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Rate Constant and Temperature Dependence for the Reaction of Hydroxyl Radicals with 2-Fluoropropane (HFC-281ea)

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Relative rate experiments were used to measure the rate constant and temperature dependence of the reaction of OH radicals with 2-fluoropropane (HFC-281ea), using ethane, propane, and ethyl chloride as reference standards. Measurements were made using both infrared spectroscopy and gas chromatography (GC). Results from the two measurement techniques were in good agreement, with the GC data being more precise. The rate at 298 K for HFC-281ea, based on the GC experiments, was found to be 5.7×10^{-13} cm^3/(molecule s), with Arrhenius *A* factor = 3.06×10^{-12} cm^3/(molecule s) and $E/R = 503$ K. A previously described estimation technique, along with an improved method to estimate the Arrhenius parameters, is used to predict a rate constant and temperature dependence for 2-fluoropropane, which is in good agreement with the experimental value. A prediction is also made for 1-fluoropropane, for which there are no data.

Introduction

It is increasingly evident that accurate assessment must be made of the consequences of injection of gaseous materials into the atmosphere that arises from urban, industrial, and natural sources. For molecules containing at least one hydrogen atom, reaction with tropospheric hydroxyl radicals is the primary pathway of removal of these compounds from the atmosphere. Therefore, atmospheric lifetimes of these gases are determined mainly by the rate at which they react with tropospheric hydroxyl radicals. Predictive rules that can accurately estimate atmospheric lifetimes are useful, and we are measuring the kinetics of key compounds to use as a basis set for forming predictive rules. In this connection, the rate constant and temperature dependence for the reaction of 2-fluoropropane, HFC-281ea, with hydroxyl radical are reported in this article. We shall examine the consequences of this information on empirical rules previously developed to predict rate constants and temperature dependencies.[2]

Experimental Section

The technique used in this work has been described in several recent publications.[2,5,6] The reaction measured is

$$\mathrm{RH + OH \rightarrow R^{\bullet} + H_2O} \qquad (1)$$

A relative method is used in which the fractional loss of reactants is compared to the fractional loss of a reference compound. The fractional loss is reported in terms of a depletion factor, DF, which is the ratio of initial concentration to final concentration. The experiments were carried out in either a stopped-flow mode or a stirred-flow mode at ambient pressure, with argon as the carrier gas. Reactant concentrations were in the range of about 100 ppm (parts per million). For the stopped-flow mode the relation of sample to reference rate constant is given by

$$k_{\text{reactant}}/k_{\text{reference}} = \ln(\text{DF})_{\text{reactant}}/\ln\,(\text{DF})_{\text{reference}} \qquad (2)$$

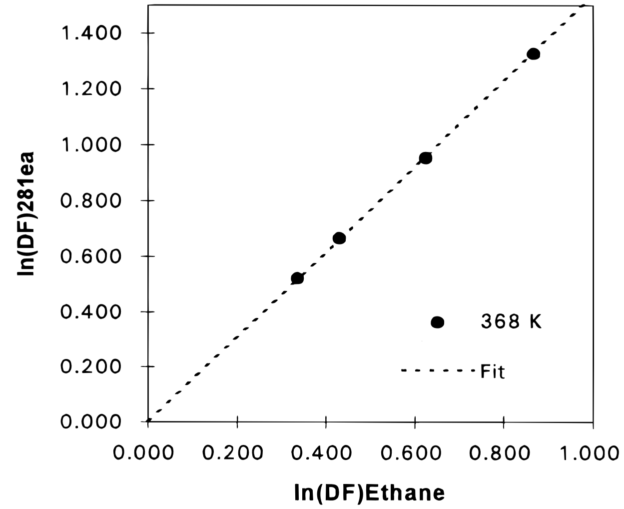

Figure 1. Plot of eq 2 for an experiment involving 281ea vs ethane at 368 K, showing linearity over a wide range of depletion factors.

For the stirred-flow mode the rate constant ratio is given by

$$k_{\text{reactant}}/k_{\text{reference}} = [(\text{DF})_{\text{reactant}} - 1]/[(\text{DF})_{\text{reference}} - 1] \qquad (3)$$

For small conversions, or for cases where the reference and reactant rate constants are approximately equal, eqs 2 and 3 are nearly equivalent. However, for other cases it is necessary to use the correct equation for the mode in which the experiment is being done.

The validity of eqs 2 and 3 was tested at each temperature by taking data over a wide range of depletion factors. An example of such data is shown in Figure 1, demonstrating good linearity as required by the equations. Systematic curvature or a nonzero intercept in these plots would indicate an error in the method, and therefore all the data were examined in this manner.

The OH radicals were produced by direct photolysis of H_2O at 185 nm or by 254 nm photolysis of O_3 [$(5-10) \times 10^{16}$ cm^{-3}] in the presence of water vapor [$(3-5) \times 10^{17}$ cm^{-3}]. The light source was a low-pressure mercury lamp, operated with a neon

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TABLE 1: Rate Constant Ratios, k_{281ea}/k_{ref}, as a Function of Temperature Using Infrared Spectroscopy

T (K)	281ea vs ethane	*T* (K)	281ea vs propane	*T* (K)	281ea vs ethyl chloride
288	2.257 ± 0.2	293	0.605 ± 0.04	293	1.715 ± 0.04
289	2.411 ± 0.2	298	0.556 ± 0.07	303	1.795 ± 0.04
298	2.671 ± 0.3	298	0.598 ± 0.06	311	1.797 ± 0.05
298	2.601 ± 0.2	323	0.510 ± 0.04	321	1.567 ± 0.06
298	2.496 ± 0.2	352	0.523 ± 0.04	333	1.773 ± 0.02
308	2.129 ± 0.3	368	0.513 ± 0.04	342	1.722 ± 0.02
315	2.349 ± 0.3	394	0.434 ± 0.03	363	1.593 ± 0.03
328	1.901 ± 0.2			378	1.590 ± 0.04
339	1.623 ± 0.1			386	1.520 ± 0.06
349	1.460 ± 0.1				
358	1.578 ± 0.1				
369	1.499 ± 0.1				
388	1.304 ± 0.1				
394	1.396 ± 0.1				

sign transformer. The experiments were done in temperature-controlled cylindrical quartz cells. The cylindrical cells were 10 cm in length and 5 cm in diameter and water-jacketed for measurements below 95 °C or wrapped with heating tape and insulating material for higher temperatures. Residence times in the cells for the stirred-flow mode were about 1 min.

All concentration measurements were made by either gas chromatography or infrared spectroscopy. For the gas chromatography measurements an SRI Model 8610 gas chromatograph equipped with flame ionization detector was used. Samples were injected into the instrument by means of a thermostated 1.00 mL sample loop. The sample loop was evacuated and the sample allowed to flow into the loop. An electronically operated valve sent the sample into the He carrier gas stream of the chromatograph. The PeakSimple Data System, Version 1.59, for Windows 3.1 controlled instrument operation, data collection, and peak integrations. A 6 ft., 1/8 in. o.d. Poropak P, 80/100 mesh column, operated at 60 or 80 °C was used for most of the separations. Infrared measurements were taken with a Nicolet 20SX FTIR, operated at 0.5 $\mathrm{cm^{-1}}$ resolution in the absorbance mode. Samples were contained in a White cell of 3 m path length. To minimize the risk of analytical errors, such as overlapping peaks in the GC analysis, measurements were made using both infrared spectroscopy and gas chromatography to measure the depletion factors as a function of temperature. Although both techniques give essentially the same results, the data obtained by the gas chromatography method have significantly less random error. The IR method is less precise for hydrocarbons, for which the less well-defined C−H bands must be relied on for the analysis.

Results

Table 1 gives the ratio results using infrared spectroscopy for HFC-281ea vs three reference compounds; ethane, propane, and chloroethane. These measurements were made in a stirred-flow mode using eq 3 to calculate the rate ratios. Table 2 presents the ratio results using gas chromatography for ethane and propane as reference compounds. Stopped-flow methods were utilized in the gas chromatography measurements, and rate constant ratios were calculated from eq 2. The absolute rates for the reaction of HFC-281ea with hydroxyl radical were calculated using both IR and GC data. The data sets are in agreement, but the GC data are preferable due to the lower random error. Table 3 gives the values of the rates of the reference materials used to calculate the rate and temperature dependence for HFC-281ea.

The resulting rate constant expression for HFC-281ea, based on the GC ratios vs ethane and propane, is

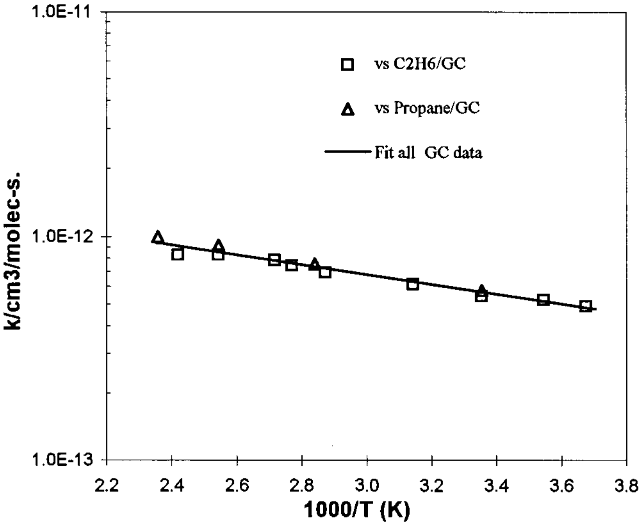

Figure 2. Rate constant data for HFC-281ea, based on the ratios as measured by GC vs ethane and propane.

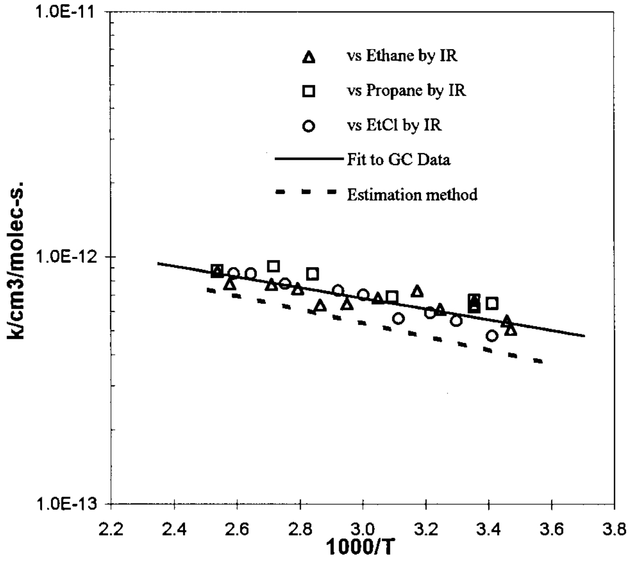

Figure 3. Comparison of the IR results with the Arrhenius line representing the GC data.

TABLE 2: Rate Constant Ratios, k_{281ea}/k_{ref}, as a Function of Temperature Using Gas Chromatography

T (K)	281ea vs ethane	*T* (K)	281ea vs propane
272	2.724 ± 0.08	270	0.541 ± 0.002
282	2.529 ± 0.03	277	0.555 ± 0.003
298	2.131 ± 0.06	284	0.523 ± 0.000
318	1.912 ± 0.03	292	0.507 ± 0.01
348	1.601 ± 0.10	298	0.517 ± 0.01
361	1.540 ± 0.01	326	0.496 ± 0.01
368	1.535 ± 0.04	352	0.467 ± 0.01
393	1.358 ± 0.03	393	0.453 ± 0.01
413	1.174 ± 0.01	424	0.432 ± 0.003

$$k(281\mathrm{ea}) = 3.06 \times 10^{-12} \exp(-503/T)\ \mathrm{cm^3/(molecule\ s)} \quad (4)$$

$$k(298\ \mathrm{K}) = 5.7 \times 10^{-13}\ \mathrm{cm^3/(molecule\ s)} \quad (5)$$

The uncertainty in k(298 K) is about 10% and the uncertainty in *E*/*R* is about 100 K. Figure 2 shows an Arrhenius plot of the data along with the least-squares fit corresponding to eq 4. Figure 3 compares the IR data with eq 4, showing that although the IR data are more scattered, they are in good agreement with the GC data.

TABLE 3: Rate Constants of the Reference Compounds Used in This Work

ref compd	Arrhenius rate constant[a]	k(298 K)[a]	source
CH_3CH_3	$1.00 \times 10^{-11}\exp(-1094/T)$	2.54×10^{-13}	Atkinson[1]
$CH_3CH_2CH_3$	$1.29 \times 10^{-11}\exp(-730/T)$	1.11×10^{-12}	DeMore and Bayes[3]
C_2H_5Cl	$5.14 \times 10^{-12}\exp(-855/T)$	2.92×10^{-13}	Herndon et al.[4]

[a] Units are cm^3/(molecule s)

TABLE 4: Current *G* Values Used in the Estimation Method

groups	G	groups	G
F	0.52	CHFCl	0.05
2F	0.34	CF_2Cl	−0.19
CF_3	−0.45	F, Cl	0.90
CH_2F	0.71	CCl_3	0.29
CHF_2	−0.07	$CFCl_2$	0.08
CH_3	1.25	Br	0.79
Cl	0.76	2Br	1.59
2Cl	1.54	BrCl	1.51
CH_2Cl	0.76	F,Br	1.2
CH_2Br	0.76	CN	0.52
$CHCl_2$	0.60	third group multiplier	0.27

TABLE 5: Preexponential Factors for the Reaction of OH with a Variety of Substrates

compd	A factor,[a] cm^3/(molecule s)
CH_3CFCl_2 (141b)	1.65×10^{-12}
CF_3CHFCF_3 (227ea)	7.07×10^{-13}
CHF_2Br (22B)	1.53×10^{-12}
CHF_2Cl (22)	9.73×10^{-13}
CH_2F_2 (32)	2.73×10^{-12}
CF_3CH_3 (143a)	1.90×10^{-12}
CF_3CH_2F (134a)	1.74×10^{-12}
$CF_3CH_2CF_3$ (236fa)	1.46×10^{-12}
CF_2HCF_2H (134)	2.05×10^{-12}
$CHBr_3$	1.36×10^{-12}
CF_2ClCCl_2H(122)	8.50×10^{-13}
$CFCl_2CHFCl$ (122a)	1.08×10^{-12}
CH_3Cl	7.46×10^{-12}
CH_3F	4.20×10^{-12}
CH_3Br	6.90×10^{-12}
$CHCl_3$	1.80×10^{-12}
CF_3OCH_3 (143aE)	2.98×10^{-12}
$CHCl_2CF_3$ (123)	7.75×10^{-13}
$CF_3CF_2CF_2OCHFCF_3$	7.44×10^{-13}
$CF_3OCHFCF_3$ (227eaE)	7.09×10^{-13}
CH_3OCH_3	1.49×10^{-11}
$c-C_6H_{12}$	3.71×10^{-11}
$c-C_5H_{10}$	2.57×10^{-11}
$c-C_3H_6$	5.15×10^{-12}
$c-C_4H_8$	1.62×10^{-11}

[a] Based on published and unpublished data from this laboratory. Some of the *A* factors differ from those originally published due to minor revisions and updates of the reference reactions.

Discussion

It is useful to compare the measured rate expression for 281ea with an estimated rate expression based on a method previously described.[2] According to this method, each reactive site is considered to be a methane derivative, and the reactivity of the C−H bonds at that site is determined by the attached groups that have replaced the H-atoms in methane. The total rate constant is obtained as the sum of the contributions from each C−H bond present in the molecule. The logarithm (base 10) of the rate constant (per H-atom) at each site is given by

$$\log(k/n) = \log k(CH_4) + G_1...G_3 \qquad (6)$$

The quantity log $k(CH_4)$ is the logarithm of the CH_4 rate constant per H-atom and is equal to −14.79, corresponding to $k(CH_4) = 6.5 \times 10^{-15}$ cm^3/(molecule s) at 298 K. The *G* terms are the contributions for the various groups, such as F, Cl, Br, CH_3, CF_3, etc., which may be present on the carbon atom in place of an H-atom. The *G* terms are determined by a fitting procedure based on a large number of well-determined rate constants at 298 K.[2] As previously discussed, a correction factor (called the third group multiplier) is necessary when three groups are present on a given carbon atom. This results from the empirically observed fact that a given group contribution is reduced when it is the third group, compared to the larger value that is appropriate when it is the only group, or is one of two groups present. The current value of the third group multiplier is 0.27. The use of eq 6 yields an estimate of the rate constant at 298 K. The current set of *G* values is listed in Table 4.

To determine the *E*/*R* or activation temperature of the reaction, we use an estimated *A* factor based on a database of reactions similar to that used to calibrate the *G* values at 298 K. In our previous description of the estimation technique, we used a fixed *A* factor of 8×10^{-13} cm^3/(molecule s) per H-atom. However, the database now includes reactions over a wider range of rate constants, and a clear dependence of *A* factor on reaction rate is now apparent. The database for the A-factor calibration is listed in Table 5, which includes those *A* factors from our previous work that are in good agreement with independent measurements by absolute methods. A plot of *A* factor per H-atom vs log(k/n(H)) for rate constants ranging over 4 orders of magnitude is shown in Figure 4. The scatter in this plot is similar in magnitude to the uncertainty in the measured *A* factors but may well be due in part to real variations in the *A* factors for these reactions. The least-squares fit to these data is as follows:

$$\log(A/n) = 0.17 \log(k/n) - 9.61 \qquad (7)$$

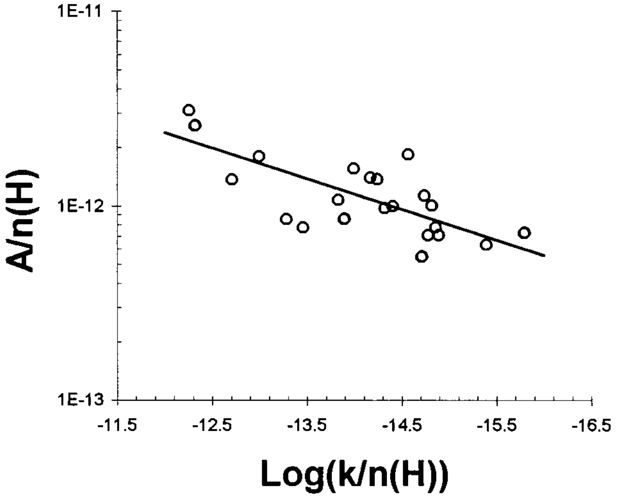

Figure 4. Plot of *A* factors vs the log of the rate constant per H-atom for several reactions.

The procedure therefore is to estimate the 298 K rate constant per H-atom at each reactive site using eq 6 and then to calculate the *A* factor for these C−H bonds using eq 7. The *E*/*R* value is then calculated from the expression,

$$E/R = -298 \ln(k/A) \qquad (8)$$

The total reaction rate at a given temperature is obtained by summing the contributions from each site. The effective overall Arrhenius parameters for the reaction are then obtained by fitting the sums over the desired temperature range to a single Arrhenius equation. This procedure is illustrated below for both *n*-propyl fluoride and isopropyl fluoride, which serves to demonstrate the interplay between *A* factors and activation temperatures factors for these two reactions.

Estimated Rate Constant for $CH_3CH_2CH_2F$:

$$-CH_3 \text{ site: } \log k/n(H) = -14.79 + G(CH_3) = -13.54$$

(The CH_3 group has been used as a surrogate for the CH_2CH_2F group.)

$$k(298\ K) = 8.7 \times 10^{-14}\ cm^3/(molecule\ s)$$
$$A = 3.7 \times 10^{-12}\ cm^3/(molecule\ s)$$
$$E/R = 1117\ K$$

$$-CH_2- \text{ site: } \log k/n(H) = -14.79 + G(CH_3) + G(CH_2F) = -12.83$$

$$k(298\ K) = 3.0 \times 10^{-13}\ cm^3/(molecule\ s)$$
$$A = 3.2 \times 10^{-12}\ cm^3/(molecule\ s)$$
$$E/R = 713\ K$$

$$-CH_2F \text{ site: } \log k/n(H) = -14.79 + G(F) + G(CH_3) = -13.02$$

$$k(298\ K) = 1.9 \times 10^{-13}\ cm^3/(molecule\ s)$$
$$A = 3.0 \times 10^{-12}\ cm^3/(molecule\ s)$$
$$E/R = 821\ K$$

The sum of these three site contributions over the temperature range 275−425 K corresponds to the following effective Arrhenius parameters:

$$k(total)_{est} = 8.9 \times 10^{-12} \exp(-818/T)\ cm^3/(molecule\ s)$$
$$k(298\ K)_{est} = 5.7 \times 10^{-13}\ cm^3/(molecule\ s)$$

Estimated Rate Constant for CH_3CHFCH_3:

$$2-CH_3 \text{ sites: } \log k/n(H) = -14.79 + G(CH_2F) = -14.08$$

(The CH_2F group has been used as a surrogate for the CH_3-CHF group.)

$$k = 5.0 \times 10^{-14}\ cm^3/(molecule\ s)$$
$$A = 6.0 \times 10^{-12}\ cm^3/(molecule\ s)$$
$$E/R = 1425\ K$$

−CHF− site:

In this case there are three groups to be accounted for; two CH_3 groups and one F. Also, this is a case where it makes a difference which group is considered to be the third group, because of the very different *G* values between methyl and the F-atom. We therefore assume the three possible cases (two identical) and take the average,

$$\text{(First case) } \log k/n(H) = -14.79 + G(F) + G(CH_3) + 0.27\, G(CH_3) = -12.68$$

$$k = 2.1 \times 10^{-13}\ cm^3/(molecule\ s)$$

(To be used twice).

$$\text{(Second case) } \log k/n(H) = -14.79 + 2G(CH_3) + 0.27G(F) = -12.15$$

$$k = 7.1 \times 10^{-13}\ cm^3/(molecule\ s)$$
$$k(average) = 3.8 \times 10^{-13}\ cm^3/(molecule\ s)$$
$$A = 1.9 \times 10^{-12}\ cm^3/(molecule\ s)$$
$$E/R = 479\ K$$

The sum of these two site contributions over the temperature range 275−425 K corresponds to the following effective Arrhenius parameters:

$$k(total)_{est} = 3.6 \times 10^{-12} \exp(-632/T)\ cm^3/(molecule\ s)$$
$$k(298\ K)_{est} = 4.3 \times 10^{-13}\ cm^3/(molecule\ s)$$

The estimation is in good agreement (within 35% at 298 K) with the experimental values from eqs 4 and 5. In Figure 3 an Arrhenius line corresponding to this estimate is shown for comparison with the experimental data.

The prediction for *n*-propyl fluoride is probably more reliable than that for isopropyl fluoride, since no third group correction is required. The predicted 298 K rate constants for the two compounds are similar, but the Arrhenius parameters differ significantly. Both compounds have the same number of H-atoms, but the individual site reactivities are quite different. For isopropyl fluoride, about 90% of the reaction occurs at the CHF site, and the overall reaction has a lower preexponential factor because there is only one H-atom. However, this is offset by a lower activation energy. The *n*-propyl fluoride has several reactive sites, each of which contributes significantly to the total reaction. This leads to a higher preexponential factor, but all the sites have relatively high activation energies. The net result is that the *n*-propyl fluoride rate constant is slightly greater than that of isopropyl fluoride. Experimental data for *n*-propyl and isopropyl bromide[4] show a similar rate constant ratio.

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