Direct Synthesis of Tris(acetylacetonato)manganese(III)

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A concentrated solution of $K[MnO_4]$ undergoes a ready reaction with acetylacetone, in the absence of any buffer, giving a very high yield of the title compound, $[Mn(acac)_3]$. The pH of the solution, recorded immediately after the formation of crystalline $[Mn(acac)_3]$, was found to be *ca.* 5. Electron impact induced mass spectrometry showed the compound to be monomeric.

TRIS(ACETYLACETONATO)MANGANESE(III), $[Mn(acac)_3]$, has been known for a long time. The compound can be synthesised by air or chlorine oxidation of a basic solution of Mn^{2+} in the presence of acetylacetone. However, this method has not been used in practice because of the deleterious effect of alkali on the end product, as well as the chances of its contamination by chloride ions. Instead, the syntheses due to Cartledge [1] and Charles [2] involving the oxidation of Mn^{2+} with $K[MnO_4]$ in the presence of acetylacetone (Hacac) have been employed. The success of this method depends markedly on the pH. The reaction mixture requires to be regulated at pH *ca.* 5 by the addition of a large amount of sodium acetate. The use of sodium acetate in such quantities must surely contaminate the end product. In the course of our studies on the synthesis of manganese(III) compounds directly from $K[MnO_4]$,[3] we have developed a method for the synthesis of $[Mn(acac)_3]$ which does not require buffer. This note reports the direct synthesis of $[Mn(acac)_3]$.

EXPERIMENTAL

Reagent-grade potassium permanganate and acetylacetone were used in the synthesis. Infrared spectra were recorded on a Perkin-Elmer model 125 spectrophotometer. The oxidation state of manganese in the compound was determined iodometrically by reduction of a known amount of the compound with acidified potassium iodide solution followed by titration of the liberated iodine with standard sodium thiosulphate solution.

The mass spectrum was recorded on a Varian MAT CH-5 mass spectrometer. The sample was introduced into the ionisation chamber using a direct insertion probe. The operation conditions were electron energy,† 70 eV; source temperature, 20 °C; resolution, 1 000; and accelerating voltage, 8 kV. The essential features of the mass spectrum run at 20 °C are given in the Table. The mass spectrometric observations were made with the field of ionising current sufficiently strong to trap primary ions.

Synthesis of Tris(acetylacetonato)manganese(III), $[Mn(acac)_3]$.—A quantity of powdered $K[MnO_4]$ (5.0 g, 31.7 mmol) was dissolved in the minimum volume of water by slight warming over a steam-bath and the solution then filtered. Distilled acetylacetone (22.0 g, 220.0 mmol) was added to the solution with vigorous stirring. The mixture was stirred for *ca.* 5 min over a steam-bath and then allowed to cool for *ca.* 10 min. The dark brown-black shiny crystals of $[Mn(acac)_3]$ were filtered off and washed several times with small amounts of acetylacetone–water (1 : 1) and finally dried *in vacuo*. The compound thus obtained was very pure and gave extremely satisfactory analysis. If desired, the compound can be recrystallised by dissolving it in the minimum volume of hot benzene followed by the addition of hot light petroleum (b.p. 40—60 °C) and then cooling at *ca.* 0 °C. The yield obtained was 9.7 g (87%). The compound does not have a sharp melting point but decomposes at *ca.* 155 °C. This method may also be used for large-scale synthesis (Found: C, 51.1; H, 6.10; Mn, 15.7. Calc. for $C_{15}H_{21}MnO_6$: C, 51.15; H, 6.00; Mn, 15.6%). The molecular weight was found to be 352 mass spectrometrically.

† Throughout this note: 1 eV ≈ 1.60 × 10^{-19} J.

Mass spectral data for $[Mn(acac)_3]$

(*a*) Major peaks

Assignment	*m/z*	Intensity (%)
$[Mn(C_5H_7O_2)_3]^+$	352	18
$[Mn(C_5H_7O_2)_2]^+$	253	100
$[Mn(C_5H_7O_2)(C_4H_4O_2)]^+$	238	34
$[Mn(C_5H_7O_2)]^+$	154	74
$[Mn(C_4H_4O_2)]^+$	139	5
Mn^+	55	0

(*b*) Metastable transitions

m/z Observed	*m/z* Calculated	Process	Fragment lost
181.8	181.84	352 → 253	$C_5H_7O_2$
223.9	223.89	253 → 238	CH_3
99.6	99.65	238 → 154	$C_4H_4O_2$
125.6	125.46	154 → 139	CH_3

RESULTS AND DISCUSSION

Direct Synthesis.—In our previous paper [3] we emphasised the role of acetylacetone as a reducing agent in the reduction of Mn^{VII}. We have now extended the use of this concept to the synthesis of $[Mn(acac)_3]$. The method described leads to the rapid synthesis of tris(acetylacetonato)manganese(III) in very high yield and analogous procedures have also been used successfully for the synthesis of $[Cr(acac)_3]$ from CrO_3 and $[Ni(acac)_2(H_2O)_2]$ from NiO(OH). Gram quantities of $[Mn(acac)_3]$ can be synthesised in less than 1 h without using any buffer. The reduction of $[MnO_4]^-$ by acetyl-

acetone and the subsequent formation of the tris chelate owing to the presence of an excess of acetylacetone (Hacac) appear to be the driving forces for the reaction. Although the present synthesis does not involve any buffer, the course of the reaction is such that it automatically maintains the pH desired for the successful formation of $[Mn(acac)_3]$. The pH of the solution measured immediately after the formation of the compound was found to be *ca.* 5. This value concurs exactly with that maintained by the addition of a large amount of sodium acetate in the syntheses of Cartledge [1] and Charles.[2] It is not possible to propose a mechanism for the present synthesis in the absence of full details of the oxidised products of acetylacetone.

Characterisation.—Tris(acetylacetonato)manganese-(III) is a dark brown-black crystalline compound, unstable in air but capable of being stored in a sealed container for months. The compound is slightly soluble in water but dissolution is accompanied by decomposition. Freshly prepared $[Mn(acac)_3]$ does not show a sharp melting point but decomposes around 155 °C. The i.r. spectrum of the compound is unambiguous and shows the characteristics of chelated acctylacetonates ($acac^-$), in agreement with the reported spectrum.[4] The molecular weight, determined mass spectrometrically, was found to be 352 suggesting that the compound is monomeric. This agrees well with the crystal structures of various forms of $[Mn(acac)_3]$ which also showed the presence of discrete $[Mn(acac)_3]$ molecules.[5,6] Chemical determination of the oxidation state of manganese in the synthesised compound gave +III, providing further support for the identity of the compound.

Mass Spectrometric Studies.—Attempts to obtain good mass spectra of $[Mn(acac)_3]$ have not always been successful.[7] It appears that the spectra of tris-(acetylacetonato)metalates markedly depend on the method of sample introduction. We favoured the direct insertion probe and introduced the sample into the ionisation chamber without any prior heating. The other conditions were similar to those maintained in our earlier experiments.[8]

The spectrum run at 20 °C (Table) showed a molecular ion signal of moderate intensity (18%) at *m/z* 352 and a base peak at *m/z* 253 due to $[Mn(acac)_2]^+$, the major fragmentation path being $[Mn(C_5H_7O_2)_3]^+ \longrightarrow [Mn(C_5H_7O_2)_2]^+ \longrightarrow [Mn(C_5H_7O_2)(C_4H_4O_2)]^+ \longrightarrow [Mn(C_5H_7O_2)]^+ \longrightarrow [Mn(C_4H_4O_2)]^+ \longrightarrow Mn^+$. The metastable peaks observed at *m/z* * 181.8, 223.9, 99.6, and 125.6 support the proposed fragmentation path and closely resemble those reported by Westmore and coworkers.[9]

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