Fluorinations with sulfur tetrafluoride and HF. 1. A reactor design for safe, routine handling of SF_4 and HF

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Abstract

A reactor has been designed and built to handle anhydrous HF and SF_4 safely for routine use in organic synthesis. The system described is completely contained and remotely operated so as to minimize any possible exposure to these dangerous materials. Furthermore, it features controls that allow the experimentalist to accurately add HF and SF_4, monitor the reaction progress and sample if necessary, as well as allowing flexibility in the work-up of the reaction.

Introduction

The development and exploration of new areas of chemistry with desirable biological properties involves the preparation of structurally diverse molecules in order to generate data for structure–activity relationships. In our work, we were interested in obtaining a variety of fluorinated molecules to be evaluated against a broad spectrum of biological targets of agricultural significance. Fluorinations with sulfur tetrafluoride [1, 2] and HF were particularly attractive since they offered a great deal of synthetic flexibility to prepare both literature and novel molecules possessing fluorine.

In planning to use these reagents we could not ignore, or take lightly, the fact that SF_4 and HF are extremely hazardous. Since exposure to these reagents can result in burns [3], and because we intended to use them on a routine basis, a reactor was designed and built that minimized chemical exposure yet allowed for convenient synthetic operations. Furthermore, this system included equipment for remote operation and the monitoring various parameters during the course of a run.

Materials

Anhydrous HF and SF_4 were purchased from Matheson* while the autoclave was made by Autoclave Engineers. Rupture discs were 3/16″ flat discs

*Frequent problems were experienced with the SF_4 purchased from Matheson when stored for periods longer than six months. The valve corroded shut on these bottles and full lecture bottles had to be returned for disposal. This reagent should be used soon after purchase.

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manufactured by BS and B Safety Systems. All valves were catalogue items produced by either Whitey or Autoclave Engineers. A Love model 1512 temperature controller and Mettler PE-11 balance were used. The lecture bottle of HF was heated using a Watlow Silicon rubber strip controlled by a Watlow temperature controller and a type J thermocouple. Lastly, the HF detector was purchased from Sensidyne Inc. as three components: an HF single channel controller; HF sensor assembly; and a controller housing.

Results and discussion

The basic design of our system is depicted in Fig. 1. We assembled our system in an explosion resistant room designed for high-pressure operations. It is conceivable that one could build a comparable unit in a suitably modified walk-in hood.

To start we had to decide on materials of construction. In contrast to hydrogen fluoride, we could find no corrosion data for SF_4. To be safe the reaction zone, *i.e.* that area of our reactor that would be exposed to extremes of temperature and pressure between valves 6 and 7 (Fig. 1), was made from Hastelloy C®. All other piping and valves used to contain these reagents were then built using Monel 400. Later we performed a crude, highly qualitative corrosion study with coupons of these metals and found that Hastelloy C®

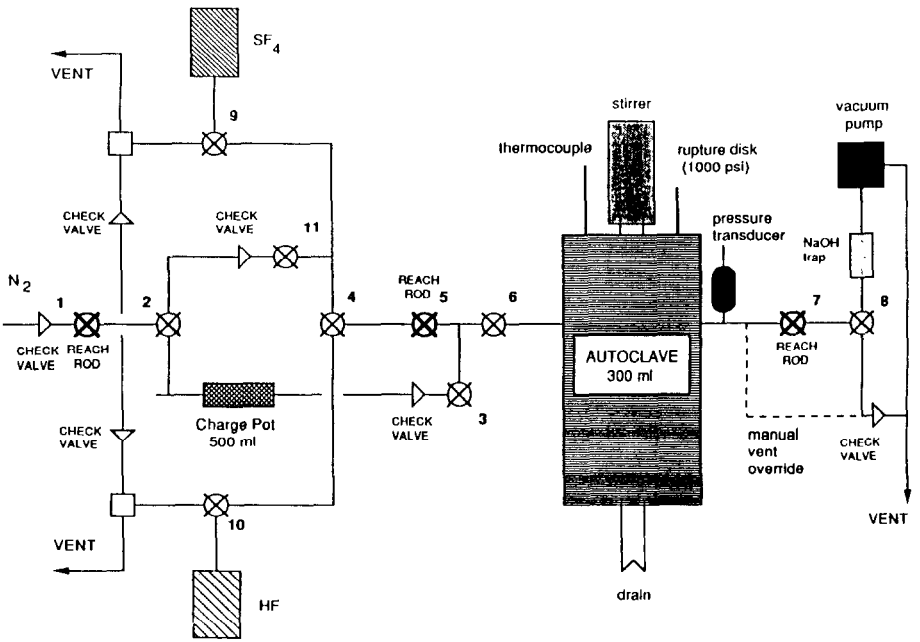

Fig. 1. Reactor with valves and piping design.

was superior to Monel 400 with regard to resistance to corrosion in the reaction zone.

The reactor consisted of a 300 ml autoclave* equipped with a stirring unit with a tachometer, a standard thermocouple, a diaphram-type pressure transducer, a sampling tube, a bottom drain valve and a heating jacket. A platinum rupture disc† rated to 1050 psi at 72 °F was installed at the attachment point of a blow-out line. The inlet valve (valve 6) was air-actuated for simple opening and closing, while the valve on the vent side of the reaction zone (valve 7) was reach-rod operated for the purpose of the controlled release of volatiles at the end of a run. Valves 1 and 5 were designed for metering nitrogen and reagents respectively and were thus reach-rod operated, while valves 2, 3, 4, 8, 9, 10 and 11 were all air-actuated. All valves were remotely operated at a panel board. An explosion-proof vacuum pump was used to evacuate the entire system for the purpose of transfering HF and SF_4 which were stored in lecture bottles. Each lecture bottle was attached to the system via flexible tubing and sat on a balance equipped for remote display. A charge pot was added to our system in order that reactions could be quenched without having to open the reactor. Lastly, we found that 1/8″ tubing was adequate for all inlet tubing, while our vent line went from 1/8″ to 1/2″ diameter out to a caustic scrubber.

Several safety features were considered in this design. First, the entire system was capable of being purged with nitrogen. Hence, sections could be isolated, flushed with inert gas and maintenance could then be performed. Secondly, a series of interlocks were installed such that in the event of a power failure or exotherm all heating would stop and had to be manually restarted. Thirdly, an HF detector was purchased and used to alert chemists regarding any potential problems. Fourthly, a manual vent valve was placed in the reaction zone for use in the event that valve 7 failed. Lastly, all sensing devices were wired to one data recorder with alarm capabilities. This enabled us to set alarm points and to have a record of several parameters monitored during a run.

In a typical reaction, reagents were charged into the autoclave which was sealed, cooled to −60 °C by a dry ice slush, and evacuated. The HF would then be distilled using a rubberized heating strip and temperature controller. Sulfur tetrafluoride was added next. This required no external heat and 120 g of this reagent have been added to 75 g HF without trouble. Valves were then secured, a heater installed and the reaction started. At the end of the reaction, the volatile reagents could be vented and scrubbed through a caustic trap or quenched by means of the charge pot.

Working with HF and SF_4 requires frequent maintenance checks on the equipment and an extremely conscientious approach to work. With these guidelines we have been able to work with these reagents safely over an

*The 300-ml size was convenient for reactions run on a 1 mmol to 0.25 mol scale.

†Other rupture discs were tried and found to be inferior to platinum. Specifically, gold-plated Inconel and Teflon-coated Monel all corroded severely.

extended period of time and have been able to perform many experiments involving the fluorination of organic substrates [4].

References

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