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The Oxidation of Metal Sulfites by Iodine for Use in Thermochemical Hydrogen Cycles*

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Thermochemical hydrogen cycles involving metal sulfates have been studied[1,2] at Los Alamos for a number of years since they offer an alternative to sulfuric acid which is corrosive and has high energy requirements for drying prior to its thermal decomposition. This abstract deals with the formation of such metal sulfates in conjunction with a low temperature hydrogen formation step.

Last year[3] we reported on the oxidation of sulfites in aqueous solution using iodine. The reactions:

$$MSO_3(c) + MgO(c) + I_2(c) \longrightarrow MSO_4(c) + MgI_2(aq) \qquad (1)$$

$$\text{where } M = Mg,\ \Delta H^o_{298} = -333.1 \text{ kJ}$$

$$M = Ca,\ \Delta H^o_{298} = -255.7 \text{ kJ}$$

$$M = Ba,\ \Delta H^o_{298} = -265.7 \text{ kJ}$$

were found to be fast (< 1 min) and quantitative when carried out in dilute solution at room temperature. MgO is used in conjunction with the sulfite since MgI_2 can be readily hydrolysed and the resultant HI thermally

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decomposed. The cycle is completed by thermally decomposing the sulfate. However, even though $BaSO_4$ and $CaSO_4$ are insoluble rendering product separation in Eq. (1) trivial, they also thermally decompose above the temperature range considered available for thermochemical hydrogen cycles:

$$MSO_4(c) \longrightarrow MO(c) + SO_2(g) + 1/2\ O_2(g)$$

$$\text{where } M = Mg,\ \Delta G^{o}_{1350} = 0$$

$$M = Ca,\ \Delta G^{o}_{1810} = 0$$

$$M = Ba,\ \Delta G^{o}_{2030} = 0.$$

Thus $MgSO_3$ seems the best candidate for reaction (1) even though $MgSO_4$ is soluble introducing a potential separation problem.

More recently, a Japanese group[4] have shown that product separation is unnecessary. They carried out reaction (1) in aqueous solution and dried the products and continued to heat them. They found there was no interaction between the HI and $SO_3(SO_2,O_2)$ emitted due to the large temperature difference (500 K) between the two evolutions.

In order to further improve the efficiency of a cycle containing this step, we set out to study reaction (1) in the absence of water. Thermodynamically, the reaction:

$$MgSO_3(c) + MgO(c) + I_2(g) \longrightarrow MgSO_4(c) + MgI_2(c)$$

is favored, $\Delta H^{o}_{298} = -105.3$ kJ, and so might reasonably be expected to proceed as written although gas/solid reactions are notorious for being kinetically slow.

Initially, therefore, we passed dry I_2 through a mixture of $MgSO_3 \cdot 6H_2O$ and MgO and measured the extent of reaction as a function of temperature by estimating gravimetrically magnesium sulfate formed. These results are shown in Fig. 1. As can be seen 67% of the total possible $MgSO_4$ (based on the stoichiometry) was found at 423 K. The passage of I_2 through the reactants took about 10 min in all cases. At this temperature, the amount of water of hydration remaining is between 2 and 3 molecules per mole of magnesium sulfite[5]. This may be critical for sulfate formation but further experimentation needs to be performed to define the role of waters of hydration. When I_2 and water vapor were passed through the solid reactant bed, no increase in products was found and in some cases a nonporous plug was formed which prevented the passage of I_2 through the solid.[5]

We have shown that reaction (3) will take place under nearly dry conditions which is energetically efficient for a thermochemical hydrogen cycle.

The heat requirements for the total cycle can be summarized:[6]

$$\begin{array}{l}
MgO(c) + SO_2(g) + 2H_2O(l) \longrightarrow MgSO_3 \cdot 2H_2O(c) \quad \Delta H^o_{298} = -141.38 \text{ kJ} \\
MgSO_3 \cdot 2H_2O(c) + MgO(c) + I_2(g) \longrightarrow MgSO_4(c) + MgI_2(c) + 2H_2O(g) \\
\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \Delta H^o_{298} = +10.01 \text{ kJ} \\
H_2O(g) \longrightarrow H_2O(l) \quad \Delta H^o_{298} = -44.0 \text{ kJ} \\
MgI_2(c) + H_2O(g) \longrightarrow MgO(c) + 2\,HI(g) \quad \Delta H^o_{298} = +59.8 \text{ kJ} \\
2HI(g) \longrightarrow H_2(g) + I_2(g) \quad \Delta H^o_{298} = +10.4 \text{ kJ} \\
MgSO_4(c) \longrightarrow MgO(c) + SO_2(g) + 1/2\ O_2(g) \quad \Delta H^o_{298} = +390.1 \text{ kJ} \\
\hline
H_2O(l) \longrightarrow H_2(g) + 1/2\ O_2(g) \quad \Delta H^o_{298} = +285.9 \text{ kJ.}
\end{array}$$

This gives a figure of merit of 0.61 without applying any exothermic heat to lower temperature endothermic steps.

Although magnesium sulfite appears promising for this oxidation, we have conducted a search for alternative metal sulfites which fit the following criteria for use:

a) sulfate must decompose in the temperature range available (< 1400 K),

b) iodide must hydrolyse easily, and

c) salts must not be rare, toxic, or expensive.

Two metals fit these criteria, they are lanthanum and titanium. For lanthanum, the triiodide hydrolyses readily only as far as the oxyiodide and lanthanum trisulfate decomposes to lanthanum dioxymonosulfate[7] at temperatures below 1400 K.

For titanium, in the tetravalent state, the iodide will be in the liquid or vapor states (mp 423 K, bp 650 K) and hydrolyses to TiO_2 ($\Delta G^{o} = 0$ at $\simeq$ 430 K). Titanium sulfate is reported[8] to decompose to TiO_2 and SO_3 at 870 K.

We propose to study these systems over the next year.

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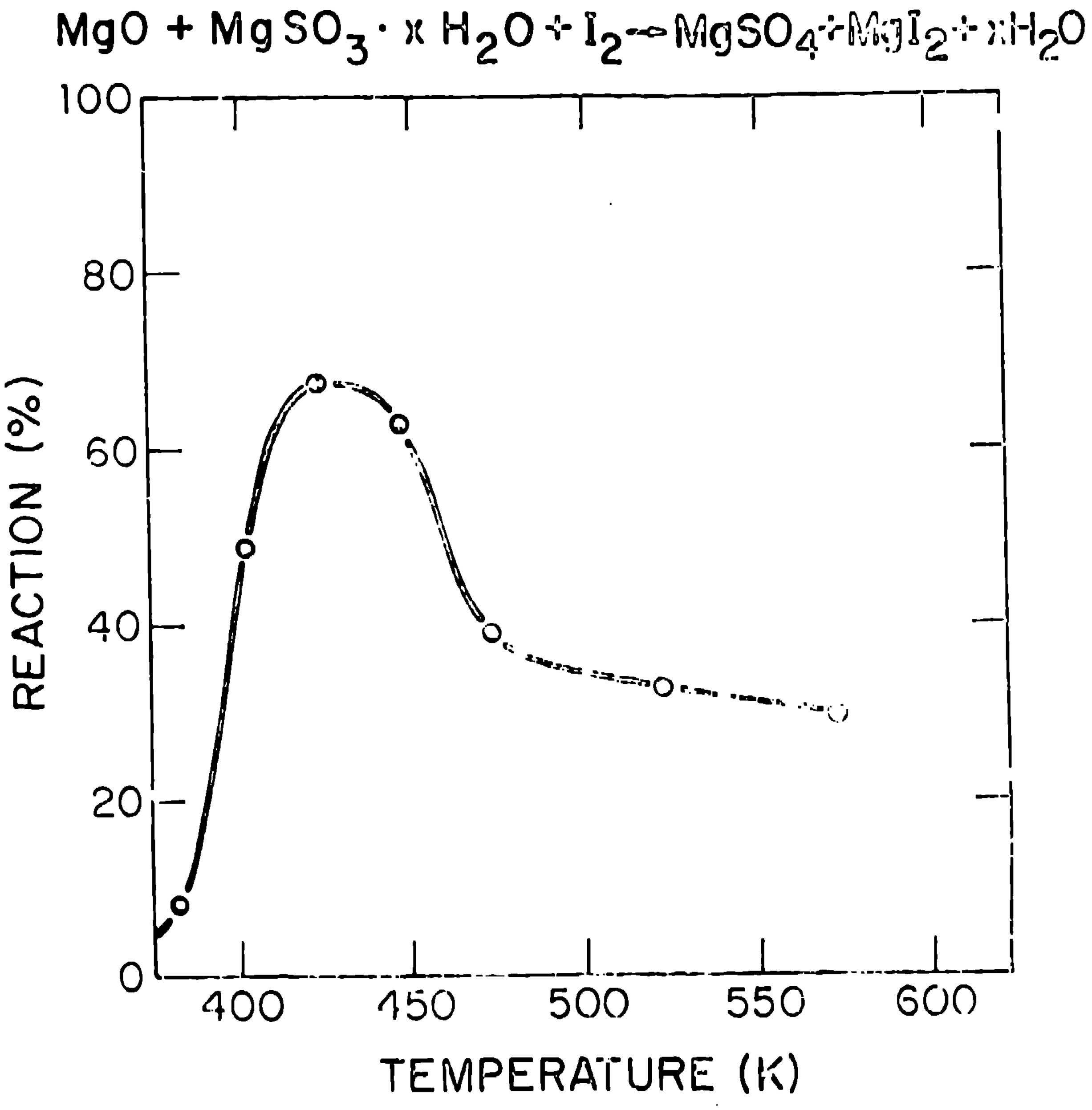
Fig. 1.



$MgO = 9.8 \times 10^{-3}$ mol

$MgSO_3 \cdot 6H_2O = 9.8 \times 10^{-3}$ mol

$I_2 = 11.8 \times 10^{-3}$ mol

$x = 0$ to 6