Direct Synthesis of Bis(acetylacetonato)nickel(II) Dihydrate and Isolation of α,α,β,β-Tetra-acetylethane as the Oxidation Product of Acetylacetone

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NiO(OH) undergoes a facile reaction with acetylacetone affording a very high yield of bis(acetylacetonato)nickel(II) dihydrate, $[Ni(acac)_2]\cdot 2H_2O$, and giving α,α,β,β-tetra-acetylethane as the oxidation product of acetylacetone.

Our interest in the area of acetylacetonates of transition metals extended to the development of new synthetic routes to such compounds [1-3] has led to an investigation of the reaction of NiO(OH) with acetylacetone (Hacac). In our previous papers [1,2] we emphasised the role of Hacac as a reducing agent in the direct synthesis of $[Mn(acac)_3]$ and $[Cr(acac)_3]$. We now wish to report the reaction between NiO(OH) and Hacac leading to the direct synthesis of bis(acetylacetonato)-nickel(II) dihydrate in a very high yield, in the absence of any buffer {unlike the synthesis of $[Ni(acac)_2]\cdot 2H_2O$ by Charles and Powlikowski [4]}, and also enabling the isolation of α,α,β,β-tetra-acetylethane as the oxidation product of Hacac, for the first time, from such a reaction.

Experimental

The chemicals used for the reactions were all reagent grade products. Infrared spectra were recorded on a Perkin-Elmer model 125 spectrophotometer. The mass spectra were recorded on a Varian MAT CH-5 mass spectrometer using a direct insertion probe (Table).

Preparation of NiO(OH).—An aqueous solution of nickel(II) chloride hexahydrate was treated with an excess of sodium hydroxide and a precipitate of $Ni(OH)_2$ was obtained. The $Ni(OH)_2$ was separated by filtration and purified by repeated washing with water until free from chloride. Nickel(II) hydroxide was then oxidised to NiO(OH) by treating an alkaline suspension of it with bromine. The black NiO(OH) thus obtained was separated by centrifugation, washed with water until free from alkali, and finally dried *in vacuo* over phosphorus pentoxide.

Reaction of NiO(OH) *with Acetylacetone.*—Acetylacetone (11.0 g, 110.0 mmol) was added to a suspension of NiO(OH), (2.0 g, 21.8 mmol) in water (*ca.* 6 cm^3) with constant stirring. An exothermic reaction occurred almost immediately. The reaction mixture was stirred mechanically until the black NiO(OH) was converted completely to a blue-green product (*ca.* 15 min). The mixture was filtered and the product washed with acetone until a green-blue filtrate had just begun to appear. The combined filtrate and washing (A) was retained for the isolation of the oxidation product of Hacac.

The compound on the filter was then recrystallised from boiling acetone by the addition of light petroleum (b.p. 40—60 °C) and subsequent cooling at *ca.* 0 °C to obtain the blue-green shiny platelet compound. The yield of $[Ni(acac)_2]\cdot 2H_2O$ was 5.3 g (82.3%) (Found: C, 40.8; H, 6.3; Ni, 20.2. Calc. for $C_{10}H_{18}NiO_6$: C, 41.0; H, 6.15; Ni, 20.05%). The compound was characterized by its i.r. spectrum, magnetic susceptibility,[5] and molar conductance.

Table. Mass spectral data for $[Ni(acac)_2]$

(*a*) Major peaks

Assignment	*m/z*	Intensity (%)
$[Ni(C_5H_7O_2)_2]^+$	256	100
$[Ni(C_5H_7O_2)(C_4H_4O_2)]^+$	241	96
$[Ni(C_5H_7O_2)(OCCH_2)]^+$	199	3
$[Ni(C_5H_7O_2)H]^+$	158	40
$[Ni(C_5H_7O_2)]^+$	157	91
$[Ni(C_4H_4O_2)]^+$	142	30
$[Ni(C_4H_3O_2)]^+$	141	23
$[Ni(C_3H_4O)]^+$	114	5
$[Ni(OCCH_2)]^+$	100	56
$[Ni(CO)]^+$ or $[Ni(C_2H_4)]^+$	86	70
Ni^+	58	16

(*b*) Metastable transitions

m/z * Observed	*m/z* * Calculated	Process	Fragment lost
226.8	226.88	256 ⟶ 241	CH_3
102.2	102.28	241 ⟶ 157	$C_4H_4O_2$
128.4	128.43	157 ⟶ 142	CH_3
91.5	91.52	142 ⟶ 114	CO
70.3	70.42	142 ⟶ 100	C_2H_2O
64.8	64.88	114 ⟶ 86	CO or C_2H_4
39.1	39.12	86 ⟶ 58	C_2H_4 or CO

Isolation of the Oxidation Product, α,α,β,β-Tetra-acetylethane from the Combined Filtrate and Washing (A).—The combined filtrate and washing (A) was concentrated by removing the solvent on a rotary vacuum evaporator, and colourless cubic crystals were obtained. The crystals were removed and washed three times with benzene and finally dried on a filter paper.

The $(CH_3CO)_2CH{-}CH(COCH_3)_2$ melts at 190 °C (lit.,[6] 191 °C) and the yield was 1.85 g (85.6%, on the basis of an electron-transfer reaction between Ni^{III} and Hacac). The compound is very sparingly soluble in water, benzene, and ether, and its various physical and chemical properties (colour, m.p., solubility, reaction with $FeCl_3$, and mass and n.m.r. spectra) compare very well with those of a specimen prepared by the action of iodine upon sodium acetylacetonate.[6]

Results and Discussion

It is evident from various reports that under the appropriate conditions Hacac is capable of acting both as a reducing agent and a chelating agent.[1,2,7,8] However, the nature of the oxidation product of acetylacetone when it acts as a reducing agent has not been established until now. We have carried out the reaction of NiO(OH) with acetylacetone leading to the direct synthesis of $[Ni(acac)_2]\cdot 2H_2O$ with oxidation of acetylacetone. One of our main concerns was to identify the oxidation product. Work up of the mother-liquor obtained after separating $[Ni(acac)_2]\cdot 2H_2O$ afforded a crystalline organic compound which has been identified as $(CH_3CO)_2CH-CH(COCH_3)_2$.

In an attempt to generalise the contention that electron-transfer reactions between higher-valent transition metal ions and acetylacetone leading to the corresponding acetylacetonates give $(CH_3CO)_2CH-CH(COCH_3)_2$ as the oxidation product, we performed the reactions of Hacac with Mn^{7+} and Cr^{6+} following the procedures described in our previous papers.[1,2] Isolation of $(CH_3CO)_2CH-CH(COCH_3)_2$ from each of the reactions, after separation of the corresponding $[M(acac)_3]$ complex, was successful again owing to the oxidation of acetylacetone; we therefore conclude that in the electron-transfer reactions of the types discussed above, acetylacetone is oxidised to $(CH_3CO)_2CH-CH(COCH_3)_2$.

The pH of the solution, recorded immediately after the formation of $[Ni(acac)_2]\cdot 2H_2O$ was found to be *ca.* 5, a situation conducive to the formation of metal–acac complexes, and concurs with that maintained by Charles and Powlikowski [4] by the addition of a large amount of sodium acetate. The chances of contamination of the product owing to the use of such a large amount of buffer can not be ruled out.[9] In view of the products isolated from the reaction of Ni^{3+}, Mn^{7+}, or Cr^{6+} with acetylacetone (*e.g.* see below), and the pH of the reaction medium, we feel that acetylacetone first undergoes

$$[Ni^{III}O(OH)] + 3\ Hacac \longrightarrow [Ni(acac)_2] + \tfrac{1}{2}(\text{'acac–acac'}) + 2\ H_2O$$

ionization giving $(CH_3CO)_2CH^-$ ($acac^-$) and H^+ (*cf.* the observed pH) followed by the oxidation of $(CH_3CO)_2CH^-$ ion to the $(CH_3CO)_2CH^{\bullet}$ radical (with corresponding reduction of the metal), which dimerises to yield $(CH_3CO)_2CH-CH(COCH_3)_2$. It appears that this route to α,α,β,β-tetra-acetylethane is relatively simpler than methods described in the literature.[6] Because of the higher yield of product, considerably shorter reaction time, and redundancy of any buffer, this method of synthesis of $[Ni(acac)_2]\cdot 2H_2O$ offers advantages over the procedure described in the literature.[4]

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