

Reports

Thermochemical Decomposition of Water Based on Reactions of Chromium and Barium Compounds

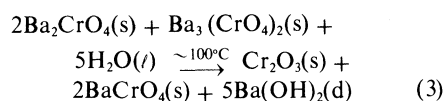
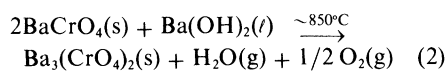
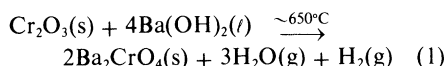
Abstract. *A potentially useful thermochemical cycle developed for the production of hydrogen and oxygen from water consists of three chemical reactions that take place in the temperature range from 400° to 1200°K. The oxidation and reduction of chromium compounds by barium hydroxide and the hydrolytic disproportionation of barium chromate(IV) and barium chromate(V), the reactions which constitute the proposed cycle, have been demonstrated.*

The production of hydrogen from water by thermochemical processes is potentially more efficient than the generation of electrical power and decomposition of water by electrolysis (1). The use of steam-hydrocarbon processes to produce hydrogen is wasteful of a valuable natural resource. Increasingly, research is being directed toward identifying and evaluating closed thermochemical cycles (2) that consume only water, thermal energy, and minimal work to provide hydrogen (and oxygen) for the future, nonpolluting "hydrogen economy" (3).

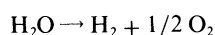
Practical considerations dictate that relatively abundant elements be utilized in these reactions and that the temperatures required not exceed 1000°C [attainable with high-temperature, gas-cooled reactors (4)]. Owing to the lack of firm thermodynamic and kinetic information and the possibility of side reactions, experimental proof that the proposed processes do occur is important.

We present here the basic chemical aspects of a newly developed three-step thermochemical cycle. It is based on the

oxidation of Cr(III) to Cr(IV) and the reduction of Cr(VI) to Cr(V), by means of Ba(OH)₂ at high temperatures, and the hydrolytic disproportionation of Ba₂CrO₄ and Ba₃(CrO₄)₂ at low temperature. The reactions are:



to give a net reaction

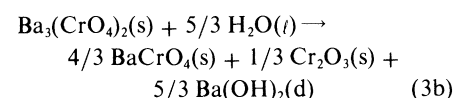
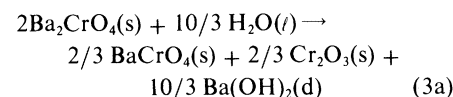


where (s), (l), (g), and (d) refer, respectively, to the states solid, liquid, gaseous, and dissolved.

The high-temperature reactions of the ground solids [with Ba(OH)₂ in excess] were conducted in a platinum crucible located in a fused quartz tube. Hydrogen or oxygen evolution was continuously monitored in an argon stream used as carrier gas. This should not be implied as an in-

dication of low evolution pressures; the presence of argon had a twofold purpose: to act as an analytical aid and to keep the partial pressure of hydrogen at a safe (flammability) level. Typical measured values were as follows: oxygen, 13 to 21 percent with an argon flow rate of 125 cm³/min; hydrogen, ~4 percent at 300 cm³/min. No attempt was made at the time these measurements were made to determine the effect of flow rate on the concentration of hydrogen or oxygen; however, we envisioned that this would be investigated at a later date. Upon virtual completion of the reactions, as indicated by the total gas evolved and the initial amounts of Cr₂O₃ or BaCrO₄, the solids were cooled under argon and then ground. Portions of the solids were leached with methanol under argon to remove unreacted Ba(OH)₂ (5). The solids were identified before and after the methanol extraction by x-ray diffraction and chemical analysis.

The hydrolysis reaction was initially studied as two separate steps:



We confirmed reaction 3 by hydrolyzing a 2 : 1 mixture of Ba₂CrO₄ and Ba₃(CrO₄)₂. The hydrolyses were conducted in a Soxhlet extractor under argon until no more Ba(OH)₂ was extracted. The remaining solids were identified by x-ray diffraction and chemical analysis. Since the Cr₂O₃ was amorphous, the presence of Cr(III) was further confirmed by electron paramagnetic resonance (6).

The chemical analyses consisted of determining the ratio of barium to chromium and the average valence of the chromium present (6). The average results from various preparations are shown compared with expected values in Table 1. The solid products resulting from the hydrolysis reactions (reaction 3) were in an intimately mixed state and could not be easily separated. However, partial separations were ob-

Table 1. Chemical analyses of reaction products.

Reaction	Compound	Barium/chromium ratio		Average chromium valence	
		Observed	Expected	Observed	Expected
1	Ba ₂ CrO ₄ *	2.08	2	3.90	4
2	Ba ₃ (CrO ₄) ₂ *	1.62	1.5	5.11	5
3a	BaCrO ₄ + Cr ₂ O ₃ †	0.36	0.33	3.94	4
3b	4BaCrO ₄ + Cr ₂ O ₃ †	0.75	0.67	5.10	5
3	2BaCrO ₄ + Cr ₂ O ₃ †	0.61	0.50	4.55	4.5
5	Ba ₃ (CrO ₄) ₃ OH		1.67	5.08	5

*Solids remaining after extraction with methanol.

†Solids remaining after extraction with water.

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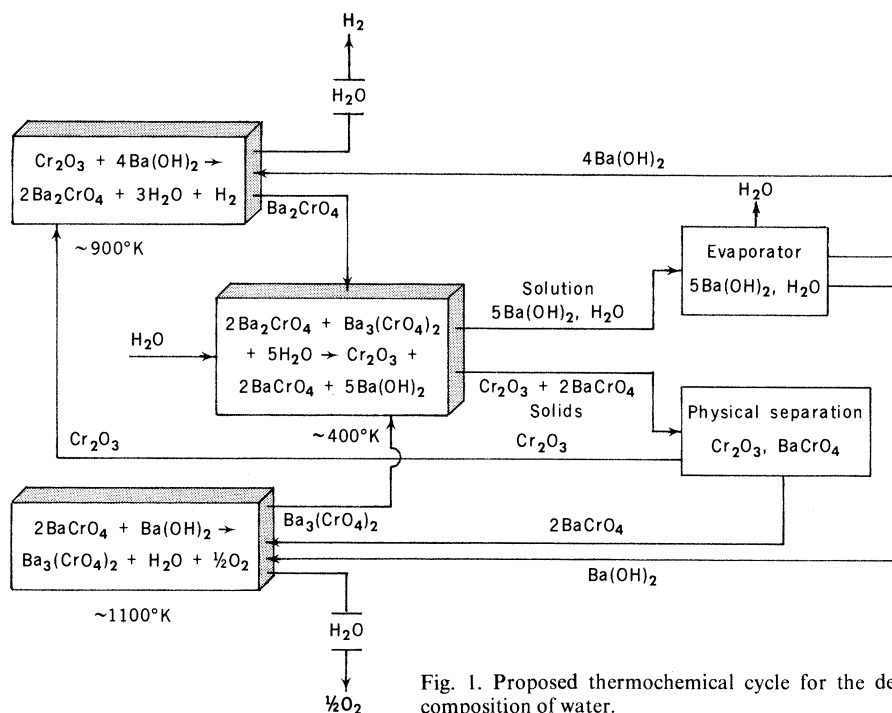
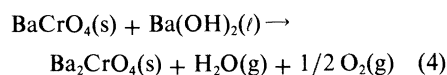


Fig. 1. Proposed thermochemical cycle for the decomposition of water.

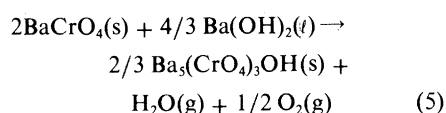
tained by zonal gradient centrifugation (6) and by density difference in high-density liquid; hence the problem does not appear to be intractable. A diagram of the proposed cycle is presented in Fig. 1.

The high-temperature reaction (reaction 1), although known to occur at 1000°C (5), was found to proceed at significantly lower temperatures, in the range 500° to 700°C. Reaction 2, first studied by Scholder and Suchy (7), was confirmed to proceed between 600° and 950°C. The work reported here has demonstrated also that the hydrolysis products of Ba_2CrO_4 are Cr_2O_3 and BaCrO_4 in a 1:1 ratio (reaction 3a), rather than BaCrO_3 as reported elsewhere (5). It was likewise demonstrated, for the first time, that the hydrolysis products of $\text{Ba}_3(\text{CrO}_4)_2$ are also Cr_2O_3 and BaCrO_4 , although in a 1:4 ratio (reaction 3b).

The recent publication (8) of the reaction



led us to consider it as a possible substitute for the oxygen evolution reaction (reaction 2). Our attempts to duplicate reaction 4, using the same experimental procedure as for reaction 2, failed to synthesize Ba_2CrO_4 . This was probably due to slow kinetics. However, during the experiment oxygen was evolved and a stable intermediate was formed, according to:



Furthermore, the apatite-like compound $\text{Ba}_5(\text{CrO}_4)_3\text{OH}$ reacts with water, disproportionating into Cr_2O_3 and BaCrO_4 in a manner similar to reaction 3b. Thus, although not shown in Fig. 1, reaction 5 may be used as a substitute for reaction 2.

The x-ray diffraction powder pattern of the solid obtained in reaction 1 was attributed to Ba_2CrO_4 by analogy to patterns of compounds of the type A_2BO_4 (prototype $\beta\text{-K}_2\text{SO}_4$) expected to be structurally similar. Thus, indexing of the unknown pattern by analogy to that of Rb_2CrO_4 (9) yielded the lattice constants of an orthorhombic unit cell containing four molecules of Ba_2CrO_4 : $a = 7.58 \pm 0.03 \text{ \AA}$, $b = 10.35 \pm 0.05 \text{ \AA}$, $c = 5.86 \pm 0.03 \text{ \AA}$, and a calculated density of $5.65 \pm 0.10 \text{ g/cm}^3$ (measured density, $5.74 \pm 0.20 \text{ g/cm}^3$) (10). The lattice constants are in very good agreement with those recently reported (8) from single crystal diffraction work.

The proposed cycle has been experimentally demonstrated and presents several attractive features, namely: (i) it consists of only three chemical reactions; (ii) the upper limit of temperature, $\sim 850^\circ\text{C}$, should be attainable without difficulty; (iii) it uses elements that are not in short supply; (iv) it does not involve the separation of multi-component gas mixtures; and (v) it appears to have suitable kinetics. Since experiments were carried out with the reagents in a stationary state (we relied on diffusion processes), it may be speculated that on a large scale where mechanical agitation would be used the kinetics of the reactions may be even more favorable and the required temperatures lower. However, sev-

eral aspects require further investigation, for example, the determination of thermochemical functions of some of the compounds, materials compatibility, and the physical separation of solids. Thus, at this preliminary stage of development of the proposed cycle we are not yet able to estimate a figure of merit for its thermal efficiency by means, for example, of the entropy-temperature diagrams developed by Abraham and Schreiner (11). If a simple process for the separation of solids can be developed that requires a modest expenditure of energy, we would expect that the present cycle (of essentially three chemical reactions) would exhibit a figure of merit which will compare favorably with those estimated for other cycles (11). It can be estimated from the three equations that about 3000 units of mass have to be manipulated in order to obtain 2 units of mass of hydrogen. Although the mass of reagents used is larger than in other published cycles (12), there are other considerations that may be compensating; for example, the number of atoms involved is comparable to those in other cycles, and thus the thermal capacity of this system would be equivalent.

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6. We thank W. R. Laing and his associates and H. W. Dunn of the Analytical Chemistry Division, M. M. Abraham of the Solid State Division, and T. Tamura of the Environmental Sciences Division, all of Oak Ridge National Laboratory, for their help with the chemical analyses, x-ray diffraction, electron paramagnetic resonance measurements, and zonal gradient centrifugation, respectively.
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13. Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation.

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