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THE THERMAL DISSOCIATION OF SODIUM HEXANITROCOBALTATE(III)

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The stoichiometry of the thermal decomposition reaction of $Na_3[Co(NO_2)_6]$ was studied by TG, DTA and mass spectrometric analysis.

The thermal properties of $Na_3K_3[Co(NO_2)_6]_2 \cdot n\ H_2O$ and $K_3[Co(NO_2)_6]$ have been investigated by Duval and co-workers [1, 2]. For the latter compound, a TG curve plateau was found from 43° to 160° which was said to be suitable for the automatic determination of cobalt. Above 160° the evolution of 3 moles of NO_2 per mole of complex took place to give the mixture, CoO + $3KNO_2$. The same type of dissociation reaction was reported for $Cs_3[Co(NO_2)_6]$ [3] and $Na_3[Co(NO_2)_6]$ [4]. Since the above data did not give very much information on the decomposition reaction stoichiometry or analysis of the reaction products, the thermal dissociation of $Na_3[Co(NO_2)_6]$ was studied in somewhat greater detail by TG, DTA and mass spectrometric analysis (MSA).

Experimental

Preparation of $Na_3[Co(NO_2)_6]$

This complex was prepared by the method of Cunningham and Perkin [5] Analysis of the compound gave % metal oxide: 23.3% found, 23.69% calc. nitrogen: 21.2% found, 20.79% calc.

Apparatus

The thermobalance, DTA apparatus, and mass spectrometer have all been previously described [6]. The heating rate for the TG and DTA experiments was 10 °C/min.

Results and discussion

The mass-loss and DTA curves of $Na_3[Co(NO_2)_6]$ and the MSA data are shown in Fig. 1.

The mass-loss curve was rather surprising for two reasons: first, the initial complex was thermally stable up to about 200°; and, second, it did not dissociate completely but rather it decomposed to an intermediate which was thermally stable to about 600°. The DTA curve showed that the complex has no phase transitions or other transitions before the first dissociation reaction at about 200°. The DTA equipment used was limited to about 500° so the dissociation reactions between 600° and 800° were not observable.

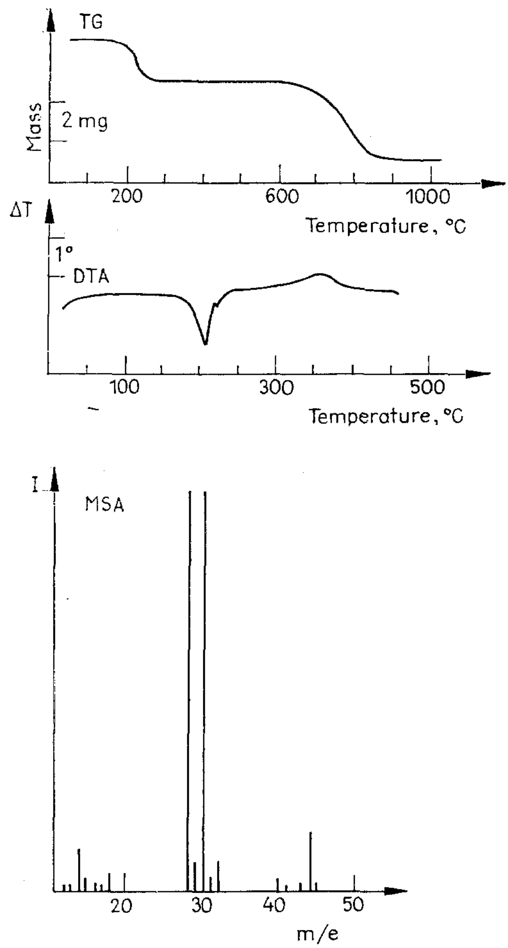

Fig. 1. TG, DTA and MSA data for $Na_3[Co(NO_2)_6]$

The MSA data revealed the presence of nitrogen, nitrogen(II) oxide [and possibly nitrogen(IV) oxide] and traces of nitrogen(I) oxide and oxygen.

The method of Saltzman [7] was used to analyze the gaseous decomposition products for nitrogen(IV) oxide. Also, by oxidizing the nitrogen(II) oxide to the higher oxidation state with oxygen, it could also be determined quantitatively in the reaction products.

Analysis of the gaseous products from the first dissociation reaction showed them to contain 18.5% nitrogen(IV) oxide and 4.4% nitrogen(II) oxide by weight. Calculation of the amount of nitrogen and oxygen present gave 1.6% nitrogen and 2.1% oxygen by weight. The small and approximately equal amounts of nitrogen and oxygen indicated that they were probably products of the hot tube dissociation of the nitrogen oxides. From these data and the TG data, the reaction stoichiometry appears to be:

$$6Na_3[Co(NO_2)_6](s) \rightarrow 18NaNO_2(s) + 2Co_3O_4(s) + 10NO_2(g) + 6NO(g) + \\ + N_2(g) + O_2(g)$$

If the nitrogen and oxygen were indeed products of the hot tube dissociation of nitrogen(II) oxide, then the actual reaction stoichiometry might have been:

$$3Na_3[Co(NO_2)_6](s) \rightarrow 9NaNO_2(s) + Co_3O_4(s) + 5NO_2(g) + 4NO(g)$$

The equipment used for the gaseous products stoichiometry was not capable of studying the dissociation reaction at 600°—800° temperature range. However, it is expected that the sodium nitrate dissociates according to the reaction:

$$NaNO_2(s) \rightarrow Na_2O(s) + NO_2(g) + NO(g)$$

so that the overall reaction is then:

$$6Na_3[Co(NO_2)_6](s) \rightarrow 9Na_2O(s) + 2Co_3O_4(s) + 17NO(g) + 19NO_2(g)$$

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RÉSUMÉ — On a examiné la décomposition thermique de $Na_3[Co(NO_2)_6]$ de point de vue stoichiométrique par les méthodes ATG, ATD et spectrométrie de masse.

ZUSAMMENFASSUNG — Es wurde über die Stöchiometrie der thermischen Zersetzung von $Na_3[Co(NO_2)_6]$ berichtet auf Grund von TG, DTA und massenspektrometrischen Untersuchungen.

Резюме — Исследована стехиометрия реакции терморaспада $Na_3[Co(NO_2)_6]$ с помощью ТГ, ДТА и масс-спектрометрического анализа.