Rate Constant for the Reaction of OH Radicals with Dichloromethane

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The rate constant for the reaction of CH_2Cl_2 with OH was measured by the flash photolysis resonance fluorescence technique over the temperature range 277−370 K to give the following Arrhenius expression: $k_{DCM} = (2.61^{+0.37}_{-0.34}) \times 10^{-12} \exp\{-(944 \pm 29)/T\}$ cm^3 molecule^{-1} s^{-1}, where the uncertainties represent 95% confidence limits associated with the statistical fitting procedure and include the contribution for the expanded uncertainties in the individual rate constant. Based on this new value, the results of recent relative studies of the OH reactions with $CHCl_2-CFCl_2$, CH_2ClBr, CH_2Br_2, and CH_2FCl have been reanalyzed.

Introduction

Dichloromethane (CH_2Cl_2 or DCM) is a minor atmospheric chlorine source.[1,2] The nonuniform distribution of DCM over the globe, with a significantly higher concentration[3,4] in the Northern hemisphere suggests its predominantly industrial origin. Due to the distinct seasonal signature in its tropospheric concentration and its relatively short atmospheric lifetime (<1 year), DCM has shown promise as an atmospheric tracer for both the determination of the global tropospheric OH concentration as well as for long-range transport of tropospheric air masses.[3] The estimated global decomposition rate of DCM in the atmosphere based on measurements of its atmospheric concentration[3,4] is about 50% higher than its estimated rate of global production.[5] The measured distribution of DCM in both the Northern and Southern hemisphere (over the North and South Atlantic)[3] also disagrees with the results of calculations based on production and emission data.[5] However, much better coincidence was shown[3,5] for tetrachloroethene ($CCl_2=CCl_2$), an industrial compound with a comparable atmospheric lifetime. Therefore, the combination of field measurements and global production data for DCM might indicate either an additional source of DCM or an error in global removal rate calculations. The key chemical process governing the loss of DCM from the atmosphere is its reaction with hydroxyl radicals in the troposphere:

$$CH_2Cl_2 + OH \rightarrow H_2O + CHCl_2$$
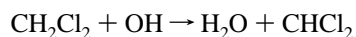
Thus, an understanding of the atmospheric budget of DCM and its utility as an atmospheric tracer depends on the degree of accuracy to which this rate constant is known.

There have been 10 studies of the reaction of OH with DCM over the last 20 years. The majority of the rate constants from absolute measurements are a factor of 2 higher than the values derived from recent relative rate measurements.[6,7] In a recent paper,[8] we calculated the OH + DCM rate constant based on the results of our absolute measurements of the rate constant for the reaction of OH with CH_2ClBr and the ratio of the OH rate constants for CH_2ClBr and DCM obtained by DeMore.[9]

We thus derived a rate constant value that lies between the results of the direct and relative studies.

Because of the unsatisfactory agreement among the previous studies, we decided to conduct careful measurements of the rate constant for the reaction between hydroxyl radicals and dichloromethane, using the flash photolysis−resonance fluorescence technique. Results of the study are presented in this paper.

Experimental Section[32]

Detailed description of the apparatus and the experimental methods employed in the studies of the present work are given elsewhere.[10,11] Therefore, only a brief overview is given here.

The principal component of the flash photolysis/resonance fluorescence (FP/RF) apparatus is a Pyrex reactor (of approximately 50 cm^3 internal volume) thermostated via a fluid circulated through its outer jacket. The reaction was studied in argon carrier gas (99.9995% purity) at a total pressure of 13.33 kPa (100.0 Torr). Dry argon, argon bubbled through water thermostated at 276 K, and DCM (2.00% and 4.00% volume fraction in argon) were premixed and flowed through the reactor at a total flow rate of 0.5−1.4 cm^3 s^{-1} STP (298.15 K and 1.013×10^5 Pa). The concentrations of the gases in the reactor were determined by measuring the mass flow rates and the total pressure using an MKS Baratron manometer. Flow rates of both argon and the H_2O/Ar mixture were measured using calibrated Tylan mass flow meters, whereas that of the DCM/Ar mixture was determined by direct measurements of the rate of pressure change in a calibrated volume. Hydroxyl radicals were produced by the pulsed photolysis (1−4 Hz repetition rate) of H_2O (introduced via the 276 K H_2O/Ar bubbler) using a xenon flash lamp focused into the reactor. The radicals were then monitored by their resonance fluorescence near 308 nm, excited by a microwave-discharge resonance lamp (280 Pa or 2.1 Torr of a ca. 2% volume fraction of H_2O in ultrahigh-purity helium) focused into the reactor center. The resonance fluorescence signal was recorded on a computer-based multichannel scaler (channel width 100 μs) as a summation of 1500−15 000 consecutive flashes. The radical decay signal at each reactant concentration ([DCM]) was analyzed as described by Orkin et al.[11] to obtain the first-order decay rate due to the reaction under study (τ^{-1}_{DCM}). The concentration of CH_2Cl_2 in the bulb with manometrically prepared mixtures was verified by UV absorption measurements from 195 to 210 nm. The spectra of pure CH_2Cl_2 and of the mixture with the same partial pressure of CH_2Cl_2 were recorded to be identical within less than 0.5%.

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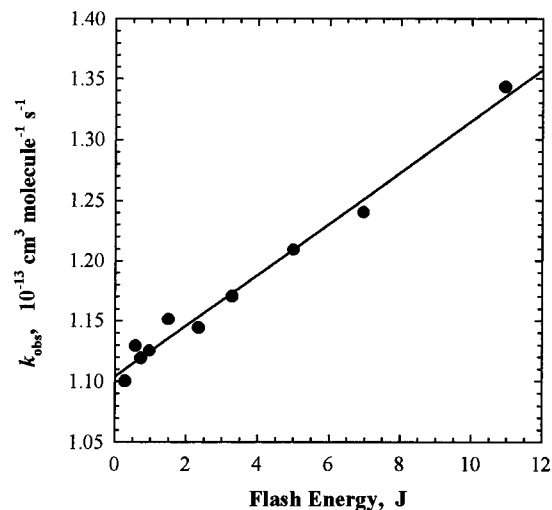
Figure 1. Dependence of the observed rate constant for the reaction of OH with DCM on flash energy obtained in our experiments at $T = 298$ K.
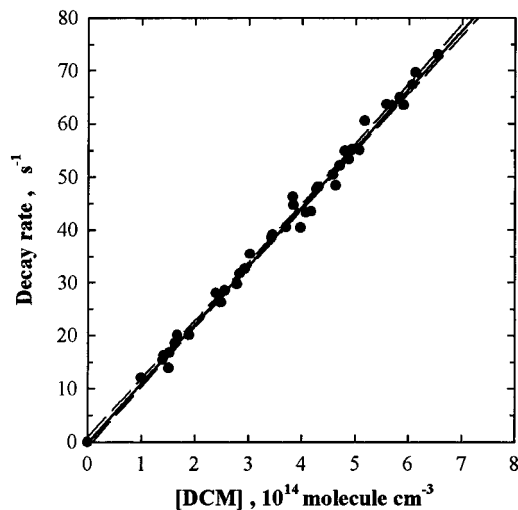

Figure 2. Plot of all first-order decay rates vs DCM concentration measured in the course of our study at $T = 298$ K at flash energy of ca. 0.3 J. Solid line is the linear least-squares fit to all points, and dashed lines are its 95% confidence intervals.

Uncertainties due to systematic effects in our measurements can be associated with such procedures as the absolute calibration of the MKS Baratron manometers (which measure the pressures in the reaction cell and in the bulb), the calibration of the temperature measurements in the reaction cell, and the decay rate measurements. The calibration of the manometers were verified to have a relative expanded uncertainty of approximately 0.5%. The expanded uncertainty of the temperature measurements in the reaction cell was around 0.2 K. The decay rate measurements were evaluated to have a relative expanded uncertainty of less than 4%. Relative expanded standard uncertainties due to systematic effects in the reactant concentrations in both the bulb mixture and the reaction cell were calculated using the root-sum-of-squares combination to yield 0.7% uncertainty in the bulb concentration and 0.9% in the reaction cell. The relative expanded uncertainty (i.e. 95% confidence level) due to all systematic effects was then calculated to be 4.2%.

The sample of dichloromethane (J. T. Baker, Inc.) used in this study was analyzed using GC and GC/MS techniques. The main impurity found was 0.029% (mole fraction) of cyclohexane, which is used as a preservative in the original sample. Preparative GC purification allowed us to decrease the total abundance of impurities to less than 0.0005%.

Results and Discussion

Rate constant measurements were complicated by the photolysis of CH_2Cl_2 by the Xe flash lamp, as in our previous study[8] of CH_2ClBr. Hence, experiments were performed at the lowest possible flash energy (corresponding to an electrical energy of approximately 0.3 J) to minimize the effect of CH_2Cl_2 photofragmentation. Additional experiments, carried out at flash energies ranging from 0.3 to 11 J, showed a clear dependence of the observed rate constant (k_{DCM}^{obs}) on flash energy (Figure 1), indicating additional photochemistry. From this figure, one can see that results obtained at the lowest flash energy were not really affected by additional photochemistry. Values of k_{DCM}^{obs} (298) were also measured at the flash energy of 3.3 J using various flash repetition rates. No dependence of the observed rate constant on variations of flash repetition rate by a factor of 4 was discernible. This indicates that additional photochemistry is due to reactions with radicals formed in the reaction volume rather than with stable products accumulating in the reactor, as was also shown for CH_2ClBr.[8] The dependence of the observed rate constant k_{DCM}^{obs} on the flash energy was found to be about 6 times less for CH_2Cl_2 than observed for CH_2ClBr. This finding is consistent with the lower absorption cross section of CH_2Cl_2 in the UV region.[6,8]

Figure 2 shows the results of our measurements at $T = 298$ K as an example of the total reproducibility of our rate constant measurements. The data in this figure were taken over a period of about 3 months, and no one measurement was rejected.

The values of k_{DCM} reported in this work were measured over the temperature range of 277–370 K, at the lowest flash energy of about 0.3 J and then slightly corrected (less than 1%) using the observed dependence of k_{DCM}^{obs} on flash energy. The resultant values of k_{DCM} are presented in Table 1 and Figure 3. The following Arrhenius expression for k_{DCM} was derived based on our results:

$$k_{DCM}(T) = (2.61^{+0.37}_{-0.34}) \times$$
$$10^{-12} \exp\{-(944 \pm 29)/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

where the uncertainties represent 95% confidence limits associated with the statistical fitting procedure and include the contribution for the expanded standard uncertainties in the individual rate constant.

For the purpose of atmospheric modeling, the region below room temperature is of the greatest interest. The above expression for the rate constant and uncertainties can be rewritten in the manner chosen by the NASA Panel for Data Evaluation,[6] as we have described previously:[11]
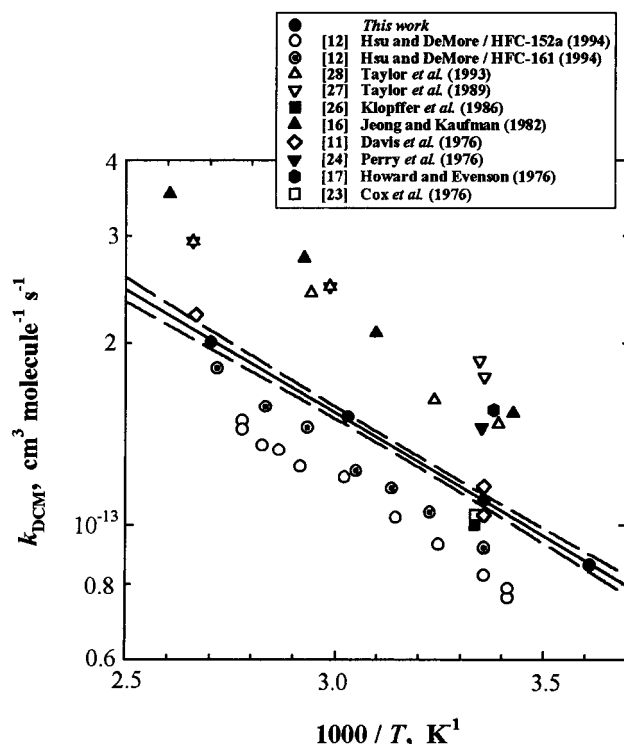
TABLE 1: Rate Constants Measured for the Reaction between OH and CH_2Cl_2

temp, K	k_{DCM}, 10^{-13} cm^3 molecule^{-1} s^{-1}	no. of determinations
277	0.86 ± 0.07^a $(0.08)^b$	3
298	1.10 ± 0.02^a $(0.05)^b$	9
330	1.51 ± 0.04^a $(0.06)^b$	3
370	2.02 ± 0.05^a $(0.06)^b$	4

^{a} Uncertainties expressed are the (95% confidence level) components due to random effects only as derived from the statistical fitting procedure. ^{b} Numbers in parentheses are the total expanded uncertainties arising from both instrumental and statistical effects.

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Figure 3. Arrhenius plot of all measured k_{DCM} values over the temperature range from 270 to 400 K and the least-squares fit to our data (solid line) with its statistical 95% confidence intervals (dashed lines).

$$k_{DCM}(T) = 1.10 \times 10^{-13} \exp\left\{-944\left|\frac{K}{T} - \frac{1}{298}\right|\right\}$$
$$cm^3 \, molecule^{-1} \, s^{-1}$$

$$f(T) = 0.05 \exp\left\{29\left|\frac{K}{T} - \frac{1}{298}\right|\right\}$$

where $f(T)$ is the uncertainty factor in the rate constant at temperature T. Here 0.05 corresponds to the root-sum-of-squares combination of the expanded uncertainties at $T = 298$ K arising from the instrumental (4.2%) and statistical effects (2%).

The results from previous studies of the reaction between OH and DCM are listed in Table 2. All of the parameters given are the results of our analysis of data from the original papers and the stated uncertainties reflect confidence intervals of Arrhenius fitting only. One previous absolute study resulted in the rate constant within 10% of the present value.[12] The other absolute measurements gave rate constants 33%−60% greater than that reported here at room temperature. We compared the other rate constants reported in those publications with the presently recommended values[6] and found no systematic trends. Hsu and DeMore[13] also determined k_{DCM} using a relative rate technique. Their values (using two different reference compounds) are about 15%−25% lower than the present result. There are no apparent errors in our measurements, either systematic or random, that can account for such differences.

More recently, CH_2Cl_2 was used as a reference[9] reactant for the relative determination of the rate constants for reactions of OH with $CHCl_2-CF_2Cl$ (HCFC-122), CH_2ClBr, CH_2Br_2, and CH_2FCl. For each of the first three, only a single absolute rate constant measurement is available. Using the value of k_{DCM} obtained in the present work, we recalculated the absolute rate constants from the ratios. The results of this recalculation are given in Table 3. There is an excellent coincidence between results of the absolute and relative determinations for the reactions of OH with $CHCl_2-CF_2Cl$ and CH_2ClBr (within 5% over the temperature range from 277 to 370 K). The CH_2FCl rate constant recalculated as indicated agrees well with absolute measurement results of refs 14, 15, and 16 while being approximately 25% less than that of ref 17 over the temperature range from 277 to 370 K and 15% higher than the room-temperature result of ref 18. The rate constant derived for CH_2Br_2 is approximately 30% higher than the absolute value reported by Mellouki et al.[19] and about 25% higher than the rate constant measured relative to OH + $(CH_3)_2CO$ at room temperature.[20] Thus, with exception of CH_2Br_2, the rate constants recalculated from the results of relative measurements are in reasonably good agreement with the published results of absolute measurements.

Atmospheric Implications

The residence time of DCM in the atmosphere can be estimated by a simple scaling procedure using methyl chloroform (MC) as a reference:[21]

TABLE 2: Summary of All Measurements of $k_{DCM}{}^a$ below $T = 425$ K[33]

$A \times 10^{12}$ (cm³ molecule⁻¹ s⁻¹)	$E/R \pm \Delta E/R$ (K)	$k_{DCM}(298) \times 10^{13}$ (cm³ molecule⁻¹ s⁻¹)	reference
		0.94^b	Cox et al., 1976[25]
		1.55 ± 0.30 ($T = 296$ K)	Howard and Evenson, 1976[18]
		1.45 ± 0.20	Perry et al., 1976[26]
4.27 ± 0.63	1094 ± 161	1.09 ± 0.10	Davis et al., 1976[12]
$4.7^{+1.4}_{-1.1}{}^c$	987 ± 84^c	1.71 ± 0.09^c	Jeong and Kaufman, 1982[17]
6.81^d	1117^d	1.60^d	Nielsen et al.., 1984[27]
		1.0^e	Klopffer et al.., 1986[28]
$2.9^{+1.5}_{-1.0}{}^c$	829 ± 139^c	1.79 ± 0.15^c	Taylor et al., 1989[29]
$5.5^{+2.8}_{-1.9}{}^c$	1073 ± 143^c	1.51 ± 0.14^c	Taylor *et al.*, 1993[30]
2.2^f	981^f	0.82^f	Hsu and DeMore, 1994[13]
3.2^g	1057^g	0.92^g	Hsu and DeMore, 1994[13]
$2.61^{+0.37}_{-0.34}$	944 ± 65	1.10 ± 0.05	this work, 1997

^{a} All values and uncertainties are derived from the data presented in original papers and reflect only statistical (2σ) scattering in Arrhenius plots. For the present work the expanded uncertainties in A, E/R, and $k(298)$ include uncertainty components due to both statistical and systematic effects. ^{b} The result of a relative determination has been recalculated using the presently recommended rate constant for the reference reaction between OH and CH_4. The reported uncertainty is stated to be a factor of 2. ^{c} Arrhenius parameters are derived from the data below $T = 425$ K. ^{d} The uncertainties are not reported in the original paper. ^{e} The reference compound and uncertainty analysis are not reported for this relative measurement. ^{f,g} Results of relative technique measurements with CH_3-CHF_2 (HFC-152a)^f, and CH_3-CH_2F (HFC-161)^g as reference compounds. Because the uncertainties were not presented in the original paper, they should be associated mainly with uncertainties of the rate constants for the OH reactions with reference compounds.

TABLE 3: Summary of Rate Constants for Reactions of OH with Haloalkanes Measured by Absolute Techniques and Those Determined Relatively to CH_2Cl_2 (See Text)

molecule	$A \times 10^{12}$ (cm^3 molecule^{-1} s^{-1})	$E/R \pm \Delta E/R$ (K)	$k_i(298) \times 10^{13}$ (cm^3 molecule^{-1} s^{-1})	reference
$CHCl_2-CF_2Cl$	$1.13^{+0.21}_{-0.16}$	918 ± 52	0.52 ± 0.02	Orkin and Khamaganov[31]
(HCFC-122)	1.31	952 ± 103	0.54 ± 0.03	DeMore[9]/this work[a]
CH_2ClBr	$4.0^{+1.1}_{-0.9}$	1069 ± 79	1.12 ± 0.04	Orkin et al. (DF/EPR)[8]
(H-1011)	$2.6^{+0.6}_{-0.5}$	930 ± 65	1.15 ± 0.02	Orkin et al. (FP/RF)[8]
	2.17	869 ± 110	1.18 ± 0.05	DeMore[9]/this work[a]
CH_2FCl			0.37 ± 0.06	Howard and Evenson[18]
(HCFC-31)	$2.8^{+1.9}_{-1.1}$	1259 ± 150	0.41 ± 0.03	Watson et al.[14]
	$5.0^{+7.2}_{-2.9}$	1432 ± 270	0.41 ± 0.05	Handwerk and Zellner[16]
			0.45 ± 0.07	Paraskevopoulos et al.[15]
	$2.04^{+0.73}_{-0.46}$	1088 ± 100	0.53 ± 0.04	Jeong and Kaufman[17]
	2.1	1161 ± 57	0.43 ± 0.01	DeMore[9]/this work[a]
CH_2Br_2	$1.91^{+0.76}_{-0.54}$	840 ± 100	1.14 ± 0.13	Mellouki et al.[19]
(H-1002)			1.2 ± 0.3	Orlando et al.[20]
	2.19	799 ± 93	1.50 ± 0.05	DeMore[9]/this work[a]

[a] Ratios of the OH reaction rate constant with the compound to that with CH_2Cl_2 obtained by DeMore[9] have been combined with the absolute value of k_{DCM} measured in this work. The quoted uncertainties are 95% confidence intervals associated with the relative rate measurements[9] only and do not include the uncertainty in the rate constant of the reference reaction.

$$\tau^{OH}_{DCM} = \frac{k_{MC}(277)}{k_{DCM}(277)}\tau^{OH}_{MC} = 0.44 \text{ years}$$

where τ^{OH}_{DCM} and $\tau^{OH}_{MC} = 5.7$ years are the atmospheric lifetimes of DCM and methyl chloroform, respectively, due to reactions with hydroxyl radicals in the troposphere, and $k_{DCM}(277)$, $k_{MC}(277) = 6.69 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} are the rate constants[6] for the reactions of OH with these substances at $T = 277$ K.

Our measurements have resulted in values for k_{DCM} that are 20%−30% lower than previously accepted for atmospheric budget estimations.[3,5] Meantime, a recent analysis of the atmospheric concentration trend of methyl chloroform[22] has resulted in a shorter calculated lifetime for methyl chloroform than used in the DCM budget analysis. Thus, the resulting correction in the DCM atmospheric lifetime is only about 10%, and the discrepancy between estimated and measured DCM atmospheric concentrations remains the same. This suggests the existence of an additional DCM source, possibly of natural origin.

Reaction with hydroxyl radicals is the main, but not the only possible, removal mechanism for DCM from the atmosphere. Dissolution in the ocean and rainout can be concurrent removal processes shortening the atmospheric lifetime. In a previous paper[8] we roughly estimated an upper limit for the rate of the ocean removal process for CH_2ClBr (based on CH_2ClBr solubility data and an assumption of relatively fast further chemical degradation) to show that it can be comparable with the OH reaction sink. The OH reaction rate constants and water solubilities[8,23] for both CH_2Cl_2 and CH_2ClBr are about the same. In the absence of relatively fast processes for chemical decomposition, however, the ocean will act simply as a temporary reservoir, not as a sink. Thus, the chemical degradation rate of DCM in ocean water will determine the relative contribution of oceanic removal to the DCM lifetime. On the basis of DCM water solubility[23] we can estimate that about 10% of total atmospheric CH_2Cl_2 is dissolved in the 75 m oceanic mixed layer.[24] Taking into account $\tau^{OH}_{DCM} = 0.44$ years, we can estimate that any degradation process must have a characteristic time shorter than 1 year to appreciably lower the atmospheric lifetime of DCM calculated for OH removal alone.

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(33) Since the submission of this manuscript we have been informed of a recent relative rate study of the title reaction by W. B. DeMore (using C_2H_6 as the reference reactant). Results of the measurements can be presented by the following Arrhenius expression: $k(T) = (2.06^{+1.1}_{-0.7}) \times 10^{-12} \exp\{-(894 \pm 140)/T\}$ with the mean rate constants being approximately 6%−9% lower than the present results over the common temperature region (298−370 K) of our respective measurements.