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SILICON HALIDE-ALKALI METAL FLAMES AS A SOURCE
OF SOLAR GRADE SILICON

Second Quarterly Report, September 1—November 30, 1977

By
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MASTER

December 1977

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AeroChem Research Laboratories, Incorporated
Princeton, New Jersey

U.S. Department of Energy

Solar Energy

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SECOND QUARTERLY REPORT

W. J. MILLER

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Approved by

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Princeton, New Jersey

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FOREWORD AND ACKNOWLEDGMENTS

This is the second quarterly progress report on a program which began 17 May 1977; it covers the period 1 September through 30 November 1977.

Major contributions to the experimental effort on the program during this report period were made by G. Roland and L. Koenig.

ABSTRACT

The experimental effort on this program has concentrated thus far on Na/SiCl₄ and K/SiCl₄ opposed jet diffusion flames in an evacuated reaction vessel; both reactants are supplied as vapors. The flames are self-igniting, fast burning and intensely chemiluminescent. Solid reaction products have been collected, separated by simple washing, and some preliminary analyses performed which indicate that the concentrations of most impurities in the reagents are reduced during the course of the Si formation process. The chemiluminescence is being characterized spectroscopically.

The products of reaction are all solids and appear as a mixture of brown (amorphous Si) and white (KCl) powders. Microscopic examination of the unwashed products reveals what seem to be agglomerates of Si particles with $< 1 \mu\text{m}$ diam. Washing with slightly acidic water easily removes the KCl.

A tubular reactor for the preparation of larger quantities of products and possibly their separation via differential deposition is now being built. Provision is also being made for the addition of hot H₂/Ar diluents and variable flow rates and pressures in this reactor.

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SUMMARY

This program is designed to test the feasibility of utilizing continuous high temperature diffusion flames of alkali metals and silicon halides as an economical source of solar grade silicon. Thermochemical calculations indicate that reactions between either sodium or potassium and any of the silicon halides are strongly exoergic and that liquid or solid silicon is the only condensed phase in any of the equilibrium product distributions.

The experimental effort on this program has concentrated thus far on Na/SiCl₄ and K/SiCl₄ flames in an evacuated reaction vessel. These flames are self-igniting, fast burning and intensely chemiluminescent. Solid reaction products have been collected, separated by simple washing, and some preliminary analyses performed. Spectroscopic characterization of the chemiluminescence has been initiated.

Vaporized reactants for the Na or K/SiCl₄ flames are obtained from two reflux columns (heat pipes) equipped with vapor outlets below the steady-state condensation points in the columns. Flows of 0.1 to 1.5 g min⁻¹ K vapor are sustained by varying the reflux column pressure between 0.1 and 1.0 atm; the halide flow is controlled independently and made to match or slightly exceed the K vapor input rate. When the halide is provided in slight excess, reaction takes place about the boundaries of the K vapor stream; the flame exhibits banded blue and green emissions (as yet unidentified) at its outside edges; K and Na atomic emission occur throughout the entire visible portion.

The products of reaction are all solids and appear as a mixture of brown and white powders. Microscopic examination of the unwashed products reveals what seem to be agglomerates of particles with < 1 μm diam. Washing with slightly acidic water removes the white powder (presumably KCl) and leaves a fine light brown powder. To date, the product has been retrieved simply from deposits on the cool reactor walls; no attempt has yet been made to collect the materials at high temperatures.

A tubular reactor for the preparation of larger quantities of products and possibly their separation via differential deposition is now being built. Provision is also being made for the addition of hot H₂/Ar diluents and variable flow rates and pressures in this reactor.

I. INTRODUCTION

This program is designed to test the feasibility of utilizing continuous high temperature diffusion flames of gaseous alkali metals and silicon halides as an economical source of high purity silicon. Thermochemical calculations¹ indicate that high flame temperatures are attained in these systems and that, for most reaction conditions and stoichiometries, silicon is the only condensed phase material in the equilibrium product distribution. The reactions have proven, as expected on the basis of prior studies,²⁻⁸ to be self-initiating, highly exothermic and fast. They thus offer considerable potential for high throughput and energetic self sufficiency.

During this quarter we have continued to pursue the examination of K/SiCl₄ flames begun during the last report period¹ and have extended the work to include experiments on the Na/SiCl₄ system. Several modifications in the apparatus have been made, the flames have been examined spectroscopically, and product characterization and separation efforts have been initiated. Also during this report period a contract modification was implemented under which the program will be expanded to include work on a laboratory analog of the Westinghouse arc-jet process⁹ in which total enthalpies comparable to those of the Westinghouse system will be obtained by preheating a stream of H₂/Ar and pre-vaporizing the sodium. The apparatus required for the latter work has been designed and is currently under construction.

II. TECHNICAL DISCUSSION

A. APPARATUS MODIFICATIONS

The overall configuration of the reactor in which the flames are sustained has remained as described in our first quarterly report¹ and shown in Fig. 1. The alkali metal vaporizer, however, has undergone several changes during this report period as the result of materials problems and undesirable performance characteristics encountered in the course of the work. The current version of the vaporizer is shown in Fig. 2. It differs from the original in that (1) a ballast chamber has been added to the upper cool portion of the tube

to absorb pressure pulses associated with "bumping" as the metal boils and (ii) the flow constricting orifice for the metal vapor has been moved to a position close to the hot tube wall. This obviates heating problems in the delivery tube and provides a flow of vapor free of condensed liquid metal droplets.

An acceptable material from which to fabricate the orifice has not yet been found. The sapphire used in our first model was found to crack and erode after three to four hours of operation; it was replaced with 304 stainless steel. The steel also erodes too rapidly. A 0.33 mm diam orifice opened to about 1 mm diam in the course of three runs of less than one hour duration each. The flow control aspect of the problem can be solved by replacing the fixed size orifice with a valve that can be adjusted to compensate for the increasing aperture size as the orifice erodes; however, the contamination introduced by erosion still predicates the use of an alternative material. These materials requirements will be a topic of prime concern in discussions to be held with Westinghouse personnel in the near future.

B. OBSERVATIONS

Reduction of SiCl_4 has now been accomplished with both K and Na. The flames in both cases are similar. To initiate the reaction, the pressure in the reactor is reduced as rapidly as possible, inducing a flow of alkali metal vapor from the generator where the pressure is maintained at 200 to 700 Torr. When it can be seen that flow of alkali metal has started, the valve on the SiCl_4 vaporizer outlet is opened and a flame is established immediately. The flow of each reactant can be varied over the range of about 0.1 to 1.5 g min^{-1} by manipulating the appropriate vaporizer pressure (these flow rates are approximations of the initial flux based on critical flow through an orifice of known diameter). When the flows are close to the stoichiometric ratio,* the flame positions itself nearly midway between the two opposed reagent

* At stoichiometry, the mass flow ratio of Na to SiCl_4 is $4(23)/170 = 0.54$ and of K to SiCl_4 , $4(39)/170 = 0.92$, in accord with the overall reactions $4 (\text{K or Na}) + \text{SiCl}_4 \rightarrow \text{Si} + 4(\text{KCl or NaCl})$.

inlets; if the flow of one reagent is reduced, the flame moves toward its inlet and, in the extreme, into the mouth of the delivery tube.

Since all of the products of these reactions are condensed phases at the cool walls of the reactor, the pressure within the chamber remains at the original pump-limited pressure throughout the run whether or not the pump is engaged. The only exception to this is the situation that obtains when the SiCl_4 is in excess; the reactor pressure then reflects the partial pressure of unreacted SiCl_4 .

The low pressure diffusion flames of both K and Na with SiCl_4 vapors exhibit chemiluminescence of several different colors; in addition to a continuum which is often but not always present, there are blue and green zones to the flame which are apparent to the naked eye. Our initial instrumental examination of this flame has been made using an f/4 Spex "Mini-mate" 0.25 m monochromator with a 1P28 photomultiplier detector. The monochromator is oriented at a right angle to the axes of the opposed reagent inlet tubes; light from the flame between the inlets is focused on the entrance slit with a 6.5 cm diam lens. Although this instrument has low resolving power, its large aperture makes it appropriate for the rapid survey work desired in preliminary experiments. The spectra of the K/ SiCl_4 flame contain strong emissions from both K, at 405 nm, and Na at 589 nm. A continuum underlies the visible portion of the spectrum with an intensity maximum near 450 nm.

A typical spectrum from a Na/ SiCl_4 flame which exhibits identical features to those from K flames with the exception of the K atom lines, is given in Fig. 3. The intensities are not corrected for the wavelength response of the grating or the detector. The strong lines at 569, 498, 467, and 450 nm (in addition to the resonance doublet at 589), are attributable to Na emission from exceptionally high energy levels. The 569 nm line, for example, arises from the 4D level of Na, nearly 100 kcal above the ground state. Excitation of this magnitude is usually the result of energy transfer processes. In the Na/ Cl_2 system the production of excited Na has been attributed² to the reactions

and

i.e., transfer of vibrational energy deposited in the diatomic product of a

highly exothermic reaction to the free atom. In the Na/SiCl₄ reaction it is difficult to account for the observed excitation levels even assuming such energy transfer processes to be fast. Future experiments will include spectroscopic observations in the near ultraviolet in search of the energetic entities responsible.

The only other identifiable features of the spectra obtained to date are lines which appear to be due to excited Si atoms. These emissions are detectable only from the brightest regions of the flames and are quite weak. This is due to the fact that the Si lines in the visible portion of the spectrum originate from very high energy levels; again, a search into the ultraviolet is indicated.

The bands in the 400-500 nm region (see Fig. 3) have not yet been identified. It is worth noting, however, that bands of a very similar nature were observed in the reaction zones of the SiCl₄/H non-equilibrium plasma jet.¹⁰ The most likely candidate emitters, then, would appear to be Si₂, SiCl or SiCl₂, although if either of the former two are responsible, they must be in extremely high energy states, as well.

C. PRODUCT CHARACTERIZATION

As noted in our last quarterly report,¹ the condensed products of reaction appear to be a mixture of brown and white powders. The configuration of the present reactor precludes determination of the time required for particle formation since there is no bulk gas flow. The deposits accumulate on all the walls of the apparatus; they adhere very loosely to the walls and do not form dense agglomerates. At some positions in the reactor the powder is nearly all white, at others, a dark brown.

A number of samples have been taken off the walls after runs with both K and Na. There are no apparent visual differences in the products of the two alkali metals. After the powders were collected, they were placed in a filter funnel and washed with distilled water and dilute HCl. After drying, the product was in the form of a dark brown cake which crumbled readily into a freely flowing powder. Examination under a metallurgical microscope revealed agglomerates of irregular shapes and sizes that appear to be composed of sub-micron roughly spherical particles.

In order to determine whether impurities in the reagents become more or less concentrated as they are converted to product, we have begun a series of analyses for heavy elements using X-ray fluorescence. Samples of the technical grade SiCl_4 reagent were hydrolyzed in distilled H_2O and the resultant SiO_2 used as the basis of comparison for product purity. No calibration standards have yet been prepared so the results to date are only qualitative. The reagent exhibits fluorescence from the contaminants Fe, Hg, Cu, Ni, Zn, and Br. The washed, brown amorphous silicon product contains no detectable Hg or Br and reduced quantities (< 10 ppm) of Cu, Ni and Zn. The Fe content of both reagents and products is highly variable; rust from the inside of the reactor and contamination by stainless steel laboratory utensils used in the washing processes are probably responsible. The experiments will be more easily controlled when product can be obtained from the flow reactor now under construction.

D. FLOW REACTOR DESIGN

The configuration of the current reactor precludes any inference as to the rates of condensation or product deposition subsequent to gas phase reaction. To achieve spatial separation related to reaction time, it will be necessary to superimpose a bulk gas flow on the system by adding an inert gas or a gas which at least does not become completely combined in the condensed phase products. The H_2 and Ar present in the reaction mixture proposed by Westinghouse fulfills these requirements in that equilibrium calculations indicate that a negligible fraction of the H_2 (and none of the Ar) undergoes reaction. An apparatus to implement the addition of these gases to our reactor has been designed and is under construction.

In essence, the new apparatus consists of a 2 m long x 15 cm diam pipe provided with concentric reagent inlets at one end, as indicated in Fig. 4, and a vacuum outlet at the other end. The reagent inlets include a central delivery tube for K vapor, an annulus immediately surrounding it for the introduction of H_2 and/or Ar and an outside annulus for halide delivery. The apparatus will have the capability of running at pressures from 1 atm down to a few Torr and the tube will be segmented to provide access for product removal. Provision has also been made for inserting a smaller diameter,

heated tube along the axis of the pipe to achieve higher linear flow rates and/or controlled temperatures in the product condensation zone.

Most of the parts and materials for this reactor have been received and its construction is proceeding. The first experiments in the new reactor should be performed in the beginning of January.

Thermodynamic calculations to determine how hot the carrier gases must be to obtain total enthalpies near or equivalent to those of the arc-jet process are currently being made. It will be impossible to heat the H_2/Ar stream to the 3500 K or so to be achieved by Westinghouse, prior to Na injection; however, it should be feasible to obtain the same total enthalpy by prevaporizing and heating the Na as well as the H_2/Ar mixture.

III. CONCLUSIONS

The most significant and obvious conclusion to be reached from the experiments to date is that the reactions between Na or K and $SiCl_4$ are rapid and self initiating. The flames are luminous and intense even at the low pressures so far employed and it appears that mixing or mass transport phenomena rather than chemical reaction kinetics will be rate limiting as the pressure is scaled up and inert gases introduced. No significant differences appear to exist between the flames of Na and K.

The reaction products, when allowed to cool via radiation or convection to the cool reactor walls, seem to be a mixture of the alkali metal salt and loosely agglomerated amorphous silicon powder. The condensation processes for these two principal products thus apparently occur separately and therefore possibly at different rates.

Heavy metal impurities in the input $SiCl_4$ are absent or lower in the silicon product and the amorphous Si is readily separated from accompanying salts by simple washing with acidified water. The extent to which impurities can be reduced via flame preparation has, however, not yet been quantitatively determined.

IV. PLANS

The construction of the new flow reactor will be the task of highest priority in the immediate future. Its completion will enable us to obtain product under better defined reaction and condensation conditions, including simulations of those which will prevail in the proposed Westinghouse apparatus. The first experiments to be performed with the new apparatus, however, will employ K/SiCl₄ flames with only H₂ added as a carrier gas. Initially, the temperature of the reactor walls downstream of the flame zone will be unregulated in order to determine whether or not a product with acceptable particulate properties can be obtained directly by simple separate condensation of salt and Si. Experiments with preheated H₂/Ar carrier gases will follow. Thermodynamic calculations are currently being conducted to determine to what temperature the carrier gases need to be heated to obtain a total enthalpy equivalent to that of the streams to be employed by Westinghouse in their arc-jet apparatus.

The existing low pressure burner apparatus will continue to be used in experiments designed to better characterize the gas phase flame chemistry. Spectroscopic examination of the flames will be extended into the near ultraviolet in an attempt to detect Si atomic emission, identify the diatomic or polyatomic emission sources and, if possible, determine local temperatures by two color pyrometry. More quantitative definition of product impurity levels and particle characteristics will also be pursued.

V. NEW TECHNOLOGY

No reportable items of new technology have been identified.

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FIG. 1 LOW PRESSURE REACTOR

FIG. 2 ALKALI METAL VAPORIZER

FIG. 3 SPECTRUM FROM LOW PRESSURE Na/SiCl₄ FLAME

FIG. 4 FLOW REACTOR INLET SECTION