CATALYTIC THERMAL DECOMPOSITION OF MAGNESIUM IODATE IN THE PRESENCE OF METAL OXIDES OR CARBON

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(Received 8 July 1983)

ABSTRACT

The catalytic thermal decomposition of intimate mixtures of $Mg(IO_3)_2$ and metal oxides (Fe_2O_3, Fe_3O_4, Cr_2O_3) or C (active carbon) was investigated by employing thermogravimetry (TG), differential thermal analysis (DTA), X-ray diffraction analysis and gas chromatography. The initial decomposition temperature of the mixtures was around 720 K which was much lower than that of pure $Mg(IO_3)_2$, around 820 K. Fe_2O_3 showed no change. Fe_3O_4 was oxidized to Fe_2O_3. Cr_2O_3 reacted with $Mg(IO_3)_2$ to form $MgCrO_4$. Active carbon also reacted with $Mg(IO_3)_2$ and was changed to CO and CO_2.

INTRODUCTION

Several investigators [1–4] have studied the thermal decomposition of $KClO_4$, NH_4ClO_4, metal sulfide and the like, and found it to be catalyzed by the addition of metal oxides. Rudloff and Freeman [5] studied the catalytic effects systematically and concluded that the catalytic activity increased with the *p*-type semiconductor character, reducing power or electrical conductivity of the metal oxides. Fe_3O_4 and Cr_2O_3 exhibit catalytic activity because not only are they *p*-type oxides but they can change irreversibly to the higher oxidization state. Nevertheless, Fe_2O_3 is an *n*-type oxide and, exceptionally, possesses catalytic activity. Furuichi et al. [6] presumed that Fe_2O_3 had a higher concentration of donor centers than the other *n*-type oxides (MgO, Al_2O_3, TiO_2, ZnO), so that the facilitated charge-transfer between Fe_2O_3 and the reactant promoted the decomposition. On the other hand, it has been reported that the decomposition was enhanced by carbon [1,7]. Its mechanism, however, has not been made evident.

In this work, the thermal decomposition of magnesium iodate in the presence of Fe_2O_3, Fe_3O_4, Cr_2O_3 or C is qualitatively studied by DTA, TG, X-ray analysis and gas chromatography. The thermal decomposition of $Mg(IO_3)_2$ is the third-step reaction [8,9] of the magnesium–iodine thermochemical cycle for water-splitting, which has been proposed by our labora-

tory [10]. The enhancement of its decomposition is very important in terms of raising the heat efficiency of the cycle.

EXPERIMENTAL

Materials

The magnesium iodate used was obtained from Yanagishima Pharmaceutical Co., Ltd. (Japan). Iron(III) oxide, iron(II) oxide, chromium(III) oxide and active carbon were obtained from Nakarai Chemicals, Ltd. (Japan). All these reagents were of guaranteed grade.

Methods

Various mixtures of $Mg(IO_3)_2$ and the metal oxides or active carbon were prepared by taking the required amounts and thoroughly grinding in an agate mortar.

Simultaneous thermogravimetric and differential thermal analyses were made in argon using a Shimadzu thermal analyzer (DT-30), where α-alumina was used as reference material. About 30–50 mg of the mixtures were taken for each run and the heating rate of the furnace was kept at 10 K min^{-1}.
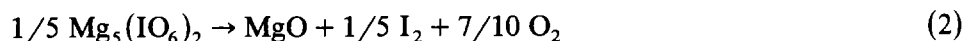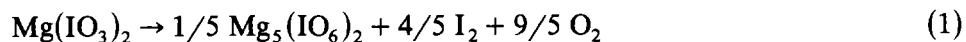
X-Ray powder diffraction patterns were taken with a Shimadzu X-ray diffractometer (XD-3) using Cu$K\alpha$ radiation.

Evolved gas from the decomposition of mixtures of $Mg(IO_3)_2$ and C was analyzed by a Shimadzu gas chromatograph (GC-R1A).

RESULTS AND DISCUSSION

Pure $Mg(IO_3)_2$

The TG and DTA results of pure $Mg(IO_3)_2$ are shown in Fig. 1. $Mg(IO_3)_2$ decomposes thermally in two steps as

$$Mg(IO_3)_2 \rightarrow 1/5\ Mg_5(IO_6)_2 + 4/5\ I_2 + 9/5\ O_2 \tag{1}$$

$$1/5\ Mg_5(IO_6)_2 \rightarrow MgO + 1/5\ I_2 + 7/10\ O_2 \tag{2}$$

The pure $Mg(IO_3)_2$ starts to decompose around 820 K and is complete around 970 K.

Mixtures of $Mg(IO_3)_2$ and Fe_2O_3

The TG and DTA curves of 1 : 0.5, 1 : 1 and 1 : 2 mixtures of $Mg(IO_3)_2$ and Fe_2O_3 are reproduced in Fig. 2. The weight loss starts at a lower
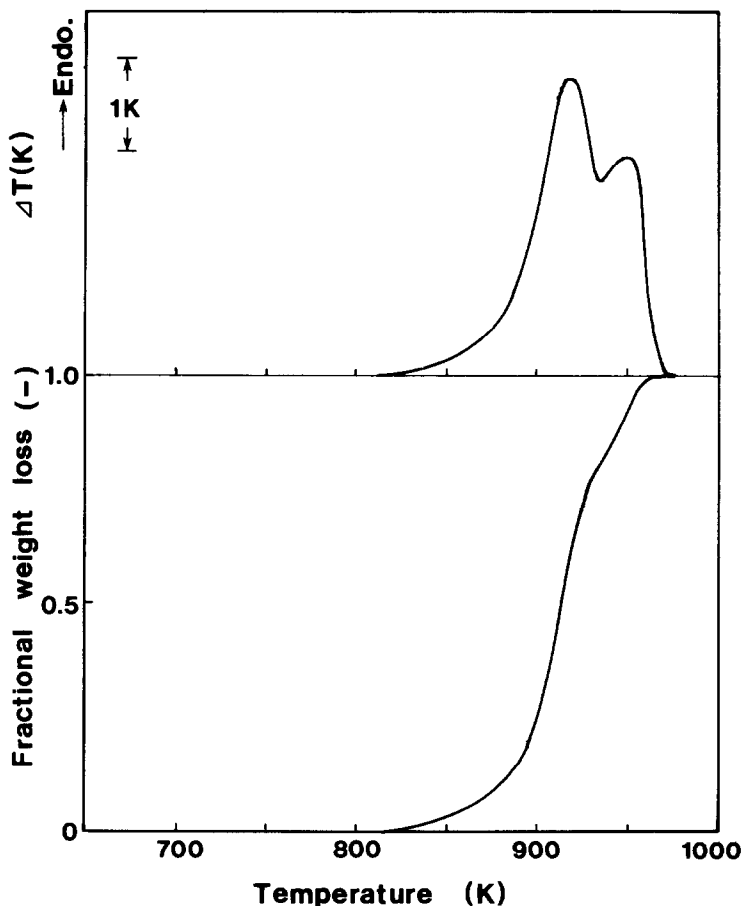
Fig. 1. TG and DTA plots for pure $Mg(IO_3)_2$.

temperature with increasing molar ratio of Fe_2O_3. The DTA curves did not show two clear peaks compared with that of pure $Mg(IO_3)_2$, while the DTA peak area per unit weight of $Mg(IO_3)_2$, which corresponds to the heat of decomposition, was almost the same as that of $Mg(IO_3)_2$. The perfectly decomposed products were examined by X-ray analysis, and it was con-firmed that Fe_2O_3 had not changed chemically.

From this, it can be said that Fe_2O_3 catalyzed the decomposition without changing chemically. If the decomposition proceeds by the charge-transfer mechanism as mentioned by Furuichi et al. [6], it can be speculated that Fe_2O_3 acts as the promotor for the decomposition.

Mixtures of $Mg(IO_3)_2$ and Fe_3O_4

TG and DTA plots of 1:0.5, 1:2 and 1:3 mixtures of $Mg(IO_3)_2$ and Fe_3O_4 are given in Fig. 3. The weight loss starts around 720 K and is

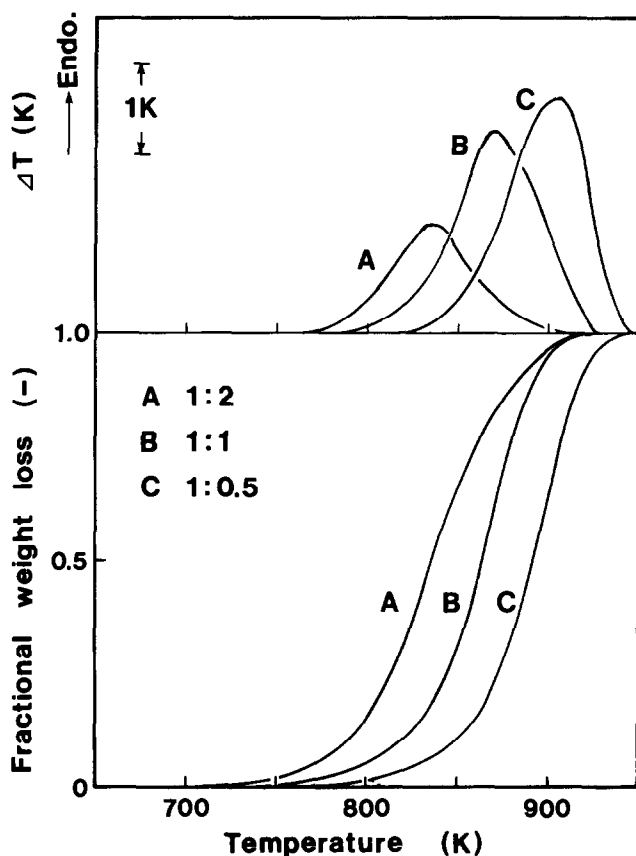Fig. 2. TG and DTA plots for mixtures of $Mg(IO_3)_2$ and Fe_2O_3.

complete around 930 K. The DTA peak appears clearly only in the case of the 1 : 0.5 mixture while the DTA peaks of 1 : 2 and 1 : 3 mixtures are small. This may be because the exotherm due to the oxidation of Fe_3O_4 ($\Delta H_{298} = -27.9$ kcal mol^{-1}) compensates the endotherm due to the decomposition of $Mg(IO_3)_2$ ($\Delta H_{298} = 87.5$ kcal mol^{-1}) according to

$$Mg(IO_3)_2 \rightarrow MgO + 2\,I_2 + 5/2\,O_2 \tag{3}$$

$$Fe_3O_4 + 1/4\,O_2 \rightarrow 3/2\,Fe_2O_3 \tag{4}$$

where Fe_2O_3 was confirmed by examining the residues of the decomposed products by X-ray analysis. Further, the formation of Fe_2O_3 was supported by observation, that is, the color of the mixtures changed from black (Fe_3O_4) to purple (Fe_2O_3) as the reaction proceeded. These results indicate that the decomposition in the presence of Fe_3O_4 is enhanced by two effects: (1) Fe_2O_3, which has a comparatively strong affinity for oxygen, probably abstracts atomic oxygen from magnesium iodate moiety; (2) the heat re-

quired for the decomposition is supplied by the exothermic heat produced on oxidation of Fe_3O_4.

Mixtures of $Mg(IO_3)_2$ and Cr_2O_3

TG and DTA plots of $1:0.3$, $1:0.5$ and $1:0.7$ mixtures of $Mg(IO_3)_2$ and Cr_2O_3 are given in Fig. 4. The weight loss starts around 720 K and is complete around 950 K. It was found by X-ray analyses that the decomposition products at around 780 K and 890 K contained $MgCrO_4$, whose color was orange-yellow, characteristic of Cr(VI). This means that Cr(III) changed to the higher oxidation state Cr(VI). The color of the final product, however, was dark green owing to Cr(III). Based on these results, the decomposition scheme of $Mg(IO_3)_2$ and Cr_2O_3 mixtures can be given as

$$Mg(IO_3)_2 + 1/2\ Cr_2O_3 \rightarrow MgCrO_4 + I_2 + 7/4\ O_2 \tag{5}$$
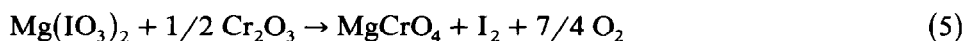
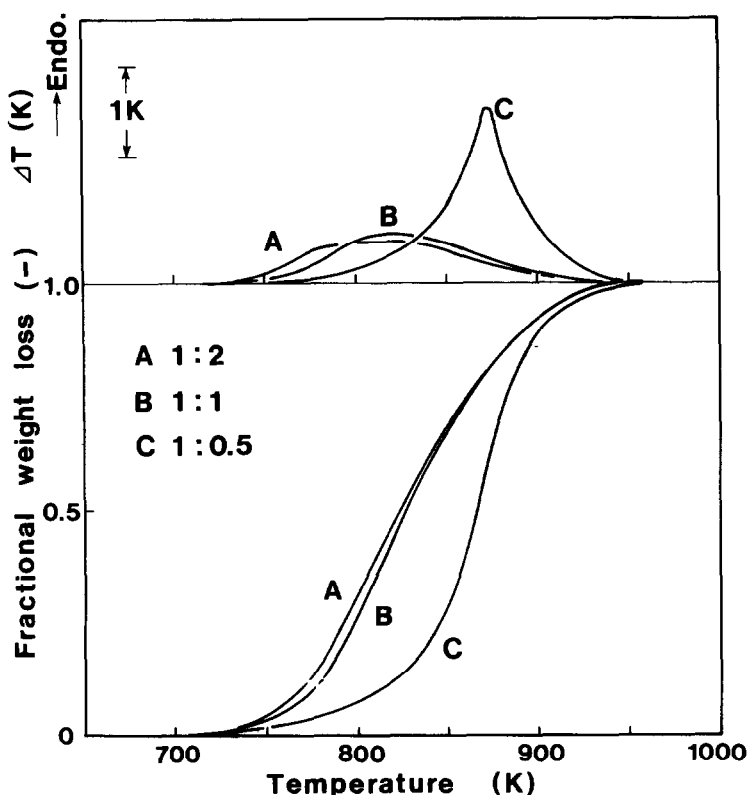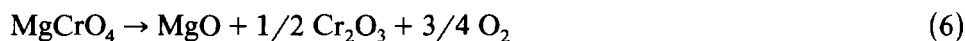and further $MgCrO_4$ decomposes as

$$MgCrO_4 \rightarrow MgO + 1/2\ Cr_2O_3 + 3/4\ O_2 \tag{6}$$

Fig. 3. TG and DTA plots for mixtures of $Mg(IO_3)_2$ and Fe_3O_4.
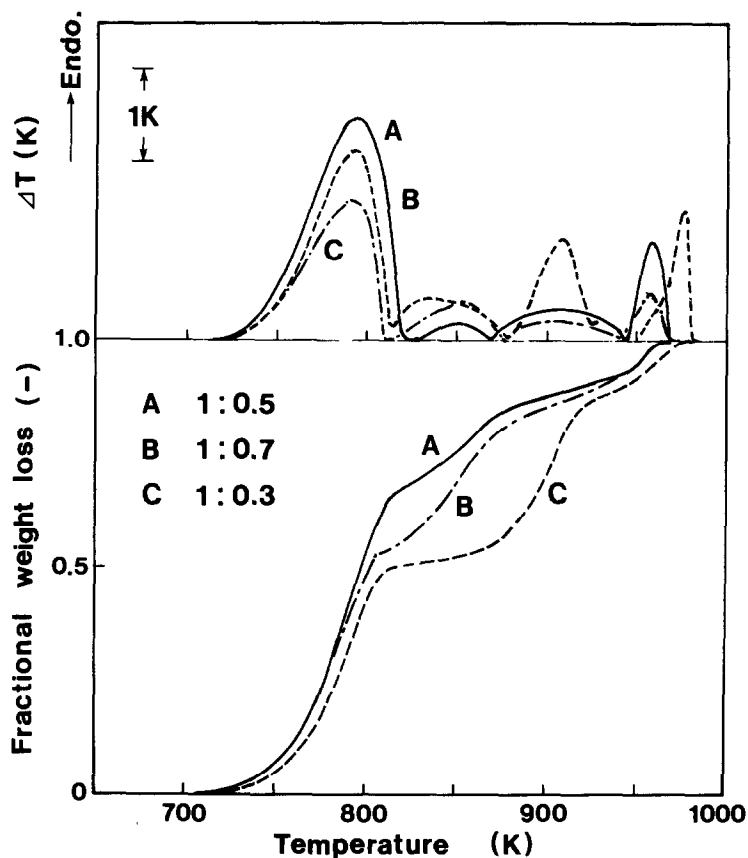
Fig. 4. TG and DTA plots for mixtures of $Mg(IO_3)_2$ and Cr_2O_4.

The first and third weight losses in Fig. 4 are attributed to the above reactions. From the patterns of the weight loss it is found that the two reactions proceeded imperfectly, as considered below. It is difficult for the solid state reaction to go to completion because the molecular motions in the solid phase are considerably limited compared with that of the liquid or gaseous state. This is more likely to occur if the mixing or the contact between solid and solid is imperfect. Simultaneously, it was found that the decomposition of $Mg(IO_3)_2$ was catalyzed, not formed $MgCrO_4$, in the presence of Cr_2O_3 since $Mg_5(IO_6)_2$ was identified in the intermediates at around 790 K by X-ray analysis. The situation may be improved by further grinding and mixing or compressing the mixtures.

Mixtures of $Mg(IO_3)_2$ and carbon

The DTA and TG curves of 1 : 0.5, 1 : 1, 1 : 2 mixtures of $Mg(IO_3)_2$ and C are shown in Fig. 5. The weight loss at around 730 K increases with an

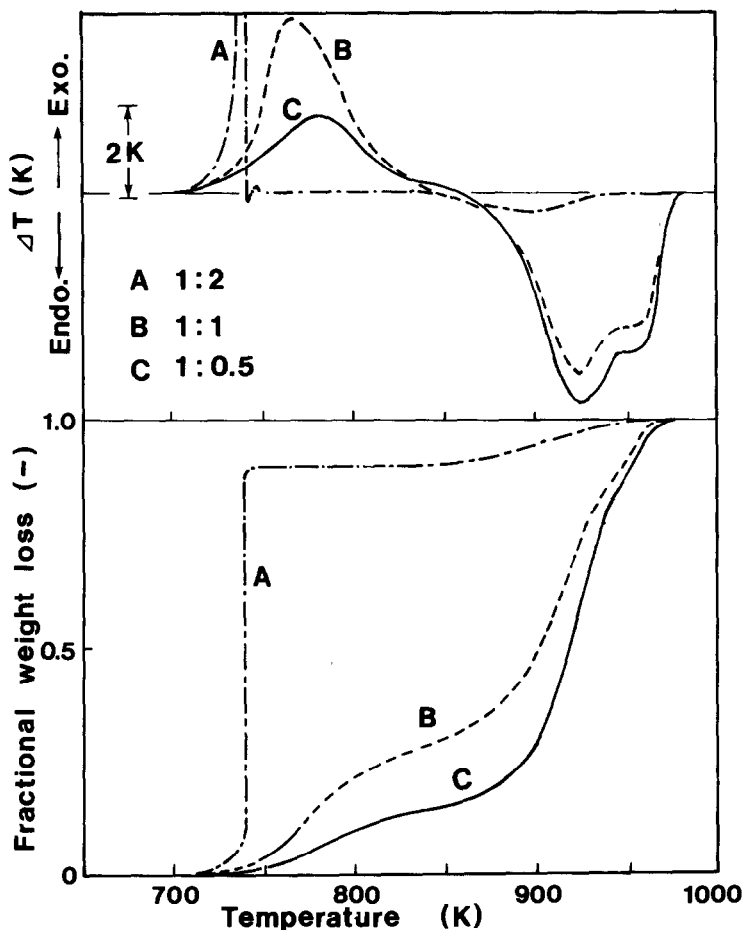Fig. 5. TG and DTA plots for mixtures of $Mg(IO_3)_2$ and C.

increase in the molar ratio of C. Hence, the amount of undecomposed $Mg(IO_3)_2$ increases with a decrease in the molar ratio of C. In the case of 1:2 mixtures, the sudden weight loss accompanying the large exotherm is observed at around 720 K. This may be attributed to both the large reducing power of carbon and the large exothermic heat produced by the reaction

$$C + O_2 \rightarrow CO + CO_2$$
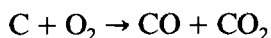
Similar phenomena were observed in the case of the mixtures with a molar ratio greater than 1:2. At the point, the evolved gas was collected and analyzed by the gas chromatograph. The gas consisted of I_2, CO_2, CO and O_2. From this, the reaction scheme is considered as

$$Mg(IO_3)_2 + x\,C \rightarrow MgO + I_2 + (x - y)\,CO_2 + y\,CO + (3 - x - y/2)\,O_2 \quad (7)$$
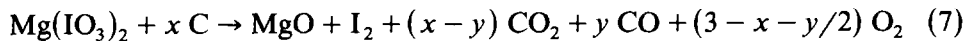
The small amount of undecomposed $Mg(IO_3)_2$ remained in the case of the

1 : 2 mixture, as seen in Fig. 5. This is perhaps due to the imperfectness of the solid–solid reaction as mentioned above. The decomposed product was only MgO because the added carbon reacted with $Mg(IO_3)_2$ and changed to CO and CO_2. Even if the excess carbon remains, it is easily removed by burning with air. This is different from the above three cases, in which they still remained in the decomposed products. Accordingly, they must be separated from the mixtures with MgO in order for them to be reused. The separation between solid and solid, however, is fairly difficult; in the case of $Mg(IO_3)_2$–C this is unnecessary, a factor which may be advantageous from a practical point of view.

CONCLUSION

It was found that the initial decomposition temperature of the intimate mixtures of $Mg(IO_3)_2$ and Fe_2O_3, Fe_3O_4, Cr_2O_3 or C was about 100 K below that of pure $Mg(IO_3)_2$. It was also found that there were three types of catalytic activity in the thermal decomposition of $Mg(IO_3)_2$. The first is like Fe_2O_3 in that it exhibits the so-called catalytic activity, that is, the catalyst itself is not changed. The second is like Fe_3O_4 or Cr_2O_3 in that they react with $Mg(IO_3)_2$ in the solid phase and form Fe_2O_3 or $MgCrO_4$, respectively; to do so reduces the decomposition temperature. The third is like carbon in that it also reacts with $Mg(IO_3)_2$, but explosively, accompanying the large exotherm and forms gaseous products, CO and CO_2.

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