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DISCLOSURE

CARBONATION OF CERIUM OXYCHLORIDE*

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We have shown that both the normal and the basic cerous carbonates, $\text{Ce}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ and CeOHCO_3 respectively, thermally decompose to yield solid ceric oxide and various gaseous products, including hydrogen, carbon monoxide, carbon dioxide and small amounts of methane(1,2). This reactivity can be incorporated into thermochemical cycles for hydrogen production by water splitting if suitable methods of converting ceric oxides back to cerous carbonates can be found. Currently, our approach to this problem is to reduce ceric oxide with hydrochloric acid, hydrolyze the resulting CeCl_3 to CeOCl , and then carbonate the CeOCl . The oxygen evolution reaction in this type of cycle is oxidation of water with chlorine in the reverse Deacon reaction.

Here we report some results on the carbonation of CeOCl and identification of a chlorocarbonate compound, previously unreported in the literature.

EXPERIMENTAL

CeOCl was made by vacuum dehydration and hydrolysis of 100 g of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ in a closed evacuated reactor system which included two condensate traps. Dehydration was done over a period of 3 h with a temperature rise from ambient (ca. 295 K) to 575 K. The hydrolysis was done at 760 K by injecting 30 cm³ H_2O with a peristaltic pump over a period of 3 h. Mol wt of the product was 192.1 by ignition (theo. 191.6). X-ray powder patterns showed only CeOCl lines.

Carbonations of CeOCl were done in glass vials placed in a stainless steel pressure vessel which was designed for magnetic stirring. CO_2 absorption was followed with a pressure gauge, but precise measurement of carbonation by pressure change in solvent reactions was obviated by high CO_2 solubility. Depending upon experimental conditions, the reaction of CeOCl with CO_2 yielded either $\text{CeClCO}_3 \cdot 3\text{H}_2\text{O}$ or $\text{Ce}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$.

Carbonate formation was measured either by thermal decomposition with the CO_2 collected, or by measured pressure changes brought about by perchloric acid decomposition of the solid sample using CaCO_3 (99.9% pure) as a standard.

Cerium was determined by ignition of samples to CeO_2 for 10 h at 1175 K. Soluble samples were first converted to oxalate before ignition.

Standard x-ray and infrared techniques were used to characterize the solid products. Gas compositions were analyzed with a HP5700A gas chromatograph equipped with a 1.8 m Supelco activated carbon column. Water of hydration of the chlorocarbonate was determined by weight differences, or inferred by changes in solution composition.

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Thermal decompositions of $\text{CeClCO}_3 \cdot 3\text{H}_2\text{O}$ were accomplished using a quartz tube pressure reactor connected to a product gas collection vessel. Only the quartz tube and contents were heated. All other pressure connections and the gas collection vessel remained at ambient temperature. The extent of decomposition was followed by pressure changes in the closed system.

RESULTS

Water-Starved Reactions Without Solvent. CeOCl absorbed only small amounts of dry CO_2 at temperatures to 550 K over extended periods of time. At lower temperatures when water was added in limited amounts, both as liquid and gas, then CO_2 uptake was greater and hydrated chlorocarbonate was formed. Reaction times were rather long. Data are listed in Table I. The last entry shows that carbonation was essentially complete at 295 K.

TABLE I
WATER STARVED REACTIONS WITHOUT SOLVENT; NO STIRRING
0.01 mol CeOCl ; 10 atm CO_2 AT START

Reaction time-h	Liquid H_2O per CeOCl^a (direct contact at start)	Temp-K	Product		
			mol wt	$\text{CO}_3^{2-}/\text{Ce}$	$\text{H}_2\text{O}/\text{CO}_3^{2-}$
232	2.00	385	--	0.87	3.19
45 ^b	4.00	355	--	0.88	--
64	0	295	283	0.89	3.19
30 ^c	4.00	295	288	0.93	3.30
15+15 ^d	4.00+4.00	295	289	0.98	3.12

a. Separate supply of H_2O provided for vapor or steam.

b. CeOCl mixed with Al_2O_3 granules.

c. CeOCl in layers ~ 0.5 mm thick.

d. Recarbonated after grinding in mortar.

Reactions in Aqueous CeCl_3 at Ambient Temperature. The disproportionation reaction:

proceeded to give stoichiometric yields when the final concentration of CeCl_3 was low (Table II). Chlorocarbonate was obtained with high starting CeCl_3 concentrations and with saturated CeCl_3 . Intermediate starting concentrations of CeCl_3 gave mixed carbonate products. This behavior indicates that the products in reaction (1) above were in equilibrium with $\text{CeClCO}_3 \cdot 3\text{H}_2\text{O}$. Two modes of chlorocarbonate formation are indicated. With saturated CeCl_3 , the aqueous phase was dehydrated, and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ was precipitated. When the

TABLE II
STIRRED AQUEOUS REACTIONS AT AMBIENT TEMPERATURE

CeCl_3 -mol/l		Elapsed Time for 95% CO_2 Absorption-h	Products	
			Soluble Ce^{3+} mol	$\text{CO}_3^{2-}/\text{Ce}$
Start	Final			
0	0.19	0.60	0.00335	1.50
0	0.50	-	0.00334	1.50
1.296	1.432	1.5	0.00198	1.24
2.564	2.666 ^a	4.3	0	1.00
3.35	3.35 ^b	14.7	0	1.00

^aThe change in Ce^{3+} concentration corresponded to removal of 0.0303 mol of H_2O to form $\text{CeClCO}_3 \cdot 3\text{H}_2\text{O}$.

^bSaturation concentration. Chlorocarbonate was identified by x-ray of air-dried product without washing.

solubility limit of CeCl_3 was not exceeded, then the solute was simply dehydrated by the 3-hydrate requirement of $\text{CeClCO}_3 \cdot 3\text{H}_2\text{O}$. $\text{Ce}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ was formed preferentially when the concentration of soluble CeCl_3 was sufficiently low.

Reactions with Acetone Solvent. Acetone- H_2O as a reaction medium was shown to be very practical for carbonation of CeOCl , since the chlorocarbonate product was easily separated by decantation. Evaporation of the solvent phase indicated only trace amounts of soluble CeCl_3 . The results in Table III show rapid carbonation with a low H_2O requirement for high yields.

It was also of interest to test reactivity of cerous carbonates with respect to chlorocarbonate formation. A stirred suspension of $\text{Ce}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (equimolar) in acetone gave a quantitative yield of $\text{CeClCO}_3 \cdot 3\text{H}_2\text{O}$ in 3 h. $\text{Ce}(\text{OH})\text{CO}_3$ was converted also by reaction with CO_2 , $2\text{H}_2\text{O}$ and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ in acetone at ambient temperature. In 3 h a product with mol wt of 284 and 2.79 $\text{H}_2\text{O}/\text{Ce}$ was obtained. With longer times, carbonation was more complete.

Thermal Decomposition Studies. Figure 1 shows two thermal decompositions which were done in the previously described closed system with the product gases allowed to accumulate and water allowed to condense in the unheated region. The magnitude of decarbonation vs. temperature is plotted. The final solid product of these decompositions was CeOCl . The upper plot obviously does not show equilibrium behavior because of the rapid heating rate, but the pressure of CO_2 at 590 K as shown in the lower plot may have been within an order of magnitude of the equilibrium pressure. It appears that extensive experimentation would be required to demonstrate and measure equilibrium behavior.

TABLE III
STIRRED REACTIONS WITH ACETONE SOLVENT AT AMBIENT TEMPERATURE
0.01 mol CeOCl₃; 15 atm. CO₂ AT START

<u>H₂O/Ce</u>	<u>Start</u>		<u>Reaction time</u> h	<u>Product</u>	
	<u>H₂O mol/l</u>			<u>mol. wt.</u>	<u>CO₃²⁻/Ce</u> <u>H₂O/CO₃²⁻</u>
2.00	1		17.0	265.6	0.66 2.73
4.00	2		17.0	277.1	0.79 2.67
8.00	4		17.0	290.9	0.95 2.68
2.00	1		4.0	270.2	0.74 2.78
4.00	2		4.0	261.6	0.68 2.45
8.00	4		4.0	290.1	0.94 3.03
4.00	2		3.0*	261.0	0.71 3.04
8.00	4		3.0*	284.0	0.91 3.29

* 10 atm CO₂ at start.

Figure 1. Decomposition of CeClCO₃·3H₂O.

Characterization of $\text{CeClCO}_3 \cdot 3\text{H}_2\text{O}$. Infrared spectra and x-ray powder diffraction data were used to characterize the solid products. Infrared spectra are shown in Fig. 2 and x-ray powder diffraction data are represented in Fig. 3 for $\text{CeClCO}_3 \cdot 3\text{H}_2\text{O}$. These are compared to other cerous carbonate compounds which are of interest. All of the preparative routes to $\text{CeClCO}_3 \cdot 3\text{H}_2\text{O}$ yield solid products whose infrared spectrum of $\text{CeClCO}_3 \cdot 3\text{H}_2\text{O}$ is quite similar to the spectrum of B-form CeOHCO_3 (3), and thus would indicate a similar environment for the carbonate group in the solid state structure of both compounds. The x-ray powder pattern of $\text{CeClCO}_3 \cdot 3\text{H}_2\text{O}$ does not resemble the patterns of any of the other carbonate phases which were considered. In order to elucidate the structure of this compound, preparations for a single-crystal x-ray structure determination have been undertaken.

Figure 2. Infrared spectra.

X-RAY HISTOGRAMS OF VARIOUS CERIOUS CARBONATE COMPOUNDS

Figure 3.

Synthesis of $\text{Ce}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ and $\text{Ce}(\text{OH})\text{CO}_3$ from CeO_2 , CO_2 and H_2O with Recycle of Reagents. The following sequence of reactions can be utilized in heat cycles:

This procedure has the advantage of no side products, but three mol of CeCl_3 must be hydrolyzed for each two mol of feed CeO_2 . In addition one mol of CeCl_3 must be dehydrated.

Further investigation of the preparation and reactivity of these various cerous carbonate phases is under way in order to find more efficient pathways for closed thermochemical cycles for water splitting.

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REFERENCES

1. E. I. Onstott, W. G. Witteman, and M. G. Bowman, Proceedings of the Twelfth Rare Earth Conference, Vail, Colorado, 1 (1976).
2. E. J. Peterson, E. I. Onstott and M. G. Bowman, Presentation at the 174th Meeting of ACS, Chicago, IL, Aug. 29-Sept. 2, 1977.
3. R. Aumont, F. Genet, M. Passaret, and Y. Thudie, C. R. Acad. Sci., Ser. C, 272(3), 314 (1971).