Thermal Decomposition of Sodium Acetylacetonate[1]

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Abstract

The thermal behavior of sodium acteylacetonate, $C_5H_7O_2^-Na^+$, and its dihydrate, $C_5H_7O_2^-Na^+ \cdot 2H_2O$, are described and interpreted for the range between room temperature and 1000° Centrigrade. Thermogravimetric analyses showed that decomposition of the dehydrated salt proceeds in two steps. The first yielded sodium carbonate at about 400° as a result of the reaction of sodium acetylacetonate with atmospheric oxygen. The second plateau at about 700° corresponded to sodium monoxide. Differential thermal analyses and differential scanning calorimetry data substantiated and extended these interpretations.

In our work on the acetylacetonates of active metals (1), it became of interest to study the stability of these salts. Since no such data appeared to be available, we undertook to study the thermal behavior of one of these salts and its hydrated form. The theory and advances of thermal analysis have been treated elsewhere (2, 3, 5, 8), and will not be dealt with here.

Experimental

Preparations

Sodium acetylacetonate, $C_5H_7O_2^-Na^+$, was prepared according to published procedures (9), recrystallized several times from dry ethanol and then dried at 110°C. Sodium acetylacetonate dihydrate crystals, $C_5H_7O_2^-Na^+ \cdot 2H_2O$, were obtained by recrystallizing the anhydrous salt from 95% ethanol/water solution.

Thermo Gravimetric Analyses

Accurately weighed samples containing between 0.2 and 0.4 g of the salt were placed in a Thermolyne furnace at a fixed temperature for about 30 min. The samples were then removed, allowed to cool in a desiccator, weighed and then subjected to higher temperatures by increments of between 20-50°C until the maximum temperature of 1000°C was reached. This procedure was repeated several times, each time using two simultaneous samples to insure reproducibility of the results.

The data were checked using an automatic DuPont 950 Thermogravimetric Analyzer in both air and nitrogen atmospheres (40 cc per min) up to 350°C at a heating rate of 5°C per min.

Differential Thermal Analyses

DTA data were obtained for both samples up to 400°C on a DuPont 900 Differential Thermal Analyzer in both air and nitrogen atmospheres (2 feet[3] per hour) at a programmed heating rate of 20°C per min using glass beads as reference.

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Differential Scanning Calorimetry

DSC curves were run for both samples up to 450°C on a Perkin-Elmer Differential Scanning Calorimeter DSC-1B in air and a 20°C per min heating rate.

Titrations

The decomposition products obtained at the two plateaus were titrated against 0.0624 N HCl according to published procedures for sodium carbonate and sodium monoxide (4). Due to the high decomposition temperatures, the product of the last plateau is fused very compactly into the crucible resulting in incomplete titrations.

Results and Discussion

The typical TGA plot for sodium acetylacetonate shows a two-step decomposition (Fig. 1). The weight loss in the first step between the starting material at room temperature (0.946 g) and the second plateau at about 400°C (0.410 g) corresponds to 56.7%. It is proposed that this decomposition takes place according to the reaction

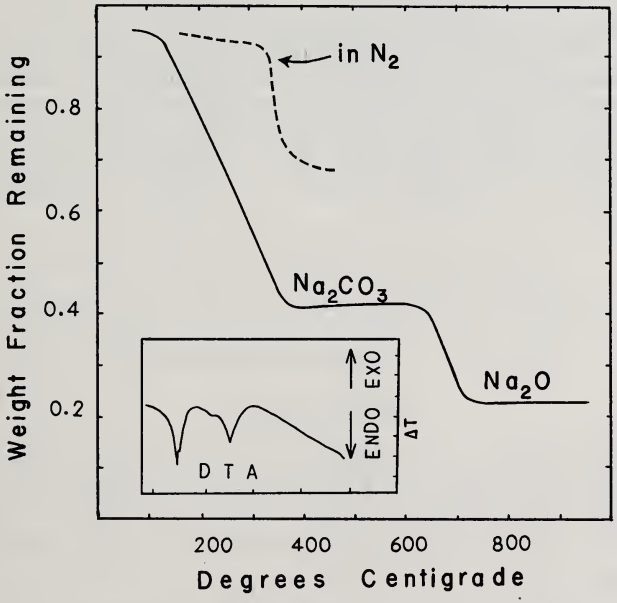

FIGURE 1. *TGA and DTA plots of sodium acteylacetonate, $C_5H_7O_2^-Na^+$, in air.*

$$2\ C_5H_7O_2^-Na^+_{(s)} + 12\ O_{2(g)} = Na_2CO_{3(s)} + 9\ CO_{2(g)} + 7\ H_2O_{(g)}$$

which requires a theoretical weight loss of 100 - [106/(2 x 122)]100 = 56.6%. The product from this plateau was identified by titration with HCl. Three typical titration data are given in Table 1. Note that the weights calculated for Na_2CO_3 based on titration results correspond very well to the actual weights of the decomposition samples. The role of oxygen in the decomposition was observed in two ways. First it was

found that rapid heating resulted in decomposition accompanied by the formation of considerable dark matter which could be eliminated by a slower heating rate and a good supply of air. Secondly, when run in nitrogen atmosphere, the decomposition sets in at a higher temperature, takes place faster, and levels off at a higher fraction of remaining weight (see dotted plot in Fig. 1), and yields more black matter than is the case with oxygen, presumably forming large amounts of elemental carbon.

TABLE 1. *Typical titrations of TGA product from 5000°C plateau with 0.1624* N *HCl.*

Sample Weight in grams	Volume of HCl in ml	Equivalents of HCl	Calculated Weight for Na_2CO_3 in grams
0.1749	53.88	3.36×10^{-3}	0.1745
0.1711	53.22	3.32×10^{-3}	0.1740
0.1748	53.56	3.34×10^{-3}	0.1770

While the above data all point to the correctness of the proposed decomposition, the expected exotherm for oxygenation does not appear on the DTA plot (see the insert in Fig. 1 which, on the same temperature scale, shows endothermic but no exothermic decomposition). The reason for this is the method by which the DTA is run using a 2 mm microtube sample holder thereby virtually eliminating air access. The DSC instrument, on the other hand, exposes the sample to the atmosphere and consequently shows the expected exothermic peak (Fig. 2).

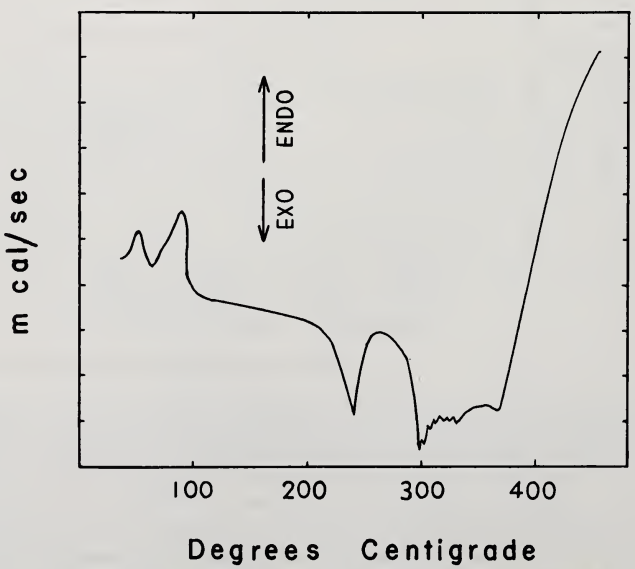

FIGURE 2. *DSC curve for sodium acetylacetonate dihydrate,* $C_5H_7O_2^-Na^+ \cdot 2H_2O$, *in air.*

The weight loss during the second step between the second plateau at about 400°C (0.410 g) and the third one at about 800°C (0.235 g) corresponds to 42.7%. It is proposed that this decomposition takes place according to the reaction

$$Na_2CO_{3(s)} = Na_2O_{(s)} + CO_{2(g)}$$

which requires a 41.5% theoretical loss of weight. Titration results (Table 2) indicate only fair agreement due to practical complications (see Experimental Section). It is noteworthy that thermodynamic calculations at 1000°K (7) show the above decomposition to be less favorable ($\Delta G_f^\circ = +42.323$ kcal/mole) than the reaction

$$Na_2CO_{3(s)} + \tfrac{1}{2}O_{2(g)} = Na_2O_{2(s)} + CO_{2(g)}$$

for which $\Delta G_f^\circ = +38.183$ kcal/mole. It appears then that kinetic factors favor the formation of Na_2O rather than that of Na_2O_2. This is substantiated by the fact that Na_2O_2 decomposes well below (460°C) the temperatures for the plateau in question, and that the decomposition was found to be independent of oxygen. At least one independent study (6) verifies these conclusions. The overall weight loss of 75.2% compares well with the predicted loss of 74.6%.

TABLE 2. *Typical titrations of TGA products from 1000°C plateau with 0.0624* N *HCl.*

Sample Weight in grams	Volume of HCl in ml	Equivalents of HCl	Calculated Weight for Na_2O in grams
0.1097	48.24	3.01×10^{-3}	0.0933
0.1054	45.35	2.83×10^{-3}	0.0877
0.0963	41.12	2.57×10^{-3}	0.0796

The hydrated salt loses its expected amount of water (22.8% by weight) in two equal and well-defined steps. The losses are detected by DTA and DSC plots as endothermic peaks.

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