Russian Journal of General Chemistry, Vol. 71, No. 6, 2001, pp. 965–967. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 6, 2001, pp. 1027–1029.

Retro-Claisen Cleavage of the β-Dicarbonyl Ligand in Alcoholysis of Group IVB Metal Chelates

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Received January 10, 2000

Abstract—Chelates of titanium, zirconium, and hafnium with β-dicarbonyl compounds react with butyl, amyl, and octyl alcohols to give metal alkoxides. The reaction is accompanied by retro-Claisen cleavage of the ligand. The reactivity of the chelates was studied in relation to the ligand structure, nature of the metal, and reaction temperature. The reaction mechanism is discussed.

Metal chelates can undergo chemical transformations resulting in changes in the coordination state of the metal and cleavage of the ligand. This factor significantly affects the thermal stability, reactivity, catalytic activity, and other properties of the chelates. Alcoholysis of metal chelates with β-dicarbonyl ligands is studied poorly.

As early as 1957, Freidlina *et al.* [1] showed that alcoholysis of tetrakis(acetylacetonato)zirconium with butyl and benzyl alcohols yields, respectively, zirconium butoxide and benzyloxide; the ligand decomposition products were not studied. Later, when studying thermal decomposition of titanium alkoxy chelates and alcoholysis of titanium bis(alkoxycarbonylacetonate) with isoamyl alcohol, we found [2] that alcoholysis with excess alcohol (or with alcohol released in decomposition of the alkoxy chelate) yields the corresponding titanium alkoxide and isoamyl acetate (in the case of acetylacetone, acetone and alkyl acetate) as products of the retro-Claisen cleavage of the chelating ligand. Wakeshima *et al.* [3] found that reactions of tetrakis(acetylacetonato)zirconium with alcohols yield zirconium dialkoxybis(acetylacetonates), acetone, and alkyl acetate.

The goal of this paper was to reveal the influence on alcoholysis of the structure of Group IVB metal chelates with β-dicarbonyl ligands.

In solutions of alcohols ROH, Group IVB metal chelates with bidentate univalent ligands L can exist in various forms: $M(OR)_3L$, $M(OR)_2L_2$ (M = Ti, Zr, Hf), $M(OR)L_3$, and ML_4 (M = Zr, Hf). In this work we studied alcoholysis of titanium dialkoxybis(acetylacetonates) and -bis(alkoxycarbonylacetonates) and of zirconium and hafnium tetrakis(acetylacetonates). Alcoholysis of these chelates with excess alcohol on heating yields, irrespective of the nature of the metal and ligand structure, metal alkoxides and products of the retro-Claisen cleavage of the ligand by the following scheme (Tables 1, 2):

M = Ti, Zr, Hf; R = *n*-Bu, *n*-Am, *i*-Am, *n*-C_8H_{17}; R' = CH_3, *i*-AmO, *n*-$C_8H_{17}O$.

As judged from the yields of the resulting alkoxides, the retro-Claisen reaction occurs to a greater extent with higher-boiling alcohols and, in the Ti–Zr–Hf series, with zirconium and hafnium. The yield of alkyl acetates is not quantitative, which means that in all cases the ligand cleavage is incomplete. The yield of acetone in all cases is lower than that of the corresponding alkyl acetate, which suggests participation of acetone in side reactions. Since the metal alkoxides were isolated in a partially hydrolyzed form, one of such reactions can be condensation of acetone with release of water. Condensation occurs apparently to a large depth, as no mesityl oxide or phorone was detected in the distillates. On the other hand, acetylacetone is also partially involved in these condensations (the IR and ^1H NMR spectra of the resulting alkoxides contained no bands or signals corresponding to the carbonyl and acetyl groups).

Thus, the retro-Claisen cleavage is the main but not the only decomposition pathway of β-dicarbonyl ligands.

Formation (and hence subsequent condensation) of acetone can be excluded by using alkoxycarbonylacetonates as chelating ligands. Indeed, in alcoholysis of

Table 1. Alcoholysis of Group IVB metal acetylacetonates with *n*-amyl alcohol[a]

Chelate	Amount of cleavage product, mol mol^{-1} ligand		Yield of alkoxide, %
	AcOAm	acetone	
$Ti(OR)_2(acac)_2$	0.66	0.47	31
$Zr(acac)_4$	0.82	0.36	65
$Hf(acac)_4$	0.41	0.21	52

[a] The chromatographic peaks of acetylacetone and excess amyl alcohol are not resolved.

Table 2. Alcoholysis of Group IVB metal acetylacetonates with *n*-octyl alcohol

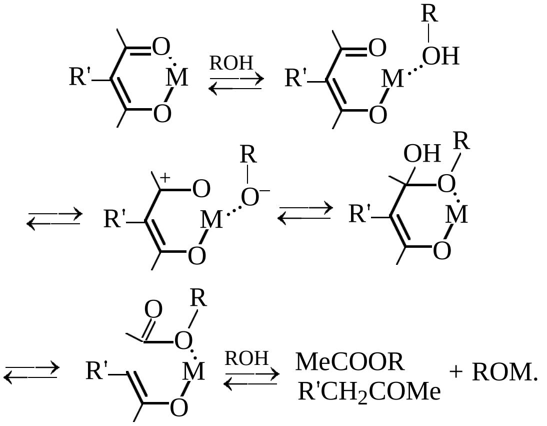
Chelate	Amount of cleavage product, mol mol^{-1} ligand		Yield of Hacac, mol mol^{-1} ligand	Yield of alkoxide, %
	$AcOC_8H_{17}$	acetone		
$Ti(OR)_2(acac)_2$	0.84	0.83	0.13	72
$Zr(acac)_4$	0.77	–	0.06	81
$Hf(acac)_4$	0.75	–	–	95

titanium alkoxycarbonylacetonates the yields of alkoxides are higher (Table 3).

The course of the retro-Claisen cleavage is governed by the reaction temperature rather than the length of the alcohol molecule. When the alcoholysis is performed with butanol at 200°C (under pressure), the yield of titanium butoxide is practically the same as the yield of the alkoxide in reaction with octanol at ambient pressure. With titanyl acetylacetonate, the reaction is essentially similar. Obviously, in this case the alkoxide cannot be isolated, but all the products of the retro-Claisen cleavage are clearly detected in the distillate.

Let us discuss the reaction mechanism.

Uehara *et al.* [4, 5] studied alcoholysis of 3-substituted acetylacetonates in the presence of transition metal ions and suggested the following mechanism involving direct decomposition of the chelate:



According to this scheme, 3,3-disubstituted β-diketone derivatives should not undergo cleavage, as they cannot form the chelates shown in the above scheme. However, 3,3-dimethylacetylacetone does undergo alcoholysis under the same conditions [5]. This contradiction can be lifted by assuming that the reactive species in alcoholysis is a chelate containing two coordination bonds with the neutral ligand (such titanium chelates are known; they were reported for the first time by Tompson [6]). Then, the mechanism of the retro-Claisen cleavage can be presented as follows:

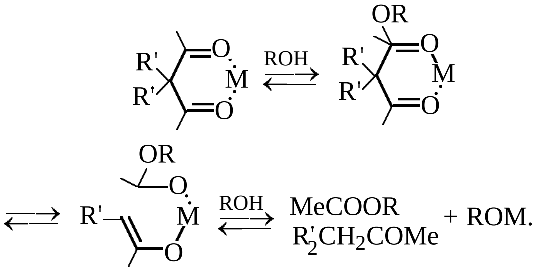


Table 3. Alcoholysis of titanium acetylacetonate and alkoxycarbonylacetonates

Chelate/alcohol	Amount of cleavage products, mol mol^{-1} ligand		Yield of alkoxide, %
	$AcOC_8H_{17}$	acetone	
$Ti(OR)_2(acac)_2/AmOH$	0.66	0.47	31
$Ti(OR)_2(AcCH_2COOAm\text{-}i)_2/i\text{-}AmOH$	0.15	0.005	50
$Ti(OR)_2(AcCH_2COOC_8H_{17}\text{-}n)_2/n\text{-}C_8H_{17}OH$	0.47	–	52

This process is more probable, since this mechanism can be operative with 3,3-disubstituted β-dicarbonyl compounds also. In our case, 3,3-dimethylacetylacetone also undergoes the retro-Claisen cleavage.

EXPERIMENTAL

Chelating agents and titanium alkoxides were distilled before use. Titanium alkoxy chelates were prepared from appropriate chemicals directly before the experiments. Titanyl acetylacetonate was prepared according to [7], and zirconium and hafnium acetylacetonates, according to [8].

Alcoholysis with butanol was performed in glass ampules in an autoclave, and alcoholysis with the other alcohols, at atmospheric pressure.

The alcoholysis products were analyzed with an LKhM-8MD chromatograph equipped with a thermal conductivity detector; the carrier gas was He, flow rate 50 ml min^{-1}; 2000 × 3-mm columns were packed with Chromaton N-AW-DMCS (0.16–0.20 mm) impregnated with 5% Carbowax 20M or 5% SE-30. The column temperature depended on the compounds to be analyzed. The substances were identified using appropriate references.

Reaction of dibutoxybis(butoxycarbonylacetonato)titanium with butanol. An autoclave was charged with 3.40 g of tetrabutoxytitanium, 3.16 g of butyl acetoacetate, and 5.92 g of butanol. The mixture was heated for 8 h at 200°C. After reaction completion, the low-boiling products were distilled off at atmospheric pressure, and the residue was vacuum-distilled. Yield of titanium butoxide 1.70 g (50%). The distillate contained, along with butanol, also butyl acetate.

Reaction of titanyl bis(acetylacetonate) with butanol was performed similarly; 2.62 g of the chelate and 7.50 g of butanol were taken. For chromatographic study, the mixture was distilled to dryness. The distillate contained butanol, acetone, and butyl acetate.

Reaction of titanium butoxide, butanol, and 3,3-dimethylacetylacetone was performed similarly; 3.40 g of titanium butoxide, 7.50 g of butanol, and 1.28 g of 3,3-dimethylacetylacetone were taken. In the reaction products, the initial diketone, methyl isopropyl ketone, and butyl acetate were detected.

Reactions of diamylbis(acetylacetonato)titanium, diisoamylbis(isoamyloxycarbonylacetonato)titanium, dioctylbis(octyloxycarbonylacetonato)titanium, tetrakis(acetylacetonato)zirconium, and tetrakis(acetylacetonato)hafnium with higher alcohols. Alcoholysis was performed at atmospheric pressure at the molar ratio chelate : alcohol = 1 : 10, with *n*-amyl, isoamyl, and *n*-octyl alcohols. The mixtures were refluxed for 1 h; the alcoholysis products were distilled off at atmospheric pressure.

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