between the oxygen and aluminum atoms in the chelate ring, giving rise to semiquinone radical **V**. An additional bromine atom is released in the presence of free *ortho*-quinone, and brominated aluminate **VI** is formed (Scheme 2).

We previously found that alkylated 1,2-benzene-diols readily react with aluminum bromide, yielding the corresponding aluminates [6]. Presumably, the formation of chelate is more favorable than formation

Table 1. Enthalpies of the reaction of *ortho*-quinones with AlBr$_3$ (bromobenzene, 16°C)

Quinone	ΔH, kJ/mol
Dimedone	105.1
1,2-Naphthoquinone	146.9
9,10-Phenanthrenequinone[a]	154.1
3,5-Di-*tert*-butyl-1,2-benzoquinone	171.2

[a] In CH$_2$Br$_2$.

Table 2. Enthalpies of the reaction of benzenediols with Al$_2$Br$_6$: ΔH_1 (1:1) and ΔH_2 (1:2) (bromobenzene, 16°C)

Phenol	ΔH_1, kJ/mol	ΔH_2, kJ/mol
4-Methoxyphenol	67.4	87.1
1,4-Benzenediol	67.4	86.7
1,3-Benzenediol	67.4	97.6
1,2-Benzenediol	98.4	132.3
1,2-Dihydroxy-naphthalene		130.6

of a dative bond. To confirm the above assumption, we performed calorimetric titration of benzenediols. The results are given in Table 2. The enthalpies of the reactions of AlBr$_3$ with 1 equiv of 4-methoxyphenol, hydroquinone, and resorcinol are almost similar. This indicates formation of similar complexes. The reaction of AlBr$_3$ with pyrocatechol is characterized by much greater heat effect. Obviously, 1,2-benzenediol, like *ortho*-quinone, gives rise to formation of chelate ring. However, unlike quinones, hydroxy protons in 1,2-benzenediol can be replaced to release hydrogen halide into the system. The presence of the conjugate acid H$^+$[AlBr$_4$]$^-$ promotes electrophilic replacement of the substituent in alkylpyrocatechols [6] (Scheme 3). Probably, analogous transformations occur in the titration of 1,2-dihydroxynaphthalene with Al$_2$Br$_6$, for the enthalpy appreciably increases as the temperature of titration rises from 5 to 16°C.
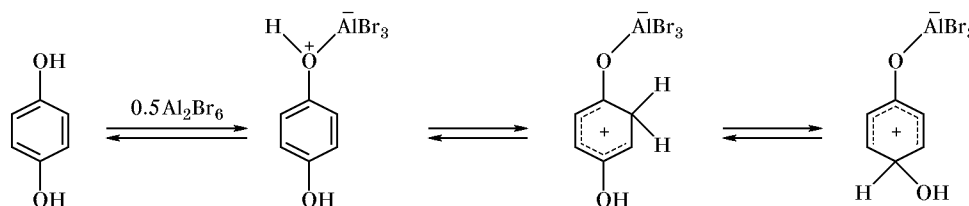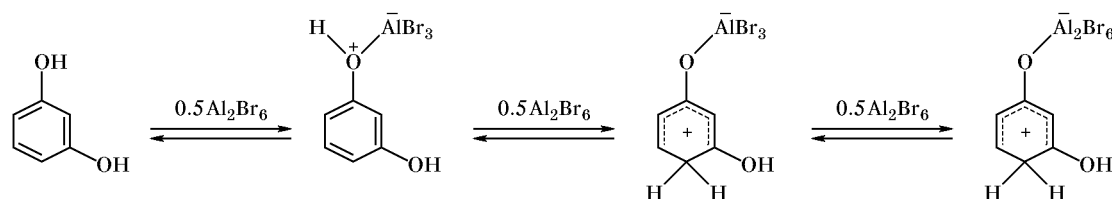
Scheme 2.
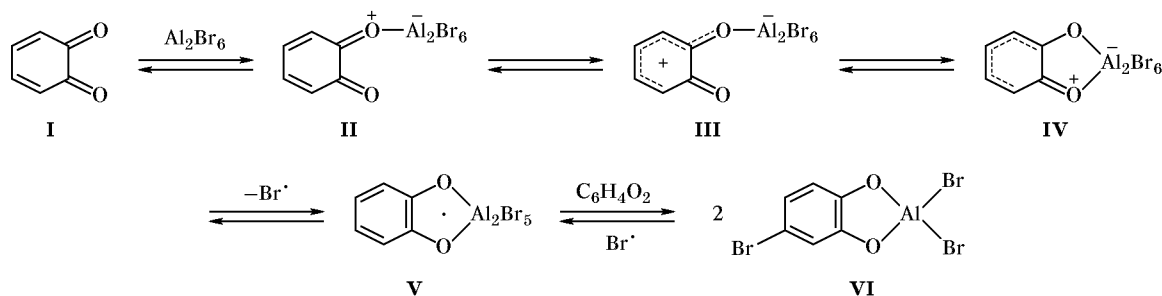
Scheme 3.
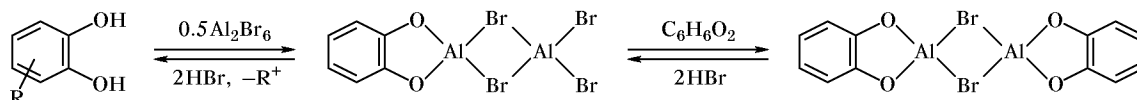
Scheme 4.

Scheme 5.

The reactions of Al_2Br_6 with hydroquinone and resorcinol differ essentially from the reaction with pyrocatechol. Proton migration from the hydroxy complex of hydroquinone to the benzene ring should give two thermodynamically unstable dipolar ions in which the free hydroxy group occupies unfavorable position. As a result, the equilibrium is displaced toward the complex involving aromatic hydroxy form (Scheme 4). The reaction of Al_2Br_6 with 4-methoxyphenol follows an analogous path. Therefore, the enthalpies of the reactions of Al_2Br_6 with hydroquinone and 4-methoxyphenol almost coincide.

By contrast, proton transfer from the hydroxy complex derived from resorcinol leads to a stable dipolar ion. For that reason resorcinol gives stable complexes of the oxo form even with weak acceptors [7]. Addition of the second molecule of $AlBr_3$ produces further stabilization of the dipolar ion ($\Delta H = 97.6$ kJ/mol; Scheme 5). It should be noted that an analogous transformation of 3,5-dimethylphenol into the complex of the ketone tautomer is characterized by an enthalpy of 92.1 kJ/mol [8].

We can conclude that complex formation of $AlBr_3$ with *ortho*-quinones and isomeric benzenediols takes different paths, depending on the arrangement of the hydroxy groups. *ortho*-Quinones and 1,2-benzenediol give rise to chelate structures, whereas 1,4-benzenediol and 4-methoxyphenol give complexes of the aromatic hydroxy form. The complex with resorcinol involves tautomeric ketone form. These differences are clearly observed in thermochemical measurements.

EXPERIMENTAL

The calorimetric titration was performed in a dry atmosphere at 16°C; the solvents were dried by the procedures described in [9]. The following compounds were used: dimedone, mp 145–148°C; 1,2-naphthoquinone, mp 115–120°C; 9,10-phenanthrenequinone, mp 206–207°C; 3,5-di-*tert*-butyl-1,2-benzoquinone, mp 113–114°C; hydroquinone, mp 169–170°C, resorcinol, mp 110–111°C; pyrocatechol, mp 105–106°C; and 4-methoxyphenol, mp 52–53°C.

In the calculation of the enthalpies of complex formation, the heat of dissociation of the dimer Al_2Br_6 was assumed to be equal to 55.7 kJ/mol [10], and the enthalpy of solvation, 21 kJ/mol [11]. The ΔT values were measured with an accuracy of ±0.01°C (the temperature was maintained with the same accuracy); and the ΔH_{exp} values were determined with an accuracy of ±2 kJ/mol.

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