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Rate Constants for Reaction of CH_2FCH_2F (HFC-152) and CH_3CHF_2 (HFC-152a) with Hydroxyl Radicals

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The rates of reaction, Arrhenius preexponential factors, and activation energies of CH_2FCH_2F (HFC-152) and CH_3CHF_2 (HFC-152a) for the abstraction reaction with hydroxyl radical were measured by a relative rate method. Temperature ranges were 287−409 and 286−403 K, respectively. Reference compounds for both reactants were ethane ($k = 1.00 \times 10^{-11}\ e^{-1094/T}$ cm^3 molec.$^{-1}$ s^{-1}) and cyclopropane ($k = 7.28 \times 10^{-12}\ e^{-1356/T}$ cm^3 molec.$^{-1}$ s^{-1}). Also, the JPL 97−4 recommendation for HFC-152a ($k = 2.4 \times 10^{-12}\ e^{-1260/T}$ cm^3 molec.$^{-1}$ s^{-1}) was used as a reference for HFC-152 vs 152a experiments. For HFC-152, the combined results yielded an Arrhenius expression of $k = 3.55 \times 10^{-12}\ e^{-1084/T}$ cm^3 molec^{-1} s^{-1}. The result for HFC-152a was $k = 1.86 \times 10^{-12}\ e^{-1183/T}$ cm^3 molec^{-1} s^{-1}. For both reactants, uncertainties in k(298 K) and E/R are believed to be less than 10% and 100 K, respectively. The experimental results are compared with predicted values based on previously observed group effects as well as the dependence of preexponential factors on the magnitude of the rate constant. The results are also compared to previously published values for these same compounds obtained by absolute methods.

Introduction

There is now an extensive body of data for the rates of hydrogen abstraction by the hydroxyl radical from atmospheric pollutants such as hydrocarbons and halocarbons.[1,6] The results have revealed several relationships among these rate constants previously obscured by lack of data or by inaccurate data. These relationships pertain primarily to the effects of different substituent groups on the rate constants[4,10] and the relationship between the preexponential factors and the magnitude of the rate constant.[7] Such criteria permit the a priori estimation of both the 298 K rate constants and temperature dependence of the reactions with high reliability.

The absolute rate constant for the reaction of hydroxyl radical with CH_2FCH_2F (HFC-152) has been measured at 298 K by Martin and Paraskevopolous[14] and by Kozlov et al.[11] in the temperature range 210−480 K. The former result is about 10% higher than the Kozlov et al.value at 298 K. Using a relative rate method, we have now measured the rate constant in the temperature range 287−409 K. Our data, based on a different experimental technique, aid in resolving the slight discrepancy between the previous results at 298 K. The data also serve as an excellent source for calibration of the CH_2F group effect, as well as a further test of the predicted temperature dependence based on k(298 K). The rate constant for hydrogen abstraction from HFC-152a is relatively well-known, but we have nevertheless conducted further measurements on that compound as a consistency test for our use of the relative rate method.

Experimental Section

The 1,2-difluoroethane, assay 97% min., was purchased from SynQuest Labs, Inc. The 1,1-difluoroethane, assay 99% min., was obtained from PCR Inc. The cyclopropane, assay 99+%, was purchased from Aldrich Chemical Co., and the ethane, assay 99%, came from Scott Specialty Chemicals.

Experimental methods were similar to those published in several recent papers.[5,7,16] Hydroxyl radicals were generated by photolyzing water vapor in the sample mixture using 185 nm radiation from a low-pressure mercury vapor lamp

$$H_2O + h\nu(185\text{ nm}) \rightarrow H + OH \qquad (1)$$

The hydroxyl radicals abstract hydrogen atoms from the reactant molecules producing water molecules and radicals

$$RH + OH \rightarrow R + H_2O \qquad (2)$$

Mixtures were prepared in a flow system which exhausted to laboratory pressure, using helium as the diluent and as the carrier gas, with flow controllers to establish the concentrations. The measurements were carried out in a stopped-flow mode. Oxygen was added to the flow to prevent possible reactant regeneration by radical disproportionation reactions. Oxygen also reacts with the hydrogen atoms formed from the photolysis of water vapor to make hydroperoxyl radicals, which do not contribute to reactant loss. The helium flow passed through a bubbler filled with water in order to produce water vapor in the final reaction mixture. The final reaction cell contained $(1-3) \times 10^{15}$ molecule cm^{-3} each of sample and reference, $(5-15) \times 10^{17}$ molecules cm^{-3} oxygen, and $(2-5) \times 10^{17}$ molecules cm^{-3} of water. The cylindrical reaction cell was made of quartz in order to pass

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TABLE 1: Rate Constants for the Reference Compounds Used in This Work[a]

reference compound	*A* factor (cm^3/molec. s)	*E*/*R* (K)	*k*(298 K) (cm^3/molec. s)	source
ethane	$(1.00 \pm 0.15) \times 10^{-11}$	1094 ± 75	2.54×10^{-13}	Atkinson (1997)
cyclopropane	$(7.28 \pm 0.5) \times 10^{-12}$	1356 ± 75	7.69×10^{-14}	Wilson et al. (2001)
CH_3CHF_2 (152a)	$(2.4 \pm 0.5) \times 10^{-12}$	1260 ± 100	3.50×10^{-14}	JPL Publication 97-4[b]

[a] Uncertainties in the Arrhenius parameters are our estimates. [b] We use the JPL recommendation for this rate constant rather than our new value to avoid any circularity in the reference basis.

185 nm radiation from the mercury vapor lamp. The dimensions of the cylindrical cell are approximately 5 cm in diameter by 10 cm long. The cell was jacketed and silicon oil used as the heat transfer agent to control its temperature by means of a temperature-controlled circulating bath. Temperatures were measured 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, of 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 data analysis.

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 Restek Corp. RTx-200 column, 105 m by 0.25 mm i.d.,1.0 micrometer film thickness, was employed for all separations. Samples were injected into the gas chromatograph by means of a programmed sample valve using a 1.00 mL sample loop. The HFC-152 measurements were made under isothermal column conditions at 35 °C. The column flow was adjusted in the range of 0.7−1.0 mL/min and a split ratio of 15 used. Single ion monitoring was employed with the detector at 1.15 kV. The M/Z fragments measured were 29.00 for ethane, 33.00 for HFC-152, 42.00 for cyclopropane, and 51.00 for HFC-152a. Retention times were adjusted to average approximately 12−13 min and produce baseline separation between peaks. Total ion monitoring was used for the HFC-152a vs cyclopropane and ethane measurements, with the column operating at 55 °C and remaining conditions being similar to that for HFC-152.

The ratio of the concentration before reaction, C_0, divided by the concentration, C, after reaction was calculated, and depletion factors, DF, were tabulated according to eq 3

$$DF = \frac{C_0}{C} \tag{3}$$

At each temperature, approximately 5 depletion factor measurements were made. Photolysis times were normally adjusted in order to keep the reactant conversion between 20% and 80%. Plots of the natural logarithms of the depletion factors of sample vs reference compounds were prepared to verify a linear relationship at each temperature measured. The rate constant ratios were calculated according to the following expression:

$$\frac{k_{\mathrm{sample}}}{k_{\mathrm{reference}}} = \frac{\ln DF_{\mathrm{sample}}}{\ln DF_{\mathrm{reference}}} \tag{4}$$

Table 1 lists the Arrhenius preexponential values (*A*), activation temperatures (*E*/*R*) and rate constants at 298 K for the reference standards.

Rate Constant Estimations

In this method, each reactive site is considered as a methane derivative, and the reactivity of the C−H bonds at that site is determined by the attached groups which replaced the H atoms in methane. The total rate constant is then obtained as the sum of the contributions for each C−H bond in the molecule. The logarithm (base 10) of the rate constant (per H-atom at 298 K) at each site is given by

TABLE 2: Current Best Fits for the *G* Values of Various Groups and the Multipliers α and *β*

group	*G* fit	group	*G* fit
F	0.62	CF_2Cl	−0.19
2F	0.37	F,Cl	1.00
CF_3	−0.52	CCl_3	0.27
CH_2F	0.60	$CFCl_2$	0.08
CHF_2	−0.25	Br	0.82
CH_3	1.29	2Br	1.61
Cl	0.81	Br,Cl	1.53
2Cl	1.65	F,Br	1.2
CH_2Cl	0.79	CN	0.52
CH_2Br	0.95	first multiplier	0.91
$CHCl_2$	0.60	second multiplier	0.31
CHFCl	0.05		

$$\log(k/n) = \log(k/n(CH_4)) + G_1 + \alpha G_2 + \beta G_3 \tag{5}$$

Equation 5 yields an estimate of the rate constant at 298 K. The quantity $\log(k/n(CH_4))$ is the logarithm of the CH_4 rate constant *per H atom*, i.e., one-fourth the total rate constant, and is equal to −14.79. Here we have taken the total methane rate constant as 6.5×10^{-15} $cm^3/molec.^{-1}$ s^{-1} at 298 K.[6] The *G* terms are the contributions for the various groups, which for HFC-152 are F and CH_2F. For HFC-152a the groups are CH_3, CHF_2, and 2F. The terms α and *β* are second and third group multipliers, respectively, and are used to reduce the *G* terms when there is more than one group attached at the reaction site. We note that in previous applications of the method only the third group multiplier was used, because the second group multiplier approximates unity. However, the present calibration includes the second group multiplier. These corrections are necessary because of the dilution effect as groups are added to progressively larger molecules. In the event of significant dependence on the choice of which groups are considered the first, second, or third, then an average of all combinations can be used. The *G* terms and the multipliers are determined by a calibration which is based on a large number of well-determined rate constants at 298 K.[4]

Previously, we were able to estimate the HFC-152 rate constant with only modest reliability, because there was no dependable calibration molecule for the CH_2F group. Compounds such as CH_3CH_2F (HFC-161) contain the group, but the rate constant is not very sensitive to the effect of the CH_2F group. The present value of *k*(298 K) for HFC-152 has been used to obtain a more reliable calibration of that group effect. The current set of *G* values and multipliers are listed in Table 2.

To determine the *E*/*R*, or activation temperature of the reaction, we use the previously described eq 6,[7] which relates the *A* factor to the magnitude of the rate constant, each

TABLE 3: Rate Constant Ratios Measured for HFC-152[a]

T (K)	HFC-152/ ethane	T (K)	HFC-152/ c-C_3H_6	T (K)	HFC-152/ HFC-152a
293	0.374 ± 0.029	287	$1.263 + 0.027$	292	2.680 ± 0.017
319	0.352 ± 0.011	300	1.264 ± 0.018	311	2.600 ± 0.028
322	0.363 ± 0.013	324	1.170 ± 0.011	360	2.485 ± 0.031
339	0.360 ± 0.006	349	1.049 ± 0.010	393	2.353 ± 0.071
355	0.358 ± 0.003	373	1.046 ± 0.005		
368	0.353 ± 0.003	409	0.980 ± 0.005		
397	0.357 ± 0.010				

[a] Errors are one standard deviation.

TABLE 4: Rate Constant Ratios Measured for HFC-152a[a]

T (K)	HFC-152a/ethane	T (K)	HFC-152a/c-C_3H_6
286	0.141 ± 0.002	290	0.458 ± 0.024
299	0.138 ± 0.005	313	0.438 ± 0.012
324	0.146 ± 0.010	332	0.406 ± 0.017
343	0.144 ± 0.013	353	0.428 ± 0.010
373	0.145 ± 0.003	372	0.404 ± 0.027
403	0.149 ± 0.005	391	0.410 ± 0.003

[a] Errors are one standard deviation.

normalized to a per-hydrogen basis

$$\log(A/n) = 0.17 \log(k/n) - 9.59 \tag{6}$$

Equation 6 is slightly changed from the original, because the calibration now includes our HFC-152 data. The E/R value is then calculated from the expression

$$E/R = -298 \ln(k/A) \tag{7}$$

Results

Relative Rate Measurements. Table 3 is a summary of the ratios measured for HFC-152 vs the reference compounds ethane, cyclopropane, and HFC-152a. Table 4 shows similar data for 152a vs the reference compounds ethane and cyclopropane. The values in Tables 3 and 4 are averaged ratios of the natural logarithms of the depletion factors at each temperature, according to eq 4.

Combining data from Tables 3 and 4 with the reference rate constants of Table 1, the results for HFC-152 and HFC 152a were calculated at each temperature. The results are plotted in Figures 1 and 2, which include recent literature data for comparison. The derived rate constants, Arrhenius A factors, and activation energies are listed in Table 5, along with previous literature results.

For relative rate measurements, the best indication of experimental accuracy is the agreement between results using independent, well-established reference rate constants. For both HFC-152 and 152a, the k(298 K) values obtained from different reference compounds are identical within a few percent and agree well with the recent absolute measurements. The E/R values for HFC-152 from different references agree within 75 K, and those for HFC-152a are within 80 K. As a conservative estimate of accuracy, we consider that the uncertainties in k(298 K) and the E/R values are 10% and ±100 K, respectively. These uncertainties encompass the recent absolute data as well, for the temperature range of our experiments.

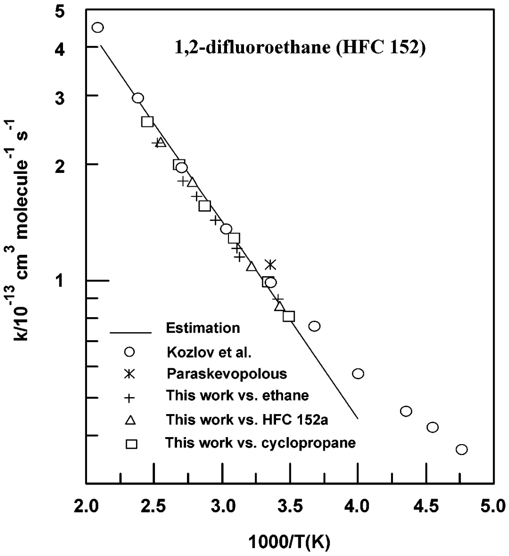

Figure 1. Arrhenius plot of the rate constants calculated for HFC-152 from the ratio data in Table 3 for the reference gases ethane, cyclopropane, and HFC-152a, combined with the values of the reference rate constants which were calculated at each temperature using the parameters given in Table 1. Also included is the Arrhenius line obtained from the estimation method, normalized to our experimental k(298 K). Previous literature data by absolute methods are included for comparison.

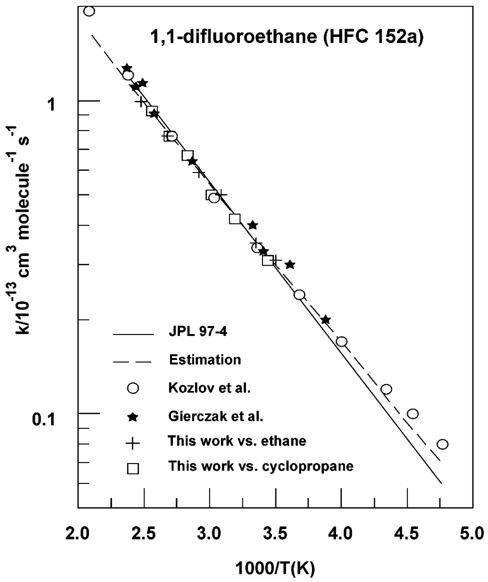

Figure 2. Arrhenius plot of the rate constants calculated for HFC-152a from the ratio data in Table 4 for the reference gases ethane and cyclopropane, combined with the values of the reference rate constants which were calculated at each temperature using the parameters given in Table 1. The nonlinear temperature dependence predicted by the estimation method is represented by the dashed line. Previous literature data by absolute measurements are included also for comparison.

Estimation of Arrhenius Parameters. For HFC-152a, we first estimate the contribution from the CH_3 site. Using eqs 5 and 6, with $n = 3$ and $G(CHF_2) = -0.25$, we find k(298 K) at that site to be 2.74×10^{-15} cm^3/molec.$^{-1}$ s^{-1}, with an A factor of 2.14×10^{-12} cm^3/molec.$^{-1}$ s^{-1}. The corresponding E/R, from eq 7, is 1985 K. The contribution from the CHF_2 site is best calculated by taking the difference between the observed total k(298 K) and the contribution from the CH_3 site. This is because estimations of the reactivity of sites containing two fluorine atoms are not very accurate, because of the unique nonlinear behavior of fluorine atoms as group constituents.[4] Using this approach, we find k(298 K) for the CHF_2 group to be $(3.52 \times 10^{-14} - 2.74 \times 10^{-15}) = 3.25 \times 10^{-14}$ cm^3/molec.$^{-1}$ s^{-1}, with $A = 1.31 \times 10^{-12}$ cm^3/molec.$^{-1}$ s^{-1} and $E/R = 1102$ K. The total rate constant is thus the sum of the rate constants for the two reactive sites in the molecule. The estimated total rate is shown in Figure 2, to compare the predicted temperature

TABLE 5: Derived Arrhenius Parameters for the Reaction of OH with CH_2FCH_2F (HFC-152) and CH_3CHF_2 (HFC-152a) and Comparison with Published Values[a,b,c]

compound	*A* factor (cm^3/molec. s)	*E*/*R* (K)	*k*(298 K) (cm^3/molec. s)	reference
CH_2FCH_2F (152)	3.14×10^{-12}	1049	9.3×10^{-14}	this work, vs ethane
	3.70×10^{-12}	1091	9.5×10^{-14}	this work, vs cyclopropane
	3.99×10^{-12}	1120	9.3×10^{-14}	this work, vs HFC-152a
	3.55×10^{-12}	1084	9.3×10^{-14}	this work, fit to all data
	3.37×10^{-12}	1043	1.0×10^{-13}	Kozlov et al. (2003)
	–	–	1.1×10^{-13}	Martin and Paraskevopolous (1983)
CH_3CHF_2 (152a)	1.71×10^{-12}	1152	3.6×10^{-14}	this work, vs ethane
	2.13×10^{-12}	1231	3.4×10^{-14}	this work, vs cyclopropane
	1.86×10^{-12}	1183	3.5×10^{-14}	this work, fit to all data
	2.10×10^{-12}	1198	3.8×10^{-14}	Gierczak et al. (1991)
	1.90×10^{-12}	1221	3.2×10^{-14}	Hsu and DeMore (1995) vs methane
	2.80×10^{-12}	1330	3.2×10^{-14}	Hsu and DeMore (1995) vs CH_3CCl_3
	2.30×10^{-12}	1252	3.4×10^{-14}	Kozlov et al. (2002)
	8.1×10^{-13}	886	4.1×10^{-14}	Liu et al. (1990)
			3.1×10^{-14}	Howard and Evenson, 296 K (1976)
	1.22×10^{-12}	1009	4.1×10^{-14}	Brown et al. (1990)
	1.78×10^{-12}	1098	4.5×10^{-14}	Nielson (1991)

[a] Arrhenius parameters and k(298 K) are from our fits to the reported data, and are not necessarily identical to those reported by the authors. [b] Fits are only for data above 272 K, because at lower temperatures some literature data are not well represented by the 2-parameter Arrhenius expression. [c] See text above for error estimates for our data.

TABLE 6: Comparison of Estimated Arrhenius Parameters for HFCs 152 and 152a with Those Obtained by the Method of Kwok and Atkinson

compound	*A* factor[a] (cm^3/molec. s)	*E*/*R*[a] (K)	*k*(298 K) (cm^3/molec. s)	source
CH_2FCH_2F (152)	4.95×10^{-12}	1183	9.3×10^{-14}[b]	this work
	7.7×10^{-12}	1272	1.1×10^{-13}	Kwok and Atkinson[12]
	3.55×10^{-12}	1084	9.3×10^{-14}	experimental
CH_3CHF_2 (152a)	1.95×10^{-12}	1197	3.5×10^{-14}[b]	this work
	5.4×10^{-12}	1500	3.5×10^{-14}	Kwok and Atkinson[12]
	1.86×10^{-12}	1183	3.5×10^{-14}	experimental

[a] From Arrhenius fits in the temperature range of our experiments, 287–409 K. [b] *k*(298 K) fit to our experimental *k*(298 K); not an estimation result.

dependence with the observed behavior. An Arrhenius fit to these data over the temperature range of our experiments, 287–409 K, yields the rate expression $k = 1.95 \times 10^{-12}\ e^{-1197/T,}$ essentially identical to the experimental temperature dependence. The predicted Arrhenius behavior shown in Figure 2 is in good agreement with the slight curvature observed by Kozlov et al. in the low-temperature range.

For HFC-152, the experimental value of *k*(298 K) is 9.36×10^{-14} cm^3/molec.$^{-1}$ s^{-1}, with four equivalent reaction sites. From eqs 6 and 7, with $n = 4$, we obtain the rate expression $k = 4.95 \times 10^{-12}\ e^{-1183/T}$ cm^3/molec.$^{-1}$ s^{-1}. In this case, both the *A* factor and *E*/*R* are slightly higher than the experimental values, although not outside the mutual uncertainties (see Figure 1).

Kwok and Atkinson[12] previously put forward an estimation method to predict rate constants for hydrogen abstraction by hydroxyl radicals from a wide variety of compounds. Their method is similar in that group values are employed, but a somewhat different approach is used for obtaining the temperature dependence. The results from their method for the present compounds in the temperature range of our experiments are shown in Table 6 and are compared with the present estimations.

In each case, their method yields excellent estimates for *k*(298 K), with Arrhenius parameters that are slightly higher than those observed experimentally, and also higher than those predicted by our method.

Discussion

As seen in Table 5 and Figure 1, the agreement for HFC-152 between the present relative rate measurements and the absolute data of Kozlov et al. is excellent in the temperature range covered by both experiments, 287–409 K. Because of the slowness of the reaction, combined with the necessity to use a less efficient method for OH generation below room temperature (photolysis of $N_2O/H_2/O_2$ mixtures), we have been unable to examine the behavior at those low temperatures where Kozlov et al. observed a marked departure from linearity in the Arrhenius plot. Because there is only one kind of C–H bond in the molecule, such departure is unexpected. The estimated temperature dependence, shown in Figure 1, does not reproduce the nonlinearity.

For HFC-152a, results from several laboratories (Table 5 and Figure 2) are in excellent agreement, and this rate constant can be considered as a reliable standard. This molecule has two kinds of C–H bonds, with widely different activation energies, as shown above by the rate constant estimation method. Because of this difference, most of the reaction occurs at the CHF_2 site. At 298 K, the CH_3 group contributes less than 10% to the total reaction rate. The low reactivity of the CH_3 group in this molecule is due to the presence of the neighboring CHF_2 group, which, as seen in Table 2, has a strongly suppressing effect on the reactivity of adjacent C–H bonds. The reactivity of the C–H bond in the CHF_2 group is similar to that of each C–H bond in CH_2FCH_2F, as shown by the similar magnitudes of *E*/*R* values for attack at these bonds. The fact that there are four such reactive C–H bonds in HFC-152, and only one in HFC-152a, accounts for fact that HFC-152 has the higher rate constant of the two compounds. These differences in reactive sites are also reflected in the Arrhenius parameters; that is, the activation temperatures are of similar magnitude, but HFC-152 has a higher *A* factor.

The rate constant estimations for these molecules demonstrate that *E*/*R* values can be calculated reliably from 298 K data, using the relationship between *k*(298 K) and *A* factor as expressed by eq 6. These calculations also provide an accurate measure of the curvature in Arrhenius plots that is to be expected from the presence of different reactive sites in a molecule.

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