Kinetics of the reactions of OH with several alkyl halides†

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The rate coefficients for the reactions of OH with methyl chloride (k_1), ethyl chloride (k_2), methylene chloride (k_3), ethyl bromide (k_4), n-propyl bromide (k_5) and isopropyl bromide (k_6) were measured over the temperature range, 220–380 K, using pulsed photolysis-pulsed laser induced fluorescence (PP-PLIF). The measured rate coefficients, k_{1-6}, (cm^3 molecule^{-1} s^{-1}) are: $k_1 = 1.3 \times 10^{-13} \, T^{0.5} \exp[-(1238)/T]$; $k_2 = 1.5 \times 10^{-13} \, T^{0.5} \exp[-637/T]$; $k_3 = 6.6 \times 10^{-14} \, T^{0.5} \exp[-721/T]$; $k_4 = 1.7 \times 10^{-13} \, T^{0.5} \exp[-641/T]$; $k_5 = 9.1 \times 10^{-14} \, T^{0.5} \exp[-157/T]$; $k_6 = 7.0 \times 10^{-14} \, T^{0.50} \exp[-145/T]$. These rate constants are compared with those from previous studies. Some trends in the reactivities are also noted. The globally averaged atmospheric lifetime for methyl chloride, CH_3Cl, with respect to loss by reaction with OH, derived from the rate constant data performed in this study is 1.3 years. The rate constants for the reaction of OH with the other compounds presented in this study are large enough to make these reactions their dominant atmospheric loss pathway.
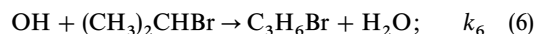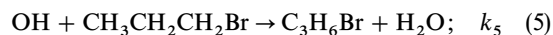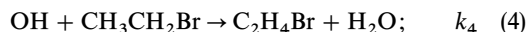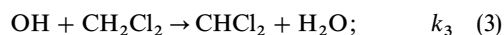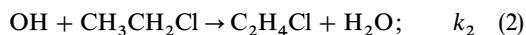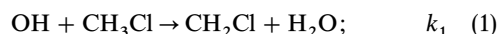
Introduction

Chlorinated and brominated alkanes are potential sources of chlorine and bromine in the stratosphere, where they can catalytically destroy ozone. These molecules are released at the Earth's surface and reach the stratosphere *via* transport. The atmospheric lifetime of the alkyl halides determines the fraction of the emitted amount that reach the stratosphere. The lifetime of a saturated organic compound, such as those studied here, is determined by its reaction with radicals (such as OH, Cl and O(^{1}D)), UV photolysis and uptake by oceans and soil. The reactions with Cl atoms and O(^{1}D) are not expected to be important for the alkyl halides studied here. The UV absorption cross sections for CH_3Cl, CH_3CH_2Cl, CH_2Cl_2 and CH_3CH_2Br are sufficiently small that their tropospheric lifetime is governed primarily by reaction with OH. In the case of the other two bromides, their reactions with OH are so rapid that none of the other loss processes are important in the troposphere.

The tropospheric concentration of CH_3Cl is about 600 pptv. CH_3Cl is believed to be the major non-industrial source of chlorine to the stratosphere. Currently, there is some discrepancy in the atmospheric budget of CH_3Cl,[1] with the emissions being estimated to be 1.2–2.5 Tg a^{-1} while the sink *via* OH reaction alone is calculated to be about 3 Tg a^{-1}. Therefore, it is necessary to examine the possibility that the calculated sink for CH_3Cl is overestimated. The two quantities that determine the loss *via* OH reaction are the atmospheric concentration of OH and the rate coefficient for the reaction of OH with CH_3Cl. Even though there have been many measurements of this rate coefficient, almost all of them have been carried out above 298 K. The only exceptions are the studies of Davis et al.[2] at 273 and 250 K and of Jeong and Kaufman[3] at 247 K. Therefore, we have measured k_1 at temperatures characteristic of the lower atmosphere (i.e., <298 K).

The other alkyl halides studied here have varied anthropogenic uses, but essentially they are all used as solvents in degreasing and specialized cleaning. They are also used in small amounts in pharmaceutical manufacturing, foam blowing and production of consumer products. In addition, currently there is a great deal of interest in n-propyl bromide because of its potential use as a solvent in replacing many of the chlorofluorocarbons. As in the case of methyl chloride, the rate coefficients for the reactions of OH with CH_2Cl_2, C_2H_5Cl and the three alkyl bromides have not been measured extensively at atmospheric temperatures.

In this paper, we report the rate coefficients for the reaction of the following alkyl halides with OH in the atmospherically important temperature range.

$$OH + CH_3Cl \rightarrow CH_2Cl + H_2O; \qquad k_1 \quad (1)$$

$$OH + CH_3CH_2Cl \rightarrow C_2H_4Cl + H_2O; \qquad k_2 \quad (2)$$

$$OH + CH_2Cl_2 \rightarrow CHCl_2 + H_2O; \qquad k_3 \quad (3)$$

$$OH + CH_3CH_2Br \rightarrow C_2H_4Br + H_2O; \qquad k_4 \quad (4)$$

$$OH + CH_3CH_2CH_2Br \rightarrow C_3H_6Br + H_2O; \quad k_5 \quad (5)$$

$$OH + (CH_3)_2CHBr \rightarrow C_3H_6Br + H_2O; \quad k_6 \quad (6)$$

Each of these reactions is exothermic to generate H_2O and a corresponding halogenated alkyl radical ($\Delta_{rxn}H°$ (298 K) ~ -18 to -22 kcal mol^{-1}), while the abstraction of a halogen atom is endothermic ($+20$ to $+30$ kcal mol^{-1}). Therefore, we assume that these reactions proceed *via* H abstraction from various possible sites.

In this paper we will describe the measurements of k_1–k_6, present the measured rate constants, compare these results

with other published work and, finally, examine briefly the atmospheric lifetime with respect to loss by reaction with OH radical.

Experimental

The rate coefficients k_1–k_6 were measured by producing OH radical in an excess of alkyl halides *via* pulsed laser photolysis of a suitable precursor and measuring its temporal profile *via* laser induced fluorescence detection (PP-LIF). In a few cases, the rate coefficients for the reactions of OD radicals with some of the alkyl halides were also measured. A detailed description of the apparatus, data acquisition methodology and data analysis is given elsewhere,[4,5] therefore, only the details necessary to understand the present measurements are described here.

Hydroxyl radical (OH) was generated by the photolysis of (1) HONO at 355 nm (third harmonic of Nd : YAG laser) or at 351 nm (XeF excimer laser) or (2) H_2O_2 at 248 nm (KrF excimer laser). Source (1) was preferred for reactions of alkyl bromides, which are more likely to be photolyzed at 248 nm. When source (2) was used, the laser fluences at 248 nm were kept sufficiently low to minimize the photolysis of alkyl halides (particularly the bromides). The OD radicals were generated by photolysis of DONO at 355 or 351 nm.

The reaction mixture, consisting of a bath gas (mainly He), OH photolytic precursor and an alkyl halide, were flowed into a thermostatted reaction cell. The gas flow rate was sufficiently rapid to essentially replenish the gas mixture in the reaction zone between photolysis pulses. The total pressure in the reactor was usually ~ 100 Torr and the bath gas was usually He. The temperature of the gas mixture in the reactor was measured in the reaction zone using a calibrated retractable thermocouple and it was accurate to (± 1 K). The OH temporal profiles were obtained by varying the delay between the photolysis and probe laser pulses. The reactions were studied under pseudo-first-order conditions in OH, such that ratio of [alkyl halide] to $[OH]_0$ was always greater than 10^4. Under these conditions, the OH temporal profiles obeyed the following expression:

$$[OH]_t = [OH]_0\, e^{-(k_i[X_i] + k_d)t} = [OH]_0\, e^{-k't} \qquad (7)$$

Where $i = 1$–6, X_i refers to the alkyl halide in reaction i, $k' = k_i[X_i] + k_d$, k_d is the first-order rate coefficient for the OH loss in the absence of alkyl halide (due to reactive and diffusive losses from the detection region) and the subscripts t and 0 refer to reaction times. A fit of the temporal profile of OH concentration (LIF signal) to eqn. (7) yielded k'. The k' values were measured as a function of alkyl halide concentration and the slopes of the plots of k' *vs.* alkyl halide concentrations yielded k_i values.

Materials

The buffer gas used in most of these experiments was UHP helium (>99.9995% pure). Hydrogen peroxide was purified to greater than 95% by flowing helium through a 70% solution of H_2O_2. Nitrous acid, HONO, was generated by drop-wise addition of 0.1 M sodium nitrite to 10% H_2SO_4 at 273 K. The HONO was swept out by helium and added to the reaction mixture. Similarly, DONO was made by using D_2SO_4 in D_2O with the $NaNO_2$. Methyl chloride and ethyl chloride were from Aldrich (99.5% and 99.7% stated purity, respectively) and used without further purification. Two samples of methylene chloride were used, one with amylene (2-methyl 2-butene) added as a stabilizer and another unstabilized sample. OH reacts rapidly with amylene ($\sim 3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}); therefore, it was necessary to remove amylene from the CH_2Cl_2 sample. A short column (50 cm long $\times$ 0.6 cm diameter) packed with concentrated H_2SO_4/$AgNO_3$ deposited on chromosorb WHP was used to remove amylene and any other unsaturated hydrocarbons from the CH_2Cl_2 sample. For each experiment the sample was passed through the purification column and the eluting gas was checked for the presence of unsaturated compounds using gas chromatography (GC). Alkyl bromides were degassed using freeze–pump–thaw cycles at dry ice temperatures. All the gas chromatography (GC) analyses, shown in Table 1, were performed using a GC equipped with a DB-1 capillary column (30 m $\times$ 0.32 mm $\times$ 3 μm) working at 50 °C and a flame ionization detector (FID). The GC analysis could not quantify Br_2 and HBr, which can contribute to the loss of OH *via* their rapid reactions with this radical. They were measured *via* UV–Visible (for detecting Br_2) and IR (for detecting HBr) absorption; the obtained Br_2 impurity levels are given in Table 1. There was no measurable HBr or HCl present in any samples of alkyl halides.

Table 1 Impurities in the alkyl halides samples used in this work determined by GC and UV analysis

| Compound	Impurity	Amount of impurity (ppmv)	Increase in k_i at 298 K (%)	$k_{OH + impurity}$/ cm^3 molecule^{-1} s^{-1}, at 298 K	Ref.
C_2H_5Cl					
	CH_3Cl	<35	<0.01	3.6×10^{-14}	This work
	Isobutane[a]	<25	<0.01		
C_2H_5Br					
	Ethanol	<5500	<5	3.3×10^{-12}	23
	Acetone	<850	<0.05	2.3×10^{-13}	6
	n-Pentane	<400	<0.5	4.1×10^{-12}	5
	Br_2[b]	<5	<0.4	4.2×10^{-11}	6
n-C_3H_7Br					
	Propane	<20	<0.01	1.1×10^{-12}	5
	n-Propanol	<1500	<0.8	5.5×10^{-12}	23
	Br_2[b]	<5	<0.4	4.2×10^{-11}	6
i-C_3H_7Br					
	Propane	<20	<0.01	1.1×10^{-12}	5
	Acetone	<1000	<0.03	2.3×10^{-13}	6
	Isopropanol	<5000	<3.5	5.3×10^{-12}	2
	n-Pentane	<600	<0.3	4.1×10^{-12}	5
	C_2H_5Br	<100	<0.01	3.4×10^{-13}	This work
	n-C_3H_7Br	<1500	<0.2	8.7×10^{-13}	This work
	Br_2[b]	<5	<0.4	4.2×10^{-11}	6

[a] Could be 1-butene, in which case the measured value of k_2 would be increased by less than 0.1%. [b] The upper limit of a possible Br_2 impurity was assigned by measuring absorption in the visible region.

Results

The measured bimolecular rate coefficients k_1–k_6 are given in Tables S1–S6.† We have also listed in those tables the other important experimental conditions that were used. The initial concentrations of hydroxyl radicals, $[OH]_0$, given in those tables, are estimated upper limits calculated from the concentration of the precursor and the photolysis laser fluence. Table 2 summarizes the results from this work. We have fit our data to two forms, $k = A \exp(-E/RT)$ and $k = AT^{0.5} \exp(-E/RT)$; the obtained values of A and E/R are listed in the table. In addition, the values of A and E/R obtained by fitting our low temperature data (i.e., $T \leqslant 300$ K) to an Arrhenius expression are also shown. The plots of the rate coefficients, k_1–k_6 (on a log scale) vs. $1/T$ are shown in Fig. 1–3.

To ensure that the measured rate coefficients are not influenced by secondary reactions, some of the experimental conditions were varied. These include buffer gas (He or N_2), and its pressures (~20 to 200 Torr), concentrations of OH precursors, initial concentrations of OH (greater than a factor of 4), photolysis laser fluence (a factor of 3) and the flow velocity (3–25 cm s^{-1}) of the gas mixture through the reaction zone. Variation of the laser fluence changed the initial concentrations of both OH and the radicals produced from the photolysis of alkyl halides. Under such variations, the measured rate coefficients remained unchanged (Table S1–S6†). This invariance showed that photolytically generated radicals, the radicals produced from reactions of OH with alkyl halides and the accumulation of any reactive end products did not contribute measurably to the obtained rate coefficients.

The alkyl halide concentration, the major parameter that determines the accuracy of the measured rate coefficient, was determined by two different methods. The first method involved the measurement of UV absorption in the gas mixture flowing through the reactor. The absorption cross sections and wavelengths used to determine the alkyl halide concentrations are given in Table 3. The absorption cross sections of the alkyl halide at 184.9 (mercury line) or 213.9 nm (zinc line) were determined by flowing the pure compound, and in some cases a manometrically prepared mixture of the compounds in helium, through an absorption cell. The length
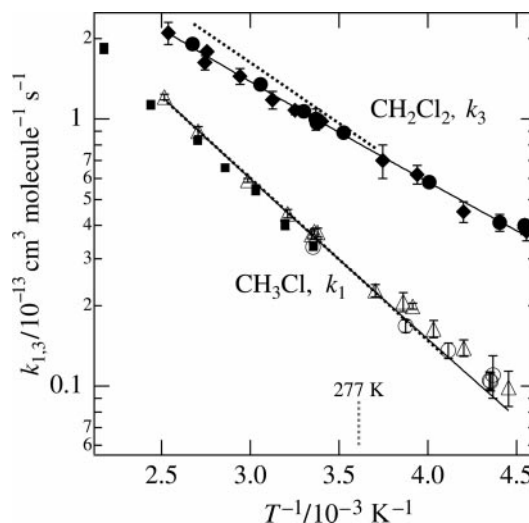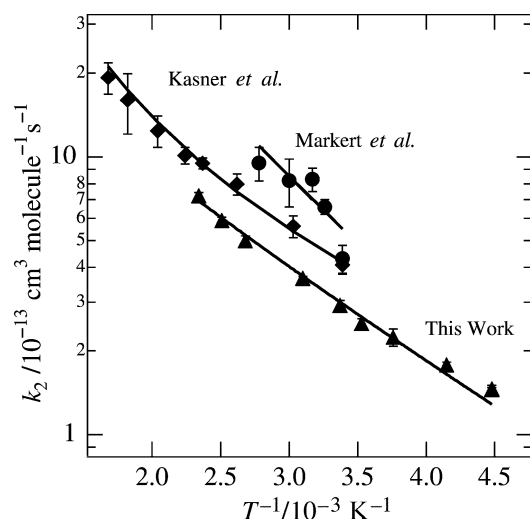

Fig. 1 The rate coefficients for reactions (1) and (3) (on a logarithmic scale) as a function of the reciprocal of temperature. The solid lines represent three parameter fits to our data given in Table 2. The dotted lines are the rate constants calculated from JPL97-4 over the temperature range of the data used to derive the recommendations. In the case of k_1, the dashed line is essentially indistinguishable from the solid line. The photolytic precursors of OH used in our measurements were H_2O_2 (◆ and △) and HONO (● and ○). The recent data from Orkin[7] is depicted by the solid dark squares. The vertical dashed bar represents the weighted mean temperature of the troposphere used to calculate the lifetimes of sufficiently long-lived species that are destroyed primarily by OH (see text).

of the absorption cell was between 25 and 100 cm, depending on the absorbance being measured. The measured absorbance varied linearly with the pressure of the compound in the cell. The absorption cross sections were derived from plots of the measured absorbance vs. the pressure in the cell. They agreed with literature values. While measuring a rate constant, the alkyl halide concentration in the gas mixture flowing through the reactor was determined in two absorption cells, one placed upstream and one downstream of the reaction cell. No systematic difference between these two determinations was

Table 2 Summary of the rate coefficient parameters for OH reactions with alkyl halides determined in this work. The values of A and E/R obtained by fitting our data to the Arrhenius expression, $k = A \exp\{-E/(RT)\}$, and A, E/R and n obtained by fitting our data to the expression $k = AT^n \exp\{-E/(RT)\}$ over the shown temperature ranges are listed

Compound	$k(298)^a$	A^a	n	$(E/R)/K$	$f(298)^{b,c}$	Temperature range/K
CH$_3$Cl (k_1)	0.036	1.24 ± 0.2	0.5	1210 ± 52		224–398
		40 ± 7	0	1401 ± 60		224–398
		18 ± 9	0	1171 ± 120	1.08	224–299
CH$_3$CH$_2$Cl (k_2)	0.30	1.5 ± 0.2	0.5	637 ± 58		223–426
		45 ± 8	0	801 ± 68		223–426
		23 ± 4	0	613 ± 50	1.08	223–297
CH$_2$Cl$_2$ (k_3)	0.10	0.66 ± 0.06	0.5	721 ± 32		219–394
		19 ± 2	0	876 ± 36		219–394
		16 ± 2	0	826 ± 40	1.14	219–302
CH$_3$CH$_2$Br (k_4)	0.34	1.7 ± 0.2	0.5	641 ± 52		233–422
		52 ± 9	0	809 ± 60		233–422
		29 ± 10	0	639 ± 98	1.07	233–297
CH$_3$CH$_2$CH$_2$Br (k_5)	0.87	0.9 ± 0.2	0.5	157 ± 62		230–386
		26 ± 6	0	305 ± 70		230–386
		15 ± 3	0	161 ± 48	1.07	230–298
CH$_3$CHBrCH$_3$ (k_6)	0.75	0.70 ± 0.04	0.5	145 ± 21		215–402
		20 ± 2	0	292 ± 23		215–402
		17 ± 2	0	250 ± 36	1.07	215–298

^{a} Units for k and A are 10^{-12} cm^3 molecule^{-1} s^{-1}. ^{b} $f(T) = f(298) \exp\left\{ \left| \frac{\Delta E_a}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right| \right\}$. ^{c} The error function, $f(298)$, includes the precision error, tabulated at 95% confidence, of the experiment as well as the estimated error in the accuracy of the rate coefficient determination.

Fig. 2 The rate coefficients for reaction (2) (on a logarithmic scale) as a function of the reciprocal of temperature. The solid line is a three-parameter fit to our data (see Table 2). The data for k_2 measured by Kasner et al.[12] and Markert et al.[13] are included for comparison.
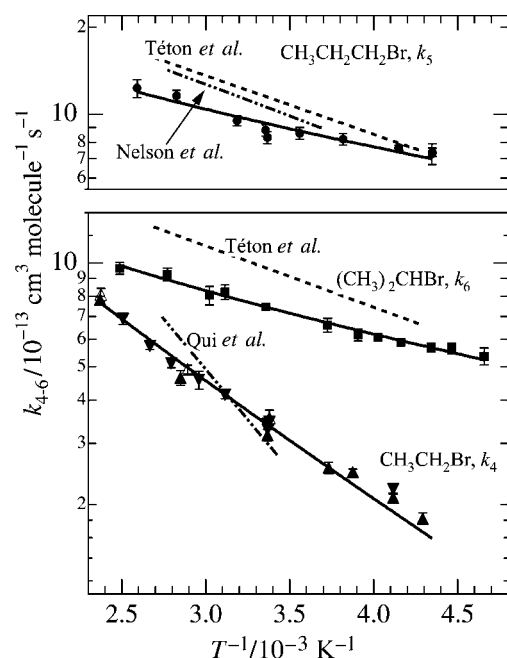
Fig. 3 The rate coefficients for reactions (4), (5) and (6) (on a logarithmic scale) as a function of the reciprocal of temperature. The solid lines are fits to a three-parameter equation discussed in the text. In the top panel, the measured values of k_5 are shown along with the fit results of Téton et al.[20] and Nelson et al.[21] In the bottom panel, both the measured values of k_4 and k_6 are shown. The fit results of Qui et al.[19] and Téton et al.[20] are also shown in the lower panel. The photolytic precursors of OH/OD in our measurements were H_2O_2 (▲), HONO (▼) and DONO (△).

Table 3 Parameters for alkyl halide concentration by UV absorption

Compound	Cross section[a] /10^{-19} cm^2	Wavelength /nm
CH_3Cl	3.00 ± 0.05	184.9
CH_3CH_2Cl	1.36 ± 0.05	184.9
CH_2Cl_2	1.2 ± 0.1	184.9
CH_3CH_2Br	4.15 ± 0.04	213.9
$CH_3CH_2CH_2Br$	4.85 ± 0.09	213.9
$(CH_3)_2CHBr$	3.94 ± 0.04	213.9

[a] The quoted errors are twice the standard deviation of several measurements.

observed. The concentrations of the alkyl halides were also determined *via* measuring the gas flow rates, using calibrated electronic mass flow meters and pressure. The concentration of alkyl halides measured by these two methods agreed with each other within the uncertainty of the measurements (< 5%). Based on these determinations, we estimate the error in alkyl halide concentration to be ⩽ 5%. The uncertainty due to temperature measurement (± 1 K) was less than 1%, leading to a combined conservative estimate of 6% uncertainty in alkyl halide concentrations.

Discussion

The rate coefficients at 298 K and the Arrhenius parameters for the OH reactions determined in the present work, along with those from previous studies, are summarized in Table 4. We will first compare our results with those from previous studies. Following this comparison, we will discuss some features of the OH–alkyl halide reactions.

It should be noted that, in experiments where OH temporal profiles are monitored, (*i.e.*, absolute methods) the presence of impurities and generation of other reactive radicals increase the measured rate coefficients. Rarely does one envision regeneration of OH *via* secondary reactions, and, hence, measure lower values of rate coefficient in reactions such as those studied here due to secondary production of OH. Thus, in the absolute measurements, all the systematic errors due to secondary reactions and presence of impurities tend to yield rate coefficients that are larger than the true value. Therefore, the lower values of the reported rate coefficients tend to be more accurate. In contrast to the absolute methods, the relative rate measurements are not hampered by the presence of impurities. Yet, the results obtained *via* relative methods have to be scrutinized. The choice of the reference reaction, the possible presence of other reactive species that could react with different rate coefficients with the reference and the studied compounds, and the loss of studied or reference compound (due to photolysis, thermal decomposition and reactions on the walls) can hamper the accuracy of this method.

It is not always possible to be completely sure of the absence of reactive impurities in the excess reagent, the alkyl halides in the present study. Therefore, the alkyl halides were analyzed for reactive impurities. Such analyses were carried out using mostly a gas chromatograph, as discussed earlier. In the case of alkyl bromides, we also determined the levels of Br_2 and HBr and found them to be negligibly small. Because we did not detect significant amounts of olefins (or Br_2 and HBr in alkyl halides), the most likely impurities in our samples that could enhance the measured rate coefficients, we believe that our measured values of the rate coefficients are accurate. With these thoughts in mind, the results of individual alkyl halides are compared with those determined by previous investigators in the following sections.

OH + CH_3Cl, k_1

The values of k_1 measured in this study are shown in Fig. 1 and listed in Table S1.† It extends k_1 to lower temperatures than in previous studies. Table 4 compares our results with those from other previous measurements. The E/R value in DeMore et al.,[6] (henceforth referred to as JPL 97-4) derived from the previous higher temperature measurements, is 1400 ± 250 K. If we include the unpublished results of Orkin[7] from 298 to 460 K with our data from 225 to 360 K, we obtain a value of $E/R = 1380$ K, which is in excellent agreement with JPL 97-4. Fitting our values of k_1 below 298 K, however, yields an E/R of 1205 ± 60 K.

The 298 K rate coefficient determined in this work is about 25% lower than that found in the studies by Jeong and Kaufman[3] carried out using a flow tube equipped with reso-

Table 4 Comparison of A, E/R, $\Delta E/R$ and n derived from this work with those from the previous measurements of k_{1-6}. The quoted uncertainties from previous studies are those quoted by the authors. The recommendations of DeMore *et al.* are also listed in the table. When a value of n is given the data were fit to the expression $k_i = AT^n e^{-E/RT}$

k_i	A^a	n	$(E/R \pm \Delta E/R)/K$	T/K	$k(298)^b$	$f(298)^c$	Technique^d	Ref.
Methyl chloride								
k_1	4.0	—	1400 ± 250	—	0.36	1.2	—	6
	3.51	—	1313 ± 55	247–483	0.426		DF-RF	3
	4.4	—	1470	293–358	0.31		Rel. Rate^e	8
	4.6	—	1455	293–358	0.35		Rel. Rate^e	8
	1.84	—	1097	245–375	0.43		FP-RF	2
	—	—	—	298	0.36		DF-LMR	10
	—	—	—	295	0.43	1.1	PR-UV	13
	—	—	—	298	0.42	1.2	FP-RF	11
	2.07	—	1205 ± 60	224–298	0.36	1.08	PLP-LIF	This work,^{f} low temp.
	4.06	—	1409 ± 60	298–400				This work,^{f} high temp.
	0.029	0.89	1447	295–955	0.51		PLP-LIF	12
	4.2×10^{-6}	1.97	599	247–483	0.41		DF-RF	3
	0.124	0.5	1210 ± 52	225–400	0.37		PLP-LIF	This work^f
Ethyl chloride								
k_2	24	—	1082	295–360	4.3	1.2	PR-UV	13
	6.2	—	805.9	295–595	4.1	1.08	PLP-LIF	12
	—	—	—	296	3.9	1.1	DF-LMR	10
	—	—	—	297	3.9	1.1	FP-RF	11
	0.15	0.5	637 ± 58	225–400	2.96		PLP-LIF	This work^f
Methylene chloride								
k_3	—	—	—	298.5	1.44		FP-RF	14
	3.8	—	1050 ± 150		1.1	1.4		6
	4.27 ± 0.63	—	1097 ± 81	245–375	1.16		FP-RF	2
	$(2.61)^{+0.37}_{-0.34}$		944 ± 29	277–370	1.10		FP-RF	17
	1.52×10^{-4}	1.58	624 ± 60	292–800	1.76		PLP-LIF	16
	4.0×10^{-3}	1.09	771 ± 48	295–955	1.52		PLP-LIF	15
	2.1	—	939	290–385	0.91		Rel Rate^e	8
	1.97	—	885 ± 40	220–298	1.00	1.14	PP-LIF	This work^f
	2.1	—	910 ± 76	220–400	1.00	1.14	PP-LIF	This work^f
	0.066	0.5	721 ± 32	220–400	1.00	1.14	PP-LIF	This work^f
Ethyl bromide								
k_4	27.7 ± 3.4	—	1344 ± 87	292–366	3.05	—	DF-RF	19
				298	2.5		Rel Rate^g	18
	0.17	0.5	641 ± 51	223–422	3.4	1.07	PP-LIF	This work^f
n-Propyl bromide								
k_5	5.29 ± 0.29	—	456 ± 31	233–372	11.7		PP-LIF	20
				298	11.8		Rel Rate^h	18
	5.75 ± 0.9	—	504 ± 50	271–363	10.3		DF-LIF	21
	0.09	0.5	157 ± 62	230–298	8.7	1.07	PP-LIF	This work^f
i-Propyl bromide								
k_6				298	8.8		Rel Rate^h	18
	3.58 ± 0.47	—	392 ± 75	233–372	9.4	—	PP-LIF	20
	0.07	0.5	145 ± 21	215–331	7.5	1.07	PP-LIF	This work^f

^{a} In units of 10^{-12} cm^3 molecule^{-1} s^{-1}. ^{b} In units of 10^{-13} cm^3 molecule^{-1} s^{-1}. The values near 298 K were converted to the 298 K value by using the E/R value of the respective studies. ^{c} $f(T) = f(298) \exp\left\{\left[\frac{\Delta E_a}{R}\left(\frac{1}{T} - \frac{1}{298}\right)\right]\right\}$. ^{d} LIF: Laser induced fluorescence detection of OH; DF: Discharge Flow tube; RF: Resonance fluorescence detection of OH; FP: Flash photolysis; LMR: Laser magnetic resonance detection of OH; PR: Pulsed radiolysis; UV: Detection of OH *via* UV absorption; PLP: Pulsed laser photolysis; PP: Pulsed photolysis. ^{e} Relative rate technique where they generate OH using O$_3$ photolysis and measure reactant concentrations relative to HFC 152a, by FTIR absorption. The reference compound was C$_6$H$_{12}$. ^{f} 95% confidence level (precision + systematic error). ^{g} Relative to the rate coefficient for the reaction of OH with C$_2$H$_6$. ^{h} Relative to the rate coefficient for the reaction of OH with c-C$_6$H$_{12}$.

nance fluorescence detection of OH (FT-RF) and by Davis *et al.*[2] carried out using a flash photolysis system with resonance fluorescence detection of OH (FP-RF). The value of k_1 calculated from the relative rate study of Hsu and DeMore[8] using OH + HFC-152a as the reference reaction (and using the JPL 97-4 values for its rate coefficient) agrees well with our data. At 299 K, the value of Hsu and DeMore is ∼12% lower than ours, while it differs by ∼5% at 277 K. At 277 K, the "average" temperature of the troposphere for the degradation of well-mixed gases *via* reactions with OH and often used to calculate the tropospheric lifetimes,[9] our measured value of k_1 is 5% higher than the JPL recommended value. It should be noted that the JPL97-4 value for this temperature is an extrapolation of the higher temperature data. Based on these results we believe that the uncertainty in the temperature dependence of k_1, $\Delta E/R$, can be reduced to ±150 K.

OH + C$_2$H$_5$Cl, k_2

Our data on k_2 are listed in Table S2† and are shown in Fig. 2. In addition to two room temperature values of Howard and Evenson[10] and of Paraskevapoulos *et al.*,[11] there are two other studies of k_2 as a function of temperature.[12,13] The results of the studies that measured k_2 as a function of temperature are compared with those from the present study in Fig. 2. All the available values of k_2 are also listed in Table 4.

Our 298 K value is the lowest reported to date. The results of Paraskevapoulos et al. may be slightly higher than the true value due to photolytic generation of C_2H_5 radicals. However, it is not clear why Howard and Evenson's value is higher than ours. It is possible that the samples of ethyl chloride used in previous investigations contained a highly reactive impurity such as ethylene or isobutene. We analyzed our samples to ensure that reactive impurities were absent. The results of Kasner et al.,[12] who measured k_2 at and above 295 K using the pulsed photolysis-laser induced fluorescence method, is consistently about 20% higher than our values. They produced OH via photolysis of N_2O with ~ 12 mJ pulse^{-1} cm^{-2} of 193 nm radiation to generate $O(^1D)$, which then reacted with H_2O vapor to give OH. Though they increased the laser fluence by roughly a factor of two (from ~ 12 to 24 mJ pulse^{-1} cm^{-2}) and found no variation in the measured value of k_2, the reaction of OH with C_2H_5 radicals produced via photolysis of C_2H_5Cl is still a concern. Kasner et al. also described the thermal decomposition of CH_3CH_2Cl to HCl and C_2H_4 in their system, which, if it occurred to a significant extent, could increase the measured OH rate coefficient. They quoted total uncertainty in their experiments to be 20%; thus their value overlaps with that reported here.

Our rate coefficients are 50% lower than the rate coefficients measured by Markert and Nielsen.[13] In their experiments carried out using the pulse radiolysis-UV absorption method (PR-UV), they use an initial concentration of OH of the order of 10^{14} molecule cm^{-3}. At these OH concentrations, secondary reactions such as the self reaction may become significant even if large concentrations of C_2H_5Cl are used. Further, it is likely that a large concentration of C_2H_5 radicals were produced in the pulsed radiolysis used to generate OH radicals. Therefore, their higher value may not be surprising.

Clearly, we have measured the lowest value of k_2 reported to date. Because we directly measured C_2H_5Cl concentration, analyzed the sample for reactive impurities, and took measures to suppress secondary reactions, we believe that our values of k_2 are the most accurate. A relative rate study of k_2 would be highly useful.

OH + CH_2Cl_2, k_3

Our data on k_3 are listed in Table S3† and are shown in Fig. 1. They are also compared with the previous determinations in Table 4. We used two different samples of methylene chloride to measure k_3 at 298 K; purified stabilized sample and the unstabilized sample. In back to back experiments, the rate coefficient of the 'purified' CH_2Cl_2 was found to be 13% higher than the unstabilized sample at 298 K. Therefore, all the data presented in this study were obtained from measurements using the unstabilized sample. This attempt clearly shows the difficulty in completely avoiding impurities, although none were detected using a GC. Clearly, we could not completely purify our samples of CH_2Cl_2.

Our measurements agree very well with the relative rate coefficients measured by Hsu and DeMore[8] when their values are rescaled for the currently recommended rate coefficients for the reference reactions. Several groups have measured k_3 and the results differ by as much as 50%. The room temperature rate constant measured by Perry et al.[14] using the flash photolysis–resonance fluorescence method, $(1.45 \pm 0.20) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} and by Taylor et al.,[15] $(1.51 \pm 0.18) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (which supersedes their earlier measurement,[16] of $(1.76 \pm 0.20) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}) are both substantially higher than our 298 K value. The more recent 298 K measurement of Villenave et al.[17] $\{(1.01 \pm 0.05) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K$\}$ and the earlier data of Davis et al.[2] $\{(1.16 \pm 0.05) \times 10^{-13}$ cm^3 molecule^{-1} s$^{-1}\}$ agree with our value. In many of these studies the presence of a highly reac-

tive stabilizer could have been a problem. As shown above, even attempts to remove the stabilizer such as amylene, are not completely successful. Taylor et al. used 193 nm photolysis of N_2O in their OH production, which could have photodissociated CH_2Cl_2 generating reactive radicals. Villenave et al., on the other hand, measured k_3 at low photolysis energies to minimize CH_2Cl_2 photolysis and also likely used purer samples of CH_2Cl_2.

OH + C_2H_5Br, k_4

Our data on k_4 are listed in Table S4† and are shown in Fig. 3. The rate coefficient k_4 has been reported in two previous studies, one at 298 K, using a relative rate method by Donaghy et al.,[18] and one as a function of temperature, in a flow tube study by Qui et al.[19] Our 298 K value, listed in Tables S4† and 4, is higher than both the two previously reported values shown in Table 4. Therefore, we carefully checked our sample for impurities and found no impurity in sufficient amounts to account for these differences.

Qui et al. determined the E/R value for reaction (4) to be 1344 K. Our k_4 values show a much weaker temperature dependence ($E/R = 730$ K) over the same temperature range (Fig. 3). The E/R values for reactions of OH with CH_3–{F, Cl, Br}, C_2H_5–{F, Cl} and other alkanes, suggest a value of 600–800 K for reaction (4). The recommended Arrhenius parameters in the temperature range, relevant to the atmosphere, given in Table 2, were calculated using the low temperature data measured in this work.

OH + n-C_3H_7Br and i-C_3H_7Br, k_5 and k_6

Our data on k_5 and k_6 are listed in Tables S5 and S6† and are shown in Fig. 3. The rate coefficients for these two reactions have been reported by Donaghy et al.,[18] Téton et al.[20] and Nelson et al.[21] Donaghy et al.[18] report k_5(298 K) and k_6(298 K) that are 33% and 17%, respectively, higher than our values. Nelson et al.[21] report a room temperature value of k_5 as 1.06×10^{-13} cm^{-3} molecule^{-1} s^{-1}, which is 20% higher than the rate constants determined here. The k_5 and k_6 values of Téton et al. (PP-LIF)[20] are also 34% and 25%, respectively, higher than our value at 298 K.

The temperature dependences of k_5 and k_6 (Fig. 3 and Table 4) reported by Téton et al.[20] are stronger than ours for both of the propyl bromide isomers. Téton et al. used 248 nm photolysis of H_2O_2 to produce OH. Therefore, the radicals produced via photolysis of alkyl bromides at 248 nm can contribute to the measured rate constant. Another possibility could be the presence of a fast reacting impurity in the alkyl bromide samples. Nelson et al.[21] also observed a steeper temperature gradient. The lowest temperature in their measurements was 271 K. They had problems due to surface removal at lower temperatures (230–250 K). The reasons for these differences are not obvious.

Curvature in Arrhenius plots. To a first approximation, over a limited range, the temperature dependence of k_1 and k_3 should follow an Arrhenius relationship, $k = A \exp(-E/RT)$ due to the presence of only one type of hydrogen (equivalent C–H bond strength) in each compound. Fig. 1 indicates that the Arrhenius plots for k_1 and k_3 are fairly linear over a limited temperature range, however, at low temperatures a slight positive deviation appears for both rate constants. Therefore, we have fit them to the expression $k = AT^n \exp(-E/RT)$, with $n = 0.5$; such a form is consistent with reaction rate theories. These fits do not lead to significantly different values of k_1 and k_3, compared to the conventional Arrhenius expression, over the temperatures of this study.

Chemically, there is more than one kind of hydrogen in ethyl chloride, ethyl bromide, isopropyl bromide and n-propyl bromide. Accordingly, if abstraction at each site followed classical Arrhenius behavior, the overall temperature dependences of k_2, k_4, k_5 and k_6 would be curved due to differences in the activation energies for the different abstraction channels. Fig. 2 and 3 clearly show that between 223 and 298 K the temperature dependence is fairly linear and at higher temperatures they tend to be higher than those obtained via extrapolation of lower temperature values. Such a behavior is consistent with the assertion that the majority of the reaction occurs via the abstraction of the weakest bound H atoms. At atmospheric temperatures these reactions preferentially yield the haloalkane radical with the highest order hydrogen removed. For example, the tertiary hydrogen can be expected to be the most likely candidate for abstraction by OH in isopropyl bromide. Abstraction of the secondary hydrogen in ethyl bromide and ethyl chloride is more exothermic than abstraction of a primary hydrogen by 3 to 4 kcal mol^{-1};[22] CH_3CHBr and CH_3CHCl are the preferred radical products.

It is interesting to note that although the tertiary hydrogen in isopropyl bromide is likely to have a lower activation energy towards abstraction by OH, this pathway is perhaps sterically hindered, as the overall rate coefficient for reaction with OH is less than that of n-propyl bromide. The possible larger contributions of the four secondary (counting the H in the CH_2Br group as secondary H) in $CH_3CH_2CH_2Br$ relative to the six primary hydrogens in i-C_3H_7Br may also be responsible for the two rate coefficients being similar in magnitude. A fit of k_6 below 300 K yields a fairly linear Arrhenius plot. This expression can be used for atmospheric purposes. It can also be assumed that the primary product of the reaction is $(CH_3)_2CBr$ radical at these temperatures. We are currently determining the site-specific H abstraction rate coefficients for the reaction of OH with n-propyl bromide.

Atmospheric implications

The absorption cross sections of CH_3Cl at wavelengths greater than 290 nm, a region of importance for photolysis in the troposphere, is less than 10^{-24} cm^2. Further, reactions with O_3, HO_2 and NO_3 with CH_3Cl are relatively slow. Even though the rate coefficient for the reaction of Cl with CH_3Cl is an order of magnitude larger[6] than k_1, the abundance of Cl is expected to be small. Therefore, the major loss process for CH_3Cl in the troposphere will be reaction with OH radicals. The tropospheric lifetimes of alkyl halides due to reaction with OH radical can be estimated using the formulation of Prather and Spivakovsky[9] by the expression

$$\frac{\tau_{RX}}{\tau_{CH_3CCl_3}} = \frac{k_{CH_3CCl_3}^{277\,K}}{k_{RX}^{277\,K}}$$

where $k_{CH_3CCl_3}^{277\,K}$ is the rate coefficient for the reaction of OH with CH_3CCl_3 at 277 K, the weighted average temperature of the troposphere for removal of species via reaction with OH. $k_{RX}^{277\,K}$ is the rate coefficient at 277 K for the reaction of OH with the alkyl halide, RX. Using the tropospheric lifetime of CH_3CCl_3 due to reaction with OH, $\tau_{CH_3CCl_3} = 4.9$ a, the tropospheric lifetime of CH_3Cl for removal via its reaction with OH was calculated to be ~ 1.3 a. This estimate is not accurate because the lifetime of CH_3Cl is still short enough to avoid complete mixing in the troposphere. The values of k_1 reported here for atmospheric temperatures are essentially those obtained from JPL 97-4 (i.e., via an extrapolation of the higher temperature data). Therefore, our rate coefficients do not alleviate the existing discrepancy in the budget of CH_3Cl that was noted in the Introduction. The atmospheric lifetimes of

CH_3CH_2Cl, CH_2Cl_2, CH_3CH_2Br, n-$CH_3CH_2CH_2Br$ and iso-$(CH_3)_2CHBr$ are short, a few days to a few months, which precludes the assignment of a globally averaged lifetime. It is important, however, to know these lifetimes on a regional scale, particularly for CH_2Cl_2, and ethyl- and propyl bromides, due to their industrial use. The substitution of n-propyl bromide for HCFC-141b as the active component of cleaning solvents does reduce the stratospheric halogen loading potential by virtue of the much higher reactivity with OH and the presence of one Br atom in place of one F and two Cl atoms. Photolysis of n-propyl bromide and i-propyl bromide in the troposphere shortens the overall atmospheric lifetime to a small extent because the non-zero absorption cross sections of the alkyl bromides in the atmospheric window region (>290 nm) (i.e., $\sim 10^{-23}$ cm^2).

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