Journal of Thermal Analysis, Vol. 21 (1981) 221–225

THERMAL DECOMPOSITION OF SODIUM CHLORATE AND CHROMIUM(III) OXIDE MIXTURES

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(Received July 17, 1980; in revised form December 15, 1980)

A study of the thermal decomposition of intimate mixtures of sodium chlorate and chromium(III) oxide in different molar ratios was made employing thermogravimetry, differential thermal analysis, chemical analysis, infrared spectroscopy and X-ray diffraction analysis. Sodium chlorate in the presence of chromium(III) oxide starts to decompose around 180°, which is much below the decomposition temperature of pure $NaClO_3$. Each mole of Cr_2O_3 consumes 8/3 moles of $NaClO_3$, undergoing oxidation to sodium dichromate.

Clorates and perchlorates are powerful oxidizing agents and give oxygen as one of the products on decomposition [1]. Our interest is to make use of the evolved oxygen during the decomposition of these salts in chemical reactions at moderate temperatures. It has been observed that Cr(III) is oxidized to Cr(VI) by potassium oxyhalates [2, 3] in the temperature range 200–400°. In an earlier report [4] we made detailed investigations on the thermal stability of sodium chlorite in presence of Cr_2O_3. The present paper reports decomposition studies made on the $NaClO_3-Cr_2O_3$ system with thermogravimetry and differential thermal analysis techniques. The products of decomposition are characterized by chemical analysis, X-ray powder diffraction patterns and infrared spectral measurements.

Experimental

Commercially-available sodium chlorate was recrystallized twice from hot water before use. Chromium(III) oxide was prepared by heating AnalaR grade CrO_3 to 500°. The different molar ratios, 1 : 2, 1 : 1, 2 : 1, 5 : 2, 8 : 3, 3 : 1, 4 : 1, 6 : 1, 8 : 1, and 10 : 1 of $NaClO_3$ and Cr_2O_3 were made by grinding the required amounts in an agate mortar for 10–15 min.

A Stanton recording thermobalance and a Netzsch differential thermal analyzer were employed for TG and DTA studies in air. The rate of heating was kept at 6° per min for TG and 10° per min for DTA studies. Constant-temperature heating experiments were carried out in air and flowing nitrogen atmospheres using a furnace whose temperature could be controlled with an accuracy of ±5°.

IR spectra were measured in the range 4000–200 cm^{-1} with Beckman IR 12 and Perkin–Elmer 257 spectrophotometers, employing KB_α pellet and nujol mull techniques. The X-ray powder diffraction patterns were taken with a Debye–Scherrer camera with a diameter of 114.6 mm using CuK_α radiation.

Chromium(VI) in the decomposition products was determined by iodometry, while chloride was determined gravimetrically after separation of the chromate as barium chromate [5].

Results and discussion

The TG and DTA runs on pure $NaClO_3$ indicate that the compound melts around 260° and decompose to NaCl and O_2 in the temperature range 440–540°, which is in agreement with the reported results [6, 7] on its thermal stability. The TG plots of ten mixtures of $NaClO_3$ and Cr_2O_3 in different molar ratios are given in Fig. 1. The results suggest that the decomposition sets in for all the mixtures around 180°, which is much below the decomposition temperature of pure $NaClO_3$. For mixture with molar ratios higher than 8 : 3, there exists a second decomposition stage in the temperature range 300–350°.

The residues obtained by heating known amounts of the mixture at 360° were found to be air-sensitive due to the absorption of moisture by the $Na_2Cr_2O_7$ formed. The residues of mixtures with molar ratios of 8 : 3 and higher were freely soluble in water, whereas those formed from lower molar ratios were incompletely soluble: the insoluble part was found to be unreacted Cr_2O_3.

The X-ray powder patterns and the IR spectra of the decomposition residues of the mixtures obtained at 360° showed the presence of $Na_2Cr_2O_7 \cdot 2\,H_2O$ and

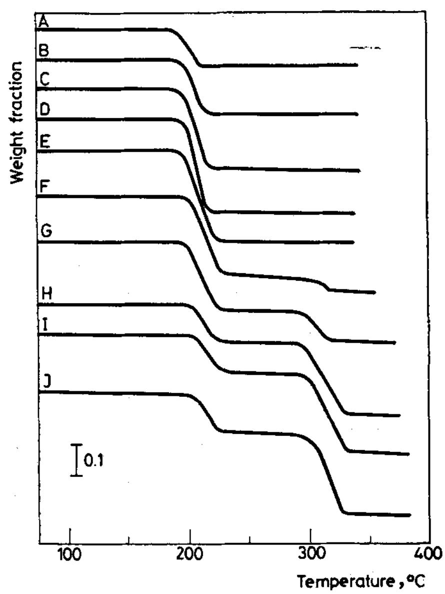

Fig. 1. TG plots of 1 : 2 (A), 1 : 1 (B), 2 : 1 (C), 5 : 2 (D), 8 : 3 (E), 3 : 1 (F), 4 : 1 (G), 6 : 1 (H), 8 : 1 (I), and 10 : 1 (J) molar ratios of sodium chlorate and chromium(III) oxide

NaCl when the stoichiometric ratio was 8 : 3 and higher, but additionally revealed the presence of Cr_2O_3 if the molar ratio was less than 8 : 3. Further, the X-ray and IR analyses of the products of decomposition obtained at 250°, corresponding to the first plateau in Fig. 1, for molar ratios 3 : 1 and higher, indicated the presence of unreacted $NaClO_3$ in addition to $Na_2Cr_2O_7 \cdot 2\,H_2O$ and NaCl. Though anhydrous sodium dichromate was formed at higher temperature, on cooling to room temperature it slowly absorbed water to yield the dihydrate.

These results, together with the analytical data on the Cr(VI) and chloride contents (Table 1), suggest the reaction to be

$$8\,NaClO_3 + 3\,Cr_2O_3 \longrightarrow 3\,Na_2Cr_2O_7 + 2\,NaCl + 6\,ClO_2 \tag{1}$$

The weight losses observed during the TG studies are given in Table 2, together with the calculated weight losses. The results are quite satisfactory, conforming the proposed reaction sequence. Thus, it is clear that when the molar ratios are greater than 8 : 3 the decomposition products at 250° are a mixture of $Na_2Cr_2O_7$, NaCl and unreacted $NaClO_3$. The excess $NaClO_3$ decomposes in the presence of $Na_2Cr_2O_7$ in the temperature range 290–330°. It has been verified in a separate experiment, by heating a mixture of $NaClO_3$ and $Na_2Cr_2O_7 \cdot 2\,H_2O$, that the latter has a catalytic influence on the decomposition of $NaClO_3$ and lowers the decomposition temperature from 440° to 280°.

In order to verify whether oxygen of the air takes part in the oxidation of Cr(III) to Cr(VI) during the decomposition, the constant-temperature heating experiments were carried out in a flowing nitrogen atmosphere for all the mixtures;

Table 1

Analytical data on the decomposition products obtained by heating $NaClO_3$–Cr_2O_3 mixtures at 360 °C

Molar ratio $NaClO_3$:Cr_2O_3	Chromium(VI), %		Chloride, %		Extent of Cr(III) oxidation, %
	Found	Calcd.*	Found	Calcd.*	
1 : 2	9.38	9.50	1.82	2.16	18.5
1 : 1	15.27	15.09	3.21	3.43	38.0
2 : 1	21.61	21.38	5.11	4.96	75.8
5 : 2	23.48	23.31	5.43	5.30	94.5
8 : 3	23.67	23.88	5.41	5.43	99.1
3 : 1	21.88	22.06	7.23	7.52	99.4
4 : 1	18.04	18.00	12.56	12.30	100.2
6 : 1	13.01	13.35	17.57	17.93	98.9
8 : 1	10.20	10.37	21.75	21.22	98.4
10 : 1	8.39	8.55	23.53	23.30	98.2

* As per reaction 1.

Table 2

Thermogravimetric data on the decomposition of sodium chlorate and chromium(III) oxide mixtures

Molar ratio $NaClO_3 : Cr_2O_3$	Weight loss, % at 200–250 °C		Weight loss, % at 300–350 °C	
	Found	Calcd.	Found	Calcd.
1 : 2	12.0	12.3		
1 : 1	19.0	19.6		
2 : 1	27.0	17.7		
5 : 2	30.0	30.2		
8 : 3	31.0	31.0		
3 : 1	28.0	28.6	32.0	32.0
4 : 1	23.0	23.4	34.0	34.2
6 : 1	17.0	17.1	37.0	37.3
8 : 1	13.0	13.5	39.0	39.0
10 : 1	11.0	11.1	40.0	40.0

the weight losses observed and the analytical results were identical with those obtained by heating the mixtures in air.

The DTA plots for $NaClO_3$ and Cr_2O_3 mixtures with molar ratios of 1 : 1, 8 : 3 and 6 : 1 are given in Fig. 2. The behaviour of mixtures with molar ratios greater than 8 : 3 is similar to that of the 6 : 1 mixture, and that of mixtures with molar ratios less than 8 : 3 is identical to that of the 2 : 1 mixture. The exotherm around 220° is ascribed to the oxidation of Cr_2O_3 to $Na_2Cr_2O_7$. The endotherm around 360° is due to the melting of $Na_2Cr_2O_7$.

For molar ratios greater than 8 : 3, additional thermal effects are observed namely an endotherm at 260° and an exotherm around 320°, which are assigned to the melting [7] and decomposition of $NaClO_3$, respectively.

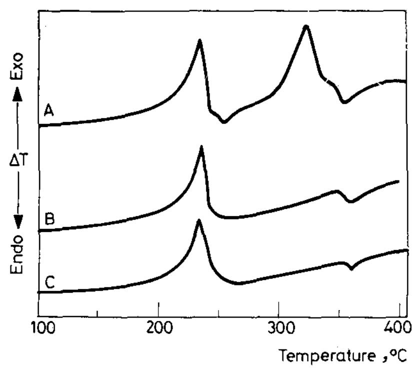

Fig. 2. DTA plots of 6 : 1 (A), 8 : 3 (B) and 2 : 1 (C) molar ratios of sodium chlorate and chromium(III) oxide

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RÉSUMÉ — On a effectué l'étude de la décomposition thermique du mélange intime de chlorate de sodium et de l'oxyde de chrome(III) en proportions molaires différentes par thermogravimétrie, analyse thermique différentielle, analyse chimique, spectroscopie infrarouge et diffraction des rayons X. En présence d'oxyde de chrome(III), le chlorate de sodium commence à se décomposer vers 180 °C, température très inférieure à celle de la décomposition du produit pur. L'oxydation d'une molécule de Cr_2O_3 en bichromate de sodium nécessite 8/3 de molécules de $NaClO_3$.

ZUSAMMENFASSUNG — Die Untersuchung der thermischen Zersetzung des Gemisches von Natriumchlorat und Chrom(III)oxid in verschiedenen Molverhältnissen wurde unter Einsatz der Thermogravimetrie, der Differentialthermoanalyse, der chemischen Analyse, der Infrarotspektroskopie und der Röntgenbeugung durchgeführt. In Gegenwart von Chrom(III)oxid beginnt die Zersetzung von Natriumchlorat um 180 °C, wesentlich unterhalb der Zersetzungstemperatur des reinen $NaClO_3$. Jedes Molekül von Cr_2O_3 verbraucht 8/3 Moleküle von $NaClO_3$ bei der Oxidation zu Natriumbichromat.

Резюме — С помощью термогравиметрии, дифференциального термического анализа, химического анализа, ИК спектроскопии и рентгенографического анализа, было изучено термическое разложение тщательно перемешанных смесей хлората натрия и окиси хрома-(III) в различных молярных соотношениях. В присутствии окиси хрома хлорат натрия начинает разлагаться при температуре около 180°, что намного ниже температуры разложения чистого хлората натрия. На каждый моль окиси хрома приходится 8:3 моля хлората натрия с окислением его до бихромата натрия.