The High Temperature Hydrolysis of Lithium Bromide[1]

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INTRODUCTION

The possibility of the hydrolysis of molten halides at high temperatures has been suggested from time to time to explain the loss of halogen observed when such halides were heated for extended periods of time. For example Eastman and Duschak (3) report a ready reaction of lead chloride with moist air to yield hydrogen chloride at low temperatures and chlorine at higher temperatures. The loss of hydrogen chloride from magnesium chloride hexahydrate when heated is well known.

Munger (7) found that, when mixtures of potassium metaphosphate and potassium fluoride are held in a molten condition for extended periods of time, there is an extensive loss of fluorine. This has been attributed by some to a hydrolytic decomposition of the melt. Most recently Hill and Andrieth (4) have explained the loss of fluorine from molten mixtures of sodium fluoride and sodium metaphosphate as being caused by a high temperature hydrolysis.

Finally Briner and Roth (2) have made an extensive study of the high temperature hydrolysis of alkali halides with and without the admixture of such substances as kaolin and silica. Briner and Roth report considerable hydrolysis.

The present study was undertaken to measure the extent of hydrolysis of molten alkali halides under controlled conditions.

EXPERIMENTAL

Two different experimental apparatuses were used in these studies. The first was a dynamic system, patterned after that of Briner and Roth, in which steam or a gas containing water vapor could be passed over the molten alkali halide. The effluent gas stream was allowed to pass through an efficient gas wash bottle. In the second experimental set up a sample of the molten salt could be subjected to atmospheres of known composition. This was a static system. In both arrangements it was possible to analyze both the alkali halide and the gas phase.

The first experiments were made using the flow system. The first halide tried was lithium iodide. As soon as the temperature reached about 100° C. a copious liberation of iodine occurred. Since oxygen had not been excluded from the system this result should have been expected in view of the reaction of lithium iodide with oxygen previously reported by Simmons and Picket (9). These investigators reported that the reaction

$$10LiI + 5O_2 \rightarrow 2LiIO_3 + 4Li_2O + 4I_2$$

readily occurs when lithium iodide is heated in the presence of oxygen. While there is some question as to the correctness of this interpretation by Simmons and Picket of the experimental data (see theoretical discussion below), there can be no question that lithium iodide is unstable when heated in the air.

In the remaining experiments lithium bromide was used. Lithium bromide was used for two reasons. First, the melting point is low enough so that it may be melted in apparatus constructed of pyrex glass. Second,

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[1] Abstracted in part from the M.S. thesis of R. T. Johansen. (1951)

thermodynamical computations indicate that lithium bromide is more easily hydrolyzed than other alkali halides except lithium iodide.

After finding that it was not possible to force pure water vapor at about atmospheric pressure through the tube containing the molten halide a gas saturation method was devised. In the modification used, a gas, first air and later nitrogen, was allowed to pass through a pair of gas wash bottles which were kept at constant temperature (about 50°C.) in a thermostat. This gas, saturated with water at the temperature of the thermostat, was then allowed to pass through the heated tube containing the molten lithium bromide. The gas was washed with water and the wash liquid analyzed for bromide ion, free bromine, and total acid.

In the first experiment using the carrier gas technic air was used to carry the water vapor into the reaction tube. Dry air was allowed to flow through the reaction tube until a temperature of about 560°C. was reached. Then the air stream was allowed to pass through the water saturators held at about 45°C. before entering the reaction tube. Large quantities of free bromine were produced. No bromide was detected in the effluent gases.

In the next experiments the air was replaced by commercial nitrogen. As long as only dry nitrogen was used no free bromine or bromide was found in the effluent gas. When wet nitrogen was used a very small amount of free bromine was sometimes detected in the effluent gas. Only a trace of bromide was found in the effluent gas. The dynamic system was abandoned when it was found that some of the water vapor taken up by the carrier gas in the saturators was not reaching the reaction chamber. Thus the actual vapor pressure of water in the reaction tube was not known. Further it was found that the salt vapor from the open gold boat was attacking the glass tube.

Two different kinds of static experiments were made. In the first the molten lithium bromide (at 560° C.) was subject to water vapor at about 6mm and 760mm pressure. The system was evacuated to about 0.5mm prior to being exposed to the water vapor. The lithium bromide was contained in a graphite tube, which was closed in such a manner that the water vapor could easily get in but only a very small amount of the salt vapor could contact the pyrex tube. The residue in the graphite tube, after reaction, was analyzed for bromide and tested for free bromine. No free bromine was found. The average amount of bromide lost in eight experiments was 0.4±0.2 per cent. This is not considered significant in view of the difficulties of handling a hydroscopic salt such as lithium bromide.

In the second group of static experiments the graphite tube containing the lithium bromide was sealed into a heavy pyrex tube and evacuated. A known weight of water was condensed into the tube by immersing the end of the tube in a dry ice bath. The tube while being cooled was connected to a small bulb of degassed water for the length of time necessary to allow the desired amount of water to be transferred. By this method sufficient water was transferred to the reaction tube to give water pressures of about four and twelve atmospheres at the temperature of the reaction. The reaction tube was heated to 547°C. and held for 30 minutes. In the experiment where the water vapor pressure was four atmospheres, 0.3 per cent of the bromide was lost from the contents of the reaction tube. In the twelve atmosphere water vapor pressure experiment a gain of 0.0 per cent in the bromide content of the reaction tube was observed. Both of these results are probably within the error of the experimental method.

CONCLUSIONS

Within the limit of the experimental uncertainty (probably 0.5 per cent) there is no evidence for the hydrolysis of lithium bromide by water vapor at the melting point of lithium bromide (547°C.). Lithium bromide does not react with dry air when heated up to about 560°C. Oxygen and water vapor, when together, react with lithium bromide to produce free bromine.

THEORETICAL DISCUSSION

Equilibrium constants for the hydrolysis of the fluorides, chlorides, bromides and iodides of lithium, sodium and potassium have been computed from the free energy of the reaction using conventional thermodynamic methods. The necessary free energy values were taken, whenever possible, from the extensive tables being prepared by the National Bureau of Standards. (8) The free energies of formation of lithium and sodium hydroxides were recalculated using modern data for the absolute entropies of the hydroxides. The entropy of lithium hydroxide has been determined by Bauer, Johnston and Kerr (1) while that for sodium hydroxide was determined by Kelly and Snyder (5). The entropies of potassium hydroxide, lithium bromide and lithium iodide have not been measured; these values were estimated. The values used were KOH $S^\circ = 16.5$, LiBr $S^\circ = 16.7$ and LiI $S^\circ = 18.0$, all in cal./deg. mole. These values agree closely with those which one would estimate using the empirical method recently published by Latimer (6). The errors in these estimated values is probably less than one entropy unit. The negative logarithm (pK) of the equilibrium constant for the reaction: $MX(s) + H_2O(g) \rightarrow MOH(s) + HX(g)$ for a temperature of 25°C. is given in Table I.

TABLE I

Equilibrium Constants, pK, for the Reaction:

$MX(s) + H_2O(g) \rightarrow MOH(s) + HX(g)$ at 25° C.

X=	F	Cl	Br	I
M				
Li	17.58	13.35	12.94	9.82
Na	20.73	23.97	24.84	23.11
K	19.90	28.77	31.03	30.61

At 25°C. none of these reactions would be expected to yield sufficient halogen halide to easily detect. All of these reactions are endothermic and consequently increasing the temperature will increase the equilibrium constant. To make an exact calculation of the influence of temperature requires knowledge of the variation of the heat of reaction with temperature as well as the heats of fusion of the alkali salts. The necessary data are not available for the majority of the substances involved. However, in the case of sodium chloride the data are available for an exact calculation. It was found that just above the melting point of sodium chloride (800°C.) the heat of the hydrolytic reaction is 30.394 Kcal compared with 31.983 Kcal at 25°C. Thus a change of about 5 per cent is produced in the heat of the reaction when the temperature is increased almost 800°. It thus appears to be satisfactory to compute the effect of temperature on the assumption that the heat of reaction is constant up to the melting point of the alkali halide. The values of the equilibrium constant have been computed at 1000°C. for each reaction. The results of these calculations are given in Table II.

TABLE II

Equilibrium Constants, pK, for the Reaction:

$MX(liq.) + H_2O(g) \rightarrow MOH(liq.) + HX(g)$ at 1000°C.

X=	F	Cl	Br	I
M				
Li	4.4	3.8	3.7	2.9
Na	5.2	6.0	6.2	5.8
K	6.1	7.2	7.9	7.2

From these calculations one may estimate the partial pressure of halogen halide in equilibrium with the salt and water vapor. The equilibrium expression for this reaction may be written:

$$\frac{a_{MOH} \cdot a_{HX}}{a_{MX} \cdot a_{H_2O}} = K$$

where the *a*'s are the activities of the various substances. If it is assumed that the two salts form an ideal liquid solution and that the gases are ideal then we may unite this expression as follows:

$$\frac{x_{MOH} \cdot p_{HX}}{x_{MX} \cdot p_{H_2O}} = K$$

where the *x*'s are mole fractions and the *p*'s are partial pressures. If the extent of the reaction is small then the mole fraction of the alkali halide would be approximately unity. If the amount of salt hydrolyzed were as great as one per cent, which is twice as great as our experiments indicate, and the partial pressure of the water vapor 10 atmospheres than the partial pressure of hydrogen bromide in the lithium bromide hydrolysis would be approximately 1mm at 547° C. At lower water vapor pressures, such as were actually used in the flow experiments, the partial pressure of HBr would be very much less than this. These calculations would appear to eliminate any extensive high temperature hydrolysis.

Thermodynamic computations have also been made of the equilibrium constants for the reaction:

$$2MX + H_2O(g) + \tfrac{1}{2}O_2 \rightarrow 2MOH + X_2(g)$$

The results are summarized in Table III.

TABLE III

Equilibrium Constants, pK for the reaction:

$2MX + H_2O(g) + \tfrac{1}{2}O_2 \rightarrow 2MOH + X_2$ at 25°C.

X=	F	Cl	Br	I
M				
Li	89.4	19.3	4.2	—18.3
Na	97.2	42.0	29.4	9.7
K	95.6	51.7	41.9	24.8

These calculations indicate that both lithium bromide and lithium iodide would be unstable when heated in moist air. Sodium iodide probably would also tend to decompose when heated in moist air. The very marked instability of lithium iodide is worthy of note as well as the great stability of the fluorides.

It has been suggested by Briner and Roth that the addition of silica or alumina to the salt will facilitate hydrolysis. A calculation for sodium chloride, silicon dioxide and water to yield sodium metasilicate and hydrogen chloride shows that at 25°C. the equilibrium constant would be about $10^{-[illegible]}$. Since the reaction is endothermic increasing the temperature will tend to increase the equilibrium constant.

Theoretical Conclusions

Thermochemical calculations indicate that the hydrolysis of alkali halides at high temperatures is possible but that the extent of the reaction would be very small unless the vapor pressure of the water were very high. The stability increases in the sequence lithium, sodium and potassium. The fluorides of sodium and potassium are less stable than the other halides but lithium fluoride is more stable than the other halides of lithium.

Both lithium bromide and lithium iodide are unstable in the presence of oxygen and water vapor when heated. This is in agreement with the experimental conclusions of this study.

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