DIRECT SYNTHESIS OF LIQUID-PHASE DIOXYGEN DIFLUORIDE

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SUMMARY

Dioxygen difluoride (O_2F_2) was produced directly in the liquid phase at temperatures above −154°C. An O_2/F_2 gas mixture was heated to 700°C and was then rapidly cooled on the outer surface of stainless steel tubes. The tubes were refrigerated by a liquid oxygen bath pressurized to >7600 torr with helium. Six grams of O_2F_2 were produced in less than an hour. Color of the viscous liquid in the O_2F_2 generator ranged from copper red to straw yellow. Different O_xF_y compounds existed simultaneously on the tubes; explanations for this phenomenon are suggested. Audible "pings" and pressure excursions occurred when liquid O_2F_2 dripped onto uncooled portions of the apparatus. An orifice at the hot/cold interface was important in obtaining significant reaction rates.
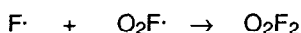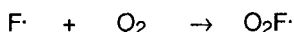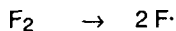
INTRODUCTION

Dioxygen difluoride was first produced from the elements in 1933 by high voltage gas discharge [1]. Production of O_2F_2 by UV photolysis [2,3], radiolysis [4], and laser photolysis [5] have been reported, and microwave [6] and thermal techniques [7] have also been successful. Each method relies on the initial dissociation of F_2 to atomic fluorine by the energy source. Dioxygen difluoride is a stronger oxidizer than elemental fluorine and has an enthalpy of formation of +4.58±0.20 kcal/mol [8]. The reported melting point of O_2F_2 is −163.5 to −154°C [1,4], with the higher temperature being accepted as more accurate [9]. The normal boiling point is −57°C [10].

Thermal generation of O_2F_2 has produced tens of grams of O_2F_2 in several hours [7]. In this method, an O_2/F_2 gas mixture is heated to 600-800°C in a nickel

tube to obtain partial dissociation of F_2. The gas is then rapidly cooled to cryogenic temperatures, and O_2F_2 collects on a cold metal wall. Liquid nitrogen (LN_2) is the usual coolant bath for this wall. The cold wall temperature remains near $-195°C$, and O_2F_2 is collected as a solid.

Some O_2F_2 is calculated to form directly in the gas phase [5], but this amount is insufficient to account for the rates observed. The mechanism by which O_2F_2 forms in the condensed state is not definitively known. It is assumed that the metastable free radical O_2F is formed as an initial product, and reaction with a subsequent F atom yields O_2F_2 [11].

$$F_2 \quad \rightarrow \quad 2\,F\cdot$$

$$F\cdot \quad + \quad O_2 \quad \rightarrow \quad O_2F\cdot$$

$$F\cdot \quad + \quad O_2F\cdot \quad \rightarrow \quad O_2F_2$$

Additional support for the O_2F intermediate is shown by low synthesis rates for KrF_2 (relative to those for O_2F_2) [12], [13]. This occurs because KrF is notably less stable than O_2F, even at 77 K, and negligible KrF_2 is produced in the gas phase [14].

As O_2F_2 collects in a thermal generator, the solid deposit retards heat flow to the cold metal wall. A temperature gradient is established in the solid, and the temperature of the free surface of O_2F_2 rises. It is unknown if O_2F_2 continues to form as a liquid above the melting point or whether O_2F_2 forms only at colder wall locations. If O_2F_2 can be produced directly in the liquid phase, it may be possible to make a generator with a steady exit stream of liquid or gaseous O_2F_2. Because no previous technique has used refrigerant temperatures above the O_2F_2 melting point, it has been unproven if O_2F_2 can be produced directly as a liquid.

The melting point of O_2F_2 is close to that of nitric oxide ($-163.6°C$). In nitric oxide (NO) distillation columns for isotope separation, the condenser temperature is maintained above the NO melting point by a pressurized liquid oxygen bath [15]. Liquid oxygen (LOX) is condensed into a closed container by a primary refrigerant bath of LN_2 at atmospheric pressure. The LOX secondary refrigerant bath is then pressurized with helium until the total pressure equals the O_2 vapor pressure at the desired condenser temperature. When heat is transferred to the LOX, O_2 boils at the elevated temperature and diffuses through the predominantly helium atmosphere to the LN_2 condenser, where LOX condenses at $-195°C$. Even higher temperatures are possible using this concept with secondary refrigerants other than oxygen [16]. The reactor for producing O_2F_2 above the melting point is based upon this concept.

APPARATUS

The heater for dissociating F_2 (Fig. 1) consisted of two 10-cm by 15-cm by 12.7-mm nickel blocks milled with a serpentine gas path (6 mm wide by 3 mm deep) and welded together. Six cartridge heaters (6 mm diameter by 10 cm long) provided up to 1 kW of power to the heater, and gas exit temperature was monitored by a chromel-alumel thermocouple in a well. The heater was insulated with 12.7-mm ceramic insulation board on all sides. Power to the heater was regulated using an autotransformer. The hot gas tube exiting the heater was fitted with a replaceable 2.3-mm orifice.

The O_2F_2 reactor (Fig. 1) was made entirely of stainless steel and was enclosed in a stainless steel vacuum jacket for thermal insulation. The hot gas flowed across a bank of 15 tubes inside a 7.5-cm diameter chamber. The distance from the orifice to the tube bank was 6 mm. The tubes were 12.7 mm o.d. by 0.9
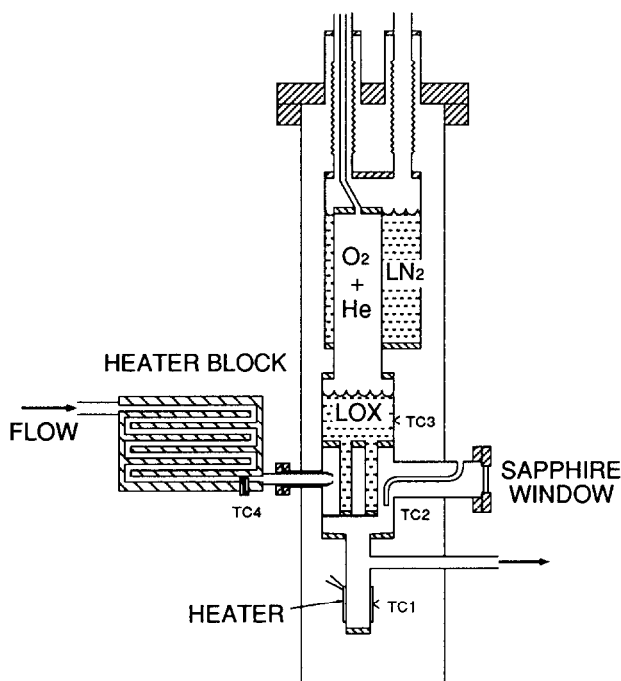

Fig. 1. Gas Heater and O_2F_2 reactor.

mm thick by 7.5 cm long, and they were in a hexagonal array on 14-mm centers. A metal plate at the bottom of the tubes forced the gas to flow across the tube bank. A sapphire window on the downstream side of the tubes allowed visual observation of portions of six of the tubes. Gas exited the reactor after flowing downwards towards a sump designed to collect liquid O_2F_2. A heater and a copper-constantan thermocouple were placed on the sump to control temperature and vapor pressure of any liquid O_2F_2 collected. Another copper-constantan thermocouple for measuring gas temperature was located in a well 6 mm behind the tubes. A third thermocouple was soldered onto the liquid oxygen chamber.

Flow of LN_2 to the condenser was regulated by an automatic level control. Valves to the pressurized oxygen chamber permitted evacuation and filling with O_2 and He. The O_2 chamber had a relief valve to prevent overpressurization. The O_2/F_2 was recirculated through the reactor by metal bellows pumps (Fig. 2). Pressure in and flow through the reactor were controlled by a throttling valve between the 16-L ballast volume and the reactor. A gas mass flowmeter measured flow entering the reactor, and transducers measured pressures in the ballast volume and on the inlet and exit sides of the reactor.
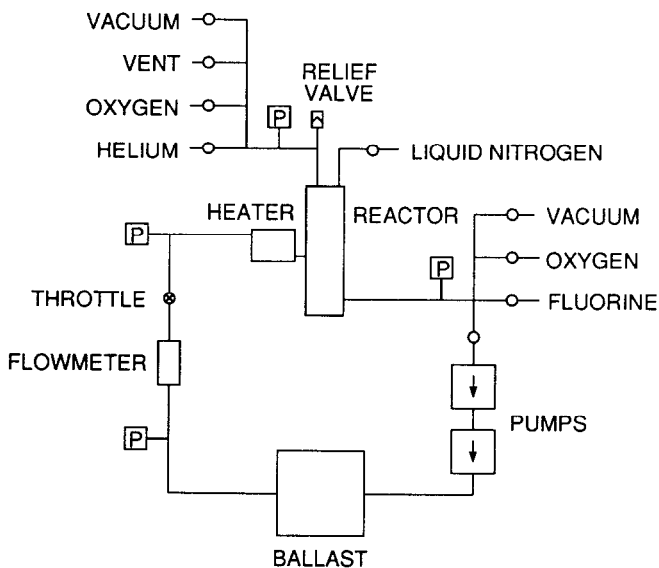

Fig. 2. Circulation loop and manifold.

EXPERIMENTAL

Following initial cooling of the condenser with LN_2, O_2 was condensed into the secondary refrigerant space. A total of 6.7 moles of O_2 was condensed, corresponding to a liquid volume of 177 cm^3 (ρ = 1.21 g/cm^3 at 75 K). (Local atmospheric pressure is 590 torr, and LN_2 boils at 75 K.) The LOX was initially pressurized to 6400 torr with helium, and the resulting temperature was −157.7°C.

The heater was warmed to approximately 700°C. The heater block glowed a dull red color, observable with room lights turned off. The ballast tank was filled to 300 torr with O_2, and F_2 was added until the total pressure was 901 torr. The gas was well-mixed due to rapid addition of the F_2.

After heater temperature and LOX bath temperature and pressure had stabilized, the throttle valve was opened to start gas circulation. Gas flow rate was maintained at 1.8–2.1 standard liters per minute (SLM). The temperature of gas exiting the heater block was held at 670–715°C. Input pressure to the reactor was held at 67–74 torr, and pressure drop through the reactor was approximately 35 torr. The ballast tank pressure began dropping immediately after gas circulation began, and liquid O_2F_2 was observed on the tubes within the first 5 minutes. The temperature of the thermocouple well behind the tubes dropped to about −70°C due to gas flow past the cold tubes. The temperature and pressure of the LOX bath rose to −154°C and 8000 torr, respectively, due to the heat load from the hot gas. Fig. 3 shows pressure in the ballast tank and temperature of the LOX bath for the first hour of the run.

After 40 minutes the helium pressure was raised to 9600 torr, and the LOX warmed to −151°C. A slight decrease occurred in the rate of drop of ballast pressure due to this change, but overall the rate was nearly constant for the experiment. The thermocouple well cooled slowly to −85°C, and the sump cooled to only −28°C.

After one hour of operation, the throttle valve was closed, and the system was left cold for two hours. During this time the sump cooled to −40°C, the thermocouple well warmed to −83°C, and the ballast pressure rose from 670 to 749 torr. When circulation was resumed, the ballast pressure again dropped steadily to ~700 torr. Then small "pings" were heard, and the ballast pressure rose rapidly to ~750 torr. The ballast pressure again dropped until pings were heard, and the pressure rose rapidly. The ballast pressure oscillated several times between 650 and 750 torr in this manner. Each time the pressure rose, the sump temperature dropped rapidly, reaching a minimum temperature of −70°C.
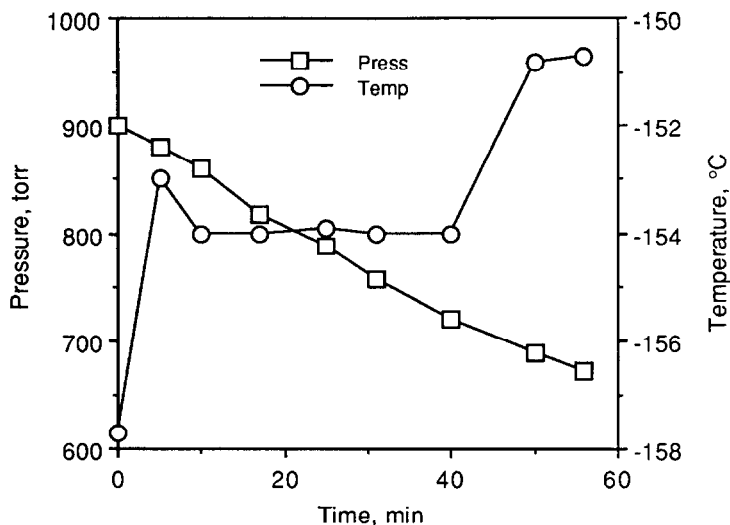
Fig. 3. Ballast tank pressure and LOX bath temperature.

At the conclusion of the experiment, the apparatus was returned to room temperature. All gas evolved from the reactor was pumped into the ballast volume, which had a final pressure of 903 torr.

The color of the condensed O_2F_2 varied, but the liquid was always a thin, uniform film which reflected light brightly. On some tubes the color was a bright copper red, while the color on other tubes was straw yellow. Both colors could be observed simultaneously on different tubes, but any one tube was always a single color. Some tubes remained uncolored but shiny, indicating a lack of condensed material. The liquid O_2F_2 appeared to have a relatively high viscosity, because it did not spontaneously drain from the tubes even when gas flow was stopped.

In an attempt to avoid O_2F_2 decomposition at the sump, O_2 was condensed into the reactor in a subsequent experiment. The sump cooled to −170°C, and the well cooled to −138°C. The O_2 was then evaporated and pumped into the ballast tank, and F_2 was added to the ballast. Gas circulation was started with the same gas temperature, flow rate, and reactor pressure as before. Ballast pressure dropped at the same rate as before, indicating production of O_2F_2, but the sump steadily warmed to −63°C.

In a further experiment, the orifice at the interface between the heater and reactor was removed. Gas circulation rate was 1.6–1.9 SLM, hot gas temperature

was 700–725°C, reactor inlet pressure was 59–65 torr, and pressure drop through the reactor was 23–27 torr. The ballast pressure dropped 30 torr in 34 minutes, and a small amount of light yellow liquid appeared on the tubes.

DISCUSSION

In previous experiments with thermally-generated O_2F_2 [7], solid O_2F_2 was collected and later allowed to warm to generate vapor. This vapor was flowed through an infrared cell, and a Nicolet 20SX FTIR infrared spectrometer was used for gas identification. The vapor was O_2F_2, identified from the O_2F_2 absorbance at 1570 cm^{-1} to avoid possible interferences from CF compounds [17]. The O_2F peak at 1490 cm^{-1} was also observed, indicating presence of O_2F as a decomposition product of O_2F_2 [13]. The primary difference between the reactors producing O_2F_2 in the earlier experiments and in the liquid O_2F_2 experiments was the temperature of the cold surface. Each reactor had similar O_2/F_2 mixtures heated to 700°C in a heater region, and the gas passed through the same size orifice to the cold wall. The same colors of condensed O_2F_2 were observed in the earlier experiments when the O_2F_2 was allowed to warm and melt, with the copper-colored material becoming straw-colored (with evolution of gas) [7].

The O_2F_2 produced was not collected in this experiment. From PVT calculations a drop of 200 torr in the ballast volume is equivalent to production of 6 g of O_2F_2. The production rate of 6 g/h of O_2F_2 (Fig. 3) is lower than the 12+ g/h rates obtained with other thermal generators for O_2F_2 [7]; however, these rates are dependent upon cooling areas. The 6 g of liquid is also the steady-state holdup of the tubes, as evidenced by the pressure oscillations. Streng [10] does not give a value of viscosity for O_2F_2, but this author estimates a value of up to 10 cp would be consistent with the slow liquid drainage from the tubes.

All the pressure drop in the ballast tank was due to formation of condensable gases, because total pressure returned to the original value after the reactor was returned to room temperature. The slight ballast pressure increase was due to heating of the gas by the pumps. By the time the last traces of colored liquid on the tubes had disappeared, the pressure was nearly at the final value. Any corrosion products (e.g., CrF_3) would require much higher temperatures to become volatile. Thus corrosion products were a small fraction (if any) of the total condensed gas. The amount of nonvolatile corrosion products was likewise small. A loss of 1 torr of ballast pressure would represent 30 mg of gas reacting.

Because of the viewport location, the only tubes with observable liquid O_2F_2 were on the downstream side of the tube bank. Following disassembly, a circular

pattern of discoloration was seen on the stainless steel tubes immediately facing the orifice. It is likely that the O_2/F_2 mixture had not cooled sufficiently to produce O_2F_2 where this attack occurred. The thermocouple well temperature (~ –85°C) also indicated the gas exiting the tube bank was not totally cooled.

Presence of the two different colors indicates different O/F ratios in the liquids. A reasonable explanation is that the yellow liquid is O_2F_2 and the red liquid contains O_2F_2 plus other oxyfluorides or trapped O_2 [4]. These colors are commonly seen (although not simultaneously) when O_2F_2 is synthesized, with the red liquid becoming yellow and with evolution of gas upon warming. The gas evolved is largely, perhaps totally, oxygen [4,7].

Two possible explanations for the simultaneous presence of different colored liquids on different tubes are as follows:

1) The inner surfaces of each tube are nearly the same temperature, due to rapid mixing of LOX inside the tubes and a high boiling heat transfer coefficient. Heat transfer from the hot gas to the tubes, however, is not the same for each tube. Depending upon the location of the tubes and the flow streamlines, the gas heat transfer coefficient is not the same for all tubes, and temperatures of the liquid films on various tubes are not identical. The stoichiometry of the O_xF_y compound or mixture formed may be temperature dependent.

2) The suspected mechanism of O_2F_2 formation involves an initial reaction of an F atom with an oxygen molecule (perhaps adsorbed O_2) to form O_2F at the metal wall. A second F atom later joins the O_2F to make O_2F_2. No more than 5 to 10% of the F_2 is dissociated at these temperatures, and some tubes will "see" a gas mixture depleted in F atoms. The stoichiometry of O_xF_y may depend on F atom availability.

The pings were probably caused by drops of liquid O_2F_2 hitting the sump. The rapid cooling of the sump is the behavior which would be expected when cold liquid droplets undergo film boiling on a warm surface. The cyclic pressure change with pings indicates a variation in the liquid holdup of the tubes between draining cycles. Whether the pings were due either to rapid decomposition of O_2F_2 (with accompanying sparks) or simply vapor explosions in droplets is not known, because the sump was not visible through the viewport. Precooling the sump with liquid oxygen was unsuccessful in permitting collection of liquid O_2F_2 because the gas passing through the reactor was not totally cooled, and the sump warmed as a result.

The orifice was important to generation of O_2F_2 in this apparatus. Without the orifice in place the production rate fell by a factor of 4. The original reason for using an orifice was to attempt to cool the gas by adiabatic expansion. Attack of the

stainless steel tubes opposite the orifice suggests the temperature was still quite high at this point. It is possible that a greater effect on generation rate is caused by the effect of an orifice on gas streamlines past the cold tubes.

CONCLUSIONS

It is possible to produce O_2F_2 directly in the liquid state. The observed production rate of 6 g/h is not extremely high, but this rate was probably limited by gas cooling rate. The reactor tubes are rather like a heat exchanger and can be scaled up for improved heat transfer. Different colors of the liquid indicate a mixture of O_2F_2 and related compounds. Explanations have been suggested for simultaneous production of different O_xF_y compounds.

The viscosity of liquid O_2F_2 is high, and the liquid does not readily drain from vertical surfaces. This high viscosity may hinder attempts to produce a flowing stream of O_2F_2. Design changes are needed to enable collection of liquid O_2F_2 in a sump region. Further experimentation is needed to assess possibilities of producing liquid O_2F_2 and vaporizing it continuously for use in potential processes.

ACKNOWLEDGMENTS

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