Rates of Reaction for Cyclopropane and Difluoromethoxydifluoromethane with Hydroxyl Radicals[†]

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The rates of reaction, Arrhenius preexponential factors, and activation energies of cyclopropane and difluoromethoxydifluoromethane, CHF_2OCHF_2 (HFOC-134), reacting with hydroxyl radical were measured by a relative method. Using ethane as the reference, eight measurements in the range from 25 to 186 °C yielded an Arrhenius fit of $k = (6.82 \pm 1.5) \times 10^{-12}e^{-(1335\pm90)/T}$ cm^3 $molecule^{-1}$ s^{-1} for the reaction of cyclopropane with hydroxyl radical. Measurements were repeated using CH_3CHF_2 (FC-152a) instead of ethane as the reference. Both measurements agreed within 3%. Nine measurements in the range from 0 to 191 °C were made of HFOC-134 using CF_3CHF_2 (FC-125) as the reference. The result was $k = (1.29 \pm 0.5) \times 10^{-12}e^{-(1895\pm100)/T}$ cm^3 $molecule^{-1}$ s^{-1} for HFOC-134. Preexponential factors for these two reactions are shown to be consistent with values predicted from a wide range of observed values for OH abstraction reactions. The rate constant results are compared to previously published values for these same compounds obtained by both relative and absolute methods.

Introduction

Rate constant measurements in chemical kinetics may be divided into absolute and relative methods. Absolute methods are the more fundamental and essential in determination of values for reaction rates. Disadvantages of absolute methods are that errors can arise due to factors such as adsorption on the surfaces of the reaction apparatus and impurities present in the reacting compounds. Relative rate measurements, on the other hand, have some advantages. Relative rate measurements can be made with less experimental difficulty, generally give better precision, and can be made faster. In the relative method, the sample compound is measured by mixing it with a reference compound whose rate is traceable to an absolute value. Since sample and reference substances are in the same container and are exposed during the measurement process to virtually identical conditions, errors tend to cancel. Relative methods are important because they can be used to verify absolute values. If the rate of a sample is determined twice by means of the relative method using two different reference compounds and both measurements yield identical results, there is strong implication that the absolute values for the two reference compounds must be accurate. If different results are obtained, either the measurement was flawed or the absolute rates for one or both reference compounds could be in error.

As discussed in ref 1, there is frequently a discrepancy between absolute and relative rate constant measurements at temperatures below about 298 K, with the absolute measurements showing a tendency to have upward curvature in the Arrhenius plots, compared to the results from relative rate measurements. In this work we present results of kinetics studies of the reaction of hydroxyl radicals with two substances, cyclopropane and difluoromethoxydifluoromethane, CHF_2-$OCHF_2$ (HFOC-134). These compounds are examples in which previous kinetics studies[1−4] show the low-temperature discrepancy. Furthermore, the compound cyclopropane is of significance for theoretical considerations because of its cyclic structure with strong C−H bonds. It is of interest to determine to what extent the kinetics parameters reflect this difference from other alkanes and cycloalkanes. The compound CHF_2OCHF_2 has practical importance because of its intended use as an industrial solvent, degreasing agent, or foaming agent. Previously published rate studies[5−7] show differences in rate behavior at lower temperatures depending on the experimental technique. Temperatures below 298 K are important for determining the lifetime of the compound in the atmosphere.

Experimental Section

The rates of reaction of hydroxyl radicals with cyclopropane and CHF_2OCHF_2 (HFOC-134) were measured repetitively at various constant temperatures. Experimental methods were similar to those published in several recent papers.[8−11] We used a relative method in which each compound studied was measured against a reference compound whose rate constant and temperature dependence for the reaction with OH had been reliably established and was traceable to an absolute measurement. The gaseous sample and reference reactants were mixed together in a quartz cell and were exposed to exactly the same conditions for each measurement. In this way errors, such as the presence of impurities and adsorption of reacting gases on the walls of the apparatus, tended to cancel. The hydroxyl radicals were generated by photolyzing water vapor that was present in the sample mixture. Photolysis was accomplished using 185 nm radiation from a low-pressure mercury vapor lamp. The hydroxyl radicals generated by photolysis abstract hydrogen atoms from the reactant molecules, producing water molecules and radicals:

$$RH + \bullet OH \rightarrow R\bullet + H_2O \qquad (1)$$

The measurements were carried out in a stopped-flow mode at ambient pressure using helium as the diluent. Reaction mixtures containing approximately 20 Torr each of sample and reference gas were prepared in 22 L containers and the

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containers were filled to 30 psi with helium. The reaction mixture was further diluted by using flow controllers to mix the sample, flowing at 3.00 sccm; with oxygen, flowing at 10.0 sccm; and helium, flowing at 187 sccm (sccm = standard cubic centimeters per minute) into the quartz reaction vessel. The helium flow went through a bubbler filled with water in order to produce water vapor in the final reaction mixture. Thus, the reaction cell contained (1−3) × 10^{15} molecules each of sample and reference per cubic centimeter, 5−15 × 10^{17} molecules oxygen per cubic centimeter, and (2−5) × 10^{17} molecules of water per cubic centimeter. Oxygen was needed to combine with the radicals produced in the reaction to prevent possible reactant regeneration by radical disproportionation reactions. In addition, oxygen reacts with the hydrogen atoms formed from the photolysis of water vapor to make hydroperoxyl radicals. Hydroperoxyl radicals are slower reacting than hydroxyl radicals and do not contribute to reactant loss.

The cylindrical reaction cells were fabricated from quartz in order to pass 185 nm radiation from the mercury vapor lamp. The dimensions of the cylindrical cells are approximately 5 cm in diameter by 10 cm long. One cell was jacketed and silicon oil used as the heat transfer agent to control its temperature in the range of 5−140 °C by means of a temperature-controlled circulating bath. For measurements above 140 °C, the temperature was controlled by an electrical rope heater wrapped around a bare quartz cell. A platinum RTD sensor inserted between the heater and the cell was used to regulate the temperature by means of a heater controller. Temperatures were measured in each cell by inserting a platinum RTD sensor directly into the reaction portion of the cell. The RTD/meter combinations used display a resolution of 0.1 °C with an accuracy of ±0.5 °C or better, as established by calibration with standards traceable to NIST. Small variations in temperature, on the order of a few tenths of a degree, during the course of each measurement period were recorded, and the average temperature was used for the experiment.

The concentrations of sample and reference in the reaction mixtures before and after reaction were measured by use of a Shimadzu GCMS QP-5000 gas chromatograph equipped with a quadrupole mass spectrometer detector. A 105 m by 0.25 mm i.d., 1.0 μm df, RTx-200 capillary column from Restek Corp. gave baseline separation of the reference and sample peaks in all cases. The column was operated isothermally at temperatures slightly above ambient. Even though the sample loop mixture contained water vapor, oxygen, sample gas, reference gas, reaction product gases, and helium, accurate measurement of the sample and reference peak areas was obtained by single ion monitoring of the intensity of the mass spectrum parent peak of sample and reference as each eluted from the column. Peak areas were calculated using Shimadzu Class 5000, version 2.00 software. The mass-to-charge ratios, *m*/*z*, used to monitor the molecules in the mass spectrometer detector for this study were 41 for cyclopropane, 30 for ethane, 51 for FC-152a (1,1-difluoroethane), 101 and 51 for FC-125 (pentafluoroethane), and 51 and 117 for HFOC-134 (difluoromethoxydifluoromethane).

After the temperature of the reaction cell was set to the desired temperature and thermal equilibrium achieved, the cell was purged with the reaction mixture for approximately 20 min. Then the cell's inlet and exit valves were closed for a few minutes and a sample was injected into the 1.00 mL sample loop of the GC/MS. This was accomplished by evacuating the sample loop, closing the valve between the vacuum pump and sample loop, and then opening the valve between the reaction cell and sample loop. In this way, a small portion of reaction mixture filled the sample loop. The contents of the sample looped was injected onto the chromatographic column and a chromatogram obtained. The cell was purged for 20 min between each reading. This amounted to flushing the cell with 5 volumes of reaction mixture. The ratio of the concentration of each gas before reaction, C_0, divided by the concentration, C, of the gas after reaction was calculated, and depletion factors, DF, were tabulated according to eq 2: At each temperature,

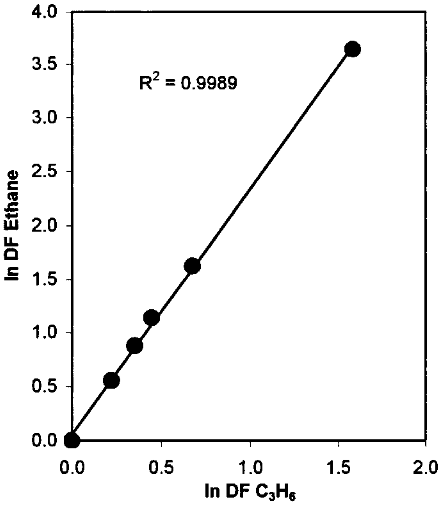

Figure 1. Natural logarithms of depletion factors for cyclopropane plotted against natural logarithms of depletion factors of ethane reference for an experiment at 459 K, showing excellent linearity over a wide range of reaction.

$$\mathrm{DF} = \frac{C_0}{C} \tag{2}$$

approximately five depletion factor measurements were made. In each measurement, the mercury vapor lamp was turned on for different periods of time in order to vary the amounts of sample and reference reacted. Photolysis times were normally adjusted in order to keep the amount of reaction between 20% and 80%. These amounts of reaction correspond to depletion factors of 1.25−5.00. Plots of the natural logarithms of the depletion factors of sample and reference were prepared to verify a linear relationship at each temperature measured. The rate constant ratios were calculated according to the following expression:

$$\frac{k_{\mathrm{sample}}}{k_{\mathrm{reference}}} = \frac{\ln \mathrm{DF}_{\mathrm{sample}}}{\ln \mathrm{DF}_{\mathrm{reference}}} \tag{3}$$

According to eq 3, the right-hand side of the equation should remain at a constant value for a particular temperature, no matter how much material was reacted. We averaged the five ratios of the logarithm depletion factors obtained at each temperature and calculated the standard deviation for the set of measurements.

Results

Figure 1 is a graph of data according to eq 3 for one case in which the reactant conversions were very large. This graph exhibits a highly linear relationship, even though the amount of reaction for the ethane reference varied between 42% and 97.5% while the cyclopropane amount reacted varied between 19% and 80%. In most experiments the conversions were not so large, but in every case excellent linearity was observed.

Table 1 is a summary of all the ratio measurements made. The rates and temperature dependencies of cyclopropane were

TABLE 1: Rate Constant Ratios, $k_{\mathrm{sample}}/k_{\mathrm{reference}}$, as a Function of Temperature

T, K	C_3H_6/C_2H_6	*T*, K	C_3H_6/CH_3CHF_2	*T*, K	CHF_2OCHF_2/CF_3CHF_2
298.3 ± 0.1	0.3017 ± 0.01	271.5 ± 0.3	2.129 ± 0.01	273.0 ± 0.5	1.129 ± 0.02
298.3 ± 0.1	0.3090 ± 0.004	278.3 ± 0.1	2.158 ± 0.1	298.7 ± 0.1	1.163 ± 0.03
323.4 ± 0.2	0.3254 ± 0.003	298.2 ± 0.1	2.121 ± 0.02	322.5 ± 0.2	1.264 ± 0.009
373.1 ± 0.3	0.3480 ± 0.004	304.3 ± 0.0	2.190 ± 0.02	348.9 ± 0.3	1.333 ± 0.01
401.3 ± 2	0.3760 ± 0.003	324.5 ± 0.2	2.181 ± 0.06	370.1 ± 0.5	1.375 ± 0.007
415.6 ± 2	0.3874 ± 0.003	348.7 ± 0.2	2.302 ± 0.05	400.8 ± 0.4	1.422 ± 0.02
444.9 ± 2	0.3969 ± 0.008	372.7 ± 0.2	2.292 ± 0.03	427.2 ± 2	1.448 ± 0.03
458.7 ± 2	0.4045 ± 0.002	399.3 ± 0.2	2.377 ± 0.05	447.7 ± 2	1.476 ± 0.01
		408.2 ± 2	2.454 ± 0.1	464.5 ± 1	1.496 ± 0.02
		424.7 ± 2	2.454 ± 0.07		
		446.6 ± 2	2.416 ± 0.1		
		463.4 ± 1.3	2.580 ± 0.1		

TABLE 2: Rate Constants for the Reaction of OH with the Reference Compounds Used in These Studies

ref compd	*A*-factor[a] (cm^3/molecule s)	*E*/*R* (K)	k_{298K} (cm^3/molecule s)	source
CH_3CH_3	$(1.00 \pm 0.15) \times 10^{-11}$	1094 ± 75	2.54×10^{-13}	Atkinson
CH_3CHF_2 (FC-152a)	$(2.4 \pm 0.5) \times 10^{-12}$	1260 ± 100	3.5×10^{-14}	JPL Publication 97-4
CF_3CHF_2 (FC-125)	$(5.6 \pm 2.0) \times 10^{-13}$	1700 ± 100	1.9×10^{-15}	JPL Publication 97-4

[a] Uncertainties in the Arrhenius parameters are our estimates.

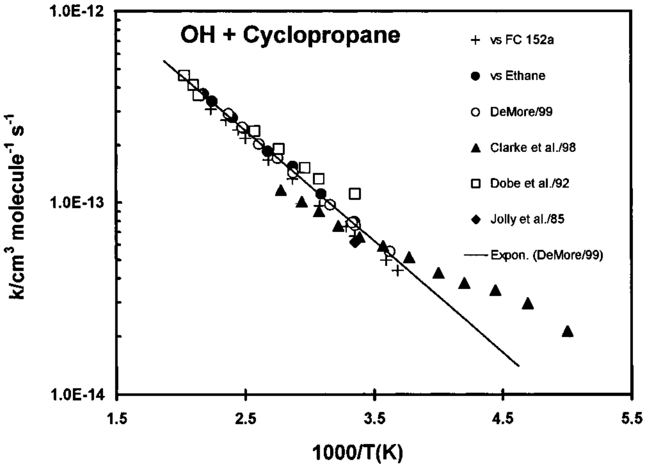

Figure 2. Arrhenius plot for the reaction of cyclopropane with hydroxyl radical. The exponential fit shown used the data set by DeMore and Bayes in ref 1.

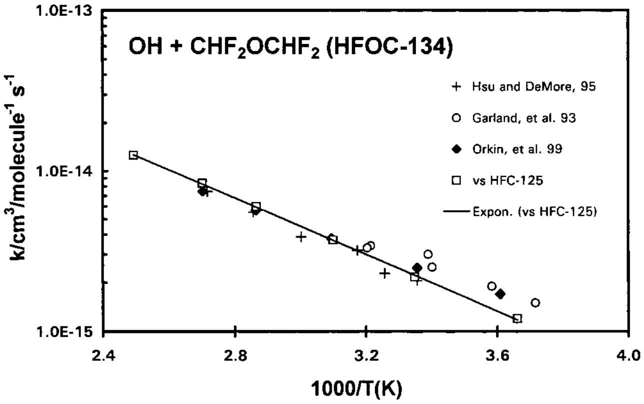

Figure 3. Arrhenius plot for the reaction of HFOC-134 with hydroxyl radical. The exponential fit shown used the data found in Table 1.

determined against two reference standards, CH_3CH_3 and CH_3CHF_2 (FC-152a). The rates and temperature dependencies of CHF_2OCHF_2 (HFOC-134) were determined using CF_3CHF_2 (FC-125) as the reference. The values in Table 1 are averaged ratios of the natural logarithms of the depletion factors at each temperature according to eq 3. The standard deviations of the measurements are significantly smaller using GC/MS single ion monitoring as compared with our previous method using GC with an FID detector.[9]

Table 2 lists the Arrhenius preexponential values (*A*), activation temperatures (*E*/*R*) and rate constants at 298 K for the three compounds used as reference standards. Combining these data with the ratio results of Table 1, the rate constants for cyclopropane and CHF_2OCHF_2 (HFOC-134) were calculated at each temperature. The results are plotted in Figures 2 and 3, and previous literature data are included for comparison. The derived specific rate constants, Arrhenius *A*-factors, and activation energies are listed in Table 3 along with results published by others.

Discussion

Figure 2 is a summary of recent results published for the reaction of cyclopropane with hydroxyl radicals using both absolute and relative methods. Our results, for both ethane and FC-152a as reference reactants, fall generally in the range of the previously published values.[1-4] They agree most closely with the data of DeMore and Bayes,[1] which was a relative rate experiment vs ethane. The relative rate results are more linear in the Arrhenius plot, and do not show the tendency toward upward curvature at lower temperatures that is characteristic of the absolute measurements. Considering that in our work two separate reference reactants give the same result, along with the fact that these experiments are perhaps less susceptible to interference than the absolute measurements, we conclude that the lack of linearity in Arrhenius plots of absolute rate data is probably due to unrecognized errors and does not represent the true temperature dependence of the rate constants.

In previous work[9] it was pointed out that preexponential factors (normalized to a per-hydrogen basis) from a large body of data on OH abstraction reactions from C−H bonds in different compounds closely follow a dependence on the magnitude of the specific rate constant at 298 K but are otherwise independent of the nature of the substrate. That relation was given as in eq 4, where *n* is the number of H-atoms in the molecule:

$$\log\left(\frac{A}{n}\right) = 0.17 \log\left(\frac{k_{298}}{n}\right) - 9.61 \qquad (4)$$

The expression applies only to molecules in which all H-atoms

TABLE 3: Derived Arrhenius Parameters for the Reaction of OH with Cyclopropane and CHF_2OCHF_2 (HFOC-134) and Comparison with Published Values[a]

substance	*A*-factor (cm^3/molecule s)	*E*/*R* (K)	k_{298K} (cm^3/molecule s)	source and method[b]
cyclopropane	$(6.82 \pm 1.5) \times 10^{-12}$	1335 ± 90	7.73×10^{-14}	this work, RR vs ethane
	$(7.68 \pm 2.0) \times 10^{-12}$	1376 ± 100	7.59×10^{-14}	this work, RR vs FC-152a
	5.15×10^{-12}	1255	7.64×10^{-14}	DeMore and Bayes,[1] RR vs ethane
	8.11×10^{-13}	723	7.17×10^{-14}	Clarke et al.,[2] HPFS-LIF
	2.69×10^{-12}	968	10.4×10^{-14}	Dobe et al.,[3] LPRF
CHF_2OCHF_2	$(1.29 \pm 0.5) \times 10^{-12}$	1895 ± 100	2.23×10^{-15}	this work, RR vs FC-125
	1.54×10^{-12}	1972	2.06×10^{-15}	Hsu and DeMore,[5] RR vs CH_3CCl_3
	6.25×10^{-13}	1643	2.52×10^{-15}	Orkin et al.,[7] FPRF
	5.68×10^{-13}	1588	2.75×10^{-15}	Garland et al.,[6] FP-LIF

[a] Uncertainties in the derived kinetics parameters include the estimated errors of the reference parameters shown in Table 2. [b] RR = relative rate; HPFS−LIF = high-pressure flow system−laser-induced fluorescence; LP−RF = laser photolysis−resonance fluorescence; FP−RF = flash photolysis−resonance fluorescence; FP−LIF = flash photolysis−laser-induced fluorescence.

are equivalent, such as ethane, HFOC-134, or cyclopropane. For more complex molecules, each type of H-atom must be considered separately.

On the basis of eq 4, the expected *A*-factors for cyclopropane and HFOC-134 are 6.4×10^{-12} and 1.4×10^{-12} cm^3 molecule^{-1} s^{-1}, respectively. As seen in Table 3, these predictions are in excellent agreement with our measured *A*-factors, thus confirming that these two reactions follow the normal pattern in this regard.

Figure 3 summarizes all results published for the reaction of CHF_2OCHF_2 with hydroxyl radicals by both absolute and relative methods. Our results agree quite well with those of DeMore and Hsu,[5] who used CH_3CCl_3 as the reference reactant. One again, the relative rate data show less of an upward drift at lower temperatures compared to the absolute data.

We are now working on measuring OH abstraction rate constants for a wide range of alkanes and cycloalkanes, with emphasis on obtaining data at even lower temperatures. With the results thus far obtained and the new values gathered, predictive rules for estimating rate data can be improved, and criteria for the evaluation of rate constant parameters can be further tested.

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