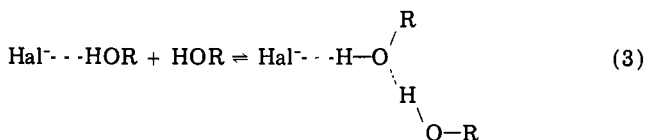


greater. These shifts to high frequencies clearly stem from the same cause as that for the trialkylammonium ion shifts studied by Lipovskii and Dem'yanova.⁷

The alternative interaction that a second alcohol molecule might display is



We think that this is less likely to occur, especially for Cl^- . Also it would give rise to two new $(\text{OH})_b$ bands, that for the primary solvent molecule being displaced to low rather than high frequency because of the increased strength of the hydrogen bond. No such *change* was detected.

Acknowledgment. We thank Mr. Scott A. Miller for early work in this field.

References and Notes

- (1) A. Allerhand and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **85**, 1233 (1963).
- (2) S. C. Mohr, W. D. Wilk, and G. M. Barrow, *J. Am. Chem. Soc.*, **87**, 3048 (1965).
- (3) H. Lund, *Acta Chem. Scand.*, **12**, 298 (1958).
- (4) J. Bufalini and K. H. Stern, *J. Am. Chem. Soc.*, **83**, 4362 (1961).
- (5) J. B. Hyne and R. M. Levy, *Can. J. Chem.*, **40**, 692 (1962).
- (6) M. J. Blandamer, T. E. Gough, and M. C. R. Symons, *Trans. Faraday Soc.*, **60**, 488 (1964).
- (7) A. A. Lipovskii and T. A. Dem'yanova, *Zh. Prikl. Spektrosk.*, **9**, 239 (1968).
- (8) W. J. Potts, "Chemical Infrared Spectroscopy", Vol. I, Techniques, Wiley, New York, N.Y., 1963.
- (9) G. P. Hoover, E. A. Robinson, R. S. McQuate, H. D. Schreiber, and J. N. Spencer, *J. Phys. Chem.*, **73**, 4027 (1969).
- (10) I. Motoyama and C. H. Jarboe, *J. Phys. Chem.*, **70**, 3226 (1966).

A Temperature Dependent Kinetics Study of the Reaction of OH with CH_2ClF , CHCl_2F , CHClF_2 , CH_3CCl_3 , $\text{CH}_3\text{CF}_2\text{Cl}$, and $\text{CF}_2\text{ClCFCl}_2$

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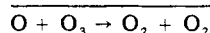
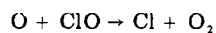
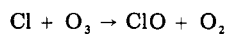
Publication costs assisted by the Georgia Institute of Technology

The flash photolysis resonance fluorescence technique has been utilized to determine the Arrhenius parameters for several reactions between the hydroxyl radical and halogenated hydrocarbons. The reactions studied, and their corresponding Arrhenius expressions in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ are shown: (1) $\text{OH} + \text{CH}_2\text{ClF} \rightarrow \text{CHClF} + \text{H}_2\text{O}$, $k_1 = (2.84 \pm 0.3) \times 10^{-12} \exp(-1259 \pm 50/T)$ (245–375) K; (2) $\text{OH} + \text{CHCl}_2\text{F} \rightarrow \text{CCl}_2\text{F} + \text{H}_2\text{O}$, $k_2 = (1.87 \pm 0.2) \times 10^{-12} \exp(-1245 \pm 26/T)$ (245–375) K; (3) $\text{OH} + \text{CHClF}_2 \rightarrow \text{CClF}_2 + \text{H}_2\text{O}$, $k_3 = (9.25 \pm 1.0) \times 10^{-13} \exp(-1575 \pm 71/T)$ (250–350) K; (4) $\text{OH} + \text{CH}_3\text{CCl}_3 \rightarrow \text{CH}_2\text{CCl}_3 + \text{H}_2\text{O}$, $k_4 = (3.72 \pm 0.4) \times 10^{-12} \exp(-1627 \pm 50/T)$ (260–375) K; (5) $\text{OH} + \text{CH}_3\text{CF}_2\text{Cl} \rightarrow \text{CH}_2\text{CF}_2\text{Cl} + \text{H}_2\text{O}$, $k_5 = (1.15 \pm 0.15) \times 10^{-12} \exp(-1748 \pm 30/T)$ (273–375) K; (6) $\text{OH} + \text{CF}_2\text{ClCFCl}_2 \rightarrow \text{products}$, $k_6 < 3 \times 10^{-16}$. Tropospheric lifetimes have been calculated for the above species by combining the rate constant data with global seasonally and diurnally averaged hydroxyl radical concentrations.

Introduction

It has been proposed that the injection of chlorinated compounds into the stratosphere will lead to a catalytic reduction in the integrated column density of ozone due to the interaction of odd oxygen (odd oxygen = $\text{O}(^3\text{P}) + \text{O}_3$) with ClO_x species ($\text{ClO}_x = \text{Cl} + \text{ClO} + \text{ClOO}$).¹ Numerous chlorinated compounds have already been shown to be present in the atmosphere and their concentrations determined by gas chromatographic detection.² These compounds can be classified into two separate groups: (a) fully halogenated, e.g., CFCl_3 , CF_2Cl_2 , and CCl_4 ; and (b) hydrogen containing, e.g., CH_3Cl , CHF_2Cl , etc. To date, no tropospheric sink mechanism has been identified for the fully halogenated compounds (i.e., the chemical lifetimes of these compounds in the troposphere far exceed the total atmospheric lifetimes that would be calculated based on stratospheric photodissociation alone). Consequently, for this type of compound, the principal atmospheric sink is believed to be vertical diffusion into the stratosphere, followed by photodissociation. However,

some caution must be exercised here as there is still considerable scatter in the published results on the tropospheric concentrations of fluorocarbons. Within the range of this scatter, there could yet exist a significant unrecognized sink mechanism.³ For those compounds reaching the lower and mid-stratosphere, photodissociation and, to a lesser extent, reaction with electronically excited atomic oxygen (O^1D), can result in the production of odd chlorine (Cl , ClO) which can directly participate in the destruction of odd oxygen:



In contrast to the fully halogenated species, those compounds containing hydrogen atoms are expected to react with hydroxyl radicals, resulting in chemical lifetimes in the troposphere significantly shorter than would be expected from photolysis alone.⁴ The relatively short lifetimes of these halocarbons (~ 1 – 20 years) would inhibit the buildup of large concentrations of these species in the troposphere, thus limiting the flux of chlorine into the stratosphere.

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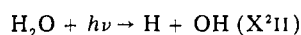
This paper presents the results of a kinetic study of the behavior of hydroxyl radicals with several C₁ and C₂ halogenated compounds. The reactions were studied over a wide range of temperature and total pressure utilizing the technique of flash photolysis-resonance fluorescence. Recent measurements of tropospheric hydroxyl radical concentrations⁵ have also permitted the calculation of tropospheric lifetimes for the various fluorocarbons studied. A comparison of our kinetic results with other recent data,⁶⁻⁹ and a discussion of the atmospheric implications of our results is presented.

Experimental Section

The experimental details and operating principles of the flash photolysis-resonance fluorescence techniques have been fully described in the literature, and only a brief summary will therefore be presented in this text.¹⁰

The reaction vessel used in this work was a jacketed black anodized aluminum cell with an internal volume of ~850 cm³. The cell temperature was controlled to within ±0.5 K by flowing methanol (240–325 K) or ethylene glycol (298–400 K) from a thermostated circulating bath through the outer jacket of the reaction vessel. An iron-constantan thermocouple was used to measure temperature, with a precision of better than 0.5 K.

As in earlier studies involving the kinetic behavior of the hydroxyl radical, photolysis of H₂O by a N₂ spark discharge lamp was used as the source of OH:¹⁰



The spark discharge lamp was normally equipped with a quartz window in order to eliminate the transmittance of light at wavelengths shorter than 165 nm, thus minimizing the production of reactive intermediates from the photodecomposition of the added reagent. Based on the known absorption spectrum of H₂O, and previously conducted actinometry using ethylene as the actinic gas, it was determined that typical OH concentrations of ~3 × 10¹¹ radical cm⁻³ were produced with an H₂O concentration of 6 × 10¹⁵ molecule cm⁻³, and a flash energy of 88 J.

Excitation of OH was accomplished via the use of a discharge-flow hydroxyl resonance lamp which primarily produced the emission characteristic of the (A²Σ⁺; v' = 0) → (X²Π; v'' = 0) transition of OH. A small fraction of the OH, produced by the photolysis of H₂O, was continuously excited by the resonance radiation emitted from the lamp. Fluorescence from excited OH was measured using a photomultiplier tube located at right angles to the lamp. As in previous studies, photon-counting electronics were used throughout this study. The intensity of the fluorescence was observed to be linearly proportional to the hydroxyl radical concentration in the reaction cell.

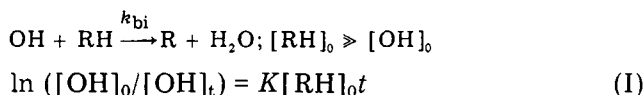
Each reaction was studied using pseudo-first-order kinetic conditions, [reagent]₀ ≫ [OH]₀ ([reagent]₀/[OH]₀ ≈ 1.5 × 10³–1.5 × 10⁵), and as expected the hydroxyl radical concentration decayed exponentially with time. Because the initial hydroxyl radical concentration was kept low to prevent secondary reactions, multiple flashes on a single gas mixture were required to produce a smooth kinetic curve. However, the number of flashes per filling of the reaction cell was limited (i.e., less than 50) so as to minimize the possible accumulation of reactive photolysis or reaction products which might participate in secondary removal of hydroxyl radicals. For this reason, several fillings of an identical gas mixture were normally used to develop a single experimental decay curve. The hydroxyl radical decay was observed to be linear for at least two half-lives.

Gas pressures of 10–5000 mTorr were measured using a MKS Baratron which was frequently checked for accuracy. High pressure measurements (10–800 Torr) were made with a two-turn Bourdon gauge (Wallace and Tiernan Type FA-145). The precision to which gas mixtures could be made up, with the exception of H₂O, was estimated to be ~3% or better. The H₂O pressure could not be metered so precisely, due to absorption on the reaction vessel surfaces.

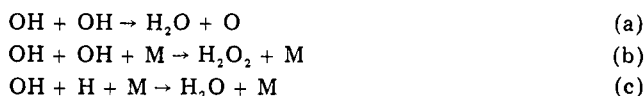
The purity of each of the halocarbons used in this study was as follows: CH₂FCl (Dupont, >99.92%); CHCl₂F (Dupont, >99.8%); CHClF₂ (Dupont, >99.8%); CH₃CCl₃ (Dow Corning, >99.95%); CH₃CF₂Cl (Dupont, >99.8%); CF₂ClCFCl₂ (Dupont, >99.9%). The helium diluent gas was Matheson Gold Label Ultra-High Purity, and was used without further purification. Even though the CH₃CCl₃ provided by Dow was uninhibited (did not contain an antioxidant), it contained trace amounts (<0.1%) of a chlorinated olefin which was removed by fractional distillation before use. The nature of the trace impurities present in each of the gases was quantitatively known, and calculations verified that they were of no importance in the present study. Each of the halocarbons were subjected to a freeze and thaw purification process prior to use.

Results and Discussion

(a) OH + C₁ and C₂ Halogenated Alkanes. Since the kinetic behavior of hydroxyl radicals with CH₂ClF (1), CHCl₂F (2), CHClF₂ (3); CH₃CCl₃ (4); CH₃CF₂Cl (5), and CF₂ClCFCl₂ (6) was studied using pseudo-first-order conditions, the hydroxyl radical decay rates could be analyzed using



where $K = k_{\text{bi}}/[\text{RH}]_0$. A wide variation in experimental conditions was performed in order to verify that kinetic complications due to secondary processes were not affecting the observed OH decay rates. These variations were normally performed at 298 K and included: H₂O pressures of 50–400 mTorr; flash energies of 45–245 J; total pressures of 40–200 Torr; and the number of flashes per single filling of the reaction cell of 25–200 (not shown in the tables). The number of flashes per filling was varied to demonstrate that the formation of significant concentrations of reactive photolytic or reaction products was unimportant. In these experiments, the measured pseudo-first-order rate constants, K , were always observed to be invariant within the expected experimental uncertainty (~5%) of the measurements. Removal of hydroxyl radicals by processes such as a-c were also shown to be

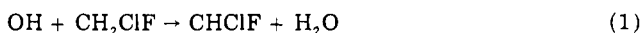


unimportant under typical operating conditions by examining the dependence of K upon flash energy, H₂O concentration, and total pressure. In these experiments, only when the flash energy was increased to 245 J were significantly higher K values (20%) measured over those obtained at lower flash energies, thus indicating some importance of radical-radical processes. Under these conditions, a ninefold increase in the radical concentration would have resulted. It should be noted, however, that no change was observed in the first-order rate constant when the flash energy was reduced from 88 to 45 J. In the calculation of K values for reactions 1–6, only data taken

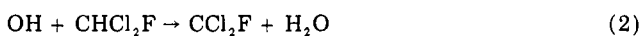
TABLE I: OH + CH₂ClF → CHClF + H₂O

Temp, K	[Reactant], mTorr	[Diluent], Torr	Flash energy, J	[Photolyte], mTorr	<i>k'</i> , s ⁻¹	<i>k</i> _{bimol} , cm ³ molecule ⁻¹ s ⁻¹
245	0	40	88	100	24	
	50	40	88	100	61	
	97	40	88	100	91	
	100	40	88	100	85	
	125	40	88	100	119	
	150	40	88	100	120	
	200	40	88	100	155	
	250	40	88	100	192	(1.65 ± 0.36) × 10 ⁻¹⁴
298	0	40	88	200	41	
	25	40	88	200	70	
	50	40	88	200	111	
	59	40	88	200	116	
	75	40	88	200	146	
	100	40	88	200	184	
	100	40	45	200	180	
	100	40	245	200	190	
	100	40	88	50	166	
	100	40	88	300	183	
	125	40	88	200	221	
	150	40	88	200	243	
	175	40	88	200	285	
	200	40	88	200	326	(4.42 ± 0.24) × 10 ⁻¹⁴
	0	200	88	200	12.5	
	50	200	88	200	79	
100	200	88	200	138		
125	200	88	200	170		
150	200	88	200	194	(3.79 ± 0.30) × 10 ⁻¹⁴	
375	25	100	88	200	95	
	40	100	88	200	135	
	50	100	88	200	154	
	75	100	88	200	219	
	100	100	88	200	280	
	125	100	88	200	350	(9.80 ± 0.34) × 10 ⁻¹⁴

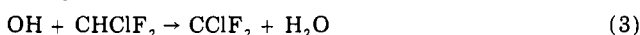
with flash energies of 88 J or less was used. The bimolecular rate constants for CH₂FCl, CHCl₂F, CHF₂Cl, CH₃CCl₃, CH₃CF₂Cl, and CF₂ClCFCl₂ were determined from a weighted least-squares treatment of the data shown in Tables I-VI. At 298 K, these *k* values are:



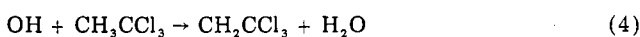
$$k_1 = (4.21 \pm 0.41) \times 10^{-14}$$



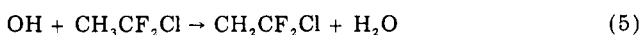
$$k_2 = (2.88 \pm 0.24) \times 10^{-14}$$



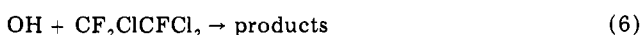
$$k_3 = (4.8 \pm 0.46) \times 10^{-15}$$



$$k_4 = (1.59 \pm 0.16) \times 10^{-14}$$



$$k_5 = (3.22 \pm 0.48) \times 10^{-15}$$



$$k_6 < 3 \times 10^{-16}$$

Units are cm³ molecule⁻¹ s⁻¹. For those reactions where several different total pressures were employed, a weighted averaged *k* value has been reported. The uncertainty limits shown for the above 298 K data, as well as those given in Tables I-VI for other temperatures, are the two σ values calculated from a weighted least-squares treatment of the data.

The temperature dependence of each reaction was studied over a nominal temperature range of ~100 deg. The limiting factors which determined the lowest temperature used in these measurements were: (a) the vapor pressure of H₂O at low temperatures; and (b) the magnitude of the rate constant. (The concentration of fluorocarbon was limited to 1500 mTorr due to electronic quenching of the A²Σ⁺ state of OH.) Figure 1 shows the

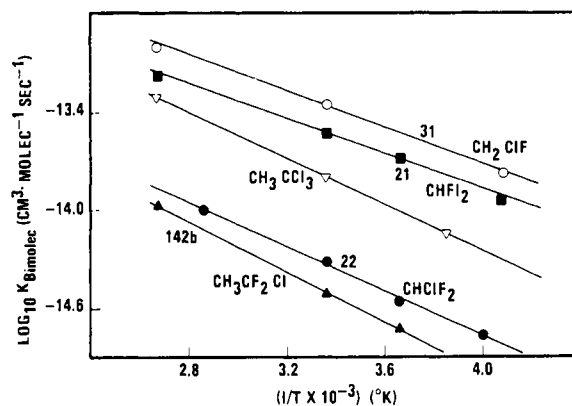


Figure 1.

Arrhenius plots for reactions 1-5. The resulting Arrhenius expressions are summarized as follows:

$$k_1 = (2.84 \pm 0.3) \times 10^{-12} \exp[-(1259 \pm 50/T)]$$

$$k_2 = (1.87 \pm 0.2) \times 10^{-12} \exp[-(1245 \pm 26/T)]$$

$$k_3 = (9.25 \pm 1.0) \times 10^{-13} \exp[-(1575 \pm 71/T)]$$

$$k_4 = (3.72 \pm 0.4) \times 10^{-12} \exp[-(1627 \pm 50/T)]$$

$$k_5 = (1.15 \pm 0.15) \times 10^{-12} \exp[-(1748 \pm 30/T)]$$

Units for the above *k* values are cm³ molecule⁻¹ s⁻¹. The activation energy has been expressed in terms of K⁻¹. The uncertainties quoted for *k*₁-*k*₅ apply only to the temperature range over which each system was studied and represent the 90% confidence limits.

Comparison and Discussion of Recent Work

A comparison of the results from this study with both published^{8,9} as well as unpublished⁷ rate data from other laboratories is shown in Table VII. It is readily seen that

TABLE II: OH + CHFCl₂ → CFCl₂ + H₂O

Temp, K	[Reactant], mTorr	[Diluent], Torr	Flash energy, J	[Photolyte], mTorr	<i>k'</i> , s ⁻¹	<i>k</i> _{bimol} , cm ³ molecule ⁻¹ s ⁻¹
245	50	40	88	100	51	
	100	40	88	100	81	
	150	40	88	100	103	
	200	40	88	100	119	
	250	40	88	100	143	
	300	40	88	100	158	
	350	40	88	100	186	
273	400	40	88	100	229	(1.12 ± 0.12) × 10 ⁻¹⁴
	75	40	88	200	102	
	100	40	88	200	120	
	150	40	88	200	161	
	200	40	88	200	196	
	250	40	88	200	240	
	300	40	88	200	270	
298	350	40	88	200	303	
	400	40	88	200	351	(2.09 ± 0.18) × 10 ⁻¹⁴
	0	40	88	200	38	
	50	40	88	200	75	
	75	40	88	200	108	
	100	40	88	200	123	
	125	40	88	200	161	
	150	40	88	200	180	
	150	40	45	200	175	
	150	40	245	200	217	
	150	40	88	50	174	
298	150	40	88	400	204	
	175	40	88	200	206	
	200	40	88	200	210	
	200	40	45	200	222	
	250	40	88	200	263	
	275	40	88	200	302	
	300	40	88	200	340	(2.99 ± 0.24) × 10 ⁻¹⁴
	0	200	88	200	12	
	50	200	88	200	60	
	100	200	88	200	98	
	125	200	88	200	115	
	150	200	88	200	140	
	175	200	88	200	173	
	200	200	88	200	185	
375	200	200	88	200	180	
	225	200	88	200	238	
	250	200	88	200	229	
	250	200	88	200	206	
	300	200	88	200	263	(2.66 ± 0.58) × 10 ⁻¹⁴
	0	100	88	200	70	
	15	100	88	200	104	
	25	100	88	200	116	
	40	100	88	200	135	
	50	100	88	200	157	
65	100	88	200	175		
75	100	88	200	206		
90	100	88	200	217		
100	100	88	200	232		
110	100	88	200	263		
125	100	88	200	298	(6.68 ± 0.82) × 10 ⁻¹⁴	

at 298 K virtually all results are in excellent agreement within the quoted experimental uncertainties. An exception to this is the compound CHClF₂ where the result quoted by Howard and Evenson is lower than that of the other two studies by ~25–30%. At present, no explanation can be forwarded for this apparent discrepancy. Howard and Evenson^{6,7} used a low pressure discharge flow system with laser magnetic resonance detection of the hydroxyl radical to determine the rate constants for reactions 1–5 at 298 K. Pitts, Atkinson, et al.,^{8,9} as in this investigation, utilized the technique of flash photolysis–resonance fluorescence to examine the kinetic behavior of reactions 2 and 3 between 298 and ~430 K. The results of the two high pressure flash photolysis studies are in excellent agreement for both reactions 2 and 3. This is especially encouraging in that the temperature ranges used in the two studies only partially overlapped, and yet the

experimental data of one study were always within the stated experimental uncertainties of that predicted from the Arrhenius expression reported from the other study. A least-squares treatment of all the data points obtained in the two temperature dependence studies of *k*₂ and *k*₃ resulted in the following evaluated Arrhenius expressions:

$$k_2 = (1.59 \pm 0.2) \times 10^{-12} \exp[-(1204 \pm 50/T)] \quad (245-423) \text{ K}$$

$$k_3 = (1.21 \pm 0.17) \times 10^{-12} \exp[-(1648 \pm 75/T)] \quad (250-434) \text{ K}$$

Atmospheric Implications of Rate Data

The chemical degradation of halogenated alkanes via hydroxyl radical attack was discussed in the Introduction with particular reference to the tropospheric lifetimes of

TABLE III: $\text{OH} + \text{CHF}_2\text{Cl} \rightarrow \text{CF}_2\text{Cl} + \text{H}_2\text{O}$

Temp, K	[Reactant], mTorr	[Diluent], Torr	Flash energy, J	[Photolyte], mTorr	k' , s^{-1}	k_{bimol} , $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
250	300	40	88	200	47	
	500	40	88	200	60	
	700	40	88	200	70	
	900	40	88	200	87	
	1100	40	88	200	93	
273	1300	40	88	200	116	$(1.70 \pm 0.40) \times 10^{-15}$
	300	40	88	200	63	
	400	40	88	200	73	
	500	40	88	200	84	
	600	40	88	200	89	
	700	40	88	200	102	
298	800	40	88	200	115	
	900	40	88	200	121	$(2.77 \pm 0.38) \times 10^{-15}$
	0	40	88	200	25	
	100	40	88	200	53	
	300	40	88	200	87	
	400	40	88	200	99	
	500	40	88	200	117	
	500	40	45	200	111	
	500	40	245	200	123	
	500	40	88	500	120	
350	600	40	88	200	131	
	700	40	88	200	141	
	800	40	88	200	166	
	900	40	88	200	178	
	960	40	88	200	190	$(4.84 \pm 0.46) \times 10^{-15}$
	0	200	88	200	15	
	400	200	88	200	66	
	600	200	88	200	90	
	700	200	88	200	114	
	800	200	88	200	128	
	900	200	88	200	151	$(4.69 \pm 1.06) \times 10^{-15}$
	0	100	88	200	34	
350	200	100	88	200	82	
	300	100	88	200	110	
	400	100	88	200	136	
	500	100	88	200	168	
	600	100	88	200	193	$(1.01 \pm 0.08) \times 10^{-14}$

TABLE IV: $\text{OH} + \text{CH}_2\text{CCl}_3 \rightarrow \text{CH}_2\text{CCl}_2 + \text{H}_2\text{O}$

Temp, K	[Reactant], mTorr	[Diluent], Torr	Flash energy, J	[Photolyte], mTorr	k' , s^{-1}	k_{bimol} , $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
260	0	40	88	200	25	
	100	40	88	200	54	
	200	40	88	200	65	
	250	40	88	200	68	
	300	40	88	200	110	
	400	40	88	200	115	
	500	40	88	200	155	
	700	40	88	200	204	
	750	40	88	200	210	
	1000	40	88	200	285	$(7.12 \pm 0.94) \times 10^{-15}$
298	0	40	88	200	38	
	100	40	88	200	87	
	150	40	88	200	117	
	200	40	88	200	140	
	250	40	88	200	150	
	300	40	88	200	205	
	400	40	88	50	280	
	400	40	88	200	255	
	400	40	88	400	273	
	405	40	88	200	249	
	500	40	88	200	285	
	800	40	88	200	450	$(1.59 \pm 0.16) \times 10^{-14}$
	200	40	245	200	171	
	400	40	245	200	270	
600	40	245	200	373	$(1.56 \pm 0.04) \times 10^{-14}$	
375	200	40	31	200	120	
	400	40	31	200	~215	$\sim 1.5 \times 10^{-14}$
	25	40	88	200	125	
	50	40	88	200	150	
	100	40	88	200	225	
	150	40	88	200	296	
	200	40	88	200	347	
	250	40	88	200	400	$(4.85 \pm 0.58) \times 10^{-14}$

TABLE V: OH + CH₃CF₂Cl → CH₂CF₂Cl + H₂O

Temp, K	[Reactant], mTorr	[Diluent], Torr	Flash energy, J	[Photolyte], mTorr	<i>k'</i> , s ⁻¹	<i>k</i> _{bimol} , cm ³ molecule ⁻¹ s ⁻¹
273	250	40	88	200	32	
	500	40	88	200	77	
	750	40	88	200	101	
	1000	40	88	200	117	
	1250	40	88	200	126	
298	1500	40	88	200	139	(1.92 ± 0.48) × 10 ⁻¹⁵
	200	40	88	200	51	
	400	40	88	200	77	
	600	40	88	200	99	
	800	40	88	200	117	
	1000	40	88	200	147	
	1200	40	88	200	156	
	1200	40	45	200	167	
	1200	40	245	200	200	
	1200	40	88	400	161	
	1400	40	88	200	177	
	1500	40	88	200	181	
	1600	40	88	200	199	(3.12 ± 0.48) × 10 ⁻¹⁵
	0	200	88	200	12.5	
	600	200	88	200	90	
800	200	88	200	117		
1000	200	88	200	116		
1400	200	88	200	172	(3.42 ± 0.68) × 10 ⁻¹⁵	
375	75	100	88	200	65	
	150	100	88	200	86	
	200	100	88		111	
	300	100	88		123	
	400	100	88		147	
	500	100	88		178	
	600	100	88		216	
	800	100	88		273	(1.09 ± 0.14) × 10 ⁻¹⁴

TABLE VI: OH + CF₂ClCFCl₂ → products

Temp, K	[Reagent], mTorr	[Diluent], Torr	Flash energy, J	[Photolyte], mTorr	<i>k'</i> , s ⁻¹	<i>k</i> _{bimol} , cm ³ molecule ⁻¹ s ⁻¹
298	250	40	88	200	27	
	500	40	88	200	36	
	750	40	88	200	31	
	1250	40	88	200	39	< 3 × 10 ⁻¹⁶

TABLE VII: Comparison of Rate Data

Compd	<i>k</i> (298K) × 10 ¹⁵ cm ³ molecule ⁻¹ s ⁻¹			Arrhenius expressions	
	This work	Ref 6,7	Ref 8,9	This work	Ref 8,9
CH ₂ ClF	42.1 ± 4	37 ± 6		2.84 × 10 ⁻¹² exp[-(1259/T)]	
CHCl ₂ F	28.8 ± 3	26 ± 4	27 ± 3	1.87 × 10 ⁻¹² exp[-(1245/T)]	1.75 × 10 ⁻¹² exp[-(1253/T)]
CHClF ₂	4.8 ± 0.3	3.4 ± 0.7	4.75 ± 0.48	9.25 × 10 ⁻¹³ exp[-(1575/T)]	1.21 × 10 ⁻¹² exp[-(1636/T)]
CH ₃ CCl ₃	15.9 ± 2	15 ± 3		3.72 × 10 ⁻¹² exp[-(1627/T)]	
CH ₃ CF ₂ Cl	3.22 ± 0.3	2.8 ± 0.4		1.15 × 10 ⁻¹² exp[-(1748/T)]	
CF ₂ ClCFCl ₂	< 0.3				

these compounds. The most significant consequence of a short tropospheric lifetime for partially hydrogenated halocarbons is that of restricting the stratospheric burden of chlorine from these compounds. Table VIII, for example, shows the results of a calculation¹¹ which gives the fraction of a given halocarbon which would diffuse into the stratosphere and photolyze as a function of its tropospheric lifetime at steady state. It can readily be seen that a lifetime of 10 years or less drastically reduces the flux of these compounds into the stratosphere at steady state (see comments on ref 11). The destruction rate for a halocarbon containing hydrogen is given by

$$-d[\text{RX}]/dt = k[\text{OH}][\text{RX}]$$

and

$$\tau_e(\text{tropospheric lifetime}) = [k[\text{OH}]_{\text{av}}]^{-1}$$

Thus, the two parameters required to calculate tropo-

TABLE VIII

Lifetime, yr	CFCl ₃	CF ₂ Cl ₂
∞	1.0	1.0
50	0.66	0.4
40	0.53	0.32
20	0.27	0.16
10	0.13	0.08

TABLE IX: Calculated Tropospheric Lifetimes

Compd	<i>k</i> _{bimol} , (265 K)	Lifetime, ^a yr
CH ₂ ClF	2.45 × 10 ⁻¹⁴	1.44
CHCl ₂ F	1.70 × 10 ⁻¹⁴	2.07
CHClF ₂	2.43 × 10 ⁻¹⁵	14.50
CH ₃ CCl ₃	8.02 × 10 ⁻¹⁵	4.39
CH ₃ CF ₂ Cl	1.57 × 10 ⁻¹⁵	22.44
CF ₂ ClCFCl ₂	< 3 × 10 ⁻¹⁶	> 117

^a Lifetime: $\ln(A_0/A) = k[\text{OH}]_{\text{av}}t$, where $\ln(A_0/A) = 1$.

spheric lifetimes are (a) the value of the bimolecular rate constant for a given OH reaction and (b) the global seasonally and diurnally averaged OH steady state concentration. In Table IX, we have calculated the tropospheric lifetimes of all six compounds investigated in this study. These calculations have been based on a weighted average temperature for the troposphere of 265 K and a global seasonally and diurnally averaged OH concentration of $9 \times 10^5 \text{ cm}^{-3}$. The latter value has been estimated using results from Crutzen's two-dimensional atmospheric model¹² and data from recent direct measurements of atmospheric OH at 32 and 21°N latitude at 7 and 11.5 km reported by Davis, McGee, and Heaps.⁵

From Table IX, it can be seen that the tropospheric lifetimes of CH_2ClF (fluorocarbon 31), CHCl_2F (fluorocarbon 21), and CH_3CCl_3 are sufficiently short that their potential impact on stratospheric ozone should be minimal. However, the predicted lifetimes for CHClF_2 (fluorocarbon 22) and $\text{CH}_3\text{CF}_2\text{Cl}$ (fluorocarbon 142) are sufficiently long that the sink for 10–20% of the anthropogenic production rate could be expected to be photodissociation in the stratosphere at steady state. Additional factors of importance, however, are that both these compounds contain only one chlorine atom per molecule in contrast to fluorocarbons 11 and 12 which contain three and two chlorine atoms, respectively. This fact combined with the predicted shorter tropospheric lifetime of fluorocarbons 22 and 142 would indicate that the potential impact of an equal source strength of these compounds compared to fluorocarbon 11 or 12 would be four to ten times less. As expected, no observable reaction was detected between OH and $\text{CF}_2\text{ClCFCl}_2$ (TF 13), suggesting a chemical lifetime in the troposphere comparable to that for fluorocarbons 11 and 12.

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References and Notes

- (1) (a) F. S. Rowland and M. J. Molina, *Rev. Geophys. Space Phys.*, **13**, 1 (1975); (b) M. J. Molina and F. S. Rowland, *Nature (London)*, **249**, 810 (1974); *Geophys. Res. Lett.*, **309** (1974); (c) S. Wofsy, M. McElroy, and N. Sze, *Science*, **187**, 535 (1975); (d) S. Wofsy and M. McElroy, *Can. J. Chem.*, **52**, 1582 (1974); (e) P. J. Crutzen, *Geophys. Res. Lett.*, **1**, 205 (1974); (f) R. J. Cicerone, R. S. Stolarski, and S. Walters, *Science*, **185**, 1165 (1974); (g) R. J. Cicerone, D. H. Stedman, and R. S. Stolarski, *Geophys. Res. Lett.*, **2**, 219 (1975); (h) P. J. Crutzen and L. S. A. Isakensen, *J. Geophys. Res.*, accepted for publication.
- (2) (a) L. E. Heidt, R. Lueb, W. Pollock, and D. H. Ehhalt, *Geophys. Res. Lett.*, **2**, 445 (1975); (b) N. E. Hester, E. R. Stephens, and O. C. Taylor, *Environ. Sci. Technol.*, **9**, 875 (1975); (c) P. W. Krey and R. J. Lagomarsino, ERDA Environment Quarterly Report HASL-294, 97 (1975); (d) J. E. Lovelock, *Nature (London)*, **252**, 292 (1974); (e) J. E. Lovelock, R. J. Maggs, and R. J. Wade, *ibid.*, **241**, 194 (1973); (f) A. L. Schmettekopf, P. O. Golden, W. R. Henderson, W. J. Harrap, T. L. Thompson, R. S. Fehsenfeld, H. I. Schiff, P. J. Crutzen, I. S. A. Isaksen, and E. E. Ferguson, *Geophys. Res. Lett.*, **2**, 393 (1975); (g) W. J. Williams, J. J. Kusters, A. Goldman, D. G. Murcray, presented at AGU, Dec, 1975; (h) P. E. Wilkness, J. W. Swinnerton, D. J. Bresson, R. A. Lamontagne, and R. E. Larson, *J. Atm. Sci.*, **22**, 158 (1975); (i) P. E. Wilkness, J. W. Swinnerton, R. A. Lamontagne, and D. J. Bresson, *Science*, **187**, 832 (1975).
- (3) N. D. Sze and M. F. Wu, *Atmos. Environ.*, submitted for publication.
- (4) D. D. Davis, G. Machado, B. Conaway, Y. Oh, and R. T. Watson, *J. Chem. Phys.*, accepted for publication.
- (5) D. D. Davis, T. McGee, and W. Heaps, *J. Geophys. Res. Lett.*, submitted for publication.
- (6) C. J. Howard and K. M. Evenson, *J. Chem. Phys.*, **64**, 197 (1976).
- (7) C. J. Howard and K. M. Evenson, *J. Chem. Phys.*, submitted for publication.
- (8) R. A. Perry, R. Atkinson, and J. N. Pitts, Jr., *J. Chem. Phys.*, **64**, 1618 (1976).
- (9) R. Atkinson, D. A. Hansen, and J. N. Pitts, Jr., *J. Chem. Phys.*, **63**, 1703 (1975).
- (10) (a) D. D. Davis, R. Schiff, and S. Fischer, *J. Chem. Phys.*, **61**, 2213 (1974); (b) D. D. Davis, R. Huie, J. Herron, W. Braun, and M. Kurylo, *ibid.*, **56**, 4868 (1972); (c) D. D. Davis and R. B. Klemm, *Int. J. Chem. Kinet.*, **4**, 367 (1972).
- (11) N. D. Sze, private communication. These calculations used the Hunter eddy diffusion coefficient. Use of any other K_z function would show a lesser dependence of flux upon lifetime. The magnitude of the effect is different for all gases and is governed by the destruction ratio (photolytic and chemical) in the stratosphere.
- (12) P. Crutzen, "Results from a 2-D Atmospheric Model", paper presented at the 4th Climatic Impact Assessment Program, Cambridge, Mass., Feb, 1975.