A temperature dependent kinetics study of the reaction of OH with CH_3Cl, CH_2Cl_2, $CHCl_3$, and CH_3Br

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Reported in this study are temperature dependent rate data for the reaction of OH with the partially halogenated methane species CH_3Cl, CH_2Cl_2, $CHCl_3$, and CH_3Br. The nominal temperature range covered was 245–375 K. The appropriate Arrhenius expressions are $k_A = (1.84 \pm 0.18) \times 10^{-12} \exp[-(2181 \pm 70/RT)]$, $k_B = (4.27 \pm 0.63) \times 10^{-12} \exp[-(2174 \pm 161/RT)]$, $k_C = (4.69 \pm 0.71) \times 10^{-12} \exp[(2254 \pm 214/RT)]$, $k_D = (7.93 \pm 0.79) \times 10^{-13} \exp[-(1766 \pm 116/RT)]$. Units are $cm^3 molecule^{-1} \cdot s^{-1}$. No simple correlations between E_{act} and C–H bond strengths were found. The impact of these halogenated species on stratospheric ozone is also discussed.

INTRODUCTION

The reactivity of OH toward partially halogenated hydrocarbons has become of increasing interest in the last few years both because of the increased level of activity in the field of fire research (with the use of halogenated species as flame retardants) and in the area of stratospheric ozone chemistry. Presented here are the final results of a flash photolysis–resonance fluorescence study which was first reported on at two scientific meetings earlier this year.[1,2] The molecules of interest in this study are CH_3Cl, CH_2Cl_2, $CHCl_3$, and CH_3Br. The details of this study as well as a discussion of the atmospheric significance of the results are presented in the following text.

EXPERIMENTAL

The flash photolysis–resonance fluorescence system used in this study was identical to that described in detail in an earlier publication.[3] For this reason, no further description will be presented here. Treatment of the experimental data from this study was also handled as before.[3] In all cases, the halogenated reactant was in large excess ($>10^3$) over the concentration of OH (typically 10^{11} molecule/cm^3); hence, pseudo-first-order kinetics prevailed.
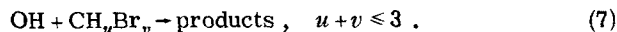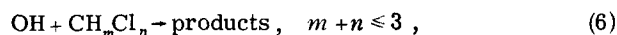
Low pressure measurements in this study (1–3000 mTorr) were made using an MKS Baratron. High pressure measurements, on the other hand, were carried out using a two turn Bourdon gauge (Wallace and Tiernan type FA145). The precision to which gas mixtures could be prepared using the above pressure gauges was estimated to be ~3% or better. The one gaseous species which could not be handled with the same precision as quoted above was H_2O. Owing to its high tendency to absorb on the walls of the reaction vessel, the H_2O pressure was typically known to only ±20% on a given gas filling. This uncertainty affected the absolute OH concentration to the extent of ±20%; however, since all experiments were carried out under pseudo-first-order kinetics, this small variation in [OH] was of no consequence.

The purity of each of the halocarbons used in this investigation was as follows: CH_3Cl (Matheson > 99.5%); CH_2Cl_2 (Fisher > 99.92%); $CHCl_3$ (Dow Corning, > 99.94%); CH_3Br (Matheson, > 99.%). The helium diluent gas was Matheson "Gold Label Ultra-High Purity" and was used without further purification.

RESULTS AND DISCUSSION

The results from this investigation have been summarized in the form of Tables I–IV. It can be seen from these tables that numerous experimental variations were carried out for each molecule studied. Of major interest are those variations performed at 298 K to test for the possible importance of secondary reactions, especially those of the radical–radical type. Those experimental parameters which were varied extensively were flash energy, total pressure, and water concentration. These experimental permutations were designed to test for reaction processes of the type

$$OH + OH + M \rightarrow H_2O_2 + M, \tag{1}$$

$$OH + OH \rightarrow H_2O + O, \tag{2}$$

$$OH + H + M \rightarrow H_2O + M, \tag{3}$$

$$OH + Cl + M \rightarrow HOCl + M, \tag{4}$$

$$OH + Br + M \rightarrow HOBr + M, \tag{5}$$

$$OH + CH_mCl_n \rightarrow products, \quad m + n \leq 3, \tag{6}$$

$$OH + CH_uBr_v \rightarrow products, \quad u + v \leq 3. \tag{7}$$

In each case, it is apparent that the rate of disappearance of OH would depend on the square power of the total radical concentration and hence on the square power of the flash intensity. These reactions, if important, should have resulted in a significant dependence of the measured pseudo-first-rate constants, K_1, on the flash intensity as well as the H_2O pressure. As can be seen from Tables I–IV, only at the very highest flash intensities (e. g., 450–500 J range) was there any significant deviation in the values of K_1. The change in the OH concentration when compared with more or less standard operating conditions, 88 J, would have been somewhat greater than a factor of 5. The increase in K_1 observed for all four molecules with this change in the OH concentration ranged from 8% to 25%. Thus, although the observed increase was small, it most certainly was indicative of secondary radical–radical processes becoming of slight importance at the highest flash intensities employed. It should be noted that further reductions in the OH concentration by nearly a fac-

TABLE I. Reaction rate data for the process $OH + CH_3Cl \rightarrow H_2O + CH_2Cl$.

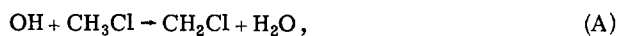| Temperature (K)	Diluent gas (Torr)	H_2O (mTorr)	CH_3Cl (mTorr)	Flash lamp window	Flash energy (J)	K_1 (s⁻¹)	$K_{bi} \times 10^{14}$ (cm³ molecule⁻¹ · s⁻¹)
350	100(He)	200	0	Suprasil	88	41	
	100	200	20	Suprasil	88	80	
	100	200	30	Suprasil	88	114	
	100	200	50	Suprasil	88	160	
	100	200	75	Suprasil	88	210	
	100	200	100	Suprasil	88	267	
	100	200	100	Suprasil	88	257	
	100	200	125	Suprasil	88	332	
	100	200	150	Suprasil	88	385	8.28 ± 0.28
298	20(He)	200	0	LiF	88	57	
	20	200	25	LiF	88	108	
	20	200	30	Suprasil	88	130	
	20	200	50	Suprasil	88	170	
	20	200	50	LiF	88	160	
	20	200	65	LiF	88	187	
	20	200	65	LiF	211	250	
	20	200	65	LiF	31	168	
	20	200	75	Suprasil	88	190	
	20	200	75	Suprasil	88	200	
	20	200	75	Suprasil	88	200	
	20	200	75	Suprasil	245	225	
	20	400	75	Suprasil	88	204	
	20	200	80	LiF	88	190	
	20	200	100	LiF	88	208	
	20	200	110	Suprasil	88	235	
	20	200	125	LiF	88	266	
	20	200	140	LiF	88	303	
	20	200	150	LiF	88	311	
	20	200	150	LiF	88	338	
	20	200	150	LiF	45	325	
	20	200	200	LiF	88	357	
	20	200	200	Suprasil	88	382	
	20	200	250	LiF	88	422	4.29 ± 0.21
	200(He)	200	50	Suprasil	88	95	
	200	200	75	Suprasil	88	126	
	200	200	150	Suprasil	88	225	
	200	200	225	Suprasil	88	312	3.98 ± 0.04
273	20(He)	200	0	Suprasil	88	70	
	20	200	30	Suprasil	88	102	
	20	200	50	Suprasil	88	130	
	20	200	75	Suprasil	88	157	
	20	200	100	Suprasil	88	185	
	20	200	120	Suprasil	88	205	
	20	200	150	Suprasil	88	240	
	20	200	200	Suprasil	88	302	3.26 ± 0.06
250	20(He)	200	0	Suprasil	88	40	
	20	200	50	Suprasil	88	80	
	20	200	65	Suprasil	88	96	
	20	200	80	Suprasil	88	118	
	20	200	95	Suprasil	88	121	
	20	200	105	Suprasil	88	135	
	20	200	120	Suprasil	88	144	
	20	200	150	Suprasil	88	190	
	20	200	175	Suprasil	88	200	2.38 ± 0.14

tor of 4 from that generated at 88 J and 200 mTorr of H_2O (typical conditions) resulted in no experimentally significant change in the measured value of K_1. It is also noteworthy that under typical operating conditions, a variation of the total pressure by a factor of 5 (5 times higher) resulted in no significant change in the value of K_1 for any of the molecules studied. We must

conclude, therefore, that under our typical operating conditions no complications were encountered as a result of radical–radical reactions. In the calculation of the bimolecular rate constants for CH_3Cl, CH_2Cl_2, $CHCl_3$, and CH_3Br, none of the high flash intensity data were included. From Tables I–IV it can be seen that at 298 K the rate constants for reaction of OH with CH_3Cl,
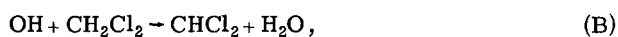
TABLE II.   Reaction rate data for the process $OH + CH_2Cl_2 \rightarrow H_2O + CHCl_2$.

Temperature (K)	Diluent gas (Torr)	H_2O (mTorr)	CH_2Cl_2 (mTorr)	Flash lamp window	Flash energy (J)	K_1 (s⁻¹)	$K_{bi} \times 10^{14}$ (cm³ molecule⁻¹ · s⁻¹)
375	100(He)	200	5	Sapphire	88	74	
	100	200	10	Sapphire	88	94	
	100	200	20	Sapphire	88	156	
	100	200	25	Sapphire	88	182	
	100	200	30	Sapphire	88	208	
	100	200	35	Sapphire	88	247	
	100	200	40	Sapphire	88	266	
	100	200	45	Sapphire	88	303	22.3 ± 0.5
298	40(He)	200	20	Sapphire	88	103	
	40	200	30	Sapphire	88	148	
	40	200	50	Sapphire	88	220	
	40	200	60	Sapphire	88	242	
	40	200	60	Sapphire	88	240	
	40	50	60	Sapphire	88	215	
	40	400	60	Sapphire	88	238	
	40	200	60	Sapphire	45	240	
	40	200	60	Sapphire	500	287	
	40	200	75	Sapphire	88	318	
	40	200	80	Sapphire	88	333	
	40	200	90	Sapphire	88	373	
	40	200	100	Sapphire	88	403	11.6 ± 0.5
	200(He)	200	50	Sapphire	88	190	
	200	200	65	Sapphire	88	222	
	200	200	80	Sapphire	88	281	
	200	200	95	Sapphire	88	344	10.4 ± 1.2
245	20(He)	100	20	Sapphire	88	43	
	20	100	40	Sapphire	88	79	
	20	100	60	Sapphire	88	120	
	20	100	80	Sapphire	88	144	
	20	100	97	Sapphire	88	200	
	20	100	120	Sapphire	88	225	4.75 ± 0.57

CH_2Cl_2, $CHCl_3$, and CH_3Br are as follows:

$$OH + CH_3Cl \rightarrow CH_2Cl + H_2O, \qquad (A)$$

$$k_A = (4.29 \pm 0.21) \times 10^{-14},$$

$$OH + CH_2Cl_2 \rightarrow CHCl_2 + H_2O, \qquad (B)$$

$$k_B = (1.16 \pm 0.05) \times 10^{-13},$$

$$OH + CHCl_3 \rightarrow CCl_3 + H_2O, \qquad (C)$$

$$k_C = (1.14 \pm 0.07) \times 10^{-13},$$

$$OH + CH_3Br \rightarrow CH_2Br + H_2O, \qquad (D)$$
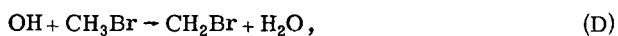
$$k_D = (4.14 \pm 0.43) \times 10^{-14}.$$

Units are cm³ molecule⁻¹ · s⁻¹. The temperature dependence of Reactions (A)–(D) was examined over the nominal temperature range of 245–375 K. Arrhenius expressions for each of the reactions investigated were determined from a weighted least squares treatment of the k_{bi} values given in Tables I–IV. The relative weighting factor for each temperature was determined by the relative number of experimental runs performed with each compound. The resulting Arrhenius expressions are given below (see also Fig. 1):

$$k_A = (1.84 \pm 0.18) \times 10^{-12} \exp - (2181 \pm 70/RT),$$

$$k_B = (4.27 \pm 0.63) \times 10^{-12} \exp - (2174 \pm 161/RT),$$

$$k_C = (4.69 \pm 0.71) \times 10^{-12} \exp - (2254 \pm 214/RT), \qquad (8)$$

$$k_D = (7.93 \pm 0.79) \times 10^{-13} \exp - (1766 \pm 116/RT)$$

Units for the above k values are cm³ molecule⁻¹ · s⁻¹. The activation energy has been expressed in terms of cal mol⁻¹ · deg⁻¹. The uncertainties quoted for k_A–k_D apply to only the temperature range over which each system was studied and represent the 90% confidence limits of the data. The indicated uncertainty limits shown in Tables I–IV for the bimolecular rate constants represent one standard deviation (1σ) as determined from a weighted least squares treatment of the data. The error limits quoted for the pre-exponential A factors in Arrhenius expressions (A)–(D) reflect 2σ error limits, whereas those for the activation energy represent 1σ. Both were determined from a weighted least squares treatment of the temperature data.

Of considerable interest with regards to the temperature dependence data is the observed trend in activation energies for the sequence CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, and CH_3Br. Summarized in Table V are the activation energies measured in this study along with the appropriate bond dissociation energies for the C–H bond in each halogenated molecule studied. Also included in Table V are the activation energies for the reaction of Cl $^2P_{3/2}$

TABLE III. Reaction rate data for the process $OH + CHCl_3 \rightarrow H_2O + CCl_3$.

Temperature (K)	Diluent gas (Torr)	H_2O (mTorr)	$CHCl_3$ (mTorr)	Flash lamp window	Flash energy (J)	K_1 (s^{-1})	$K_{bi} \times 10^{14}$ (cm^3 molecule$^{-1} \cdot s^{-1}$)
375	100(He)	200	10	Suprasil	88	90	
	100	200	20	Suprasil	88	148	
	100	200	25	Suprasil	88	183	
	100	200	30	Suprasil	88	195	
	100	200	35	Suprasil	88	230	
	100	200	40	Suprasil	88	260	
	100	200	45	Suprasil	88	290	21.8 ± 1.4
298	40(He)	200	20	Suprasil	88	93	
	40	200	30	Suprasil	88	139	
	40	200	40	Suprasil	88	182	
	40	200	50	Suprasil	88	206	
	40	50	50	Suprasil	88	200	
	40	200	50	Suprasil	45	213	
	40	200	50	Suprasil	500	263	
	40	200	57	Suprasil	88	242	
	40	200	65	Suprasil	88	260	
	40	200	75	Suprasil	88	308	
	40	200	80	Suprasil	88	322	
	40	200	90	Suprasil	88	377	
	40	200	100	Suprasil	88	380	11.4 ± 0.7
	200(He)	200	25	Suprasil	88	87	
	200	200	35	Suprasil	88	132	
	200	200	50	Suprasil	88	171	
	200	200	75	Suprasil	88	260	
	200	200	100	Suprasil	88	362	11.0 ± 0.5
245	40(He)	50	20	Suprasil	88	40	
	40	50	40	Suprasil	88	73	
	40	50	50	Suprasil	88	96	
	40	50	60	Suprasil	88	99	
	40	50	75	Suprasil	88	122	
	40	50	80	Suprasil	88	124	
245	40(He)	50	100	Suprasil	88	165	
	40	50	100	Suprasil	88	168	
	40	50	120	Suprasil	88	218	
	40	50	150	Suprasil	88	254	
	40	50	200	Suprasil	88	328	
	40	50	200	Suprasil	88	360	4.39 ± 0.28

with several of the same molecules examined in this study.

From Table V, it is apparent that there is no simple correlation between C–H bond strength and the measured OH activation energies from this study. There is, of course, a major decrease in the activation energy in going from CH_4 to CH_3Cl or CH_3Br, which would seem to correlate with a significant decrease in the respective C–H bond energies. However, it is interesting to see no such trend develop in the case of chlorine atom attack on these same two molecules. For this reaction system, even though there appears to be a systematic error in one or both of the studies by Clyne et al.[7] and Watson and Davis,[8] there is good agreement between both of these direct measurements that chlorine atom attack on CH_4 and CH_3Cl results in the same activation energy. In comparing OH activation energies for the compounds CH_3Cl, CH_2Cl_2, and CCl_3H, we see that within the experimental uncertainty of the measurements it can be concluded that the activation energies are either unchanged or that they might

show a slight positive increase in going from CH_3Cl and CCl_3H. This insignificant change in activation energy is to be compared with an ~4 kcal change in the C–H bond energy between CH_3Cl and CH_2Cl_2 and $CHCl_3$. For chlorine atom attack on CH_3Cl, CH_2Cl_2, and $CHCl_3$, no obvious conclusions can be drawn, in that the data of Fettis and Knox[6] show a quite different trend in activation energies than do the data of Clyne et al.[7] At the present time, therefore, these authors can only speculate that there are probably several factors which might explain individually or collectively the observed activation energy bond correlations for both the OH and Cl reaction systems. These include (1) erroneous assignments of C–H bond strengths for some of the halogenated methanes, (2) incorrect measurements of the respective activation energies, and (3) the strong electronic repulsion effects of neighboring chlorine atoms to the incoming OH and/or Cl radical attack.

A comparison of the results from this study with published as well as unpublished rate data from other laboratories is shown in Table VI. From this table of

TABLE IV. Reaction rate data for the process $OH + CH_3Br \rightarrow H_2O + CH_2Br$.

Temperature (K)	Diluent gas (Torr)	H_2O (mTorr)	CH_3Br (mTorr)	Flash lamp window	Flash energy (J)	K_1 (s^{-1})	$K_{bi} \times 10^{14}$ (cm^3 molecule$^{-1} \cdot s^{-1}$)
350	100(He)	200	25	Suprasil	88	90	
	100	200	50	Suprasil	88	119	
	100	200	75	Suprasil	88	186	
	100	200	100	Suprasil	88	216	
	100	200	100	Suprasil	45	220	
	100	200	125	Suprasil	88	259	
	100	200	150	Suprasil	88	300	
	100	200	200	Suprasil	88	380	6.08 ± 0.4
298	20(He)	200	25	Suprasil	88	100	
	20	200	50	Suprasil	88	128	
	20	200	75	Suprasil	88	166	
	20	200	100	LiF	88	192	
	20	200	100	Suprasil	88	190	
	20	200	100	Suprasil	45	198	
	20	200	100	Suprasil	500	263	
	20	50	100	Suprasil	88	180	
	20	400	100	Suprasil	88	192	
	20	200	125	Suprasil	88	253	
	20	200	150	Suprasil	88	277	
	20	200	200	LiF	88	322	4.14 ± 0.43
	200(He)	200	0	Suprasil	88	13	
	200	200	50	Suprasil	88	84	
	200	200	100	Suprasil	88	148	
	200	200	150	Suprasil	88	202	3.89 ± 0.03
273	20(He)	200	30	LiF	88	95	
	20	200	50	Suprasil	88	108	
	20	200	75	LiF	88	134	
	20	200	100	LiF	88	171	
	20	200	125	LiF	88	205	
	20	200	150	LiF	88	229	
	20	200	150	LiF	45	227	
	20	200	150	LiF	320	260	
	20	200	175	LiF	88	250	
	20	200	200	LiF	88	270	
	20	200	250	LiF	88	294	3.16 ± 0.15
244	20(He)	100	50	LiF	88	93	
	20	100	75	LiF	88	100	
	20	100	100	LiF	88	131	
	20	100	125	LiF	88	143	
	20	100	150	LiF	88	160	
	20	100	150	LiF	45	150	
	20	100	150	LiF	320	202	
	20	100	175	LiF	88	193	
	20	100	206	LiF	88	221	
	20	100	250	LiF	88	243	2.01 ± 0.12

compiled results, it is readily seen that at 298 K virtually all results are in excellent agreement within the quoted experimental uncertainties. In the study by Howard and Evenson,[5] a discharge flow system with

laser magnetic resonance of OH was used to examine the reaction of the OH radical with CH_3Cl, CH_2Cl_2, $CHCl_3$, and CH_3Br. Perry, Atkinson, and Pitts,[9] as in this investigation, employed the flash photolysis–reso-

TABLE V. Correlation of E_{act} with C–H bond strengths.[4,5]

	$OH + CH_yX_z \rightarrow H_2O + CH_{y-1}X_z$			$Cl(^2P_{3/2}) + CH_yX_z \rightarrow HCl + CH_{y-1}X_z$		
		C–H(kcal/mol)	E_{act} (cal/mol)	Fettis and Knox[6]	Clyne et al.[7]	Watson and Davis[8]
CH_4	CH_3–H	103	3400 Ref. 3		3580	2437
CH_3Cl	$CClH_2$–H	99	2181 This work	3300	3574	2557
CH_2Cl_2	CCl_2H–H	95	2174 This work	2980	2980	
$CHCl_3$	CCl_3–H	95	2254 This work	3340	2760	
CH_3Br	$CBrH_2$–H	97	1766 This work			

TABLE VI. Comparison of rate data for reaction of OH with halogenated methane species.[a]

	298			Temperature dependence	
	Howard and Evenson[5]	Perry, Atkinson, and Pitts[9]	This work	Perry, Atkinson, and Pitts[9]	This work
CH_3Cl	$(3.6 \pm 0.8) \times 10^{-14}$	$(4.4 \pm 0.3) \times 10^{-14}$	$(4.29 \pm 0.21) \times 10^{-14}$	$4.1 \times 10^{-12} \exp - (2700 \pm 300/RT)$ (298–423) K	$(1.84 \pm 0.18) \times 10^{-12} \exp - (2181 \pm 70/RT)$
CH_2Cl_2	$(15.5 \pm 3.4) \times 10^{-14}$	$(14.5 \pm 2.0) \times 10^{-14}$	$(11.6 \pm 0.5) \times 10^{-14}$		$(4.27 \pm 0.6) \times 10^{-12} \exp - (2174 \pm 16RT)$
$CHCl_3$	$(10.1 \pm 1.5) \times 10^{-14}$		$(11.4 \pm 0.7) \times 10^{-14}$		$(4.69 \pm 0.71) \times 10^{-12} \exp - (2254 \pm 214/RT)$
CH_3Br	$(3.5 \pm 0.8) \times 10^{-14}$		$(4.14 \pm 0.43) \times 10^{-14}$		$(7.93 \pm 0.79) \times 10^{-12} \exp - (1766 \pm 105/RT)$

[a]All units are in cm^3 molecule$^{-1} \cdot$ s^{-1}.

nance fluorescence technique in their study. In the one system, CH_3Cl, where another temperature dependence study has also been completed, by Perry, Atkinson and Pitts,[9] apparently only fair agreement exists. In this case, the experimental uncertainties do not allow for overlapping activation energies, the differences between the E_{act} values being 20%–25%. However, the results obtained in these studies are in excellent agreement both at 298 and 350 K. The value of k_1 measured by Perry et al. at 423 K is only ~18% greater than would be predicted from Arrhenius expression (A) obtained in this study. A least squares fit of all the data points (this study and Perry et al.) resulted in the following Arrhenius expression:

$$k_1 = (2.47 \pm 0.37) \times 10^{-12} \exp - (2353 \pm 94/RT) \quad (250–423)K.$$

All data points are within 10% of that predicted by this expression.

The atmospheric significance of the OH reaction rate study reported in this work lies in the prediction of reliable tropospheric lifetimes for the halogenated methanes. The concern about these halogenated methanes

involves their possible impact on stratospheric ozone due to either chlorine[10] or bromine[11] catalytic ozone destruction processes, i.e.,

$$Cl + O_3 \rightarrow ClO + O_2 \quad (9)$$

$$\frac{ClO + O \rightarrow Cl + O_2}{O + O_3 \rightarrow O_2 + O_2} \quad (10)$$

or

$$Br + O_3 \rightarrow BrO + O_2 \quad (11)$$

$$\frac{BrO + O \rightarrow Br + O_2}{O + O_3 \rightarrow O_2 + O_2}. \quad (12)$$
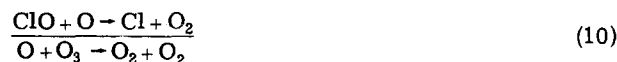
The extent to which the compounds CH_3Cl, CH_2Cl_2, $CHCl_3$, and CH_3Br could provide halogen atoms to promote the catalytic cycles 9, 10 and 11, 12 is predicated on their rate of destruction in the troposphere via attack from atmospheric OH. This destruction rate,

$$-d[CH_yX_z]/dt = k[OH][CH_yX_z]$$

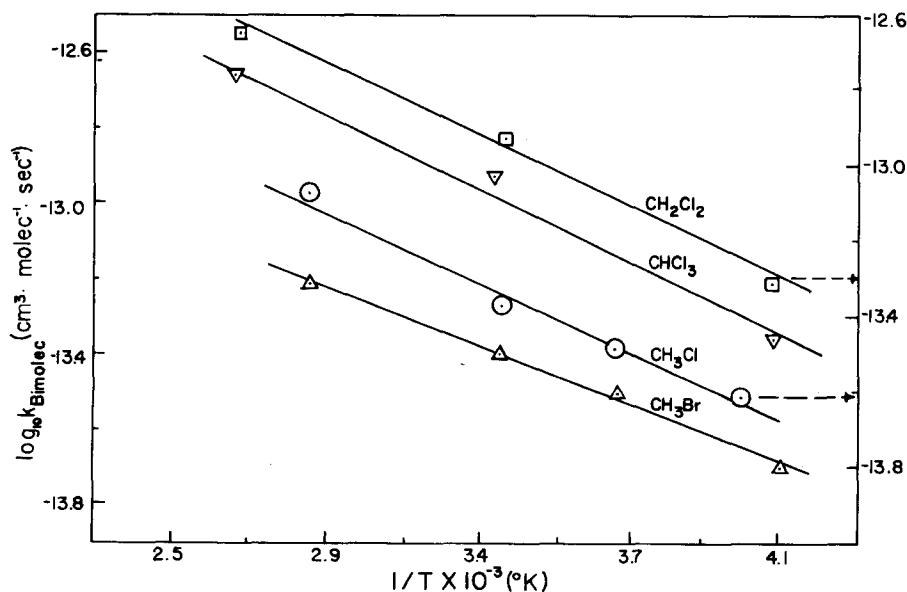or, more appropriately, the average tropospheric life-

FIG. 1. Arrhenius plot of temperature data on the reaction of OH with CH_3Cl, CH_2Cl_2, $CHCl_3$, and CH_3Br.

TABLE VII. Tropospheric lifetimes for the molecules CH_3Cl, CH_2Cl_2, $CHCl_3$, and CH_3Br.

Compound	K_{265}	Lifetime (years)
CH_3Cl	3.0×10^{-14}	1.19
CH_2Cl_2	8.7×10^{-14}	0.39
$CHCl_3$	6.4×10^{-14}	0.56
CH_3Br	2.7×10^{-14}	1.32

time of a partially halogenated species, is controlled (1) by the value of the bimolecular rate constant for OH attack, and (2) on the global seasonally averaged OH steady state concentration. In Table VII we have calculated the tropospheric lifetimes of all four compounds investigated in this study. These calculations have been based on a weighted average temperature for the troposphere of 265 K and a seasonally, diurnally averaged OH concentration of 9×10^5 OH's/cm³. The latter value has been estimated using results from Crutzen's 2-D atmospheric model[12] and data from recent direct measurements of atmospheric OH at 32 and 21 °N latitude at 7 and 11.5 km by Davis, McGee, and Heaps.[13]

Thus, on the basis of the lifetimes calculated in Table VII, it can be seen that all compounds have very short tropospheric lifetimes and their potential impact on stratospheric ozone should be minimal.

ACKNOWLEDGMENTS

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