

THE THERMAL DECOMPOSITION OF MAGNESIUM CHLORIDE DIHYDRATE

ANDREW K. GALWEY and GENEVIÈVE M. LAVERTY

Department of Pure and Applied Chemistry, The Queen's University of Belfast, Belfast BT9 5AG (Gt. Britain)

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ABSTRACT

The kinetics and mechanism of the isothermal decomposition of magnesium chloride dihydrate in nitrogen have been studied between 623–803 K. The principal products of reaction were identified as MgO and HCl: the progress of reaction was monitored by titrating the acid evolved with standard alkali. The stoichiometry is satisfactorily represented by



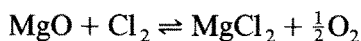
The effects of prevailing water vapour pressure, reaction temperature and sample precrushing were investigated. Electron microscopy was used to examine the textures of partly and fully decomposed salts, confirming that reaction proceeded in the solid state. The kinetic observations fitted the contracting area rate equation from which the activation energies were found to be $110 \pm 5 \text{ kJ mol}^{-1}$ in dry N_2 and $75 \pm 7 \text{ kJ mol}^{-1}$ in 10 Torr water vapour.

The mechanism of this decomposition is discussed with consideration of the close similarity of kinetic behaviour with that of the reaction of MgCl_2 (anhydrous) with O_2 .

INTRODUCTION

On heating, many hydrated crystalline salts evolve water to yield a lower hydrate, or anhydrous salt, by a reaction that characteristically proceeds at a reactant–product interface [1]. Studies of such rate processes have contributed notably towards advancing the theory of solid-state reaction kinetics [1]. However, the evolution of molecular water of crystallization is not the only possible chemical process, and alternative reactions may proceed through intracrystalline interactions of lattice water with other constituents of the salt. An example of this type of behaviour, the subject of the present article, is the solid state decomposition of magnesium chloride dihydrate ($\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$) above 620 K, from which the principal products are MgO and HCl.

Several articles in the literature support the view that hydrolytic reactions occur during the decomposition of $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$. Kelley [2], from consideration of the energy changes and equilibria data for the dehydrations, hydrolyses and decompositions of the various hydrates of magnesium chloride, concluded that dehydration without hydrolysis can only be expected in an atmosphere of HCl gas. The dihydrate tends to give the hydroxychloride, $\text{Mg}(\text{OH})\text{Cl}$. Moldenhauer [3] observed that between 623 K and 778 K water vapour reacts with solid MgCl_2 to yield $\text{Mg}(\text{OH})\text{Cl}$, which is decomposed to MgO and HCl above 778 K. Markowitz [4] concluded, from energy considerations, that above 700 K direct decomposition of magnesium perchlorate to MgO becomes possible. Below this temperature, the relative amounts of MgCl_2 and MgO in the solid product may depend on the composition of the gas phase, if the equilibration reaction



is sufficiently rapid.

Ball [5] has reported a mechanistic study of the reaction of MgCl_2 with O_2 . The low temperature reaction (618–693 K) is controlled by the rate of advance of a reactant–product interface and the activation energy E is 74.0 kJ mol^{-1} . At higher temperatures (713–753 K) the mechanism changes to control by diffusion of Cl_2 gas, the activation energy is reduced (41.2 kJ mol^{-1}) and there is considerable loss of entropy in the formation of the transition state.

The hydrolytic decomposition of $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ may involve $\text{Mg}(\text{OH})_2$ as an intermediate. The dehydration of $\text{Mg}(\text{OH})_2$ has been the subject of several kinetic and mechanistic studies. Gordon and Kingery [6] have concluded from rate and microscopic observations (510–640 K) that crack formation and propagation, resulting from strain at the oxide–hydroxide interface, exerts an important control on the kinetic behaviour. Dehydroxylation of thin crystals obeyed first-order kinetics, while the reaction of thicker crystals fitted the contracting area [1] rate equation, and $E = 126 \pm 20 \text{ kJ mol}^{-1}$. Hancock and Sharp [7] identify the decomposition of $\text{Mg}(\text{OH})_2$ as an interface advance reaction and Sharp [8] concludes that $E = 84 \text{ kJ mol}^{-1}$. Freund et al. [9] find the rate of interface progress to be irregular and spasmodic. At any advancing hydroxide–oxide contact, intervals of diffusion control are interrupted by local crack formation, with product detachment.

The present article reports a kinetic and microscopic investigation of the thermal decomposition of $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$; this reaction appears not to have been previously studied in detail. The major products identified are MgO and HCl and the reaction mechanism is discussed in the context of the extensive background information provided by the articles cited above.

EXPERIMENTAL

Reactant salt

Commercially supplied $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ was heated for 1 h at 673 K in air and the product stored thereafter in a dry atmosphere. The composition of this prepared reactant approximately agreed with expectation for $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ (theoretical values in parentheses): H, 2.85% (3.07%); Cl, 49.2% (54.0%); and Mg, 17.95% (18.5%). The discrepancies can be ascribed to the presence of 2–3% $\text{Mg}(\text{OH})_2$. The prepared salt dissolved completely to give a clear solution in cold water, showing that it contained no MgO.

Method

The kinetics of the isothermal decomposition of $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ were measured by titration of the HCl evolved. During reaction, each sample of salt was maintained at constant temperature (± 2 K) in a stream of N_2 . This flowing gas was passed as a stream of fine bubbles through water containing phenolphthalein indicator and maintained alkaline. The time at which the acid, released by the reaction, decolourized the indicator was noted and a further volume (usually 0.05 ml) of standard alkali (0.1 M NaOH) was immediately added. The influences of temperature, water vapour pressure and reactant precrushing on the kinetics of decomposition of $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ were studied.

During reaction, each salt sample (0.010 ± 0.001 g) was retained in a silica reaction vessel and spread thinly to minimize gas diffusion effects. Isothermal rate studies were completed between 623 and 803 K. In one series of experiments the N_2 gas was predried by passage through a cold trap (78 K). In other experiments the influence of water vapour (10 Torr) on the decomposition at 620–700 K was investigated by pre-passage of the N_2 through water thermostatted at the appropriate temperature. Rates of salt decomposition in 5 and 15 Torr water vapour were also measured.

Other variations in reaction conditions are described at appropriate places in the text below.

Electron microscopy

Samples of the prepared reactant, the product, and the salt decomposed to various known extents (α , fractional reaction) were examined in a Jeol 35CF scanning electron microscope. Portions of each sample were lightly crushed after reaction to enable the textures of internal surfaces to be observed. Each prepared specimen was lightly coated with gold before being placed in the microscope.

RESULTS AND DISCUSSION

Reaction stoichiometry

Yields of product HCl, measured by titration, corresponded to at least 90%, and usually 95–100%, of those expected to result from quantitative conversion of the chloride in the reactant to HCl. The weight of the residues corresponded to expectation for MgO, within the limits of measurement accuracy. Reaction stoichiometry is, therefore, satisfactorily represented by $\text{MgCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{MgO} + 2\text{HCl} + \text{H}_2\text{O}$

No detectable quantity of soluble chloride could be found in the residue by precipitation tests with AgNO_3 . Electron microprobe analyses (Jeol Superprobe 733) of the products of the completed reaction detected a small proportion of chloride in the residue, corresponding to ca. 2 mol.% $\text{Mg}(\text{OH})\text{Cl}$. This confirms that the reaction is most satisfactorily represented by the above equation.

Electron micrographs

Each reactant sample was crushed before kinetic study, and similarly treated unreacted salt was examined in the electron microscope; representative photographs are shown in Fig. 1. This salt included spherical aggregates which appeared to have melted and fused together, probably as the higher hydrate during the heat pretreatment (Fig. 1a). Closer examination of fracture surfaces showed the irregular distribution of particle sizes and shapes (Fig. 1b).

At $\alpha = 0.50$ (reactant decomposed for 86 min at 653 K in dry N_2) the texture of the solid was closely similar to that of the original reactant (Fig. 2; compare Fig. 1a). The only difference found was some evidence of slight surface roughening. When $\alpha = 0.75$ (reaction for 180 min at 653 K) the irregular structure of the reactant was still present (Fig. 3). On completion of reaction, i.e. $\alpha = 1.00$ (100 min at 673 K), the residue was composed of an aggregate of very finely divided particles (Fig. 4a). The surface textures of the individual particles were generally similar to those of the starting material (Fig. 4b).

On completion of decomposition in water vapour ($\alpha = 1.00$; 130 min reaction in 10 Torr H_2O at 623 K), the residual product appeared to be somewhat more aggregated than the residue obtained from the reaction in dry N_2 (Fig. 5).

The electron microscope observations indicate that the texture of the reactant undergoes very little change during the reaction, except that in the final stages it becomes somewhat more finely divided. There was no evidence of melting or sintering and we conclude, therefore, that reaction

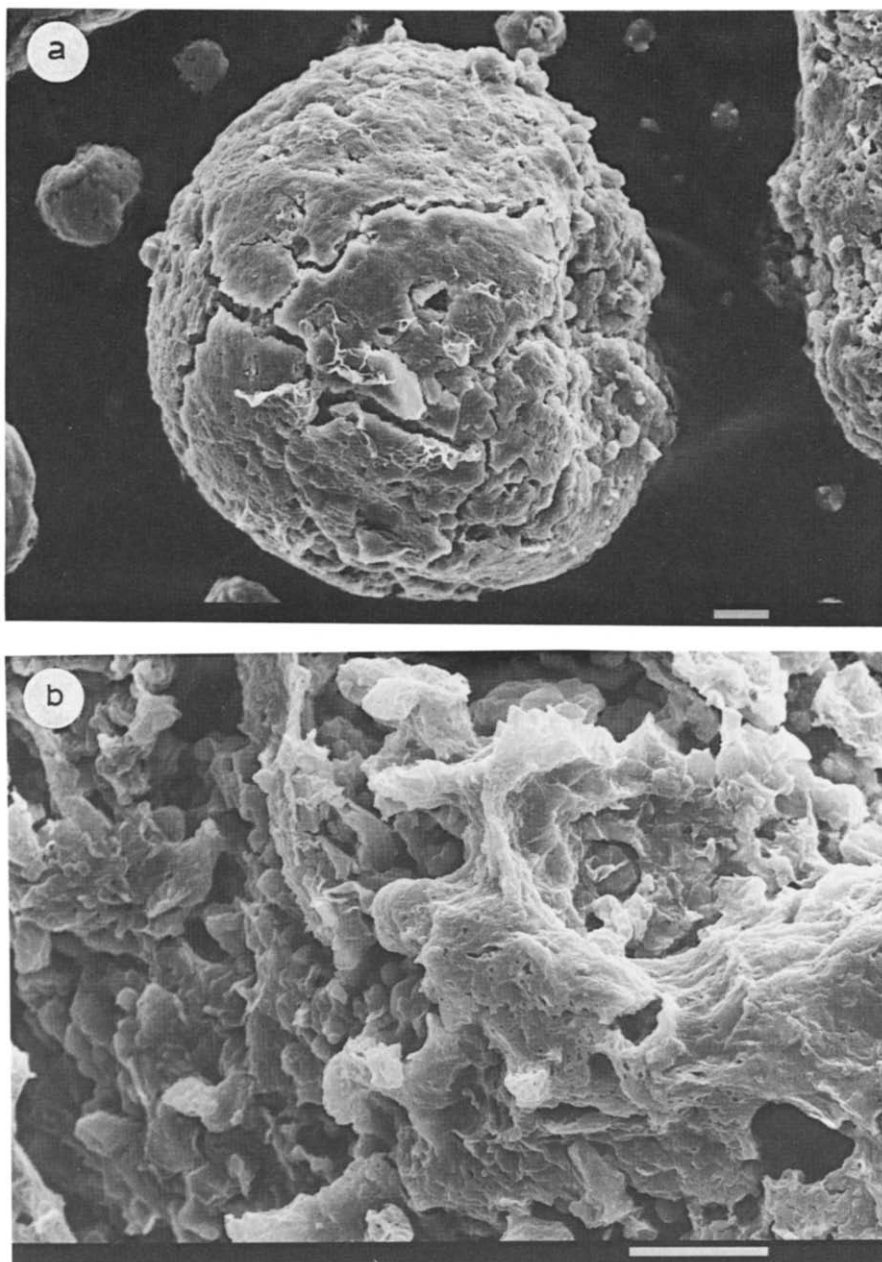


Fig. 1. Scanning electron micrographs (SEM) of the prepared reactant used in the present study of the isothermal decomposition of $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$. Scale bars, 10 μm .

occurred in the solid state. It is also concluded that water vapour may confer some mobility on the reactant, because the residual textures are different from those obtained under dry conditions (compare Figs. 4a and 5).

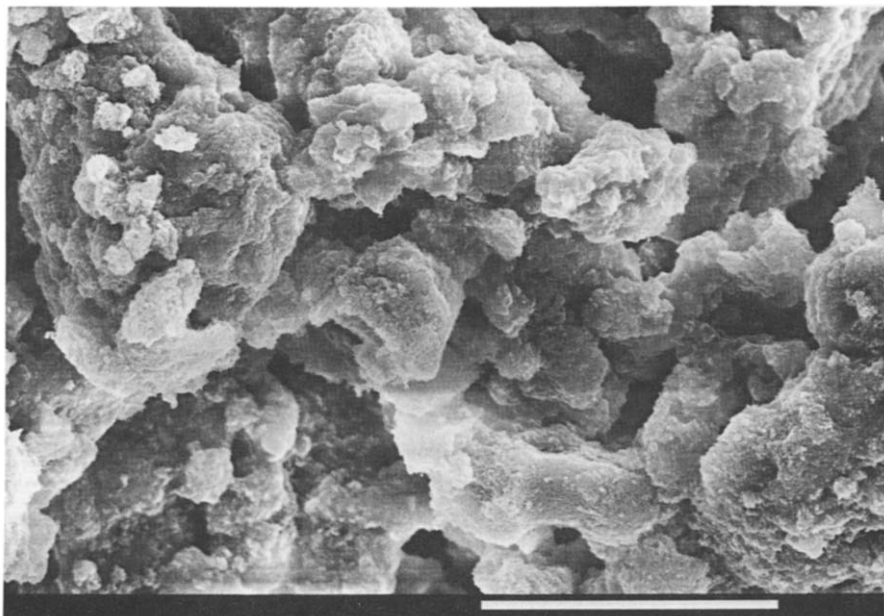


Fig. 2. SEM of $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ decomposed to $\alpha = 0.50$, heated for 86 min at 653 K in dry N_2 . Scale bar, 10 μm .

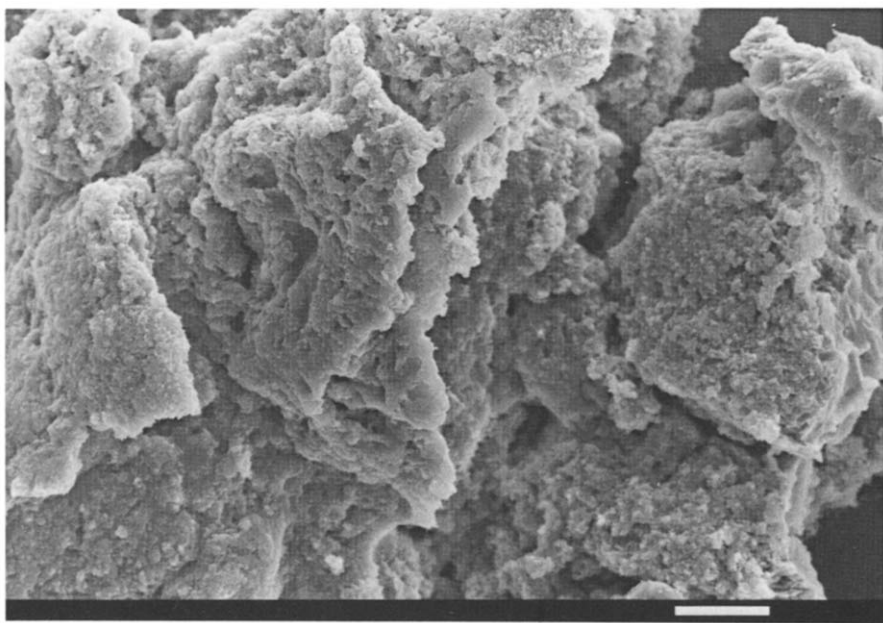


Fig. 3. SEM of $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ decomposed to $\alpha = 0.75$, heated for 180 min at 653 K in dry N_2 . Scale bar, 10 μm .

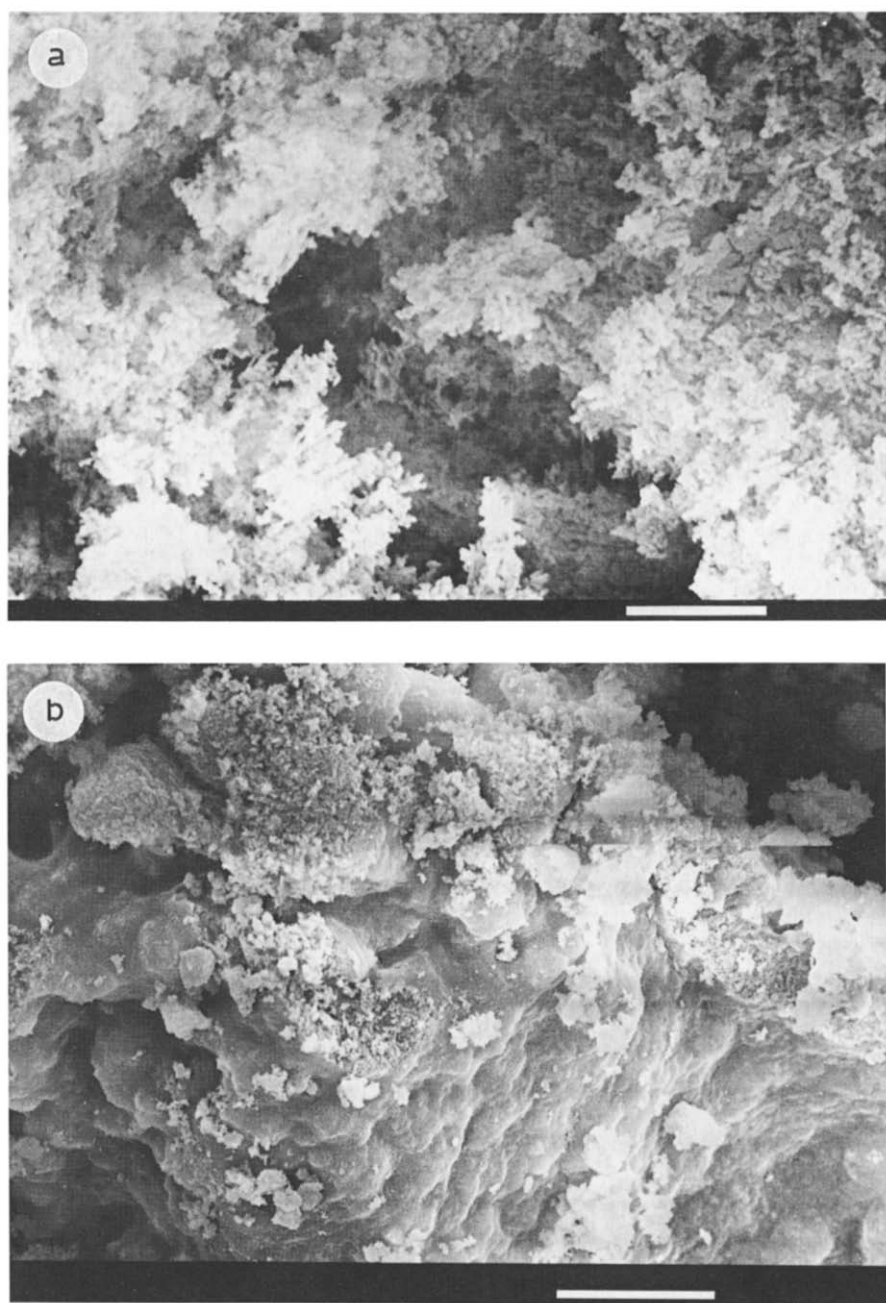


Fig. 4. SEM of $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ completely decomposed ($\alpha = 1.00$; heated for 100 min at 673 K in dry N_2). Scale bars: (a), 1.0 μm and (b), 10 μm .

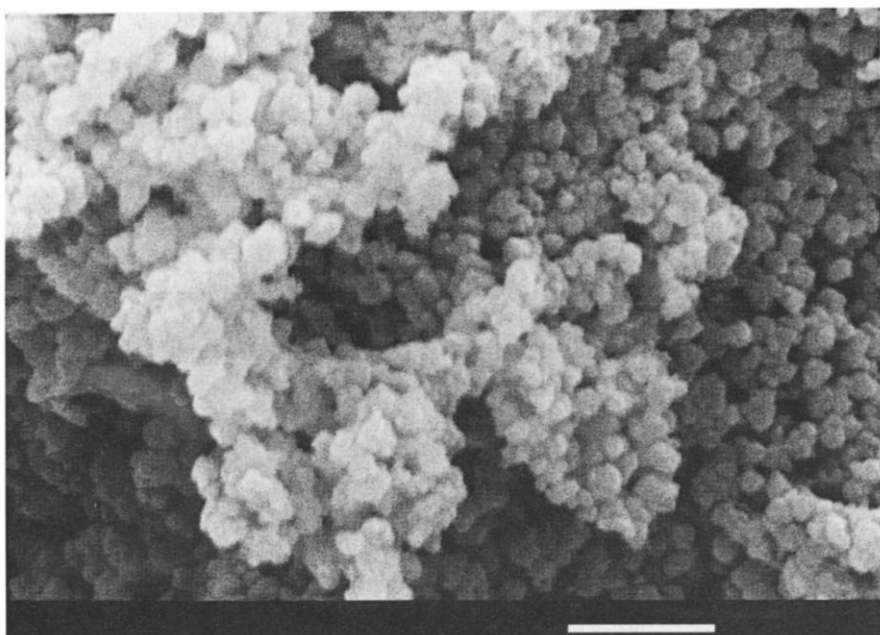


Fig. 5. SEM of $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ completely decomposed ($\alpha = 1.00$; heated for 130 min at 623 K in N_2 containing 10 Torr water vapour). Scale bar, 1.0 μm .

Kinetic measurements

Decomposition of $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ in dry N_2

Typical α -time plots for the HCl evolution reaction during isothermal decomposition of $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ in dry N_2 at various temperatures 623–703 K are shown in Fig. 6a. The reaction was predominantly deceleratory: three sections of these α -time curves require individual consideration.

The initial stage ($0 < \alpha < 0.12$) This rate process was completed relatively rapidly, and kinetic characteristics were not separately resolved in the temperature range of the present study. This rapid reaction is ascribed to facile decomposition at surfaces of finely divided material or in regions of poorly recrystallised salt generated during the heat pretreatment.

The main reaction ($0.12 < \alpha < 0.7$ – 0.9) This rate process was slightly deceleratory. Data fitted the contracting area, the contracting volume and the first-order rate equations [1] (see also the dehydroxylation [6–8] of $\text{Mg}(\text{OH})_2$), from which obedience to the contracting area equation is identified as being the most satisfactory (see Fig. 6b, which shows the data from Fig. 6a). The activation energy for this reaction was $110 \pm 5 \text{ kJ mol}^{-1}$ (623–703 K).

Reactant precrushing significantly enhanced the rate of salt decomposition; this observation strongly supports the kinetic conclusion that the main

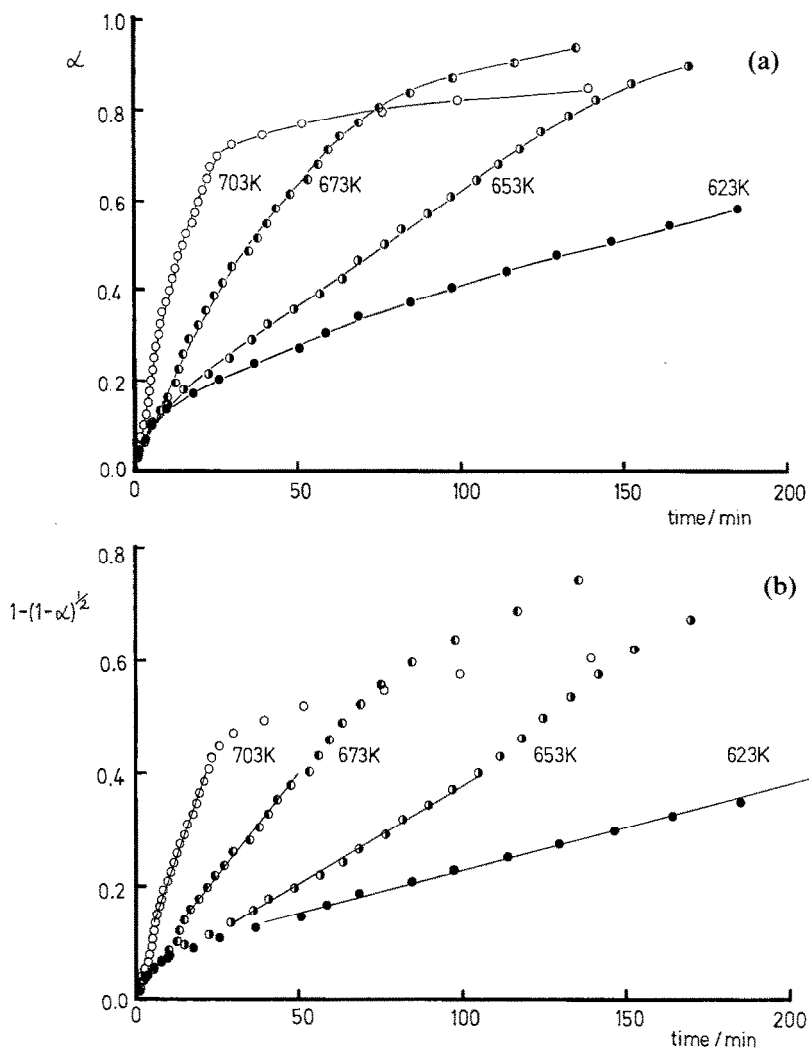


Fig. 6. Isothermal decomposition of $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ in dry N_2 : (a) fractional decomposition α -time plots, (b) obedience of data in (a) to contracting area equation, $1 - (1 - \alpha)^{1/2} = kt$.

reaction proceeds by a contracting envelope mechanism through interface advance.

The contracting area equation gave a slightly better fit than the contracting cube expression. Although the crystal structure of $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ could not be found in the literature, the crystals are described as "crystalline plates" [10]. Anhydrous MgCl_2 is known [11] to have a layer arrangement of Mg^{2+} and Cl^- ions, and these descriptions are consistent with our proposal that decomposition of the dihydrate may proceed in two dimensions rather than three.

The later slower reaction ($\alpha > 0.7-0.9$) Reactions studied at the highest temperatures characteristically included this final slow deceleratory process, the onset of which occurred at progressively lower α values (0.7–0.9) as the reaction temperature was increased. The diminution in rate was more pronounced than could be ascribed to the obedience of any of the usual [1] rate expressions. We conclude, therefore, that a different, slower process occurred during the final stages of salt decomposition. This reaction is ascribed to the intervention of $\text{Mg}(\text{OH})\text{Cl}$, whose decomposition is known to occur above 780 K [10]. It is expected that this reaction will be slow, but perceptible, during the longest experiments (20 h) at the highest temperatures of the present studies (703 K). Variations in the range of obedience to the contracting area expression are seen in Fig. 6b. This kinetic contribution arises from the intermediate formation of $\text{Mg}(\text{OH})\text{Cl}$; its decomposition increases with temperature and the significance of the final slow process rises accordingly. Microprobe analyses confirmed the presence of a small proportion of chloride in the residues from reactions completed throughout the entire temperature range of the present work.

The rate discontinuity in the α –time curve, most evident at 703 K in Fig. 6, is therefore ascribed to a change in reaction mechanism during the final stages ($\alpha > \text{ca. } 0.8$). α –time curves for decompositions at lower temperatures, however, apparently proceeded to completion in a finite time. We believe that this is due to the formation of smaller amounts of $\text{Mg}(\text{OH})\text{Cl}$ at lower reaction temperatures. The observation that these rate processes proceed to completion relatively rapidly also supports the kinetic conclusion that reaction is controlled by an interface advance mechanism, because first-order reactions become very slow during the final stages. The same interpretation is consistent with the microscopic observation that decomposition is accompanied by roughening of all reactant surfaces, since a porous product layer may not influence chemical changes proceeding at the interface.

It was also observed that the kinetics of reaction in dry O_2 (760 Torr O_2 at 703 K) were indistinguishable from the reaction in dry N_2 .

Decomposition of $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ in N_2 containing 10 Torr H_2O

The pattern of kinetic behaviour for salt decomposition in 10 Torr H_2O was identical with that described above, except for a significant overall increase in reaction rate (Fig. 7). This relative increase varied across the temperature interval studied from $\times \text{ca. } 5$ at 623 K to $\times \text{ca. } 1.5$ at 703 K, corresponding to a reduction in the magnitude of the apparent activation energy to $75 \pm 7 \text{ kJ mol}^{-1}$. Again, the most satisfactory kinetic representation was obedience to the contracting area equation, though the fits to the contracting cube and first-order expressions were only slightly inferior. The influence of variations of water vapour pressure between 5 and 15 Torr on reaction rates at 703 K was small.

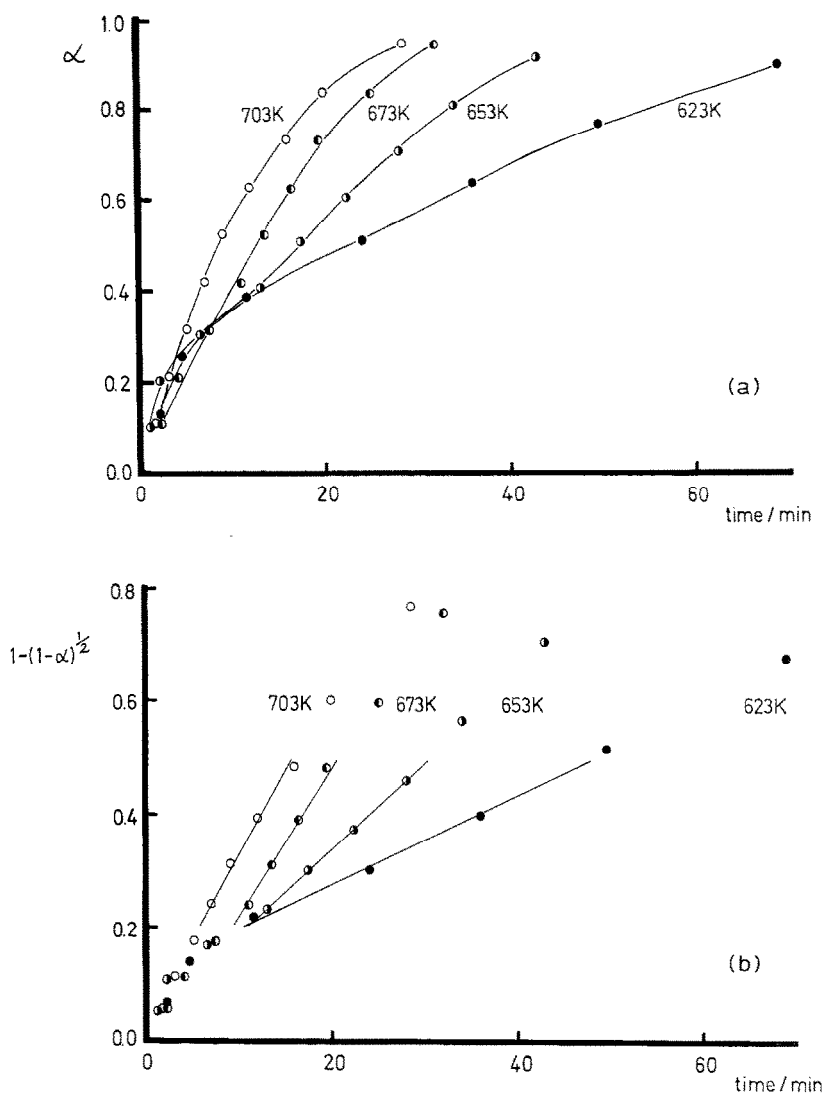


Fig. 7. Isothermal decomposition of $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ in N_2 containing 10 Torr H_2O : (a) α -time plots, (b) obedience of data in (a) to contracting area equation, $1-(1-\alpha)^{1/2} = kt$.

Microscopic evidence showed that the texture of the residual product from reactions in water vapour was less finely divided than from decompositions in dry N_2 . This is evidence that water may promote mobility of the reactant constituents resulting in the aggregation of MgO . However, the texture developed was open, permitting access of H_2O to the reaction zone, and the influence of water vapour in accelerating chemical change was maintained throughout each decomposition.

REACTION MECHANISM

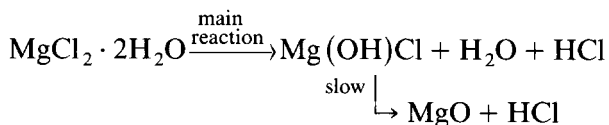
The following stoichiometric equation represents the overall and predominant chemical changes occurring at the advancing reactant–product interface:



Undoubtedly there is hydroxyl ion formation within the active zone of chemical change but the lifetime of any $\text{Mg}(\text{OH})_2$ intermediate (decomposes at 510–640 K [6]) is expected to be short at the present reaction temperatures (623–703 K). Crystalline $\text{Mg}(\text{OH})_2$ is probably not formed but facile proton transfers yield the rapidly volatilized products HCl and H_2O .

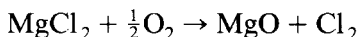
The acceleration of the decomposition reaction observed when water vapour was present in the reaction vessel is evidence that H_2O participates in the dynamic equilibria existing within the advancing zone of chemical activity (Cl^{-} , OH^{-} , H_2O , Mg^{2+} , O^{2-}). Temperature-dependent changes in the concentrations of these entities explain the variation in activation energy that is found for reactions in water vapour. This also confirms that water vapour, or, more probably, its dissociation products formed after adsorption on the reactant surface, participate in the essential steps controlling the present reaction.

Throughout reactions at lower temperatures, and during the greater part of all the present studies, the production of $\text{Mg}(\text{OH})\text{Cl}$ was small or negligible. This compound can be formed [3] by the reaction of MgCl_2 with water vapour between 623 and 778 K but decomposition becomes rapid [10] only above 780 K. Thus, if formed, $\text{Mg}(\text{OH})\text{Cl}$ can be expected to persist, but under the present reaction conditions only small amounts were detected:



It is concluded, therefore, that $\text{Mg}(\text{OH})\text{Cl}$ is not a significant intermediate in the present reaction, under the experimental conditions imposed.

The kinetics of the present main reaction show a remarkably close similarity to the behaviour reported by Ball [5] for the reaction



The temperature intervals across which both processes obeyed the contracting area expression were virtually identical (618–693 K [5] and 623–703 K here). The value of E for the present reaction in water vapour (75 kJ mol⁻¹) was close to that [5] for the reaction in O_2 (74 kJ mol⁻¹) and the influence of pressure of gaseous reactant on rate was small. Both reactions gave the same residual product (MgO) and the presence of gaseous oxygen did not influence the present reaction. These similarities, amounting to

identical chemical behaviour, are evidence that the same determining factors control both reactions. From this we must conclude that the parameters determining reactivity do not directly derive from the oxygen-containing participant. Control of the reaction rate must, therefore, reside in the common features of reaction, the chemical properties of MgCl_2 and/or MgO .

At the reaction interface, proton transfer is a necessary precursor step before HCl evolution and in the release of water from intermediate hydroxyl. The equilibria involving these groups within the zone of chemical change will result in progressive product formation when there is irreversible generation of the stable MgO residue. This may arise in the temperature interval associated with increasing stability of MgO (as compared with the reactants) or when the reactant MgCl_2 interacts with surface-held oxygen or oxide (as in OH^- or H_2O). Chemical change follows proton transfer steps, participating in dynamic equilibria at the appreciably mobile reactant surface, yielding a residual, stable product (MgO) that does not prevent the escape of the volatile products (H_2O and HCl).

ACKNOWLEDGEMENTS

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