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**TROPOSPHERIC HYDROXYL CONCENTRATIONS AND THE LIFETIMES OF  
HYDROCHLOROFLUOROCARBONS (HCFCs)**

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## ABSTRACT

Three-dimensional fields of modeled tropospheric OH concentrations are used to calculate lifetimes against destruction by OH for many hydrogenated halocarbons, including the CFC alternatives (hydrochlorofluorocarbons or HCFCs). The OH fields are taken from a 3-D chemical transport model (Spivakovsky et al., 1989) that accurately simulates the global measurements of methyl chloroform (derived lifetime of 5.5 yr). The lifetimes of various hydro-halocarbons are shown to be insensitive to possible spatial variations and seasonal cycles. It is possible to scale the HCFC lifetimes to that of methyl chloroform or methane by using a ratio of the rate coefficients for reaction with OH at an appropriate temperature, about 277 K.

## 1. INTRODUCTION

Synthetically produced halocarbons that contain chlorine and bromine, often called chlorofluorocarbons (CFCs) and halons, pose a direct threat to the stratospheric ozone layer (e.g., NASA/WMO, 1986; Watson et al., 1988) and also contribute substantially to the greenhouse forcing of the climate (Ramanathan, 1975; Lacis et al., 1981). A single characteristic of CFCs and halons that aggravates these environmental problems is their long atmospheric lifetimes; most are destroyed only by ultraviolet sunlight in the stratosphere. As a result of these environmental concerns, there will soon be international restrictions on CFC growth as agreed upon in the Montreal Protocol, and there is now a search for alternative fluorocarbons, environmentally acceptable substitutes (AFEAS Workshop, 16-17 May 1989, Boulder Colorado). One key property of these alternative compounds must be a short atmospheric residence time, implying efficient loss in the troposphere or at the Earth's surface.

Many of the suggested alternative fluorocarbons contain hydrogen (hydrochlorofluorocarbons or HCFCs), and atmospheric loss of these HCFCs is dominated by reaction with tropospheric OH. Their buildup in the atmosphere (units: kg) will be controlled by the ratio of emissions ( $\text{kg yr}^{-1}$ ) to atmospheric destruction ( $\text{yr}^{-1}$ ). The globally averaged, annual mean lifetime (yr) of the HCFCs (against atmospheric loss) is defined as the global atmospheric content (kg) divided by the total annual loss ( $\text{kg yr}^{-1}$ ).

In this report we derive the lifetime of HCFCs and other hydrogenated halocarbons in two ways. The primary method involves modelling the OH distribution from first principles, specifying or predicting the HCFC distribution, and then integrating the HCFC loss over the globe (e.g., Logan et al., 1981). The tropospheric OH fields are calculated from a global 3-D climatology of sunlight, temperature,  $\text{O}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{NO}_x$ ,  $\text{CO}$ ,  $\text{CH}_4$  and other hydrocarbons (see Spivakovsky et al., 1989). Uncertainties in the calculated OH concentrations occur not only with the kinetic model, but also with the global climatologies of the other trace gases and cloud-cover needed as input to the photochemical model.

The OH fields used here were developed and applied to study methyl chloroform in a 3-D Chemical Transport Model (CTM). With the CTM, we specified sources, global transport and chemical losses of  $\text{CH}_3\text{CCl}_3$  in order to simulate the latitudinal and seasonal patterns, and the global trends (see Spivakovsky et al., 1989). Similar CTM modelling of all the HCFCs is impractical and would require also a history and geographical location of emissions. Instead, the four-dimensional OH field (latitude x longitude x altitude x time) is applied here to test various hypotheses on the sensitivity of HCFC lifetimes to their tropospheric distribution; it is used also to test the accuracy of scaling the HCFC lifetimes to an assumed methyl chloroform lifetime.

## TROPOSPHERIC HYDROXYL

The second method for deriving HCFC lifetimes selects a reference species with a global budget and atmospheric lifetime (against OH destruction) that is thought to be well understood (see Makide and Rowland, 1981). The lifetime of methyl chloroform,  $\text{CH}_3\text{CCl}_3$ , derived from the ALE/GAGE analysis is often used (Prinn et al., 1987) and is then scaled by the ratio of the rate coefficients for reaction with OH (Hampson, Kurylo and Sander, AFEAS, 1989),  $k(\text{OH} + \text{CH}_3\text{CCl}_3)/k(\text{OH} + \text{HCFC})$ , to calculate the HCFC lifetime. Possible errors in this approach are associated with the assumed lifetime for  $\text{CH}_3\text{CCl}_3$ , and with the use of a single scaling factor that does not reflect the different spatial distribution of the HCFCs. This scaling approximation is tested here for plausible global patterns in the HCFC concentration and for different temperature dependence of the rate coefficients.

The tropospheric chemistry model for OH is described in Section 2. We calculate the global losses for methane and methyl chloroform in Section 3, and then compare the results for methyl chloroform with other published values. The integrated losses for a range of possible distributions of an HCFC are given in Section 4. HCFC lifetimes and uncertainties are discussed in Section 5.

## 2. THE CHEMICAL MODEL

The lifetimes calculated here for the HCFCs, as well as for  $\text{CH}_3\text{CCl}_3$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$  and  $\text{CH}_4$ , use global distributions of OH from the photochemical model developed for the 3-D Chemical Transport Model (CTM developed at GISS & Harvard). The model for tropospheric OH is based on a 1-D photochemical model (an updated version of Logan et al., 1981; DeMore et al., 1987) that has been used to parameterize OH concentrations as a function of sunlight and other background gases (see Spivakovsky et al., 1989). This parameterized chemistry has been used to calculate a three-dimensional set of mean OH concentrations for the CTM grid over one year: the diurnally averaged OH concentrations are stored at 5-day intervals with a spatial resolution of 8 degrees latitude by 10 degrees longitude over 9 vertical layers (see Prather et al., 1987 for CTM documentation) for a total of more than 1/2 million values, even at this coarse resolution. The 5-day average temperatures at each grid point are also stored.

The local independent variables needed to derive OH concentrations are taken from the parent General Circulation Model (5-day averages of pressure, temperature, water vapor and cloud cover; see Hansen et al., 1983) and from observed climatologies ( $\text{CO}$ ,  $\text{O}_3$ ,  $\text{CH}_4$ ,  $\text{NO}_x$ ,  $\text{H}_2\text{O}$  above 500 mbar and stratospheric ozone column). The observational database for most of these species is insufficient to define the necessary 4-D fields, and we have assumed zonally uniform distributions with smooth variations over latitude, altitude and season for most species. One exception is that from the available data we are able to differentiate between the continental and the maritime troposphere up to 3 km altitude. See Spivakovsky et al. (1989) for details of the assumed trace-gas climatology and the chemical parameterization.

The annual averages of the zonal mean OH concentrations are shown in Table 1a; Table 1b gives the corresponding annual average temperatures. Hydroxyl concentrations are highest in the middle troposphere over the tropics. The OH density peaks at 700-800 mbar because cloud cover and Rayleigh scattering reduce solar ultraviolet light below 800 mbar.

The global loss of a gas that reacts with OH is the integral over a wide range of conditions in temperature, density and trace gas abundance. The integrand is extremely non-linear, and thus, the average loss

Table 1a. Annual Average OH concentration ( $10^4 \text{ cm}^{-3}$ )

		LATITUDE																							
P(mbar)		90S	84S	76S	68S	60S	52S	44S	36S	28S	20S	12S	4S	4N	12N	20N	28N	36N	44N	52N	60N	68N	76N	84N	90N
100										20	26	43	40	35	30	26	19								
150										43	51	68	59	54	49	44	34								
200		33	32	30	25	25	24	30	38	52	57	65	58	52	48	43	36	30	21	17	18	17	20	22	20
300		31	27	24	21	23	26	33	43	62	76	80	77	72	65	59	50	39	28	21	20	21	28	32	33
500		41	36	32	30	36	45	63	81	119	131	135	147	141	124	118	108	80	61	45	40	34	41	46	44
700		51	44	41	42	43	51	68	89	139	154	159	180	182	171	159	139	111	88	64	58	56	53	56	32
800			42	40	44	36	48	65	89	144	157	152	168	168	159	155	140	130	108	79	67	77	52	56	32
900				31	32	14	21	35	65	114	124	123	130	134	135	126	110	116	90	62	53	59	23	26	20
1000					20	11	16	28	52	92	105	103	112	112	112	107	88	86	63	43	40	46	17	21	10

Table 1b. Annual Average Temperature ( $^{\circ}\text{K}$ )

		LATITUDE																							
P(mbar)		90S	84S	76S	68S	60S	52S	44S	36S	28S	20S	12S	4S	4N	12N	20N	28N	36N	44N	52N	60N	68N	76N	84N	90N
100										207	204	203	202	202	202	203	206								
150										215	215	215	215	215	216	216	215								
200		206	209	209	211	212	213	214	217	222	225	225	226	226	225	223	220	217	215	214	214	214	214	214	215
300		216	217	216	219	221	224	228	233	239	244	246	246	247	246	245	241	236	231	227	225	223	222	222	217
500		232	236	237	240	244	247	252	257	263	268	270	270	270	270	269	266	260	255	250	248	245	244	242	225
700		247	248	248	254	259	263	267	272	277	282	283	283	283	284	283	280	275	270	265	262	259	258	256	235
800			255	256	258	264	268	273	278	283	287	288	289	289	289	289	286	280	275	270	267	264	262	261	239
900				264	262	268	273	278	283	288	291	293	293	294	294	294	291	285	279	275	270	267	265	263	244
1000					267	271	276	282	287	291	295	297	297	297	298	297	293	289	283	277	272	268	268	267	246

Quantities are the annual zonal average of the 4-D fields described in the text.

No values for OH or T are reported for the extra-tropical stratosphere (above 200 mbar).

At higher pressures over Antarctica the number of points are insufficient to report a zonal average.

Table 2. Global Average OH concentrations

<u>integrating kernel</u>	<u>OH (<math>10^4 \text{ cm}^{-3}</math>)</u>	<u>effective T (K)</u>
dm	80	
exp(-1000/T) dm	96	259
exp(-1700/T) dm	105	262
exp(-1800/T) dm	106	263
exp(-2300/T) dm	111	265
(1 + 0.6/P) dm	91	
dz	65	

Integrals over mass (dm, from the surface to 100 mbar) are weighted by different factors: exponential in temperature (e.g., -1700/T for  $\text{CH}_4$ ), and linear in pressure (i.e.,  $1 + 0.6/P$  for CO). Integrals over volume (dz) preferentially weight the lower atmospheric densities in the upper troposphere. Use of the average OH with the effective temperature in the exponential gives the correct global integral.

## TROPOSPHERIC HYDROXYL

is not equal simply to the product of averages (Makide and Rowland, 1981). It is misleading to report a single "global average OH concentration" without qualifying it as to the averaging kernel. The global OH concentrations averaged over the atmosphere (100-1000 mbar with no stratospheric contribution) are reported here in Table 2 for a variety of integrating kernels. The average OH is largest,  $111 \times 10^4 \text{ cm}^{-3}$ , when weighted appropriately (by mass) for loss of an HCFC with a large exponential factor of  $-2300/T$ . A larger temperature dependence result in greater average OH because the OH densities are maximal at high temperatures in the tropics (see Table 1). The spatially averaged OH density is smallest,  $65 \times 10^4 \text{ cm}^{-3}$ , because of the large volumes of air in the upper troposphere with low OH concentrations. The effective temperatures given in Table 2 are those needed to get the correct globally averaged integral, and should not be confused with the optimal scaling temperature in Section 4. (The scaling temperature must also account for the change in mean OH as the temperature dependence varies.)

### 3. GLOBAL LOSS OF $\text{CH}_3\text{CCl}_3$ AND $\text{CH}_4$

The globally integrated losses for methane and for methyl chloroform are calculated by integrating the loss frequency (OH and temperature fields described above) using realistic, but fixed tropospheric distributions for  $\text{CH}_4$  and  $\text{CH}_3\text{CCl}_3$ . Tropospheric reactions with OH dominate the loss of both species, but stratospheric losses cannot be ignored and are used in place of OH densities in layer 9 (0-70 mbar) globally and in layer 8 (70-150 mbar) outside the tropics. The stratospheric losses are calculated from a 1-D vertical diffusion model for stratospheric chemistry evaluated at the appropriate latitude and season.

The assumed conditions and resulting atmospheric losses of  $\text{CH}_4$  and  $\text{CH}_3\text{CCl}_3$  are summarized in Table 3. The lifetime of methane is 8.7 yr with about 6% of the loss occurring in the stratosphere and more

**Table 3.** Global budgets for  $\text{CH}_4$  and  $\text{CH}_3\text{CCl}_3$

	<u><math>\text{CH}_4</math></u>	<u><math>\text{CH}_3\text{CCl}_3</math></u>
Rate coefficient		
$k(\text{X} + \text{OH})$	$2.3 \times 10^{-12} e^{-1700/T}$	$5.0 \times 10^{-12} e^{-1800/T}$
Concentration		
NH (<28°/>28°)	1700/1700 ppb	140/150 ppt
SH	1600 ppb	110 ppt
Atmospheric content	$4580 \times 10^{12} \text{g}$	$2930 \times 10^9 \text{g}$
Atmospheric losses		
total	$524 \times 10^{12} \text{g}$	$534 \times 10^9 \text{g}$
tropics (2-6 km)	$270 \times 10^{12} \text{g}$	$260 \times 10^9 \text{g}$
stratosphere	$29 \times 10^{12} \text{g}$	$53 \times 10^9 \text{g}$
Lifetime	8.7 yr	5.5 yr

Budgets based on integration of 4-D tropospheric OH fields with zonally fixed, non-seasonal distributions as noted. Stratospheric profiles and losses are included.

than half in the tropical middle troposphere. The lifetime of methyl chloroform is 5.5 yr. Stratospheric loss for methyl chloroform is about three times more rapid than for methane because photolysis of  $\text{CH}_3\text{CCl}_3$  becomes important in the stratosphere. Again the tropical middle troposphere accounts for about half of the global loss.

Methyl chloroform is usually chosen as a reference species for tropospheric loss, with a "known" atmospheric lifetime based on the ALE/GAGE analysis of Prinn et al. (1987). We compare the lifetimes in Table 3 for  $\text{CH}_3\text{CCl}_3$  with those from the ALE/GAGE analysis and the recent 3-D CTM simulations (Spivakovsky et al., 1989). The ALE/GAGE analysis uses observations of  $\text{CH}_3\text{CCl}_3$  at 5 surface sites, industry data for atmospheric emissions, and a 9-box atmospheric model, to derive an annual average global lifetime of 6.3 yr with a reported 1-sigma range of 5.4-7.5 yr. Errors in the lifetime due to uncertainties in the atmospheric emissions used in the ALE/GAGE study have been reduced by recent analyses of  $\text{CH}_3\text{CCl}_3$  sources from industry surveys (Midgley, 1989) and from observations (Prather, 1988).

When the same OH and temperature fields are used in the complete CTM simulation of  $\text{CH}_3\text{CCl}_3$  (Spivakovsky et al., 1989) the integrated loss correctly includes all correlations of OH and temperature with  $\text{CH}_3\text{CCl}_3$  concentrations. The 3-D CTM simulation showed that the standard OH field (with a resulting lifetime of 5.5 yr) and the OH field scaled by a factor of 0.75 (with a lifetime of 7.1 yr) bracket the observations. This range, however, does not include uncertainties in the observations (i.e., absolute calibration) or in the sources. The observed seasonal cycle of  $\text{CH}_3\text{CCl}_3$  in the southern hemisphere is not a direct measure of the absolute OH concentrations; however, its accurate simulation in the CTM provides some confirmation of the integrated seasonal variation of the modeled OH fields in the southern hemisphere. Such comparisons emphasize the mid-latitude photochemistry which has the largest seasonal variations, and they are independent of absolute calibration and sources because they depend on the relative (%) changes in  $\text{CH}_3\text{CCl}_3$ .

It is difficult to find other globally distributed trace gases with well defined sources and trends that can be used to test global OH concentrations. For example, Derwent and Volz-Thomas (AFEAS, May, 1989; Volz et al., 1981) have used carbon monoxide, both  $^{14}\text{CO}$  and  $^{12}\text{CO}$ , to test and recalibrate the OH fields in their 2-D model. Another possibility, HCFC-22 ( $\text{CHF}_2\text{Cl}$ ) has limited data on hemispheric abundances, trends and sources. Data for HCFC-22 are sparse and barely able to define the hemispheric ratio and instantaneous trend ( $\text{N/S} = 89/77$  ppt,  $+6.5$  ppt/yr in 1985, see NASA/WMO, 1986). Furthermore, significant uncertainties exist currently for the absolute calibration and atmospheric emissions of most HCFCs. HCFC-22 is used as an intermediate chemical in the production of other compounds, and thus its release is only a fraction of production. Recent estimates of HCFC-22 emission (130 Gg/yr in 1985, M. McFarland, personal communication) are twice as large as previous values, and are now barely able to reconcile the current atmospheric budget from the limited observations noted above.

It is not possible at present to put a formal "one-sigma" accuracy on the OH fields used here, either from first principles, or from constraints using the methyl chloroform budget. The uncertainty factor for the OH fields is chosen to be 1.3 and is applied to the lifetimes for HCFCs in Section 5.

## TROPOSPHERIC HYDROXYL

### 4. SENSITIVITY OF HCFC LIFETIME TO GLOBAL DISTRIBUTION

We use the 4-D fields of OH and temperature to understand how to predict the lifetime of one species relative to another. Specifically, how can the lifetime of one species be scaled to another with a different spatial-temporal distribution and loss rate? Idealized tropospheric distributions are used to examine the sensitivity of HCFC lifetime to (a) the temperature dependence of their reaction rates with OH, (b) large interhemispheric gradients, (c) enhanced concentrations in the boundary layer near sources, and (d) seasonal cycles in concentration.

a. Sensitivity to rate coefficient:  $k = A \times \exp(-B/T)$

Two species, X and Y, with the same global distribution and with rate coefficients for reaction with OH that differ only by a constant factor,  $k(\text{OH} + X)/k(\text{OH} + Y) = \text{constant}$ , will have lifetimes that scale inversely by the same factor. In most cases, however, the rate coefficients have different temperature dependence, B, or pressure dependence (as in the case of CO). We investigate the dependence of HCFC lifetime on values of B ranging from 0 to 2300 K, by integrating the loss for an atmospheric tracer that is uniformly distributed throughout the troposphere and stratosphere. The A coefficient was selected to match the CH<sub>4</sub> rate,  $k = 2.3\text{E-}12 \times \exp(-B/T) \text{ cm}^3 \text{ s}^{-1}$ , and stratospheric losses were not included.

The integrated global loss rates are given in Table 4a; lifetimes range from 81 yr (B = 2300 K) to 0.02 yr (B = 0 K). In Figure 1 we show the error associated with predicting the lifetime by scaling to a reference lifetime (9.42 yr at B = 1700 K) using an appropriate temperature in the ratio of reaction rates. This scaling temperature is not necessarily the mean temperature of the OH losses, but includes also the shift in the reaction-weighted mean OH as a function of reaction rate (see Section 2 and Table 2). The optimal temperature for scaling the lifetimes is 277 K, and the resulting errors are less than 2% over the range 800 K < B < 2300 K. Use of a temperature 10 K warmer or colder yields errors in the lifetime of order 10% when scaling the reference case (B = 1700 K) to greater (2300 K) or smaller (1000 K) activation energies.

b. Sensitivity to interhemispheric gradient

HCFCs released predominantly from industrialized countries in the northern mid-latitudes will establish a global distribution similar to that for CFCs (see Prather et al., 1987). The north-to-south latitudinal gradient will have an interhemispheric absolute difference about equal to one year's emissions, and higher concentrations will build up over the presumed continental sources at mid-latitudes. The sensitivity of HCFC lifetimes to their interhemispheric gradient will depend on hemispheric asymmetries in the OH fields (and temperatures in so far as they affect the rate coefficients). The base case described above assumes a uniformly distributed tracer with OH reaction rates appropriate for CH<sub>4</sub>, and the perturbed case includes doubling the abundance in either hemisphere uniformly. Results are shown in Table 4b. For a factor of 2 asymmetry in the HCFC distribution, the lifetime changes by only 1.5%. Thus the effective OH loss is about 9% greater in the northern hemisphere. Spivakovsky et al. (1989) note that the higher concentrations of CO in the northern hemisphere (reducing OH) are more than offset by the higher levels of O<sub>3</sub> and NO<sub>x</sub>.



**Table 4.** Lifetime for species x against tropospheric OHa. Sensitivity to rate coefficient  $k(\text{OH} + \text{X}) = A/\exp(-B/T)$ 

<u>A (cm<sup>3</sup> s<sup>-1</sup>)</u>	<u>B (K)</u>	<u>lifetime (yr)</u>
2.3E-12	2300	81.2
2.3E-12	2000	27.7
2.3E-12	1700	9.42
2.3E-12	1500	4.58
2.3E-12	1100	1.08
2.3E-12	500	.120
2.3E-12	0	.019

## b. Sensitivity to interhemispheric ratio

<u>NH:SH</u>	<u>lifetime (yr)</u>
2:1	9.28
1:1	9.42
1:2	9.57

## c. Sensitivity to boundary layer enhancements

<u>enhancement</u>	<u>lifetime (yr)</u>
none	9.42
+ 10% (global)	9.33
+ 10% (global, land)	9.35
+ 10% (> 30°N)	9.42
+ 10% (> 30°N, land)	9.41
+ 100% (> 30°N)	9.37
+ 100% (> 30°N, land)	9.33

## d. Sensitivity to seasonal cycle

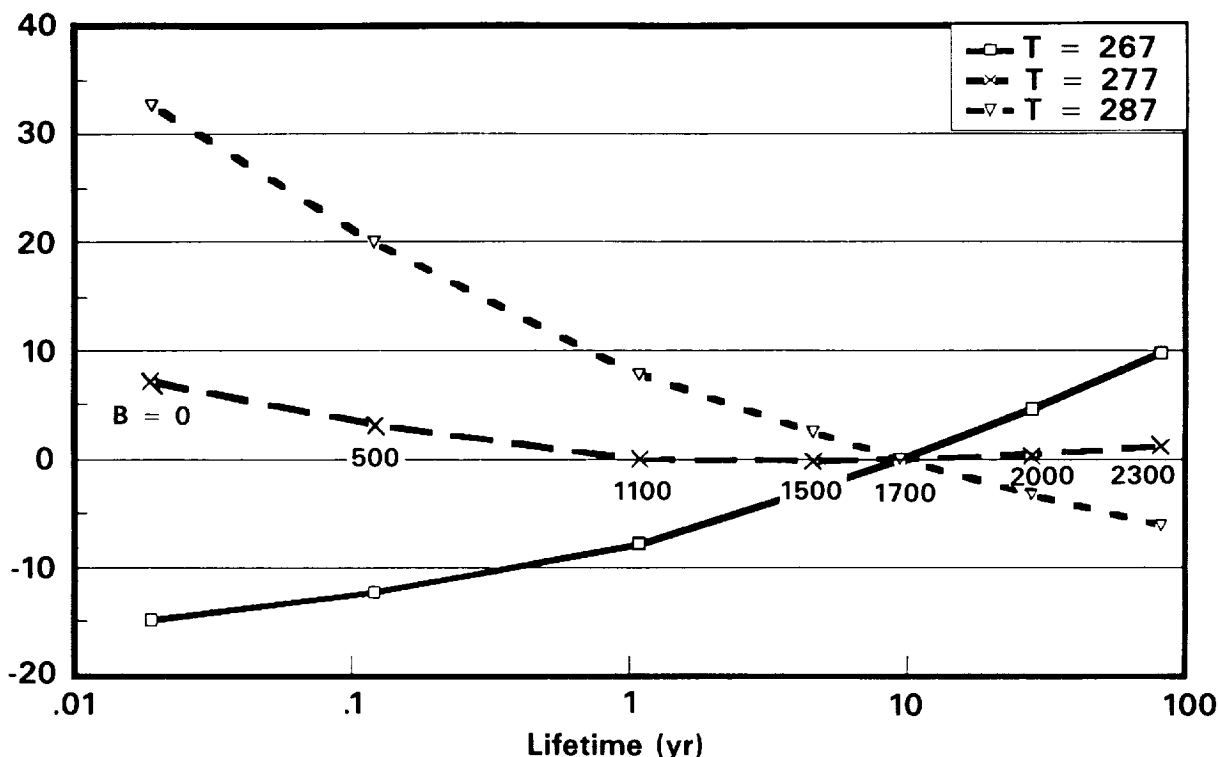
<u>amplitude</u>	<u>lifetime (yr)</u>
none	9.42
± 1%	9.43
± 10%	9.52
± 50%	9.97

Except where noted X has a uniform mixing ratio throughout the troposphere and stratosphere, but no loss in the stratosphere. Default values are  $k(\text{OH} + \text{X}) = 2.3 \times 10^{-12} \exp(-1700/T)$ , boundary layer defined as 984-850 mbar, and no seasonal cycle.

The assumed seasonal cycle is: positive in winter, (DJF > 30°N) & (JJA < 30°S), negative in summer, (JJA > 30°N) & (DJF < 30°S).

TROPOSPHERIC HYDROXYL

% ERROR BY SCALING:  $k = A \exp(-B/T)$



**Figure 1.** Error (%) in predicting HCFC lifetimes by scaling the rate coefficient for reaction with OH. The lifetime against OH destruction is calculated by integrating the 4-D fields of OH and T with a rate coefficient  $k = 2.3E-12 \exp(-B/T)$  and a uniformly distributed tracer. The reference case is chosen to be  $B = 1700$  K with a lifetime of 9.42 yr. A range of values for B from 0 K to 2300 K is considered (see Table 4a, noted on graph). Three different effective temperatures (267 K, 277 K and 287 K) have been chosen to predict a lifetimes by scaling the "known" result for  $B = 1700$  K. Minimum error occurs for  $T = 277$  K.

c. Sensitivity to enhancement in the boundary layer

Enhanced abundances of  $CFCl_3$  and  $CF_2Cl_2$  are both observed and predicted in the lower troposphere over much of the northern mid-latitudes, especially near continental sources. A similar buildup of HCFCs would be expected. We examine the sensitivity of HCFC lifetimes to boundary layer enhancements in the lowest 1.5 km for several assumptions: northward of  $30^\circ N$ , globally, over land, or over land and ocean. The reference case is that with methane kinetic rates as above. The net effect of boundary layer enhancements, as shown in Table 4c, is negligible ( $< 1\%$ ) if they are less than 100% and are restricted to the northern mid-latitudes as expected. If there were a globally uniform source, and hence accumulation in the boundary layer over the tropics also, then a +10% enhancement in the lowest 1.5 km would increase losses and reduce the lifetime by at most 1%.

d. Sensitivity to seasonal cycles

Seasonal variations in the concentrations of a gas should be included when calculating the OH losses. In most cases the seasonal cycle is driven by the corresponding variations in OH, and, thus, the lowest

concentrations of the trace gas occur slightly after the greatest OH levels (i.e., late summer). This anticorrelation of OH and trace gas increases the lifetime of the gas relative to that calculated with a fixed concentration. As shown in Table 4d, this effect is negligible ( $<0.2\%$ ) for a gas like  $\text{CH}_4$  with a lifetime of about 9 yr and an observed seasonal amplitude of  $\pm 1.5\%$ . Since large seasonal variations occur only in short-lived species, we would not expect the seasonal amplitude for an HCFC to exceed  $\pm 10\%$  (corresponding to a 1% increase in lifetime) unless the lifetime were very short, less than 1.5 yr. The seasonal effect is so small because the majority of OH loss occurs in the tropics, as noted above, where OH concentrations do not vary significantly with season.

In summary, a short-lived HCFC with a lifetime of about 0.5 yr might be expected to have a seasonal amplitude of  $\pm 25\%$  (lifetime correction:  $+2.5\%$ ), a north:south interhemispheric ratio of 2:1 (lifetime correction:  $-1.5\%$ ), and a boundary layer enhancement north of  $30^\circ\text{N}$  over land of 100% (lifetime correction:  $-1\%$ ). The sum of these corrections tend to cancel, or be very small, and thus the lifetime predicted from a uniform distribution should be a reasonably accurate,  $\pm 10\%$ , evaluation of the true lifetime.

## 5. SUMMARY OF HCFC LIFETIMES

The lifetimes of HCFCs and other hydrohalocarbons are reported in Table 5. These lifetimes are calculated directly from the tropospheric OH fields using the recommended rate coefficients (Hampson, Kurylo and Sander, AFEAS, 1989) and a fixed, uniform distribution of trace gas (labelled TROP-OH). They have been augmented (labelled TOTAL) with much smaller stratospheric losses that include estimated destruction by OH and photolysis. Stratospheric OH loss is scaled by rate coefficients at a temperature of 250 K to an assumed methane (stratosphere only) loss rate of  $1/160 \text{ yr}^{-1}$ ; stratospheric photolysis is assumed only for species with a  $-\text{CCl}_3$  group ( $1/60 \text{ yr}^{-1}$ ) or a  $-\text{CCl}_2$  group ( $1/120 \text{ yr}^{-1}$ ) and is based on the lifetimes of  $\text{CFCl}_3$  and  $\text{CF}_2\text{Cl}_2$ . An additional column of lifetimes in Table 5 (labelled SCALED) has been calculated by ratioing the rate coefficients (scaling temperature of 227 K) and multiplying by the methyl chloroform lifetime of 6.3 yr. As expected from the analyses in this report the two approaches agree very well.

An attempt has been made to estimate uncertainty factors for HCFC lifetimes in the same manner as in the kinetics reviews. We identify the uncertainty in the reaction rate of 277 K and then multiply by the estimated uncertainty factor for the OH fields (1.3). The uncertainty associated with a non-uniform distribution is significant only for HCFCs with lifetimes less than 1 yr, and has been increased. The final uncertainty quoted in Table 5 is representative of the likely range, but cannot be treated as a formal statistical error.

Although the ALE/GAGE analysis of the total atmospheric residence time for  $\text{CH}_3\text{CCl}_3$  agrees with the chemical model's lifetime for destruction by OH, the combined uncertainties in the two lifetimes cannot rule out another sink, such as hydrolysis (Wine and Chameides, AFEAS, 1989), with a lifetime as short as 25 yr.

There is a clear need for other trace species that can be used to test the tropospheric abundance of OH. Such species must have accurate histories of emissions and good, absolutely calibrated measurements. In situ atmospheric tests of the kinetic model for OH should possibly focus on the tropical middle troposphere where most of the destruction of HCFCs will occur.

## TROPOSPHERIC HYDROXYL

**Table 5.** Atmospheric Lifetimes for the HCFCs & other Halocarbons

species	A	B	LIFETIME (yr)		uncertainty		(CFC)
			TROP-OH	TOTAL	SCALED	f	
CH <sub>3</sub> F	5.4E-12	1700	4.0	3.8	4.1	1.8	
CH <sub>2</sub> F <sub>2</sub>	2.5E-12	1650	7.2	6.8	7.3	1.7	
CHF <sub>3</sub>	7.4E-13	2350	302.	289.	310.	2.3	
CH <sub>2</sub> FCI	3.0E-12	1250	1.42	1.33	1.44	1.8	
CHFCI <sub>2</sub> *	1.2E-12	1100	2.10	1.89	2.10	1.6	
CHF <sub>2</sub> CI	1.2E-12	1650	15.1	14.2	15.3	1.6	(22)
CH <sub>3</sub> CH <sub>2</sub> F	1.3E-11	1200	0.27	0.25	0.28	5.	
CH <sub>2</sub> FCH <sub>2</sub> F	1.7E-11	1500	0.62	0.58	0.63	5.	
CH <sub>3</sub> CHF <sub>2</sub>	1.5E-12	1100	1.65	1.53	1.68	1.8	(152a)
CH <sub>2</sub> FCHF <sub>2</sub>	2.8E-12	1500	3.76	3.54	3.81	3.	
CH <sub>3</sub> CF <sub>3</sub>	2.6E-13	1500	40.5	38.1	41.	3.	
CHF <sub>2</sub> CHF <sub>2</sub>	8.7E-13	1500	12.1	11.4	12.3	3.	
CH <sub>2</sub> FCF <sub>3</sub>	1.7E-12	1750	15.3	14.4	15.5	1.8	(134a)
CHF <sub>2</sub> CF <sub>3</sub>	3.8E-13	1500	27.7	26.1	28.1	3.	(125)
CH <sub>3</sub> CFCl <sub>2</sub> *	2.7E-13	1050	7.6	6.7	7.8	1.7	(141b)
CH <sub>3</sub> CF <sub>2</sub> CI	9.6E-13	1650	18.8	17.8	19.1	1.7	(142b)
CH <sub>2</sub> CICF <sub>2</sub> CI	3.6E-12	1600	4.2	4.0	4.2	3.	
CH <sub>2</sub> CICF <sub>3</sub>	5.2E-13	1100	4.7	4.4	4.8	1.8	
CHCl <sub>2</sub> CF <sub>3</sub> *	6.4E-13	850	1.55	1.42	1.59	2.0	(123)
CHFCICF <sub>3</sub>	6.6E-13	1250	6.5	6.0	6.6	1.8	(124)
CH <sub>4</sub>	2.3E-12	1700	9.4	8.9	9.6		
CH <sub>3</sub> CI	1.7E-12	1100	1.45	1.35	1.48		
CH <sub>3</sub> Br	6.0E-13	820	1.48	1.37	1.53		
CH <sub>3</sub> CCl <sub>3</sub> **	5.0E-12	1800	6.2	5.4	6.3		

Rate coefficients are in units of  $\text{cm}^3 \text{s}^{-1}$ ,  $k = A \exp(-B/T)$ .

TROP-OH lifetimes include only the integrated loss with respect to OH in the troposphere. TOTAL lifetimes include the small additional losses estimated to occur in the stratosphere as described below. SCALED lifetimes are keyed to the CH<sub>3</sub>CCl<sub>3</sub> lifetime of 6.3 yr (Prinn et al., 1987) and the ratio of the rate constants at 277 K.

Species marked (\*) with 2 Cl's on one C are assumed to have a lifetime of 120 yr with respect to stratospheric photolysis; methyl chloroform (\*\*) is assumed to have a stratospheric lifetime of 60 yr due to photolysis. Stratospheric loss due to reaction with OH is scaled to the CH<sub>4</sub> stratospheric lifetime (160 yr) and rate coefficient at 250 K.

The lifetime uncertainty factor (f) is assumed here to be the product of the kinetic factor (at 277 K), the uncertainty in the OH fields (1.3), and an additional uncertainty factor for HCFCs with short lifetimes.

## VI. DEGRADATION MECHANISMS

Combined Summary and Conclusions

Fluorine-Containing Products in Atmospheric Degradation Table

*Tropospheric Reactions of the Haloalkyl Radicals Formed from Hydroxyl Radical Reaction with a Series of Alternative Fluorocarbons*

**Roger Atkinson**  
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*Degradation Mechanisms of Selected Hydrochlorofluorocarbons in the Atmosphere: An Assessment of Current Knowledge*

**Richard A. Cox**  
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DIDCOT, Oxfordshire, United Kingdom  
and  
**Robert Lesclaux**  
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*An Assessment of Potential Degradation Products in the Gas-Phase Reactions of Alternative Fluorocarbons in the Troposphere*

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*Atmospheric Degradation Mechanisms of Hydrogen Containing Chlorofluorocarbons (HCFC) and Fluorocarbons (HFC)*

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**COMBINED SUMMARY AND CONCLUSIONS**

Tropospheric reaction with the OH radical is the major and rate determining loss process for the HFCs and HCFCs in the atmosphere.

There are virtually no experimental data available concerning the subsequent reactions occurring in the atmospheric degradation of these molecules. By consideration of data for degradation of alkanes and chloroalkanes it is possible to postulate the reaction mechanisms and products formed in the troposphere from HCFC and HFCs. However, the results are subject to large qualitative and quantitative uncertainty, and may even be incorrect.

The current level of support for laboratory work is inadequate to enable significant improvement in the state of knowledge in this area in the near future.

Using the above mentioned analysis, a large variety of chlorine and fluorine containing intermediate products such as hydroperoxides, peroxy nitrates, carbonyl halides, aldehydes and acids can be expected from the degradation of the 8 proposed CFC substitutes. These are listed in the accompanying Table.

Based on the available knowledge of gas phase chemistry only four of these products appear to be potentially significant carriers of chlorine to the stratosphere. These are  $\text{CClFO}$ ,  $\text{CF}_3\text{CClO}$ ,  $\text{CClF}_2\text{CO}_3\text{NO}_2$  and  $\text{CCl}_2\text{FCO}_3\text{NO}_2$ . However physical renewal processes may reduce this potential. In addition, the possibility of pathways and products not predicted by the arguments-by-analogy are a cause for concern.

A large part of the uncertainty of the mechanistic details of the HCFC oxidation arises from all insufficient knowledge of the thermal stability and reactivity of halogenated alkoxyradicals. In particular, the mechanism of oxidation of the  $\text{CF}_3\text{O}$  radical, which is assumed to produce  $\text{CF}_2\text{O}$ , is not known for atmospheric conditions and needs further study.

Particular attention should be paid to obtaining data on the photochemistry, gas phase reactivity and solubility of the carbonyl, acetyl and formyl halides, in order to assess their removal rates and mechanisms.

Based on current knowledge, the products identified are unlikely to cause significant changes to the effective greenhouse warming potential of the 8 proposed CFC substitutes. This conclusion would be modified if long-lived products such as  $\text{CF}_3\text{H}$  were formed by unidentified pathways.

Laboratory tests and atmospheric measurements are urgently needed to test the validity of the proposed degradation mechanisms for HCFCs and HCFs.

## DEGRADATION MECHANISMS

### Fluorine-Containing Products in the Atmospheric Degradation of Selected Fluorocarbons

Compound	Formula	Atom & Radical	Carbonyl	Acid	Hydroxide	Nitrate
HCFC 123	HCCl <sub>2</sub> CF <sub>3</sub>	CF <sub>3</sub> CCl <sub>2</sub> OO CF <sub>3</sub> CCl <sub>2</sub> O CF <sub>3</sub> OO CF <sub>3</sub> O	CF <sub>3</sub> CClO		CF <sub>3</sub> CCl <sub>2</sub> OOH CF <sub>3</sub> OOH CF <sub>3</sub> OH	CF <sub>3</sub> CCl <sub>2</sub> OONO <sub>2</sub> CF <sub>3</sub> OONO <sub>2</sub> CF <sub>3</sub> ONO <sub>2</sub>
HCFC 141B	CCl <sub>2</sub> FCH <sub>3</sub>	CCl <sub>2</sub> FCH <sub>2</sub> OO CCl <sub>2</sub> FCH <sub>2</sub> O CCl <sub>2</sub> F <sub>2</sub> OO CCl <sub>2</sub> F <sub>2</sub> O CCl <sub>2</sub> FC(O)OO	CCl <sub>2</sub> FCHO  CClFO	  CCl <sub>2</sub> FC(O)OOH CCl <sub>2</sub> FC(O)OH	CCl <sub>2</sub> FCH <sub>2</sub> OOH CCl <sub>2</sub> F <sub>2</sub> OOH	CCl <sub>2</sub> FCH <sub>2</sub> OONO <sub>2</sub> CCl <sub>2</sub> F <sub>2</sub> OONO <sub>2</sub> CCl <sub>2</sub> FC(O)OONO <sub>2</sub>
HCFC 142b	CClF <sub>2</sub> CH <sub>3</sub>	CClF <sub>2</sub> CH <sub>2</sub> OO CClF <sub>2</sub> CH <sub>2</sub> O CClF <sub>2</sub> OO CClF <sub>2</sub> O CClF <sub>2</sub> C(O)OO	CClF <sub>2</sub> CHO  CF <sub>2</sub> O	  CClF <sub>2</sub> (O)OOH CClF <sub>2</sub> C(O)OH	CClF <sub>2</sub> CH <sub>2</sub> OOH CClF <sub>2</sub> OOH	CClF <sub>2</sub> CH <sub>2</sub> OONO <sub>2</sub> CClF <sub>2</sub> OONO <sub>2</sub> CClF <sub>2</sub> C(O)OONO <sub>2</sub>
HCFC 22	CHClF <sub>2</sub>	CClF <sub>2</sub> OO CClF <sub>2</sub> O	CF <sub>2</sub> O		CClF <sub>2</sub> OOH	CClF <sub>2</sub> OONO <sub>2</sub>
HCFC 124	CHClFCF <sub>3</sub>	CF <sub>3</sub> CClFOO CF <sub>3</sub> CClFO CF <sub>3</sub> OO CF <sub>3</sub> O	CF <sub>3</sub> CFO		CF <sub>3</sub> CClFOOH CF <sub>3</sub> OOH CF <sub>3</sub> OH	CF <sub>3</sub> CClFOONO <sub>2</sub> CF <sub>3</sub> OONO <sub>2</sub> CF <sub>3</sub> ONO <sub>2</sub>
HCF 134a	CH <sub>2</sub> FCF <sub>3</sub>	CF <sub>3</sub> CHFOO CF <sub>3</sub> CHFO  CF <sub>3</sub> OO CF <sub>3</sub> O CFO	CHFO CF <sub>3</sub> CHFO		CF <sub>3</sub> CHFOOH CF <sub>3</sub> OOH CF <sub>3</sub> OH CF(O)OOH	CF <sub>3</sub> CHFOONO <sub>2</sub> CF <sub>3</sub> OONO <sub>2</sub> CF <sub>3</sub> ONO <sub>2</sub> CF(O)OONO <sub>2</sub>
HFC 52a	CHF <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub> CF <sub>2</sub> Oo CH <sub>3</sub> CF <sub>2</sub> O CHF <sub>2</sub> CH <sub>2</sub> OO CHF <sub>2</sub> CH <sub>2</sub> O CHF <sub>2</sub> OO CHF <sub>2</sub> O CHF <sub>2</sub> C(O)OO  CFO	CF <sub>2</sub> O  CHF <sub>2</sub> CHO  CHFO	    CHF <sub>2</sub> C(O)OOH CHF <sub>2</sub> C(O)OH CF(O)OOH	CH <sub>3</sub> CF <sub>2</sub> OOH CHF <sub>2</sub> CH <sub>2</sub> OOH CHF <sub>2</sub> OOH	CH <sub>3</sub> CF <sub>2</sub> OONO <sub>2</sub> CHF <sub>2</sub> CH <sub>2</sub> OONO <sub>2</sub> CHF <sub>2</sub> OONO <sub>2</sub> CHF <sub>2</sub> C(O)OONO <sub>2</sub> CF(O)OONO <sub>2</sub>
HCF 125	CHF <sub>2</sub> CF <sub>3</sub>	CF <sub>3</sub> CF <sub>2</sub> OO CF <sub>3</sub> CF <sub>2</sub> O  CF <sub>3</sub> OO CF <sub>3</sub> O	CF <sub>2</sub> O CF <sub>3</sub> CFO		CF <sub>3</sub> CF <sub>2</sub> OOH CF <sub>3</sub> OOH CF <sub>3</sub> OH	CF <sub>3</sub> CF <sub>2</sub> OONO <sub>2</sub> CF <sub>3</sub> OONO <sub>2</sub> CF <sub>3</sub> ONO <sub>2</sub>