

Chapter 4.

Laboratory Studies of Halocarbon Loss Processes

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Chapter 4

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Chapter 4: Laboratory Studies of Halocarbon Loss Processes

4.0 Summary

- Improved laboratory data have been obtained from reactions of OH with 14 different halocarbons. The most significant changes were those in reactions with HCFC-141b (CH_3CFCl_2), HCFC-142b ($\text{CH}_3\text{CF}_2\text{Cl}$), HFC-125 (CHF_2CF_3) and HFC-143a (CH_3CF_3). The largest change in rate constant at atmospheric temperatures is a decrease of about 30% for HCFC-141b.
- New evaluations of reaction rates of $\text{O}(^1\text{D})$ with 8 different halocarbons were obtained. The branching ratios for the quenching of $\text{O}(^1\text{D})$ to $\text{O}(^3\text{P})$ were also obtained. In addition, reaction rates of Cl (chlorine) with 18 different halocarbons were measured and the rates of reactions of NO_3 (nitrogen trioxide) with various halocarbons were found to be very slow (room temperature rates slower than $3 \times 10^{-18} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$).
- Absorption cross sections (including temperature dependence) were re-evaluated for CFC-11, CFC-12, CFC-113, CFC-114 ($\text{CClF}_2\text{CClF}_2$), CFC-115 (CClF_2CF_3) and the halons. Hydrolysis rates and Henry's Law constants for methyl chloroform and carbon tetrachloride have been reviewed in the context of recent data.

4.1 Introduction

The determination and interpretation of the atmospheric lifetimes of halocarbons both by inference from observed tropospheric trends and by calculation from atmospheric models requires a quantitative understanding of the important chemical and physical loss processes. This chapter contains a critical evaluation of laboratory data relevant to halocarbon loss processes in the atmosphere. The scope of the review includes the gas phase reactions of halocarbons with OH, O(¹D) and Cl, photolysis of selected halocarbons, and heterogeneous loss (dissolution and hydrolysis) of methylchloroform (CH₃CCl₃) and carbon tetrachloride (CCl₄). The specific contents of the review are discussed below.

The predominant loss process for hydrohalocarbons is by reaction with OH radicals in the troposphere. Because of the need to determine the degradation rates of HFCs and HCFCs in the troposphere and to calculate accurately their ozone depletion potentials (ODPs), a large body of new work has appeared on OH reactions with these species. For this review, the data base for the reaction of OH radicals with 14 important HFCs and HCFCs was updated, and temperature dependent rate coefficients were evaluated.

Reactions of O(¹D) with HFCs and HCFCs are unimportant in the troposphere, but may be important in the stratosphere for certain compounds. In this review, new rate constants for O(¹D) with 8 halocarbons as well as the branching ratio for quenching of O(¹D) to O(³P) by the halocarbon are given. Other possible gas phase chemical destruction mechanisms for CFC substitutes include reaction with Cl and NO₃, although both processes are probably unimportant in the atmosphere compared to the reactions mentioned above. Recommendations for Cl reactions with 18 halocarbons are presented here.

CFCs, HFCs and HCFCs display continuous absorption in the 175-250 nm spectral region making photolysis of the compounds an important destruction process only in the stratosphere. The absorption spectra of halons extend to wavelengths longer than 300 nm, and they can therefore be photodissociated in the troposphere. In this review, UV absorption cross sections and their temperature dependences are given for CFCs 11, 12, 113, 114, 115 and halons 1202, 1211, 1301 and 2402. Lyman-α (121.6 nm) cross sections are given for CFCs 13, 114 and 115.

To assess the heterogeneous loss of CH₃CCl₃ and CCl₄, hydrolysis rates and Henry's Law constants are evaluated.

4.2 Reactions of OH with HFCs and HCFCs

There have been several recent reviews of rate constants for the reactions of OH with HFCs and HCFCs under atmospheric conditions. The most recent include a comprehensive assessment as part of the Alternative Fluorocarbon Environmental Acceptability Study (AFEAS, 1989), and periodic reviews by the NASA Panel for Data Evaluation (DeMore *et al.* [1990, 1992]) and the IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry (Atkinson *et al.* [1989, 1992]). Because of the importance of these reactions in the assessment of the environmental impact of fluorocarbon substitutes, there have been many new studies of OH reaction rates in the last few years and considerable progress has been made in extending the rate constant data base over a wide temperature range. This section updates the work on OH reactions and provides a critical review of a subset of the data base with recommendations for rate constants to be used in atmospheric modelling.

Since the publication of the AFEAS (1989) and DeMore *et al.* (1990) reviews, several new studies have been published or submitted for publication. These include the work of Nelson *et al.* (1990), DeMore (1992), Finlayson-Pitts *et al.* (1992) and Talukdar *et al.* (1992) on methyl chloroform, Talukdar *et al.* (1991) on HFC-32, HFC-125, HCFC-141b and HFC-143a, Zhang *et al.* (1991) on HCFC-225ca and HCFC-225cb, Zhang *et al.* (1992) on HCFC-141b, HCFC-142b and HFC-134a, Nelson *et al.* (1992) on HCFC-225ca, HCFC-225cb and HCFC-243cc, DeMore (1993) on HFC-125, HFC-134a and HFC-152a and Nielsen (1991) on HFC-152a. This new work has significantly enlarged the kinetic data base on OH reactions with CFC replacements. In addition, the first results have been reported on three new C₃ HCFC compounds, namely, HCFC-225ca, HCFC-225cb and HCFC-243cc.

A detailed discussion of the sources of experimental uncertainty in the measurement of rate parameters of the reactions of OH with HFCs and HCFCs is beyond the scope of this review. For this information the reader should consult several of the referenced experimental papers including Gierczak *et al.* (1991), Zhang *et al.* (1992) and Wayne *et al.* (1992). With the exception of the studies of Nelson *et al.* (1990) and DeMore (1992,1993), the reactions considered here were investigated by measuring the first-order loss of OH in the presence of a large excess of the compound of interest. For reactions whose bimolecular rate constants are less than about $10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, measurements of the OH decay rate can lead to an overestimation of the rate constant unless extreme care is taken to exclude interferences from faster secondary reactions of OH, such as with impurities or with reaction products arising from the initial OH attack. While problems associated with interfering reactions are sometimes difficult to detect, they often manifest themselves in one of several ways. For example, the rate constants for such faster reactions generally have smaller temperature dependencies than that of the primary reaction being studied. Hence, appreciable interference due to them can be seen as a non-linearity (upward curvature at low temperatures) in an Arrhenius plot. In addition, the contribution of secondary reaction interferences associated with reaction products is dependent on the initial radical concentration. These contributions can therefore be assessed by measuring changes in the observed rate constant at different initial OH concentrations and can be eliminated by performing experiments at extremely low OH concentrations. Wayne *et al.* (1992) have also highlighted the possible role of bimolecular wall reactions in studies carried out in discharge flow reactors. As discussed in AFEAS (1989), certain early studies such as those of Clyne and Holt (1979a,b) may have suffered from interferences and were therefore not considered in the evaluation.

In the studies by Nelson *et al.* (1990) and DeMore (1992a,b), a relative rate technique was used in which OH is allowed to react with both the compound of interest and a reference compound such as CH_3Cl or CH_4 in a steady-state photolysis reactor. Rate constants are determined relative to the reference compound by measuring the relative disappearance rates of the compound and the reference. This method is insensitive to the presence of impurity hydrocarbons and secondary reactions of OH, provided that the only loss pathway for the compound and the reference is by the initial OH attack. In addition, uncertainties in the absolute rate constant for the reference reaction factor into the final uncertainty for the OH rate constant obtained using this method.

In this review, Arrhenius parameters were derived from plots of $\ln k$ vs. $1/T$ for data below 400 K (Table 4.2-1). It was found that the evaluated data base showed linear Arrhenius behavior for all but three compounds: HFC-32, HCFC-123 and HFC-134a. For these compounds, the preferred Arrhenius parameters were derived by ignoring the data below room temperature. Changes to the data base since the publication of AFEAS (1989) and DeMore *et al.* (1990) have resulted in significant changes to the recommendations for the OH reactions with three compounds: HCFC-141b, HCFC-142b and HFC-143a. Of these, the most significant change is for HCFC-141b where the recommended rate constant at 277 K (the weighted mean tropospheric temperature) has decreased by nearly 30%. Improvements in the purity of the available fluorocarbon samples and in the detection sensitivity of the kinetic apparatus are primarily responsible for these changes. The recommended values for k_{298} that appear in Table 4.2-1 were derived from the temperature dependence expressions in all cases. This approach differs slightly from that used in the AFEAS evaluation in which values of k_{298} were obtained from room temperature rate constant measurements and the value of the Arrhenius pre-exponential factor was adjusted to fit the k_{298} value using the activation energy derived from the recommended studies. Uncertainty estimates (corresponding to approximately one standard deviation) on the rate constants presented in the next three tables (Tables 4.2-1, 4.3-1 and 4.4-1) may be calculated using the uncertainty factor on the rate constant at 298 K, $f(298)$, together with the Arrhenius temperature coefficient uncertainty ($\Delta E/R$) according to the formalism adopted by the NASA Panel for Data Evaluation (DeMore *et al.* [1990,1992]). Thus, the uncertainty ($\approx 1\sigma$) factor at any temperature, T , is given by

$$f(T) = f(298) \exp\{(\Delta E/R)(1/T - 1/298)\}.$$

Table 4.2-1. Recommended rate constants and uncertainties for reactions of OH with selected HFCs and HCFCs.

Reactant	Name	$10^{12} \cdot A^1$	$E/R \pm \Delta E/R^2$	$10^{15} \cdot k_{298}^1$	f(298)	Note
CHF ₂ Cl	HCFC-22	1.2	1650 ± 300	4.7	1.3	4.2.1
CH ₂ F ₂	HCFC-32	1.9	1550 ± 300	10	1.3	4.2.2
CHCl ₂ CF ₃	HCFC-123	0.77	900 ± 300	38	1.3	4.2.3
CHFClCF ₃	HCFC-124	0.66	1250 ± 300	10.0	1.3	4.2.4
CHF ₂ CF ₃	HFC-125	0.56	1700 ± 300	1.9	1.3	4.2.5
CH ₂ FCF ₃	HCFC-134a	1.7	1750 ± 300	4.8	1.3	4.2.6
CH ₃ CCl ₃	methyl chloroform	1.8	1550 ± 150	10.0	1.1	4.2.7
CH ₃ CFCl ₂	HCFC-141b	1.3	1600 ± 300	6.0	1.3	4.2.8
CH ₃ CF ₂ Cl	HCFC-142b	1.4	1800 ± 200	3.3	1.2	4.2.9
CH ₃ CF ₃	HFC-143a	1.6	2100 ± 300	1.4	1.3	4.2.10
CH ₃ CHF ₂	HFC-152a	1.5	1100 ± 200	37	1.2	4.2.11
CF ₃ CF ₂ CHCl ₂	HCFC-225ca	1.5	1250 ± 200	23	1.3	4.2.12
CF ₂ ClCF ₂ CHClF	HCFC-225cb	0.55	1250 ± 200	8.3	1.3	4.2.13
CH ₃ CF ₂ CFCl ₂	HCFC-243cc	0.77	1700 ± 300	2.6	2.0	4.2.14

¹ Units are cm³ molecule⁻¹ s⁻¹

² Units are K

Notes

4.2.1 OH + CHF₂Cl. The data base for this reaction is well established and there have been no new data recently. The preferred values are derived from a fit to all data below 400 K except the rate constants of Clyne and Holt (1979b), which have a significantly larger temperature dependence than all the other studies. The unpublished data of Orkin *et al.* (private communication), while not considered, agree well with the recommendation. The recommendation for k_{298} is derived from the Arrhenius line.

4.2.2 OH + CH₂F₂. The temperature dependence of the preferred rate expression is derived from the data of Jeong and Kaufman (1982a), Talukdar *et al.* (1991) below 400 K and the room temperature data of Howard and Evenson (1976a) and Nip *et al.* (1979). The recommendation for k_{298} is derived from the Arrhenius line. Although the data of Clyne and Holt (1979b) are consistent with the data from the other studies, this study is not included in the least squares fit.

4.2.3 OH + CHCl₂CF₃. The preferred rate expression is derived from the temperature dependence data below 400 K of Nielsen (1991), Gierczak *et al.* (1991), Liu *et al.* (1990), Watson *et al.* (1979), and the room temperature data of Howard and Evenson (1976b). The recommended value of k_{298} is derived from the temperature dependence expression. The data of Brown *et al.* (1990a) and Clyne and Holt (1979b) were not considered.

4.2.4 OH + CHFClCF₃. The preferred rate expression is derived from the temperature dependence data of Gierczak *et al.* (1991), Watson *et al.* (1979), and the room temperature data of Howard and Evenson (1976b). The recommended value of k_{298} is derived from the temperature dependence expression.

4.2.5 OH + CHF₂CF₃. The preferred rate expression is derived from the temperature dependence data of Talukdar *et al.* (1991) and the room temperature data of Martin and Paraskevopoulos (1983) and DeMore (1993). Due to the large discrepancy between the room temperature rate constant of Clyne and Holt (1979b) and those of Martin and Paraskevopoulos and Talukdar *et al.*, the Clyne and Holt data were ignored. The data from Brown *et al.* (1990a) were not considered due to the likelihood of impurities. The preferred value of k_{298} is taken from the recommended temperature dependence expression.

4.2.6 OH + CH₂FCF₃. The preferred rate expression was derived from the data of Gierczak *et al.* (1991) above 243 K, Liu *et al.* (1990), the 270 K data of Zhang *et al.* (1992) and the room temperature data of Martin and Paraskevopoulos (1983), and DeMore (1993). The recommended value of k_{298} is obtained from the temperature dependence expression. The data of Jeong *et al.* (1984), Brown *et al.* (1990a), Clyne and Holt (1979b), and Orkin *et al.* (private communication) were not considered.

4.2.7 OH + CH₃CCl₃. The recommendation is based on the absolute rate studies of Talukdar *et al.* (1992) and Finlayson-Pitts *et al.* (1992) and the relative rate study of DeMore (1992) with CH₄ as a reference. The average value of k₂₉₈ from these studies is 35-55% lower than those obtained previously by Watson *et al.* (1977), Chang and Kaufman (1977), and Clyne and Holt (1979a) and 23% lower than the k₂₉₈ value extrapolated from the higher temperature absolute measurements of Nelson *et al.* (1990). The k₂₉₈ values obtained by Jeong and Kaufman (1979) and Kurylo *et al.* (1979) agree reasonably well with the recommended studies but have considerably larger temperature dependences. Talukdar *et al.* (1992) have speculated that the earlier studies may have been affected by impurities, surface decomposition of CH₃CCl₃ and secondary reactions of OH. The relative rate technique used by DeMore (1992) is insensitive to hydrocarbon impurities and yields rate constant ratios which are extremely consistent with those calculated from the absolute values obtained by Talukdar *et al.* (1992) and by Vaghjiani and Ravishankara (1991) for the OH + CH₃CCl₃ and OH + CH₄ reactions, respectively.

4.2.8 OH + CH₃CFCl₂. The preferred rate expression is significantly different from that in AFEAS (1989) and DeMore *et al.* (1990) due to the recent data of Talukdar *et al.* (1991) and Zhang *et al.* (1992). The above two reviews were based on the results of Liu *et al.* (1990) and the preliminary data of Talukdar *et al.* which showed noticeable curvature in the Arrhenius plots. The reaction rate at the lowest temperature, being so slow, is most likely to be affected by impurities and/or secondary reactions. The use of higher-purity samples and improved OH detection sensitivity in the studies of Talukdar *et al.* and Zhang *et al.* resolved the problem of Arrhenius curvature. The new results imply an A-factor which is more consistent with similar H-abstractions by OH. The temperature dependence expression is derived from the data of Zhang *et al.* (1992), Liu *et al.* (1990) at 330 K and above, and the data of Talukdar *et al.* above 253 K. The temperature dependence data of Brown *et al.* (1990a) were not considered because the relatively large rate constants and Arrhenius curvature are suggestive of sample impurities. The recommended value of k₂₉₈ is obtained from the temperature dependence expression.

4.2.9 OH + CH₃CF₂Cl. The recommended rate expression is derived from a fit to the temperature dependence data of Gierczak *et al.* (1991), Liu *et al.* (1990), Watson *et al.* (1977) and Handwerk and Zellner (1978), the 270 K data of Zhang *et al.* (1992) and the room temperature data of Howard and Evenson (1976b), Paraskevopoulos *et al.* (1981). The value of k₂₉₈ was derived from the rate expression. The data from Brown *et al.* (1990a) and Clyne and Holt (1979b) were not considered.

4.2.10 OH + CH₃CF₃. The only temperature dependence data for this reaction are those of Talukdar *et al.* (1991) and Clyne and Holt (1979b). Due to the large discrepancy between the room temperature rate constant of Clyne and Holt (1979b) and that measured by Martin and Paraskevopoulos (1983), and the generally poor agreement between the Clyne and Holt data and that of other workers for several other halomethanes and haloethanes, the Clyne and Holt data were ignored. The recommended rate expression is derived from a fit to the temperature dependence data of Talukdar *et al.* for T ≥ 261 K and the room temperature point of Martin and Paraskevopoulos. The recommended value of k₂₉₈ is derived from the rate expression.

4.2.11 OH + CH₃CHF₂. The preferred rate expression is derived from the temperature dependence data of Nielsen (1991), Gierczak *et al.* (1991), Liu *et al.* (1990) and the room temperature data of Howard and Evenson (1976b), Handwerk and Zellner (1978), and Nip *et al.* (1979). The data of Brown *et al.* (1990a) and Clyne and Holt (1979b) were not considered. The recommended value of k₂₉₈ is obtained from the temperature dependence expression.

4.2.12 OH + CF₃CF₂CHCl₂. The preferred rate expression is derived from the temperature dependence data of Nelson *et al.* (1992) and Zhang *et al.* (1991a). The data of Brown *et al.* (1990b) were ignored. The recommended value of k₂₉₈ is obtained from the temperature dependence expression.

4.2.13 OH + CF₂ClCF₂CHClF. The preferred rate expression is derived from the temperature dependence data of Nelson *et al.* (1992) and Zhang *et al.* (1991a). The recommended value of k₂₉₈ is obtained from the temperature dependence expression.

4.2.14 OH + CH₃CF₂CFCl₂. The preferred rate expression is derived from the temperature dependence data of Nelson *et al.* (1992). The recommended value of k₂₉₈ is obtained from the temperature dependence expression.

4.3 Reactions of O(¹D) with CFCs, HFCs and HCFCs

The rate constants for the reactions of O(¹D) with various CFCs, HFCs and HCFCs that were reported before 1989 have been reviewed in DeMore *et al.* (1990). In that review, the total rate constants for the removal of O(¹D) are recommended and the branching ratios for the quenching of O(¹D) to O(³P) measured by various investigators are listed. Recently, Warren *et al.* (1991) and Ravishankara *et al.* (1993) have studied the reactions of O(¹D) with HCFCs/HFCs and with CFCs, respectively. They directly measured the overall rate constants for the loss of O(¹D),

$k[O(^1D)$ loss], and the branching ratio, ϕ , for the production of $O(^3P)$ in these reactions. These are the only new data on the $O(^1D)$ reactions with CFCs and HCFCs since DeMore *et al.* (1990). The rate coefficients for the loss of the HCFC are calculated from the measured or recommended values of $k[O(^1D)$ loss] and ϕ . The recommended values are listed in Table 4.3-1. It is assumed that these rather fast $O(^1D)$ reactions will not exhibit any temperature dependence and hence the E/R for the overall reactions is taken to be zero. In addition, the branching ratios for the two channels are also assumed to be independent of temperature.

Table 4.3-1. Recommended rate constants and uncertainties for reactions of $O(^1D)$ with selected CFCs and HCFCs. Rate constants are given for $O(^1D)$ loss ($k(O(^1D))$), reaction plus quenching, and fluorocarbon loss (k_X , reaction only).

Reactant	Name	$10^{10} \cdot k(O(^1D))$ $\text{cm}^3 \text{s}^{-1}$	$f(298)$	$10^{10} \cdot k_X$	$f(298)$ $\text{cm}^3 \text{s}^{-1}$	Notes
CFCl_3	CFC-11	2.3	1.2	1.7	1.3	1
CF_2Cl_2	CFC-12	1.4	1.3	1.2	1.4	1
CF_3Cl	CFC-13	0.87	1.3	0.60	1.5	2
CCl_4		3.3	1.2	2.8	1.3	1
CHF_2Cl	HCFC-22	1.0	1.2	0.72	2.0	1
$\text{CFCl}_2\text{CF}_2\text{Cl}$	CFC-113	2.0	2.0	1.5	2.0	2
$\text{CF}_2\text{ClCF}_2\text{Cl}$	CFC-114	1.3	1.3	1.0	1.8	2
$\text{CF}_3\text{CF}_2\text{Cl}$	CFC-115	0.50	1.3	0.15	2.0	2
CF_3CHCl_2	HCFC-123	2.0	1.3	1.6	1.5	2
CF_3CHFCl	HCFC-124	0.86	1.3	0.60	1.5	2
CH_3CFCl_2	HCFC-141b	2.6	1.3	1.8	1.5	2
$\text{CH}_3\text{CF}_2\text{Cl}$	HCFC-142b	2.2	1.3	1.6	1.5	2

Notes

1. Recommendation from DeMore *et al.* (1992).
2. Recommendation based on the work of Warren *et al.* (1991) and Ravishankara *et al.* (1993) who have measured the total rate coefficient for the deactivation of $O(^1D)$ by selected CFCs and the branching ratio for the quenching of $O(^1D)$ to $O(^3P)$.

4.4 Other Loss Processes for HFCs and HCFCs

In addition to photolysis and the reactions with OH and $O(^1D)$, the CFC substitutes may be degraded in the atmosphere via reactions with the nitrate free radical (NO_3) and atomic chlorine (Cl). NO_3 reaches its highest concentration at night and is known to be an important oxidizer of many atmospheric species. In the case of the HCFCs and HFCs, which are saturated halocarbons, the reaction with NO_3 is expected to be very slow. A recent relative rate study of NO_3 with several CFC substitutes (CHF_2Cl , CF_3CHCl_2 , CH_3CFCl_2 , $\text{CH}_3\text{CF}_2\text{Cl}$ and CH_3CHF_2) by Haar *et al.* (1991) showed that these reactions are indeed very slow, all with rate constants less than $3 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

The other possible loss process, reaction with Cl, can be evaluated from the available laboratory kinetics data as summarized in Table 4.4-1. Most of the data for the reactions of Cl with HFCs and HCFCs are based on relative rate studies. The 298 K rate constants for the reactions of Cl with HFCs and HCFCs correlate extremely well with the corresponding reactions of OH suggesting that both radicals react with these compounds by hydrogen abstraction at the same sites.

Table 4.4-1 Recommended rate constants and uncertainties for the reactions of Cl with selected HFCs and HCFCs.

Reactant	Name	$10^{11} \cdot A$ $\text{cm}^3 \text{s}^{-1}$	$E/R \pm \Delta E/R$ K	k_{298} $\text{cm}^3 \text{s}^{-1}$	f(298)	Notes
CH ₂ Cl ₂		3.1	1350 ± 500	3.3x10 ⁻¹³	2.0	4.4.1
CHCl ₃		0.49	1240 ± 500	7.6x10 ⁻¹⁴	3.0	4.4.2
CHFCl ₂	HCFC-21	---	---	2.1x10 ⁻¹⁴	1.5	4.4.3
CH ₂ FCI	HCFC-31	2.1	1390 ± 500	1.9x10 ⁻¹³	3.0	4.4.4
CH ₂ F ₂	HFC-32	1.7	1630 ± 500	7.1x10 ⁻¹⁴	3.0	4.4.5
CH ₃ F	HFC-41	0.48	770 ± 500	3.6x10 ⁻¹³	1.5	4.4.6
CHCl ₂ CF ₃	HCFC-123	---	---	1.2x10 ⁻¹⁴	1.5	4.4.7
CHFClCF ₃	HCFC-124	---	---	2.7x10 ⁻¹⁵	2.0	4.4.8
CH ₂ CICF ₃	HCFC-133a	0.18	1710 ± 500	5.9x10 ⁻¹⁵	3.0	4.4.9
CHF ₂ CHF ₂	HCFC-134	0.82	2430 ± 500	2.4x10 ⁻¹⁵	3.0	4.4.10
CH ₂ FCF ₃	HCFC-134a	---	---	1.4x10 ⁻¹⁵	3.0	4.4.11
CH ₃ CFCl ₂	HCFC-141b	---	---	2.2x10 ⁻¹⁵	1.5	4.4.12
CH ₃ CF ₂ Cl	HCFC-142b	---	---	3.9x10 ⁻¹⁶	3.0	4.4.13
CH ₂ FCHF ₂	HCFC-143					4.4.14
→CH ₂ FCF ₂		0.55	1610 ± 500	2.5x10 ⁻¹⁴	3.0	
→CHFCHF ₂		0.77	1720 ± 500	2.4x10 ⁻¹⁴	3.0	
CH ₃ CF ₃	HFC-143a	1.2	3880 ± 500	2.6x10 ⁻¹⁷	5.0	4.4.15
CH ₂ FCH ₂ F	HFC-152	2.6	1060 ± 500	7.5x10 ⁻¹³	3.0	4.4.16
CH ₃ CHF ₂	HFC-152a					4.4.17
→CH ₃ CF ₂		0.64	950 ± 500	2.6x10 ⁻¹³	1.5	
→CH ₂ CHF ₂		0.72	2390 ± 500	2.4x10 ⁻¹⁵	3.0	
CH ₃ CH ₂ F	HFC-161					4.4.18
→CH ₃ CHF		1.8	290 ± 500	6.8x10 ⁻¹²	3.0	
→CH ₂ CH ₂ F		1.4	880 ± 500	7.3x10 ⁻¹³	3.0	

Notes

4.4.1 Cl + CH₂Cl₂. The recommended value is based on results of the relative rate study of Tschuikow-Roux *et al.* (1988) normalized to the value of the rate constant for the reference reaction (Cl + CH₄) recommended in DeMore *et al.* (1992). The room temperature value is in good agreement with results of the relative rate study of Niki *et al.* (1980). The higher results of Clyne and Walker (1973) were not used.

4.4.2 Cl + CHCl₃. The recommended value is based on results of the relative rate study of Knox (1962) normalized to the values of the rate constants for the two reference reactions (Cl + CH₄ and Cl + CH₃Cl) recommended in this evaluation. The higher results of Clyne and Walker (1973) were not used.

4.4.3 Cl + CHFCl₂. The recommended values is based on results of the relative rate study of Tuazon *et al.* (1992) normalized to the value of the rate constant for the reference reaction (Cl + CH₄) recommended in DeMore *et al.* (1992). The results of Glavas and Heicklen (1985) were not considered.

4.4.4 Cl + CH₂FCI. The recommended value is based on results of the relative rate study of Tschuikow-Roux *et al.* (1988) normalized to the value of the rate constant for the reference reaction (Cl + CH₄) recommended in DeMore *et al.* (1992). The recent k_{298} value of Tuazon *et al.* (1992) is smaller than the recommendation.

4.4.5 Cl + CH₂F₂. The recommended value is based on results of the relative rate study of Tschuikow-Roux *et al.* (1985) normalized to the value of the rate constant for the reference reaction (Cl + CH₄) recommended in DeMore *et al.* (1992).

4.4.6 Cl + CH₃F. The recommended value is based on results of the direct study of Manning and Kurylo (1977) using the flash photolysis-resonance fluorescence technique. The results of the relative rate study of Tschuikow-Roux *et al.* (1988) are in

good agreement at room temperature but show a stronger temperature dependence, which is encompassed within the error limits. The recommendation for k_{298} is in excellent agreement with the recent value of Tuazon *et al.* (1992).

4.4.7 $\text{Cl} + \text{CHCl}_2\text{CF}_3$. The recommended value is based on results of the direct study of Warren and Ravishankara (private communication) using the pulsed photolysis-resonance fluorescence technique, and the relative rate study of Wallington and Hurley (1992) at room temperature. The recommendation for k_{298} is in excellent agreement with the recent value of Tuazon *et al.* (1992).

4.4.8 $\text{Cl} + \text{CHFClCF}_3$. The recommended value is based on results of the direct study of Warren and Ravishankara (private communication) using the pulsed photolysis-resonance fluorescence technique. The recommendation for k_{298} is in excellent agreement with the recent value of Tuazon *et al.* (1992).

4.4.9 $\text{Cl} + \text{CH}_2\text{ClCF}_3$. The recommended value is based on results of the direct study of Jourdain *et al.* (1978) using the discharge flow-mass spectrometric technique to monitor the decay of the HCFC in the presence of a large excess of Cl atoms.

4.4.10 $\text{Cl} + \text{CHF}_2\text{CHF}_2$. The recommended value is based on results of the relative rate study of Yano and Tschuikow-Roux (1986) normalized to the value of the rate constant for the reference reaction ($\text{Cl} + \text{C}_2\text{H}_6$) recommended in DeMore *et al.* (1992).

4.4.11 $\text{Cl} + \text{CH}_2\text{FCF}_3$. The recommended value is based on results of the relative rate study of Wallington and Hurley (1992). The recommendation for k_{298} is in excellent agreement with the recent value of Tuazon *et al.* (1992).

4.4.12 $\text{Cl} + \text{CH}_3\text{CFCl}_2$. The recommended value is based on results of the direct study of Warren and Ravishankara (private communication) using the pulsed photolysis-resonance fluorescence technique and the relative rate study of Wallington and Hurley (1992) at room temperature.

4.4.13 $\text{Cl} + \text{CH}_3\text{CF}_2\text{Cl}$. The recommended value is based on results of the relative rate study of Wallington and Hurley (1992). The recommendation for k_{298} is in excellent agreement with the recent value of Tuazon *et al.* (1992).

4.4.14 $\text{Cl} + \text{CH}_2\text{FCHF}_2$. The recommended values for the two reaction channels are based on results of the relative rate study of Tschuikow-Roux *et al.* (1985) normalized to the value of the rate constant for the reference reaction ($\text{Cl} + \text{CH}_4$) recommended in DeMore *et al.* (1992).

4.4.15 $\text{Cl} + \text{CH}_3\text{CF}_3$. The recommended value is based on results of the relative rate study of Tschuikow-Roux *et al.* (1985) normalized to the value of the rate constant for the reference reaction ($\text{Cl} + \text{CH}_4$) recommended in DeMore *et al.* (1992).

4.4.16 $\text{Cl} + \text{CH}_2\text{FCH}_2\text{F}$. The recommended value is based on results of the relative rate study of Yano and Tschuikow-Roux (1986) normalized to the value of the rate constant for the reference reaction ($\text{Cl} + \text{C}_2\text{H}_6$) recommended in DeMore *et al.* (1992).

4.4.17 $\text{Cl} + \text{CH}_3\text{CHF}_2$. The recommended values for the two reaction channels are based on results of the relative rate study of Yano and Tschuikow-Roux (1986) normalized to the value of the rate constant for the reference reaction ($\text{Cl} + \text{C}_2\text{H}_6$) recommended in DeMore *et al.* (1992). The overall rate constant value is in good agreement with results of the relative rate study of Wallington and Hurley (1992) at room temperature. The recommendation for k_{298} is in excellent agreement with the recent value of Tuazon *et al.* (1992).

4.4.18 $\text{Cl} + \text{CH}_3\text{CH}_2\text{F}$. The recommended value is based on results of the relative rate study of Tschuikow-Roux *et al.* (1985) normalized to the value of the rate constant for the reference reaction ($\text{Cl} + \text{CH}_4$) recommended in DeMore *et al.* (1992).

4.5 Ultraviolet Absorption Cross Sections

Ultraviolet absorption cross sections have been re-evaluated for CFC-11, 12, CFC-113, 114 and 115, and Halon 1301, 1211, 1202 and 2402 in this section based on recent work or new interpretations of older work. Absorption of Lyman- α radiation at 121.6 nm by long-lived CFCs has not been previously considered in lifetime calculations. Ravishankara *et al.* (1993) have recently measured Lyman- α cross sections for several fluorocarbons and have shown that photolysis at this wavelength has an effect on the lifetime calculated for CFC-115. For the purpose of atmospheric modelling, the absorption of a photon leads to the dissociation of the molecule, *i.e.* the quantum yield for dissociation is unity. For molecules that contain more than one Cl atom, the chlorine contained in the photodissociation fragment is assumed to be released fairly rapidly via subsequent reactions.

Evaluated temperature dependent cross sections are given in Tables 4.5-1 through 4.5-6 in the form of power series that are derived from least squares fits to the data. The basis for each of the recommendations is given below.

There have been several recent studies of the temperature dependences of the cross sections for HFCs and HCFCs [Gillotay and Simon (1991a, 1991b), Orlando *et al.* (1991)]. Because photodissociation is only a minor pathway for their removal, absorption spectra of these compounds have not been evaluated here.

Table 4.5-1 *Ultraviolet absorption cross sections vs. temperature (T) and wavelength (λ) for CFC-11 (CFCl₃)*

The equation giving the absorption spectrum at 298 K is:

$$\ln(\sigma) = a_0 + \sum_{i=1}^4 a_i(\lambda-205)^i$$

where

$$a_0 = -42.57847$$

$$a_1 = -0.1463296$$

$$a_2 = -1.866467 \times 10^{-3}$$

$$a_3 = 1.648604 \times 10^{-5}$$

$$a_4 = 4.882447 \times 10^{-8}$$

The units for σ are cm² molecule⁻¹.

Using these values at different wavelengths as standard, σ_{298} , the absorption spectrum at other temperatures is given by,

$$\frac{\sigma_{298}}{\sigma_T} = (a_0 + \sum_{i=1}^2 a_i(\lambda-205)^i) \exp \left((b_0 + \sum_{i=1}^4 b_i(\lambda-205)^i) \frac{1}{T} \right)$$

where

$$a_0 = 0.539095439$$

$$a_1 = -0.0190050642$$

$$a_2 = 4.36706795 \times 10^{-5}$$

$$b_0 = 169.001053$$

$$b_1 = 12.9541961$$

$$b_2 = 0.330676979$$

$$b_3 = 2.37078050 \times 10^{-3}$$

$$b_4 = -4.2522029 \times 10^{-5}$$

The fit is valid only over the temperature range 210-270 K and wavelength range 180-230 nm.

4.5.1 CFC-11 and CFC-12

The absorption cross sections of CFCl₃ (CFC-11) and CF₂Cl₂ (CFC-12) as a function of wavelength between 175 and 230 nm at 298 K have been measured by various investigators with reasonably good agreement ($\pm 6\%$ between 175 and 215 nm) being obtained. The recommended 298 K values were obtained by averaging the data from Merienne *et al.* (1990), Simon *et al.* (1988a), Bass and Ledford (1976), Robbins (1976) and Chou *et al.* (1977). The data of Hubrich *et al.* (1977) were not included in the average because they increase the standard deviation of the polynomial fit with respect to the rest of the data. The earlier data of Rowland and Molina (1975) are assumed to be superseded by the results of Chou *et al.* (1977) from the same group. The temperature dependence of the absorption cross sections for CFC-11 was established using the measured values of Simon *et al.* (1988a) at 270, 250, 230 and 210 K, Hubrich and Stuhl (1980) at 208 K, Bass and Ledford (1976) at 223 K, and Chou *et al.* (1977) at 252, 232 and 213 K along with the 298 K values recommended here. The results of Green and Wayne (1976/77) were not included. The derived expressions for CFC-11 are given in Table 4.5-1. The expression for the temperature dependence of the cross sections for CFC-12 was taken from Table 4.5-2 of DeMore *et al.* (1990).

Table 4.5-2 Ultraviolet absorption cross sections vs. temperature (T) and wavelength (λ) for CFC-12 (CF_2Cl_2)

The equation giving the absorption spectrum at 298 K is:

$$\ln(\sigma) = a_0 + \sum_{i=1}^4 a_i(\lambda-205)^i$$

where

$$\begin{aligned} a_0 &= -45.07771 \\ a_1 &= -0.2426733 \\ a_2 &= -1.184626 \times 10^{-3} \\ a_3 &= 5.685441 \times 10^{-5} \\ a_4 &= -6.110005 \times 10^{-7} \end{aligned}$$

The units for σ are $\text{cm}^2 \text{molecule}^{-1}$.

Using these values at different wavelengths as standard, σ_{298} , the absorption spectrum at other temperatures is given by,

$$\sigma_T = \sigma_{298} \exp[4.1 \times 10^{-4}(\lambda-184.9)(T-298)]$$

where

$$\begin{aligned} \sigma_{298} &= \text{cross section at 298 K} \\ \lambda &= \text{wavelength in nm} \\ T &= \text{temperature in K} \end{aligned}$$

4.5.2 CFC-113, 114 and 115

The recommended absorption cross sections for these molecules in the 185-230 nm wavelength range as a function of temperature are based on the measurements of Simon *et al.* (1988b). The derived expressions are given in Table 4.5-3. The values measured at 298 K by Chou *et al.* (1978), at 298 and 208 K by Hubrich and Stuhl (1980) and at 298 K by Robbins (1976) are in good agreement with the recommended values. The absorption cross sections at 121.6 nm (Lyman- α) from the measurements of Ravishankara *et al.* (1993) are listed in Table 4.5-4.

Table 4.5-3 Ultraviolet absorption cross sections vs. temperature (T) and wavelength (λ) for CFC-113, CFC-114 and CFC-115

$$\log_{10} \sigma(\lambda, T) = \sum_{n=0}^4 A_n \lambda^n + (T-273) \sum_{n=0}^4 B_n \lambda^n$$

taken from Simon *et al.* (1988b)

CCl_2FCClF_2

$$\begin{aligned} A_0 &= -1087.9 & B_0 &= 12.493 \\ A_1 &= 20.004 & B_1 &= -2.3937 \times 10^{-1} \\ A_2 &= -1.3920 \times 10^{-1} & B_2 &= 1.7142 \times 10^{-3} \\ A_3 &= 4.2828 \times 10^{-4} & B_3 &= -5.4393 \times 10^{-6} \\ A_4 &= -4.9384 \times 10^{-7} & B_4 &= 6.4548 \times 10^{-9} \end{aligned}$$

T range: 210-300 K
 λ range: 182-230 nm

Table 4.5-3 ContinuedCClF₂CClF₂

$A_0 = -160.50$	$B_0 = -1.5296$
$A_1 = 2.4807$	$B_1 = 3.5248 \times 10^{-2}$
$A_2 = -1.5202 \times 10^{-2}$	$B_2 = -2.9951 \times 10^{-4}$
$A_3 = 3.8412 \times 10^{-5}$	$B_3 = 1.1129 \times 10^{-6}$
$A_4 = -3.4373 \times 10^{-8}$	$B_4 = -1.5259 \times 10^{-9}$

T range: 210-300 K
 λ range: 172-220 nm

CClF₂CF₃

$A_0 = 5.8281$	$B_0 = 0$
$A_1 = -2.9900 \times 10^{-1}$	$B_1 = 0$
$A_2 = 1.3525 \times 10^{-3}$	$B_2 = 0$
$A_3 = -2.6851 \times 10^{-6}$	$B_3 = 0$

T range: 210-300 K
 λ range: 172-204 nm

Table 4.5-4 Absorption Cross Sections at 121.6 nm, Lyman- α radiation, at 298 K

Compound	Cross Section $10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$
CF ₃ Cl (CFC-13)	8.12 ± 0.54
CF ₂ ClCF ₂ Cl (CFC-114)	36.0 ± 2.2
CF ₃ CF ₂ Cl (CFC-115)	4.57 ± 0.37

All data from Ravishankara *et al.* (1993)

4.5.3 Halons 1301 (CF₃Br), 1211 (CF₂ClBr), 1202 (CF₂Br₂) and 2402 (C₂F₄Br₂)

Absorption cross sections for these compounds have been measured by various investigators. Molina *et al.* (1982) (CF₃Br, CF₂ClBr, CF₂Br₂ and C₂F₄Br₂ at 298 K), Giolando *et al.* (1980) (CF₂ClBr at 298 K), and Robbins (1976) (C₂F₄Br₂ at 298 K). Gillotay and Simon (1989) and Burkholder *et al.* (1991) have measured the cross sections of all four compounds as a function of temperature. The recommended values were obtained by averaging the results of Burkholder *et al.* and Gillotay and Simon over the wavelength ranges where they overlap. The recommendation is given in Table 4.5-5.

Table 4.5-5 Ultraviolet absorption cross sections vs. temperature (T) and wavelength (λ) for the Halons
$$\ln \sigma (\lambda, T) = [A_0 + \sum_{i=1}^4 A_i (\lambda - \lambda_0)^i] \cdot [1 + (296 - T) \cdot (B_0 + \sum_{i=1}^4 B_i (\lambda - \lambda_0)^i)]$$

Molecule	λ_0 (nm)	i	A_i	B_i
CF ₂ Br ₂ (H-1202)	263.1184	0	-43.61707	1.024236 (-4)
		1	-0.1392279	5.173454(-6)
	235-304	2	-8.847585(-4)	2.582280(-8)
		3	1.423058(-5)	-1.222894(-11)
		4	-6.439138(-8)	6.541614(-12)
CF ₂ ClBr (H-1211)	253.9698	0	-44.65328	1.05987(-4)
		1	-0.1205495	5.10452(-6)
	220-304	2	-8.133584(-4)	5.367804(-8)
		3	4.626312(-6)	2.196723(-10)
		4	5.079764(-10)	7.275262(-12)
CF ₃ Br (H-1301)*	244.8952	0	-47.038912	2039623(-4)
		1	-0.1629549	8.248259(-6)
	214-283	2	-1.155689(-3)	-5.445033(-8)
		3	1.995283(-5)	-3.638785(-9)
		4	2.916192(-9)	-1.39492(-11)
C ₂ F ₄ Br ₂ (H-2402)	229.885	0	-42.49031	9.66205(-6)
		1	-0.08344399	1.987599(-6)
	190-279	2	-1.356491(-3)	5.150506(-8)
		3	3.17866(-6)	5.837533(-10)
		4	7.715186(-8)	6.946091(-13)

* In the wavelength range 190 to 213 nm, the cross sections are temperature independent and are given by σ (in units of 10^{-19} cm^2) = $3.1885074 \times 10^{-3} - 6.0996270 \times 10^{-1} (\lambda) + 4.3419069 \times 10^{-1} (\lambda^2) - 1.3618646 \times 10^{-3} (\lambda^3) + 1.5869473 \times 10^{-6} (\lambda^4)$. This should be added to the temperature dependent part to get the cross sections in the photolytically active region for this molecule.

CF₂Br₂ and CF₂ClBr absorb only weakly at wavelengths longer than 300 nm but the calculated photolytic lifetimes are very sensitive to the cross sections in this spectral region. While there are cross section data beyond 300 nm, the agreement between different studies is not particularly good. Therefore, we have extrapolated the recommended cross sections by assuming that $\log(\sigma)$ varies linearly with wavelength beyond 300 nm at each temperature. This assumption, however, introduces considerable uncertainty into the evaluated cross sections in this spectral region. The calculated parameters for these extrapolations are listed in Table 4.5-6.

Table 4.5-6 Extrapolated ultraviolet absorption cross sections vs. temperature (T) for CF₂Br₂ and CF₂ClBr
$$\ln \sigma (\lambda, T) = (A_0 + \sum_{i=1}^4 A_i (T-251.2)^i) + (B_0 + \sum_{i=1}^4 B_i (T-251.2)^i) \cdot (\lambda - 290)$$

Molecule	i	A_i	B_i
CF ₂ Br ₂ (H-1201) 300-340nm	0	-48.31973	-0.1783530
	1	1.257516(-2)	4.518468(-4)
	2	3.009917(-7)	5.862273(-6)
	3	8.530738(-10)	1.196068(-8)
	4	-1.468803(-10)	-3.751400(-9)
CF ₂ ClBr (H-1211) 300-340nm	0	-50.63382	-0.1918624
	1	1.782180(-2)	7.636243(-4)
	2	4.275152(-7)	1.772590(-5)
	3	3.070216(-10)	-1.847984(-7)
	4	-2.047512(-10)	-6.537606(-9)

4.6 Rate of Hydrolysis and Henry's Law Constant for CH₃CCl₃ and CCl₄

CH₃CCl₃.

In order to assess the possible fate of methylchloroform in the oceans and in fresh water, it is necessary to know the rate of decomposition and the Henry's Law constant in water as a function of temperature. It is also necessary to measure these constants in water approximating the salinity of ocean water in order to determine whether there are any effects due to ionic strength.

The major hydrolysis pathways for methylchloroform in water are shown below:



Haag and Mill (1988) and Gerkens and Franklin (1989) have shown that at 25° C, the formation of 1,1-dichloroethylene is, respectively, about 22% and 27% of the overall process, whereas Jeffers *et al.* (1989) did not detect any 1,1-dichloroethylene. The pre-exponential factor, A, the activation energy, E_a, the rate constant at 25° C, k, and the lifetime, τ, are given in Table 4.6-1. The data from the three groups are in reasonable agreement, although there is some discrepancy in the activation energy and A-factor. The mean lifetime at 25° C is 1.35 years with a deviation from the mean of about 20%. Trusty *et al.* (1991) repeated the work of Jeffers *et al.* using zero dead-volume ampoules and found that the rate constant at 115° C was within 17% of the Jeffers *et al.* value. Major sources of error include head space correction and the accuracy of the analytical method. Haag *et al.* had about a 33% dead volume in their reaction ampoules, Gerkens *et al.* about 6% and Jeffers *et al.*, practically zero.

Table 4.6-1. Rate Constants for the aqueous decomposition of methylchloroform.

A-factor (s ⁻¹)	E _a (kJ mol ⁻¹)	k ¹ , 25°C (s ⁻¹)	τ (Yr)	Ref.
1.1x10 ¹³	118	2.33x10 ⁻⁸	1.35	Haag and Mill (1988)
1.26x10 ¹³	117.8	2.89x10 ⁻⁸	1.10	Gerkens and Franklin (1989)
4.93x10 ¹²	116.1	2.25x10 ⁻⁸	1.40	Jeffers <i>et al.</i> (1989)

¹The rate constant is determined from: $k = A \exp(-E_a/RT)$

There are very few data available regarding the effect of salinity on the rate of methylchloroform decomposition. A few kinetic runs were carried out by Gerkens *et al.* comparing the rates in distilled and salt water. Any differences observed were small, and it is difficult to determine whether they would be statistically significant.

Gossett (1987), Ashworth (1988) and Leighton and Calo (1981) have determined the values for the Henry's Law constant for methylchloroform as a function of temperature. Henry's Law relates to the solubility of gases in a solvent as shown by equation (3) below,

$$X' = p'/H' \quad (3)$$

where, X' = concentration of the gas in the solvent

p' = partial pressure of the gas above the solvent

H' = Henry's Law constant in units of (pressure/concentration)

The coefficients for the Henry's Law correlation equation are given in Table 4.6-2. Gossett (1987) and Ashworth (1988) used an EPICS (Equilibrium Partitioning In Closed Systems) method where nearly identical amounts of a volatile solute are added to two sealed serum bottles having different water volumes. The concentration of the solute in the vapor phase is determined by gas chromatography, and the Henry's Law constant is calculated from the vapor concentrations in the two bottles. Leighton and Calo used an equilibrium cell, where the concentrations of methylchloroform were determined in the gas and aqueous phases using gas chromatography. Results from the two groups which used the EPICS method are in very good agreement while the results from the equilibrium cell are about 15% higher, which could be due to difficulties in the gas chromatographic measurements.

Table 4.6-2 Coefficients for the correlation equation of Henry's Law for methylchloroform and carbon tetrachloride (units T, K; H, atm m³ mole⁻¹)

Investigator	ln H = A - B/T			
	Methylchloroform		Carbon tetrachloride	
	A	B	A	B
Gossett (1987)	9.777	4133	11.29	4411
Ashworth (1988)	7.351	3399	9.739	3951
Leighton and Calo (1981)	10.81	4391	11.09	4381

Ashworth *et al.* (1988) and Dilling (1977) have also measured the Henry's Law constant for methylchloroform in distilled water at 25°C. These results, along with the 25°C results from the temperature dependence investigations, are compared in Table 4.6-3. The value obtained by Ashworth *et al.*, who used a batch air stripping method, agrees within 2% with the value obtained by Ashworth who used the EPICS procedure. There is, however, a 75% discrepancy with the value of Dilling who used a method which required the measurement of the vapor pressure and solubility of methylchloroform. This discrepancy may be due to difficulties in measuring solubilities at low levels.

Table 4.6-3 Henry's Law constants at 25°C for methyl chloroform and carbon tetrachloride in water.

Investigator	H (atm m ³ mole ⁻¹)	
	Methyl chloroform	Carbon tetrachloride
Gossett (1987)	0.0172	0.0304
Ashworth (1988)	0.0174	0.0295
Leighton and Calo (1981)	0.0200	0.0274
Dilling (1977)	0.0302	

The presence of ionic species in the water will lower the solubility of the gas in the solvent (the salting out effect). Gossett (1987) has used the EPICS procedure to determine the activity coefficient, γ , of the solute in the solvent as a function of the ionic strength. A plot of $\log \gamma$ vs. the ionic strength yields a straight line where the slope is the salting out coefficient as shown by equation 4 below.

$$\log \gamma = k I \quad (4)$$

where, k = salting out coefficient (L mole⁻¹)

I = ionic strength

His value for the salting out coefficient of methylchloroform is 0.193 (L mole⁻¹) at 20°C.

CCl₄.

Jeffers *et al.* (1989) measured the decomposition of carbon tetrachloride dissolved in water as a function of temperature and obtained the following expression for the decomposition rate constant:

$$k \text{ (s}^{-1}\text{)} = 6.783 \times 10^{10} \exp(-114.5/RT)$$

where the activation energy is given in kJ mol⁻¹. The resulting decomposition half-lives are 431, 81.8, 37.4 and 17.4 years at temperatures of 10, 20, 25 and 30°C, respectively. Coefficients for the correlation equation determined by Gossett (1987), Ashworth (1988) and Leighton and Calo (1981) are given in Table 4.6-2. The results of Ashworth (1988) at 25°C using a batch stripping method are compared with the results at 25°C from the temperature dependence studies in Table 4.6-3. The results from all these studies are in very good agreement.

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