THE REACTION OF THE ALKALINE EARTH METAL OXIDES WITH IODINE IN THE PRESENCE OF WATER AS PART OF A THERMOCHEMICAL HYDROGEN CYCLE[†]

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Abstract—When iodine was reacted with aqueous alkaline earth metal oxides (MgO, CaO, SrO and BaO) both metal iodate and iodide were formed. However these reactions were never complete. The percentage of products obtained was increased with excess I_2 and water, and higher molecular weight oxide. Both single and mixed oxides were used. Product separation between insoluble iodate and soluble iodide was often incomplete, and much I_2 remained occluded on the insoluble reaction product when MgO was one reactant. The results show that, from the mixed oxides examined, the highest yield (76%) and best product separation was obtained using 5MgO/BaO, which may be of value in a thermochemical hydrogen cycle.

INTRODUCTION

Recently a search has been underway to identify chemical reactions which may be useful in thermochemical H_2 cycles for water splitting[1]. One reaction thus identified is that of I_2 with aqueous base resulting in a simultaneous oxidation (to IO_3^-) and reduction (to I^-)

$$3I_2 + 6OH^- \rightarrow IO_3^- + 5I^- + 3H_2O_1$$
 (1)

Oxygen is produced by thermal decomposition of the iodate and hydrogen by hydrolysis of iodide and subsequent decomposition of HI. Since the iodates of the alkaline earth metal oxides are insoluble (except for Mg) and the iodides are soluble, product separation is simple. This is a desirable feature in a cycle. Thermodynamically the reactions

$$I_2(c) + MO(c) \xrightarrow{H_2O} 5/6MI_2(aq) + 1/6M(IO_3)_2(c)$$
 (2)

$$I_2(c) + M(OH)_2(c) \xrightarrow{H_2O} 5/6MI_2(aq) + 1/6M(IO_3)_2(c)$$

 $H_2O(lq)$ (3)

are, in general, favored (M = Mg, Ca, Sr or Ba). The enthalpy of all these reactions are negative (except for eqn (3), M = Mg) indicating that there is sufficient driving force for them to go completely. These enthalpies are listed in Table 1[2-4]. The reactions

$$5/6MgO(c) + 1/6M(OH)_{2}(c) + I_{2}(c) \xrightarrow{H_{2}O} 5/6MgI_{2}(aq) + 1/6H_{2}O(lq) + 1/6M(IO_{3})_{2}(c)$$
(4)

where M = Ca, Sr or Ba are also favored (Table I). The latter are particularly useful in cycles since Mgl₂ hydrolyses readily ($\Delta G^{\circ} \sim 0$ at 180°C, $\Delta H_{298}^{\circ} = +58.0$ kJ) unlike the other iodides (Ca, Sr, Ba) in the series.

This work was therefore undertaken to determine pertinent details of these reactions, such as the rate, extent and separation of products between solid and solution phases. Both the MgO and CaO cases have been previously examined [5, 6] as part of thermochemical cycles, but few chemical details are available. Mixed alkaline earth oxides have also been postulated [7].

The reactions were studied by analyzing the products both in the solid and solution phases. The effort was divided into an initial study at room temperature and pressure‡ and high dilution using different oxides, and a repeat at high temperature, pressure and concentration for single oxides, mixed oxides and paraperiodates.

EXPERIMENTAL

The metal oxide(s) and I_2 were ground together and placed, with water, in a Teflon cell in a stainless steel cylinder (Parr Bomb). The cell was covered with teflon and nickel foil caps to reduce the possibility of I_2 reacting with steel. Water was also placed directly in the cylinder to equalize pressure inside and outside the cell. The whole was pressurized with helium to 141 psi and heated at 150°C for specified lengths of time, generally one hour. On cooling, the vessel was dismantled and the reaction products analyzed.

After filtration, the solid residue was washed with water and acetone, and analyzed by its X-ray powder diffraction pattern and by thermal decomposition. In cases involving MgO, much I_2 remained occluded to the precipitate even after washing; this I_2 was removed by heating to 400°C. For the mixed oxide runs, the X-ray of the solid residue only showed the higher atomic weight iodate (except for 5CaO/SrO). However, after heating to 1000°C, the two oxides were both easily seen, and the evolved I_2 was estimated using standard sodium thiosulfate. The filtrate was analyzed for iodide, using a specific iodide electrode, and for iodate, by estimating the liberated iodine obtained on acidification after extraction of the free I_2 with p-xylene. The pH was also taken.

All the oxides and Ca and Ba iodate hydrates were obtained commercially. Hydrated Sr and Mg iodates were made and characterized by thermal decomposition and X-ray powder diffraction patterns, as were also the anhydrous iodates and paraperiodates. The patterns of the anhydrous iodates are not available in the literature; the product patterns obtained were compared with anhydrous iodates which were prepared and analyzed.

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[‡]Atmospheric pressure at Los Alamos is 11.4 psi.

(10)

Table 1. $\Delta H_{298}^{\circ}kJ$ for the following reactions:

$$I_2(c) + MO(c) \xrightarrow{H_20} 5/6MI_2(aq) + 1/6M(IO_3)_2(c)$$
 (2)

 $I_{2}(c) + M(OH)_{2}(c) \xrightarrow{H_{2}O} 5/6MI_{2}(aq) + 1/6M(IO_{3})(c) + H_{2}O(Iq)$ (3) $I_{2}(c) + 5/6MgO(c) + 1/6M(OH)_{2}(c) \xrightarrow{H_{2}O} 5/6MoL(ac)$

$$\frac{1}{2} \int \partial M g O(c) + \int \partial M (\partial H) g(c) + \int \partial M g G(c) + \int \partial M (\partial H) g(c) + \int \partial M (\partial H)$$

$$+ 1/6M(IO_3)_2(c) + 1/6H_2O(Iq)$$
 (4)

$$1/3M_5(IO_6)_2(c) + 4/3I_2(c) \xrightarrow{H_2O} 2/3M(IO_3)_2(c) + MI_2(aq)$$
 (9)

$$MgO(c) + \frac{1}{18M_5}(IO_6)_2(c) + \frac{12}{18I_2(c)} \xrightarrow{\Pi_2O} \frac{5}{18M}(IO_3)_2 + MgI_2(aa)$$

Where M = Mg, Ca, Sr or Ba

Equation						
Metal	2	3	4	9	10	
Mg	- 27.2	+ 9.8				
Ca	- 77.2	- 12.1	- 26.9			
Sr	- 126.3	- 43.1	- 34.3	- 10.6	- 34.3	
Ba	- 154.9	- 52.5	- 37.8	- 17.5	- 37.7	

RESULTS

(1) Initial study

The reactions (2-4) were studied by monitoring the change in pH of the reacting mixture as a function of time. Resultant plots are shown in Fig. 1. As the reactions proceeded, the solubility of the hydroxide decreased due to the increase in the metal ion concentration as the iodide formed. Equilibrium was established before all the available oxide had been consumed. For BaO and CaO the initial high pH decreased rapidly and then slowly. For MgO and 5MgO/BaO the starting pH was lower than in the previous cases and quickly declined to reach an equilibrium value which was relatively high due to the greater insolubility of MgO (Table 2). Thus, even though the reaction was fast, the pH of the product suggested that the extent of the reaction was low. In order to encourage greater reaction, the conditions were changed. The new conditions chosen, 150°C and 141 psi initial pressure for 1 hr, did show more complete reaction, as indicated by a lower final pH (e.g. in Fig. 1, case B pH was 9.5, while when run at high temperature and pressure the pH was 7.7). Carrying the reaction out in a closed container guaranteed that the I₂ and water could not vaporize away. The amount of water was kept small to decrease the amount of iodate in solution, and to decrease the energy necessary to dry the metal iodide. Although a reaction time of 1 hr was used in general, the same product yields were obtained when the time was shortened to 10 min.

(2) Single oxides at high temperature and pressure

All the oxides were run under the conditions described above. The X-ray powder diffraction patterns of the solid products showed that for Mg and Sr the precipitated iodates were anhydrous, whereas for Ba and Ca the monohydrates were formed. The reaction temperature was above the dehydration temperatures for Mg, Ca and Sr iodates (57.5, 57.5 and 55.0°C) respectively, but below that for Ba (200°C)[8]. The hydrate formation for Ca(IO₃)₂ appears to be an anomaly.



Fig. 1. MO + $I_2 \longrightarrow 1/6M(IO_3)_2 + 5/6MI_2$ room temperature MO = 0.16 mol 1⁻¹.

Table 2. Solubilities, g/100 cm³

Metal	Metal oxide	Metal iodate at 60°C	Metal iodate nH ₂ O	Iodate hydrate at 35°C
Mg	0.0006 (25°C)	13.2	4	9.83
Ca	0.131 (10°C)	0.62	1	0.48
Sr	0.69 (20°C)	0.28	1	0.33
Ba	3.48 (20°C)		1	0.05

In the Mg case the solid reaction product was brown. This brown color could not be removed by washing (acetone or *n*-butanol) or by suction. However, the brown component was removed by heating to 400°C and I₂ was formed. The brown color was therefore thought to be due to adsorbed I₂[9]. An alternative explanation for the brown color is the formation of a solid solution Mg(IO₃)(I), which has to give the same X-ray pattern as Mg(IO₃)₂. After the heat treatment the X-ray patterns of both Mg(IO₃)₂ and MgO were seen. The reaction MgO/I₂ was also tried in the absence of water, but no reaction took place, although I₂ adsorption was observed.

A parameter study was undertaken using MgO, varying the amount of water and I_2 as shown in Table 3. The mole-% values given in this Table (and subsequent Tables) are calculated by the ratio of the total moles of iodate found to the moles of iodate which would be formed if the reaction represented by eqn (2) was entirely transformed to products. This ratio is expressed as a percentage.

The total extent of reaction was greater at higher water and iodine mole ratios, but the amount of iodate in solution also increased. Thus, the conditions which promote high product yields also produce soluble iodates, so that complete separations were not accomplished.

Also shown in Table 3 are the results using Ca, Sr, and Ba oxides. All experiments were carried out with at least a 2-fold excess of I_2 , to reduce the possibility of forming

Table 3. Reaction of single oxides, MO, H₂O and I₂ at 150°C for 1 hr, 141 psi initial pressure, MO = 3.5×10^{-3} mole

м	I2/MO	H ₂ O	Solid M(IO ₃) ₂ mole-%	Solution M(IO ₃) ₂ mole-%
Mg	2	15	17	24
Mg	2	30	10	44
Mg	2	93	9	58
Mg	4	15	38	13
Mg	4	43	20	59
Ca	2	15	65	6
Sr	2	17	63	6
Ba	2	16	84	4

 $MO + I_2 \xrightarrow{H_2O} 5/6MI_2 + 1/6M(IO_3)_2$

basic metal salts. The iodide analyses agreed with the stoichiometry of eqn (2) (i.e. $5 \times \text{total}$ iodate) to within 2%, when a 2 mole excess of I_2 was used. With a 4 mole I_2 excess agreement was not as close, suggesting that some of the iodide was coprecipitated with the iodate in the form of a solid solution. The Ca, Sr, and Ba oxides all showed higher product yields than Mg, BaO gave the greatest. No brown color was seen.

Even though these yields were relatively high and the product separation good, the metal oxides alone will not give adequate efficiencies in thermochemical cycles since the metal iodides are not easily hydrolyzed.

(e.g.
$$BaI_2 + H_2O \rightarrow BaO + 2HI, \Delta G^\circ = 0 \text{ at } 2,705^\circ\text{C}, \Delta H_{298}^\circ = + 339.7 \text{ kJ}$$
) (5)

(3) Mixed oxides at high temperature and pressure

(a) MgO and CaO

By studying the mixed oxide reactions it was hoped to be able to combine the properties of the individual oxides and thus optimize the product yields and separations. For example, $Ba(IO_3)_2$ is the least soluble iodate and MgI_2 is the most readily hydrolysed iodide. However, $Ba(IO_3)_2$ requires a temperature of 1000°C to form BaO.

$$5\text{MgO} + \text{Ca(OH)}_2 + 6\text{I}_2 \xrightarrow{\text{H}_2\text{O}} 5\text{MgI}_2 + \text{Ca(IO}_3)_2 + \text{H}_2\text{O}.$$
(6)

The insoluble product was dark brown and gave the power pattern of anhydrous calcium iodate, with one extra line at a *d* value of 4.6 Å. As in the case of pure MgO, this brown color could only be removed by heating to 400°C, which corresponded to the removal of the extra line and the production of I_2 . On further heating to 800°C, Ca(IO₃)₂ decomposed to CaO, I_2 and O_2 . The X-ray pattern showed both Ca and Mg oxides.

The iodate analysis results are shown in Table 4. The mole-% values being calculated from the ratio of the amount of iodate found to the maximum which could be formed theoretically. By comparing the results of Tables 3 and 4 it is clear that, by substituting 1/6MgO with CaO both the product separation and the amount of precipitated iodate was increased. As before, increasing the moles of I₂ and water raised the product yield, but also raised the soluble fraction of iodate.

Table	4.	React	ion	of	MgO	and	CaO	with	H_2O	and	I2,
150°C,	11	nr, 141	psi :	initi	al pre	ssure	. Mg()/CaC	= 5,	MgO	=
				5.	0 × 10	⁻³ mo	ole			Ũ	

$5/6MgO + 1/6Ca(OH)_2 + I_2 \xrightarrow{H_2O} 5/6MgI_2 + 1/6Ca(IO_3)_2$						
I ₂ /MgO + CaO	H ₂ O/MgO + CaO	Solid Ca(IO ₃) ₂ mole-%	Solution Mg(IO ₃) ₂ mole-%			
2	15	29	8			
2	44	35	18			
2	92	40	23			
4	15	47	10			
4	43	49	45			
4	92	26	48			
6	48	47	38			

The reaction time was varied between 10 min and 19 hr, but this had little effect on the product yields. Equilibrium was established after 10 min.

(b) MgO and SrO or BaO

As in the previous cases, the insoluble products were dark brown and gave the X-ray patterns of anhydrous $Sr(IO_3)_2$ and hydrated $Ba(IO_3)_2$ respectively with an additional line at 4.6 Å. This line disappeared together with the brown color after heating to 400°C.

MgO was seen in the product X-rays after heating to 1000°C. The analysis results are shown in Table 5. Again, these show that replacment of 1/6MgO by Sr or Ba oxides increase the amount of iodate formed, a greater proportion of this being in the solid phase.

(c) Mixed oxides not involving MgO

In order for this study to be comprehensive, the reactions of the combinations 5CaO/BaO, 5CaO/SrO and 5SrO/BaO were also examined. In the first and last cases, hydrated barium iodate precipitated. However, for 5CaO/SrO, hydrated calcium iodate was formed, in the reverse of the general trend seen in all other examples [a small amount of $Sr(IO_3)_2$ coprecipitated, since after heating to 1000°C, both SrO and CaO were seen in the powder patern].

All the solid phase products were white in contrast to the mixed oxide runs involving MgO. The quantitative data is displayed in Table 6.

(4) Paraperiodates at high temperature and pressure

Metal paraperiodates are formed as an intermediate in the decomposition of metal iodates to oxides [10, 11].

Table 5. Reaction of MgO with SrO or BaO, H₂O and I₂, 150°C, 1 hr, 141 psi initial pressure, MgO/MO = 5, MgO = 5.0×10^{-3} mole M = Sr or Ba

 $5/6MgO + 1/6M(OH)_2 + I_2 \longrightarrow 5/6MgI_2 + 1/6M(IO_3)_2$

м	I ₂ /MgO + MO	H ₂ O/MgO + MO	Solid M(IO ₃) ₂ mole-%	Solution Mg(IO ₃) ₂ mole-%
Sr	2	12	34	8
Sr	4	53	52	18
Ba	2	13	48	6
Ba	4	39	62	6
Ba	4	77	68	8
Ba	8	64	35	8

Table 6. Reactions of mixed metal oxides, H_2O and I_2 . 150°C, 1 hr, 141 psi initial pressure, $M^1O = 0.7 \times 10^{-3}$ mole

 $1/6M^{1}O + 5/6M^{11}O + I_{2} \longrightarrow 1/6M^{1}(IO_{3})_{2} + 5/6M'I_{2}$

M	M ¹¹	Solid mole-%	Solution mole-%
Ba	Ca	66Ba(IO ₃) ₂ · H ₂ O	3Ca(IO ₃) ₂
Sr	Ca	53Ca(IO ₃) ₂ · H ₂ O	10Sr(IO ₃) ₂
Ba	Sr	75Ba(IO ₃) ₂ ·H ₂ O	4Ba(IO ₃) ₂

$$M(IO_3)_2(c) \to 1/5M_5(IO_6)_2(c) + 9/5O_2(g) + 4/5I_2(g)$$
(7)

$$1/5M_5(IO_6)_2(c) \rightarrow MO(c) + 7/10O_2(g) + 1/5I_2(g).$$
 (8)

The temperature of the paraperoidate decomposition increases $Mg \rightarrow Ca \rightarrow Sr \rightarrow Ba$ (650, 800, 900, 1000°C). Depending on the maximum temperature available for a thermochemical H₂ cycle, the reactions of Sr and Ba paraperiodates with I₂ may be important in order to obtain recyclisation

$$1/3M_{5}(IO_{6})_{2}(c) + 4/3I_{2}(c) \xrightarrow{H_{2}O} 2/3M(IO_{3})_{2}(c) + MI_{2}(aq)$$
(9)

or, if reacting in conjunction with MgO,

$$MgO(c) + 1/18M_{5}(IO_{6})_{2}(c) + 22/18I_{2}(c)$$

$$\xrightarrow{H_{2}O} 5/18M(IO_{3})_{2}(c) + MgI_{2}(aq). \quad (10)$$

Since these reactions are again thermodynamically favored (Table 1) they were studied. However, as is shown in Table 7, although $Ba_5(IO_6)_2$ gave favorable yields by itself, when mixed with MgO little reaction took place, showing little interaction between $Ba_5(IO_6)_2$ and MgO.

DISCUSSION

The X-ray patterns of the insoluble reaction products, even though they are all iodate's, fall into two distinct groups:

(1) Those which are brown and have an additional line at a d value of 4.6Å found for reactant mixtures MgO/CaO, MgO/SrO, MgO/BaO [for MgO as a single oxide, although the product is brown there is no line at 4.6Å].

(2) Those which are white and give X-ray patterns of pure iodates. It is surprising in case 1) that the iodine, if merely occluded, hangs so tenaciously to the product. Therefore a solid solution could be formed between I_2 , MgO and the iodate. This would account for the additional line in the X-ray, but the presence of both MgO and I_2 do not deform the crystal lattice of the iodate. One interesting observation seen for 5MgO/CaO is that the amount of I_2 from heating the insoluble reaction product is the same below 400°C as above which suggests the following sequence:

$$Ca(IO_3)(I_3)_2 \xrightarrow{<400^{\circ}C} Ca(IO_3)(I) + I_2$$
(11)

$$Ca(IO_3)(I) \xrightarrow{>400^{\circ}C} CaO + I_2 + O_2.$$
(12)

However, the weight loss measurements more closely support decomposition of the iodate

$$Ca(IO_3)_2 \rightarrow CaO + I_2 + 5/2O_2. \tag{13}$$

When I_2 dissolves in a highly alkaline solution an equilibrium is immediately set up [12]

$$I_2 + 2OH^- \rightleftharpoons OI^- + I^- + H_2O,$$
 (14)

with the hypoiodite decomposing at a measurable rate to iodate and iodide

$$3OI^- \to IO_3^- + 2I^-.$$
 (15)

Table 7. Reactions of Sr or Ba paraperiodates, H₂O and I₂ 150°C, 1 hr, 141 psi initial pressure

(a) $Ba_5(IO_6)_2 + 4I_2 \xrightarrow{H_2O} 3BaI_2 + 2Ba(IO_3)_2$ $Ba_5(IO_6)_2 = 5.5 \times 10^{-4}$ mole.

(a)				
	I2/Ba5(IO6)2	H2O/Ba5(IO6)2	Insoluble iodate mole-%	Soluble iodate mole-%
	16	200	85	2
(b)	$18MgO + M_5(IO_6)_2 + 22I_2$	$\xrightarrow{H_{2}O} 18MgI_2 + 5M(IO_3)_2$		
	$M_5(IO_6)_2 = 3.6 \times 10^{-4} \text{ mol}$	e.	Insoluble jodate	Soluble jodate
М	$I_2/18MgO + M_5(IO_6)_2$	$H_2O/18MgO + M_5(IO_6)_2$	mole-%	mole-%
D		······		
Dà	2.5	18	8	1
Ба Ва	2.5 4.6	18 87	8 15	1

With alkali (>4M) the following rate law has been found

$$\frac{-d[OI^-]}{dt} = k_1[OI^-]^2 + k_2 \frac{[OI^-]^2[I^-]}{[OH^{-1}]}.$$

At lower alkalinities or with excess I_2 no satisfactory rate law has, as yet, been established, many species being present at equilibrium [13, 14]. But, with the established rate law, increasing the base and I_2 concentration will increase the rate of the reaction. The reaction rate has been shown to be fast (Fig. 1).

The limiting factor in establishing an equilibrium favorable to product formation is the decreased solubility of the oxide (or hydroxide) in the presence of I^- ions[15] (due to the common ion effect of the metal ion). This overrides the highly negative enthalpies of the reactions. The increased solubility accounts for the increase in product yield obtained on passing down the series, Mg to Ba. Solubility also accounts for the separation of iodate between the two phases allowing much Mg(IO₃)₂ to exist in solution. Ba(IO₃)₂, however, is so insoluble that little is formed in solution even in relatively dilute conditions.

CONCLUSIONS

In none of the cases studied are the reactions complete; the degree of reaction increasing with atomic weight. Good product separation is only obtained when using BaO.

From the viewpoint of the production of H_2 thermochemically, the mixture 5MgO/BaO offers the most promise. In this case product separation was good, and the extent of the reaction was high; further, MgI₂ is easily hydrolyzed. However, the temperature available has to be 1000°C or higher, in order to convert $Ba_{s}(IO_{6})_{2}$ back to the oxide.

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REFERENCES

- 1. R. H. Wentorf and R. E. Hanneman, Science 185, 311 (1974).
- Selected Values of Thermodynamic Properties, NBS Tech. Note 270–6.
- J. Bousquet, J. C. David, D. Mathurin and G. Perachon, Bull. Soc. Chim. Fr. 3991 (1968).
- Handbook of Chemistry and Physics, 55th Edn. Chemical Rubber Publishing Co. (1974-5).
- K. Fujii, W. Kondo, W. Mizuta and T. Kumagai. Int. J. H₂ Energy 2, 413 (1977).
- W. Kondo, S. Mizuta, T. Kumagai, Y. Oosawa, Y. Takemori and K. Fujii, Proc. 2nd World H₂ Energy Conf. p. 909 (1978).
- S. Mizuta, W. Kondo, T. Kumagai and K. Fujii, Int. J. H₂ Energy 3, 407 (1978).
- Gmelin, 27 Mg (B) 197, Gmelin, 28 Ca (B) 629, Gmelin, 29 Sr Erg. 243 and Gmelin, 30 Ba Erg. 400.
- 9. R. C. Dunn and H. H. Pomeroy, J. Phys. Chem. 51, 981 (1947).
- G. S. Sanyal and K. Nag, J. Inorg. Nucl. Chem. 39, 1127 (1977).
- 11. S. Peltier and C. Duval, Anal. Chim. Acta 1, 360 (1947).
- 12. C. H. Li and C. F. White, J. Am. Chem. Soc. 65, 335 (1943).
- Comprehensive Chemical Kinetics, Vol. 6, p. 400. Editors C. H. Bamford and C. F. H. Tipper, Elsevier (1972).
- 14. E. L. C. Forster, J. Phys. Chem. 7, 640 (1903).
- 15. A. Seidell, Solubilities of Inorganic and Metal Organic Compounds, Van Nostrand (1940).