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Complexes of Cyclohexadienones with Aluminum Bromide

Yu. S. Shchedrin and A. V. Golounin

Krasnoyarsk Institute of Chemistry and Chemical Technology, Siberian Division,
Russian Academy of Sciences, Krasnoyarsk, Russia
Siberian State Technological University, Krasnoyarsk, Russia

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Abstract—Saturated and aromatic monofunctional ketones form with $AlBr_3$ only 1 : 1 adducts, β-diketones bind 2 mol of $AlBr_3$, and methylated cyclohexadienones form both 1 : 1 and 1 : 2 complexes.

Ample physicochemical evidence shows that in donor–acceptor complexes of ketones with metal halides the former function as monofunctional bases [1]. Systematic studies on the thermochemistry of $AlBr_3$ reaction with a series of ketones allowed an interrelationship between the enthalpy of complex formation and the electronic and steric effects of groups adjacent to the carbonyl function to be established [2, 3]. However, 1 : 2 complexes of ketones have also been reported [4–6]. Furthermore, the isomerization of polymethylated phenols, initiated by complex formation, have been treated in terms of formation of 1 : 2 complexes between cyclohexadienones and $AlBr_3$ [7, 8]. It still not quite clear, whether aromatic and saturated ketones are capable, under certain conditions, of forming 1 : 2 complexes or the above findings are a result of imperfect analytical techniques and experimental errors.

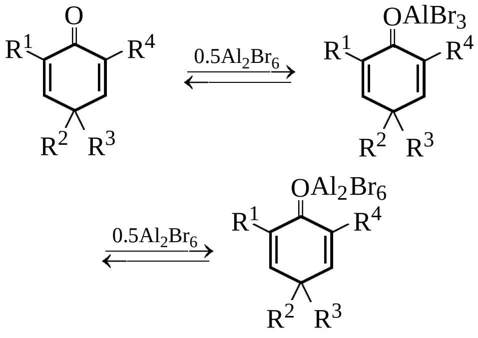
To find out if 1 : 2 adducts can actually be formed, we performed calorimetric titration of a series of saturated, aromatic, and unsaturated ketones with $AlBr_3$ (direct and back) in a bromobenzene solution. The enthalpies were calculated by the following equation (see also [8]), and the experimental results are listed in the table.

$$\Delta H_c = \Delta H_e + 0.5\ \Delta H(Al_2Br_6) - \Delta H_S.$$

Here ΔH_c (kJ/mol) is the enthalpy of complex formation, ΔH_e is the experimental enthalpy, ΔH (Al_2Br_6) is the enthalpy of bond cleavage in the dimer Al_2Br_6, and ΔH_S is the enthalpy of solvation of the complex.

As judjed from the calorimetric titration curves, monofunctional aliphatic and aromatic ketones **I**–**IV**, including benzophenone (**I**) which has been mentioned in [4–6] as a ketone capable of forming a 1 : 2 complex, give exclusively 1 : 1 complexes with enthalpies of ~100 kJ/mol even in the presence of a considerable excess of $AlBr_3$.

According to [7, 8], we might expect formation of both 1 : 1 and 1 : 2 complexes from cyclohexadienones and $AlBr_3$.



Entalpies of formation of 1 : 1 (1 : 2) complexes of ketones with $AlBr_3$ [bromobenzene, 16°C (kJ/mol)[a]]

Ketone	$-\Delta H_e$	$-H_c$
Benzophenone (**I**)	64.9	99.7
Acetophenone (**II**)	65.1	99.9
Ethyl methyl ketone (**III**)	65.7	100.5
Cyclohexanone (**IV**)	66.6	101.3
Acetylacetone (**V**)	66.2	100.0
5,5-Dimethylcyclohexane-1,3-dione (**VI**)	70.3	105.1
4-Dichloromethyl-4-methyl-2,5-cyclohexadienone (**VII**)	65.8 (122.2)	100.6 (157.0)
4-Dichloromethyl-2,4,6-trimethyl-2,5-cyclohexadienone (**VIII**)	66.6 (123.5)	101.4 (158.3)
6-Dichloromethyl-2,3,4,5,6-pentamethyl-2,4-cyclohexadienone (**IX**)	69.0 (128.0)	103.8 (162.8)
2-Dichloromethyl-2-methyl-1,2-dihydronaphthalen-1-one (**X**)	(95.4)	(130.2)

[a] Parenthesized are ΔH_{e2} and ΔH_{c2} values.

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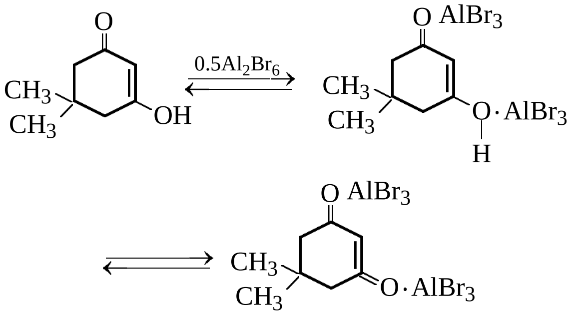
The plot of Δt against the molar fraction of $AlBr_3$ in cyclohexadienone solutions gives evidence for the above speculations. Actually, the plot for titration of ketone **VII** with a solution of $AlBr_3$ shows an inflection point at a 1:1 reactant ratio, while that for titration of a solution of $AlBr_3$ with a solution of ketone **VII** shows an inflection point at a 1:2 ratio. Further increase in the concentration of $AlBr_3$ in the solution produces no heat effect, implying lack of formation of more complex adducts.

Earlier we showed that the basicity of methylated cyclohexadienones is insensitive to the number and position of methyl substituents in the ring [8–10]. It seemed interesting to find out if this tendency is preserved in reactions of substituted cyclohexadienones with aluminum bromide. To this end, we determined the enthalpies of these reactions for cyclohexadienones **VII**–**IX** with various degree of methylation.

The enthalpies of formation of the 1:1 and 1:2 adducts of ketone **VII** are 100.6 and 157.0 kJ/mol, respectively. The same pattern is characteristic of the other methylated cyclohexadienones; therewith, numerically, the enthalpies vary only slightly (see table), thus providing evidence for the assumptions in [7, 8]. Note, however, that the ΔH_c value for the reaction of 2-dichloromethyl-2-methyl-1,2-dihydronaphthalen1-one (**X**) with 2 mol of $AlBr_3$ already differs from those for complexes of methylated cyclohexadienones.

It might be expected that reactions of β-diketones with $AlBr_3$ would give 1:2 complexes, and their enthalpies of formation would be close to ΔH_c for 1:2 cyclohexadienone complexes. The experiment shows that the reaction of acetylacetone **V** with excess Al_2Br_6 results in evolution of 100.0 kJ/mol, which is roughly equal to the enthalpy effect of 1:1 adduct formation, even though the composition of the resulting complex is 1:2. The contradiction if lifted is one takes into account that the ketone is bifunctional and, consequently, like monofunctional ketones, has 1 mol of the halide per one carbonyl group. The fact that β-diketones are enolized in solutions only slightly affects the enthalpy effect, since the keto–enol isomerization of these compounds is accompanied by weak enthalpy changes.

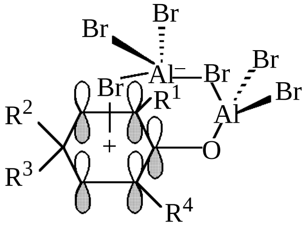


According to titration data, dimedone (**VI**) forms a 1:2 adduct with an enthalpy 1of 05.1 kJ/mol, which is one more evidence for the general tendency of complex formation of ketones.

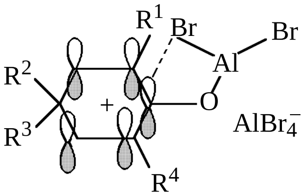
The observed differences in the behavior of saturated, aromatic, and unsaturated cyclic ketones in their reactions with $AlBr_3$ are explained, first, by complexation-induced structural changes of ketones. In saturated ketones, coordination with $AlBr_3$ produces transformation of the double C=O bond into sesquialteral {as evidenced by the fact that ν(C=O) shifts from 1690 cm^{-1} in free ketones to 1560–1570 cm^{-1} in coordinated ketones [4]}, and, therewith, the positive charge is localized on the carbonyl carbon atom.

Cyclohexadienones in the process under consideration convert into particles structurally similar to hydroxybenzenonium ions [11], where the positive charge is delocalized over the conjugation system.

Moreover, in hydroxybenzenonium adducts the Al_2Br_6 fragment can rotate about the O–Al bond and thus stabilize in the dienyl ring plane either by electrostatic or *p*,*π* interaction. The Al_2Br_6 dimer may well disproportionate with liberation of the $AlBr_4^-$ anion. This situation is illustrated by structures **A** and **B**.



A



B

Assignment to adducts of structure **A** or **B** can be based on the ^{27}Al NMR and IR spectra. As shown in [6], the IR spectrum of the complex of hexamethyl-2,5-cyclohexadienone contains no absorption band at 450 cm^{-1} (anion $AlBr_4^-$). Moreover, the ^{27}Al NMR spectrum [15] shows no $AlBr_4^-$ signal, implying that the complex is most likely dipolar.

To conclude, monofunctional saturated and aromatic ketones, as well as β-diketones form with $AlBr_3$ adducts containing 1 mol of the aluminum halide per each carbonyl group. The energy of the donor–acceptor bond in the complexes is 100±2 kJ/mol. Methylated cyclohexadienones can form both 1:1 and 1:2 complexes. The enthalpy of formation of the 1:1 cyclohexadienone complexes is 102±2 kJ/mol, and that of the 1:2 complexes, 158±2 kJ/mol.

EXPERIMENTAL

6-Dichloromethyl-2,3,4,5,6-pentamethyl-2,4-cyclohexadienone, 4-dichloromethyl-2,4,6-trimethyl-, 4-dichloromethyl-4-methyl-2,5-cyclohexadienones, as well as 2-dichloromethyl-2-methyl-1,2-dihydronaphthalen-1-one were synthesized by chloromethylation of pentamethyl-, 2,4,6-trimethyl-, and 4-methylphenols, as well as 2-methyl-1-naphthol [12].

Calorimetric titration was performed in a dry atmosphere by the direct and back procedures at 16°C. The solvent was C_6H_5Br (C_p 0.23). The enthalpies of dimer dissociation and solvation were taken to be 55.7 [13] and 21 kJ/mol [14], respectively. The temperature measurements and thermostating were performed to an accuracy of ±0.01°C. The ΔH values were determined to an accuracy of ±2 kJ/mol.

The reagents used had the following boiling and melting points (°C): acetophenone 202, benzophenone 306, cyclohexanone 157, 5-dichloromethyl-2,3,4,5,6-pentamethyl-2,4-cyclohexadienone 57.5–58.5, 4-dichloromethyl-2,4,6-trimethyl-2,5-cyclohexadienone 37.5–38.5, 4-dichloromethyl-4-methyl-2,5-cyclohexadienone 53–55, 2-dichloromethyl-2-mehyl-1,2-dihydronaphthalen-1-one 67–68, 3-hydroxy-5,5-dimethyl-2-cyclohexenone 145–146, and acetylacetone 140.

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