Thermochimica Acta, 184 (1991) 205–212
Elsevier Science Publishers B.V., Amsterdam

Kinetics and mechanism of thermal decomposition of magnesium perchlorate catalysed by metal metavanadate additives

A.M. El-Awad, R.M. Gabr and M.M. Girgis

Chemistry Department, Faculty of Science, Assiut University, Assiut (Egypt)

(Received 7 November 1990)

Abstract

The thermal decomposition of magnesium perchlorate, $Mg(ClO_4)_2$, was studied non-isothermally and isothermally. Under non-isothermal conditions it was found that $Mg(ClO_4)_2$ decomposes through a stepwise release of oxygen forming unstable intermediates which produce MgO, not $MgCl_2$, as a final decomposition product. The kinetic parameters of the decomposition reaction were deduced employing a computer-oriented kinetic analysis of the $\alpha - t$ data obtained under isothermal conditions in the temperature range 300–500 °C. This indicates that the decomposition process is governed by the Ginstling–Brounshtein equation. In order to evaluate the effect of additives on the catalytic thermal decomposition reaction, the decomposition of $Mg(ClO_4)_2$ was followed in the presence of CuV_2O_6 and MgV_2O_6 catalysts. The results show that CuV_2O_6 had a remarkable catalytic acceleration effect while addition of MgV_2O_6 retarded the decomposition of $Mg(ClO_4)_2$. These effects are discussed on the basis of the redox couple, $Cu^{2+} + e^- \rightleftharpoons Cu^+$, which promotes the decomposition reaction via a charge-transfer mechanism. In the case of MgV_2O_6 addition, the retarding effect seems to arise from the hindrance of gaseous oxygen evolution. Finally, the effect of additives was followed kinetically and a modified catalytic mechanism is proposed.

INTRODUCTION

Whilst studying the thermal behaviour of solids in order to identify the mechanism of their decomposition process and those properties which are responsible for their thermal behaviour [1–3], we have carried out detailed thermal analytical and kinetic investigations on the decomposition of perchlorates [1], which have found technological applications in explosives, pyrotechnics and propellants [4]. The effect of additives on the catalytic thermal decomposition of perchlorates is of special interest; however discrepant results have been reported in this field. Freeman and Anderson [5] proposed that the rate-controlling step is the transfer of an electron from the perchlorate ion to the positive hole in p-type semiconducting additives. Other workers [1,6,7] have explained their results in terms of an electron-transfer mechanism and an oxygen abstraction model [8]. In the present

0040-6031/91/$03.50

study an attempt was made to obtain detailed information on the thermal decomposition process of magnesium perchlorate which so far has not been reported. Also, the correlation between the mechanism of the catalysed thermal decomposition of magnesium perchlorate and the nature of the catalysts added, namely CuV_2O_6 and MgV_2O_6, are discussed with special reference to their electronic properties.

EXPERIMENTAL

All the reagents used in the present investigation were of analytical grade (BDH Chemicals). The DTA and TGA of magnesium perchlorate were carried out using a 1090 DuPont thermal analyser with a heating rate of 10 °C min^{-1}. Magnesium perchlorate was mixed in an agate mortar with 10% (wt./wt.) copper metavanadate (CuV_2O_6) or magnesium metavanadate (MgV_2O_6) as thermally stable solid catalysts. The α–t data, where α is the fraction decomposed at time t, of pure magnesium perchlorate and its mixtures with the catalysts were obtained as described elsewhere [3] in the temperature range 300–500 °C using a Sartorius electrobalance (Type 2004 MP6). The sample temperature was adjusted using a Heraus temperature controller, type TRK. A Philips X-ray diffractometer (model PW 1710) was used to record d values for the residual decomposition product of magnesium perchlorate. The IR investigations were carried out on a Perkin–Elmer 580 B spectrophotometer, using the KBr technique. The catalysts used in this study were prepared as described by Mocala and Ziolkowski [9], and the formation of CuV_2O_6 and MgV_2O_6 was well characterized by X-ray analysis.

RESULTS AND DISCUSSION

Superimposed TG and DTA curves for pure magnesium perchlorate are shown in Fig. 1. The TG curve (curve (a) in Fig. 1) has two distinct well-separated steps in the range 385–415 °C, each step consisting of two consecutive stages. It is evident from the percentage weight loss (Table 1) that the decomposition process of $Mg(ClO_4)_2$ proceeds via a stepwise release of oxygen forming chlorate, chlorite, hypochlorite and finally magnesium oxide.

The percentage weight loss found at the end of the decomposition process suggests that the overall equation for the decomposition is

$$Mg(ClO_4)_2 \rightarrow MgO + Cl_2 + 7/2O_2 \qquad (1)$$

From a comparison with the ASTM cards [10], the X-ray diffraction pattern of the residual decomposition products reveals the presence of MgO only (d spacing values 2.11, 1.49 and 1.22 Å) which is supported by the appearance of the characteristic IR band of MgO at 542 cm^{-1} [11]. There is

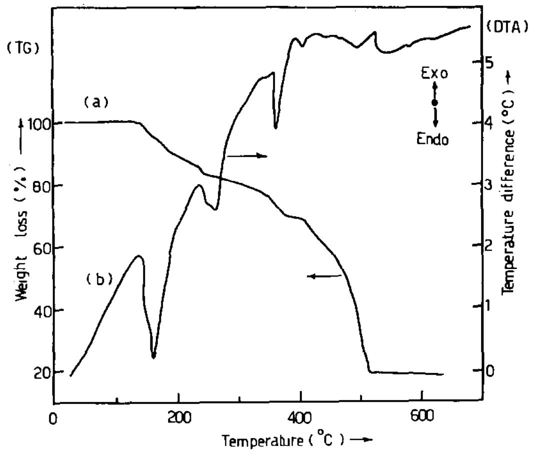

Fig. 1. TG (a) and DTA (b) curves for magnesium perchlorate.

no evidence for the presence of $MgCl_2$ in the residual products as suggested before [12]. These findings are in accordance with the thermodynamic data reported by Markowitz [13].

Further information can be obtained from the DTA curve (curve (b) in Fig. 1). The curve starts to deflect towards the endothermic direction at

TABLE 1

Suggested thermal decomposition scheme for magnesium perchlorate according to the TG data

Compound	% Weight loss		Decomposition range (°C)
	Found	Calculated	
$Mg(ClO_4)_2$			
↓			150–250
$Mg(ClO_3)_2$	14.70	14.34	
↓			250–385
$Mg(ClO_2)_2$	29.20	28.67	
↓			415–460
$Mg(ClO)_2$	43.50	43.00	
↓			460–525
MgO	82.10	81.94	

TABLE 2

The rate constants for the three-dimensional diffusion decomposition of pure $Mg(ClO_4)_2$ in the temperature range 300–500 °C

Temperature (°C)	300	350	400	450	500
$10^4 k$ (s^{-1})	0.06	0.15	0.38	0.75	1.49

about 150 °C and gives a broad endothermic peak corresponding to the initial decomposition stage. The reason for the broadening of this peak is that the initial stage proceeds via the following consecutive reactions [14]:

$$ClO_4^- \rightarrow ClO_3^- + O \tag{2}$$

$$ClO_4^- + O \rightarrow ClO_3^- + O_2 \tag{3}$$

Both are characterized by endothermic effects and the broad peak obtained represents a summation of these effects. The next two endothermic peaks commencing at 250 and 375 °C correspond to the melting of chlorate, as proved by visual examination, and the reversible liquid state decomposition of chlorate to chlorite respectively:

$$ClO_3^- \rightleftharpoons ClO_2^- + O \tag{4}$$

Evidence for the reversibility of reaction (4) can be deduced from the fact that the decomposition rate of chlorate (TG) is very slow; this is consistent with the conclusion drawn by Acheson and Jacobs [15]. This is followed by a small endothermic peak which starts at the beginning of the second main decomposition step and corresponds to the decomposition of chlorite to hypochlorite, which rapidly decomposes to the final products:

$$Mg(ClO_2)_2 \rightarrow Mg(ClO)_2 + O_2 \tag{5}$$

$$Mg(ClO)_2 \rightarrow MgO + Cl_2 + \tfrac{1}{2}O_2 \tag{6}$$

It should be noted that the formation of MgO at the end of the decomposition reaction is accompanied by a solidification process, as demonstrated by the exothermic peak at 525 °C.

Further studies were carried out in order to elucidate the kinetic parameters of the thermal decomposition reaction of $Mg(ClO_4)_2$. Figure 2 shows the α–t curves obtained under isothermal conditions in the temperature range 300–500 °C. The computer-oriented kinetic analysis was performed for each set of α and t data using the different kinetic equations describing such reactions [2]. The results indicate that the Ginstling–Brounshtein equation (three-dimensional diffusion)

$$(1 - \tfrac{2}{3}\alpha) - (1 - \alpha)^{2/3} = kt \tag{7}$$

gives the best fit of the data, with a correlation coefficient very close to unity. Accordingly, one can conclude that the rate of the decomposition reaction is controlled by the rate at which the gaseous products can diffuse away from the reaction centres [16]. This conclusion provides further support for the suggestion that eqn. (4) represents the rate-controlling step, where ClO_3^- will only decompose readily when the oxygen can escape easily.

Application of the Arrhenius equation using the data depicted in Table 2

$$k = A\exp(-E_a/RT) \tag{8}$$

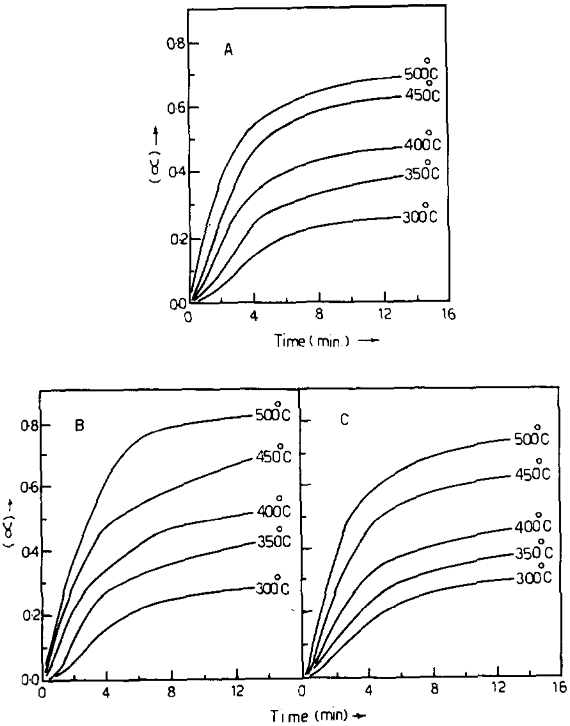

Fig. 2. Plots of α vs. temperature for the isothermal decomposition of magnesium perchlorate: A, pure; B, mixed with 10 wt.% CuV_2O_6 catalyst; C, mixed with 10 wt.% MgV_2O_6 catalyst.

where E_a is the energy of activation and A is the pre-exponential factor, provides the two values $E_a = 58.35$ kJ mol^{-1} and $\ln A = 9.5$ for the thermal decomposition reaction of $Mg(ClO_4)_2$ (see curve a in Fig. 3).

It has been stated that the decomposition of perchlorates involves an electron-transfer process [6]; this was checked by examining the thermal

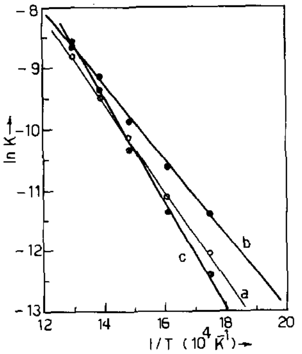

Fig. 3. Arrhenius plots for the isothermal decomposition of magnesium perchlorate: curve a, pure; curve b, mixed with 10 wt.% CuV_2O_6 catalyst; curve c, mixed with 10 wt.% MgV_2O_6 catalyst.

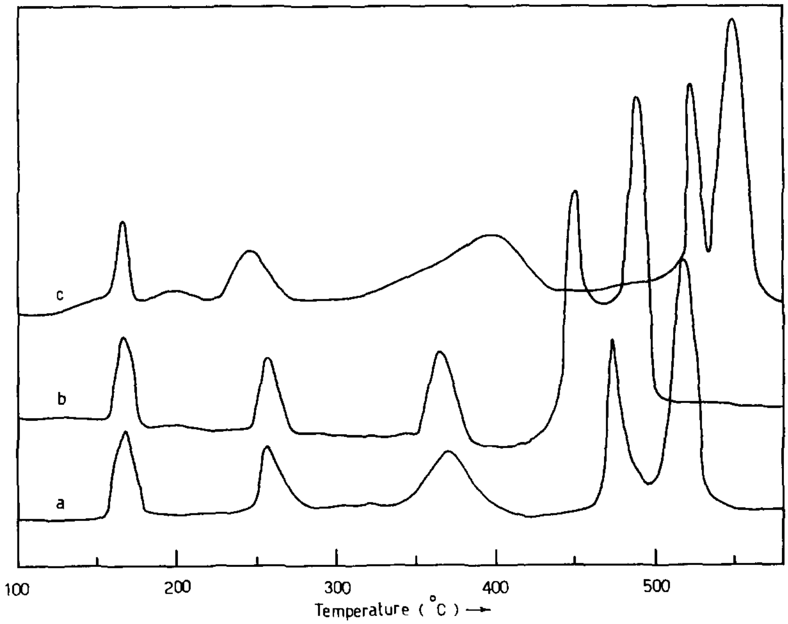

Fig. 4. DTG curves for the decomposition of magnesium perchlorate, pure and mixed with catalysts (symbols as in Fig. 3).

behaviour of $Mg(ClO_4)_2$ in the presence of two different additives, namely CuV_2O_6 and MgV_2O_6. Both were thoroughly characterized structurally [9,17] and pre-examined in another catalytic test reaction which involves an electron transfer [17]. Typical DTG curves for pure $Mg(ClO_4)_2$ and $Mg(ClO_4)_2$ mixed with CuV_2O_6 and MgV_2O_6 (Fig. 4) suggest that the decomposition of $Mg(ClO_4)_2$ is affected differently by the presence of each additive. Copper metavanadate (CuV_2O_6) does not alter the low temperature decomposition stage but accelerates the high temperature one considerably, while the presence of magnesium metavanadate MgV_2O_6 retards the decomposition in the high temperature region and has no influence in the low temperature range. From these findings, it is reasonable to assume a modified catalytic mechanism involving an electron transfer between the material to be decomposed and the additive. Accordingly, the enhancement role of the copper-containing catalyst could be interpreted in terms of the ease of establishing the redox cycle $Cu^{2+} + e^- \rightleftharpoons Cu^+$ [1]. Considering the different opinions [6,18] on the catalytic decomposition of perchlorates, one can suggest the following equation to describe the role of Cu^{2+} addition:

$$Cu^{2+} + ClO_3^- \xrightarrow[\mathrm{I}]{} Cu^+ + ClO_2^{\cdot} + O \xrightarrow[\mathrm{II}]{} Cu^{2+} + ClO_2^- + \tfrac{1}{2}O_2 \qquad (9)$$

As seen from eqn. (9), the high electron acceptability of Cu^{2+} enables the decomposition reaction to be initiated (through step I in eqn. (9)) forming a chlorite radical, and copper(II) becomes reduced to copper(I); once the chlorite radical is formed, the next stage is a transfer of an electron from copper(I) (through step II in eqn. (9)). Thus the accelerating effect observed in the case of addition of copper-containing catalysts may be the result of the redox couple $Cu^{2+} + e^- \rightleftharpoons Cu^+$ being so readily established that the two stages, I and II, occur simultaneously. It seems likely that eqn. (9) represents the rate-determining step. Furthermore, it is easy to understand on the basis of the absence of the redox couple, why MgV_2O_6 did not accelerate the magnesium perchlorate decomposition. Only one observation need be considered in such a case; that is why the DTG peak characterizing the chlorate decomposition becomes shifted to a higher temperature with a broadening in its shape. This retardation may be explained in terms of electronic effects which probably enable the Mg^{2+} in MgV_2O_6 to distort the electron distribution sufficiently for Mg^{2+} to be bound to the oxygen produced from the decomposition reaction, a situation that renders the escape of oxygen more hindered and the backward reaction [15] in $ClO_3^- \rightleftharpoons ClO_2^- + O$ much more favoured than in the case of pure $Mg(ClO_4)_2$ or $Mg(ClO_4)_2$ plus CuV_2O_6 mixture. This assumption finds support [19] from the fact that the closed-shell configuration of both Mg^{2+} and O^{2-} represents filled 2p shells and empty 3s shells; because O^{2-} ions have a negative ionization potential of 9 eV and Mg^{2+} has an electron affinity of 15 eV, the reaction

$$Mg^{2+} + O^{2-} \rightarrow Mg^+ + O^- \qquad (10)$$

occurs spontaneously by an electron excitation from the 2p band of the O^{2-} ions to the 3s band of the Mg^{2+} ions releasing 24 eV.

Finally, the decomposition of $Mg(ClO_4)_2$ in the presence of 10% (wt./wt.) CuV_2O_6 and MgV_2O_6 additives was followed isothermally in the temperature range of 300–500 °C. The decomposition data represented as α–t curves are shown in Fig. 2. The computer-oriented kinetic analysis was performed as in the case of pure $Mg(ClO_4)_2$ and the results indicate that the three-dimensional diffusion (Ginstling–Brounshtein) equation is still valid to describe such data. The values of k are listed in Table 3.

In order to relate the observed behaviour of the additives to a parameter indicative of their catalytic activity, the activation energy values were obtained using the Arrhenius equation (eqn. (8)). The values are $E_a = 49.37$

TABLE 3

The rate constants for the three-dimensional diffusion decomposition reaction of $Mg(ClO_4)_2$ mixed with 10% (wt./wt.) CuV_2O_6 and MgV_2O_6 catalysts, in the temperature range 300–500 °C

Mixture	$k \times 10^4$				
	300 °C	350 °C	400 °C	450 °C	500 °C
$Mg(ClO_4)_2 + CuV_2O_6$	0.113	0.249	0.531	0.967	1.65
$Mg(ClO_4)_2 + MgV_2O_6$	0.041	0.124	0.336	0.836	1.66

and 70.63 kJ mol^{-1} with ln $A = 9.23$ and 9.37 for $Mg(ClO_4)_2$ plus CuV_2O_6 and $Mg(ClO_4)_2$ plus MgV_2O_6 respectively. The fact that the E_a values lie in the sequence $Mg(ClO_4)_2$ plus CuV_2O_6 < pure $Mg(ClO_4)_2$ < $Mg(ClO_4)_2$ plus MgV_2O_6, i.e. the decrease in the E_a value parallels the accelerating effect of the additives, provides further support for our findings concerning the accelerating effect of CuV_2O_6 and the retarding effect of MgV_2O_6.

REFERENCES

1 A.M. El-Awad, A.A. Said and K.M. Abd El-Salaam, Thermochim. Acta, 126 (1988) 17.
2 A.M. El-Awad and R.M. Mahfouz, J. Therm. Anal., 35 (1989) 1413.
3 R.M. Gabr, A.M. El-Awad and M.M. Girgis, J. Therm. Anal., (1991) in press.
4 P.W.M. Jacobs and H.M. Whitehead, Chem. Rev., 69 (1969) 551.
5 E.S. Freeman and D.A. Anderson, Nature, 206 (1965) 378.
6 M. Shimokawabe, R. Furuichi and T. Ishii, Thermochim. Acta, 20 (1977) 347.
7 W.K. Rudloff and E.S. Freeman, J. Phys. Chem., 74 (1970) 3317.
8 M.M. Markowitz and D.A. Boryta, J. Phys. Chem., 69 (1965) 1114.
9 K. Mocala and J. Ziolkowski, J. Solid State Chem., 69 (1987) 299.
10 Powder Diffraction File (Inorganic Phases), JCPDS International Center for Diffraction Data, U.S.A., 1984.
11 R.A. Nyquist and R.O. Kagel, Infrared Spectra of Inorganic Compounds, Academic Press, New York, 1971, p. 9.
12 A.A. Zinov'ev and L.J. Cludinova, Zh. Neorg. Khim., 1 (1956) 1722.
13 M.M. Markowitz, J. Inorg. Nucl. Chem., 25 (1963) 407.
14 R.J. Acheson and P.W.M. Jacobs, Can. J. Chem., 47 (1969) 3031.
15 R.J. Acheson and P.W.M. Jacobs, J. Phys. Chem., 74 (1970) 281.
16 P.D. Garn, in H. Kambe and P.D. Garn (Eds.), Thermal Analysis: Comparative Studies on Materials, Wiley, New York, 1974, pp. 100.
17 M.M. Girgis, R.M. Gabr and A.M. El-Awad, submitted for publication.
18 E.S. Freeman and W.K. Rudloff, in R.C. Mackenzie (Ed.), Differential Thermal Analysis, Vol. 1, Academic Press, New York, 1970, Chapter 12.
19 N.B. Hannay, Treatise on Solid State Chemistry, Vol. 2, Plenum, New York, 1975, p. 283.