Rate Constants for the Reactions of Hydroxyl Radical with Several Fluoroethers by the Relative Rate Method

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Relative rate experiments were used to measure ratios of chemical kinetics rate constants as a function of temperature for the reactions of OH with eight fluoroethers, including $CF_3OCF_2CHF_2$, $CF_3OCF_2CHFCF_3$, $CHF_2CF_2OCHF_2$, $CF_3CHFCF_2OCH_2CF_3$, $(CF_3)_2CHOCHF_2$, $CF_2HCF_2OCH_2CF_3$, $CHF_2CF_2OCHFCF_3$, and $CF_3CH_2OCH_2CF_3$. The temperature ranges were about 270−400 K. Each compound was measured against at least two references. Results are compared with previous data where available. An approach using model compounds for the approximate estimation of rate constants for the fluoroethers is discussed. Observed temperature dependences for fluoroethers from the present work and some literature work are shown to be accurately predictable, based on a previously determined correlation of k_{298K} with the pre-exponential factor, A, in the Arrhenius equation $k = Ae^{-E/RT}$.

Introduction

In recent years partially fluorinated ethers have become of interest as possible substitutes for chorofluorocarbons and other halocarbons for many industrial applications. The fluoroethers are inert with respect to ozone depletion in the atmosphere, but it is necessary to know the atmospheric lifetime in order to assess possible global warming effects. Since the lifetime is determined primarily by the rate of attack by hydroxyl radical, laboratory measurements of the abstraction rate constants are required. These rate constants are also of general interest as a class of reactions in chemical kinetics. In the present work, we have measured the rate constants and their temperature dependences for eight fluoroethers of possible industrial significance, and have further investigated the general problem of predicting such data in advance. The measurement technique is the relative rate method, which is reliable when accurate reference rate constants are available.

Relative Rate Measurements. The technique used in this work has been described in several recent publications.[1−3] Rate constants and temperature dependences for fluoroethers reacting with OH radicals according to eq 1 were measured by a relative method:

$$R{-}H + {\cdot}OH \rightarrow R{\cdot} + HOH \tag{1}$$

Measurements were made in the range of about 270 to 400 K. Each compound studied was measured relative to at least two reference standards whose rate constants were traceable to published values of absolute rates. Equation 2 defines the relationship that exists between the rates of sample and reference:

$$k_{sample}/k_{reference} = [\ln(C_0/C_{final})_{sample}]/[\ln(C_0/C_{final})_{reference}] \tag{2}$$

Concentrations before and after reaction, C_0 and C_{final}, were measured by means of a GC/MS, using single ion monitoring. For each temperature, the reaction times were adjusted so that sample depletions were between 80% and 20%. Sample and reference gases (each $\sim 7 \times 10^{14}$ molecules per cm^3) were mixed together in cylindrical quartz cells, 5 cm diameter by 10 cm long. Helium was added to the reaction mixture to dilute the samples and maintain the pressure at 1 atm. The cells were jacketed and a thermostatic circulator filled with low viscosity silicon oil was attached to the cell and adjusted to the desired temperature.

The hydroxyl radicals were generated by photolysis of water vapor ($1{-}5 \times 10^{17}$ cm^{-3}), using a low-pressure mercury vapor lamp:

$$H_2O + h\upsilon\ (185\ nm) \rightarrow H + OH \tag{3}$$

Loss of fluoroether samples by photolysis is not a problem owing to the low cross sections of those compounds.[4] A small amount of O_2 ($2 - 5 \times 10^{17}$ molecules cm^{-3}) was added to remove H atoms and the resulting alkyl radicals. The latter is important in order to avoid possible reactant reformation by radical−radical reactions. In every case it was verified that rate constant ratios calculated from eq 2 were independent of the sample depletions. Reference rate constants used in these studies are summarized in Table 1.

Results and Discussion

Rate Constant Measurements. Table 2 lists the ratio measurements at different temperatures for the various reference compounds. Table 3 summarizes results from each reference compound, including the reference rate constant used, the

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TABLE 1: Reference Rate Constants Used in This Study

reference compound	*A*-factor (cm^3 molecule^{-1} s^{-1})	*E*/*R* (K)	k_{298K} (cm^3 molecule^{-1} s^{-1})	reference
CF_3CF_2H (HFC-125)	5.6×10^{-13}	1700	1.9×10^{-15}	JPL 97-4[15]
CF_3CHFCF_3 (HFC-227ea)	5.0×10^{-13}	1700	1.7×10^{-15}	JPL 97-4[15]
CF_3CFH_2 (HFC-134a)	1.5×10^{-12}	1750	4.2×10^{-15}	JPL 97-4[15]
CH_3CF_3 (HFC 143a)	1.8×10^{-12}	2170	1.2×10^{-15}	JPL 97-4[15]
CH_3CHF_2 (HFC-152a)	2.4×10^{-12}	1260	3.5×10^{-14}	JPL 97-4[15]
CH_2F_2 (HFC-32)	1.9×10^{-12}	1550	1.0×10^{-14}	JPL 97-4[15]
CH_2FCH_2F (HFC-152)	3.6×10^{-12}	1084	9.5×10^{-14}	Wilson et al.[3]
CH_3CH_2F (HFC-161)	5.0×10^{-12}	923	2.3×10^{-13}	Kozlov et al.[16]*

*Our fit to their data in temperature range 272−420K, to match range of the present experiments.

TABLE 2: Experimental Results for the Rate Constant Ratios

T (K)	ratio	*T* (K)	ratio	*T* (K)	ratio	*T* (K)	ratio
$CF_3OCF_2CHF_2$ vs HFC-125		$CF_3OCF_2CHF_2$ vs HFC-227a		$CF_3OCF_2CHFCF_3$ vs HFC-125		$CF_3OCF_2CHFCF_3$ vs HFC-227ea	
269	1.132	273	1.288	270	0.974	284	1.142
276	1.124	294	1.282	299	0.939	288	1.135
288	1.129	316	1.280	329	0.908	294	1.134
298	1.096	338	1.283	363	0.883	296	1.120
309	1.089	365	1.271	385	0.867	310	1.111
322	1.071	397	1.263	404	0.852	315	1.128
332	1.077					324	1.099
343	1.067					334	1.117
358	1.055					342	1.097
370	1.055					353	1.085
386	1.043					371	1.074
406	1.042					402	1.050
						406	1.080
$CHF_2CF_2OCHF_2$ vs HFC-134a		$CHF_2CF_2OCHF_2$ vs HFC-143a		$CF_3CHFCF_2OCH2CF_3$ vs HFC-134a		$CF_3CHFCF_2OCH2CF_3$ vs HFC-227ea	
266	0.744	287	2.473	272	2.361	270	6.55
276	0.725	306	2.346	276	2.326	275	6.18
281	0.746	327	2.096	287	2.246	298	5.58
293	0.728	348	1.975	292	2.294	323	5.15
299	0.745	383	1.839	313	2.005	348	5.04
314	0.725	407	1.700	324	1.974	374	4.92
321	0.746			332	2.016	404	4.78
335	0.718			338	1.937		
342	0.752			352	1.904		
361	0.736			363	1.933		
369	0.750			391	1.816		
394	0.740			391	1.816		
406	0.756			407	1.742		
$(CF_3)_2CHOCHF_2$ vs HFC-134a		$(CF_3)_2CHOCHF_2$ vs HFC-143a		$CF_2HCF_2OCH_2CF_3$ vs HFC-152a		$CF_2HCF_2OCH_2CF_3$ vs HFC-32	
312	0.633	284	2.24	270	0.252	273	0.882
367	0.709	289	2.28	272	0.261	279	0.935
369	0.713	296	2.22	289	0.284	291	0.854
		307	2.08	293	0.264	303	0.818
		309	2.13	312	0.275	331	0.805
		317	2.18	322	0.276	380	0.756
		332	1.97	341	0.316	382	0.773
		341	2.00	352	0.308	399	0.815
		347	1.90	363	0.326		
		360	1.89	371	0.308		
		379	1.78	389	0.342		
		393	1.78	407	0.344		
		398	1.76				
$CF_2HCF_2OCH_2CF_3$ vs HFC-161		$CF_2HCF_2OCH_2CF_3$ vs HFC-227ea		$CHF_2CF_2OCHFCF_3$ vs HFC-152		$CHF_2CF_2OCHFCF_3$ vs HFC-161	
322	0.0494	407	5.076	347	0.052	398	0.0269
$CHF_2CF_2OCHFCF_3$ vs HFC-32		$CHF_2CF_2OCHFCF_3$ vs HFC-125		$CF_3CH_2OCH_2CF_3$ vs HFC-152a		$CF_3CH_2OCH_2CF_3$ vs HFC-161	
267	0.359	274	2.547	268	4.423	275	0.559
277	0.360	294	2.345	279	3.815	283	0.570
284	0.356	306	2.227	289	3.974	307	0.576
290	0.362	333	2.164	299	3.570	347	0.601
299	0.350	354	2.048	312	3.482	383	0.586
312	0.349	381	1.959	324	3.362	407	0.582
324	0.364	403	1.965	339	3.497		
347	0.349			354	3.214		
363	0.365			369	3.182		
380	0.361			399	2.874		
399	0.366			409	2.818		
407	0.377						

TABLE 3: Compounds Studied and Rate Constant Results for Each Reference Compound

		result		
reference compound	temp range (K)	*A*-factor (cm^3 molecule^{-1} s^{-1})	*E*/*R* (K)	k$_{298K}$ (cm^3 molecule^{-1} s^{-1})
		$CF_3OCF_2CHF_2$		
HFC-125	269−406	4.85 × 10^{-13}	1628	2.05 × 10^{-15}
HFC-227ea	273−397	6.10 × 10^{-13}	1685	2.13 × 10^{-15}
		$CF_3OCF_2CHFCF_3$		
HFC-125	270−404	3.67 × 10^{-13}	1593	1.75 × 10^{-15}
HFC-227ea	284−406	4.53 × 10^{-13}	1635	1.88 × 10^{-15}
		$CHF_2CF_2OCHF_2$		
HFC-134a	266−406	1.14 × 10^{-12}	1758	3.12 × 10^{-15}
HFC-143a	287−407	1.26 × 10^{-12}	1805	2.94 × 10^{-15}
		$CF_3CHFCF_2OCH_2CF_3$		
HFC-134a	272−407	1.46 × 10^{-12}	1511	9.17 × 10^{-15}
HFC-227ea	270−404	1.57 × 10^{-12}	1534	9.14 × 10^{-15}
		$(CF_3)_2CHOCHF_2$		
HFC-134a	312−369	2.06 × 10^{-12}	1992	2.57 × 10^{-15}
HFC-143a	284−398	1.63 × 10^{-12}	1906	2.71 × 10^{-15}
		$CF_2HCF_2OCH_2CF_3$		
HFC-152a	270−407	1.46 × 10^{-12}	1497	9.62 × 10^{-15}
HFC-32	273−399	1.07 × 10^{-12}	1425	8.95 × 10^{-15}
HFC-161	322	−	k_{322K} =	1.4 × 10^{-14}
HFC-227ea	407	−	k_{407K} =	3.9 × 10^{-14}
		$CHF_2CF_2OCHFCF_3$		
HFC-32	267−406	7.83 × 10^{-13}	1592	3.75 × 10^{-15}
HFC-125	274−403	6.19 × 10^{-13}	1478	4.34 × 10^{-15}
HFC-152	347	−	k_{347K} =	8.18 × 10^{-15}
HFC-161	398	−	k_{398K} =	1.32 × 10^{-14}
		$CF_3CH_2OCH_2CF_3$		
HFC-152a	268−409	3.31 × 10^{-12}	963	1.31 × 10^{-13}
HFC-161	275−407	3.23 × 10^{-12}	961	1.29 × 10^{-13}

temperature range, and the calculated rate constant for that reference gas. Table 4 shows the best fit rate constants derived from the combined data from all references and compares the results with previous work. Figures 1-8 show results graphically, along with data from earlier studies.

$CF_3OCF_2CHF_2$. This compound was studied versus the two references CF_3CF_2H and CF_3CHFCF_3 in the temperature range 269−406 K. Figure 1 shows good agreement among data from both references and also with the 298 K point of Andersen et al.[5] As shown in Table 4, the latter authors also calculated Arrhenius parameters for the reaction which are in excellent agreement with the present experimental values.

$CF_3OCF_2CHFCF_3$. This compound was studied versus the two references CF_3CF_2H and CF_3CHFCF_3 in the temperature range 270−406 K. As shown in Figure 2, the results for the two references agree well and are in approximate agreement (24% higher) with the 296 K data point of Wallington et al.[6] The latter data point is from a relative rate study in which the reference compounds were ethene and acetylene, with OH abstraction rate constants 8.66 × 10^{-12} and 8.5 × 10^{-13} cm^{3}molecule^{-1}s^{-1}, respectively. These are in accord within 2% of the recommendations of ref 15, JPL-97-4. The two resulting values for $CF_3OCF_2CHFCF_3$ were in good agreement, 1.43 × 10^{-15} and 1.42 × 10^{-15} cm^{3}molecule^{-1}s^{-1}, respectively. However, a referee has suggested that the authors' assumption that $CF_3OCF_2CHFCF_3$ loss could be monitored by measuring the product $CF_3C(O)F$ with an assumed 100% yield may have produced a rate constant somewhat lower than the correct value, in the event that the actual yield was less than 100%.

$CHF_2CF_2OCHF_2$. This compound was studied versus the reference gases CF_3CH_2F and CH_3CF_3 at 266−407 K, with good agreement for the two references (Figure 3). The earlier relative rate work of Chen et al.[7] shows good agreement with the temperature dependence of our study (see Table 4), but their rate constants are about 28% lower at all temperatures. The reference reactants for the Chen et al. measurements were $C_2F_5OCH_3$ and n-$C_3F_7OCH_3$, which have apparently

TABLE 4: Overall Fits to Data from All Reference Compounds for Fluoroethers Studied in This Work and Comparison with Previous Work[a]

A-factor (cm^3 molecule^{-1} s^{-1})	*E*/*R* (K)	k$_{298K}$ (cm^3 molecule^{-1} s^{-1})	source
		$CF_3OCF_2CHF_2$	
(5.24 ± 0.29) × 10^{-13}	1648 ± 18	2.08 × 10^{-15}	this work
(6.5 × 10^{-13})[b]	(1685)[b]	(2.26 ± 0.18) × 10^{-15}	Andersen et al.[5]
		$CF_3OCF_2CHFCF_3$	
(4.07 ± 0.32) × 10^{-13}	1609 ± 26	1.84 10^{-15}	this work
−	−	(1.43 ± 0.28) × 10^{-15}	Wallington et al.[6]
		$CHF_2CF_2OCHF_2$	
(1.24 ± 0.09) × 10^{-12}	1792 ± 23	3.02 × 10^{-15}	this work
(7.58 ± 3.30) × 10^{-13}	1720 ± 130	2.36 × 10^{-15}	Chen et al.[7]
		$CF_3CHFCF_2OCH_2CF_3$	
(1.49 ± 0.08) × 10^{-12}	1517 ± 19	9.17 × 10^{-15}	this work
($1.67^{+1.05}{}_{-0.65}$) × 10^{-12}	1560 ± 140	8.90 × 10^{-15}	Chen et al.[10]
		$(CF_3)_2CHOCHF_2$	
(1.65 ± 0.08) × 10^{-12}	1912 ± 17	2.70 × 10^{-15}	this work
1.52 × 10^{-12}	909 ± 500	7.2 × 10^{-14}	Brown et al.[11]
		$CF_2HCF_2OCH_2CF_3$	
(1.29 ± 0.13) × 10^{-12}	1469 ± 33	9.35 × 10^{-15}	this work
1.49 × 10^{-12}	1520 ± 170	(9.08 ± 0.91) × 10^{-15}	Tokuhashi et al.[12]
($1.36^{+0.52}{}_{-0.37}$) 10^{-12}	1470 ± 90	9.80 10^{-15}	Chen et al.[10]
		$CHF_2CF_2OCHFCF_3$	
(6.86 ± 0.07) 10^{-13}	1538 ± 35	3.93 10^{-15}	this work
		$CF_3CH_2OCH_2CF_3$	
(3.28 ± 0.19 × 10^{-12}	962 ± 19	1.30 × 10^{-13}	this work
($2.32^{+0.46}{}_{-0.41}$) × 10^{-12}	790 ± 47	1.64 × 10^{-13}	Orkin et al.[4]

[a] Errors for our work are one standard deviation of the least-squares fit and do not reflect uncertainties in the reference rate constant or other possible systematic errors. Errors for previous work are those given by the authors. [b] Values in parentheses were calculated by Andersen et al. from a correlation between *A*-factors and k_{298K} similar to the correlation used in the present work.

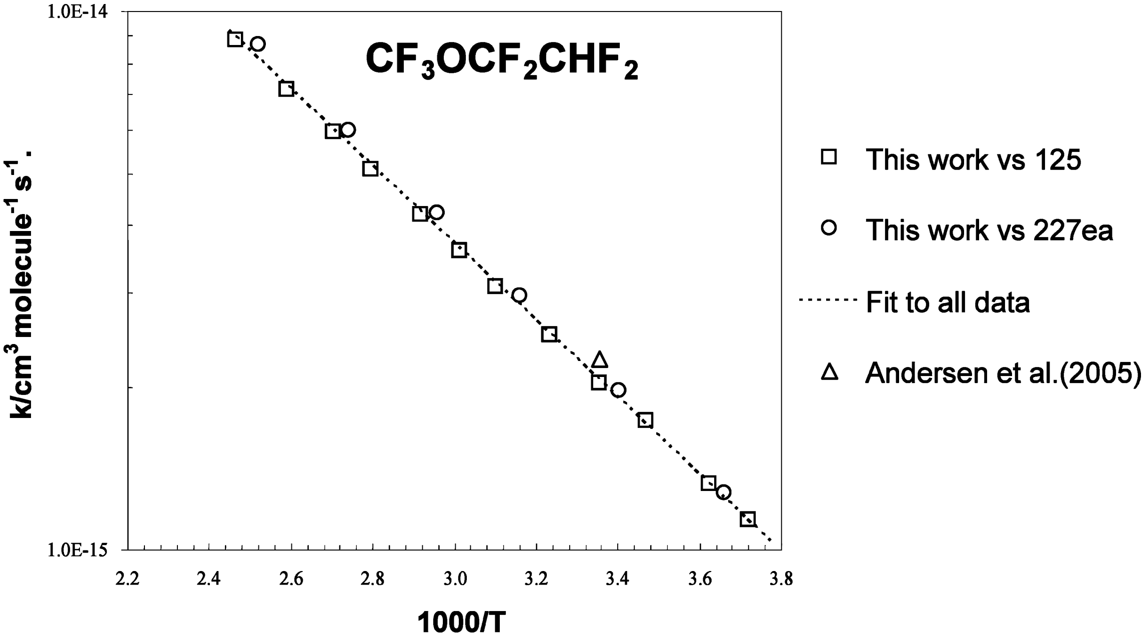

Figure 1. Rate constant results for $CF_3OCF_2CHF_2$ and comparison with previous work.

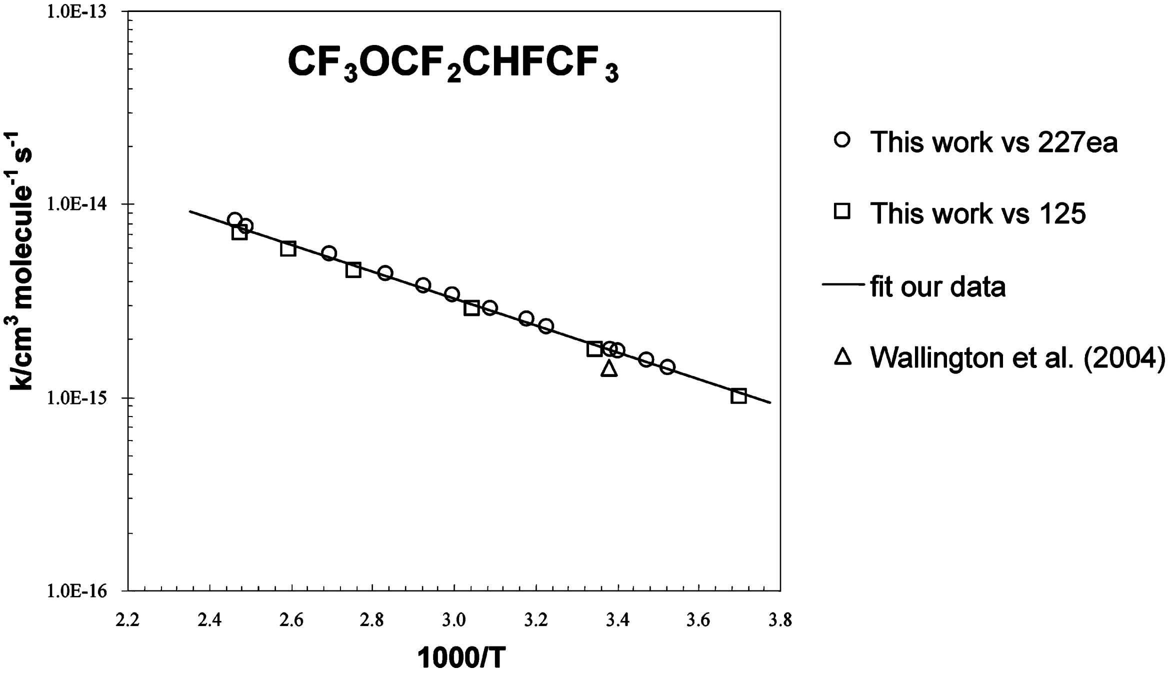

Figure 2. Rate constant results for $CF_3OCF2CHFCF_3$ and comparison with previous work.

well-established rate constants.[8] For example, a relative rate study at 294 K by Ninomiya et al.[9] gave a rate constant for n-$C_3F_7OCH_3$ (1.2×10^{-14} $cm^3molecule^{-1}s^{-1}$), which is essentially identical to that used by Chen et al. The reference reactants for the Ninomiya et al. study were CH_4 and CH_3Cl, using JPL 97-4 rate constants). Thus the reason for the discrepancy for $CHF_2CF_2OCHF_2$ does not seem to be due to errors in the reference rate constants.

$CF_3CHFCF_2OCH_2CF_3$. This compound was studied versus CF_3CH_2F and CF_3CHFCF_3 at temperatures of 270−407 K, with good agreement between the two datasets (Figure 4). In addition, relative rate results of Chen et al.[10] versus CH_3CCl_3 and CH_4 (using rate constants from ref 15, JPL 97-4) in the temperature range 268−308 K are in excellent agreement.

$(CF_3)_2CHOCHF_2$. Reference gases for this study were CF_3CHFCF_3 and CH_3CF_3, with measurements in the range 284−398 K. As seen in Figure 5, results from the two references are in excellent agreement. An early discharge flow/resonance fluorescence study by Brown et al.[11] reported data points at 299 and 422 K for this compound (7.3×10^{-14} and 1.77×10^{-13} cm^3 $molecule^{-1}$ s^{-1}, respectively), but these values are more than an order of magnitude higher than the present results and may have been affected by impurities in the sample. These data points are not shown in Figure 5, but are included in Table 4.

$CF_2HCF_2OCH_2CF_3$. This compound was studied over the temperature range 270−407 K versus the references CH_3CHF_2, CH_2F_2 CH_3CH_2F, and CF_3CHFCF_3. As seen in Table 2, the latter two references have rate constants that are too different from that of the subject compound and therefore were not used in the overall fit shown in Table 4. Nevertheless the results are in good agreement with the other data (see Figure 6), attesting to the accuracy of our analytical method. Figure 6 shows

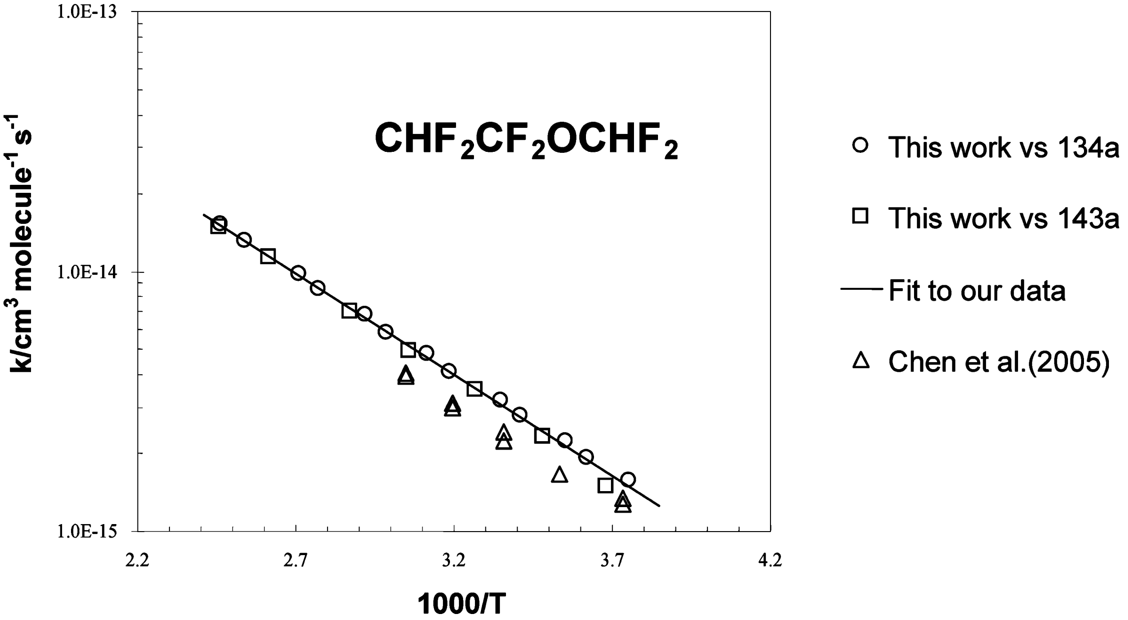

Figure 3. Rate constant results for $CHF_2CF_2OCHF_2$ and comparison with previous work.

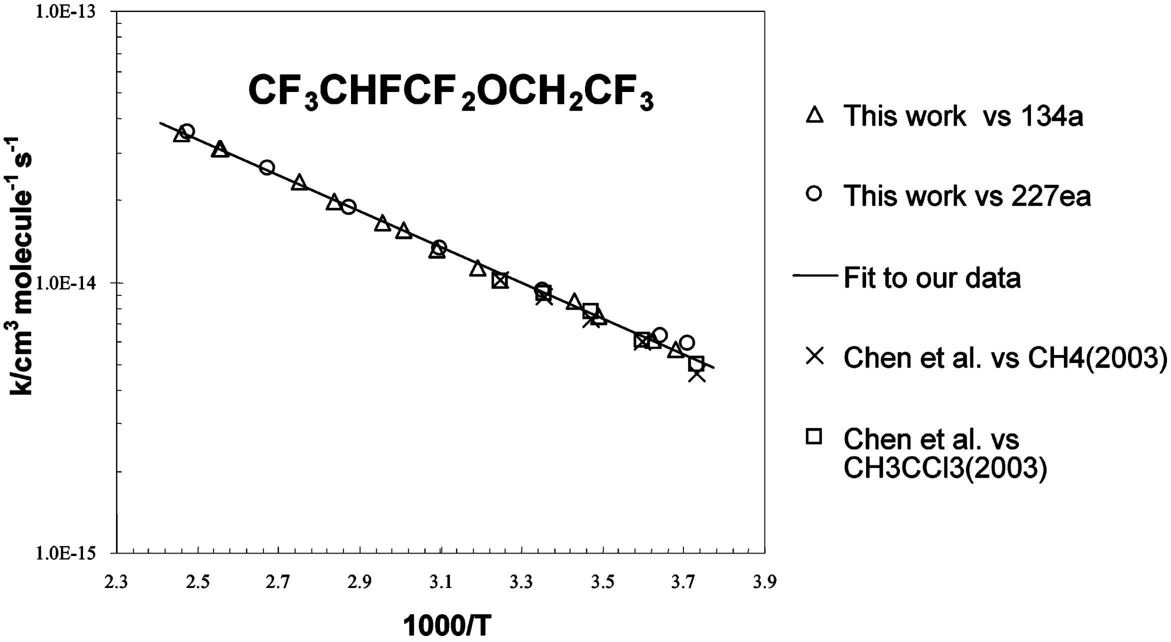

Figure 4. Rate constant results for $CF_3CHFCF_2OCH_2CF_3$ and comparison with previous work.

excellent agreement with the relative rate measurements of Chen et al.[10] over the temperature range 268−308 K, and absolute measurements of Tokuhashi et al.[12] over the range 250−430 K. The Chen et al. data were taken versus different reference gases (CH_3CCl_3 and CHF_2Cl, *k*'s from JPL 97-4) from those of our study.

$CHF_2CF_2OCHFCF_3$. This compound was studied over the temperature range 267−407 K versus four references, CH_2F_2, CF_3CF_2H, CH_2FCH_2F, and CH_3CH_2F. Experiments showed that the latter two references have rate constants that are too fast by about a factor of 10 to be ideal references for this reaction, and these results were not used in the overall data fit (Table 4). Again, however, the results are in reasonable agreement with data from the other reference gases (see Figure 7). We are not aware of any previous work on this reaction.

$CF_3CH_2OCH_2CF_3$. This reaction was studied versus CH_3CF_2H and CH_3CH_2F in the temperature range 268−409 K, with good agreement between results for the two references. (Figure 8). Absolute data by Orkin et al.[4] are higher than our data for unknown reasons, since those authors made efforts to remove impurities which can cause absolute measurements to be too high.

Rate Constant Estimations at 298 K. The group additivity (SAR) approach for estimation of OH abstraction reaction rate constants is only partially successful for the fluorinated ethers.[12] There are several reasons for this, including the fact that the database for calibration of group effects is still somewhat limited, and there are many separate groups for which calibration is necessary. The problem is compounded by the nonlinear behavior of some highly fluorinated groups. For example, no single group value for CF_3O can account for the influence of that group in the series of compounds CF_3OCH_3, CF_3OCH_2F, and CF_3OCHF_2. This behavior is analogous to that of the F atom in the sequence CH_3F, CH_2F_2, and CF_3H, which requires different group values for the F atom depending on the number present in the molecule. The CF_3O group indeed behaves much

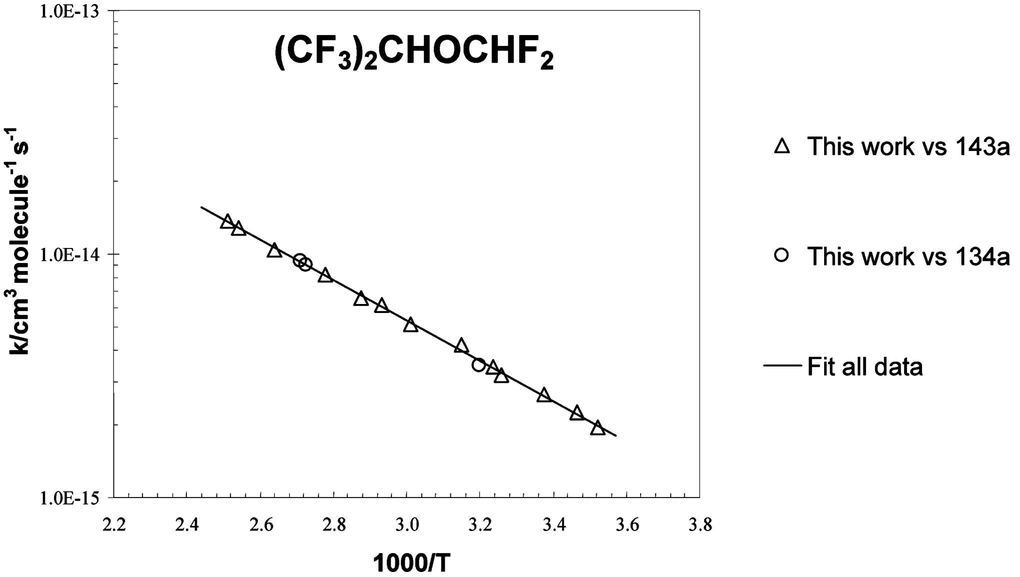

Figure 5. Rate constant results for $(CF_3)_2CHOCHF_2$.

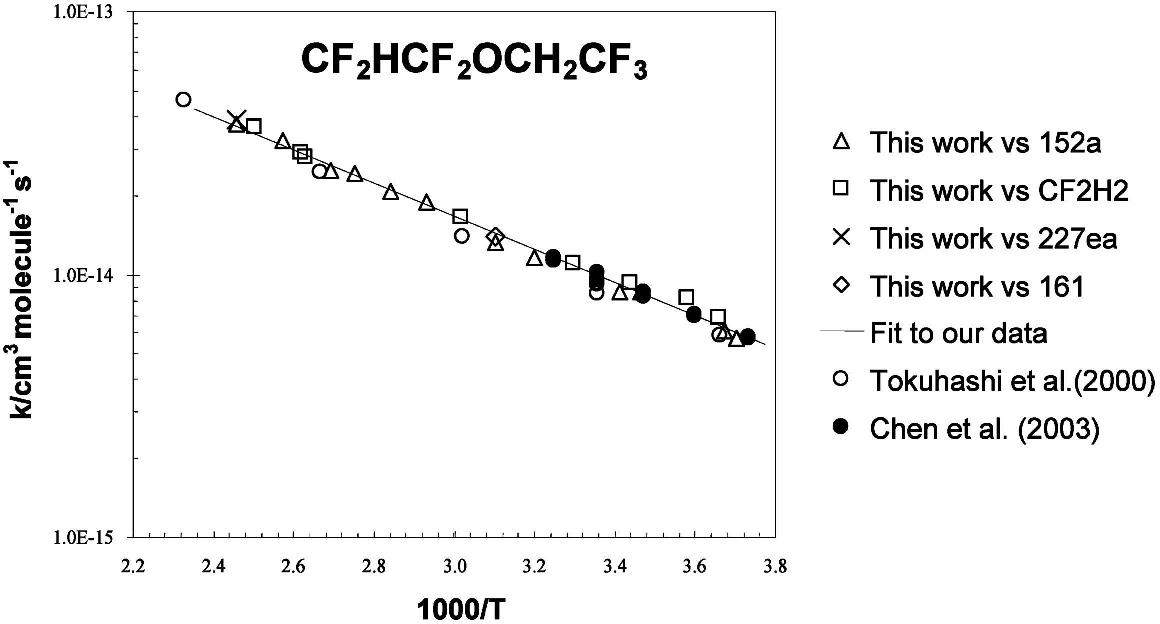

Figure 6. Rate constant results for $CF_2HCF_2OCH_2CF_3$ and comparison with previous work.

like an F atom in its effect on the OH abstraction rate constants.[13]

For this reason an alternative approach based on comparison with model or analogous compounds has been used with some success in place of the SAR method.[5,12] The fact that CF_3O behaves like F can be used for the selection of model compounds, such that, for example, CF_3OCH_3 has a rate constant similar to that of CH_3F.[5,13] In some cases it is also possible to use the F atom as a surrogate for CF_2HO and similar groups such as CF_3CF_2O. Some examples of model selection for compounds studied in the present work are shown in Table 5, including the estimated Arrhenius parameters as discussed below.

Calculations of the Arrhenius Parameters. Although estimation of k_{298K} is difficult for fluoroethers, Arrhenius parameters (the quantities A and E/R in the equation $k = Ae^{-E/RT}$) can usually be calculated from reliable experimental values of k_{298K}. The simplest case is where there is only one type of C−H bond in the molecule. The method is the same as that previously employed in our treatment of hydrocarbons,[1] and utilizes the following equations:[14]

$$E/R/(K) = -509 \log(k_{298}/n) - 5771 \qquad (4)$$

$$\log(A/n) = 0.2581 \log(k_{298}/n) - 8.411 \qquad (5)$$

The quantity k_{298}/n is the rate constant per C−H bond, and similarly for A/n. The units of k and A are cm³ molecule⁻¹ s⁻¹. Table 6 shows the application of this method to nine fluoroethers which have a single type of C−H bond, including six fom the literature and three from the present work. The E/R fit is illustrated graphically in Figure 9, showing a high degree of fidelity to the experimental data. It should be pointed out that the derivation of eqs 4 and 5 is not based on data for any fluoroethers.

Compounds with different C−H bonds can also be treated, but then it is necessary to have some basis for separating the contributions of the different C−H bonds to the overall k_{298K}. Each site must be treated separately, and the sum of the rates at all sites gives the total rate constant as a function of

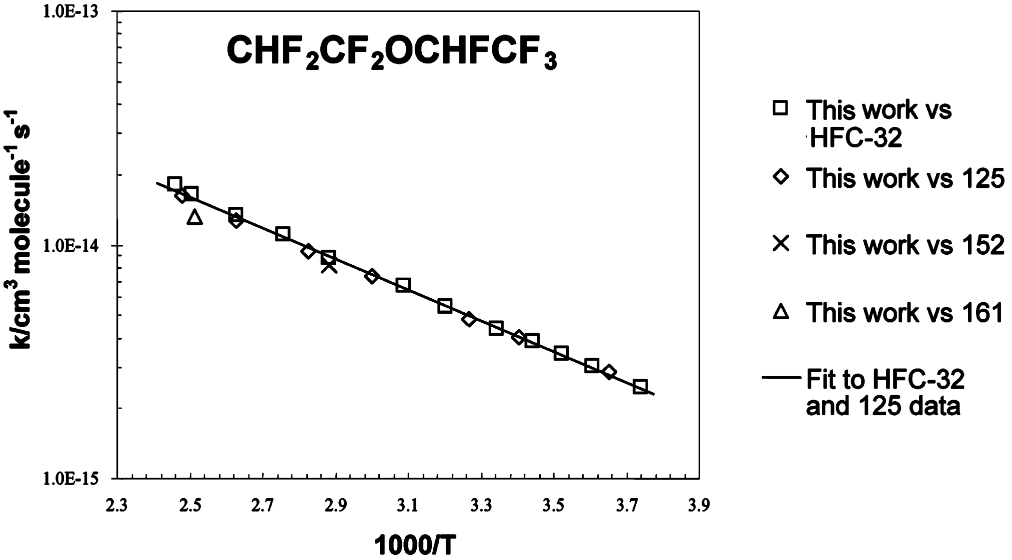

Figure 7. Rate constant results for $CHF_2CF_2OCHFCF_3$.

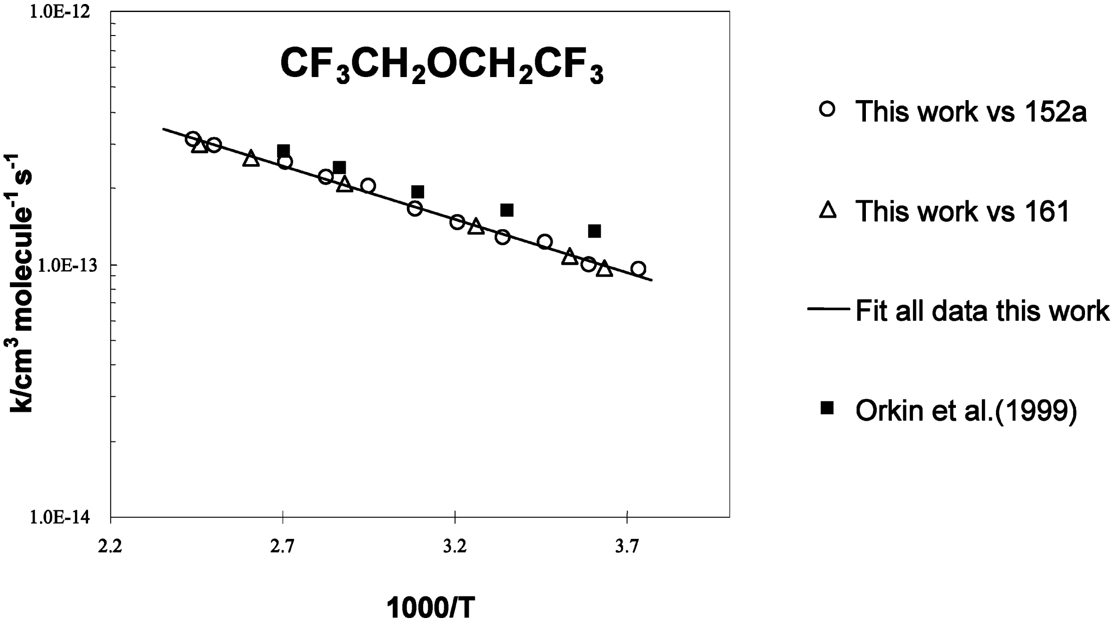

Figure 8. Rate constant results for $CF_3CH_2OCH_2CF_3$ and comparison with previous work.

temperature. One method is to use models to represent reactivities at the different sites. Table 5 shows results of this approach for six of the compounds studied in the present work. (Two of the compounds in Table 5 contain only a single type of C−H bond but are nevertheless included to illustrate the model approach). The other two compounds studied, $CF_2HCF_2OCH_2CF_3$ and $CF_3CH_2OCH_2CF_3$, do not have obvious analogues. By contrast, we note in Table 5 that the compound $CHF_2CF_2OCHF_2$ has three possible models, all of which give similar predictions for the rate parameters. The average error of the k_{298K} predictions in Table 5 is only 23%. However, such accuracy cannot be expected for all models.

For the most part the model Arrhenius parameters in Table 5 are similar to the experimental values. One exception is $CHF_2CF_2OCHFCF_3$, for which the observed *A*-factor and *E*/*R* are lower than the model prediction which is based on the assumption that there are two reactive sites, each similar to CF_3CF_2H. This suggests that one site is more reactive than CF_3CF_2H and is predominant. Indeed, the experimental A-factor of 6.9×10^{-13} cm³molecule⁻¹s⁻¹ is similar to that predicted by eq 5 (7.4×10^{-13} cm³molecule⁻¹s⁻¹) for a single C−H bond with $k_{298K} = 3.93 \times 10^{-15}$ cm³molecule⁻¹s⁻¹. It is probable, in our opinion, that CHF_2- is the more reactive site in this molecule. Thus the good agreement of the experimental k_{298K} with the model prediction is somewhat fortuitous in this case.

Conclusions

Rate constants for the eight fluoroethers studied in this work by relative rate methods are in good agreement for data from at least two reference reactants, and for the most part are in agreement with previous literature data. The poorest agreement with earlier work is for $CHF_2CF_2OCHF_2$ and $CF_3CH_2OCH_2CF_3$. Further work is needed for these compounds, especially the former.

Estimates of fluorocarbon rate constants by the SAR method are presently of limited utility, but estimates can often be made based on analogous or model compounds.

Observed temperature dependences for fluoroethers which contain a single type of C−H bond are shown to be accurately predictable, using a previously determined[14] correlation of k_{298K} with the pre-exponential factor, *A*, in the Arrhenius equation *k*

TABLE 5: Comparison of Experimental and Model Rate Constant Parameters for Six Compounds Studied in This Work

		rate constant parameters	
compound/(model)	*A*-factor (cm^3 $molecule^{-1}$ s^{-1})	*E*/*R* (K)	k_{298K} (cm^3 $molecule^{-1}$ s^{-1})
$CF_3OCF_2CHF_2$	5.24×10^{-13}	1648	2.08×10^{-15}
(CF_3CHF_2)	5.6×10^{-13}	1700	1.86×10^{-15}
$CHF_2CF_2OCHF_2$	1.24×10^{-12}	1792	3.02×10^{-15}
($CF_3OCHF_2 + CF_3OCF_2CHF_2$)	1.18×10^{-12}	1838	2.47×10^{-15}
$CHF_2CF_2OCHF_2$	1.24×10^{-12}	1792	3.02×10^{-15}
($CF_3CHF_2 + CF_3H$)	8.61×10^{-13}	1793	2.10×10^{-15}
$CHF_2CF_2OCHF_2$	1.24×10^{-12}	1792	3.02×10^{-15}
($CF_3CHF_2 + CF_3OCF_2H$)	8.98×10^{-13}	1782	2.27×10^{-15}
$CF_3OCF_2CHFCF_3$	4.07×10^{-13}	1609	1.84×10^{-15}
(CF_3CHFCF_3)	5.00×10^{-13}	1700	1.66×10^{-15}
$(CF_3)_2CHOCHF_2$	1.63×10^{-12}	1906	2.71×10^{-15}
($CF_3CHFCF_3 + 0.5CHF_2OCHF_2$)	1.32×10^{-12}	1831	2.82×10^{-15}
$CHF_2CF_2OCHFCF_3$	6.86×10^{-13}	1538	3.93×10^{-15}
(2 x CF_3CHF_2)	1.12×10^{-12}	1700	3.73×10^{-15}
$CF_3CHFCF_2OCH_2CF_3$	1.49×10^{-12}	1517	9.17×10^{-15}
($CF_3CFH_2 + CF_3CHFCF_3$)	2.00×19^{-12}	1736	5.88×10^{-15}

TABLE 6: Comparison of Experimental and Calculated Arrhenius Parameters for Some Fluoroethers Having a Single Type of C−H Bond[a]

	experimental parameters			calculated parameters		
compound	*A*-factor	*E*/*R*	k_{298K}	*A*-factor	*E*/*R*	source of experimental data
CF_3OCF_2H	3.18×10^{-13}	1964	4.37×10^{-16}	4.21×10^{-13}	2048	Hsu and DeMore[13]
CF_2HOCF_2H	1.29×10^{-12}	1895	2.22×10^{-15}	1.07×10^{-12}	1841	Wilson et al.[2]
CF_3OCH_3	2.09×10^{-12}	1554	1.13×10^{-14}	2.21×10^{-12}	1571	Hsu and DeMore[13]
$CF_3OCF_2CHF_2$	5.24×10^{-13}	1648	2.08×10^{-15}	6.30×10^{-13}	1702	this work
$CH_3OCF_2CF_3$	1.90×10^{-12}	1510	1.20×10^{-14}	2.24×10^{-12}	1559	Tokuhashi et al.[8]
$CF_3OCF_2CHFCF_3$	4.07×10^{-13}	1609	1.84×10^{-15}	6.11×10^{-13}	1730	this work
$CH_3OCF_2CF_2CF_3$	2.06×10^{-12}	1540	1.17×10^{-14}	2.22×10^{-12}	1563	Tokuhashi et al.[8]
$CH_3OCF(CF_3)_2$	1.94×10^{-12}	1450	1.49×10^{-14}	2.37×10^{-12}	1509	Tokuhashi et al.[8]
$CF_3CH_2OCH_2CF_3$	3.28×10^{-12}	962	1.30×10^{-13}	5.12×10^{-12}	1095	this work

[a] Units of k_{298K} and the *A*-factor are cm^3 $molecule^{-1}$ s^{-1} and units of *E*/*R* are degrees K.

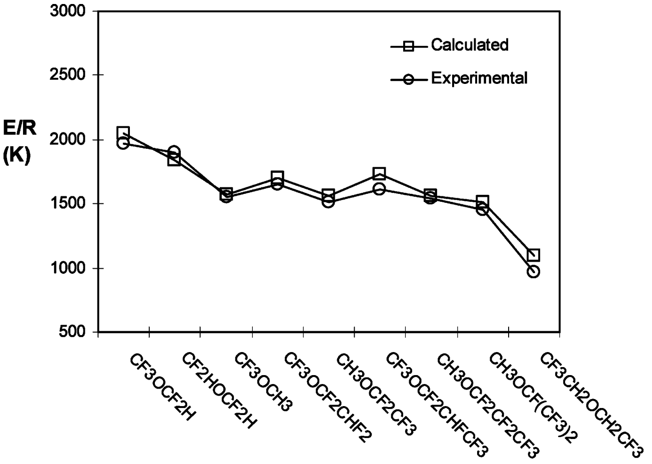

Figure 9. Comparison of experimental and calculated E/R values for fluoroethers having a single type of C−H bond.

$= Ae^{-E/RT}$. This indicates that OH abstractions from fluoroethers show the same behavior with regard to Arrhenius parameters as other substrates such as halocarbons or hydrocarbons.

Fluoroethers with multiple types of C−H bonds can sometimes be treated by a model approach using analogous compounds which breaks down the overall reaction rate into its components at the various sites, and thereby permits estimation of the overall Arrhenius parameters for the reaction.

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