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Thermochemical Splitting of Water and Carbon Dioxide with Cerium Compounds*

C. E. BAMBERGER and PAUL R. ROBINSON

Chemistry Division of Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, Tenn. 37830, U.S.A.

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Cerium(IV) oxide reacts with solid or molten $Na_4P_2O_7$ at 750–950 °C to form sodium cerium(III) phosphate, $Na_3Ce(PO_4)_{2(s)}$, $Na_3PO_{4(s)}$, and $O_{2(g)}$. The mixture of $Na_3Ce(PO_4)_{2(s)}$ with $Na_3PO_{4(s)}$ reacts at similar temperatures with $Na_2CO_{3(l)}$ and steam to produce $CeO_{2(s)}$, $Na_3PO_{4(s)}$, $CO_{2(g)}$, and $H_{2(g)}$. In the absence of steam, carbon monoxide forms instead of $H_{2(g)}$. Treatment of aqueous Na_3PO_4 with $CO_{2(aq)}$ at 0–50 °C yields solutions of Na_2HPO_4 and $NaHCO_3$, which are separated by crystallization. These salts condense at >200 °C to form $Na_4P_2O_{7(s)}$ and $Na_2CO_{3(s)}$, respectively, thus completing the thermochemical cycle. The cycle splits either H_2O or CO_2, depending upon whether steam is used in the reaction of Na_2CO_3 with $Na_3Ce(PO_4)_2$.

Introduction

Thermochemical cycles for water-splitting [1] employ thermal energy to drive a cyclic series of chemical reactions, the sum of which is just: H_2O + Thermal Energy = $H_2 + 1/2O_2$. Solar furnaces [2] or nuclear reactors [3] can supply the necessary thermal input, thereby avoiding the consumption of fossil fuels for the production of hydrogen. While it is possible to use electricity from these sources to electrolyze water into H_2 and O_2, Funk [4] has suggested that thermochemical cycles might be a more efficient way of converting thermal energy into chemical energy in the form of burnable H_2. Because the energy required to decompose CO_2 into CO and oxygen is quite similar to that required to decompose water at about 1000 K, this concept is also applicable to CO_2. Thus, the splitting of CO_2 can also provide a means for producing a fuel and a chemical intermediate.

The present work began with the observation [5] that cerium(IV) pyrophosphate, CeP_2O_7, thermally decomposes into cerium(III) phosphate at >700 °C. This is interesting because cerium(IV) oxide, CeO_2, cannot be thermally decomposed at such low temperatures. Thus, we sought to develop a thermochemical cycle based upon the chemistry of cerium phosphate. While many proposed cycles are derived solely from calculations, we continued our experimental approach to the development of thermochemical cycles. As in the past, the advantage of this approach was borne out by the discovery of compounds and of chemical reactions that were previously unknown.

In this report, we describe the results of these studies, which led to an experimentally proven thermochemical cycle that splits both CO_2 and H_2O.

Experimental

A. Reagents

CeO_2 (99.9% pure) was purchased from Gallard-Schlesinger.

$CePO_4$ was prepared by reducing CeO_2 with 47% HI (Mallinckrodt). The resulting solution was filtered, and then treated with excess H_3PO_4 (85%). Impure $CePO_4$ precipitated. This was collected by filtration and purified three times by boiling an aqueous suspension of the solid for an hour. The purified product was analyzed by X-ray powder diffraction [7].

Li_3PO_4 was prepared by mixing $LiOH \cdot H_2O$ (Fisher Chemical) with a stoichiometric amount of 85% H_3PO_4 (Mallinckrodt). The resulting Li_3PO_4 was washed several times with deionized water and fired in air in a platinum dish to 500 °C. It was analyzed by titration with HCl, which showed the solid to be $Li_3PO_4 \cdot 0.02H_2O$ (EW = 38.73 g).

All other reagents were 'Analytical' or 'Reagent' grade, and were used without purification. In some cases, $Na_4P_2O_7 \cdot 10H_2O$ and $Na_2CO_3 \cdot xH_2O$ were vacuum-dried prior to use.

B. High-Temperature Experiments

The high-temperature reactions were run as follows: The reactants were ground together and placed into a platinum boat, which was covered with Pt-foil and introduced into a fused quartz tube. A tube furnace was then used to heat the solids. A con-

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tinuously flowing stream of Ar or He at essentially one atm pressure was used to purge air from the tube, and to carry evolved gases away from the solids and into continuously operating measurement devices – a Gow-Mac Model 20-150 thermal conductivity analyzer for H_2 or CO, and a Beckman Model 741 oxygen analyzer. A solution of $Ba(OH)_2$ was used to trap CO_2 as $BaCO_3$, and a $CaSO_4$ column was used to dry the gases prior to analysis. Solids were analyzed by neutron activation and by powder X-ray diffraction [7]. 'Slow-heating' experiments are those in which a thermal controller was used to increase the reaction temperature at a steady rate of 5.4 °C/min. 'Fast-heating' experiments are those in which the reactants were introduced into a pre-heated furnace, which brought them from room temperature to the desired temperatures within 4–6 min; the thermal controller was then used to maintain reaction temperatures at a fairly constant (±3 °C) value. Yields were arbitrarily measured after 7 min, and after completion of the reactions.

C. Low-Temperature Experiments

Reactions of CO_2 with Na_3PO_4 were carried out in thermostated aqueous solutions at 0–80 °C. Typically, CO_2 at 10^5Pa was bubbled through solutions of Na_3PO_4 (0.2–3.0 *M*), or through slurries of Na_3PO_4 mixed with CeO_2. The reactions reached completion within 30 min. When the resulting solution was cooled to 0 °C, a precipitate formed; it was primarily $Na_2HPO_4 \cdot xH_2O$. The solutions contained mostly $NaHCO_3$, which was recovered by careful evaporation of the solvent. The compositions of all solutions and precipitated solids were determined by addition of a known excess of $HCl_{(aq)}$, followed by boiling to drive off $CO_{2(g)}$ and potentiometric back-titration with standardized NaOH. Additional details of these experiments are given in Table I.

Results

Equations 1–5 show in outline the chemical reactions that comprise the cycle:

$$2CeO_{2(s)} + 3Na_4P_2O_{7(s)} \xrightarrow{850\text{–}950\ ^\circ C} 2Na_3Ce(PO_4)_{2(s)} + 2Na_3PO_{4(s)} + \tfrac{1}{2}O_{2(g)} \tag{1}$$

$$2Na_3Ce(PO_4)_{2(s)} + 3Na_2CO_{3(l)} \xrightarrow{750\text{–}900\ ^\circ C} 2CeO_{2(s)} + 4Na_3PO_{4(s)} + 2CO_{2(g)} + CO_{(g)} \tag{2}$$

$$2Na_3Ce(PO_4)_{2(s)} + 3Na_2CO_{3(l)} + H_2O_{(g)} \xrightarrow{750\text{–}900\ ^\circ C} 2CeO_{2(s)} + 4Na_3PO_{4(s)} + 3CO_{2(g)} + H_{2(g)} \tag{2'}$$

$$6Na_3PO_{4(d)} + 6CO_{2(d)} + 6H_2O_{(l)} \xrightarrow{5\text{–}50\ ^\circ C} 6Na_2HPO_{4(s)} + 6NaHCO_{3(d)} \tag{3}$$

$$6Na_2HPO_{4(s)} \xrightarrow{>250\ ^\circ C} 3Na_4P_2O_{7(s)} + 3H_2O_{(g)} \tag{4}$$

$$6NaHCO_{3(s)} \xrightarrow{>200\ ^\circ C} 3Na_2CO_{3(s)} + 3H_2O_{(g)} + 3CO_{2(g)} \tag{5}$$

The designations (s), (l), (g), and (d) refer respectively to the states solid, liquid, gas, and dissolved. The sum of eqns. 1, 2, 3–5 yields the overall reaction

$$\text{heat} + CO_2 \longrightarrow CO + \tfrac{1}{2}O_2$$

and the sum of eqns. 1, 2′, 3–5 gives

$$\text{heat} + H_2O \longrightarrow H_2 + \tfrac{1}{2}O_2$$

Figure 1 shows typical curves for the pressures of evolved oxygen (eqn. 1) as a function of time and temperature in slow-heating experiments. When CeO_2

TABLE I. Typical Treatment of a Reaction Product (CeO_2 + Na_3PO_4) with CO_2 in H_2O.

Initial Composition	Treatment	Products	
1. 2.70 g (15.5 mmol) CeO_2 3.52 g (22.1 mmol) Na_3PO_4 2.12 g (20.0 mmol) Na_2CO_3	52 ml H_2O; 22 °C; 1 atm $CO_{2(g)}$; 30 min	Solid:	2.59 g (15.1 mmol) CeO_2
		Solution:	48.9 mmol $NaHCO_3$; 35.0 mmol Na_2HPO_4
2. Solution from above	Evaporated to 28 ml; cooled to 0 °C	Solid:	7.20 g (19.1 mmol) $Na_2HPO_4 \cdot 12H_2O$; 0.35 g (4.2 mmol) $NaHCO_3$
		Solution:	23.0 mmol $NaHCO_3$ 2.5 mmol Na_2HPO_4

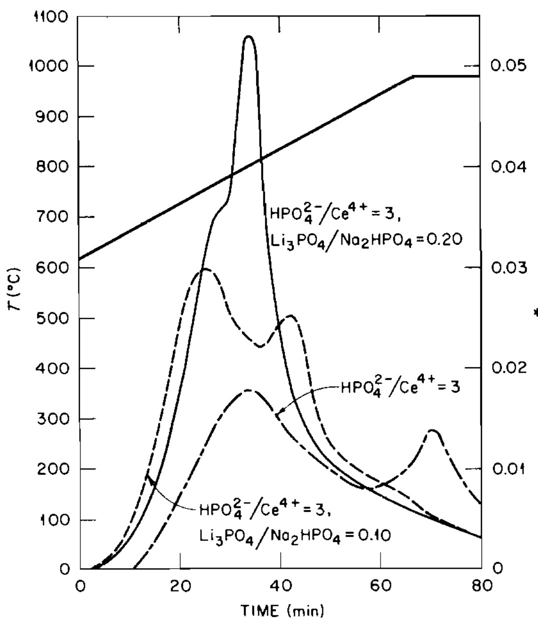

Fig. 1. Pressures of evolved O_2 as a function of time, temperature, and mol-% Li_3PO_4 during 'slow-heating' of CeO_2–Na_2HPO_4 mixtures (eqns. 1 + 4). The heavy, slanted line indicates the increase in temperature with time. The $P^*_{O_2}$ is the 'partial pressure' of O_2 in a stream of Ar flowing at 100 ml/min.

was fired with pure Na_2HPO_4 or $Na_4P_2O_7$ (eqns. 1 and 4), the O_2 pressures consistently reached two maxima. This can be explained in terms of the phase behavior of the system Na_2O–P_2O_5 [8], which shows that a eutectic mixture melting at 945 °C forms when the composition of the system corresponds to about 70 mol-% $(Na_4P_2O_7)_{1/2}$ (m.p. 994 °C) and 30 mol-% Na_3PO_4 (m.p. 1583 °C). Since Na_3PO_4 is produced from $Na_4P_2O_7$ as the reaction proceeds, the mixture of solids may melt when the eutectic composition is reached, thereby providing better contact between the reactants and causing a corresponding increase in the rate of O_2-evolution. This led us to add Li_3PO_4 to the mixtures of CeO_2 with Na_2HPO_4 or $Na_4P_2O_7$, in order to lower the temperature at which these reactants formed a melt. As Fig. 1 shows, its addition resulted in increasingly higher pressures of O_2 evolved at a given temperature as the mol-% of Li was increased.

Figure 2 summarizes the results of fast-heating experiments for Reaction 1. Measurable evolution of O_2 begins at temperatures below 780 °C. Above 900 °C, no significant increase in the rate of O_2-generation is observed. The effect of added Li_3PO_4 is also apparent in this figure, especially in the temperature range 780–880 °C: With a $Li_3PO_4/Na_4P_2O_7$ molar ratio of 0.20, the rate of O_2-evolution is four times higher than the rate without lithium. However, above about 930 °C, the effect of added lithium is negligible.

Figure 3 shows the results of fast-heating experiments for Reaction 2. Evolution of CO begins at about 720 °C, and reaches a maximum rate at above 970 °C. The presence of Li_3PO_4 improves reaction rates at 720–830 °C, but may actually slow down the evolution of CO at temperatures above 900 °C. Excess Na_2CO_3 has no measurable effect on the kinetics of the reaction.

It was not possible for us to conduct fast-heating experiments in Reaction 2′ because the rapid expansion of steam would have created too large a surge of

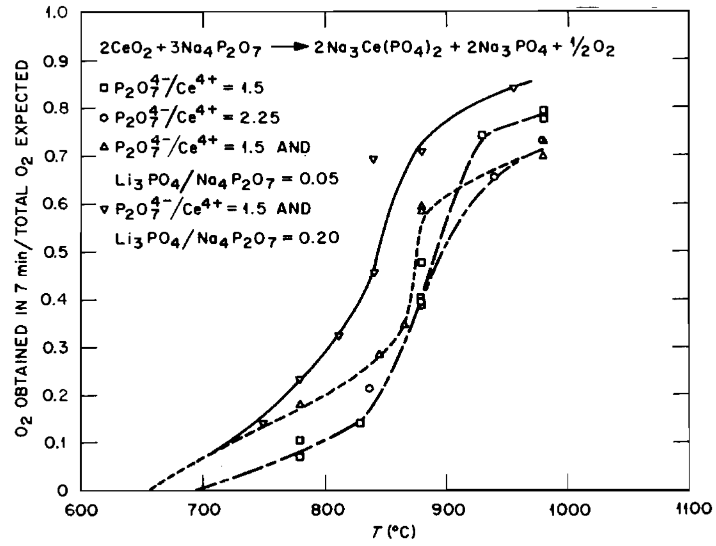

Fig. 2. (O_2 obtained in 7 min) ÷ (Total expected O_2) as a function of temperature and mol-% Li_3PO_4 during 'fast-heating' of CeO_2–$Na_4P_2O_7$ mixtures (eqn. 1).

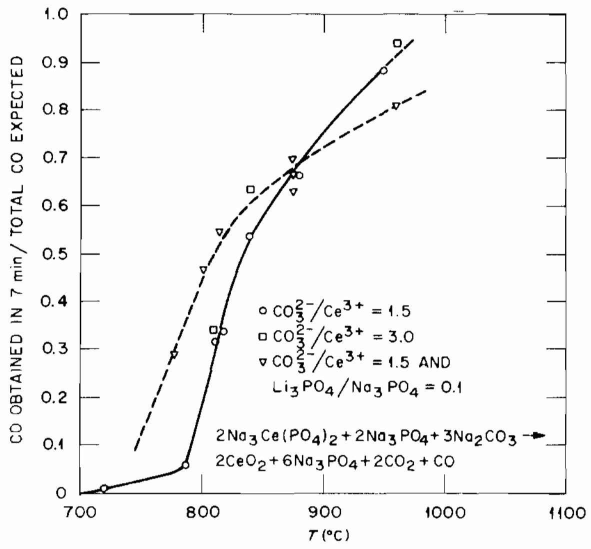

Fig. 3. (CO obtained in 7 min) ÷ (Total expected CO) as a function of temperature and mol-% Li_3PO_4 during 'fast-heating' of $Na_3Ce(PO_4)_2$–Na_2CO_3 mixtures (eqn. 2).

pressure. However, slow heating experiments showed that the evolution of H_2 occurred at the same temperatures and pressures as the evolution of CO. Also, the rate of H_2-production is essentially independent of the rate at which steam was passed through the system. This implies that the rate-limiting steps in the generation of H_2 *via* Reaction 2′ is the production of CO, which then reacts with H_2O *in situ* to form hydrogen:

$$CO + H_2O \rightarrow CO_2 + H_2$$

Equation 3 greatly oversimplifies the reaction between aqueous Na_3PO_4 and CO_2. Between pH 8 and 13, H_2CO_3, HCO_3^-, CO_3^{2-}, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, OH^-, and Na^+ are present in different amounts at equilibrium, the position of which depends upon the temperature, the pressure of CO_2, and the relative amounts of solvent and solute being used. Table I describes a typical Reaction 3 experiment. Proper selection of reaction conditions can lead to 95% separation of $NaHCO_3/Na_2CO_3$ from Na_2HPO_4 in a single crystallization with pure water as the solvent. If a 50/50 (v/v) mixture of H_2O/CH_3OH is used, 100% separation can be achieved in a single step.

We presently prefer to treat the products of Reaction 2 – CeO_2 and Na_3PO_4 – with the CO_2 evolved from another Reaction 2 and just enough water to dissolve the resulting $NaHCO_3$ and Na_2CO_3. This also separates the CO_2 from the other gases – H_2 or CO. The less-soluble Na_2HPO_4 is left behind with insoluble CeO_2, and these solids are fired together to yield O_2 (eqns. 1 and 4). The carbonate-containing solution is evaporated to give a mixture of $NaHCO_3$ and Na_2CO_3, which is used in eqn. 2.

The use of Li_3PO_4 as described above to improve the rates of Reactions 1 and 2 does not complicate the cycle to any great extent. It was chosen because Li_3PO_4 is only very slightly soluble, and therefore remains precipitated with the CeO_2.

It is possible to use sodium *meta*phosphate, $(NaPO_3)_3$, to replace $Na_4P_2O_7$ in eqn. 1, in which case half as many moles of acid phosphate are needed to release an equivalent amount of oxygen. The temperatures at which CeO_2 reacts with $(NaPO_3)_3$ are also lower, by about 100 °C. The disadvantage of using *meta*phosphate arises in eqns. 3 and 4. High pressures (2–5 atm) of CO_2 are required to convert aqueous Na_3PO_4 totally to NaH_2PO_4 (as opposed to Na_2HPO_4) which is then separated and fired to above 250 °C to form $(NaPO_3)_3$ and $H_2O_{(g)}$.

When lithium salts completely replace sodium salts in the cycle, the temperatures of eqns. 1 and 2 are lowered by 50–100 °C. However, Reaction 3 again becomes more complicated. As we mentioned above, Li_3PO_4 is only slightly soluble. Furthermore, Li_2HPO_4 does not exist. These facts forced us to use higher pressures of CO_2 (2–5 atm) to effect conversion of Li_3PO_4 to LiH_2PO_4, which we then recycled to Reaction 1. When we used Li-salts, we also found that no double lithium–cerium phosphate forms [6]. Therefore, the products of eqn. 1 when Li replaces Na are $CePO_4$, Li_3PO_4, and O_2.

When potassium salts are used in place of sodium salts, Reaction 1 requires temperatures of over 1100 °C. The addition of 10 mol-% Li_3PO_4 lowers this to about 950 °C. The temperatures required for Reaction 2 remain at 750–900 °C. A possible advantage of using K-salts could be their lower tendency to hydrate; drying them would therefore require less heat than either the Li- and Na-salts. Consequently, their use could make the cycle more practical than it would be with salts of the other alkali metals. Additionally, K_2HPO_4 is soluble in methanol while K_2CO_3, $KHCO_3$, and K_3PO_4 are all insoluble. Therefore, we can use this solvent to separate the K_2HPO_4 from the other K-salts quite easily. Again, because Li_3PO_4 is insoluble, its presence does not greatly complicate the separations used in the cycle.

A suggested flow-scheme for the process is outlined in Fig. 4. Subsequent to our elucidation of the chemistry involved in this cycle, its thermal efficiency could be estimated. This preliminary calculation, which was based upon both experimental and estimated thermodynamic parameters, gave an efficiency of $\leqslant$39% for H_2 production [9]. This value is low compared to those reported for some other thermochemical cycles [10], but other characteristics of the $CeO_2/CePO_4$ cycle could make its overall cost lower: First of all, the required temperatures are well within those achievable by present day solar furnaces and high-temperature gas-cooled reactors. Secondly, none of the chemicals are overly corrosive: We have

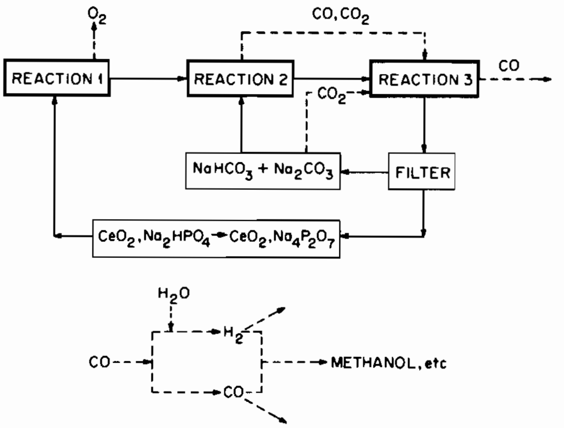

Fig. 4. Proposed scheme for the cycle.

run Reaction 1 in alumina and magnesia containers, and Reaction 2 in copper boats with no observable ill-effects. These should be compared to the expensive materials – tantalum or zirconium metals – which are proposed for use in other cycles [10]. Thirdly, separation of the products of Reaction 3 need not be 100% complete: If either the bicarbonate or the acid phosphate is contaminated by the other, they will simply react to form Na_3PO_4:

$$2Na_2HPO_4 + 2NaHCO_3 \rightarrow 2Na_3PO_4 + 2CO_2 + H_2O$$

Incomplete separation would require that relatively more heat be used, but no loss of reagents would be caused by side-reactions. The fourth advantage is the availability and low cost of the necessary materials. We have successfully run through the cycle using CeO_2 contaminated with 5% by weight of other rare earth oxides. Since such low-grade CeO_2 is much cheaper than pure CeO_2, the cost of the cerium will not make initial capital investments prohibitively high. Additionally, the required use of CO_2 in Reaction 3 also accomplishes the separation of the gases evolved thus avoiding an extra energy-consuming step.

Finally, the unique ability of this cycle to split both CO_2 and H_2O makes it quite versatile. The CO which is formed could be burned or used to make H_2. The CO and H_2 could be reacted together to generate CH_3OH, CH_4, and other organic chemicals.

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