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THE EFFECT OF ALKALI-CHLORIDE ON THE THERMAL HYDROLYSIS OF HYDRATED MAGNESIUM-CHLORIDE

S. Shoval, Geological Studies Group, Everyman's University,
Tel Aviv, Israel
S. Yariv, Department of Inorganic and Analytical Chemistry,
The Hebrew University of Jerusalem, Jerusalem, Israel.

ABSTRACT

DTA, TG and DTG curves were recorded for mixtures of hydrated $MgCl_2$ with NaCl, KCl and CsCl. Infrared spectra of the mixtures were recorded after they had been heated to several temperatures. CsCl forms a stable solid solution with $MgCl_2$ and the thermal hydrolysis of the salt is prevented. The solid solution formed with KCl is less stable than that formed with CsCl and hydrated Mg is thermally hydrolyzed to a small extent. No solid solution is formed with NaCl and $MgCl_2$ is thermally hydrolyzed in the presence of this salt.

INTRODUCTION

The thermal hydrolysis of hydrated magnesium chloride has been investigated by several methods, including DTA(1). In the first step of the heating process water evaporates and the monohydrate is obtained. In the continuation of the thermal treatment the following thermal hydrolysis (deprotonation reaction) proceeds in two steps

1. $Mg(OH_2)Cl_2 \rightarrow Mg(OH)Cl + HCl$
2. $Mg(OH)Cl \rightarrow MgO + HCl.$

Simultaneously, further dehydration of the monohydrate occurs as follows:

$MgCl_2.H_2O \rightarrow MgCl_2 + H_2O.$

The end-product of the thermal hydrolysis is the oxy-chloride $Mg_{1+x}OCl_{2x}$. In a previous publication we showed that grinding cesium halide salts with various sodium salts gives rise to a mechanochemical reaction in which solid solutions of the sodium halide and water molecules in the cesium halide matrix are formed(2). Preliminary experiments have shown that such a solid solution is formed when $MgCl_2$ is ground with CsCl. In the present communication we shall describe the effect of the formation of the salt solution on the thermal hydrolysis of the hydrated $MgCl_2$.

MEASURING METHODS

DTA, TG and DTG of mixtures containing 1.5 mg $MgCl_2.6H_2O$, 13.5 mg alkali chloride and 15 mg calcined alumina, or 1.5 mg $MgCl_2.6H_2O$ and 28.5 mg calcined alumina were recorded using a Stanton instrument. Powder $MgCl_2.6H_2O$ and disks of NaCl, KCl or CsCl containing 10% $MgCl_2$ were heated to various tempratures for 48h and IR spectra were recorded using a Perkin Elmer IR Spectrophotometer, model 597.

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RESULTS AND DISCUSSION

DTA, TG and DTG

DTA, TG and DTG curves of hydrated magnesium chloride are shown in Fig. 1. The first endothermic effect at 120°C corresponds to congruent or incongruent melting with the formation of tetrahydrate. The second and third endothermic effects at 155° and 180°C correspond to boiling of the solution and the passing of the tetrahydrate into the dihydrate. The subsequent endothermic effects correspond to a further dehydration to the monohydrate, accompanied by decomposition. The peak at 275°C corresponds to deprotonation of water and the liberation of HCl. The peak at 455°C corresponds to deprotonation of OH and the formation of anhydrous MgO(1). There is a very good correlation between the DTA, TG and DTG curves. The DTA cooling curve of $MgCl_2$ is also given in the figure. This curve proves that indeed all the endothermic peaks are associated with thermal weight loss and that no other types of phase transition occur.

The DTA, TG and DTG curves of $MgCl_2$ ground with NaCl are very similar to those of pure $MgCl_2$. This indicates that no reaction occurs between NaCl and $MgCl_2$ during the grinding process or, if a solid solution between $MgCl_2$ and NaCl is formed, the complex is not thermally stable. The small shifts of the deprotonation peaks to lower values are attributed to the presence of excess chloride in the system when the mixture NaCl-$MgCl_2$ is studied.

The DTA, TG and DTG curves of $MgCl_2$ mixtures with KCl or CsCl differ from those of pure $MgCl_2$. Only two peaks are observed in temperatures below 220°C. According to IR spectra they represent dehydration of the salt mixtures. No endothermic peak is observed in the temperature range 220°-300°C. It appears as if there is no hydrolysis of hydrated $MgCl_2$ or deprotonation of water molecule at this temperature range. A very small endothermic peak at 375°C in the KCl mixture may be due to thermal hydrolysis of hydrated Mg^{2+} which occurs at high temperatures to a very small extent. As will be shown in the next section, this is in agreement with the IR study. Endothermic peaks at 495°C and 525°C in CsCl are not associated with peaks in the DTG curves and are assumed to be phase transitions rather than dehydroxylation. The reversible phase transitions are shown in the DTA cooling curves. The TG curves show a very slow weightloss at temperatures above 350°C and 450°C in the KCl and CsCl mixtures, respectively. As will be shown in the next section, these mixtures hold water at high temperatures. This high-temperature weightloss is due to the loss of water, either by deprotonation and liberation of HCl or by the liberation of H_2O molecules. The endothermic peak at 475°C in KCl seems to be associated with this reaction. This is proved from the DTA cooling curve.

Infrared spectra of thermal treated samples

$MgCl_2$ powder

Hydroxyl ion formation can be observed from the appearance of bands at 3550-3620 cm^{-1}. $MgCl_2$ heated at 190°C showed a negligible amount of hydroxyl giving rise to a shoulder at a 3580 cm^{-1} and weak absorptions at 415 and 515 cm^{-1}. After heating the powder at 250°C a small broad band was detected at 3580cm^{-1}. Together with the increments of the bands at 410 and 515 cm^{-1}, this indicates that a thermal hydrolysis of the salt occurs at this temperature. The thermal hydrolysis of the powder continues at 300°C, as can be seen from the relative intensification of characteristic bands at 410, 520 and 3587 cm^{-1}. When the powder is heated for three days at 350°C the nature of the hydroxy salt changes and new hydroxyl groups are obtained, as can be seen from appearance of new bands at 3560 and 3620 cm^{-1}. A complete change in the spectrum is observed after heating the powder at 400°C. At this stage the hydroxy-salt is dehydroxylated and $Mg_{1+x}OCl_{2x}$ is obtained. All the bands which characterize hydroxyl groups disappear and a broad Mg(Cl)-O band is observed at 505 cm^{-1}.

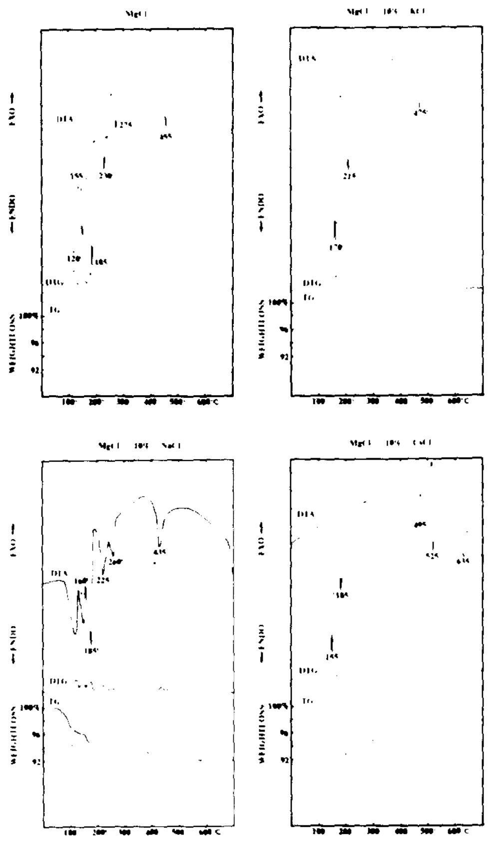

Fig 1: DTA (heating curve - solid line and cooling curve - broken line) TG and DTG of $MgCl_2 \cdot 6H_2O$ and of mixtures of alkali chlorides.

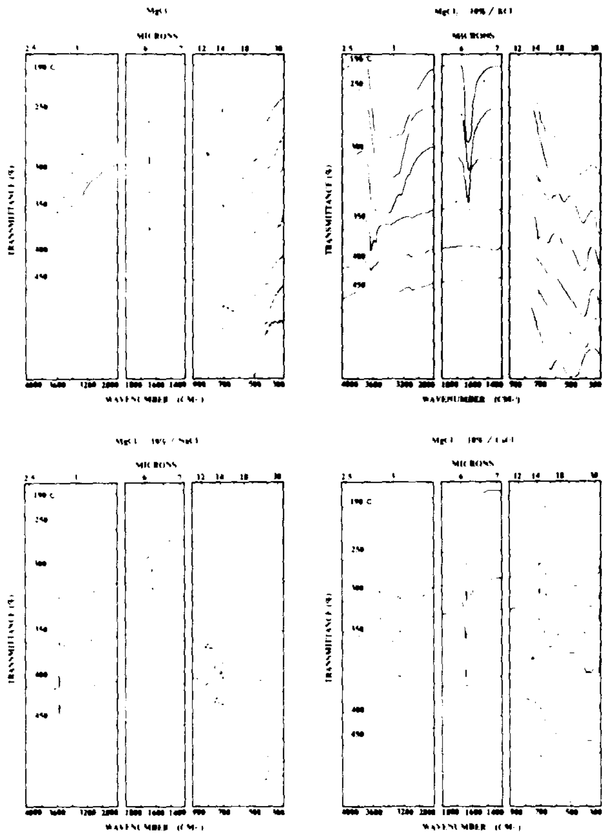

Fig 2: IR spectra of $MgCl_2$ thermally treated (a) as powder; (b)-(d) in alkali chloride disks. First curve at 450°C - unground; second curve - disk reground three times.

Disks of $MgCl_2$ in NaCl, KCl or CsCl matrices

The effect of temperature on the IR spectra of NaCl, KCl or CsCl disks containing 10% $MgCl_2$ can be observed from Fig 2. The spectra obtained after the thermal treatment of the NaCl disk are in very good agreement with the DTA results. Dehydration increases with the rise in temperature. Almost complete dehydration is obtained at 300°C. A sharp OH band at 3555 cm^{-1} is observed after heating the disk at 250°C. An additional OH band is observed at 3585 cm^{-1} after heating the disk at 300°C. As well, the thermal hydrolysis gives rise to bands at 410, 527 and 640 cm^{-1}.

In agreement with the DTA observations, IR spectra recorded in a CsCl disk do not show thermal hydrolysis of hydrated Mg. Although the intensity of the water bands decrease with the rise in temperature, they persist at temperatures as high as 400°C. No OH groups were detected during the thermal treatment.

KCl disks keep water to a very high temperature such as 350°C. Only traces of OH groups were detected after the disk had been heated at 300°C. These bands at 3560 and 3620 cm^{-1} increased in intensity at 350°C but decreased again at 400°C. They completely disappeared at 450°C.

Spectra obtained at 450°C of all salt mixtures differ from that of $MgCl_2$ heated to the same temperature as powder. The salt mixtures heated to 450°C give an Mg-O absorption band at 410 cm^{-1}, whereas the powder of the pure salt gives an Mg-O absorption band at 505 cm^{-1}. Since the latter is attributed to the second order compound Mg_2OCl_2 (namely Mg(Cl)-O groups), we assume that the absorbance at 410 cm^{-1} should be attributed to the first order oxide MgO. The second order oxide is obtained in the absence of alkali halide salt due to the evaporation of water molecules occurring simultaneously with the thermal deprotonation. At the end of the process not enough O^{2-} remains in the system to form a first order magnesium oxide. On the other hand, in the presence of alkali chloride, that fraction of water which separates from $MgCl_2$ without hydrolysis, reacts with the alkali chloride as follows:

$$H_2O + 2Cl^- \rightarrow 2HCl + O^{2-}$$

and at the end of the process enough O^{2-} is present in the system to form mainly a first order magnesium oxide.

CONCLUSIONS

CsCl forms a solid solution of hydrated $MgCl_2$ which prevents thermal hydrolysis of the hydrated magnesium salt. KCl also forms a solid solution of hydrated $MgCl_2$. The thermal stability of this solid solution is not as high as that of CsCl and a thermal hydrolysis of $MgCl_2$ occurs to a small extent. No stable solid solution is formed in NaCl and the thermal hydrolysis of a NaCl-$MgCl_2$ mixture is similar to that of a pure $MgCl_2$.

In the presence of alkali chloride water molecules which are separated from $MgCl_2$, react with the alkali-chloride and HCl evaporates. Due to the presence of excess O^{2-} a first order oxide, MgO is obtained at the end of the thermal treatment.

REFERENCES

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