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SOLID STATE REACTIONS IN THE POTASSIUM IODATE AND MOLYBDENUM(VI) OXIDE SYSTEM

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The reaction between potassium iodate and molybdenum(VI) oxide in mixtures of different mole ratios has been investigated employing TG and DTA techniques in static air atmosphere. The products are characterised by infrared spectroscopy, chemical analysis and X-ray diffraction studies. The studies indicate the formation of mono-, di-, tri- and tetramolybdates of potassium from mixtures with 2:1, 1:1, 2:3 and 1:2 mole ratios of $KIO_3:MoO_3$. The kinetics of the reaction was followed and the energy of activation values were computed.

An interesting aspect of the decomposition of halogenoxyacids and their salts is that they are extremely sensitive to the presence of additives. Detailed studies have been made on the influence of transition metal oxides during the thermal decomposition of various halates like $KClO_4$ [1, 2], $KClO_3$ [4], $TlClO_4$ [3], $NaClO_2$ [5], $Ba(ClO_4)_2$ [6] etc. In presence of Cr(III) oxide for instance, these salts decompose at strikingly low temperatures and further, oxidise the Cr(III) to Cr(VI) compounds. Thus a study of the interaction of MoO_3 with KIO_3 appeared relevant and the results of the study using TG and DTA techniques are reported in this paper. The products are characterised by infrared spectroscopy, chemical analysis and X-ray powder diffraction studies. The kinetics of the reaction was followed by the Coats–Redfern [7] method and the activation energy values have been calculated.

Experimental

Analytically pure grade KIO_3 was used as such. Molybdenum(VI) oxide was obtained by heating reagent grade $H_2MoO_4 \cdot H_2O$ at 400° until the dehydration was complete. The MoO_3 so obtained was stable upto 790° after which it started subliming.

Reaction mixtures were prepared by grinding together KIO_3 and MoO_3 in mole ratios of 1:3, 1:2, 2:3, 1:1, 2:1 and 3:1 in an agate mortar for 10–15 min.

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Thermogravimetry and differential thermal analysis were done in air using a Stanton simultaneous thermal analyser 783 instrument at a linear heating rate of 10 deg/min. Constant temperature heating experiments were carried out in air using a furnace whose temperature could be controlled with an accuracy of ± 5°.

IR spectra were recorded in the range 2000–400 cm^{-1} with a Perkin–Elmer 983 spectrophotometer employing KBr pellet technique. The X-ray powder diffraction patterns were recorded in a Philips diffractometer using CuK_α radiation.

Results and discussion

The TG and DTA runs of pure KIO_3 indicate that it melts at 560° with an endotherm and immediately decomposes to KI in the range 560–600°.

The TG curves of various mixtures are shown in Fig. 1 which indicate a single step reaction for all the mixtures except for the 3 : 1 mixture wherein two steps are observed. Noticeably, in all the case, the mass loss sets in at a temperature of ~435° which is much below the decomposition temperature of either of the reactants. The temperature of the completion of the reaction ranges from 475° for the 1 : 3 mixture and gradually increases to 525° for the 2 : 1 and to 600° for the 3 : 1 mixture. Thus,

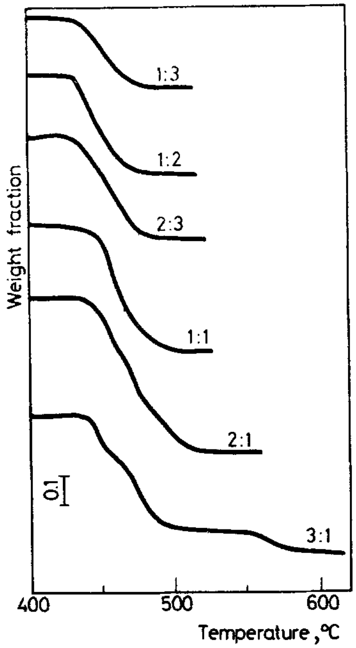

Fig. 1 TG curves of mixtures of KIO_3 and MoO_3 in different mole ratios

with a decrease in the proportion of MoO_3 in the mixtures, the temperature range of the reaction increases. This in turn indicates that the presence of a greater proportion of MoO_3 accelerates the reaction.

The products obtained by heating the mixtures to 600° were crystalline and water insoluble in the case of 1 : 3, 1 : 2, 2 : 3 and 1 : 1 mixtures. The products from 2 : 1 and 3 : 1 mixtures were hygroscopic and contained free iodide.

The IR spectrum of the product from the mixture with 1 : 2 mole ratio exhibited bands at 960m, 945s, 935m, 920s, 900s, 890s, 870s, 755s, 620s, 580s, 555s, 520s, 470m and 430m cm^{-1} corresponding to $K_2Mo_4O_{13}$ [8], the residue from the 2 : 3 mixture showed bands at 940s, 905m, 890s, 870m, 730s, 560s, 535m, 478m cm^{-1} corresponding to $K_2Mo_3O_{10}$ [8] and the product from the 1 : 1 mixture had bands at 930m, 905m, 870s. 720s, 705s, 570w, 480m and 402m cm^{-1} due to $K_2Mo_2O_7$ [8]. The products from 2 : 1 and 3 : 1 mixtures both exhibited a very strong and broad band around 830 cm^{-1} characteristic of K_2MoO_4 [9]. The product from the 1 : 3 mixture showed IR bands due to MoO_3 in addition to bands due to $K_2Mo_4O_{13}$. The X-ray diffraction patterns of the products from 1 : 3, 1 : 2, 2 : 3 and 1 : 1 mixtures corresponded to the literature reported values [10] for $K_2Mo_4O_{13} \cdot MoO_3$, $K_2Mo_4O_{13}$, $K_2Mo_3O_{10}$ and $K_2Mo_2O_7$ respectively.

These results point out that KIO_3 and MoO_3 react in stoichiometric ratios of 1 : 2 to give the potassium tetramolybdate, in 2 : 3 ratio to give potassium trimolybdate, in 1 : 1 ratio to give potassium dimolybdate and in 2 : 1 ratio to give the potassium molybdate. This is further confirmed by the percentage mass loss values obtained from the TG curves which agree well with the values calculated on the basis of the reaction schemes proposed in Table 1. The excess KIO_3 in the 3 : 1 mixture decomposes to give KI in the second step as seen in the TG curve.

The DTA curves of the different mixtures are shown in Fig. 2. The reaction of the 1 : 3 mixture which takes place in the narrowest range of temperature is manifested

Table 1 Thermogravimetric data as compared to the mass loss calculated on the basis of the proposed reaction schemes

$KIO_3 : MoO_3$ mole ratio	Mass loss, %		Temp. range of reaction, °C	Reaction scheme proposed
	obsd.	calcd.		
1 : 3	24.10	25.85	435–475	$KIO_3 + 3MoO_3 \rightarrow 1/2\ K_2Mo_4O_{13} + MoO_3 +$ $+ (1/2\ I_2\uparrow + 5/4\ O_2\uparrow)$
1 : 2	32.70	33.27	435–480	$KIO_3 + 2MoO_3 \rightarrow 1/2\ K_2Mo_4O_{13} +$ $+ (1/2\ I_2\uparrow + 5/4\ O_2\uparrow)$
2 : 3	38.89	38.84	435–495	$2KIO_3 + 3MoO_3 \rightarrow K_2Mo_3O_{10} + (I_2\uparrow + 5/2\ O_2\uparrow)$
1 : 1	45.65	46.65	440–500	$KIO_3 + MoO_3 \rightarrow 1/2\ K_2Mo_2O_7 + (1/2\ I_2\uparrow + 5/4\ O_2\uparrow)$
2 : 1	55.29	58.38	440–525	$2KIO_3 + MoO_3 \rightarrow K_2MoO_4 + (I_2\uparrow + 5/2\ O_2\uparrow)$
3 : 1	47.72	48.59	440–600	$3KIO_3 + MoO_3 \rightarrow K_2MoO_4 + KI + (I_2\uparrow + 4O_2\uparrow)$

as one endotherm at 435°. In the higher ratios of 1 : 2, 2 : 3 and 1 : 1, the number of endotherms gradually increases indicating a complex reaction that sets in these mixtures, while in 2 : 1 and 3 : 1 mixtures, there is also an exotherm interposed between the endotherms. Besides, the sharp endotherms at ~560° for the 1 : 3 and 1 : 2 mixtures and 565° for the 2 : 3 mixture are assigned to the melting of $K_2Mo_4O_{13}$ and $K_2Mo_3O_{10}$ respectively, formed as products in these ratios. The 560° endotherm for the 3 : 1 mixture corresponds to the melting followed by decomposition of the excess unreacted KIO_3.

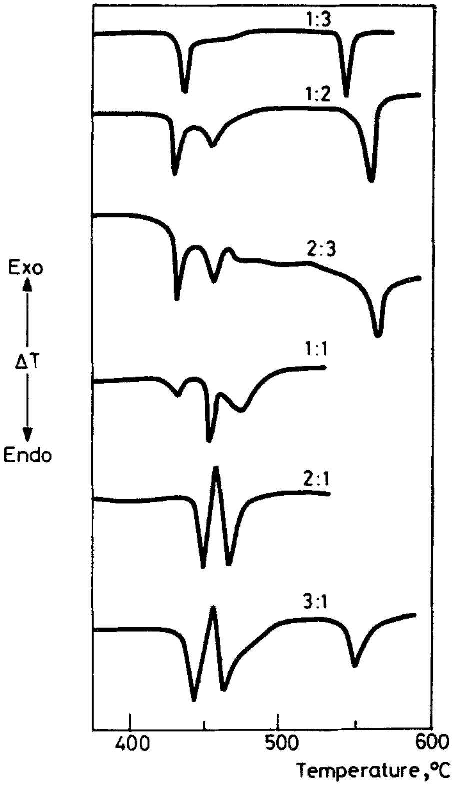

Fig. 2 DTA curves of mixtures of KIO_3 and MoO_3 in different mole ratios

The kinetics of the reaction was followed by the Coats–Redfern method [7] and the energy of activation was calculated. The values, given in Table 2, are found to be of the same magnitude ~84 kJ/mol indicating that the same type of mechanism operates in all these reactions.

Table 2 Activation energy values calculated by the Coats–Redfern method

KIO_3 : MoO_3 mole ratio	E_a value, kJ/mol
1 : 3	79
1 : 2	75
2 : 3	84
1 : 1	88
2 : 1	71
3 : 1	79

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Zusammenfassung — In umbewegter Luftatmosphäre wurde mittels TG- und DTA-Verfahren die Reaktion zwischen Kaliumjodat und Molybdän(VI)-oxid in Gemischen mit unterschiedlichen Molverhältnissen untersucht. Die Produkte werden mit Hilfe von IR-Spektroskopie, chemischer Analyse und Röntgendiffraktionsuntersuchungen beschrieben. Die Untersuchungen an der Reaktion von Gemischen mit einem KIO_3 : MoO_3 Molverhältnis von 2 : 1, 1 : 1, 2 : 3 und 1 : 2 zeigen die Bildung von Mono-, Di-, Tri- bzw. Tetramolybdat des Kaliums. Die Reaktionskinetik wurde untersucht und die Aktivierungsenergien berechnet.

Резюме — Методом ТГ и ДТА в статической атмосфере воздуха исследована реакция между иодатом калия и окисью шестивалентного молибдена, взятых в различных молярных соотношениях. Образующиеся продукты были охарактеризованы ИК спектроскопией, химическим и рентгенофазовым анализом. Установлено образование моно-, ди-, три- и тетрамолибдатов калия в смесях с молярным соотношением KIO_3 : MoO_3 равным 2 : 1, 1 : 1, 2 : 3 и 1 : 2. Прослежена кинетика реакции и вычислены энергии активации.