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Tropospheric OH and the Lifetimes of Hydrochlorofluorocarbons

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Hydrochlorofluorocarbons (HCFCs) may be used as alternatives for the chlorofluorocarbons (CFCs). Lifetimes for the HCFCs are predicted here in two ways: integrating their loss with a global model, and scaling to another compound with a better known lifetime. Both approaches are shown here to yield similar results. Three-dimensional fields of modeled tropospheric OH concentrations are used to calculate lifetimes against destruction by OH for the HCFCs and other hydrogenated halocarbons. The OH fields are taken from a three-dimensional chemical transport model [*Spivakovsky et al.*, 1990a] 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 effect [*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 [*WMO*, 1990]. 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 abundance in the atmosphere (units: kg) will be controlled by the ratio of emissions (kg yr^{-1}) to atmospheric destruction (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 (kg yr^{-1}).

In this report we derive the lifetime of HCFCs and other hydrogenated halocarbons in two ways. The primary method involves modeling 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 three-dimensional climatology of sunlight, temperature, O_3, H_2O, NO_x, CO, and CH_4 [see *Spivakovsky et al.*, 1990a]. 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 (CH_3CCl_3) in a three-dimensional Chemical Transport Model (CTM). With the CTM, we specified sources, global transport and chemical losses of CH_3CCl_3 in order to simulate the latitudinal and seasonal patterns, and the global trends [*Spivakovsky et al.*, 1990a]. Similar CTM modeling 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.

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 [*Makide and Rowland*, 1981]. The lifetime of methyl chloroform 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 et al.*, 1990], $k(OH+CH_3CCl_3)/k(OH+HCFC)$, to calculate the HCFC lifetime. Possible errors in this approach are associated with the assumed lifetime for CH_3CCl_3, and with the use of a single scaling factor that does not reflect the different spatial distribution of the HCFCs coupled with the variations in OH and rate coefficient. 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 the uncertainties in the derived values are discussed in section 5.

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2. The Chemical Model

The lifetimes calculated here for the HCFCs, as well as for CH_3CCl_3, CH_3Cl, CH_3Br and CH_4, use global distributions of OH from the photochemical model developed for the three-dimensional Chemical Transport Model (CTM) developed at GISS and Harvard. The model for tropospheric OH is based on a one-dimensional 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 [*Spivakovsky et al.*, 1990b]. This parameterized chemistry has been used to calculate a three-dimensional set of mean OH concentrations for the CTM grid over one year. The OH concentrations are averaged over 5-day intervals with a spatial resolution of 8° latitude by 10° longitude and nine vertical layers, i.e., a total of more than 1/2 million values, even at this coarse resolution (see *Prather et al.* [1987] for CTM documentation). 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 (CO, O_3, CH_4, NO_x, H_2O above 500 mbar, and stratospheric ozone column). The observational database for most of these species is insufficient to define the necessary four-dimensional fields, and the model assumes 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.* [1990b] 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 enhance solar ultraviolet light in this region while reducing it in the lower troposphere.

The global loss (L) of a gas that reacts with OH (rate coefficient, k) is the integral over a wide range of conditions in temperature (T), pressure (p) and trace gas abundance (mixing ratio by mass, f)

$$L = \int k(T,p)\, OH(x,y,p)\, f(x,y,p)\, dm \qquad (1)$$

where the mass element dm is proportional to the product of dx (longitude) by dy (latitude) by dp (pressure). Each factor of the integrand varies nonlinearly over the domain, and thus the loss L will not be equal to the product of the averages, a point made by *Makide and Rowland,* [1981]. It is misleading to report a single "global average OH concentration ($\langle OH \rangle$)" without qualifying it as to the averaging kernel ($k\, f\, dm$).

$$\langle OH \rangle = L \,/ \int k(T,p)\, f\, dm \qquad (2)$$

TABLE 1a. Annual Average OH Concentration (10^4 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 (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	225	226	226	225	223	220	217	215	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 four-dimensional fields described in the text.
No values for OH or T are reported for the extratropical stratosphere (above 200 mbar).
At higher pressures over Antarctica the number of points is insufficient to report a zonal average.

Values of <*OH*> calculated here assume a constant *f* and are integrated over the troposphere (*dp* from surface to 100 mbar); they are reported in Table 2 for a variety of integrating kernels. The effective "average" temperature (<*T*>) can be defined by

$$L = <OH>\, k(<T>) \int f\, dm \qquad (3)$$

and thus used to derive a lifetime, $1/<OH>k(<T>)$.

Using a rate coefficient of the form, $k(T) = A\ exp(-B/T)$, the maximum value of <*OH*>, 111 x 10^4 cm^{-3}, corresponds to the largest value of *B*, 2300 K, because the OH densities are maximal at high temperatures in the tropics (see Table 1). The volume-averaged OH density is smallest, 65 x 10^4 cm^{-3}, because the large volumes of low density air in the upper troposphere have low OH concentrations.

3. Global Loss of CH_3CCl_3 and 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 CH_4 and CH_3CCl_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 integrated stratospheric losses are a small fraction of the total for the gases considered here (<10%); they are not explicitly integrated with the tropospheric OH losses, but are included in the net atmospheric lifetimes given here.

The assumed conditions and resulting atmospheric losses of CH_4 and CH_3CCl_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 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 CH_3CCl_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 CH_3CCl_3 with those from the ALE/GAGE analysis and the recent three-dimensional CTM simulations [*Spivakovsky et al.*, 1990a]. The ALE/GAGE analysis uses observations of CH_3CCl_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 CH_3CCl_3 sources from industry surveys [*Midgley*, 1989] and supported further by inferred emissions based on observations [*Prather*, 1988].

When the OH and temperature fields are used in the complete CTM simulation of CH_3CCl_3 [*Spivakovsky et al.*, 1990a] the integrated loss correctly includes all correlations of OH and temperature with variations in CH_3CCl_3 concentrations. The three-dimensional CTM simulation showed that the computed 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 CH_3CCl_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 with the largest seasonal variation and, further, are independent of absolute calibration and sources when the relative (%) changes in CH_3CCl_3 are considered.

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. In one case, *Derwent and Volz-Thomas* [1990] have used carbon monoxide, both ^{14}CO and ^{12}CO, to test and recalibrate the OH fields in their two-dimensional model [*Volz et al.*, 1981]. Another possibility, HCFC-22 (CHF_2Cl) 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 (N/S = 89/77 ppt, +6.5 ppt/yr in 1985, see *NASA/WMO*, [1986]. Furthermore, significant uncertainties

TABLE 2. Global Average OH Concentrations

Integrating Kernel	<OH> (10^4 cm^{-3})	<T> (K)
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 + 0.6p) dm	91	
dz	65	

The global average <OH> is integrated over mass (dm, from the surface to 100 mbar) with different weighting factors (exponential in temperature or linear in pressure) and over volume (dz). The effective temperature <T> giving the correct global integral is defined in the text.

TABLE 3. Global Budgets for CH_4 and CH_3CCl_3

	CH_4	CH_3CCl_3
Rate coefficient k(X+OH)	$2.3x10^{-12}e^{-1700/T}$	$5.0x10^{-12}e^{-1800/T}$
Concentration		
NH (<28°/>28°)	1700 ppb	140/150 ppt
SH	1600 ppb	110 ppt
Atmospheric content	4580 x 10^{12}g	2930 x 10^9g
Atmospheric losses		
total	524 x 10^{12}g	534 x 10^9g
tropics (2-6 km)	270 x 10^{12}g	260 x 10^9g
stratosphere	29 x 10^{12}g	53 x 10^9g
Lifetime	8.7 yr	5.5 yr

Budgets based on integration of four-dimensional tropospheric OH fields with zonally fixed, nonseasonal distributions as noted. Stratospheric profiles and losses are included.

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. MacFarland, personal communication, 1989) 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 in the integrated OH fields is estimated to be ±25 %, and we choose to apply an uncertainty factor of 1.3 to the lifetimes for HCFCs in section 5.

4. Sensitivity of HCFC Lifetime to Global Distribution

We use the four-dimensional 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 (1) the temperature dependence of their reaction rates with OH; (2) large interhemispheric gradients; (3) enhanced concentrations in the boundary layer near sources; and (4) seasonal cycles in concentration.

4.1. *Sensitivity to Rate Coefficient: k = A 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(OH+X)/k(OH+Y) = 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_4 rate, k = 2.3E-12 exp(-B/T) cm^3 s^{-1}, and stratospheric losses were not included.

The lifetimes for values of B ranging from 0 K to 2300 K are given in Table 4a. 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 T_{scal} in the ratio of reaction rates. This scaling temperature should not be equal to the effective temperature $\langle T \rangle$ defined in section 2, because the scaling of lifetimes must also include the shift in $\langle OH \rangle$ as a function of reaction rate (see Table 2). The optimal T_{scal} 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 of about 10% when scaling the reference case (B = 1700 K) to greater (2300 K) or smaller (1000 K) activation energies.

4.2. *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 [*Prather et al.*, 1987]. In the tropics the absolute north-to-south difference will be equal to about one year's emissions averaged over the globe. At mid-latitudes higher concentrations will build up over the presumed continental sources. 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_4, and the perturbed cases include 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%. One can derive that the effective OH loss is about 9% greater

TABLE 4a. Lifetime for Species X Against Tropospheric OH: Sensitivity to Rate Coefficient k(OH+X) = A exp(-B/T)

A (cm^3 s^{-1})	B (K)	Lifetime (yr)
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

Except where noted, X has a uniform mixing ratio throughout the troposphere and stratosphere, but no loss in the stratosphere. Default values are k(OH+X) = 2.3 x 10^{-12} exp(-1700/T) and no seasonal cycle. The boundary layer is defined as 984-850 mbar. The assumed seasonal cycle is: positive in winter, (DJF >30°N) and (JJA <30°S), negative in summer, (JJA >30°N) and (DJF <30°S).

TABLE 4b. Lifetime for Species X Against Tropospheric OH: Sensitivity to Interhemispheric Ratio

NH:SH	Lifetime (yr)
2:1	9.28
1:1	9.42
1:2	9.57

TABLE 4c. Lifetime for Species X Against Tropospheric OH: Sensitivity to Boundary Layer Enhancements

Enhancement	Lifetime (yr)
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

TABLE 4d. Lifetime for Species X Against Tropospheric OH: Sensitivity to Seasonal Cycle

Amplitude	Lifetime (yr)
none	9.42
± 1 %	9.43
±10 %	9.52
±50 %	9.97

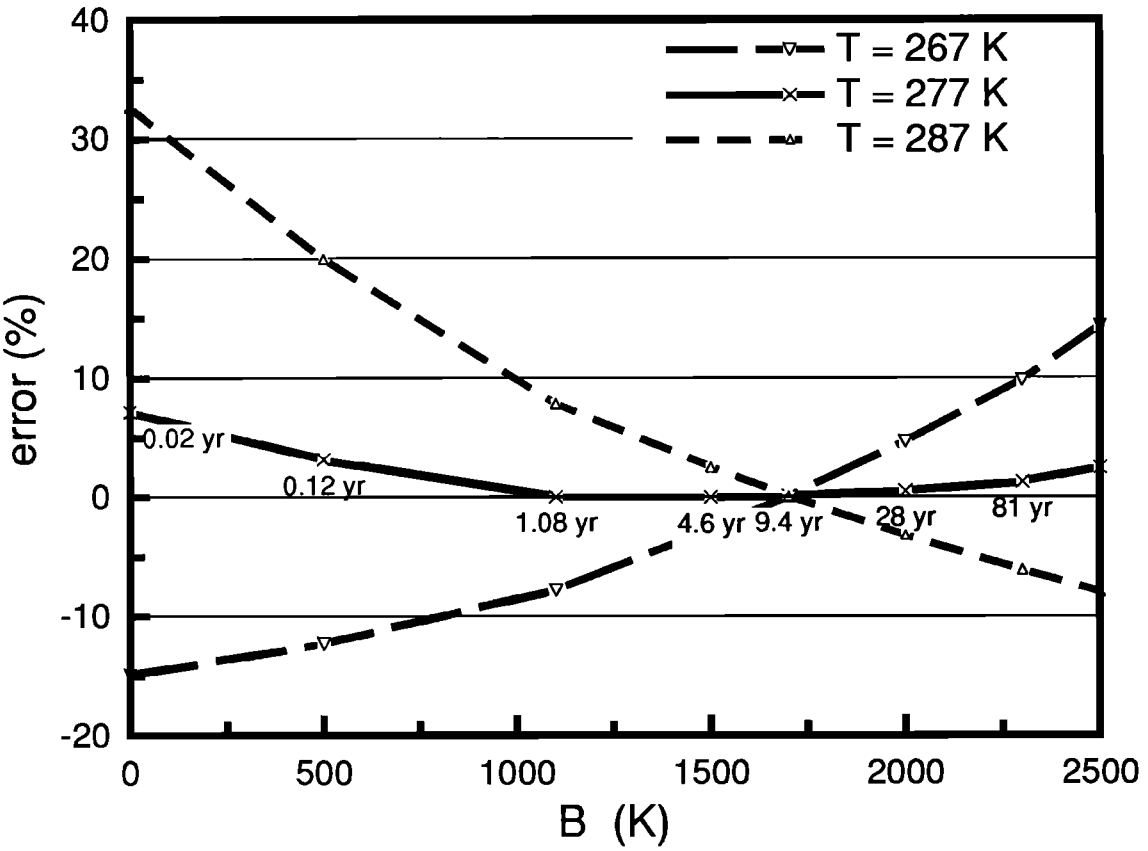

Fig. 1. Error (%) in predicting HCFC lifetimes by scaling the rate coefficient for reaction with OH. The lifetime against OH destruction is calculated by integrating the four-dimensional fields of OH and T with a rate coefficient k = 2.3E-12 exp(-B/T) and a uniformly distributed tracer. The reference case is chosen to be B = 1700 K (lifetime = 9.42 yr). Lifetimes for different values of B are noted on graph. Three different scaling temperatures (267 K, 277 K, and 287 K) have been chosen to predict the lifetimes by scaling the "known" result for B = 1700 K.

in the northern hemisphere. *Spivakovsky et al.* [1990a] note that the higher concentrations of CO in the northern hemisphere (reducing OH) are more than offset by the higher levels of O_3 and NO_x.

4.3. *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°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%.

4.4. *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 CH_4 with a lifetime of about 9 yr and an observed seasonal amplitude of ±1.5%. Since large seasonal variations occur only in short-lived species, we would not expect the seasonal amplitude for an HCFC to exceed ±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 about 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°N over land of 100% (lifetime correction: -1%). The sum of these corrections tends to cancel, or be very small, and thus the lifetime predicted from a uniform distribution should be an accurate evaluation of the true lifetime to within 10%.

5. SUMMARY OF HCFC LIFETIMES

The lifetimes for HCFCs and other hydrohalocarbons are reported in Table 5. These lifetimes are calculated directly

TABLE 5. Atmospheric Lifetimes for the HCFCs and Other Halocarbons

Species	(CFC)	A	B	Lifetime (yr)			Uncertainty
				Trop-OH	Total	Scaled	f
CH_3F		5.4e-12	1700	4.0	3.8	4.1	1.8
CH_2F2		2.5e-12	1650	7.2	6.8	7.3	1.7
CHF_3		1.5e-12	2650	434.	418.	452.	2.3
CH_2FCl		3.0e-12	1250	1.42	1.33	1.44	1.8
$CHFCl_2$*		1.2e-12	1100	2.10	1.89	2.10	1.6
CHF_2Cl	(22)	1.2e-12	1650	15.1	14.2	15.3	1.6
CH_3CH_2F		1.3e-11	1200	0.27	0.25	0.28	5.
CH_2FCH_2F		1.7e-11	1500	0.62	0.58	0.63	5.
CH_3CHF_2	(152a)	1.5e-12	1100	1.65	1.53	1.68	1.8
CH_2FCHF_2		2.8e-12	1500	3.76	3.54	3.81	3.
CH_3CF_3		6.0e-13	1750	43.2	40.9	44.	3.
CHF_2CHF_2		8.7e-13	1500	12.1	11.4	12.3	3.
CH_2FCF_3	(134a)	1.7e-12	1750	15.3	14.4	15.5	1.8
CHF_2CF_3	(125)	8.9e-13	1750	29.1	27.6	30.	3.
CH_3CFCl_2*	(141b)	4.2e-13	1200	8.5	7.4	8.6	1.7
CH_3CF_2Cl	(142b)	9.6e-13	1650	18.8	17.8	19.1	1.7
CH_2ClCF_2Cl		3.6e-12	1600	4.2	4.0	4.2	3.
CH_2ClCF_3		5.2e-13	1100	4.7	4.4	4.8	1.8
$CHCl_2CF_3$*	(123)	6.4e-13	850	1.55	1.42	1.59	2.0
$CHFClCF_3$	(124)	6.6e-13	1250	6.5	6.0	6.6	1.8
CH_4		2.3e-12	1700	9.4	8.9	9.6	
CH_3Cl		1.7e-12	1100	1.45	1.35	1.48	
CH_3Br		6.0e-13	820	1.48	1.37	1.53	
CH_3CCl_3**		5.0e-12	1800	6.2	5.4	6.3	

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

The trop-OH lifetimes include only the integrated loss with respect to OH in the troposphere. The total lifetimes include the small additional losses estimated to occur in the stratosphere as described below. The scaled lifetimes are keyed to the CH_3CCl_3 lifetime of 6.3 yr [*Prinn et al.*, 1987] and the ratio of the rate constants at 277 K.

Species marked (*) with two chlorine atoms on the same carbon 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_4 stratospheric lifetime (160 yr) and rate coefficient at 250 K. Stratospheric loss due to $O(^1D)$ ($<1/200\ yr^{-1}$) is not included.

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.

from the tropospheric OH fields using the recommended rate coefficients [*Hampson et al.*, 1990] and a fixed, uniform distribution of trace gas (labeled TROP-OH). They have been augmented (labeled 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 $1/160\ yr^{-1}$; stratospheric photolysis is assumed to be important only for species with a $-CCl_3$ group ($1/60\ yr^{-1}$) or a $-CCl_2$ group ($1/120\ yr^{-1}$) and is based on the lifetimes of $CFCl_3$ and CF_2Cl_2. Stratospheric loss due to reaction with $O(^1D)$ has not been included, but is constrained to be very small ($<1/200\ yr^{-1}$) because of the limited abundance of $O(^1D)$. An additional column of lifetimes in Table 5 (labeled SCALED) has been calculated by taking the ratio of the rate coefficients (scaling temperature of 277 K) and multiplying by the methyl chloroform lifetime of 6.3 yr. As expected from the analyses in this report the two approaches agree well.

An attempt has been made to estimate uncertainty factors for HCFC lifetimes in the same manner as in the recent JPL kinetics reviews [*DeMore et al.*, 1987]. We identify the uncertainty in the reaction rate at 277 K and then multiply by the estimated uncertainty factor for the OH fields (1.3). The uncertainty associated with a nonuniform distribution is significant only for HCFCs with lifetimes less than 1 yr, and the corresponding uncertainty factors have 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 CH_3CCl_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*, 1990], 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.

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