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Rate Constants and Temperature Dependences for the Reactions of Hydroxyl Radical with Several Halogenated Methanes, Ethanes, and Propanes by Relative Rate Measurements

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Rate constants of 15 OH reactions with halogen-substituted alkanes, C1 to C3, were studied using a relative rate technique in the temperature range 283−403 K. Compounds studied were CHF_2Cl (22), CHF_2Br (22B), CH_3F (41), CH_2F_2 (32), CHF_3 (23), $CHClFCCl_2F$ (122a), $CHCl_2CF_3$ (123), $CHClFCF_3$ (124), CH_3CF_3 (143a), CH_3CH_2F (161), CF_3CHFCF_3 (227ea), $CF_3CH_2CF_3$ (236fa), $CF_3CHFCHF_2$ (236ea), and $CHF_2CF_2CH_2F$ (245ca). Using CH_4, CH_3CCl_3, CF_3CF_2H, and C_2H_6 as primary reference standards (JPL 92-20 rate constants), absolute rate constants are derived. Results are in good agreement with previous experimental results for six of the compounds studied, including CHF_2Cl, CHF_2Br, CH_2F_2, CH_3CF_3, $CHFClCFCl_2$, and CF_3CHFCF_3. For the remainder the relative rate constants are lower than those derived from experiments in which OH loss was used to measure the reaction rate. Comparisons of the derived Arrhenius *A* factors with previous literature transition-state calculations[2,3] show order of magnitude agreement in most cases. However, the experimental *A* factors show a much closer proportionality to the number of H atoms in the molecule than is evident from the transition state calculations. For most of the compounds studied, an *A* factor of $(8 \pm 3)E{-}13$ cm^3/(molecule s) per C−H bond is observed. A new measurement of the ratio $k^{CH_3CCl_3}/k^{CH_4}$ is reported that is in good agreement with previous data.

Introduction

Most atmospheric species which have at least one C−H bond are destroyed in the atmosphere by OH attack. To estimate the atmospheric lifetimes of such species, accurate data for the rate constants and their temperature dependences are needed. Such data are especially useful when referenced to methylchloroform, because that compound is used as a standard for atmospheric lifetimes of species removed by OH.[4] A considerable body of data has accumulated for these reactions. (See ref 1 for a compilation.) The bulk of the data have been obtained by measuring the rate of disappearance of OH in the presence of the reactant. However, such measurements are vulnerable to OH loss by reaction with impurities, secondary or side reactions, and wall reactions. As a consequence many rate constants obtained in that manner are effectively upper limits to the correct rate constants, and thus they imply shorter atmospheric lifetimes than is actually the case. Also, the uncertainty makes the data less useful for tests of theory, such as comparison of preexponential factors with those calculated from transition-state theory[2,5] or for calibration of rate constant estimation methods such as that of Atkinson.[6] Correlations with abstraction reactions of other species such as Cl, Br, and I may be obscured.

Measurements of the consumption of two compounds in the presence of OH can give very accurate ratios of rate constants. This method has the advantage of being insensitive to impurities, secondary reactions, or wall losses which may affect the measurements based on OH loss. If CH_3CCl_3 is included in the relative database, then the results can be used for atmospheric lifetime calculations without regard to the absolute accuracy of any of the rate constants. Further, if a reliable absolute rate constant is available, such as is believed to be the case for the $OH + CH_4$ reaction,[1] then the relative data can be placed on an absolute basis by including CH_4 as a reference standard. In the present work we report relative rate measurements, traceable to CH_4, CH_3CCl_3, and other reference gases, for 15 halogenated methanes, ethanes, and propanes. In a few cases the results agree very well with previous measurements based on OH loss, but often the latter are higher than those from the relative rate results. The experimental preexponential factors are examined for their dependence on the number of hydrogen atoms in the molecules and are compared with recent transition-state predictions.

Experimental Section

The relative rate technique used in this work has been described in several recent publications.[7−9] The method involves measurement of the fractional losses of the reactant compound and a reference compound in the presence of OH. The OH radicals are produced by UV photolysis of O_3 ((5−10) × 10^{16} cm^{-3}) in the presence of water vapor ((3−5) × 10^{17} cm^{-3}) in a slow-flow, temperature-controlled photochemical cell. For reactants such as HFCs which do not absorb 185 nm radiation, direct photolysis of H_2O at 185 nm may also be used for OH production. The H atoms produced in the H_2O photolysis are converted to the relatively unreactive HO_2 in the presence of O_2. The cylindrical cell is 10 cm in length and 5 cm in diameter and is either water-jacketed (for the O_3 photolysis experiments) or wrapped with heating tape and insulating material for the H_2O photolysis experiments. Residence times in the cell for the slow-flow mode are about 1 min. To obtain high conversion ratios, experiments are sometimes operated in a stopped-flow mode where the reactant mixture is expanded into the IR cell for analysis after several minutes of irradiation. This method is most useful for reactant pairs which have slow rate constants. All experiments are at atmospheric pressure.

The rate constant ratio is obtained from the relation

$$k_{\mathrm{reactant}}/k_{\mathrm{reference}} = \ln(\mathrm{DF})_{\mathrm{reactant}}/\ln(\mathrm{DF})_{\mathrm{reference}} \quad \text{(I)}$$

The quantity DF (depletion factor) is defined as

$$\mathrm{DF} = (\text{initial concn})/(\text{final concn}) \quad \text{(II)}$$

Initial reactant and reference concentrations are in the range

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TABLE 1: Rate Constants of the Primary Reference Compounds Used in This Work

reference compound	Arrhenius rate constant[a]	k(298 K)
CH_4	2.9E−12exp(−1820/T)	6.5E−15
CH_3CCl_3	1.8E−12exp(−1550/T)	1.0E−14
CF_3CF_2H	5.6E−13exp(−1700/T)	1.9E−15
C_2H_6	8.7E−12exp(−1070/T)	2.4E−13

[a] All from ref 1.

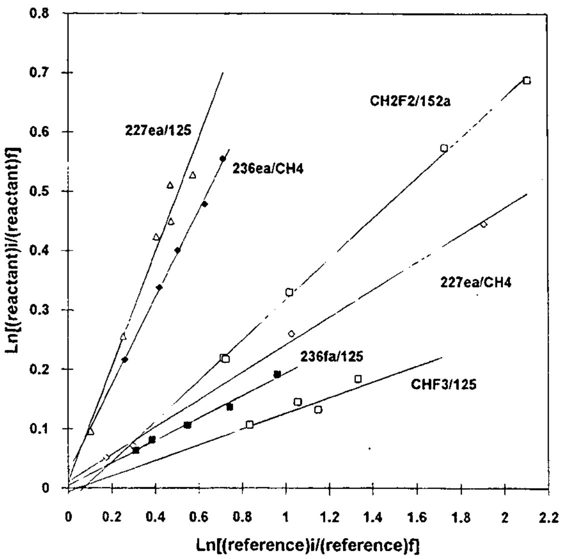

Figure 1. Tests of the linear dependence between depletion factors of reactant and reference gases, as predicted from eq 1.

$10^{14}-10^{15}$ cm^{-3}, and depletion factors are normally about 1.1−1.5. Concentrations are monitored with a Nicolet 20SX FTIR operated at 0.5 cm^{-1} resolution in the absorbance mode using a White cell with a 3 m path length. After irradiation, and before entering the FTIR cell, the mixture flows through a trap at about −20 °C to remove the bulk of the H_2O, which would interfere with the IR analysis. The light source is a low-pressure Hg lamp. Flow controllers are used to maintain constant flows of reactant mixture (10 Torr each of the two reactants plus 1000 Torr of Ar, stored in two 5-L bulbs), the O_2/O_3 input (flowing from a commercial ozonizer), and the Ar carrier. Argon is used because of its low quenching efficiency for $O(^1D)$. The experiments are usually conducted in a light-on, light-off mode for repeated measurements of the depletion factors. Approximately 15 min are required for concentrations to stabilize between cycles.

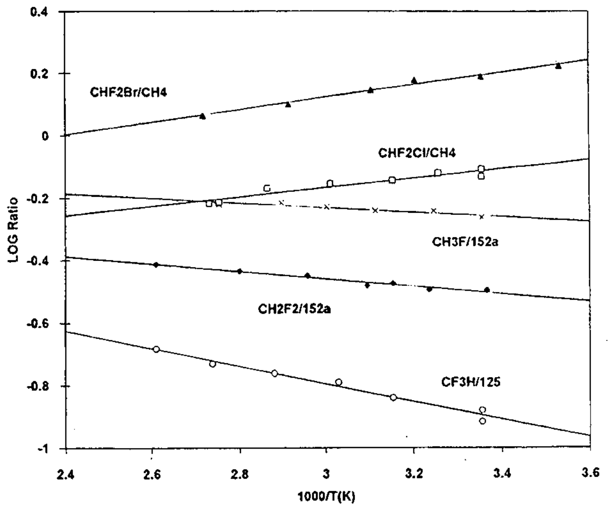

Figure 2. Arrhenius plots of rate constant ratio data for the halogenated methanes.

Reactant regeneration by secondary chemistry could be a source of error, but in the presence of O_2 (which scavenges radical products) this is improbable and there is no evidence that it occurs. Results for rate constant ratios are tested for any dependence on the extent of reaction, which would indicate a complication due to secondary chemistry. No such dependence has been found in O_2-containing mixtures. In mixtures with no O_2, CH_4 regeneration has been observed, as evidenced by a decreasing CH_4 loss with increasing extent of photolysis. However, O_2-free mixtures are not generally used.

It is also necessary for OH to be the only radical species removing the reactants. Other possible reactant species are $O(^1D)$ (from O_3 photolysis), halogen atoms (which may be produced in secondary chemistry), and various haloalkoxy or peroxy radicals. Attack of $O(^1D)$ on the reactants is minimized by using a large excess (factor of 300−500) of H_2O over the reactants. Computer simulations show that errors in the rate constant ratio less than 3% are expected under these conditions. In any case it is often possible to compare results in O_3

TABLE 2: Ranges of Depletion Factors for Relative Rate Measurements of Halogen-Substituted Alkanes

reactant	reference	depletion factor range: reactant	depletion factor range: reference
CHF_2Cl (HFC-22)	CH_4	1.10−1.14	1.14−1.24
CHF_2Br (HFBC-22B)	CH_4	1.11−1.31	1.07−1.23
CH_3F	CH_3CF_2H (HFC-152a)	1.70−2.05	1.34−1.55
CH_2F_2	CH_3CF_2H (HFC-152a)	1.20−2.01[a]	1.82−8.25[a]
CHF_3	CHF_2CF_3 (HFC-125)	1.04−1.28[a]	1.70−4.37[a]
$CHClFCCl_2F$ (HCFC-122a)	CH_3CF_2H (HFC-152a)	1.12−1.23	1.27−1.58
$CHCl_2CF_3$ (HCFC-123)	CH_3CF_2H (HFC-152a)	1.18−1.42	1.25−1.55
$CHFClCF_3$ (HCFC-124)	CH_4	1.13−1.22	1.12−1.17
$CHFClCF_3$ (HCFC-124)	CHF_2CHF_2 (HFC-134)	1.16−1.28	1.13−1.25
CH_3CF_3 (HFC-143a)	CH_4	1.03−1.33	1.16−4.23
CH_3CF_3 (HFC-143a)	CHF_2CF_3 (HFC-125)	1.11−1.65	1.17−2.18
CH_3CF_2H (HFC-152a)	CH_4	1.24−2.03	1.04−1.24
CH_3CF_2H (HFC-152a)	CH_3CCl_3	1.36−2.34	1.10−1.42
CH_3CH_2F (HFC-161)	C_2H_6	1.13−1.30	1.21−1.43
CF_3CHFCF_3 (HFC-227ea)	CH_4	1.06−1.57[a]	1.41−6.89[a]
CF_3CHFCF_3 (HFC-227ea)	CHF_2CF_3 (HFC-125)	1.04−1.10	1.06−1.12
		1.10−1.70[a]	1.11−1.82[a]
$CF_3CH_2CF_3$ (HFC-236fa)	CHF_2CF_3 (HFC-125)	1.02−1.04	1.08−1.15
		1.06−1.26[a]	1.36−2.53[a]
$CF_3CHFCHF_2$ (HFC-236ea)	CH_4	1.23−2.00[a]	1.30−2.81
$CHF_2CF_2CH_2F$ (HFC-245ca)	CH_4	1.08−1.17	1.06−1.15

[a] Stopped flow measurement.

TABLE 3: Experimental Results for Rate Constant Ratios, k/k_{ref}, for Halogen-Substituted Methanes

CHF_2Cl		CHF_2Br		CH_3F		CH_2F_2		CHF_3	
T (K)	$k/k_{ref}{}^a$	T (K)	$k/k_{ref}{}^a$	T (K)	$k/k_{ref}{}^c$	T (K)	$k/k_{ref}{}^c$	T (K)	$k/k_{ref}{}^d$
298	0.777	283	1.672	298	0.543	297	0.318	298	0.132
298	0.736	298	1.549	308	0.571	309	0.320	298	0.121
307	0.755	312	1.508	321	0.573	317	0.335	317	0.145
317	0.717	322	1.399	333	0.585	323	0.330	330	0.162
332	0.700	343	1.258	345	0.609	338	0.355	347	0.173
349	0.676	368	1.159	363	0.602	357	0.368	365	0.185
363	0.611					383	0.386	383	0.208
366	0.606								

[a] CH_4. [b] C_2H_6. [c] HFC-152a. [d] HFC-125. [e] HFC-134. [f] HFC-161 were the reference compounds.

TABLE 4: Experimental Results for Rate Constants Ratios, k/k_{ref}, for Halogen-Substituted Ethanes

$CHClFCCl_2F$ (HCFC-122a)		$CHClFCF_3$ (HCFC-124)				CH_3CF_3 (HFC-143a)			
T (K)	$k/k_{ref}{}^c$	T (K)	$k/k_{ref}{}^a$	T (K)	$k/k_{ref}{}^e$	T (K)	$k/k_{ref}{}^a$	T (K)	$k/k_{ref}{}^d$
294	0.446	298	1.164	298	1.293	298	0.212	298	0.630
294	0.467	298	1.217	298	1.180	298	0.199	313	0.653
298	0.481	313	1.134	298	1.272	314	0.210	330	0.714
308	0.460	328	1.054	298	1.244	328	0.189	351	0.755
328	0.444	345	1.013	308	1.216	346	0.241	383	0.823
345	0.425	358	0.936	321	1.194	374	0.242		
351	0.458	366	0.975	334	1.077	403	0.240		
358	0.426			356	1.092				
362	0.430			356	1.042				

$CHCl_2CF_3$ (HCFC-123)		CH_3CHF_2 (HFC-152a)				CH_3CH_2F (HFC-161)	
T (K)	$k/k_{ref}{}^c$	T (K)	$k/k_{ref}{}^a$	T (K)	$k/k_{ref}{}^g$	T (K)	$k/k_{ref}{}^b$
298	0.947	298	4.77	298	3.28	285	0.671
298	0.972	303	4.456	298	3.22	298	0.714
313	0.906	308	4.337	298	3.24	298	0.657
320	0.893	308	4.790	298	3.19	298	0.657
324	0.833	308	4.812	308	3.07	308	0.708
332	0.862	318	4.087	313	2.98	318	0.708
345	0.839	333	3.850	313	3.14	329	0.695
358	0.765	333	3.896	333	2.75	338	0.733
359	0.767	358	3.506	333	3.19	351	0.752
359	0.790	358	3.384	358	2.88	358	0.722
				358	2.82	364	0.762

[a] CH_4. [b] C_2H_6. [c] HFC-152a. [d] HFC-125. [e] HFC-134. [f] HFC-161. [g] CH_3CCl_3 were the reference compounds.

TABLE 5: Experimental Results for Rate Constant Ratios, k/k_{ref}, for Halogen-Substituted Propanes

CF_3CHFCF_3 (HFC-227ea)				$CF_3CH_2CF_3$ (HFC-236fa)		$CF_3CHFCHF_2$ (HFC-236ea)		$CHF_2CF_2CH_2F$ (HFC-245ca)	
T (K)	$k/k_{ref}{}^a$	T (K)	$k/k_{ref}{}^d$	T (K)	$k/k_{ref}{}^d$	T (K)	$k/k_{ref}{}^a$	T (K)	$k/k_{ref}{}^a$
296	0.243	298	0.991	298	0.198	298	0.796	286	1.154
320	0.255	310	0.864	298	0.192	320	0.746	286	1.151
338	0.242	323	0.938	306	0.186	333	0.723	298	1.241
355	0.250	347	0.934	312	0.185	350	0.706	298	1.170
361	0.224	358	0.930	323	0.208	366	0.690	310	1.157
398	0.230	358	0.972	333	0.210	380	0.668	310	1.142
		367	0.875	344	0.235			319	1.117
				354	0.240			319	1.106
				355	0.246			331	1.135
				367	0.273			331	1.134
								345	1.056
								345	1.119
								364	1.041
								364	1.022

[a] CH_4. [b] C_2H_6. [c] HFC-152a. [d] HFC-125. [e] HFC-134. [f] HFC-161 were the reference compounds.

photolysis experiments with those from H_2O photolysis experiments. No significant difference has ever been observed in these comparisons. Errors due to halogen atoms are prevented in experiments with O_3 because of rapid scavenging by the O_3. In general, reactions of secondary radicals are unimportant because of the normally low reactivity and relatively low rate of production compared to OH.

Direct photolysis of reactants is a potential complication. However, the HFCs (hydrofluorocarbons) are transparent to both 185 and 254 nm radiation, and the HCFCs (hydrofluorochlorocarbons) are transparent to 254 nm, which is the only wavelength used for those compounds. Tests are made for unsuspected complications by measuring rate constant ratios with more than one reference compound and have not found any case in which the results differ significantly.

The technique is very accurate for rate constant ratio determinations because the depletion factors can be measured with great precision (approximately 0.1−0.3%) by the FTIR technique. The FTIR measurements of the depletion factors are based on at least two measurements, one being an absorbance measurement at a fixed wavelength of a strong IR band of the compound (sometimes two bands are used as a further test of consistency). Absorbance has been found to be linear with reactant concentrations for the compounds used in this work.

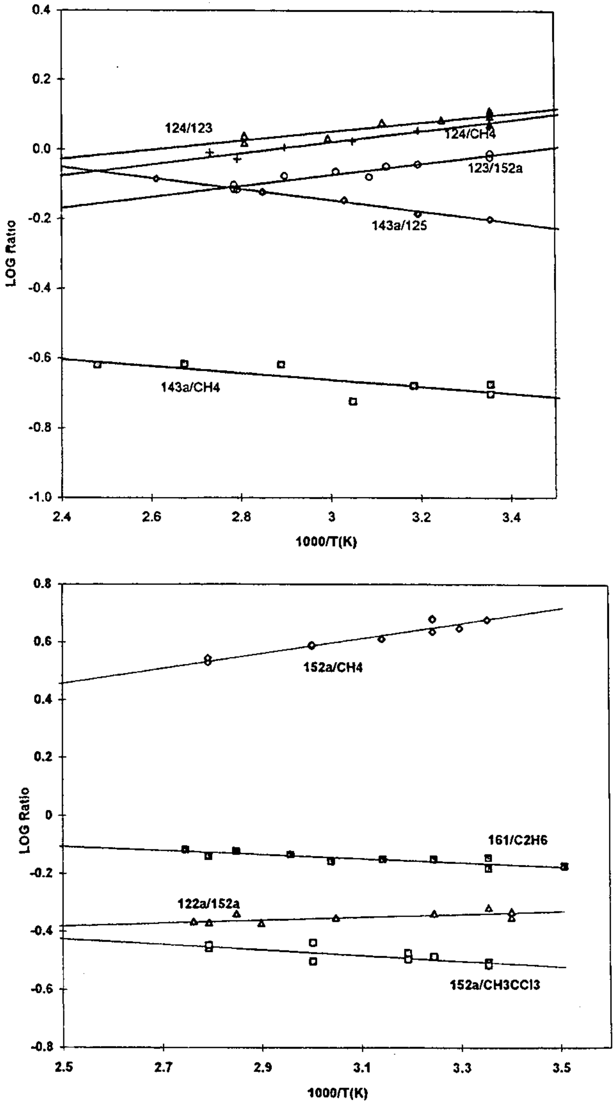

Figure 3. Arrhenius plots of rate constant ratio data for some halogenated ethanes.

The absorbance method is accurate provided that there is no overlap with the spectrum of the second reactant, and product spectra do not interfere. Product interference is tested for by subtracting a reference spectrum of the compound in question, and noting any product spectra which may have remained. A second measure of the concentration is the subtraction factor, which is the factor by which the reference IR spectrum must be multiplied for exact subtraction of the spectral features of that compound. The subtraction factor ratio is used in addition to the absorbance ratios to determine the depletion factors. The best indication of the accuracy of the measurements is the fact that results obtained with depletion factors as small as 1.03 do not differ significantly from those with much larger depletions.

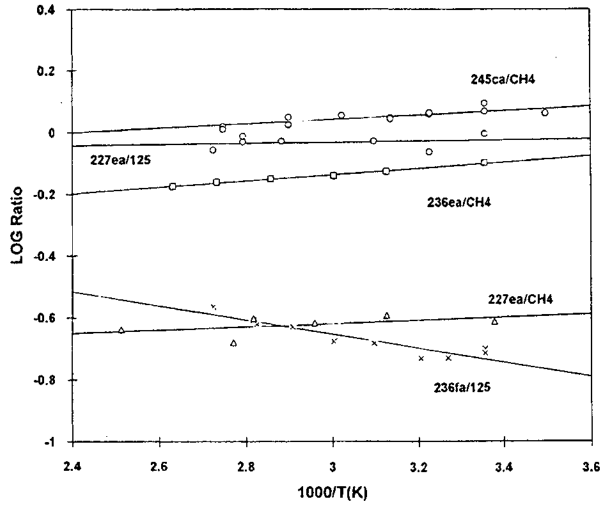

Figure 4. Arrhenius plots of rate constant ratio data for some halogenated propanes.

Several factors are involved in the choice of reference compounds: (1) the accuracy of the absolute rate constant; (2) the magnitude of the rate constant (which should be similar to the rate constant to be compared); (3) the IR spectral bands should be strong and well-defined and should not interfere with those of the reactant. From the standpoint of absolute accuracy, CH_4 is a good choice, the rate constant having been carefully measured using high-purity samples, and with great care to avoid errors due to secondary chemistry.[10] Ethane is useful as a standard for faster reactions, the OH rate constant being about 37 times faster than that of CH_4 at 298 K. However, the C_2H_6 rate constant is not known as accurately as that of CH_4, despite

TABLE 6: Ratios Measured and Their Temperature Dependences

reactant	reference	k/k_{ref}[a]	ratio at 298 K
	Halogen-Substituted Methanes		
CHF_2Cl (HFC-22)	CH_4	(0.24 ± 0.03) exp(342 ± 45)/T	0.76
CHF_2Br (HFBC-22B)	CH_4	(0.33 ± 0.03) exp(460 ± 31)/T	1.54
CH_3F	HFC-152a	(0.99 ± 0.10) exp(−174 ± 35)/T	0.55
CH_2F_2	HFC-152a	(0.80 ± 0.06) exp(−277 ± 24)/T	0.32
CHF_3	HFC-125	(1.14 ± 0.08) exp(−654 ± 44)/T	0.13
	Halogen-Substituted Ethanes		
$CHClFCCl_2F$ (HCFC-122a)	HFC-152a	(0.31 ± 0.04) exp(117 ± 42)/T	0.46
$CHCl_2CF_3$ (HCFC-123)	HFC-152a	(0.28 ± 0.03) exp(365 ± 36)/T	0.95
$CHFClCF_3$ (HCFC-124)	CH_4	(0.35 ± 0.04) exp(367 ± 40)/T	1.20
$CHFClCF_3$ (HCFC-124)	HFC-134	(0.46 ± 0.07) exp(300 ± 52)/T	1.26
CH_3CF_3 (HFC-143a)	CH_4	(0.43 ± 0.12) exp(−223 ± 90)/T	0.21
CH_3CF_3 (HFC-143a)	HFC-125	(2.16 ± 0.14) exp(−370 ± 21)/T	0.62
CH_3CF_2H (HFC-152a)	CH_4	(0.64 ± 0.13) exp(599 ± 67)/T	4.8
CH_3CF_2H (HFC-152a)	CH_3CCl_3	(1.53 ± 0.28) exp(220 ± 57)/T	3.2
CH_3CH_2F (HFC-161)	C_2H_6	(1.16 ± 0.13) exp(−158 ± 36)/T	0.68
	Halogen-Substituted Propanes		
CF_3CHFCF_3 (HFC-227ea)	CH_4	(0.17 ± 0.05) exp(117 ± 105)/T	0.25
CF_3CHFCF_3 (HFC-227ea)	HFC-125	(0.83 ± 0.22) exp(38 ± 89)/T	0.94
$CF_3CH_2CF_3$ (HFC-236fa)	HFC-125	(1.26 ± 0.41) exp(−580 ± 109)/T	0.18
$CF_3CHFCHF_2$ (HFC-236ea)	CH_4	(0.36 ± 0.01) exp(231 ± 12)/T	0.78
$CHF_2CF_2CH_2F$ (HFC-245ca)	CH_4	(0.67 ± 0.07) exp(164 ± 34)/T	1.16

[a] Errors shown are standard deviation. Actual uncertainties are approximately a factor of 1.3 in the *A* factor ratios and 75−125 K in the *E*/*R* values.

TABLE 7: Halogenated Methanes: Derived Rate Constants and Comparisons with Previous Work

reactant	*A* factor	*E/R*	*k*(298 K)	reference
CHF_2Cl (HCFC-22)	1.2*E*−12	1636	5.0*E*−15	Atkinson et al.[20]
	9.2*E*−13	1575	4.7*E*−15	Watson et al.[21]
	9.5*E*−12	2315	4.0*E*−15	Clyne and Holt[22]
	2.1*E*−12	1782	5.3*E*−15	Handwerk and Zellner[23]
			4.6*E*−15	Paraskevopoulos et al.[24]
	1.3*E*−12	1670	4.8*E*−15	Jeong and Kaufman[11]
	1.2*E*−12	1650	4.7*E*−15	JPL 92-20
	8.1*E*−13	1516	5.0*E*−15	Orkin and Khamaganov[25]
	7.1*E*−13	1478	5.0*E*−15	this work[a]
CHF_2Br (HBFC-22)	7.4*E*−13	1300	9.4*E*−15	Talukdar et al.[26]
	7.4*E*−13	1300	9.4*E*−15	JPL 92-20
	9.3*E*−13	1326	1.1*E*−14	Orkin and Khamaganov[27]
	9.6*E*−13	1360	1.0*E*−14	this work[a]
CH_3F (HFC-41)			1.6*E*−14	Howard and Evenson[13]
			2.2*E*−14	Nip et al.[28]
	8.2*E*−12	1890	1.5*E*−14	Jeong and Kaufman[11]
	5.4*E*−12	1700	1.8*E*−14	JPL 92-20
	1.7*E*−12	1300	2.2*E*−14	Schmoltner et al.[12]
	2.2*E*−12	1449	1.7*E*−14	this work[c]
CH_2F_2 (HFC-32)			7.8*E*−15	Howard and Evenson[13]
			1.2*E*−14	Nip et al.[28]
	4.4*E*−12	1766	1.2*E*−14	Jeong et al.[19]
	1.6*E*−12	1470	1.2*E*−14	Talukdar et al.[17]
	1.9*E*−12	1550	1.0*E*−14	JPL 92-20
	1.8*E*−12	1552	9.8*E*−15	this work[c]
CHF_3 (HFC-23)			2.0*E*−16	Howard and Evenson[13]
	3.0*E*−12	2910	2.0*E*−16	Jeong and Kaufman[11]
	6.9*E*−13	2300	3.1*E*−16	Schmoltner et al.[12]
	see Figure 9			Kurylo et al.[14]
	1.5*E*−12	2650	2.1*E*−16	JPL 92-20
	6.4*E*−13	2354	2.4*E*−16	this work[d]

[a] CH_4. [b] C_2H_6. [c] HFC-152a. [d] HFC-125. [e] HFC-134. [f] HFC-161 were the reference compounds.

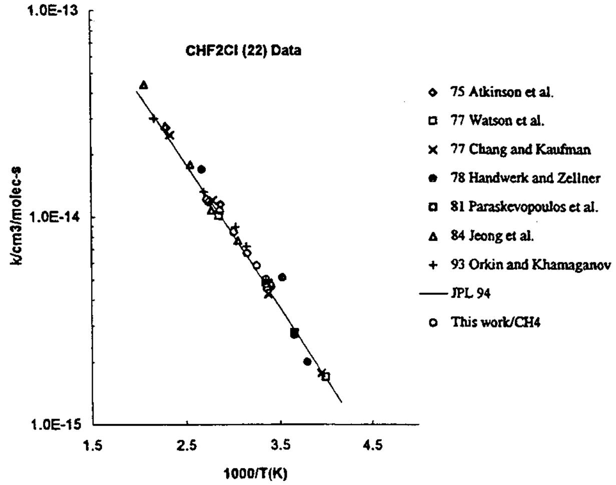

Figure 5. Arrhenius plot of data for CHF_2Br (HBFC-22B).

the fact that many studies have been reported.[1] Earlier results from this laboratory indicate, however, that the rate constant for C_2H_6 is consistent with that of CH_4 to within about 10%.[9] As mentioned in the Introduction, CH_3CCl_3 is a standard for atmospheric lifetimes, and the rate constant has also been carefully measured.[1] We have found that the recommended rate constants[1] for CH_4, CH_3CCl_3, and C_2F_5H (HFC-125) give consistent results to within 3% or better at 298 K, when used as common references for the same gas; for example, HFC-134a[7] or HCFC-141b.[8] The E/R values appear to be mutually consistent to within about 75 K. These three compounds, along with C_2H_6 are the primary references for our work. The rate constants used (Table 1) are those of the JPL 92-20 evaluation. In addition to these primary references, we also use secondary references, such as HFC-134a, HFC-134, HFC-152a, or HFC-161, where the rate constants have been determined in our own work and are based on one or more of the primary references. These secondary references are often more suitable than any of the primary references because of the position of the IR bands or the magnitude of the rate constants.

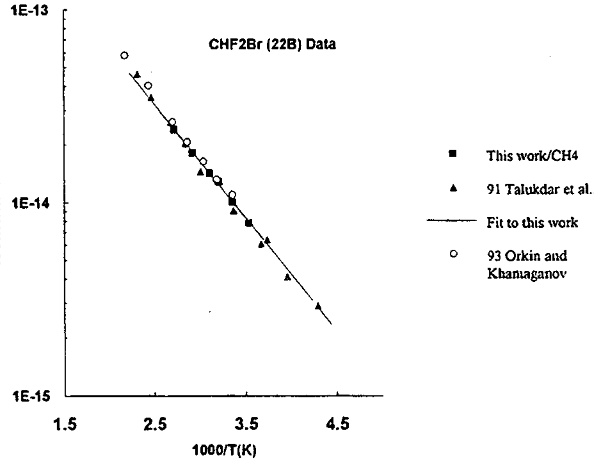

Figure 6. Arrhenius plot of data for CH_3F (HFC-41).

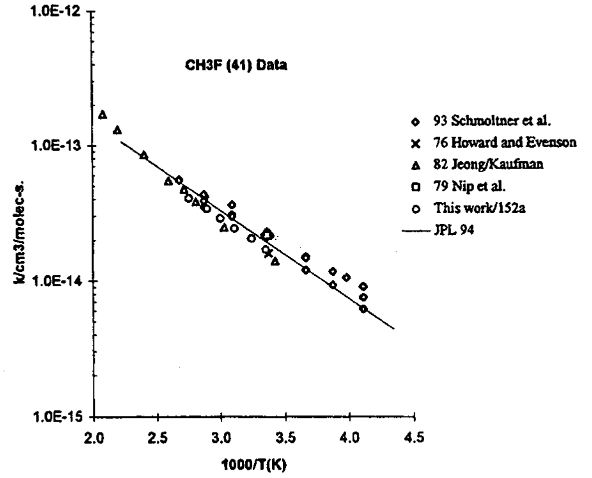

Figure 7. Arrhenius plot of data for CH_2F_2 (HFC-32).

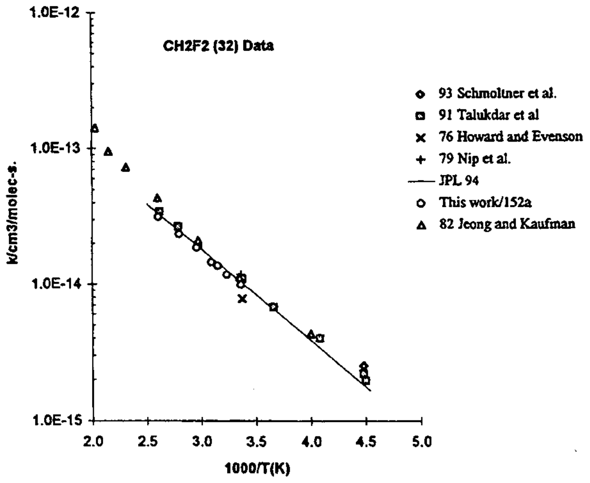

Figure 8. Arrhenius plot of data for CH_2F_2 (HFC-32).

Results

Figure 1 shows data from six experiments using the stopped-flow method. The lines are unrestricted linear least-squares fits to the data. The results show a linear dependence between depletion factors of reactant and reference compounds and a

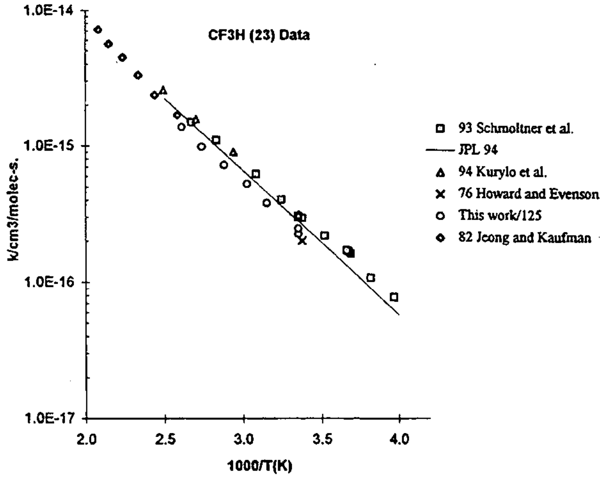

Figure 9. Arrhenius plot of data for CF_3H (HFC-23).

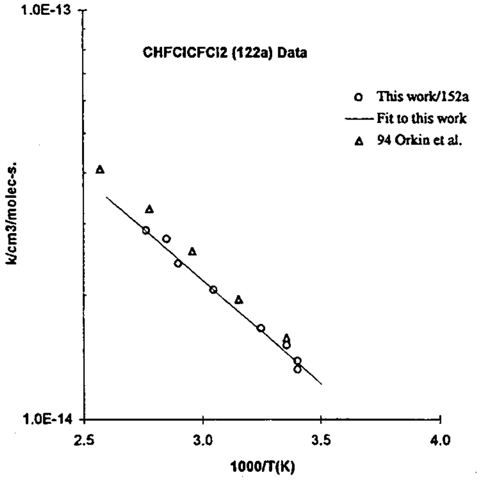

Figure 10. Arrhenius plot of data for $CHFClCFCl_2$ (HCFC-122a).

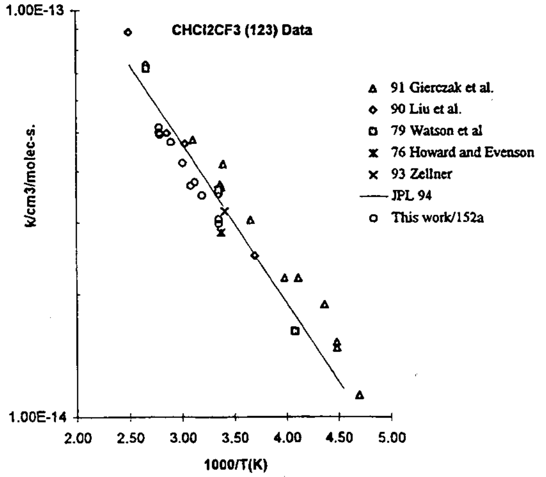

Figure 11. Arrhenius plot of data for $CHCl_2CF_3$ (HCFC-123).

near-zero intercept, as expected from eq I. This indicates the absence of problems resulting from reactant regeneration or product spectral interference.

Table 2 lists the extent of depletions that were obtained for each reactant pair in all the present experiments. Each data point is the average of three or four depletion ratios, which were measured in successive light-on, light-off cycles at a given temperature.

Data for the temperature dependences of the rate constant ratios are listed in Tables 3−5 for the methanes, ethanes, and propanes. These data are plotted in Figures 2−4, and the derived Arrhenius expressions are summarized in Table 6. The resulting rate constants are listed in Tables 7−9, along with comparisons with previous measurements. Figures 5−19 show graphically the data and the comparisons with other work. The lines labeled "JPL 94" in Figures 5−19 are the rate constant recommendations which will appear in the next edition of the JPL/NASA data evaluation.

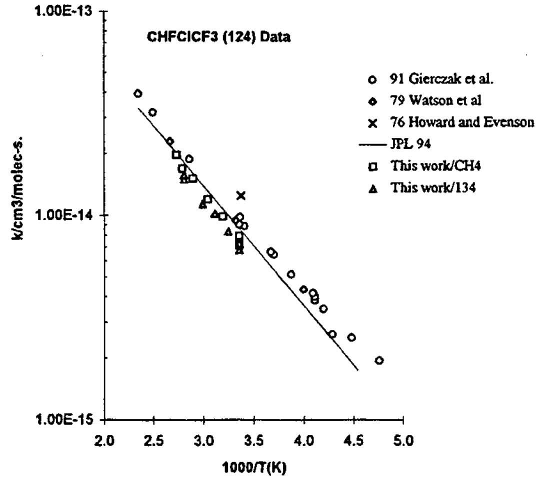

Figure 12. Arrhenius plot of data for $CHFClCF_3$ (HCFC-124).

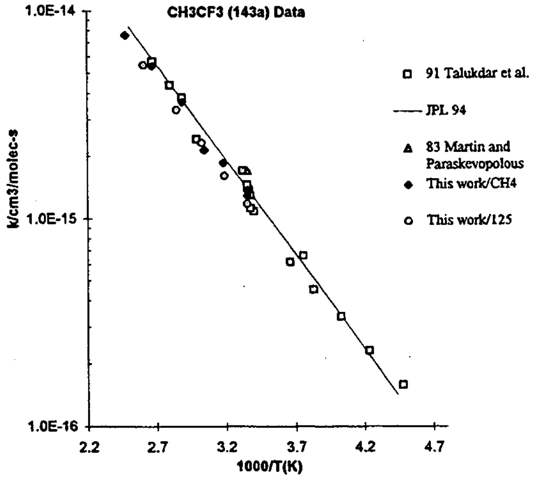

Figure 13. Arrhenius plot of data for CH_3CCl_3 (HFC-143a).

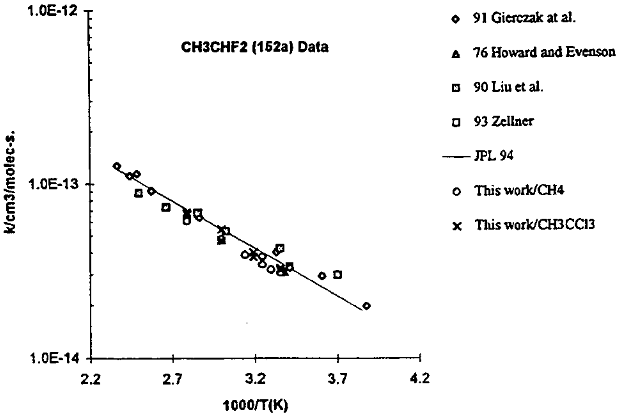

Figure 14. Arrhenius plot of data for CH_3CHF_2 (HFC-152a).

Methanes. For the five halogenated methanes studied, agreement is reasonably good among the present and previous measurements. This is especially true for CHF_2Cl (HCFC-22), CHF_2Br (HBFC-22B), and CH_2F_2 (HFC-32), which therefore appear to have well-established rate constants. For CH_3F, our data are in excellent agreement with that of Jeong and

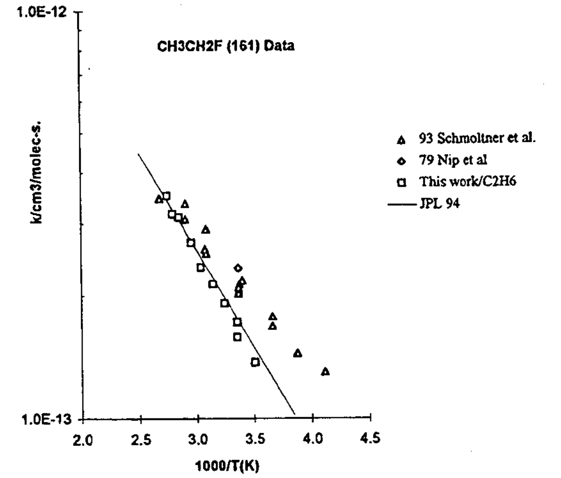

Figure 15. Arrhenius plot of data for CH_3CH_2F (HCFC-161).

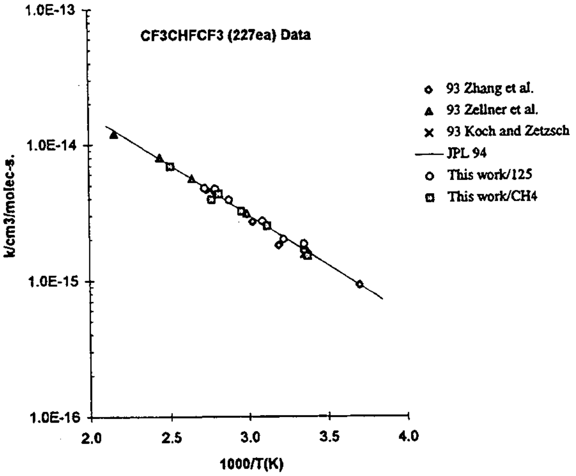

Figure 16. Arrhenius plot of data for CF_3CHFCF_3 (HFC-227ea).

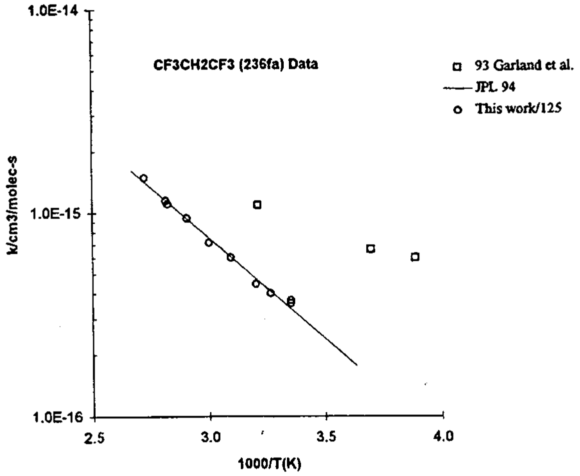

Figure 17. Arrhenius plot of data for $CF_3CH_2CF_3$ (HFC-236fa).

Kaufman,[11] but slightly lower than the results of Schmoltner et al.[12] The compound CF_3H has a low rate constant for the OH reaction, and therefore was measured by Jeong and Kaufman only at higher temperatures. Our data at lower temperatures are in good agreement with their extrapolated data, as well as that of the earlier room temperature measurement of Howard and Evenson.[13] The more recent results of Schmoltner et al.[12] and Kurylo et al.[14] are in good agreement with each other but slightly higher than the others.

Ethanes. Our result for $CHClFCCl_2F$ (HCFC-122a, Figure 10) is in excellent agreement with an unpublished measurement by Orkin et al.,[15] who obtained $K = 1.0E-12 \exp(-1240/T)$ in the temperature range 298−460 K using a fast-flow/EPR technique. From Figures 11 and 12, it is apparent that our data for $CHCl_2CF_3$ (HCFC-123) and $CHFClCF_3$ (HCFC-124) are lower than some of the absolute measurements[16] but in good agreement with others.

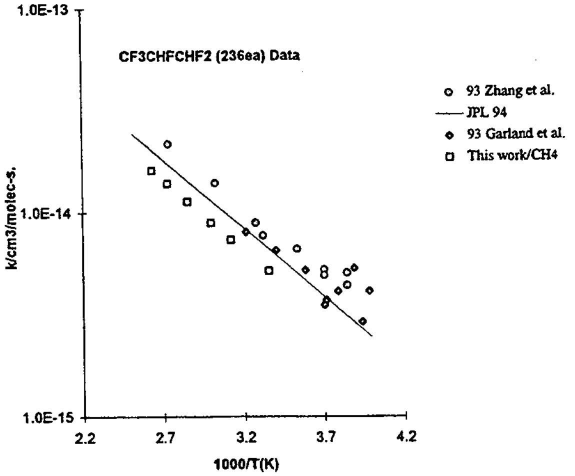

Figure 18. Arrhenius plot of data for CF_3-$CHFCHF_2$ (HFC-236ea).

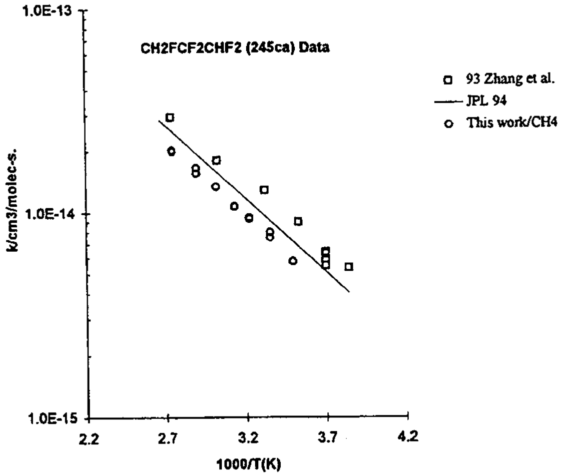

Figure 19. Arrhenius plot of data for $CH_2FCF_2CHF_2$ (HFC-245ca).

Since we use CH_3CHF_2 (HFC-152a) as a secondary reference, the ratio was determined against both CH_4 and CH_3CCl_3 as primary references. These two results are in excellent agreement (Table 8 and Figure 14), but both are slightly lower than the absolute measurements. For the secondary reference rate constant, we use the average value $K = 2.3E-12 \exp(-1275/T)$.

The HFC-143a reaction rate is quite slow, but nevertheless there is generally good agreement between the absolute and relative measurements (Figure 13). On the other hand, the CH_3-CH_2F (HFC-161, Figure 15) rate constant is large and therefore spurious OH losses should be relatively unimportant, especially considering that no significant impurities were detected in the HFC-161.[12] Nevertheless, as seen in Figure 15, our results deviate considerably from the absolute measurements, particularly in the lower temperature range. It is unlikely that our rate constant for this reactant is incorrect, because it has been substantiated in previous work[9] in which we obtained rate data for HFC-161, relative to CH_2Cl_2, which in turn was measured relative to HFC-152a and CH_4. These data are quite compatible with our present rate constant for HFC-161. Nonetheless, additional studies of this rate constant are warranted.

Propanes. Agreement among all reported data sets is excellent for CF_3CHFCF_3 (HFC-227ea). However, for all the

TABLE 8: Halogenated Ethanes: Derived Rate Constants and Comparisons with Previous Work

reactant	*A* factor	*E*/*R*	*k*(298 K)	reference
$CHClFCCl_2F$ (HCFC-122a)	7.1*E*−13	1158	1.5*E*−14	this work[c]
	1.0*E*−12	1240	1.6*E*−14	Orkin[15]
$CHCl_2CF_3$ (HCFC-123)			2.8*E*−14	Howard and Evenson[13]
	1.4*E*−12	1102	3.5*E*−14	Watson et al.[29]
	1.1*E*−12	1040	3.4*E*−14	Liu et al.[30]
	6.5*E*−13	840	3.9*E*−14	Gierczak et al.[16]
	1.1*E*−12	940	4.7*E*−14	Nielson[31]
	7.0*E*−13	900	3.4*E*−14	JPL94
			3.2*E*−14	Zellner et al.[32]
	6.4*E*−13	910	3.0*E*−14	this work[c]
$CHFClCF_3$ (HCFC-124)			1.2*E*−14	Howard and Evenson[13]
	6.1*E*−13	1244	9.4*E*−15	Watson et al.[29]
	4.4*E*−13	1150	9.3*E*−15	Gierczak et al.[16]
	8.0*E*−13	1350	8.6*E*−15	JPL94
	7.3*E*−13	1380	7.1*E*−15	this work[e]
	1.0*E*−12	1453	7.7*E*−15	this work[a]
CH_3CF_3 (HFC-143a)			1.7*E*−15	Martin and Paraskevopoulos[33]
	2.1*E*−12	2200	1.4*E*−15	Talukdar et al.[17]
	1.6*E*−12	2100	1.4*E*−15	JPL 94
	1.3*E*−12	2043	1.4*E*−15	this work[a]
	1.2*E*−12	2070	1.2*E*−15	this work[e]
CH_3CHF_2 (HFC-152a)			3.5*E*−14	Handwerk and Zellner[23]
			3.7*E*−14	Nip et al.[28]
	9.6*E*−13	940	4.1*E*−14	Liu et al.[30]
	3.9*E*−12	1370	3.9*E*−14	Nielson[31]
	1.0*E*−12	980	3.7*E*−14	Gierczak et al.[16]
	2.4*E*−12	1260	3.5*E*−14	JPL 94
			3.3*E*−14	Zellner et al.[32]
	1.9*E*−12	1221	3.1*E*−14	this work[a]
	2.8*E*−12	1330	3.2*E*−14	this work[g]
CH_3CH_2F (HFC-161)			2.3*E*−13	Nip et al.[28]
	7.0*E*−12	1100	1.7*E*−13	JPL 94
	2.7*E*−12	750	2.2*E*−13	Schmoltner et al.[12]
	1.0*E*−11	1228	1.6*E*−13	this work[b]
	7.0*E*−12	1152	1.5*E*−13	this work[c]

[a] CH_4. [b] C_2H_6. [c] HFC-152a. [d] HFC-125. [e] HFC-134. [f] HFC-161. [g] CH_3CCl_3 were the reference compounds.

other cases the agreement is poor. In some cases, our rate constants are lower than the absolute data by a nearly constant factor which is independent of temperature. The results for HFC-236ea (factor of about 1.7) and HFC-245ca (factor of about 1.5) are examples of this behavior.

Discussion

Utility of the Relative Rate Method. The relative rate method as used in the present work is intrinsically very simple and appears to yield quite accurate temperature-dependent ratio data. The method is essentially immune to impurity effects and secondary reactions. The small standard deviations of the data as seen in Table 6 demonstrate that random errors are minor. Reproducibility of a rate constant ratio in a given experiment is normally about 3%. The reference standards we have used (Table 1) have been intercompared in our experiments and are in excellent agreement. The derived rate data are sufficiently accurate, particularly on a relative basis, to permit some conclusions concerning rate data which were previously obscured either by experimental error or by uncertainties in the application of transition state theory. These are discussed below.

Comparisons between Relative and Absolute Rate Constants. There is no case in which our relative rate constant is systematically higher than the absolute rate constant. Similar comparisons were seen in previous work.[7−9] This may be due to the influence of reactions with impurities or secondary chemistry in the absolute experiment, in which any loss of OH contributes to the measured rate constant. However, there is no clear pattern to the disagreements, and other factors may be involved. There is no consistent correlation with the magnitude of the rate constant, which might have been expected if impurity effects or secondary chemistry were the only source of discrepancies between the two methods.

TABLE 9: Halogenated Propanes: Derived Rate Constants and Comparison with Previous Work

reactant	*A* factor	*E*/*R*	*k*(298 K)	reference
CF_3CHFCF_3 (HFC-227ea)	3.7*E*−13	1615	1.6*E*−15	Nelson et al.[34]
	3.6*E*−13	1610	16*E*−15	Zhang et al.[35]
	3.8*E*−13	1596	1.8*E*−15	Zellner et al.[36]
			1.6*E*−15	Koch and Zetzsch[37]
	5.0*E*−13	1700	1.7*E*−15	JPL 94
	4.9*E*−13	1703	1.6*E*−15	this work[a]
	4.6*E*−13	1662	1.8*E*−15	this work[d]
$CF_3CH_2CF_3$ (HFC−236fa)	2.0*E*−14	906	9.6*E*−16	Garland et al.[38]
			5.2*E*−16	Kolb et al.
	7.1*E*−13	2280	3.4*E*−16	JPL 94
	7.0*E*−13	2280	3.4*E*−16	this work[d]
$CH_3CHFCHF_2$ (HFC-236ea)	2.0*E*−13	1006	6.8*E*−15	Garland et al.[38]
	1.0*E*−12	1430	8.5*E*−15	Zhang et al.[35]
	1.2*E*−12	1550	6.6*E*−15	JPL 94
	1.1*E*−12	1589	5.1*E*−15	this work[a]
$CHF_2CF_2CH_2F$ (HFC-245ca)	2.9*E*−12	1660	1.1*E*−14	Zhang et al.[35]
	2.4*E*−12	1660	9.1*E*−15	JPL 94
	2.0*E*−12	1656	7.5*E*−15	this work[a]

[a] CH_4. [b] C_2H_6. [c] HFC-152a. [d] HFC-125. [e] HFC-134. [f] HFC-161 were the reference compounds.

Comparison of *A* Factors from Experiments and Transition-State Theory (TST). Table 10 compares experimental *A* factors (present and earlier work)[7−9] and those from TST calculations of Cohen and Benson[2] and Jeong and Kaufman.[3] This table includes only those compounds in which all the C−H bonds are identical.

There are two points of comparison to be made, one being the absolute values and the other being the relative values. Our derived *A* factors depend, of course, on those of the primary reference rate constants we have used, mainly CH_4, CH_3CCl_3, and CF_3CHF_2. The average *A* factor per H atom is (6.3 ± 1.0)-*E*−13. On the basis of these, our experimental *A* factors are, on average, in reasonable agreement with the TST calculations (factor of 2 or better). There are, however, some substantial individual disagreements. For example, the *A* factors for CH_3CF_3, CH_3F, CH_3Cl, and HCFCs 140 and 141b in the Cohen and Benson predictions are high (about a factor of 3) compared to our experimental results. The exact reason for this is not obvious, other than that contributions to the TS entropy from sources such as internal rotation are difficult to estimate. On the other hand, the very low *A* factor (4.8*E*−13) calculated by Jeong and Kaufman for HFC-134a appears to be the result of a low estimate for the entropy of the transition state (only 7.1 eu difference between the entropy of the reactant and the TS model, whereas replacement of H by OH usually produces an increase in entropy of at least 10 eu). It thus appears that uncertainties in estimating the entropy of the TS occasionally result in substantial disagreements among different sets of TST calculations and also with the experimental results.

From Table 10 it is apparent that an *A* factor per H-atom of about (8.0 ± 3.0)*E*−13 $cm^3/(molecule\ s)$ can be used to estimate the total *A* factor for molecules with a single type of C−H bond. It must be emphasized that this is only a general guideline, and variations within this range will almost certainly occur. For example, the *A* factors of the chloromethanes seem to fall on the high side of the average. It must be borne in mind, however, that this discrepancy is comparable to the experimental error (in relative *A* factors) of about a factor of 1.3, and it is therefore

TABLE 10: Comparison of Some Transition-State Theory *A* Factors with Experimental Values[a]

reactant	*A*(TST) CB[b]	*A*(TST) JK[c]	*A*(exp) this work	*A*(TST)/*n*(H) CB[b]	*A*(TST)/*n*(H) JK[c]	*A*(exp)/*nH* this work
CH_3Cl	110	62	44[d]	37	21	15
CH_2Cl_2	47	28	22[d]	23	14	11
	47		32[d]	23		16
$CHCl_3$	9.9	12	12[d]	9.9	12	12
CH_3F	110	62	23	37	21	7.7
CH_2F_2	45	15	18	22	7.5	9.0
CHF_3	16	12	6.4	16	12	6.4
CHF_2Cl (22)	14	15	7.1	14	15	7.1
CH_2FCl (31)	45	15		22	7.5	
$CHFCl_2$ (21)	13	11		13	11	
$CHFClCCl_2F$ (122a)			7.1			7.1
$CHCl_2CF_3$ (123)	6.3		6.4	6.3		6.4
$CHFClCF_3$ (124)	7.4		10	7.4		10
CHF_2CF_3 (125)	10		5.6	10		5.6
CH_2ClCF_2Cl (132b)	21	9.3		10	4.7	
CH_2ClCF_3 (133a)	23			11		
CHF_2CHF_2 (134)	25		21[e]	12		11
			15[e]	12		7.5
			12[e]	12		6.0
CH_2FCF_3 (134a)	32	4.8	15	16	2.4	7.5
			13	16		6.5
			12	16		6.0
CH_3CCl_3 (140)	71	25	18	24	8.3	6.0
CH_3CFCl_2 (141b)	74		14[g]	25		4.7
CH_3CF_3 (143a)	130		12	43		4.0
CF_3CHFCF_3 (227ea)	12		4.6	12		4.6
			4.9	12		4.9
CHF_2Br (Ha-1201)	12		9.6	14		9.6
			avgs:	av 19	11	7.8
			st devs	9.9	5.5	3.1

[a] Units are 1.0*E*−13 cm^3/(molecule s). [b] Cohen and Benson.[2] [c] Jeong and Kaufman.[3] and Jeong et al.[19] [d] From Hsu and DeMore.[9] Different values are from different reference gases. [e] From DeMore.[7] Different values are from different reference gases. [f] *A* factor from JPL 92-20.[1] [g] Experimental *A* factor from Huder and DeMore.[8]

not necessarily certain that these deviations are significant. We also note that C_2H_6 has an *A* factor per H atom of 1.5*E*−12 cm^3/(molecule s) (Table 1), which is on the high side of the average. There are also deviations on the low side of the average, the largest of which seem to occur for molecules such as CH_3CX_3, where X represents a halogen atom. In this case the deviations are consistent and are more certainly real. The database is not sufficiently accurate or broad enough to fully characterize the detailed dependence of the *A* factor on the reactant structure. The principal utility of the average *A* factor would be to detect very large experimental errors in rate constant data. Measured *A* factors which fall significantly (more than a factor of 1.5) outside the above range should be regarded as suspect, particularly when they are on the low side. This is because most of the errors in absolute rate data produce low *A* factors.

For molecules with different C−H bonds the situation is more complicated, since the overall reaction rate constant is in effect the sum of rate constants for reaction at the different sites. It is necessary to know the relative contributions to the overall rate constant in order to deduce the effective *A* factor.

A more important comparison between experiment and TST is with the relative values of the *A* factors. These comparisons are independent of the accuracies of the *A* factors of the reference compounds. The most striking feature of the data in Table 11 is that the experimental *A* factor ratios are for the most part remarkably consistent with a simple proportionality to the number of H atoms. This is of course related to the fact that a "generic" *A* factor per H atom can be used to represent most of the data. Again, however, there are some exceptions. Molecules with the structure CH_3CX_3 have relative *A* factors which are consistently low by an amount (up to a factor of 1.8), which is outside the estimated experimental error in relative *A* factors of about a factor of 1.3. This is related to the fact that the absolute *A* factors for these molecules fall on the low side of the average. With regard to the TST predictions, the ratios show no discernible dependence on the number of H atoms. This is because uncertainties in the TS entropy estimates produce substantial variations (factor of 3 or more) in the predictions. As a result, no meaningful information on the relative *A* factors can be detected by that method.

TABLE 11: Experimental *A* Factor Ratios Compared to Transition-State Theory Predictions

reactant pair	exp[a]	statistical[b]	TS (JK)	TS (CB)
$CHCl_3/CH_2Cl_2$	0.55	0.50	0.43	0.21
$CHCl_3/CH_3Cl$	0.27	0.33	0.19	0.09
CH_3F/CH_2F_2	1.24	1.5		2.4
CH_3Br/CH_3Cl	1.02	1.00		0.83
CHF_2Cl/CH_4	0.24	0.25	0.16	
CHF_2Br/CH_4	0.33	0.25		
CH_4/CF_3CFH_2	2.24	2.0	19.2	
CF_3CF_2H/CF_3CFH_2	0.48	0.50		0.31
CF_3CFH_2/CF_2HCF_2H	0.85	1.0		1.3
CF_3CF_2H/CF_2HCF_2H	0.48	0.50		0.4
$CHFClCF_3/CF_2HCF_2H$	0.46	0.50		0.3
$CHFClCF_3/CH_4$	0.35	0.25		
CHF_3/CF_3CF_2H	1.14	1.00		1.6
CH_3CCl_3/CF_3CFH_2	1.22	1.5	5.2	2.2
CH_3CCl_3/CF_2HCF_2H	0.84	1.5		2.8
CH_3CCl_2F/CH_4	0.49	0.75		
CH_3CCl_2F/CH_3CCl_3	0.79	1.00		1.0
CH_3CF_3/CH_4	0.43	0.75		
CH_3CF_3/CF_3CF_2H	2.16	3.00		13.0
CF_3CHFCF_3/CH_4	0.17	0.25		
CF_3CHFCF_3/CF_3CF_2H	0.83	1.00		1.2
$CF_3CH_2CF_3/CF_3CF_2H$	1.26	2.00		

[a] Ratios measured either directly or calculated from ratios measured against a common reference. [b] Ratio expected for strict proportionality to number of hydrogen atoms.

Application to Rate Constant Estimation Methods. Because of the large number of compounds for which OH rate

TABLE 12: Rate Constant Ratio $k^{CH_3CCl_3}/k^{CH_4}$

Arrhenius form	value at 298 K	source	reference
0.418 exp(379/*T*)	1.49	152a as common reference	this work
0.544 exp(301/*T*)	1.49	134a as common reference	DeMore[7]
0.62 exp(263/*T*)	1.50	141b as common reference	Huder and DeMore[8]
0.62 exp(291/*T*)	1.65	direct ratio measurement	DeMore[18]
0.62 exp(270/*T*)	1.53	absolute rate constants	JPL 92-20[1]

constant data are required, and the substantial cost of individual measurements, techniques such as that of Atkinson[6] have been developed for the estimation of rate constants. These methods are based on group effects and require calibration from existing data. However, the absolute rate constants are often substantially in error, and as a consequence the estimation methods are difficult to calibrate and test. The relative rate data are much more suitable for this purpose. We are developing a modified estimation technique based on the relative rate constants (to be published separately) which shows promise of calculating OH rate constants at 298 K with an accuracy comparable to the experimental results.

The Ratio $k^{CH_3CCl_3}/k^{CH_4}$. The two 152a ratios measured with CH_4 and CH_3CCl_3 as references provide an additional measurement of the ratio $k^{CH_3CCl_3}/k^{CH_4}$, which is important in connection with the atmospheric lifetime of CH_4.[4] The result is shown in Table 12, along with previous determinations against other references[7,8] and by a direct ratio measurement.[7] All the measurements against a common reference are in excellent agreement with each other (better than 1%) and with the ratio calculated from the absolute rate constants as recommended in JPL 92−20. The ratio obtained earlier in the direct measurement[18] is about 10% higher (at 298 K) and should now be considered less reliable than the combined ratios and the ratio of absolute rate constants. The average value, $k^{CH_3CCl_3}/k^{CH_4} = 0.55\ \exp(300/T)$, is suggested for atmospheric use. This corresponds to $k^{CH_3CCl_3}/k^{CH_4} = 1.62$ at an average tropospheric temperature of 277 K.

Conclusions

The relative rate method for OH reaction rates produces accurate and self-consistent rate constant data which are well-suited for atmospheric lifetime calculations, tests of rate theory, and calibration of empirical estimation techniques.

Calculations of atmospheric liftimes for OH abstraction which are based solely on rate constants determined by measurements of OH loss must be regarded with caution. The true lifetimes may be substantially longer, and the implications for ozone depletion and global warming will be correspondingly greater.

Transition-state theory usually predicts the correct order of magnitude for *A* factors of OH abstraction reactions. Uncertainties in the estimation of the transition-state entropy limit the accuracy to a factor of about 3.

For the HFCs and HCFCs studied, the *A* factors for OH abstraction are closely, but not exactly, proportional to the number of H atoms.

For *A* factor predictions in the temperature range of the present experiments, the assumption of 8.0*E*-13 cm^3/(molecule s) per H atom (for cases where all C−H bonds are identical) yields an *A* factor which will usually be accurate to within a factor of 1.3. Experimental *A* factors which differ greatly from this value near room temperature should be regarded as suspect.

The ratio of $k^{CH_3CCl_3}/k^{CH_4} = 0.55\ \exp(300/T)$, with an uncertainty of about 2% at tropospheric temperatures.

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