

respectively).<sup>5</sup> The first two reactions have relatively negative enthalpy changes which are close to one another, and the last two reactions are considerably less exothermic. That reaction 2 is more exothermic and reaction 3 less exothermic than might be expected on the basis of a smooth trend with less heat evolution in each successive step<sup>26</sup> is consistent with the special stability of the dichloro species, which is produced in reaction 2 and consumed in reaction 3.

The complexes of thallium(III) ion and chloride ion are very much more stable than are complexes of chloride ion and transition metal ions of charge 3+, e.g., chromium(III) ion<sup>27</sup> and iron(III) ion.<sup>14</sup> At  $I = 3 M$ , values of  $Q_1$  for reactions of these two metal ions are  $\sim 0.2$  and  $6.6$  l. mole<sup>-1</sup>, respectively,  $\sim 10^7$ -fold smaller

- (26) W. M. Latimer and W. L. Jolly, *J. Am. Chem. Soc.*, **75**, 1548 (1953).  
 (27) H. S. Gates and E. L. King, *ibid.*, **80**, 5011 (1958).

than the value of  $Q_1$  for reaction of thallium(III) ion and chloride ion. This enormous difference, arising presumably because of differences in the type of bonding, is due to the difference in enthalpy changes; the entropy changes are similar, +17.2, +16.1, and +14.5 cal. mole<sup>-1</sup> deg.<sup>-1</sup> for the reaction  $M^{3+} + Cl^- = MCl^{2+}$  for  $M^{3+} = Cr^{3+}$ ,  $Fe^{3+}$ , and  $Tl^{3+}$ , respectively. The values of  $\Delta S^\circ$  for reactions of different metal ions with a particular anion seem, therefore, to depend largely upon the value of  $\Delta Z^2$ . The small variation of these values may reflect an expected less positive partial molal entropy for a complex with a stronger metal-ligand bond.

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## The Thermal Decomposition of Zinc Acetylacetonate Hydrate

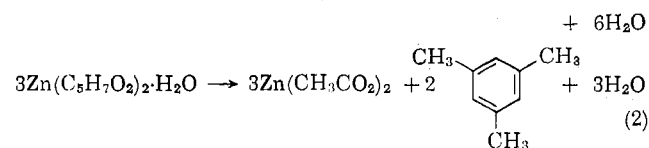
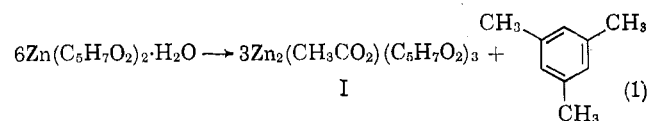
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Zinc acetylacetonate hydrate undergoes on heating a decomposition to form mesitylene and acetate ions, the latter being found in the novel compound  $Zn_2(CH_3CO_2)(C_6H_7O_2)_3$ . Anhydrous zinc acetylacetonate does not undergo this decomposition under analogous experimental conditions. The acetate compound and an analogous benzoate may also be obtained by an independent route.

Although zinc acetylacetonate is known to have low thermal stability,<sup>2</sup> little attention has been paid to its decomposition products. Some volatile decomposition products from a series of other metal acetylacetonates were shown by von Hoene<sup>3</sup> to include acetone, carbon dioxide, acetylacetone, and methane.

We have found that zinc acetylacetonate hydrate at elevated temperatures, preferably at 130° in an inert solvent, undergoes a remarkable decomposition reaction according to the equations



Anhydrous zinc acetylacetonate does not undergo this decomposition under the conditions used in these ex-

periments. When the reaction is carried out in open systems such as refluxing xylene, only part of the starting material decomposes according to (1) to yield the acetate-containing compound I, while its major part is found as anhydrous zinc acetylacetonate. When the escape of water is prevented by the use of a sealed tube, the reaction proceeds further to form zinc acetate (eq. 2).

The volatile products of the reaction were collected, separated, and analyzed using vapor phase chromatographic and infrared techniques. Mesitylene (1,3,5-trimethylbenzene) was shown to be the main product along with acetone and traces of acetylacetone. In one reaction, in which xylene was used as a solvent, a mixture of mesitylene and its isomer pseudocumene (1,2,4-trimethylbenzene) was noted.

Some ambiguity is connected with the acetate-containing compound I. While its empirical formula is well confirmed (see Experimental part), its structure remains an open question. Molecular weight determinations in chloroform, dioxane, and camphor gave ambiguous results. Conductivity measurements carried out in chloroform and nitrobenzene indicated little or no ionic dissociation taking place in these solvents. The compound may be recovered unchanged from solutions

- (1) National Academy of Sciences Research Fellow.  
 (2) R. G. Charles and M. A. Pawlikowski, *J. Phys. Chem.*, **62**, 440 (1958).  
 (3) J. von Hoene, R. G. Charles, and W. M. Hickam, *ibid.*, **62**, 1098 (1958).

of chloroform, while in solutions with the basic solvents pyridine and formamide, adducts of zinc acetylacetonate are readily formed, *viz.*,  $\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2 \cdot \text{C}_5\text{H}_5\text{N}$  and  $\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2 \cdot \text{H}_2\text{NCHO}$ , respectively.

When zinc acetate dihydrate is dissolved in an excess of hot acetylacetonate, the same compound I precipitates out of the cooled solution, identical in all respects with the product obtained *via* the thermal decomposition. In order to explain the fact that only three out of four acetate groups are replaced by acetylacetonate, we assume that a six-coordinated tris(acetylacetonato)zincate anion is formed, thus leading to a formula such as  $\text{Zn}[\text{CH}_3\text{CO}_2][\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_3]$ . The tris(acetylacetonato)zincate anion has previously been described by Dwyer.<sup>4</sup>

An analogous compound,  $\text{Zn}_2(\text{C}_6\text{H}_5\text{CO}_2)(\text{C}_5\text{H}_7\text{O}_2)_3$ , was prepared from zinc benzoate and acetylacetonate. This latter compound is one of a series under current investigation.

### Experimental

**Zinc Acetylacetonates.**—Metal acetylacetonates are prepared by numerous methods, each slightly different in procedure.<sup>5</sup> Since we were interested in obtaining both the hydrated and the anhydrous zinc acetylacetonate in high purity, we prepared these complexes by the following techniques.

(A) **Zinc Acetylacetonate Hydrate.**—To a stirred aqueous solution of 100 g. of freshly distilled acetylacetonate (1 mole) and 40 g. of sodium hydroxide (1 mole) was slowly added an aqueous solution of 144 g. of zinc sulfate heptahydrate (0.5 mole). The resulting precipitate was washed with water and dried. Recrystallization from acetylacetonate followed by washing with petroleum ether yielded 105 g. of zinc acetylacetonate hydrate (75%) with m.p. 145–146° (opaque melt).

*Anal.* Calcd. for  $\text{ZnC}_{10}\text{H}_{14}\text{O}_4 \cdot \text{H}_2\text{O}$ : C, 42.55; H, 5.73. Found: C, 42.80; H, 5.72.

(B) **Zinc Acetylacetonate.**—The anhydrous form of zinc acetylacetonate is obtained most easily by sublimation of the hydrate at a pressure of 0.1 mm. and a bath temperature of 110°. It melts at 127° to a clear melt.<sup>6</sup>

*Anal.* Calcd. for  $\text{ZnC}_{10}\text{H}_{14}\text{O}_4$ : C, 45.57; H, 5.35. Found: C, 45.05; H, 5.41.

**Formation of I. (A) Decomposition of Zinc Acetylacetonate Hydrate.**—Decomposition of zinc acetylacetonate hydrate was carried out in refluxing toluene, xylene, or tetralin. The following semiquantitative decomposition was carried out in tetralin.

Zinc acetylacetonate hydrate (20 g., 0.071 mole) was dissolved and heated with about 100 ml. of tetralin in a sealed tube at 130° for 24 hr. After cooling, 7.4 g. of I (0.015 mole, fine powder) and 7.6 g. of zinc acetate (0.041 mole, leaf-like crystals) were obtained and mechanically separated. For analysis of I see section B.

The filtrate was fractionally distilled by use of a spinning-band column. At 55°, 2 ml. of almost pure acetone (0.027 mole) was collected. A fraction of 3.75 ml. was collected between 85 and 204°. Vapor phase chromatography of the second fraction indicated the presence of mesitylene as well as traces of acetone

and acetylacetonate. A semiquantitative estimation using peak areas and standard reference curves with known compounds gave 0.019 mole of mesitylene or 60% of the amount calculated from application of eq. 1 and 2.

(B) **Reaction of Zinc Acetate and Acetylacetonate.**—Zinc acetate dihydrate (21.9 g., 0.1 mole) was dissolved in 50 ml. of acetylacetonate and filtered hot. On cooling, 21.3 g. of I (87%) crystallized out of solution; after filtration and washing with petroleum ether the melting point was 198–200°. A mixture melting point with the product obtained in method A showed no depression.

*Anal.* Calcd. for  $\text{Zn}_2\text{C}_{17}\text{H}_{24}\text{O}_8$ : C, 41.92; H, 4.97; Zn, 26.84; mol. wt., 487.14. Found: C, 42.31; H, 5.06; Zn, 26.02 (average values from several samples); mol. wt. in camphor, 259; in dioxane, 246; in chloroform (Mechrolab vapor pressure osmometer), 346, 348, 386.

The proton magnetic resonance spectrum of I shows two peaks at +5.5 and +2.15 p.p.m. against tetramethylsilane (solvent deuteriochloroform) with a ratio of 1:7 within the limits of error.  $\text{Zn}_2(\text{CH}_3\text{CO}_2)(\text{CH}_3\text{—C(O)—CH—CO—CH}_3)_3$  demands three protons on  $(\text{HC=})$ — groups and 21 protons on methyl groups.

The infrared spectrum of I is almost identical with that of zinc acetylacetonate; the latter's reported absorption<sup>7</sup> at 769  $\text{cm.}^{-1}$  is, however, shifted to 800  $\text{cm.}^{-1}$ .

**Reactions of I. (A) Decomposition with Acid.**—I (0.8751 g.) was decomposed with 50% phosphoric acid and the volatile products were separated by steam distillation. Acetic acid and acetylacetonate were determined by potentiometric titration with 0.1 N NaOH. From 1.80 mmoles of I there were obtained 1.52 mmoles of acetic acid and 4.63 mmoles of acetylacetonate. Thus, the ratio acetic acid:acetylacetonate amounts to 1:3.05.

(B) **With Pyridine.**—I (3 g.) was dissolved in 10 ml. of pyridine with slight heating. Removal of the excess pyridine *in vacuo* gave 4.08 g. of yellowish crystals with m.p. 122–127°, which after two recrystallizations from cyclohexane gave white  $\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2 \cdot \text{C}_5\text{H}_5\text{N}$ , m.p. 121°.

*Anal.* Calcd. for  $\text{ZnC}_{15}\text{H}_{19}\text{NO}_4$ : C, 52.57; H, 5.59; N, 4.09. Found: C, 51.84; H, 5.52; N, 4.04.

(C) **With Formamide.**—A solution of I in hot formamide gave on cooling large crystals, which after recrystallization from ethanol had m.p. 166°. The composition was  $\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2 \cdot \text{HCONH}_2$ .

*Anal.* Calcd. for  $\text{ZnC}_{11}\text{H}_{17}\text{NO}_5$ : C, 42.81, H, 5.55; Zn, 21.18. Found: C, 42.47; H, 5.61; Zn, 21.16.

Both the pyridine and formamide adducts can also be obtained from zinc acetylacetonate under similar conditions. Identical melting points, mixture melting points, and elemental analyses were found.

**Zinc Benzoate Acetylacetonate.**—Zinc benzoate, prepared from the reaction of zinc oxide and benzoic acid, was dissolved in hot acetylacetonate. The powder which formed on cooling was recrystallized from acetylacetonate and washed with alcohol and ether to give  $\text{Zn}_2(\text{C}_6\text{H}_5\text{CO}_2)(\text{C}_5\text{H}_7\text{O}_2)_3$ , m.p. 243–245° dec.

*Anal.* Calcd. for  $\text{Zn}_2\text{C}_{22}\text{H}_{26}\text{O}_8$ : C, 48.11; H, 4.77; Zn, 23.81. Found: C, 49.12; H, 4.79; Zn, 22.59.

**Thermal Decomposition of Zinc Acetylacetonate Hydrate.**—A 5-g. sample of zinc acetylacetonate hydrate was heated in a sealed tube at 130° for 60 hr. The contents became partly liquid. After removal of the volatile products, 3.8 g. of solid zinc acetate remained. The volatile products were acetylacetonate and mesitylene as shown by vapor phase chromatography.

**Acknowledgment.**—We are indebted to Mr. Carmine DiPietro of these Laboratories for carrying out the microanalyses and to the National Academy of Sciences for the opportunity given to G. R. to work at the U. S. Army Natick Laboratories.

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(6) D. P. Graddon and D. G. Weeden, *Australian J. Chem.*, **16**, 980 (1963), have reported the conversion of zinc acetylacetonate hydrate to its anhydrous form by dehydration in a  $\text{P}_2\text{O}_5$  drying pistol. by heating the monohydrate in an oven for 18 hr. at 105°, and by azeotropic distillation of the monohydrate in toluene. Their reported anhydride had a melting point of 152°. According to our experiments, these conditions would have been severe enough to convert partially the zinc acetylacetonate hydrate to acetate-containing compounds and thus account for the higher melting point.