Enclosed flow tube injector system for low temperature kinetic studies

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A new enclosed injector system for low temperature kinetic studies is described. This system offers a number of advantages over more conventional designs of moveable inlet injectors. The enclosed injector prevents the introduction of contaminants into the flow reactor. In conventional designs, ambient contaminants adsorbed onto the outside of the injector could be transported into the flow reactor. The enclosed injector exposes the reactant gas to the same length of inlet tubing at a uniform temperature regardless of the injector position. In addition, the enclosed injector minimizes temperature gradients in the flow reactor caused by heat transfer along the injector. This is a particular problem when the flow reactor is operated near atmospheric pressure at reduced temperatures. Finally, this design is significantly more compact than conventional injector designs. This system has been successfully employed in studies of the heterogeneous reaction of N_2O_5 with sulfuric acid aerosols over the temperature range 225–293 K.

I. INTRODUCTION

The flow tube technique has been one of the most widely used methods to acquire kinetic data. Initially employed around 1930 to study reactions of atomic hydrogen and oxygen with various compounds,[1,2] this technique was later applied by many researchers to study important reactions of atoms and radicals. For a comprehensive review of this technique, its extensive applications, and the associated detection methods, the reader is referred to the review by Howard.[3]

Figure 1 shows a schematic diagram of a typical flow tube reactor employing a moveable inlet injector. Reactants, such as atomic or molecular radicals, are introduced through one of the sidearms and mixed with the main carrier gas flow entering the other sidearm. The carrier flow generally defines the physical properties of the flow reactor gas stream while a temperature-regulated jacket defines the maximum length of the reaction zone. An additional reactant is introduced into the flow tube through the moveable injector. Kinetic measurements are carried out by varying the distance between the point where the two reactants are mixed and the detector. In addition to the moveable inlet injector shown in the figure, variations on this technique include moveable detectors, moveable discharge sources, and a series of fixed position inlet and/or sampling ports along the flow reactor length.

Because of its simplicity, a large number of kinetic studies employ moveable injector designs similar to Fig. 1. However, this simple design presents several practical disadvantages when carrying out laboratory studies simulating the earth's stratosphere where temperatures of interest typically range between 210 and 240 K. Stratospheric reactions are generally studied using pressures below ambient, thus placing stringent requirements on the integrity of the sliding injector seal. This becomes particularly important when water vapor and/or other trace ambient gases may be involved in

the reactions under study. For water vapor in particular, adsorption onto the cold outer wall of the injector can produce a significant "leak" into the reactor, even for reactor pressures near ambient. An additional complication arises when the warm injector, which is initially near ambient temperature, is moved into the cold flow reactor. This introduces temperature gradients, which may result in turbulence, especially at high flow reactor pressures. Such turbulence in turn can contribute to the background wall decay rate as well as cause an uncertainty in the knowledge of the velocity profile and therefore in the conversion of injector position into residence time.

Finally, some gases of stratospheric interest, such as dinitrogen pentoxide (N_2O_5), decompose both homogeneously and heterogeneously in the warm sections of a moveable injector. With the simple design of Fig. 1, the extent of decomposition changes with injector position since the temperature profile along the injector changes. As a result, the background wall decay may become large, severely complicating the data analysis, as will be further discussed in Sec. III.

The above problems would clearly be greatly reduced if the injector is completely isolated from the ambient environment and maintained at a uniform temperature. In the present design, we accomplish this by mounting the entire injector and drive mechanism in a temperature-controlled enclosure. The drive mechanism is connected to a crank, which is external to the enclosure, through a vacuum seal. Reactant gas is introduced into the moving injector by means of a coiled Teflon tube. Details of the design are given in Sec. II. An additional advantage of this design is that it requires a total length of only twice the desired injector travel; traditional designs require a length of three times this travel. The present injector design has been used successfully in measur-
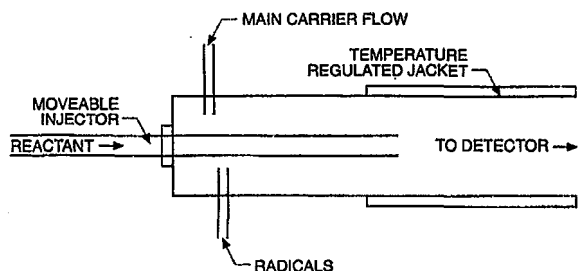
FIG. 1. Schematic of typical flow tube reactor with a moveable inlet injector.

ing the reaction probability of N_2O_5 with sulfuric acid aerosols at stratospheric temperatures.[4]

II. ENCLOSED INJECTOR DESIGN

Figure 2 shows a detailed schematic of the enclosed injector, associated components, and the suspended flow reactor (27). The injector system is constructed from a triple-wall stainless steel cylinder 106.7 cm long×12.7 cm in diameter. Stainless steel flanges are welded on both ends. Viton O rings (24) form a seal between the inner chamber and the plates at the top (2) and bottom (23) of the injector enclosure as well as the seal (25) for the flow reactor (27).

Ethanol coolant is circulated between the inner and middle walls while the outer annulus serves as an insulating vacuum jacket. The base plate (23) contains a number of vacuum feedthroughs for a thermocouple, the coolant inlet, and the gas and aerosol inlets. A slow flow of dry air enters and exits through needle valves connected to ports in the base (28) and top (29) flanges, respectively. The enclosure pressure is controlled by these needle valves and is monitored by a pressure gauge connected to the inlet port. The enclosure pressure and temperature are maintained near those of the flow reactor.

One reactant gas (N_2O_5 in the present study) enters the system through the inlet port (20), and passes through a coiled length of 3 mm o.d. PFA Teflon tubing (17). This Teflon coil contracts or expands as the injector moves. The gas then passes through a Teflon elbow (15), through the Delrin connector head (12) and into the injector tube (16). This tube consists of a 120 cm length of 6.35 ± 0.05 mm o.d. glass-lined stainless steel tube (Scientific Glass Engineering, Inc., Austin, TX). Precision o.d. tubing is needed to effect a good sliding seal over the entire range of injector travel. The glass-lined stainless steel injector achieves the stiffness of stainless steel and the inertness of glass. A Thompson linear ball bearing (13), mounted in the Delrin connector head, slides on a linear guide shaft (7). This acts as a guide for movement of the injector. A Warner R-0502 ball nut assembly (11) is also mounted on the Delrin connector and runs on a Warner ball lead screw (1). The lead screw is supported on both ends by ball bearings (4) mounted in the top and bottom plates. The lead screw protrudes through the top plate and is sealed by a Teflon-encapsulated Viton O ring (6) mounted in the top plate. An identical O ring (18) forms the sliding seal around the injector near the bottom of the enclosure. This seal achieves the inertness of Teflon and the mechanical sta-
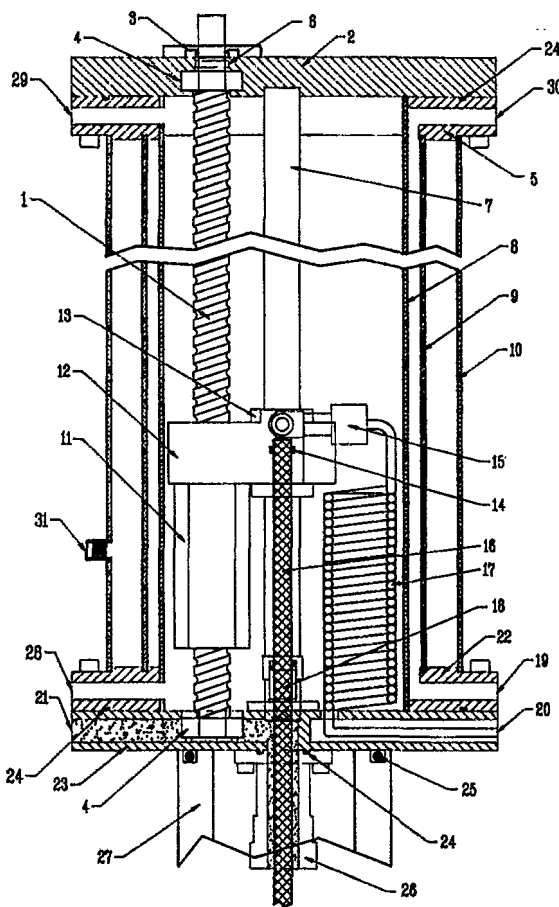

FIG. 2. Detailed enclosed injector design showing the following parts: (1) ball lead screw, (2) aluminum top plate, (3) external chevron seal, (4) ball bearing, (5) top plate sealing flange, (6) Teflon-encapsulated Viton O ring, (7) linear guide shaft, (8) inner wall, (9) middle wall, (10) outer wall, (11) ball nut, (12) Delrin connecting head, (13) linear ball bearing, (14) O ring, (15) Teflon elbow, (16) glass-lined stainless steel injector, (17) Teflon coil for reactant gas, (18) injector sliding seal fitting containing Teflon-coated Viton O ring, (19) coolant inlet, (20) reactant gas inlet, (21) aerosol inlet (the aerosol flow path is schematically illustrated by the small dots), (22) base plate sealing flange, (23) stainless steel base plate, (24) O ring, (25) flow reactor sealing O ring, (26) Cajon fitting for aerosol inlet diffuser cone, (27) flow reactor, (28) purge gas inlet, (29) purge gas outlet, (30) coolant outlet, (31) vacuum pump out port.

bility of Viton. A Chevron seal (3) external to the top of the injector chamber prevents ambient moisture from reaching the internal O ring and causing ice buildup. This Chevron seal is readily changed without opening up the chamber enclosure.

The injector is moved in and out of the flow reactor by turning an external crank; this crank (not shown) is coupled to the lead screw via a pair of toothed timing pulleys. The pulleys and lead screw, which protrude from the injector enclosure, are enclosed in a loose-fitting plastic bag which is flushed with dry nitrogen to prevent ice buildup. Since the injector and the Teflon coil are completely enclosed in a constant temperature environment, the extent of decomposition of the reactant gas does not change with injector position. A stainless steel guide rod (not shown) passes through the center of the Teflon coil and into the base plate to prevent the Teflon coil from entangling with the injector tube.

The main carrier gas, containing a second reactant (sulfuric acid aerosol in the present experiment), is precooled using an external heat exchanger (not shown), and is introduced into the flow reactor through a port in the base plate (21) of the injector enclosure. The aerosol flow passes through a channel in this plate and into the flow reactor through a glass diffuser cone. The diffuser cone is attached to the base flange by an ultra-Torr fitting (26).

III. SYSTEM PERFORMANCE

The performance of the enclosed injector system can be judged by the integrity of the sliding injector seal, the magnitude of flow reactor temperature gradients, the degree of reactant gas decomposition with injector movement, and the ease of system use without encountering major problems.

With a Teflon-encapsulated Viton O ring forming the seal around the injector (18), the enclosed injector system has been in operation for over eight months at temperatures of 215–293 K without any major problems. The Viton seal initially employed was eventually attacked by the acidic aerosol, which caused a dramatic increase in the injector sliding friction. The more inert Teflon seal deformed at lower temperatures resulting in leakage. Leakage across this seal can have a number of detrimental effects on low temperature kinetic studies. In addition to those discussed in Sec. I such leakage will (1) affect the gas flow rate and therefore the residence time in the flow reactor, (2) introduce impurities from the injector enclosure into the flow reactor, and (3) introduce corrosive flow reactor gas and aerosol into the injector enclosure leading to corrosion of the injector drive mechanism. The Teflon-encapsulated injector O-ring seal maintained an excellent sliding seal throughout the temperature range 215–293 K, even with a 227 Torr pressure differential across the seal; we measured no change in the injector enclosure pressure as the flow reactor pressure was reduced. In addition, the total gas flow entering the reactor was typically within 3% of that measured at the output, again implying a good sliding seal.

Calibrated thermocouples were used to measure the aerosol inlet temperature at the exit of the glass cone and the wall temperature at the exit of the flow reactor. Temperature gradients were typically $\leqslant 0.2$ K over the above temperature range. At 273 K, no temperature gradient was measured. Under similar flow and pressure conditions, the injector system of Fig. 1 by comparison resulted in temperature gradients of 0.5 and 0.8–1.5 K at operating temperatures of 273 and 243 K, respectively.

The degree of reactant gas decomposition as a function of injector position is quantitatively measured by the background wall decay rate (k_{wall}). This rate, which is measured in the absence of aerosol, is dependent upon the condition of the flow reactor walls, the presence of flow reactor temperature gradients, and the degree of reactant gas thermal decomposition with injector movement. As discussed in Sec. I, thermal gradients will cause turbulence and this may contribute to the wall decay rate. In contrast to the enclosed injector described here, such a situation has in fact been observed using the simple injector system. For example at a flow tube temperature of 273 K and a temperature gradient of 0.5 K,
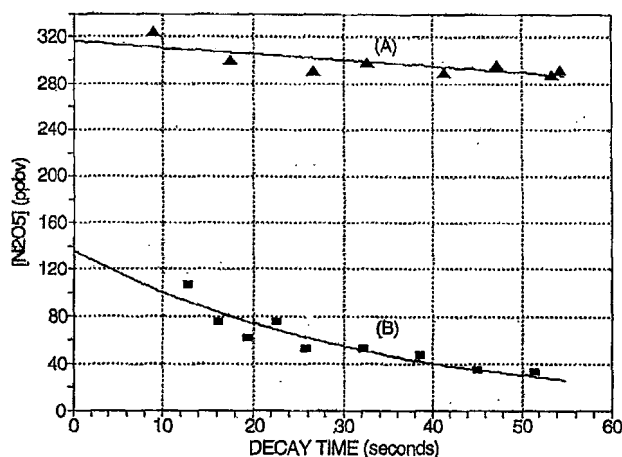

FIG. 3. Background N_2O_5 wall decay curves for the enclosed injector system (profile A) and the simple injector system (profile B) shown in Fig. 1. Similar conditions of temperature (273 K), relative humidity (~0.6%), and flow velocity (1.6 cm s^{-1}) were used to record both profiles. Profile A results in k_{wall}=0.00175 s^{-1} while profile B yields a k_{wall}=0.034 s^{-1}. These decay rates were obtained from an exponential fit of the background N_2O_5 concentration as a function of time.

we sometimes measured k_{wall} values a factor of 1.6–3.7 times higher than that predicted by diffusional transport (Gormley and Kennedy).[5]

As previously mentioned, the extent of decomposition for gases like N_2O_5 will change with injector position using the design of Fig. 1. As one increases the fraction of the injector length protruding into the warm environment, more N_2O_5 will thermally decompose to NO_2. This results in a larger apparent k_{wall}, as shown by the comparisons of Fig. 3. As can be seen, the background N_2O_5 decay for the enclosed injector (profile A, k_{wall}=0.00175 s^{-1}) is over an order of magnitude smaller than that for the simple injector (profile B, k_{wall}=0.034 s^{-1}) under similar conditions of temperature (273 K), relative humidity (~0.6%), and flow velocity (1.6 cm s^{-1}). As the k_{wall} values become larger, it becomes more difficult to separate out the gas phase reaction rate from those occurring on the walls, particularly when the former is small. In addition, as we often observe, high k_{wall} values are frequently associated with a high variance. This in turn degrades the precision in the determination of reaction probability. In this particular case, the enclosed injector system results in a reaction probability a factor 6 more precise than the simple injector system.

In the present low temperature kinetic studies, water is a reactant. Thus minimizing leakage of ambient water vapor into the flow reactor, from either the O-ring seal (25) or the sliding injector seal (18), is extremely important for achieving stratospheric water vapor concentrations below 10 parts-per-million by volume (ppmv). The present injector design achieves this. For example, at a flow tube temperature of 234 K, air with a controlled water vapor concentration was added to the flow reactor and the concentration in the flow leaving the reactor was measured by tunable diode laser absorption spectroscopy (see Ref. 4 for details). With a water vapor mixing ratio of 7.9 ppmv, the measured concentration was

within 1.8 ppmv of the added concentration, indicating a negligible ambient air leak rate.

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