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SOLID STATE REACTION BETWEEN DICHROMATES AND OXALATES

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The thermal investigation of the reaction taking place between dichromates and oxalates in the solid state has been done taking two systems of potassium dichromate-potassium oxalate and sodium dichromate-sodium oxalate. The techniques employed include thermogravimetry, differential thermal analysis, infrared spectroscopy and X-ray diffraction studies. The results indicate a stoichiometric reaction of dichromate and oxalate in 1:1 ratio to give the corresponding chromate as the sole product.

Althoaugh dichromates are known to be strong oxidising agents, not much is reported in literature [1, 2] on solid state decomposition reactions. A study of reactions between dichromates and oxalates has been made to understand the mechanism and the product formation in solid state. The systems taken for the present study are potassium dichromate and potassium oxalate; and sodium dichromate and sodium oxalate. The studies have been made using TG, DTA, IR and XRD techniques.

Experimental

The chemicals used ($K_2Cr_2O_7$, $K_2C_2O_4 \cdot H_2O$, $Na_2Cr_2O_7 \cdot 2H_2O$ and $Na_2C_2O_4$) were all of reagent grade. Reaction mixtures were made in the mole ratios of 1:3, 1:2, 1:1, 2:1 and 4:1 for the $K_2Cr_2O_7$ and $K_2C_2O_4$ system and 1:2, 1:1, 2:1, 3:1 and 4:1 for the $Na_2Cr_2O_7$ and $Na_2C_2O_4$ system by intimate mixing and grinding of the reactants.

TG and DTA studies were carried out using a Stanton simultaneous thermal analyzer–783 in static air atmosphere at a linear heating rate of 10 deg/min. Infrared spectra were recorded on a Perkin–Elmer 983 instrument in the range 2000–400 cm^{-1} employing KBr pellet technique. The X-ray powder diffractograms were obtained from a Philips diffractometer using CuK_α radiation.

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Results and discussion

$K_2Cr_2O_7$–$K_2C_2O_4 \cdot H_2O$ system

In accordance with the literature [3] pure $K_2Cr_2O_7$ melts with a sharp endotherm at 398° and starts decomposing at 500° while $K_2C_2O_4 \cdot H_2O$ undergoes dehydration with an endotherm at 120°, a reversible phase change with an endotherm at 400° and decomposes at 520–575°. The decomposition of potassium oxalate is accompanied by an endotherm followed by an exotherm at 569 and at 573°, respectively, with the formation of K_2CO_3 as the final product.

The TG curves of reaction mixtures with various mole ratios are given in Fig. 1. In all the cases the initial mass loss registered around 120° corresponds to the loss of

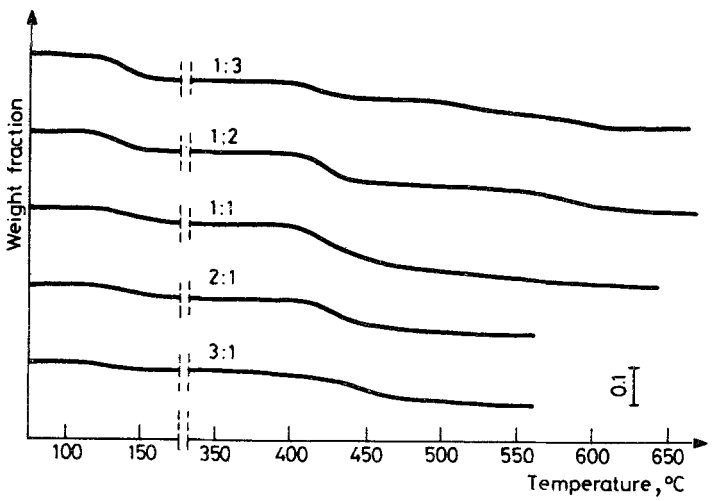

Fig. 1 TG curves for mixtures with various mole ratios of $K_2Cr_2O_7$ and $K_2C_2O_4 \cdot H_2O$

the appropriate number of water molecules from $K_2C_2O_4 \cdot H_2O$ in the mixtures. The subsequent mass loss, due to the reaction, sets in at 390° in all the mixtures and occurs in two stages for mixtures with 1 : 3 and 1 : 2 mole ratios and in a single step for those with 1 : 1, 2 : 1 and 4 : 1 mole ratios.

The TG data of the different mixtures and IR data of the products obtained from these mixtures are listed in Table 1. The IR band positions correspond to those of K_2CO_3 [5] and K_2CrO_4 [5] for 1 : 3 and 1 : 2 ratios, pure K_2CrO_4 in 1 : 1 and a mixture of K_2CrO_4, $K_2Cr_2O_7$ [5, 6] and Cr_2O_3 [4] for 2 : 1 and 4 : 1 mole ratios. The X-ray powder diffraction patterns of the products show lines with d_{hkl} values [7] which confirm the results from infrared spectroscopy.

The DTA curves of the mixtures are shown in Fig. 2. The endotherm at 120° for the mixtures can be assigned to the dehydration of $K_2C_2O_4 \cdot H_2O$ while the

Table 1 TG and IR data of mixtures of $K_2Cr_2O_7$ and $K_2C_2O_4 \cdot H_2O$

$K_2Cr_2O_7 : K_2C_2O_4 \cdot H_2O$ mole ratio	Percentage mass loss				IR frequencies (cm^{-1}) of the products obtained			
	Dehydration		Total loss					
	obsd.	calcd.	obsd.	calcd.	$K_2Cr_2O_7$	K_2CrO_4	K_2CO_3	Cr_2O_3
1 : 3	6.28	6.38	20.53	21.51	—	890s, 855m	1450vs, 900vw, 865m	—
1 : 2	5.30	5.43	19.80	20.59	—	890s, 855m	1450vs, 900vw, 865m	—
1 : 1	3.23	3.76	18.13	18.80	—	890s, 855m	—	—
2 : 1	2.80	2.33	13.70	14.70	—	890s, 855m	—	625m, 560m, 400w
4 : 1	1.28	1.32	8.41	8.38	950s, b, 905s, 890s, 795s, 760s, 565m, 450w	890s, 855m	—	625m, 560m, 400w

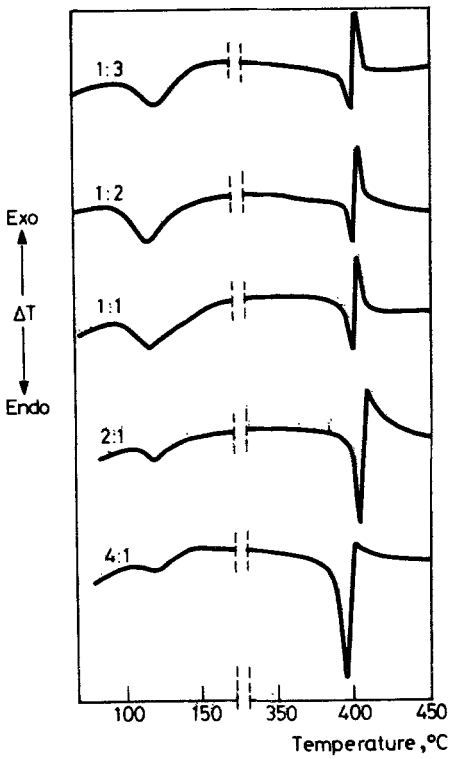

Fig. 2 DTA curves for mixtures with various mole ratios of $K_2Cr_2O_7$ and $K_2C_2O_4 \cdot H_2O$

endotherm at 400° could be due to the phase change of both reactants, $K_2Cr_2O_7$ and $K_2C_2O_4$. The exotherm immediately following the endotherm could be assigned to the reaction of the dichromate in the melt state and the oxalate to give the chromate.

Thus it is seen that $K_2Cr_2O_7$ undergoes a stoichiometric reaction with $K_2C_2O_4$ in 1 : 1 mole ratio to give K_2CrO_4. The excess $K_2C_2O_4$ in mixtures with 1 : 3 and 1 : 2 mole ratio decomposes to form K_2CO_3 in the second step while the excess $K_2Cr_2O_7$ in 2 : 1 and 4 : 1 ratios undergoes only partial decomposition to K_2CrO_4 and Cr_2O_3. The results are summarised in the following equations:

$$xK_2Cr_2O_7 + K_2C_2O_4 \rightarrow (x-2)K_2Cr_2O_7 + 3K_2CrO_4 + 1/2\,Cr_2O_3 \qquad (1)$$
$$x > 1$$

$$K_2Cr_2O_7 + yK_2C_2O_4 \rightarrow (y-1)K_2CO_3 + 2K_2CrO_4 \qquad (2)$$
$$y > 1$$

$$K_2Cr_2O_7 + K_2C_2O_4 \rightarrow 2K_2CrO_4 \qquad (3)$$

The mass loss calculated (Table 1) on the basis of the proposed reaction schemes agrees well with the percentage mass loss observed from the TG curves.

$Na_2Cr_2O_7$–$Na_2C_2O_4$ system

Reaction mixtures in this system were made in the mole ratios of 1:2, 1:1, 2:1, 3:1 and 4:1 of $Na_2Cr_2O_7$:$Na_2C_2O_4$. Pure $Na_2C_2O_4$ melts with decomposition in the range 560–585°. This is manifested as a small endotherm followed by a sharp exotherm at 560°.

Due to the hygroscopic nature of $Na_2Cr_2O_7 \cdot 2H_2O$, the samples are heated to 150° to complete dehydration and the reaction mixtures were made at 70–80° with the anhydrous $Na_2Cr_2O_7$ and maintained in thoroughly dried atmosphere.

The thermogravimetric curves for the reactions are given in Fig. 3. The first step for all mixtures ranging between 330–370°, corresponds to the decomposition of at

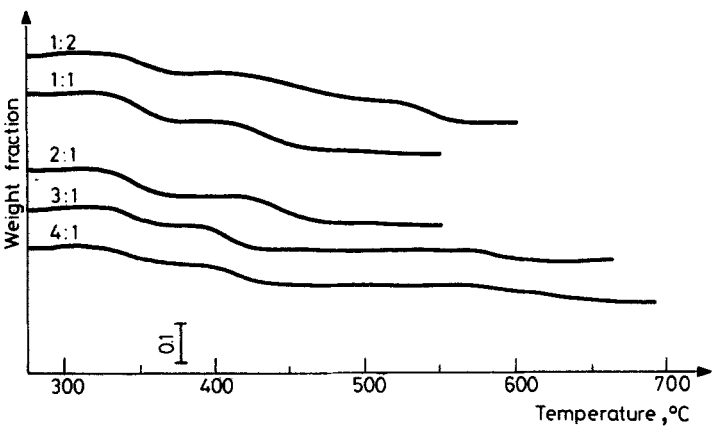

Fig. 3 TG curves for mixtures with various mole ratios of $Na_2Cr_2O_7$ and $Na_2C_2O_4$

least two molecules of sodium dichromate to give sodium chromate and chromium(III) oxide. The second step between 425 and 475° for 1:2, 1:1 and 2:1 mixtures and between 400–430° for 3:1 and 4:1 mixtures is due to the reaction between the Cr(III) oxide formed and the $Na_2C_2O_4$ to give Na_2CrO_4 as the product. The last step from 525 to 560° for the 1:2 mixture is due to the decomposition of the excess $Na_2C_2O_4$ to give Na_2CO_3 and the corresponding step from 570–640° for 3:1 and 4:1 mixtures is the decomposition of the excess $Na_2Cr_2O_7$.

The DTA curves shown in Fig. 4, exhibit an endotherm at 350°, in all the mixtures, corresponding to the melting of $Na_2Cr_2O_7$. Simultaneously, $Na_2Cr_2O_7$

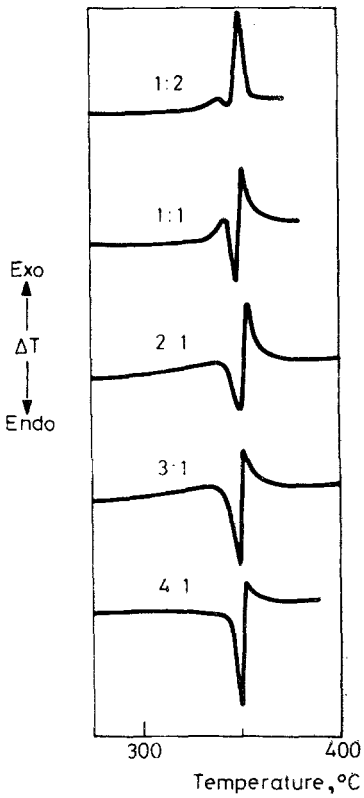

Fig. 4 DTA curves for mixtures with various mole ratios of $Na_2Cr_2O_7$ and $Na_2C_2O_4$

undergoes an exothermic decomposition to give Na_2CrO_4 and Cr_2O_3. This Cr_2O_3 further reacts with $Na_2C_2O_4$ to give the chromate.

The IR frequencies of the final products in each of the reactions are listed in Table 2. The bands are assigned to a mixture of Na_2CrO_4 [5] and Na_2CO_3 [5] for the 1 : 2 mixture, pure Na_2CrO_4 [5] for the 1 : 1 mixture and a mixture of Na_2CrO_4 and Cr_2O_3 [4] for 2 : 1, 3 : 1 and 4 : 1 mole ratios. Based on the results, the following reaction schemes are proposed:

$$x\mathrm{Na_2Cr_2O_7} + \mathrm{Na_2C_2O_4} \rightarrow (x+1)\mathrm{Na_2CrO_4} + \left(\frac{x-1}{2}\right)\mathrm{Cr_2O_3} \qquad (4)$$

$x > 1$

$$\mathrm{Na_2Cr_2O_7} + \mathrm{Na_2C_2O_4} \rightarrow 2\mathrm{Na_2CrO_4} \qquad (5)$$

$$\mathrm{Na_2Cr_2O_7} + y\mathrm{Na_2C_2O_4} \rightarrow (y-1)\mathrm{Na_2CO_3} + 2\mathrm{Na_2CrO_4} \qquad (6)$$

$y > 1$

Table 2 TG and IR data of mixtures of $Na_2Cr_2O_7$ and $Na_2C_2O_4$

$Na_2Cr_2O_7$:$Na_2C_2O_4$ mole ratio	Mass loss, %		IR frequencies (cm^{-1}) of the products obtained		
	obsd.	calcd.	Na_2CrO_4	Na_2CO_3	Cr_2O_3
1:2	18.85	18.87	950m, 915m, sh, 890s, 855s, 680m	1755m, 1440vs, 880s, 705m	—
1:1	17.75	18.18	950m, 915m, sh 890s, 855s, 680m	—	
2:1	14.40	14.59	950m, 915m, sh, 890s, 855s, 680m	—	625m, 560m, 400w
3:1	13.23	13.10	950m, 915m, sh, 890s, 855s, 680m	—	625m, 560m, 400w
4:1	12.53	12.18	950m, 915m, sh, 890s, 855s, 680m	—	625m, 560m, 400w

The percentage mass losses calculated on the basis of these reactions are tabulated in Table 2, which agree well with the observed values.

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Zusammenfassung — Anhand der Systeme Kaliumdichromat-Kaliumoxalat bzw. Natriumdichromat-Natriumoxalat wurde eine thermische Untersuchung der Festkörperreaktion zwischen Dichromaten und Oxalaten durchgeführt. Dazu wurden thermogravimetrische, differentialthermoanalytische, IR-spektroskopische und Röntgendiffraktionsverfahren angewendet. Im Ergebnis zeigte sich eine stöchiometrische Reaktion von Dichromat und Oxalat im Verhältnis 1:1, die das entsprechende Chromat als einziges Produkt liefert.

Резюме — Методами ТГ, ДТА, ИК спектроскопии и рентгенофазового анализа проведено исследование твердотельной реакции между бихроматами и оксалатами на примере двух систем бихромат калия — оксалат калия и бихромат натрия — оксалат натрия. Результаты показали, что реакция дихромата и оксалата при стехиометрическом их соотношении 1:1 приводит к образованию соответствующего хромата в качестве единственного продукта.