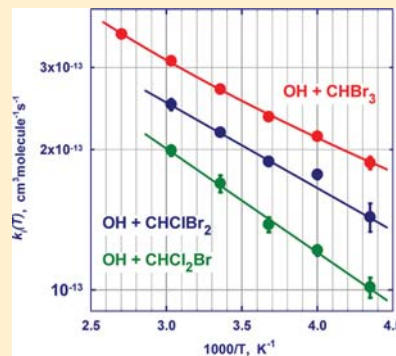


Measurements of Rate Constants for the OH Reactions with Bromoform (CHBr₃), CHBr₂Cl, CHBrCl₂, and Epichlorohydrin (C₃H₅ClO)Vladimir L. Orkin,* Victor G. Khamaganov,[†] Sergey N. Kozlov,[‡] and Michael J. Kurylo[§]

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ABSTRACT: Measurements of the rate constants for the gas phase reactions of OH radicals with bromoform (CHBr₃) and epichlorohydrin (C₃H₅ClO) were performed using a flash photolysis resonance-fluorescence technique over the temperature range 230–370 K. The temperature dependences of the rate constants can be represented by the following expressions: $k_{\text{BF}}(230\text{--}370\text{ K}) = (9.94 \pm 0.76) \times 10^{-13} \exp[-(387 \pm 22)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_{\text{ECH}}(230\text{--}370\text{ K}) = 1.05 \times 10^{-14} (T/298)^{5.16} \exp(+1082/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Rate constants for the reactions of OH with CHCl₂Br and CHClBr₂ were measured between 230 and 330 K. They can be represented by the following expressions: $k_{\text{DCBM}}(230\text{--}330\text{ K}) = (9.4 \pm 1.3) \times 10^{-13} \exp[-(513 \pm 37)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_{\text{CDBM}}(230\text{--}330\text{ K}) = (9.0 \pm 1.9) \times 10^{-13} \exp[-(423 \pm 61)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The atmospheric lifetimes due to reactions with tropospheric OH were estimated to be 57, 39, 72, and 96 days, respectively. The total atmospheric lifetimes of the Br-containing methanes due to both reaction with OH and photolysis were calculated to be 22, 50, and 67 days for CHBr₃, CHClBr₂, and CHCl₂Br, respectively.



1. INTRODUCTION

The release of bromine-containing organic compounds into the atmosphere is of interest because of their potential adverse impact on stratospheric ozone¹ and their important role in tropospheric ozone chemistry. Bromoform (CHBr₃) is the largest source of bromine in the atmosphere with an estimated bromine (Br) emission rate of 0.45–1.4 MT/year.¹ Bromoform is characterized as a very short-lived substance (VSLS) with an estimated atmospheric lifetime of ca. 24 days¹ due to photolysis and reaction with OH in the troposphere. It is predominantly oceanic in origin with tropical macroalgae constituting an important source. The concentration of bromoform in the marine boundary layer exhibits very large variability and can significantly exceed the concentration of CH₃Br in coastal areas.² Although its concentration decreases from the boundary layer to the upper troposphere, bromoform and other VSLS are still thought to contribute to the stratospheric bromine abundance and, thus, to the catalytic cycle for stratospheric ozone depletion along with the principal, more stable, contributor, methyl bromide (CH₃Br). Two other mixed Cl/Br-trihalomethanes (CHBr₂Cl and CHBrCl₂) have been observed in smaller amounts^{2,1} and also appear to have natural oceanic origins.

Although photolysis seems to be the main atmospheric sink of CHBr₃, the contribution of the reaction with OH to the total removal rate has been estimated to be only a factor of 2 smaller. However, this estimate is based on results from a single study³ of the reaction between CHBr₃ and OH performed only above room temperature.

The present paper reports results of our study of the reaction between OH and CHBr₃ over the temperature range of atmospheric interest. The measurements were performed using our recently modified flash photolysis–resonance fluorescence

(FP-RF) apparatus with very careful analysis of the purity of different samples of bromoform, including on-site purification. We also report the results of some earlier studies of the reactions between OH and CHBr₂Cl and CHBrCl₂ using our FP-RF apparatus prior to its modification. We have also studied the OH + CHBr₃ reaction using this earlier version of the apparatus and aspects of these results are also included.

In addition, we have obtained data for the rate constant of the reaction between OH and epichlorohydrin (ECH, chloromethyl oxirane, C₃H₅ClO) because this compound was added as a stabilizer in some of our bromoform samples to prevent oxidation. Epichlorohydrin is an important commercial chemical, with a global annual demand of over one million tons.⁴ It is a versatile chemical intermediate used in a wide variety of applications with approximately 3/4 of the world's consumption being used to make epoxy resins and elastomers increasingly used in applications such as corrosion protection coatings as well in the electronics, automotive, aerospace industries, etc. It is also used as a precursor in the production of a variety of specialty chemicals.

Details of these studies of reactions 1 through 4 are presented below.



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2. EXPERIMENTAL SECTION⁵

2.1. OH Reaction Rate Constant Measurements.

General descriptions of the apparatus and the experimental method used to measure the OH reaction rate constants are given in previous papers.^{6–9} Modifications to the apparatus and the measurement procedure, which resulted in significant improvements in the accuracy and precision of the obtained kinetic data, were recently detailed.^{9,10} In particular, the gas handling system was completely rebuilt and a new reaction cell and photomultiplier installed.

The principal component of the FP-RF apparatus is a double-walled Pyrex reactor (of approximately 180 cm³ internal volume) equipped with quartz windows. The reactor is temperature controlled by circulating methanol or water between the outer walls and is located in an evacuated metal housing to prevent ambient water condensation during low temperature measurements. This also prevents extraneous absorption of the UV radiation from the flash lamp used to produce OH radicals. Reactions were studied in argon carrier gas at a total pressure of 4 kPa (30.0 Torr). Flows of dry argon, argon bubbled through water thermostatted at 276 K, and dilute mixtures of each reactant were passed through the reactor at a total flow rate between 0.21 and 2.4 cm³ s⁻¹, STP. The reactant mixtures diluted with Ar were prepared in a 10 L glass bulb equipped with Teflon/glass valve. The concentrations of the gases in the reactor were determined by measuring the gas flow rates and the total pressure with MKS Baratron manometers. Flow rates of argon, the H₂O/argon mixture, and the reactant/argon mixture were measured and maintained using MKS mass flow controllers directly calibrated for every mixture. The calibration procedures for the mass flow controllers and manometers as well as the uncertainties associated with gas handling have been described in detail.⁹ The total uncertainty of the kinetic results was estimated to be ~2% to 2.5% in the absence of chemical complications for measurements performed after the recent modification of the apparatus and in the measurement procedures.⁹ As stated above, only $k_{\text{BF}}(T)$ and $k_{\text{ECH}}(T)$ were measured by using this modified apparatus. The total uncertainty of our earlier data for the rate constants of the reactions between OH and CHClBr₂ and CHCl₂Br ($k_{\text{CDBM}}(T)$ and $k_{\text{DCBM}}(T)$) reported here can be estimated as ~8%.

Hydroxyl radicals were produced by the pulsed photolysis of H₂O, injected via the 276 K argon/water bubbler. The OH radicals were monitored by their resonance fluorescence near 308 nm, excited by a microwave-discharge resonance lamp (0.8 kPa or 6 Torr of a mixture of H₂O in UHP helium) focused into the reactor center. Resonantly scattered radiation from the center of the reaction cell was collimated by the reactor window/lens assembly and detected by a cooled photomultiplier operating in the photon counting mode. The resonance fluorescence signal was recorded on a computer-based multichannel scaler (using a channel width of 100 μs) as a summation of 2000–20 000 consecutive flashes. The entire temporal OH profile was recorded and coadded following each flash, thereby minimizing any possible effects of small flash-to-flash variations of the initial OH concentration and drift of the resonance lamp intensity.

In the absence of any reactant in the reactor, the temporal decay of [OH] is associated with its net diffusion out of the

irradiated (photolysis) zone. This relatively long “background” decay was always recorded with a 2.5 Hz flash repetition rate to ensure in complete disappearance of the OH between consecutive flashes. [OH] decays were then recorded at various reactant concentrations with a flash repetition rate of 5 Hz, or 10 Hz for faster data collection except at small reactant concentrations when the low repetition rate was still required. The test experiments revealed no effect of the repetition rate on the measured decay rate at higher reactant concentrations. The procedure for deriving the reaction rate constant from such data has been described by Orkin et al.⁷ and in subsequent papers.^{9,11}

At each temperature the rate constant was determined from a fit to all of the decay rates obtained at that temperature. The temperatures for the measurements were chosen to be approximately equally distant along the Arrhenius 1/*T* scale in order to have them equally weighted in the fitting procedure for determining the temperature dependence. Experiments were always performed at two temperatures that are widely used in other studies, *T* = 298 and 272 K. The first is standard room temperature, used in evaluations and presentations of the rate constants while the second is the temperature used in estimations of atmospheric lifetimes.¹²

2.2. Materials. The purity of the bromoform (CHBr₃) sample was one of the main concerns in this study and required substantial efforts to be resolved. Bromoform is a liquid at room temperature with a saturated vapor pressure of a few Torr. Liquid bromoform is easily oxidized when exposed to the atmosphere. Therefore, commercial bromoform always contains a small amount of various stabilizers such as ethanol, amylene, or epichlorohydrin. We studied a number of samples obtained from various suppliers and describe below the purity information for the samples that were used to obtain the data reported here. We have highlighted with italicized text the impurities whose presence in a sample could result in an overestimation of the measured reaction rate constant due to their reaction with OH. Halogenated methanes found as impurities have OH reactivities similar to that of bromoform (Sander et al.¹³ and our results reported below) and do not contribute appreciably to the OH decays at the levels indicated. Fully halogenated methanes do not undergo reaction with OH. Molecular bromine, Br₂, which is very reactive toward OH,¹³ can be a potential impurity in the samples of Br-containing methanes. Fortunately, because Br₂ absorbs visible light, even a contamination level as low as ca. 0.01% is readily visible with the naked eye in transparent liquid samples. Analysis of the liquid samples of bromoform using a spectrophotometer revealed no detectible absorption near 400 nm, thereby allowing us to estimate the bromine concentration to be less than ca. 0.002%.

Two different samples of bromoform were obtained from Chem Service, Inc. Our GC/MS/FID analysis of the first sample (stated purity of 99.3%) indicated the presence of ethanol, CH₃CH₂OH (~0.02%), CH₂Br₂ (0.06%), and epichlorohydrin (0.27%). Our GC/MS/FID analysis of the second sample (stated purity of 99.4%) showed amylene, (CH₃)₂C=CHCH₃ (0.05%), dimethylcyclopropane (0.2%), CHCl₃ (0.03%), CH₂Br₂ (0.05%), CHCl₂Br (0.03%), CHClBr₂ (0.35%), and CBr₄ (0.2%). Epichlorohydrin and amylene serve as stabilizers in the first and second sample, respectively. Both different stabilizing compounds and the impurity footprints indicate the different origins of these samples. The use of samples of different origin minimizes possible kinetic

interferences due to nondetected impurities, whose presence in both samples at identical amounts is highly unlikely.

Test experiments with the second sample resulted in noticeably higher derived rate constants when compared with the results obtained with the first sample. Moreover, these results were different depending on the CHBr_3/Ar mixture preparation procedure. A liquid (degassed) bromoform sample was stored in a small (100 mL) glass bulb equipped with a Teflon valve. When the sample degassing was completed, the bulb was usually connected to the vacuum gas preparation rack in the “valve-down” position to allow liquid phase sampling for the preparation of CHBr_3/Ar mixtures. Standard mixtures (1.5%) were prepared in a 10 L glass bulb equipped with a Teflon valve by pressurizing 400 Pa (3.00 Torr) of CHBr_3 with Ar to 26.67 kPa (200.0 Torr). Thus, this 3 Torr CHBr_3 sample contains the same amount of impurities as the bulk liquid sample that was analyzed. Alternatively, the small storage bulb with liquid bromoform could be connected to the gas preparation vacuum system in the “valve-up” position to allow gas phase sampling for preparing CHBr_3/Ar mixtures. Experiments performed using mixtures prepared in this second manner typically resulted in much larger measured reaction rate constants. This is not surprising since the different volatilities of CHBr_3 and the reactive hydrocarbon impurities (amylene and dimethylcyclopropane) resulted in the vapor phase being enriched with these more volatile compounds.

We used the amylene stabilized bromoform sample to prepare a stabilizer-free sample of CHBr_3 through a low temperature vacuum distillation. Use of this sample is described later in this paper.

The sample of bromoform, CHBr_3 that was used in our earlier study performed with our older FP-RF apparatus was obtained from Aldrich with stated purity of 99.8%. Our GC/MS/FID analysis of that sample indicated ethanol, $\text{CH}_3\text{CH}_2\text{OH}$ (0.02%), CH_2Br_2 (0.3%), epichlorohydrin (0.26%), and CBr_4 (0.5%).

The sample of epichlorohydrin used in this study was obtained from Fluka (stated purity of 99.9%). We found acetone (0.05%) to be the main impurity.

The samples of dichlorobromomethane, CHCl_2Br , stabilized with potassium carbonate (stated purity of 98%) and chlorodibromomethane, CHClBr_2 , (stated purity of 97%) were obtained from Lancaster Synthesis Inc. Our GC/MS/FID analysis of the CHCl_2Br indicated CHCl_3 (0.16%), CCl_3Br (0.31%), and CCl_2Br_2 (1.0%) as the main impurities. Smaller amounts of $\text{CH}_3\text{C}(\text{O})\text{OCH}_3$ (0.005%), $\text{CH}_3\text{C}(\text{O})\text{OH}$ (0.009%), CH_2Cl_2 (0.012%), and CCl_4 (0.004%) were found as well. Our GC/MS/FID analysis of the CHClBr_2 indicated acetones, $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ (0.8%), $\text{CH}_2\text{ClC}(\text{O})\text{CH}_3$ (0.003%), $\text{CH}_2\text{BrC}(\text{O})\text{CH}_3$ (0.08%), tetrahydrofuran, $\text{C}_4\text{H}_8\text{O}$ (0.01%), toluene (0.005%), CHCl_2Br (0.3%), CHBr_3 (0.17%), CH_2Br_2 (0.06%), CCl_3Br (0.004%), and CCl_2Br_2 (0.04%).

We used 99.9995% purity argon (Spectra Gases Inc.) as a carrier gas in all kinetic experiments and preparation of reactant mixtures.

3. RESULTS

3.1. OH + CHBr_3 . Kinetic Study of OH + CHBr_3 . Bromoform (as well as the two other trihalomethanes) has a very strong UV absorption¹³ and, therefore, rate constant measurements were complicated by its photolysis. Reactions between OH and products of CHBr_3 photolysis resulted in a small overestimation of the derived rate constant even at the

lowest flash energies used in the study. Hence, sets of experiments at various flash energies were performed at each temperature to derive the correct rate constant for the reaction between OH and CHBr_3 . We have used and analyzed this approach in earlier studies of halogenated methanes.^{8,14}

Figure 1 shows the measured rate constant for the reaction between OH and CHBr_3 at various flash lamp energies. Each

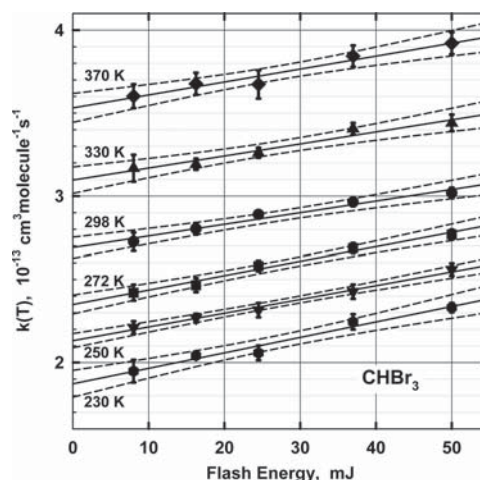


Figure 1. Results of measurements of the rate constant for the reaction between OH and CHBr_3 at various flash lamp energies; the results obtained at different temperatures are shown with different symbols. The best fits to the data at each temperature (solid lines) are shown with their 95% confidence intervals (dashed lines). The intersects with $k(T)$ axis are the rate constants $k_{\text{BF}}(T)$ at these temperatures with their 95% confidence intervals.

point shown in this figure was obtained from the combined fit to all data points measured at the particular temperature and flash energy. The total number of measurements at each temperature is shown in Table 1. The results obtained at each temperature exhibit a linear dependence on flash energy indicated by the solid lines in Figure 1, with their confidence intervals corresponding to two standard errors indicated by the dashed lines. An extrapolation of these linear dependences to “zero” flash energy yields the rate constant for the reaction between OH and CHBr_3 , $k_{\text{BF}}(T)$, not complicated by the secondary chemistry. The intersection of the dashed lines gives the statistical two standard error for $k_{\text{BF}}(T)$. These data are presented in Table 1 as the bold highlighted numbers. Note, that the dependences shown in Figure 1 have approximately the same slopes, which is indicative of reactions with products of CHBr_3 photolysis (probably, CHBr_2 radicals), rather than secondary reactions with a product of the primary reaction between CHBr_3 and OH (CBr_3 radicals).⁸

Along with the reactions with CHBr_3 photolysis products, there are two other potential complications in studying the bromoform reaction: the low vapor pressure of bromoform and the presence of reactive stabilizers in the bromoform samples. The saturated vapor pressure of bromoform is only 0.7 kPa (5.3 Torr) at room temperature and becomes as small as 1.7 Pa (0.013 Torr) at 230 K.¹⁵ This raises a concern about possible bromoform adsorption on the surfaces of the gas handling system and the reaction cell, especially at lowest temperatures. Test experiments were performed using mixtures containing larger (3%) and smaller (0.5%) concentrations of bromoform in the storage bulb, different storage bulbs (10 and 5 L), and

Table 1. Rate Constants Measured in the Present Work for the Reaction of OH with CHBr_3^a

T, K	$k_{\text{BF}}(T) \times 10^{13}$	CHBr_3	
E, mJ	$\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$10^{14} \text{ molecule/cm}^3$	test experiments conditions
230	1.87 ± 0.06 (110)	0.648–3.13	
<i>8 mJ</i>	<i>1.95 ± 0.07 (22)</i>		epichlorohydrin stabilized sample
	<i>1.92 ± 0.07 (8)</i>		vacuum distilled sample
250	2.13 ± 0.03 (69)	0.43–6.17	
<i>8 mJ</i>	<i>2.21 ± 0.04 (19)</i>		epichlorohydrin stabilized sample
	<i>2.18 ± 0.03 (8)</i>		vacuum distilled sample
272	2.35 ± 0.04 (81)	0.47–6.63	
<i>8 mJ</i>	<i>2.42 ± 0.05 (13)</i>		epichlorohydrin stabilized sample
	<i>2.42 ± 0.08 (6)</i>		vacuum distilled sample
298	2.69 ± 0.04 (203)	0.96–6.05	
<i>8 mJ</i>	<i>2.73 ± 0.05 (20)</i>		epichlorohydrin stabilized sample
	<i>2.79 ± 0.02 (16)</i>		vacuum distilled sample
	<i>3.22 ± 0.10 (6)</i>		amylene stabilized (liquid sampling)
	<i>4.53 ± 0.17 (5)</i>		amylene stabilized (gas sampling)
<i>25 mJ</i>	<i>2.89 ± 0.02 (66)</i>		
	<i>2.89 ± 0.04 (8)</i>		1.5% mixture, flow rate 100%
	<i>2.92 ± 0.07 (11)</i>		1.5%, flow rate 200%
	<i>2.94 ± 0.02 (7)</i>		0.5% mixture, flow rate 100%
	<i>2.86 ± 0.04 (8)</i>		3.0% mixture, flow rate 200%
	<i>2.87 ± 0.05 (14)</i>		3.0% mixture, flow rate 340%
	<i>2.86 ± 0.05 (5)</i>		1.5% mixture, 100 days old
330	3.11 ± 0.06 (100)	0.44 – 6.12	
<i>16 mJ</i>	<i>3.19 ± 0.03 (25)</i>		epichlorohydrin stabilized sample
	<i>3.13 ± 0.05 (10)</i>		vacuum distilled sample
370	3.53 ± 0.06 (68)	0.43 – 6.04	
RRSD^b	1.4% (two parameter Arrhenius dependence)		

^aThe uncertainties in the final bold highlighted values are two Standard Errors from the least-squares fit of a straight line to the measured rate constant versus the flash energy as described in the text (Figure 1). They do not include the estimated instrumental/systematic uncertainty of ca. 2%. The uncertainties in the rate constants measured in test experiments at particular flash energies are two standard errors from the least-squares fit of a straight line to the measured OH decay rates versus the reactant concentrations and do not include the instrumental/systematic uncertainty. The bold-highlighted data are intersects from the fit to all measurements at various flash energies performed at the particular temperature and 4.00 kPa (30.0 Torr) total pressure using a 1.5% mixture. These data are shown in Figure 1 and were used to derive the temperature dependences of this reaction rate constant. The total number of experiments is shown in parentheses for each temperature. ^bRelative residual standard deviation (RRSD)¹⁰ is shown to uniformly represent the data deviation from the best fit temperature dependence.

different total gas flow rates through the gas handling system and the reaction cell (a factor of 3.5). The standard 1.5% mixtures were “aged” in the storage bulb between a half day and 100 days before measurements. None of these variations resulted in noticeable changes in the measured rate constants. Results of some of these test experiments performed at $T = 298$ K with a medium flash energy are presented in Table 1 with italicized text. Quantitative UV absorption analysis of the sample taken from the storage bulb confirmed the content of our 1.5% standard manometrically prepared mixture. Thus, we are confident in our determination of the CHBr_3 concentration in our rate constant measurements.

Figure 2 shows the results of a test experiment performed to illustrate a possible complication from bromoform condensation or adsorption on the cell walls at the lowest temperature of 230 K. The solid points represent the results of our standard [OH] decay rate measurements, which were used to derive the rate constant as a slope of the fitted solid line. When this set of measurements was complete, we continued to increase the flow rate of the 1.5% CHBr_3/Ar mixture through the cold reactor and an additional set of decay rate measurements was obtained (open circles at the highest calculated concentrations). Figure 2 clearly illustrates that removal of bromoform on the cold reaction cell walls inhibits increasing its gas phase concen-

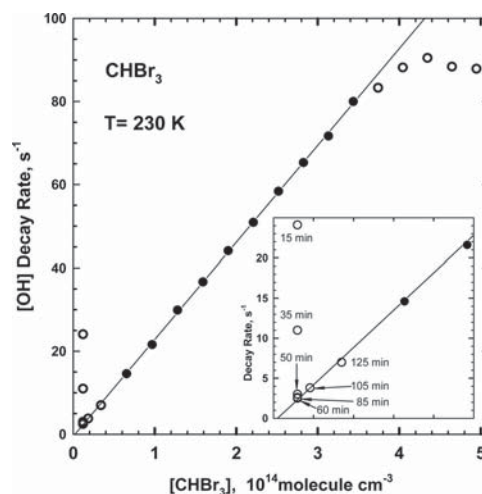


Figure 2. Result from a low temperature experiment for determining $k_{\text{BF}}(230 \text{ K})$, illustrating the effects of condensation of bromoform at higher concentrations.

tration. We observed a similar, but less pronounced, effect of such low temperature condensation of the reactant in our study of the reaction between OH and $\text{CF}_3\text{CH}_2\text{OH}$.¹⁰ In order to

check the possible effects of such behavior on any subsequent measurements, we decreased the flow rate of the CHBr_3/Ar mixture by a factor of 40 to a very low level and continued measuring the $[\text{OH}]$ decay rates. The results are shown in Figure 2 as the low concentration open circles, expanded in the figure insert. The first measurement was done in ca. 15 min after the CHBr_3/Ar flow rate was decreased (the highest of the open circles). Additional measurements of the $[\text{OH}]$ decay rate were performed with the same reactant flow rate after 35 min, 50 min, 60 min, and 85 min. It appears that, over this time interval, the condensed bromoform evaporated and the gas phase concentration in the reactor returned to its correct low value of $[\text{CHBr}_3] = 1.2 \times 10^{13}$ molecule/ cm^3 calculated from the flow rate - the corresponding low $[\text{OH}]$ decay rate being finally observed. Two additional data points were taken at slightly higher CHBr_3 concentrations (after 105 and 125 min) to confirm that the effects of reactant condensation were no longer in evidence - the measured points were consistent with the originally derived linear dependence shown by the solid line.

Stabilizer Free Bromoform. As stated earlier, one of the most challenging aspects of this study involved dealing with the possible effects of reactive chemicals used by manufacturers to stabilize bromoform against oxidation when in contact with ambient air. Our original kinetic measurements were performed using a sample stabilized with epichlorohydrin ($\text{C}_3\text{H}_5\text{ClO}$) for which no data were available on its reactivity toward OH. In our latest experiments presented in Figure 1 and Table 1, we primarily used a sample with the same stabilizer. However, we also performed measurements of the rate constant, $k_{\text{ECH}}(T)$, for the reaction between epichlorohydrin (ECH) and OH over the entire range of temperatures to demonstrate the lack of any appreciable effect (0.1% to 0.2% over the entire temperature range) of this impurity on our results. The results of our measurements of the rate constant for the reaction between OH and epichlorohydrin, $k_{\text{ECH}}(T)$, are presented below. The presence of 0.02% of ethanol as an impurity in our CHBr_3 sample can contribute only 0.2% to 0.36% over the entire temperature range.

We also studied samples of bromoform stabilized with amylene (2-methyl-2-butene, $(\text{CH}_3)_2\text{C}=\text{CHCH}_3$). As expected, with the much more volatile amylene stabilizer, the effect on the measured rate constant depends on the method of sampling, being predictably larger when the vapor phase was used to prepare the CHBr_3/Ar mixtures. For example, experiments at $T = 298$ K resulted in $\sim 18\%$ and $\sim 66\%$ overestimations of the measured rate constant when the reactant mixture was prepared from the liquid phase and gas phase of amylene stabilized bromoform, respectively (see Table 1).

Despite being able to obtain an essentially "stabilizer independent" rate constant for the reaction of OH with bromoform using a sample stabilized with epichlorohydrin, we conducted a series of additional experiments with a sample of bromoform, which was free of any chemical stabilizers. Using a sample of bromoform stabilized with amylene, we prepared a stabilizer-free bromoform sample using low temperature vacuum distillation. On the basis of the very different saturated vapor pressures of bromoform and amylene, we were able to selectively remove the amylene by continuous pumping with a turbomolecular pump through a condenser maintained at ca. -50 C. The saturated vapor pressure of amylene at -50 C exceeds that of bromoform by a factor of $\sim 10^3$.¹⁵ We were

unable to detect any residual amylene in a sample of CHBr_3 distilled in such a manner indicating that we succeeded in reducing its concentration by a factor of at least 30–40. Our GC/MS/FID analysis of the original sample indicated ca. 0.2% of very similar impurity (similar GC retention time and mass spectrum), which could be assigned to *cis*-1,2-dimethylcyclopropane. This larger impurity was also no longer detectable in the distilled sample, thus suggesting a lowering of its concentration by a factor of more than 200. This distilled bromoform sample was rapidly oxidized when the storage flask was opened to expose the liquid sample to the ambient atmosphere. The transparent colorless distilled sample turned into a dark brown liquid within a very short period of time. A similarly distilled sample, which was never exposed to the atmosphere after distillation, still remains stable (exhibits no visible changes) a year after purification.

Experiments were performed using this stabilizer-free sample of CHBr_3 over the entire range of temperatures and at various flash lamp energies. The rate constants measured using this sample were not statistically different from those obtained with an epichlorohydrin stabilized sample. Therefore, we combined all the data obtained with both samples to derive the rate constants presented in Figure 1 and Table 1. Some of the results obtained at lowest flash energy (where the measurements are less affected by the chemistry caused by the photolysis of bromoform) with both samples are presented in Table 1. Note that the range of flash energy variations in our experiments is wider than the extrapolation range by a factor of more than 5 and the rate constants measured at lowest flash energies exceed the "correct" reaction rate constants, $k_{\text{BF}}(T)$, obtained from an extrapolation (bold highlighted data in Table 1) by only 1.5% to 4%.

In conclusion, we are confident that the derived reaction rate constants are not affected by either secondary chemistry or the presence of reactive impurities. An Arrhenius fit to the bold highlighted data set in Table 1 (solid circles in Figure 3) is shown by the solid line in the figure and corresponds to the expression:

$$k_{\text{BF}}(230\text{--}370 \text{ K}) = (9.94 \pm 0.76) \times 10^{-13} \exp\{-(387 \pm 22)/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (5)$$

The data deviation from the fitted line can be numerically represented by the relative residual standard deviation (RRSD) introduced in recent papers,^{10,16} $\text{RRSD} = 1.4\%$. Assuming confidence in the derived uncertainties of the data points, we can apply a rigorous χ^2 -test to check the statistical "goodness" of the two-parameter fit represented by eq 5 and that of a higher level of fitting. The χ^2 -test yields a probability of $P = 0.04$ for expression 5. The commonly accepted probability of "significant" deviation is $P < 0.05$.¹⁷ This means that, based on the individual statistical uncertainties of the data points, there is a 96% chance that their deviation is due to something other than random scattering alone and suggests that a different fit be examined. A three-parameter fit to the same data yields

$$k_{\text{BF}}(230\text{--}370 \text{ K}) = 4.35 \times 10^{-13} (T/298)^{0.844} \exp\{-143/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (6)$$

This expression has an associated RRSD value of 1.0% and the χ^2 -test yields a probability of $P = 0.26$, suggesting a much

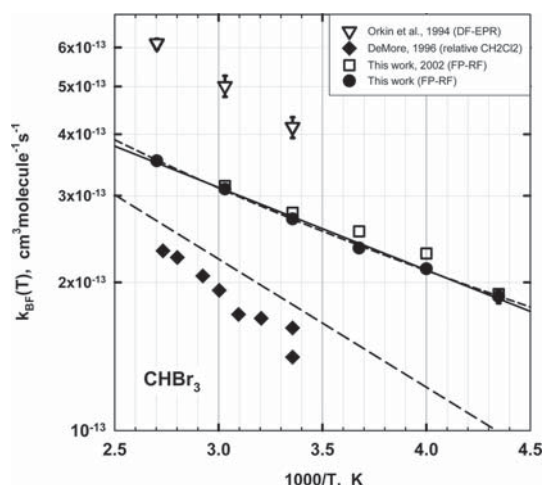


Figure 3. Available results for the rate constant of the reaction between OH and CHBr_3 , $k_{\text{Br}}(T)$: (∇) DF-EPR measurements,¹⁸ (\blacklozenge) relative rate measurements by DeMore,³ (\square) our earlier measurements using FP-RF, and (\bullet) this study. The solid and short-dashed lines show two-parameter and three-parameter fits to our data, respectively. The current JPL 10-6 recommendation¹³ is shown with the long-dashed straight line.

better representation of the data. On a purely statistical basis such a conclusion is correct. However, when one considers the degree of accuracy needed for atmospheric modeling, data representations yielding P values slightly less than 0.05 appear to be quite adequate. In fact, the dependences given by eqs 5 and 6 and shown in Figure 3 yield nearly equivalent rate constants over the temperature range of atmospheric interest with a difference of less than 6% when extrapolated to $T = 200$ K. Hence, we recommend use of the simple Arrhenius temperature dependence given by expression 5. The recommended room temperature rate constant derived in this study is

$$k_{\text{Br}}(298 \text{ K}) = (2.69 \pm 0.10) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (7)$$

where the indicated total uncertainty includes the statistical two standard error of intersects in Figure 1 and listed in Table 1 plus the estimated 2% instrumental uncertainty.

Figure 3 also shows the results from the only published study of this reaction, a relative rate investigation by DeMore (diamonds).³ The current recommendation for this rate constant, which is based on the rate constant ratios measured by DeMore³ and the current recommendation for the rate constant of the reference reaction between OH and CH_2Cl_2 , is shown with the dashed line.¹³ The results of our measurements yield $k_{\text{Br}}(T)$ that are 80% larger than the value originally reported by DeMore at room temperature,³ 50% larger than the currently recommended value¹³ at room temperature, and 80% larger at $T = 230$ K. The reason for such a difference is not clear.

We also show results of our earlier study of this reaction using our FP-RF apparatus prior to the aforementioned improvements (squares). Based on results of the present study of both the bromoform and epichlorohydrin reactions, we know that these earlier data were not affected by the presence of stabilizer (epichlorohydrin) in the sample. Nevertheless, these earlier data are less accurate and more scattered, being 1% to 8% larger.

Results of a discharge-flow/EPR study reported in a conference proceedings¹⁸ are also shown as the triangles in Figure 3. The sample of CHBr_3 used in that study was later analyzed to reveal a small impurity of isopentanol, which was probably added as a stabilizer. Based on its reactivity toward OH,¹⁹ an amount of isopentanol as small as $\sim 1\%$ could explain the difference between the DF-EPR data and our current results.

3.2. OH + $\text{C}_3\text{H}_5\text{ClO}$ (Epichlorohydrin). The results of the rate constant measurements for the reaction between OH and epichlorohydrin are presented in Table 2 and shown in Figure

Table 2. Rate Constant Measured in the Present Work for the Reaction of OH with Epichlorohydrin^a

T , K	$k_{\text{ECH}}(T) \times 10^{13}$, $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$[\text{ECH}]$, $10^{14} \text{ molecule/cm}^3$
230	3.05 ± 0.05 (30)	0.89–6.7
240	3.15 ± 0.04 (10)	0.89–6.7
250	3.21 ± 0.03 (15)	0.89–6.7
260	3.36 ± 0.05 (23)	0.89–5.9
272	3.50 ± 0.06 (8)	0.89–6.7
285	3.76 ± 0.06 (11)	0.89–6.6
298	3.93 ± 0.04 (24)	0.72–6.2
313	4.26 ± 0.06 (11)	0.90–4.6
330	4.77 ± 0.09 (15)	0.73–4.7
350	5.32 ± 0.08 (11)	0.73–4.1
370	5.96 ± 0.09 (32)	0.45–4.1
RRSD ^b	0.79% (three parameter Arrhenius dependence)	

^aThe uncertainties are two Standard Errors from the least-squares fit of a straight line to the measured OH decay rates versus the reactant concentrations and do not include the estimated systematic uncertainty. The number of experiments is shown in parentheses for each temperature. We estimate the total uncertainty of our measurements to be less than 3%. ^bRelative residual standard deviation (RRSD) is shown to uniformly represent the data deviation from the best fit temperature dependence.

4. In contrast with the studies of CHBr_3 , CHClBr_2 , and CHCl_2Br the variation of flash energy by a factor of 2–3 resulted in less than 1.5% change of the measured reaction rate constant for epichlorohydrin. The Arrhenius plot exhibits a

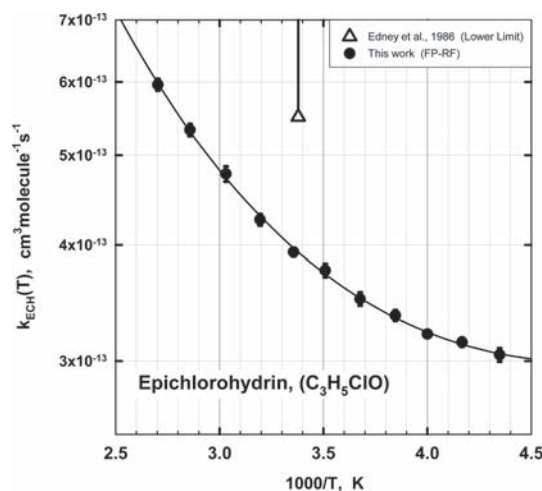


Figure 4. Results of the rate constant measurements for the reaction between OH and epichlorohydrin ($\text{C}_3\text{H}_5\text{ClO}$): (\triangle) a lower limit estimated from a chemical mechanism²⁰ and (\bullet) this study.

positive temperature dependence with very pronounced curvature at lower temperatures. This temperature dependence can be represented using a three-parameter modified Arrhenius expression as

$$k_{\text{ECH}}(230\text{--}370\text{ K}) = 1.05 \times 10^{-14} (T/298)^{5.16} \exp\{+1082/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (8)$$

This dependence represents the data with a statistical probability $P = 0.21$ calculated from the χ^2 -square test. The characteristic data deviation represented by the relative residual standard deviation is $\text{RRSD} = 0.8\%$. Acetone in the amount of 0.05% was the main reactive impurity in the sample of epichlorohydrin. It is slightly less reactive toward $\text{OH}^{\text{I}3}$ than epichlorohydrin and cannot affect the results of our measurements. Therefore, we believe that the total uncertainty (statistical plus systematic) of the measured reaction rate constant, $k_{\text{ECH}}(T)$, is associated only with the uncertainty of our measurements, which can be estimated as less than 3% and^{9,10}

$$k_{\text{ECH}}(298\text{ K}) = (3.97 \pm 0.12) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (9)$$

The only other reported results for this rate constant is an estimated lower limit at room temperature,²⁰ which is also shown in Figure 4.

3.3. Studies of OH + CHBr_3 , CHCl_2Br , and CHClBr_2 Conducted with the Old FP-RF Apparatus. As mentioned earlier, we studied the reactions between OH and the three trihalomethanes (CHBr_3 , CHCl_2Br , and CHClBr_2) several years ago using an older version of our experimental assembly that did not permit as accurate and precise a determination of reaction rate constants as does the present version. We used an epichlorohydrin stabilized sample of bromoform and, with no information available at that time on the reactivity of OH toward epichlorohydrin, we had concerns about the presence of reactive impurities including stabilizers in all available samples. After completion of the current study of the reaction between OH and CHBr_3 we have revisited these older data with the primary aim of presenting information on the reactions of OH with CHCl_2Br and CHClBr_2 . These two compounds are smaller sources of atmospheric bromine¹ in comparison to CHBr_3 . Nevertheless, it is worthwhile to provide information on their OH reaction rate constants at atmospheric temperatures.

The experimental procedure was essentially the same although we used a different gas handling system. We used substantially smaller concentrations of reactants in the storage bulb, typically 0.2% in contrast with 1.5% in the present experiments. Also, we used substantially larger flash energies for these earlier measurements since our OH detection was somewhat less sensitive. As discussed above, both the new and old data sets for CHBr_3 yield reasonably consistent results, lending confidence to the kinetic results obtained for the CHCl_2Br and CHClBr_2 reactions. Figures 5 and 6 illustrate the changes in the measured rate constants with the flash energy. Note, that the data presented in these two figures supports our assertion that the increase in the measured rate constant with the flash energy is due to the reaction between OH and reactant photolysis products. The essentially temperature independent slope for each compound supports this assumption.^{8,14} In addition, the absolute change in the

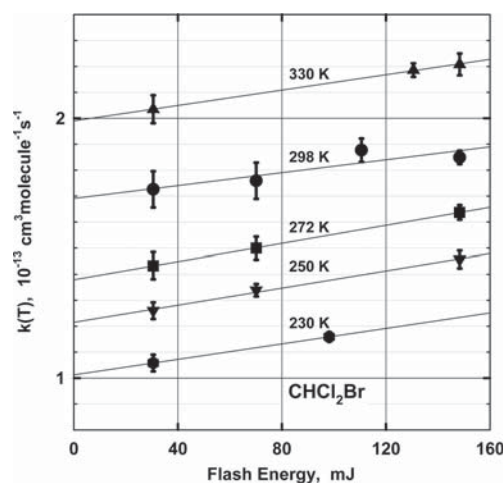


Figure 5. Results of our FP-RF measurements of the rate constant for the reaction between OH and CHCl_2Br at various flash lamp energies; the results obtained at different temperatures are shown with different symbols.

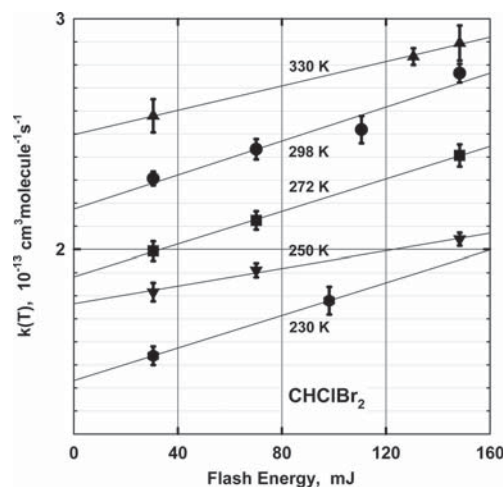


Figure 6. Results of our FP-RF measurements of the rate constant for the reaction between OH and CHClBr_2 at various flash lamp energies; the results obtained at different temperatures are shown with different symbols.

measured rate constant with the flash energy is consistent with the increasing yield of photolysis products, CHCl_2 , CHClBr , and CHBr_2 , respectively that can undergo the reaction with OH and affect the derived reaction constant.

In spite of the limited number of measurements the data in Figures 5 and 6 are reasonably consistent. The only visible outlier is the data set obtained for CHClBr_2 at $T = 250\text{ K}$. We would have expected a steeper dependence of the measured rate constant on flash energy, similar to the dependences at the other temperatures. The smaller slope for the 250 K data results in an overestimation of the intercept, i.e., $k_{\text{CDBM}}(250\text{ K})$. The rate constants of both reactions obtained as intercepts in Figures 5 and 6 are presented in Table 3 and are shown in Figure 7 along with current results for CHBr_3 .

A two-parameter Arrhenius fit to the CHCl_2Br data yields the following expression:

Table 3. Results of Rate Constants Measurements for Reactions of OH with CHCl_2Br and CHClBr_2 ^a

T, K	$k_{\text{DCBM}}(T) \times 10^{13}$, $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$[(\text{CHCl}_2\text{Br})]$, $10^{14} \text{ molecule/cm}^3$	$k_{\text{CDBM}}(T) \times 10^{13}$, $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$[\text{CHClBr}_2]$, $10^{14} \text{ molecule/cm}^3$
230	1.01 ± 0.05 (19)	0.93–9.4	1.43 ± 0.04 (14)	0.96–8.0
250	1.22 ± 0.03 (25)	0.66–4.4	1.76 ± 0.04 (24)	0.67–4.4
272	1.38 ± 0.05 (26)	0.61–4.0	1.88 ± 0.04 (17)	0.72–5.0
298	1.69 ± 0.07 (52)	0.56–3.9	2.17 ± 0.03 (67)	0.57–6.2
330	1.99 ± 0.05 (22)	0.95–5.6	2.50 ± 0.07 (18)	0.72–5.0

^aThe uncertainties are two Standard Errors from the data points obtained at the lowest energy for each temperature and do not include the estimated systematic uncertainty. The number of experiments is shown in parentheses for each temperature. We conservatively estimate the total uncertainty of these measurements to be $\sim 8\%$.

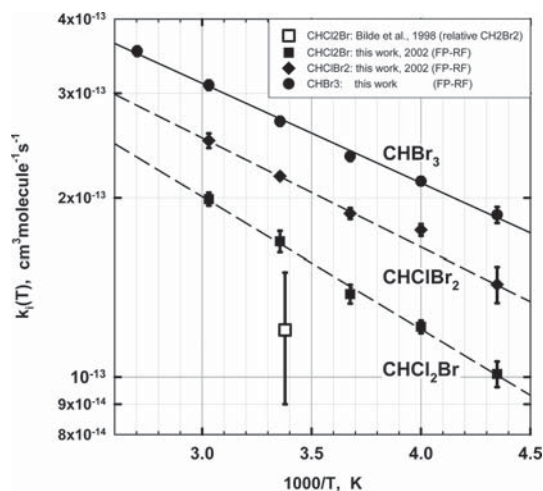


Figure 7. Results of rate constants measurements for reactions of OH with CHCl_2Br and CHClBr_2 : (■) $k_{\text{DCBM}}(T)$ reported here, (□) $k_{\text{DCBM}}(T)$ from relative rate measurements by Bilde et al.,²² (◆) $k_{\text{CDBM}}(T)$ reported here, and (●) $k_{\text{BF}}(T)$ measured in this study (shown for comparison).

$$k_{\text{DCBM}}(230\text{--}330 \text{ K}) = (9.4 \pm 1.3) \times 10^{-13} \exp\{-(513 \pm 37)/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (10)$$

Our impurity analyses revealed only fully halogenated compounds in any substantial amounts, CCl_2Br_2 (1%) and CCl_3Br (0.3%). If not corrected, the presence of these nonreactive compounds would result only in a slight underestimation of the measured rate constant because of a $\sim 1.3\%$ overestimation of the CHCl_2Br concentration. Thus, this small correction was made in deriving the rate constants used in calculating expression 10. Although $\text{CH}_3\text{C}(\text{O})\text{OH}$ is more reactive¹³ toward OH than CHCl_2Br , its contribution to the measured rate constant does not exceed 0.1% because of the small abundance of this impurity. $\text{CH}_3\text{C}(\text{O})\text{OCH}_3$ has a reactivity²¹ similar to that of CHCl_2Br and does not affect the result because of its small amount. We therefore conclude that our results for CHCl_2Br are not affected by the possible reactions of OH with reactive impurities in the reactant sample. Based on the analysis of possible instrumental uncertainties and the data obtained for CHBr_3 in both our old and new studies, we estimate the total uncertainty in the rate constants for the reactions of OH with both CHCl_2Br and CHClBr_2 to be $\sim 8\%$. Thus the room temperature rate constant for CHCl_2Br can be expressed as

$$k_{\text{DCBM}}(298 \text{ K}) = (1.67 \pm 0.13) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (11)$$

There is only one published experimental determination of this reaction rate constant at room temperature by a relative rate technique.²² This result, shown in Figure 7 as the open square, is $\sim 25\%$ smaller than the 298 K rate constant reported here although its reported uncertainty nearly extends to our data.

As mentioned earlier and seen in Figure 7, the rate constant for the CHClBr_2 reaction at $T = 250 \text{ K}$ appears to be an outlier from the other data. Given that it was determined from the intercept of a flash energy dependence plot (see Figure 6) that had a suspiciously low slope (probably an artifact of the limited amount of data), we have excluded this data point, $k_{\text{CDBM}}(250 \text{ K})$, from the fit when deriving our recommended rate constant temperature dependence.

$$k_{\text{CDBM}}(230\text{--}330 \text{ K}) = (9.0 \pm 1.9) \times 10^{-13} \exp\{-(423 \pm 61)/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (12)$$

However, if this point had not been excluded a very similar Arrhenius expression would have been derived since the data point at 250 K is only $\sim 9\%$ larger than calculated using expression 12. The room temperature rate constant for the CHClBr_2 reaction can be expressed as

$$k_{\text{CDBM}}(298 \text{ K}) = (2.17 \pm 0.17) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (13)$$

where the estimated total uncertainty of $\sim 8\%$ is indicated. Our sample of CHClBr_2 contained as much as 0.8% of acetone impurity. However, due to the very similar reactivities of both compounds toward OH^{13} the presence of this impurity could result in less than a 0.15% underestimation of the measured rate constant. The much smaller amounts of chlorinated and brominated acetone impurities are not expected to have any effect on the measured rate constants. The presence of low amounts of very reactive tetrahydrofuran²³ (0.01%) and toluene²⁴ (0.005%) impurities also result in insignificant overestimations of the measured rate constant by 0.8% and 0.15%, respectively, at room temperature. Therefore, the presence of reactive impurities in the sample of chlorodibromomethane does not affect results of our measurements. There are no other data on the rate constant of this reaction reported in the literature.

4. DISCUSSION

In this paper we report the first measurements of rate constants for the reactions of OH with epichlorohydrin, CHBr_3 ,

CHClBr₂, and CHCl₂Br over the temperature range of atmospheric interest. Although the reported data for the reactions of CHClBr₂ and CHCl₂Br are somewhat less accurate than those of CHBr₃, they demonstrate a trend in reactivity with increasing Br-substitution, an increase in the room temperature rate constant by ca. 30% with each additional Br atom. In addition, the temperature dependence becomes slightly weaker with increasing Br substitution.

These kinetic data allow us to estimate the atmospheric lifetime of epichlorohydrin and revise slightly the presently recommended atmospheric lifetimes of three halogenated methanes. The atmospheric lifetime of a compound due to its reaction with tropospheric hydroxyl radicals, τ_i^{OH} , can be estimated using a simple scaling procedure that is based on the results of field measurements²⁵ and detailed atmospheric modeling:¹²

$$\tau_i^{\text{OH}} = \frac{k_{\text{MCF}}(272)}{k_i(272)} \tau_{\text{MCF}}^{\text{OH}} \quad (14)$$

where τ_i^{OH} and $\tau_{\text{MCF}}^{\text{OH}}$ are the lifetimes of a compound under study and methyl chloroform (MCF), respectively, due to reactions with hydroxyl radicals in the troposphere only, and $k_i(272 \text{ K})$ and $k_{\text{MCF}}(272 \text{ K}) = 6.14 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ are the rate constants for the reactions of OH with the substances under study and methyl chloroform,¹³ respectively, at $T = 272 \text{ K}$. The value of $\tau_{\text{MCF}}^{\text{OH}} = 6.13$ years was calculated from the measured lifetime of MCF of 5.0 years (reported in the latest WMO/UNEP ozone assessment¹) after taking into account an ocean loss of 89 years and a stratospheric loss of 39 years. Applying this method to the epichlorohydrin yields an estimated atmospheric lifetime due to reaction with OH of ~ 39 days. However, it should be noted that the use of such a scaling procedure for atmospheric lifetime estimation assumes that the chemical is well mixed throughout the troposphere, as is methyl chloroform. The estimated lifetime for epichlorohydrin is significantly shorter than the characteristic time of mixing processes in the troposphere and, therefore, its true local atmospheric lifetime will depend on the local chemical environment in which its emissions occur (including such aspects as latitude, season, etc.). Nevertheless, for such very short-lived substances (VSLs) these estimated lifetimes can be used for comparisons with similar compounds. This saturated hydrocarbon with a single Cl-substitution is not expected to have any strong absorption of solar UV radiation. Photolysis of such a compound in the stratosphere is associated with the lifetime exceeding ~ 200 years¹ and, therefore, cannot compete with the OH reaction in removing it from the atmosphere.

Similar estimations of atmospheric lifetimes due to reactions of CHBr₃, CHClBr₂, and CHCl₂Br with OH yield ~ 57 , ~ 72 , and ~ 96 days, respectively. However, these compounds also have strong absorption of near UV radiation, further shortening their atmospheric lifetimes. Because of these short lifetimes, the same caveats associated with using the scaling procedure described above apply here. The total atmospheric lifetime (τ_i^{total}) due to both photolysis and reaction with OH is calculated as¹

$$(\tau_i^{\text{total}})^{-1} = (\tau_i^{\text{OH}})^{-1} + (\tau_i^{\text{ph}})^{-1} \quad (15)$$

where τ_i^{OH} and τ_i^{ph} are atmospheric lifetimes due to reaction with OH and photolysis for compound i . The modeled lifetimes due to photolysis were taken from WMO-2010.¹ The estimated lifetimes for all four compounds calculated using the

MCF scaling procedure are presented in Table 4. Also shown in parentheses in Table 4 are lifetimes calculated using the

Table 4. Atmospheric Lifetimes Estimated under Assumption of the Well-Mixed Atmosphere^a

molecule	atmospheric lifetime, days			
	OH reaction	photolysis ¹	total, this work	total, WMO-2010 ¹
CHBr ₃	57 (48)	36	22 (20)	(24)
CHBr ₂ Cl	72 (60)	161	50 (44)	(59) ^b
CHBrCl ₂	96 (80)	222	67 (59)	(78) ^b
Epichlorohydrin	39 (33)		39 (33)	

^aLifetimes in parentheses were calculated following the procedure employed in WMO-2010 for VSLs, which assumes an average tropospheric OH concentration of $1 \times 10^6 \text{ molecule/cm}^3$ and the OH reaction rate constant at $T = 275 \text{ K}$. ^bThe OH reaction rate constant was estimated for WMO-2010¹ based on the available data for similar molecules.

procedure employed in WMO-2010 for determining τ^{OH} for VSLs. In WMO-2010 a uniform atmospheric OH concentration of $[\text{OH}] = 1 \times 10^6 \text{ molecule/cm}^3$ was assumed together with an average temperature of 275 K. This approach results in OH lifetimes that are systematically $\sim 20\%$ lower than those obtained using the more generally accepted MCF scaling procedure described here and are subject to the same above-mentioned caveats for estimating lifetimes of VSLs. If we were to use this same method, we would obtain the OH reactive lifetimes and total lifetimes given in parentheses in Table 4. These latter numbers are what should be compared to the WMO-2010 recommendations. It should be further noted, however, that in the absence of experimental reaction rate data for CHBr₂Cl and CHBrCl₂, the lifetimes of these two compounds in WMO-2010 were based on estimated reactivities toward OH.

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Notes

The authors declare no competing financial interest.

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