Relative Thermal Stability of Ammonia Derivatives of the Magnesium Halides

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Formation of basic salts of magnesium from the hydrolysis of Grignard reagents is a well-known reaction. Similarly, Grignard reagents react with ammonia to produce amide salts in which the amide radical, NH_2, is exactly analogous to the hydroxyl group, OH , in the ordinary hydrolysis reaction.

These ammonobasic salts had not been investigated as definite compounds, however, until recently (3). Just as many chemical compounds combine with water to form hydrates, these ammonobasic salts apparently form ammoniates when treated with excess ammonia in a non-aqueous medium. These reactions are illustrated in the following chemical equations:

    1. Hydrolysis with hydrate formation:
       $RMgBr + (x+1) H_2O \rightarrow Mg(OH)Br \cdot xH_2O + RH$

    2. Ammonolysis with ammoniate formation:
       $RMgBr + (x+1) NH_3 \rightarrow Mg(NH_2)Br \cdot xNH_3 + RH$

The "R" in the above equations represents certain alkyl radicals.

By ammonolysis of Grignard reagents in the above manner, amoniates of the bromide, iodide and chloride of amidomagnesium have been prepared. The relative ease with which the ammonia of solvation in these three ammonobasic salts can be removed is a measure of the relative stability of the ammoniates and is of theoretical interest. Stability of the completely desolvated compounds is also significant. It has been found convenient to compare the rates of desolvation as functions of temperature and pressure.

<div align="center">EXPERIMENTAL</div>

PREPARATION. Ethylmagnesium bromide, ethylmagnesium iodide and isopropylmagnesium chloride were prepared according to standard procedure in ether solutions of ethyl bromide, ethyl iodide and isopropyl chloride, respectively, by reaction with excess magnesium. These Grignard reagents were then filtered from the excess magnesium and slowly added to an ether or benzene solution of ammonia gas through which excess ammonia gas was kept bubbling. In each case a fine white suspension was obtained. The product was then separated from the liquid medium by filtration. The products thus obtained were identified by analyses as ammoniates of magnesium amide bromide, magnesium amide iodide and magnesium amide chloride, respectively, and were subjected to further treatment such as desolvation.

ANALYSIS. One of the most critical steps in the analysis was solution of the sample without loss of ammonia. Early experience showed that the products liberated ammonia at a rapid rate when treated with alcohol or water, and that some ammonia was lost by attempting to dissolve the sample in an open container. The following procedure was devised to avoid loss of ammonia. The sample was quickly transferred from a weighing bottle into a glass stoppered Erlenmeyer flask. Both containers were stoppered immediately. The weighing bottle was reweighed to obtain the weight of sample by difference. Then the stem of a 150 ml. separatory funnel was inserted into a one hole rubber stopper which fitted the Erlenmeyer flask. The separatory funnel was half filled with water and the stopcock opened. Sometimes, a gas would bubble slowly up through the water solution, but gradually a vacuum was created inside the flask which tended to suck the water into the flask. Just before all the water had been added, 100 ml. of sulfuric acid, diluted 1:4, were added to the separatory funnel. The flask was gently swirled during the addition of sulfuric acid in order to dissolve the sample completely. The separatory funnel was then removed from the flask, and the lower portion rinsed with distilled water. The solution was transferred quantitatively to a volumetric flask and diluted to volume. This solution was used for halogen, nitrogen and magnesium analyses.

HALOGEN ANALYSIS. Approximately 0.1 N. silver nitrate and potassium thiocyanate solutions were prepared and standardized. A slightly modified

Volhard procedure was found applicable to analyses for iodide, bromide and chloride. This modification consisted of using sulfuric acid for solution of the sample rather than nitric acid. The presence of sulfuric acid was necessary for the magnesium analysis and was found to have no appreciable effect on the halogen analysis. Ferric ammonium sulfate was the indicator used.

NITROGEN ANALYSIS. The Kjeldahl method for the determination of nitrogen was used. No digestion was required since the amide group was readily converted into ammonia which was distilled from a concentrated sodium hydroxide solution into a 5% boric acid solution, and titrated to a methyl red end-point with standard hydrochloric acid solution. The apparatus used in these Kjeldahl determinations was of the semimicro, self-emptying, steam distillation type, operating on the same principle as the apparatus described by Parnas (1). A nitrogen determination could be run in approximately twenty minutes with the apparatus in continuous operation.

MAGNESIUM ANALYSIS. Magnesium was determined gravimetrically as magnesium sulfate. The procedure consisted of evaporating an aliquot of the unknown solution over a hot plate. Particular care had to be taken to prevent spattering near the end of the evaporation. This is a modification of a standard procedure (4) and has been used by one of the authors (2) in the determination of magnesium in magnesium bromide. Though limited in scope, this method has been found to be precise when no interfering metallic ions are present.

DESOLVATION. In attempts to remove the ammonia of solvation, the products were heated at various temperatures under reduced pressure for prolonged periods of time. These rates of desolvation data form the basis for comparison of the relative thermal stability of ammoniates of the magnesium amide halides.

In each case, the sample under investigation was placed in a 300 ml. round bottom flask which was immersed in a wax bath at the desired temperature. The pressure in the flask was then reduced by using oil pump vacuum. After definite intervals of time, samples were withdrawn for analysis.

A convenient notation which quickly shows the degree of desolvation of the samples is the nitrogen to halogen ratio. These ratios were obtained directly from analytical data. By considering the nitrogen to halogen ratio in the compounds postulated, the convenience of this notation becomes apparent. For example:

		N/X
Desolvated product	$Mg(NH_2)X$	1
Monoammoniate	$Mg(NH_2)X \cdot NH_3$	2
Diammoniate	$Mg(NH_2)X \cdot 2NH_3$	3

The "X" in the above formulas represents any halide.

DISCUSSION

Since magnesium amide iodide was desolvated so slowly below 160° C., very few data were taken on this compound below that temperature. Similarly, since the ammoniates of magnesium amide chloride were so unstable above 160° C., only lower temperature data are included here. Magnesium amide bromide, however, was investigated over the entire range of temperatures as shown in Table I.

TABLE I

TEMP.(°C.)	TIME (HRS.)	N/I	N/Br	N/Cl
30	0	3.4	3.1	3.5
	35	3.3	2.6	2.6
125	0		2.0	2.3
	2		1.6	1.6
	4		1.4	1.3
	6		1.3	1.2
	12		1.3	1.1
140	0		3.5	3.1
	2		1.3	1.2
	4			1.0
	10		1.1	
160	0	3.5	3.6	3.5
	2	2.2	1.5	1.3
	6	1.3	1.1	1.0
	14	1.2	1.1	1.0
180	0	3.4	3.6	
	2	1.2		
	4	1.1		
	6	1.1	1.1	
	8	1.1	1.0	
195	0	3.5	3.4	
	4	1.1	1.0	
	8	1.0	1.0	
300	1	1.0	1.0	1.0

This table allows comparison of the chloride derivative with the bromide at lower temperatures and comparison of the iodide with the bromide at higher temperatures.

The samples had sufficient vapor pressure even at 30° C. to be slowly desolvated, but it is apparent that the diammoniates are relatively stable at this low temperature. As the temperature is raised, the diammoniates have higher dissociation pressures so that the ammonia of solvation can be removed more easily. Thus, the chloride can be completely desolvated at 140° C. in only four hours, whereas the bromide retains some of its ammonia of solvation after ten hours at 140° C. Further evidence that the chloride loses its ammonia of solvation at a more rapid rate than the bromide is shown by the nitrogen to halide ratios of the chloride and bromide at the end of twelve hours at 125° C. In spite of the fact that the bromide was initially a lower ammoniate than the chloride, there was still more ammonia of solvation on the bromide at the end of twelve hours, thus indicating that the chloride has a higher dissociation pressure than the bromide.

Similarly, it has been shown that the iodide ammoniate has a lower dissociation pressure than the bromide ammoniate at the same temperature. At 160° C. the bromide ammoniate shows a consistently lower nitrogen to halide ratio than does the iodide, in spite of the fact that initially the bromide was ammoniated to a greater extent than the iodide.

It is significant to note that as the temperature is raised to 180-195° C., the rates of desolvation become more nearly equal, thus indicating that all three of the magnesium amide halide ammoniates have high dissociation pressures and are desolvated at quite rapid rates at these higher temperatures. At 300° C. they have such high dissociation pressures that they are all desolvated in an hour or less. Rapid heating of the ammoniates at very high temperatures as a means of preparing the desolvated products has not been too satisfactory, however, because the products appear to undergo incipient fusion while being desolvated at these higher temperatures.

Although analyses indicate the desolvated product in each case, this tendency toward fusion results in a hard, compact, lumpy mass which is rather difficult to break up and handle. Desolvation at lower temperatures under reduced pressure produces a fine white powder. The desolvated products have been heated above 300° C. without apparent change except for a slight darkening which is undoubtedly due to traces of organic impurities.
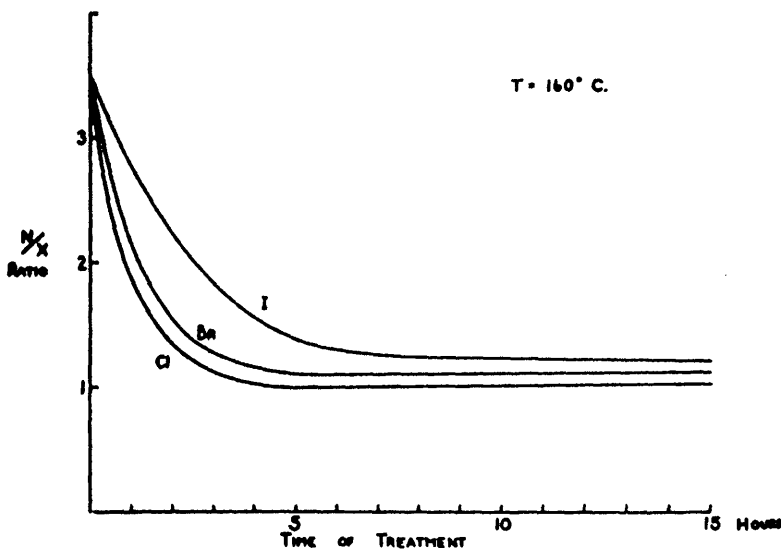

FIGURE 1.

A direct comparison of the relative stabilities of the three compounds at the same temperature, 160° C., is shown in Figure 1. It is quite evident that the rate at which the ammoniate of magnesium amide chloride decomposes is much faster than for the ammoniate of magnesium amide bromide. Likewise, the dissociation pressure of the ammoniate of magnesium amide bromide is greater than that of the ammoniate of magnesium amide iodide.

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