2000

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A Versatile Apparatus for Measuring Kinetics of Gaseous Reactions by a Relative Method

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Abstract

It is important that accurate, reproducible values for the rates of chemical reactions occurring in the atmosphere be obtained. The value of accurate kinetics measurements is to improve the accuracy of mathematical models used to forecast the state of the atmosphere. We describe a versatile, robust apparatus for obtaining atmospheric reaction rate values and their temperature dependencies by a relative method. This relative method has the advantage over absolute methods in that errors due to impurities and adsorption on walls of the reaction apparatus are minimized. In addition, relative values serve as an important verification for absolute values. The apparatus serves to mix sample and reference gases, used in the studies, with helium, water vapor and oxygen and deliver them to a quartz reaction cell whose temperature can be controlled between of -50 C and +350 C. Reaction is carried out by use of a low pressure mercury vapor lamp radiating the sample for different periods of time. The mercury lamp produces hydroxyl radicals in the presence of the water vapor in the reaction mixture. The hydroxyl radicals abstract hydrogen atoms from the sample molecules. Oxygen is needed to mimic reaction conditions in the atmosphere which is rich in oxygen. Measurement of the concentrations of unreacted and reacted mixtures are obtained by injecting these samples into a gas chromatograph having a mass spectrometer detector, GC/MS. Analysis of the rates of reaction of cyclopropane and difluoromethoxydifluoromethane, CHF_2OCHF_2, (HFOC-134) with hydroxyl radicals yields the following results: For cyclopropane, a rate of $7.85 \times 10^{-14} s^{-1}$ at 298.15 K and an activation energy, E/R, of 1323 was obtained. For HFOC-134, a rate of $2.23 \times 10^{-15} s^{-1}$ at 298.15 K and an activation energy, E/R, of 1895 was obtained.

Introduction

Because of questions raised concerning the impact of people upon their environment, especially the atmosphere, there is great need for accurate values of the rates of chemical reactions occurring in Earth's atmosphere (Belton, 1990; Albritton and Watson, 1991; Finlayson-Pitts and Pitts, 2000). It is important to know atmospheric lifetimes of gaseous pollutants arising from natural and man-produced sources (DeMore, 1997; Taylor, 1999). In this report we describe an apparatus and a method to acquire these values.

Absolute Methods.--Gaseous chemical kinetics rate measurements may be divided into absolute and relative methods (Finlayson-Pitts and Pitts, 2000). The absolute method involves making measurements of the concentration of each reactant after steady-state flow has been achieved, both before and after the reaction has occurred. This is most often done by use of a concentric tube apparatus in which one reactant flows through a central tube while the other reactant flows through a surrounding outer tube. Reaction progress is measured at different distances from the point of mixing after reaction has been initiated. Elaborate, powerful vacuum systems are required for absolute measurements. Also, there are considerable opportunities for error, such as the presence of impurities and loss of reactants by adsorption on the walls of the containing apparatus. Detection schemes used to monitor the concentrations must be very specific, sensitive and accurate and are usually sophisticated and expensive. However, absolute methods are fundamental. Without them there would be no way of having the true, absolute values for reaction rates and temperature dependencies.

Relative Methods.--Relative methods for measuring chemical kinetics rates and temperature dependencies are also important and are simpler to perform. In this method, the rates of a reaction are measured relative to a standard reference compound whose rate has already been determined and traceable to an absolute measurement. Many errors are minimized and often cancel in the measuring process. This is because both the compound whose rate is to be determined and the standard compound are mixed together and exposed to exactly the same conditions as they flow through the reaction apparatus and are measured. Generally, the presence of trace impurities has little effect. There is additional benefit from measuring chemical kinetics rates by the relative method. They provide an important verification of the absolute rates. For example, let us measure an unknown rate two times and each time the rate of the unknown is measured using a different standard. If the same value of the unknown rate is obtained using the two different standards, each traceable to a different absolute measurement, strong evidence is provided that not only is the rate for the unknown correct, but that the absolute rates for the standard compounds are also correct.

The relative method can also provide reaction rate information accurately, less expensively, and in greater abundance than the absolute method. It can serve as a check on the accuracy of absolute values. Many different types of gaseous kinetic rates may be measured using this method. The following are examples:

- Thermolysis Reactions
- Photo-initiated reactions with oxygen
- Halogen free radical reactions
- Photo-initiated reactions with ozone
- Photo-initiated reactions with nitric oxide
- Photo-initiated reactions with hydroxyl radicals

In this report a relative rate apparatus and method is described that can be used to measure chemical reaction rates and temperature dependencies of rates reproducibly and accurately.

Theory

Our kinetic studies are focused on reactions of gaseous atmospheric pollutants as they react with hydroxy radicals. Past atmospheric research has revealed that hydroxyl radical reaction with organic compounds is the predominate, and perhaps only, pathway by which organic and other compounds are removed from the atmosphere (Atkinson, 1989). Furthermore, hydroxyl radical reaction is of primary importance in combustion processes. A hydroxyl radical abstracts a hydrogen atom from organic compounds, producing water and leaving an organic radical:

$$R\text{-}H + \cdot OH \rightarrow R\cdot + HOH$$

This reaction is a second order reaction. The rate equation for this reaction is simplified by the fact that the concentration of one of the reactants, the hydroxyl radical, is present in constant amount during the course of a reaction, just as it is in the atmosphere. The equations necessary to calculate hydroxyl reaction rates using the relative method are simple. Because sample and reference compounds are in the same reaction cell for the same amount of time, t, the concentration of hydroxyl radical, $C_{\cdot OH}$, and time, t, cancel from the defining equations yielding a simple relationship between the rate constants for sample and reference compounds.

$$\frac{\text{Rate}_S}{\text{Rate}_R} = \frac{-\dfrac{dC_S}{dt}}{-\dfrac{dC_R}{dt}} = \frac{k_S[C_S][C_{\cdot OH}]}{k_R[C_R][C_{\cdot OH}]} = \frac{k_S[C_S]}{k_R[C_R]}$$

$$\frac{\displaystyle\int_{C_{S\,Initial}}^{C_{S\,Final}} \frac{d[C_S]}{[C_S]}}{\displaystyle\int_{C_{R\,Initial}}^{C_{R\,Final}} \frac{d[C_R]}{[C_R]}} = \frac{\displaystyle\int_{t=0}^{t=t} k_S\, dt}{\displaystyle\int_{t=0}^{t=t} k_R\, dt} = \frac{\ln\left\{\dfrac{C_{S\,Initial}}{C_{S\,Final}}\right\}}{\ln\left\{\dfrac{C_{R\,Initial}}{C_{R\,Final}}\right\}} = \frac{\ln(DF_S)}{\ln(DF_R)} = \frac{k_S \times t}{k_R \times t} = \frac{k_S}{k_R}$$

$$k_{Sample} = k_{Reference} \times \frac{\ln(DF_{Sample})}{\ln(DF_{Reference})}$$

In this derivation, S and R refer to sample gas and reference gas, respectively. The concentrations of the reactants in moles per liter are denoted by a subscripted C. The specific rate constants are defined as k_S and k_R for sample and reference gases, respectively. The time of reaction is given by t. The depletion factor for sample and reference are labeled as DF. The depletion factor is defined as the concentration of sample (or reference) gas before reaction divided by the concentration of sample (or reference) gas after reacting for a period of time equal to t.

Materials and Methods

Sample and Reference Preparation and Storage.--Figure 1 shows a schematic of the apparatus. Each subsection of the apparatus will be described, beginning with the sample/reference container. The sample and reference gas mixtures are prepared and stored in containers normally used to hold propane for recreational vehicles and barbecue grills. The containers have a water capacity of 21.7 L (47.6 lb.). They can be pressurized to a maximum of 1654 kPa (240 psi). The steel compressed gas cylinders (DOT/ICC 4B-240) are purchased new and fitted with a brass adapter that screws into the outlet and terminates in a 1/2 inch NPT male fitting. These adapters can be purchased from any gas company that sells and fills the propane containers. The 1/2 inch NPT male fitting is connected by means of a 1/2 inch NPT male fitting to 1/8 inch Swagelok™ tube connector for attachment to the vacuum lines and the reaction apparatus. The containers are evacuated to a fraction of a torr pressure before filling them with the sample and reference gases. The on-off valves of these containers exhibit almost no leakage at low pressures. The sample gas is admitted into the evacuated container to a pressure of approximately 2.67 kPa (20 Torr) using normal vacuum techniques. The reference gas, 2.67 kPa, is then introduced into the same container. Finally, ultra high purity helium is added to the tank until the total pressure is 207 kPa (30 psi). The reaction mixture must stand for several hours to insure complete mixing. All vacuum and low pressure readings are obtained using a MKS Type 690A Absolute Baratron™ Pressure Transducer connected to a MKS Type 670A High Accuracy Signal Conditioner. The final pressure was measured with a 152.4 mm Ashcroft Type 1082 Test Gauge having a stated accuracy of 0.25%.

Dilution and Mixing of Sample and Reference Gases for Reaction.--Once the sample container is filled and mixing completed, it is attached to the reaction apparatus using stainless steel 1/8 inch Swagelok™ fittings and 1/8
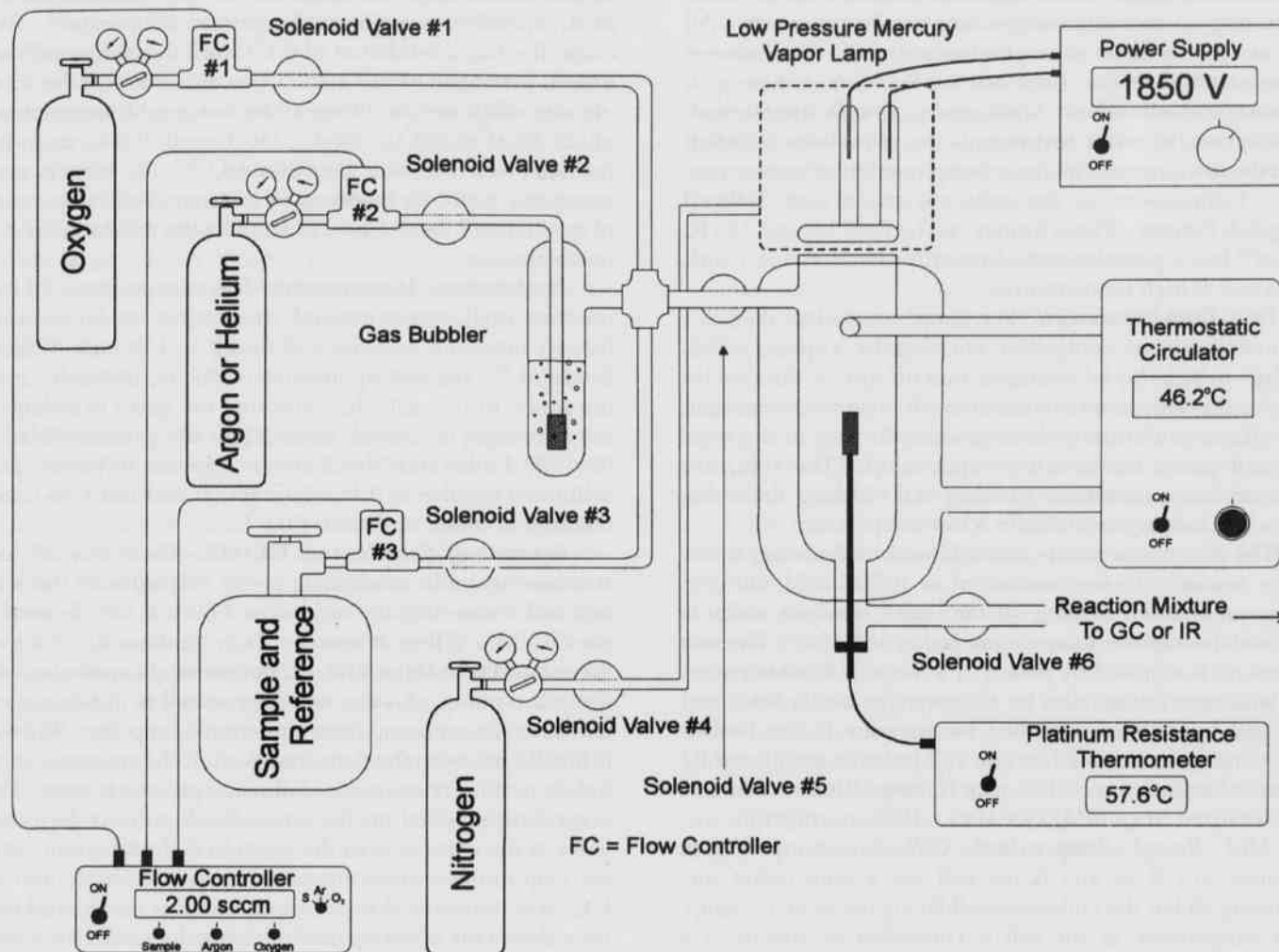
Fig. 1. Schematic of apparatus.

inch Teflon™ tubing. The sample mixture is diluted with additional ultra high purity helium and oxygen by means of stainless steel Swagelok™ 1/4 inch Tee connectors before entering the reaction chamber. The oxygen and helium are supplied by means of conventional Type H tanks fitted with pressure regulators adjusted to deliver these gases at 172 kPa (25 psi). The pressure regulators used are Model 11 Series (Two Stage) General Purpose High-Flow Regulators manufactured by Scott Specialty Gases. The sample, helium and oxygen gases have their flow into the reaction cell accurately controlled by means of Hastings Model HFC-202 Mass Flowcontrollers connected to a Hasting Model 400 Power Supply. The power supply is a combination power supply and readout device that can control up to four flow controllers. The flow controllers were calibrated for an upstream pressure of 172 kPa and downstream pressure of 101 kPa. The helium controller (HFC 202D) was calibrated

to deliver 0 to 500 sccm (standard cubic centimeters per minute) helium. The oxygen controller (HFC-202B) was calibrated to deliver 0 to 50 sccm oxygen, and the sample controller (HFC-202A) was calibrated to deliver 0 to 10 sccm helium. The accuracy and linearity of the controllers are guaranteed to have less than 1% error with a repeatability error of less than 0.1%. The helium gas is fed into a glass bubbler apparatus which can be used to saturate the helium with water vapor needed to produce hydroxyl radicals when irradiated by the low pressure mercury vapor lamp. The flow through the water bubbler can be diverted by means of a two-way stopcock to deliver dry helium gas when desired. This stopcock is not shown in Fig. 1. The final diluted gas mixture can be sent into the reaction chamber or diverted to an exhaust line by solenoid valves. The exhaust line is not shown in Fig. 1. All gases are eventually vented outside the building through 1/4 inch Teflon™ tubing.

Reaction Cells.--Three different reaction cells are used depending on the temperature range to be measured. All cells are in the shape of a cylinder having a 5 cm diameter and a length of 10 cm. Each cell has 9.53 mm (3/8 in.) o.d. entrance and exit tubes. Additionally, all cells are fabricated of quartz in order to transmit the ultraviolet radiation from the low pressure mercury lamp required to cause reaction. Connections to the cells are made with Teflon™ Swagelok Fittings. These fittings can be used to near 350 K. Teflon™ has a phase transition near this temperature which limits use at high temperatures.

Low Temperature Cell.--For temperatures less than 273 K the cell used is completely enclosed by a quartz jacket through which liquid nitrogen boil-off gas is directed to achieve the low temperatures desired. The waste nitrogen boil-off gas is ultimately directed onto the face of the reaction cell facing the mercury vapor lamp. The cold, dry nitrogen keeps frost from forming and blocking the radiation while helping to maintain a low temperature.

The low temperatures are achieved by inserting a cartridge heater into the bottom of a 30 L liquid nitrogen Dewar and slowly boiling off the liquid nitrogen which is directed through the temperature jacket of the cell. The rate of boil-off is adjusted by means of a Variac. A rubber stopper with tight fitting holes for the cartridge heater leads and nitrogen boil-off line maintain the pressure in the Dewar. The temperature of the reaction cell jacket is monitored by means of a platinum RTD sensor (Omega PR-11-2-100-1/8-9-E) attached to an OMEGA 4201A PC2 controller.

Mid Range Temperature Cell.--For temperatures between 273 K to 400 K the cell has a fluid jacket surrounding all but the end of the cell facing the mercury lamp. The temperature of the cell is controlled by means of a Neslab Constant Temperature Bath/Circulator, Model RTE-111 that controls in the range -25°C to + 150°C. Dow Corning Silicon Fluid, Dow Corning 200™ fluid with 50 centistokes viscosity at 273 K is used as the heat transfer fluid. We measured the absorbance of this fluid in a 1.00 cm quartz cell and found the fluid is transparent in the visible region of the electromagnetic spectrum down to 254 nm where the absorbance is 0.037. Below 254 nm the absorbance rises steadily to a value of 1.000 at approximately 210 nm for the 1.00 cm path length. This information is useful if filtering of the higher energy (shorter wavelength) radiation from the mercury vapor lamp is required.

High Temperature Cell.--For reaction temperatures higher than 400 K a simple quartz cell with no jacket is used. The cell is wrapped with a 10 ft. OMEGALUX™ FGR-100 500 watt/120 volt rope heater. The maximum allowable temperature for this heater rope is 755 K. The temperature of the cell is controlled by inserting a 100-ohm inch o.d. platinum RTD sensor, = 0.00385, between the cell and the heater rope. The RTD sensor (Omega PR-11-2- 100-1/8-9-

E) and heater rope are connected to an OMEGA 4201A PC2 controller to maintain the desired temperature. The controller has a resolution of 0.1°C and measures and controls in the region of ±199.9°C. The sensor/controller module was calibrated by Omega Engineering at temperatures of -25°C, 0°C, 50°C, 100°C, 150°C and 190°C to insure readings were accurate to within ±0.1°C. In theory, measurements could be made up to the transition temperature of the Teflon™ fittings used to connect the cell to the rest of the apparatus.

Temperature Measurement.--The temperature of the reaction itself was measured by placing an RTD probe directly into the reaction cell using a 1/2 inch Teflon™ Swagelok™ Tee and appropriate reducing fittings to mate the probe to the cell while allowing the gases to escape to the measuring or exhaust lines. The Cole-Parmer Model P-08117-90 Probe and Thermometer Module 02155-54 were calibrated together at 0°C, 50°C, 100°C and 150°C to insure readings accurate to within ±0.1°C.

Injection of Samples into GC/MS.--There is a 1/8 inch stainless steel tube originating at the exit valve of the reaction cell connecting the cell to the 1.00 mL sample loop of the GC/MS. There is another inch stainless steel tube on the exhaust side of the 1.00 mL sample loop connecting with a vacuum pump. A valve has been placed in this line to isolate the vacuum pump from the sample loop line. When it is time to measure the concentrations of the reactants either before or after reaction, the following process is used. First a vacuum is pulled on the entire gas line from the closed valve at the exit outlet of the reaction cell through the sample loop to the vacuum pump. To admit a sample into the GC/MS, the valve at the vacuum pump is closed and then the valve to the cell is opened allowing the gases in the reaction cell to fill the 1.00 mL sample loop. Once this is done, the GC/MS program is started. After the sample in the 1.00 mL sample loop has been admitted into the GC/MS and the exit valve on the reaction cell is closed, the vacuum pump valve is again opened to evacuate the sample loop in preparation for the next sample.

Solenoid Valves Used to Control Gas Flows.--All the valves used to control the flow of gases through and around the reaction cell are two-way electronic solenoid valves with a 2.778 mm orifice. The Burkert 1/8 in. NPT Miniature Solenoid Valves are operated by a 24 VDC power supply through a series of miniature SPST toggle valves. With no power applied, these valves are closed and open upon application of +24 VDC to the coils. If the valves are left open for more than a very few minutes, there is considerable heating of the gases in contact with the valve housing. Therefore, some of the valves will be replaced in the future with valves that are normally open when there is no power to them in order to reduce heating effects from the valving system. Another feature to be implemented is a valve dri-

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ver that reduces current flow once the valve has been operated. Neptune Research and Development produce these CoolDrive™ Valve Drivers.

Low Pressure Mercury Vapor Lamp.--A low pressure mercury vapor lamp is used for producing the hydroxyl radicals necessary for reaction. The lamp is fabricated in the form of a flat coil of approximately 7.62 cm. It is powered by use of a 2 kV transformer powered directly from house 120 VAC having an SPST switch and fuse. The lamp produces a large amount of ozone in the laboratory when operated. Therefore, it has been placed in an acrylic box with a nitrogen purge to prevent the formation of ozone from atmospheric oxygen. The face of the box is open at the coil end of the lamp and the cell is mounted within 2 or 3 mm of the lamp.

Operation of the Apparatus.--A typical experiment is performed by first adjusting the flows from the sample container, oxygen tank and helium tank. In the measurements for cyclopropane we used 3.00 sccm for sample flow, 10.00 sccm for oxygen flow and 187.0 sccm for the helium saturated with water vapor flow. The thermostat circulator is adjusted to the desired temperature and the reaction cell is purged for 20 minutes. This amounts to five cell volumes sweeping through the cell to insure the cell is filled with the reactant gases at the proper concentration. Next, the cell inlet and outlet are closed for 4 minutes. The cell is opened to the evacuated sample loop line leading to the GC/MS. The unreacted sample and reference gases in the cell are measured with the GC/MS instrument, and the peak areas of each are recorded. The cell is again purged for 20 minutes and cell inlet and outlet valves are closed. The low pressure mercury vapor lamp is turned on so that hydroxyl radical production can take place. Usually, the lamp is on for 2 to 10 minutes. The reacted sample and reference concentrations are measured and recorded with the GC/MS instrument. After purging for 20 more minutes another "off

cycle" is carried out. Each time the cell is isolated the temperature is recorded at the beginning and end of the isolation period. The temperature is reported as the average temperature of all these measurements. This procedure continues until 5 measurements are made with times adjusted so that the amount of reaction occurring varies between 20 percent reacted to 80 percent reacted. This completes the rate measurement for one temperature.

Results and Discussion

We measured the rate of reaction for HFOC-134 (CHF_2OCHF_2) using FC-125 (CHF_2CF_3) as the reference. HFOC-134 is a product of commercial interest to DuPont Chemical Company for possible use as a refrigerant, foaming agent and/or degreasing solvent. The results are tabulated in Table 1 along with values obtained from previously published sources. The values obtained in our laboratory are quite close to those of which were measured at Jet Propulsion Laboratory (DeMore, 1997) also by the relative method. The other measurements were obtained using absolute methods (Garland et al., 1993). This comparison shows the difficulty of making absolute measurements that are reproducible.

Table 2 gives the results of our measurements along with those at Jet Propulsion Laboratory (DeMore, 1997), at Harvard (Donahue et al., 1998) and Dobe et al. (1992). The relative measurements at two different laboratories using two different reference materials again agree more closely than those obtained using absolute methods.

Conclusions

As the results tabulated in Table 1 and Table 2 show, the relative method of kinetic rate determinations is accurate and reproducible. The values we obtained for the rate con-

Table 1. Comparison of Results for Difluoromethoxydifluoromethane, HFOC-134

	A, s^{-1}	E/R , Kelvin	k (298 K), s^{-1}	Reference
Wilson (Wilson et al., 2000)	1.29×10^{-12}	1895	2.23×10^{-15}	FC-125
DeMore (DeMore and Bayes, 1999)	1.54×10^{-12}	1972	2.05×10^{-15}	CH_3CCl_3
Orkin (Orkin et al., 1994)	6.25×10^{-12}	1643	2.52×10^{-15}	Absolute
Garland (Garland et al.,1993)	5.68×10^{-13}	1588	2.76×10^{-15}	Absolute

Table 2. Comparison of Results for Cyclopropane

	A, s^{-1}	E/R , Kelvin	k (298 K), s^{-1}	Reference
Wilson (Wilson et al., 2000)	6.64×10^{-12}	1323	7.85×10^{-14}	Ethane
Wilson (Wilson et al., 2000)	6.85×10^{-12}	1376	6.68×10^{-14}	FC-152a
DeMore (DeMore and Bayes, 1999)	6.80×10^{-12}	1337	7.64×10^{-14}	Ethane
Donahue (Donahue et al., 1998)	1.63×10^{-12}	949	6.76×10^{-14}	Absolute
Dobe (Dobe et al., 1992)	3.96×10^{-12}	1089	1.03×10^{-13}	Absolute

stants and temperature dependencies of these two compounds agree quite well with similar measurements made at other laboratories. Having established our ability to make these kinds of measurements and having tested our apparatus, we will now begin to measure other compounds that are precursors to the tropospheric formation of ozone. The first compound to be measured will be isobutane using butane as a reference. These two compounds differ by the single tertiary hydrogen on isobutane. Knowledge of the rate of these compounds will allow us to make predictive statements as to the reactivity of primary versus tertiary hydrogens.

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