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THE REACTION OF METAL ACETYLACETONATES WITH CHLORAL[1)]

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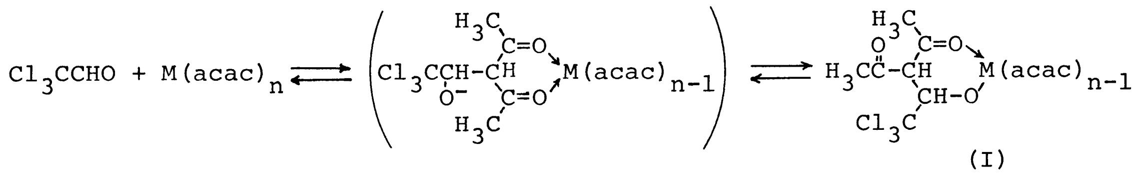
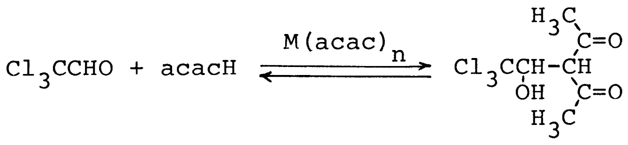
The reaction of metal acetylacetonate($M(acac)_n$) with chloral has been investigated from the viewpoint of the catalyses of $M(acac)_n$ in the crossed aldol reaction of chloral with acetylacetone, and in the polymerization of chloral.

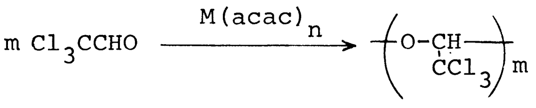
Metal acetylacetonate($M(acac)_n$) is known to have quasi-aromatic characters and to undergo electrophilic substitutions at the 3-position on the chelate ring.[2)] The present paper shows that $M(acac)_n$ also undergoes aldol reaction with chloral at the 3-position on the chelate ring and that the adduct I is an intermediate of $M(acac)_n$-catalyzed aldol reaction between chloral and acetylacetone (acacH), and that of retrograde aldol reaction of 3-(1-hydroxy-2,2,2-trichloroethyl) 2,4-pentanedione (A), and furthermore, an active species of $M(acac)_n$-induced polymerization of chloral.

 (1)

(I)

 (2)

(A)

 (3)

The Reaction of Chloral with $M(acac)_n$. Attempts to isolate the adduct I from reaction mixtures were unsuccessful, presumably because this complex was unstable and readily decomposed to chloral and $M(acac)_n$. However, there are several spectral evidences to support the existence of I in equilibrium with chloral and $M(acac)_n$. Powdered crystals of $Co(acac)_2$ and $Cu(acac)_2$ rapidly change their colors on exposure to the vapor of chloral from pink to blue and from blue to green, respectively. The infrared spectrum (KBr disk) shows the presence of $\nu_{C=O}$(saturated ketone) at 1700 cm^{-1}, which is not detectable in chloral or $M(acac)_2$(M=Co, Cu), independently. On standing the specimens in air, this band disappears with the restoration of color. The cycle can be repeated many times. The similar color change of Co(acac)$_2$ by the addition of chloral is also observed in tetrahydrofuran solution. The spectra of solutions containing constant amounts of Co(acac)$_2$ and varying quantities of chloral are shown in Fig. 1.

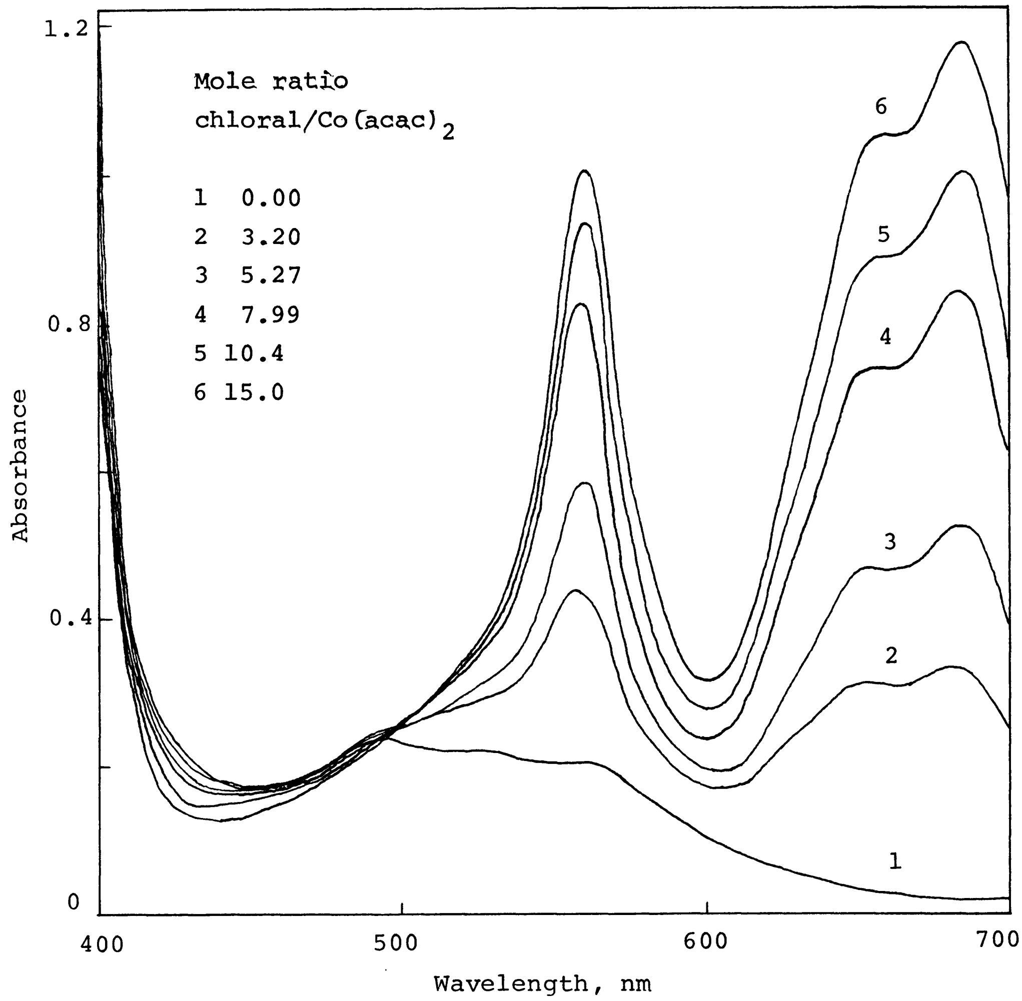


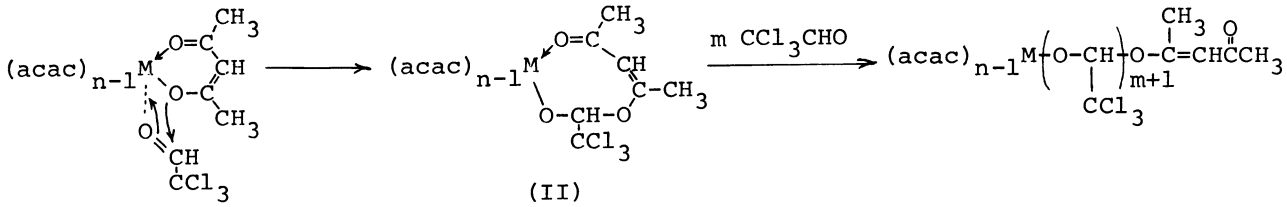
Fig. 1. Spectra of tetrahydrofuran solutions of Co(acac)$_2$ containing varying amounts of chloral. Concentration of chelate, $1.65\times10^{-2}M$.

From these results and another one (isolation of aldol condensate A and analysis of terminal group of polychloral, which will be described below), we tentatively propose an aldol condensate structure I for the M(acac)$_n$-chloral complex. However, the possibility of a charge-transfer complex, which may be formed by an electron transfer from M(acac)$_n$ to chloral, cannot be excluded.

Aldol Reaction between Chloral and Acetylacetone. To a mixture of 5.79 g (57.8 mmol) of acetylacetone and 8.48 g (57.5 mmol) of chloral, 0.339 mmol of M(acac)$_n$ (M= Mg^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}) is added and the solution is cooled on an ice bath for 24 hr. The product, which precipitates at this point, is poured into 20 m*l* of ligroin to give a white crystal of 3-(1-hydroxy-2,2,2-trichloroethyl) 2,4-pentanedione (A). The yield in the presence of Mg(acac)$_2$ is 91 %. Co(acac)$_3$ and Cr(acac)$_3$ are ineffective as the catalyst. mp 83°C (from benzene-ligroin). Found: C, 34.09; H, 3.62 %. Calcd for $C_7H_9O_3Cl_3$: C, 33.97; H, 3.67 %. IR spectrum (KBr disk): 3420(s), 3300(s), 1690(vs), 1410(m), 1360(s), 1320(m), 1275(w), 1180(s), 1150(s), 1090(s), 940(m), 830(w), 805 cm^{-1} (s). UV spectrum ($CHCl_3$): λ_{max} 290 nm, ε_{max} 140. NMR spectrum(CCl_4): 7.67τ(6H, singlet, $COC\underline{H}_3$), 5.35τ (3H, multiplet, $O\underline{H}$, $Cl_3CC\underline{H}(OH)$, and $C\underline{H}(COCH_3)_2$). IR and NMR spectra show the absence of the band or signal due to enol and the spectral evidence is compatible with structure A for the aldol condensate. It is interesting to note that A can exist only in keto form. The formation of A suggests that chloral reacts with $M(acac)_n$ at the 3-position of $M(acac)_n$ and that the intermediate I may be involved in the present aldol reaction. Aldol reaction of chloral with acetylacetone is also catalyzed by piperidine and gives the same product A in a yield of 85 %.

The aldol reaction is reversible and A is converted to chloral and acetylacetone in the presence of $M(acac)_n$ in chloroform. The retrograde reaction is confirmed from the change of the spectra (IR, UV, and NMR) of the reaction mixture, which show the formation of chloral and acetylacetone. The retrograde reaction can be followed conveniently by the measurement of UV absorption band (273 nm) of acetylacetone, because absorbance of A and chloral at 273 nm may be regarded as negligible in comparison with the absorbance of acetylacetone. The rate of the retrograde aldol reaction is found to be first order with respect to $M(acac)_n$, and the order of the activity of $M(acac)_n$ as the catalyst is as follows: $Mg^{2+} > Co^{2+} > Ni^{2+} > Zn^{2+} > Cu^{2+}$. This order is opposed to that of stability constants of $M(acac)_2$. $Co(acac)_3$ and $Cr(acac)_3$ are ineffective as the catalyst.

Initiation of Polymerization of Chloral. Otsu *et al.*[3] have reported that some $M(acac)_n$ can induce the polymerization of chloral and that a possible mechanism of initiation is as follows:



(II)

This mechanism, however, seems to be inconsistent with our aldol reaction described above. So, further experiments were carried out to rationalize the mechanism of initiation of the $M(acac)_n$-induced polymerization of chloral.

It was found that the order of activities of $M(acac)_n$ as the initiator of the polymerization[3] is essentially the same as obtained for the retrograde aldol reaction of A. Thus, the aldol reaction catalyzed by $M(acac)_n$ seems to be closely related to the initiation of polymerization of chloral. In order to confirm that the aldol reaction of chloral with $M(acac)_n$ occurs at the 3-position of $M(acac)_n$ prior to the initiation of polymerization, the effect of the replacement of the hydrogen atom at the 3-position of $Cu(acac)_2$ was investigated. Table 1 shows that the replacement of a hydrogen at the 3-position by *n*-butyl or benzyl group results in a markedly decreased rate of polymerization. On the other hand, the replacement at the 1-position results in a slight change of the rate.

A low molecular weight polymer was obtained by the polymerization with large amounts of $Co(acac)_2$ in tetrahydrofuran followed by thorough washings with acetone containing small amounts of hydrochloric acid to remove unreacted and terminal cobalt acetylacetonates. The IR spectrum of this polychloral shows the existence of the band due to keto form of β-diketone (saturated ketone) at 1695 cm^{-1} and the absence of the band due to unsaturated ketone.

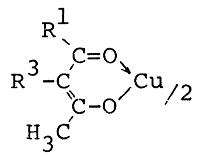
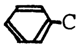
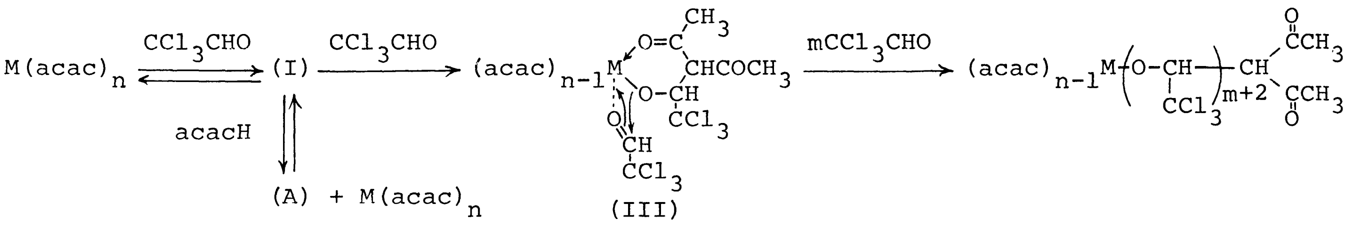


Table 1. Polymerization of Chloral by Copper(II) β-Diketonates
chloral: 5 m*l*, THF: 5 m*l*, chelate: 1.1×10^{-2} *M*, at 0°C.

Cu(II) β-Diketonate		Yield
R^1	R^3	(%/20 min)
CH_3	H	5.27
$CH_2{=}C(CH_3)$	H	3.26
$(CH_3)_3C$	H	4.83
CH_3	$CH_3CH_2CH_2CH_2$	0
CH_3	CH_2	0

In views of our studies on the $M(acac)_n$-catalyzed aldol reaction of chloral with acetylacetone and on the polymerization of chloral described above, the mechanism of initiation previously proposed should be somewhat ammended; Formation of the active alcoholate (I) by the aldol reaction is followed by the subsequent insertion of chloral to polychloral in a similar manner as metal alcoholate-induced polymerization of aldehyde.$^{4)}$ In the presence of large amounts of acetylacetone, I gives no polychloral but the aldol condensate (A). A more possible mechanism is as follows:



Detailed mechanistic study is now in progress.

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