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Novel Reactions of Metal Acetylacetonates with Formaldehyde in Relation to Formose Reaction

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The reaction of metal acetylacetonates with formaldehyde in water or methanol gave 4-hydroxy-3,3-bis(hydroxymethyl)-2-butanone and 5-oxa-3,3-bis(hydroxymethyl)-2-hexanone, respectively.

"Formose reaction",1) the base-catalyzed condensation of formaldehyde to produce the mixture of carbohydrates, has been the subject of interest. But the formation of complex products mixture limits the utility of this reaction, and urges us to improve the selectivity. Inorganic bases,2) organic bases,3) and clay have been used for the formose reaction, but there are few attempts to use metal complexes as the catalyst.4) Reported here are the attempts to use metal acetylacetonates for the formose reaction.

Into the solution of 0.90 g (30 mmol) of formaldehyde in 20 ml of water was added 1.0 mmol of metal acetylacetonate, and the mixture was heated at 60 °C for 20 h under N_2 atmosphere. After the removal of water and the unreacted formaldehyde, the products were trimethylsilylated and analyzed by gas chromatography(GC). From various metal acetylacetonates, the same product was obtained as a major product. The GC pattern was simple and the peak area of the main products exceeded 90% on the use of acetylacetonates of various kinds of metals such as Li, Mg, Ca, Al, Co(II), Mn(II), and Mn(III) as shown in Fig.1. The conversion5) of the formaldehyde was 8 - 28%.

The reaction mixture with $Co(acac)_2$ was treated with cation exchange resin and purified by column chromatography on silica gel(acetone/chloroform) to give the major product as a clear light-brown syrup. IR, ^1H and ^{13}C NMR spectra suggest the product to be 4-hydroxy-3,3-bis(hydroxymethyl)-2-butanone (**1**). **1** was confirmed by preparing authentic sample by the different method.6) Quantitative analysis of the silylated product by GC using n-tetradecane as an internal standard gave 0.056 g (0.38 mmol) of **1** from 1.0 mmol of $Co(acac)_2$.

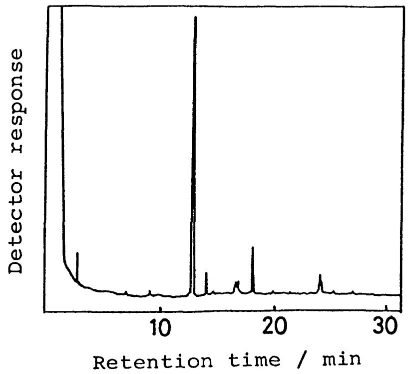
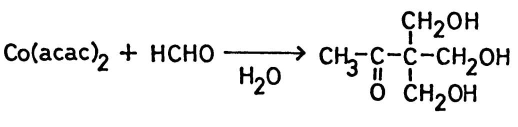


Fig.1. The gas chromatogram of the TMS derivative of the products obtained from $Co(acac)_2$/formaldehyde/H_2O at 60 °C for 20 h.



$$\mathrm{Co(acac)_2} + \mathrm{HCHO} \xrightarrow[\mathrm{H_2O}]{} \mathrm{CH_3{-}\underset{\overset{\|}{O}}{C}{-}\overset{CH_2OH}{\underset{CH_2OH}{C}}{-}CH_2OH}$$

1

The same procedure was followed using methanol as solvent. A different product was obtained as a single peak on gas chromatogram (selectivity by GC analysis; >90%) from acetylacetonates of various metals such as Mg, Ni(II), Co(II), Fe(II), Fe(III), Mn(II), and Mn(III) as shown in Fig.2. The product from Mn(III)(acac)$_3$ was treated similarly to give a syrup. IR spectrum of the syrup was similar to that of **1**. Molecular weight was obtained from C.I. mass spectrum (isobutane and ammonia) as 162, and the presence of -OCH$_3$, identified by ^{13}C-NMR spectrum [(CDCl$_3$) δ 58.767(q) ppm] suggested 5-oxa-3,3-bis(hydroxymethyl)-2-hexanone,(**2**), a novel compound. ^{1}H-NMR spectrum was consistent with the structure. The quantitative analysis of the silylated product by GC using pentaerythritol as an internal standard gave 0.046 g (0.28 mmol) of **2** from 1.0 mmol of Mn(acac)$_3$. The conversion of formaldehyde was 20%.

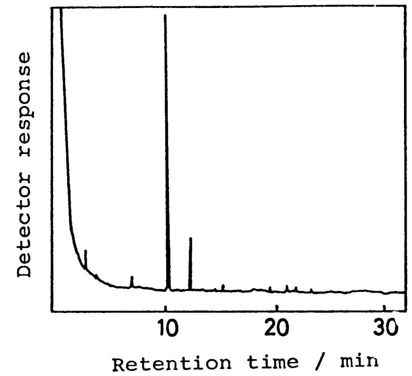
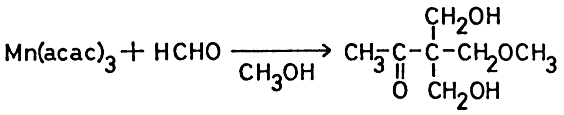


Fig.2. The gas chromatogram of the TMS derivative of the products obtained from Mn(acac)$_3$/formaldehyde/CH$_3$OH at 60 °C for 20 h.



$$\mathrm{Mn(acac)_3 + HCHO \xrightarrow[CH_3OH]{} CH_3-\underset{\underset{O}{\|}}{C}-\overset{\overset{CH_2OH}{|}}{\underset{\underset{CH_2OH}{|}}{C}}-CH_2OCH_3}$$

2

Since **1** and **2** have acetyl group, it is reasonable to consider that **1** and **2** are formed from C-C bond cleavage of the ligand and the condensation with formaldehyde and the solvent. The reaction clarified here is a new type of reaction of acetylacetone ligand. Though the mechanism is not clear now, it is interesting that only one OH group was methylated selectively by methanol. The selective condensations of the ligand with formaldehyde and the solvents reported here could lead to the finding of new catalysts or co-catalysts for the selective formose reaction.

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