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EVALUATED RATE CONSTANTS FOR SELECTED HCFC'S AND HFC'S WITH OH AND $O(^1D)$

Robert F. Hampson and Michael J. Kurylo
Center for Chemical Technology
National Institute of Standards and Technology
Gaithersburg, Maryland 20899

Stanley P. Sander
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California 91109

INTRODUCTION

The anthropogenic release of chlorofluorocarbons (CFC's) can cause significant perturbations to the odd oxygen budget of the stratosphere through catalytic processes. The partially halogenated CFC's react much more quickly in the troposphere than their fully halogenated counterparts. The substitution of hydrofluorocarbons (HFC's) and hydrochlorofluorocarbons (HCFC's) for fully halogenated species in industrial applications may therefore lessen the problem of catalytic ozone destruction in the stratosphere. In order to evaluate the effects of HCFC releases we must achieve a reasonable understanding of the rates and mechanisms of the reactions of HCFC's and HFC's with other tropospheric constituents. The chemistry of HCFC's and HFC's in the troposphere is controlled by reactions with OH in which a hydrogen atom is abstracted from the halocarbon to form water and a halo-alkyl radical. The halo-alkyl radical subsequently reacts with molecular oxygen to form a peroxy radical. The reactions of HCFC's and HFC's with $O(^1D)$ atoms are unimportant in the troposphere but may be important in producing active chlorine or OH in the stratosphere.

Scope

This paper is a critical evaluation of the available data on the reactions of OH and $O(^1D)$ with selected partially hydrogenated C_1 and C_2 haloalkanes. Of the 6 C_1 and 36 C_2 HFC's and HCFC's that exist, eight compounds have been identified as being of particular interest to the fluorocarbon industry as possible CFC substitutes. These include HCFC-22 (CHF_2Cl), HCFC-152a (CH_3-CHF_2), HFC-134a (CH_2F-CF_3), HFC-125 (CHF_2-CF_3), HCFC-142b (CH_3-CF_2Cl), HCFC-124 ($CHFCl$-CF_3), HCFC-141b (CH_3-$CFCl_2$) and HCFC-123 ($CHCl_2$-CF_3). Accordingly, the reactions of OH and $O(^1D)$ with these compounds were evaluated where data existed and estimated where experimental results were not available. In addition, all other C_1 and C_2 HCFC's and HFC's for which kinetic data existed were included. These are HFC-41 (CH_3F), HFC-32 (CH_2F_2), HFC-23 (CHF_3), HCFC-31 (CH_2FCl), HCFC-21 ($CHFCl_2$), HFC-161 (CH_3-CH_2F), HFC-152 (CH_2F-CH_2F), HFC-143 (CH_2F-CHF_2), HFC-143a (CH_3-CF_3), HFC-134 (CHF_2-CHF_2), HCFC-133a (CH_2Cl-CF_3) and HCFC-132b (CH_2Cl-CF_2Cl) for a total of 20 HFC and HCFC species being reviewed. There are currently temperature dependence OH reaction rate data for all the compounds in the first group. In the second group, there are room temperature OH kinetics data for all species, but temperature dependence data are lacking for HFC-161 and HFC-152. We have also included evaluations for CH_3CCl_3 and CH_2Cl_2 since these compounds play a role in most chlorine-ozone modeling scenarios. An evaluation for CH_4 was included because of its important role in atmospheric HO_x chemistry. The previous kinetics studies of the species of interest, including the temperature ranges and measurement techniques are summarized in Table 1.

Reactions of HFC's and HCFC's with OH

Several recent evaluations of OH reaction rate data for these species have been published including DeMore et al. (1987) (hereafter called NASA (1987)), Atkinson et al. (1989) (hereafter called IUPAC (1989)), Atkinson (1989) and Cohen and Westberg (1988). The emphasis of all these evaluations with the exception of the last one has been on data relevant to atmospheric modelling. Because the Cohen and Westberg review is oriented toward high temperature combustion conditions, the recommendations from their evaluation are not included. No single review encompasses the data for all the reactions considered here. In addition, this review includes data from the recent, unpublished studies of Kurylo (1989) and Ravishankara (1989)

Table 1. Laboratory studies of the reactions of OH with C_1 and C_2 HFC's and HCFC's.

Reference	Fluorocarbon Number	Technique[1]	Temp. Range (K)
Atkinson et al. (1975)	22	FP/RF	297-434
Davis et al. (1976)	30	FP/RF	245-375
Howard and Evenson (1976a)	21,22,23,30,31,32,41	DF/LMR	296
Howard and Evenson (1976b)	123,124,133a,140 142b,152a	DF/LMR	296
Perry et al. (1976)	21,30	FP/RF	298-423
Watson et al. (1977)	21,22,31,140,142b	FP/RF	250-350
Chang and Kaufman (1977)	21,22	DF/RF	250-400
Handwerk and Zellner (1978)	22,31,133a,142b,152a	FP/RA	260-370
Ernst et al. (1978)	23	FP-ST/RA	1000-1500
Clyne and Holt (1979a)	140	DF/RF	293-425
Clyne and Holt (1979b)	21,22,23,32,123,125 133,134,134a,142b,143 143a,152a	DF/RF	293-425
Jeong and Kaufman (1979)	140	DF/RF	250-480
Kurylo et al. (1979)	140	FP/RF	222-363
Nip et al. (1979)	23,32,41,152a,161	FP/RA	297
Watson et al. (1979)	123,124,132b	FP/RF	250-375
Singleton et al. (1980)	161	GC/MS	298
Paraskevopoulos et al. (1981)	21,22,31,142b	FP/RA	297
Jeong and Kaufman (1982a)	21,22,23,30,31,32,41	DF/RF	250-480
Martin & Paraskevopoulos (1983)	125,134a,143,143a,152	FP/RA	298
Jeong et al. (1984)	132b,134a	DF/RF	250-470
Ravishankara (1989)	134a,141b,142b 152a,123	LP/FP/LIF & DF/LMR	235-425
Kurylo (1989)	123,134a,141b,142b 152a	FP/RF	270-400

[1]DF - discharge flow, FP - flash photolysis, GC - gas chromatography, LMR - laser magnetic resonance, LP - laser photolysis, MS - mass spectrometry, RA - resonance absorption, RF - resonance fluorescence, ST - shock tube.

which are not included in the previous evaluations. Ten of the twenty reactions reviewed here were previously evaluated in NASA (1987). Of these ten, the new rate data encompass five of the ten reactions.

The format of this evaluation combines aspects of the NASA and IUPAC review formats. For each reaction, there is a set of data sheets listing the rate constants and measurement temperatures from every paper where data are presented. Also included are the Arrhenius parameters derived in the original study and in subsequent reviews. The recommended Arrhenius parameters from this evaluation are then listed with the uncertainties in k_{298} and E/R. The data sheet includes a note which discusses the studies and temperature ranges which were considered in the review. Finally a plot of ln k vs. 1/T is presented for each reaction showing the data from the original studies and the line derived from the recommended Arrhenius parameters. In all cases, the temperature limits for the recommended rate expression are 220 to 400 K. This temperature restriction was made due to the observed Arrhenius curvature for several of the reactions over more extended temperature ranges. The recommended rate expressions and uncertainties are summarized in Table 2. The data point symbols on the plots are identified in Table 4.

For virtually every reaction evaluated, the experimental data were obtained from studies which monitored the loss of OH in the presence of excess halocarbon. For relatively slow reactions, which proceed under conditions where the rate constant is 10^{-15} cm^3 $molecule^{-1}$ s^{-1} or less, this procedure can lead to an overestimation of the true rate constant due to the presence of trace reactive impurities or to secondary reactions involving the primary radical product. One of the early studies (Clyne and Holt, 1979a,b) may have suffered from such interferences. Because of these discrepancies the Clyne and Holt results were not considered in the evaluation.

For those reactions for which temperature dependence data did not exist or were available only from the Clyne and Holt study, we chose to estimate the value of E/R and back-calculate the A-factor using k_{298}. Reasonable values of E/R can be estimated from compounds appearing in a homologous series, and by noting that most values of E/R for reactions of OH with halocarbons lie between 1000 and 2000 K. An alternative approach would have involved estimating, or calculating from transition state theory, the A factor and using k_{298} to obtain E/R. These two approaches yield similar results if the data are not extrapolated very far from room temperature and, thus, are nearly equivalent for the calculation of ozone depletion or greenhouse warming potentials. These two estimation procedures can result in significant differences when used for extrapolations over a wide temperature range. In particular, they can yield disparate predictions when there are no direct kinetic data for either the species of interest or for one of similar structure. In addition, it should be noted that several OH + fluorocarbon reactions have experimentally derived A factors which are lower than expected for hydrogen abstraction (assumed to be the dominant pathway for these reactions). While this may be due to systematic experimental errors of the type mentioned earlier, it appears to be particularly characteristic of the highly fluorinated compounds.

Reactions of HFC's and HCFC's with $O(^1D)$

Recommended rate constants for the reactions of HFC's and HCFC's with $O(^1D)$ are given in Table 3. Rate constant values for the $O(^1D)$ reactions are associated with actual chemical reaction (leading to chemical breakdown of the HCFC or HFC) and do not include contributions due to simple physical deactivation (quenching) of the excited oxygen atom. Force and Wiesenfeld (1981) determined that chemical reaction played a dominant role in the overall interaction with all halomethanes they studied except for

Table 2. Recommended rate constants and uncertainties for reactions of OH with selected HFC's and HCFC's.

Reaction	Fluorocarbon Number	A[1]	E/R ± ΔE/R[2]	k_{298}[1]	f(298)
$OH + CHFCl_2$	HCFC-21	1.2(-12)	1100 ± 150	3.0(-14)	1.1
$OH + CHF_2Cl$	HCFC-22	1.2(-12)	1650 ± 150	4.7(-15)	1.1
$OH + CHF_3$	HFC-23	1.5(-12)	2650 ± 500	2.1(-16)	1.5
$OH + CH_2Cl_2$	30	5.8(-12)	1100 ± 250	1.4(-13)	1.2
$OH + CH_2FCl$	HCFC-31	3.0(-12)	1250 ± 200	4.5(-14)	1.15
$OH + CH_2F_2$	HFC-32	2.5(-12)	1650 ± 200	1.0(-14)	1.2
$OH + CH_3F$	HFC-41	5.4(-12)	1700 ± 300	1.8(-14)	1.2
$OH + CH_4$	50	2.3(-12)	1700 ± 200	7.7(-15)	1.2
$OH + CHCl_2CF_3$	HCFC-123	6.4(-13)	850 ± 250	3.7(-14)	1.2
$OH + CHFClCF_3$	HCFC-124	6.6(-13)	1250 ± 300	1.0(-14)	1.2
$OH + CHF_2CF_3$	HFC-125	8.9(-13)	1750 ± 500	2.5(-15)	2.0
$OH + CH_2ClCF_2Cl$	HCFC-132b	3.6(-12)	1600 ± 400	1.7(-14)	2.0
$OH + CH_2ClCF_3$	HCFC-133a	5.2(-13)	1100 ± 300	1.3(-14)	1.3
$OH + CHF_2CHF_2$	HFC-134	8.7(-13)	1500 ± 500	5.7(-15)	2.0
$OH + CH_2FCF_3$	HFC-134a	1.7(-12)	1750 ± 300	4.8(-15)	1.2
$OH + CH_3CCl_3$	140	5.0(-12)	1800 ± 300	1.2(-14)	1.3
$OH + CH_3CFCl_2$	HCFC-141b	4.2(-13)	1200 ± 300	7.5(-15)	1.3
$OH + CH_3CF_2Cl$	HCFC-142b	9.6(-13)	1650 ± 250	3.8(-15)	1.2
$OH + CH_2FCHF_2$	HFC-143	2.8(-12)	1500 ± 500	1.8(-14)	2.0
$OH + CH_3CF_3$	HFC-143a	6.0(-13)	1750 ± 500	1.7(-15)	2.0
$OH + CH_2FCH_2F$	HFC-152	1.7(-11)	1500 ± 500	1.1(-13)	2.0
$OH + CH_3CHF_2$	HFC-152a	1.5(-12)	1100 ± 200	3.7(-14)	1.1
$OH + CH_3CH_2F$	HFC-161	1.3(-11)	1200 ± 300	2.3(-13)	2.0

1 units are cm^3 $molecule^{-1}$ s^{-1}
2 units are K

Table 3. Recommended rate constants and uncertainties for reactions of $O(^1D)$ with selected HFC's and HCFC's.

Reaction	Fluorocarbon Number	A[1]	E/R ± ΔE/R[2]	k_{298}[1]	f(298)
$O(^1D)$ + $CHFCl_2$	HCFC-21	1.9(-10)	0 ± 100	1.9(-10)	1.3
$O(^1D)$ + CHF_2Cl	HCFC-22	1.0(-10)	0 ± 100	1.0(-10)	1.3
$O(^1D)$ + CHF_3	HFC-23	1.9(-12)	0 ± 500	1.9(-12)	3.0
$O(^1D)$ + CH_2F_2	HFC-32	5.0(-11)	0 ± 100	5.0(-11)	2.0
$O(^1D)$ + CH_3F	HFC-41	1.0(-10)	0 ± 100	1.0(-10)	2.0
$O(^1D)$ + $CHCl_2CF_3$	HCFC-123	2.3(-10)	0 ± 100	2-3(-10)	2.0
$O(^1D)$ + $CHFClCF_3$	HCFC-124	1.0(-10)	0 ± 100	1.0(-10)	3.0
$O(^1D)$ + CHF_2CF_3	HFC-125	5.0(-11)	0 ± 100	5.0(-11)	2.0
$O(^1D)$ + CH_2ClCF_2Cl	HCFC-132b	1.7(-10)	0 ± 100	1.7(-10)	2.0
$O(^1D)$ + CH_2ClCF_3	HCFC-133a	1.6(-10)	0 ± 100	1.6(-10)	2.0
$O(^1D)$ + CH_2FCF_3	HFC-134a	5.0(-11)	0 ± 100	5.0(-11)	3.0
$O(^1D)$ + CH_3CFCl_2	HCFC-141b	1.5(-10)	0 ± 100	1.5(-10)	3.0
$O(^1D)$ + CH_3CF_2Cl	HCFC-142b	1.4(-10)	0 ± 100	1.4(-10)	2.0
$O(^1D)$ + CH_3CF_3	HFC-143a	6.0(-11)	0 ± 100	6.0(-11)	2.0
$O(^1D)$ + CH_3CHF_2	HFC-152a	1.0(-10)	0 ± 100	1.0(-10)	3.0

1 units are cm^3 $molecule^{-1}$ s^{-1}
2 units are K

highly fluorinated species. Of the species considered here, only for CF_3H is physical deactivation important. For these species absolute rate constants have been reported in the following studies: Fletcher and Husain (1976) for HCFC-21 and HCFC-22; Davidson et al. (1978) for HCFC-21 and HCFC-22; and Force and Wiesenfeld (1981) for HFC-23 and HFC-41. In the first two studies overall rate constants for collisional deactivation were reported, while in the study by Force and Wiesenfeld both the overall rate constants and those for chemical reaction were determined. Green and Wayne (1976) conducted a competitive study in which the rate constants only for the chemical reactions were determined relative to the reaction with N_2O for HCFC-22, HFC-32, HCFC-123, HFC-125, HCFC-132b, HCFC-133a, HCFC-142b, and HFC-143a. The values given here are based upon a value of 1.2(-10) cm^3 $molecule^{-1}$ s^{-1} for the rate

Table 4. Symbols used in Data Plots for Reactions of OH with HFC's and HCFC's.

Symbol	Reference(s)
■	Howard and Evenson (1976a), Howard and Evenson (1976b)
△	Watson et al. (1977), Watson et al. (1979), Davis et al. (1976)
□	Handwerk and Zellner (1978)
●	Nip et al. (1979), Paraskevopoulos et al. (1981), Martin and Paraskevopoulos (1983)
◇	Clyne and Holt (1979a,b)
▽	Jeong and Kaufman (1979, 1982a), Jeong et al. (1984)
▼	Chang and Kaufman (1977)
◆	Atkinson et al. (1975), Perry et al. (1976)
○	Ravishankara (1989)
▲	Kurylo et al. (1979), Kurylo (1989)

constant of the reference reaction of $O(^1D)$ with N_2O. For HCFC-124, HFC-134a, HCFC-141b, and HFC-152a no data have been reported. For the reactions with these species the values given here have been estimated by analogy with reactions of similar species for which data exist. In these cases an uncertainty factor of three was assigned. Only for HCFC-21 and HCFC-22 do data exist over a range of temperature. The temperature independencies recommended here for all $O(^1D)$ reactions are based upon the temperature independencies observed for reactions with these two species and with several CFC's.

Uncertainties

All of the uncertainties are one standard deviation, 1σ. Hence, 95% confidence limits are given by 2σ. The uncertainty (1σ) at any temperature can be calculated from the expression:

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

$OH + CHFCl_2$ (HCFC-21) $\rightarrow H_2O + CFCl_2$

Rate Coefficient Data

Temp. K.	$10^{15} \cdot k$ cm^3 $molecule^{-1}$ s^{-1}	Reference
296	26	Howard and Evenson (1976a)
298	27	Perry et al. (1976)
349	48	
422	91	
245	11.2	Watson et al. (1977)
273	20.9	
298	28.8	
375	66.8	
241	12.8	Chang and Kaufman (1977)
250	17.3	
288	27.0	
296	30.4	
380	71.7	
396	75.2	
293	35.4	Clyne and Holt (1979b)
330	65.7	
373	97.7	
413	152	
297	33.9	Paraskevopoulos et al. (1981)
250	18.8	Jeong and Kaufman (1982a)
295	33.7	
315	42.5	
354	58.5	
392	78.6	
433	105	
483	148	

RATE CONSTANTS

$$OH + CHFCl_2 \text{ (HCFC-21)} \rightarrow H_2O + CFCl_2$$

Derived Arrhenius Parameters

$10^{12}\cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp. K	Reference
1.75	-	1253	298-422	Perry et al. (1976)
1.87	-	1245	245-375	Watson et al. (1977)
1.16	-	1073	241-396	Chang and Kaufman (1977)
4.79	-	1400	293-413	Clyne and Holt (1979b)
1.19	-	1052	250-483	Jeong et al. (1984)
Reviews and Evaluations				
0.86	-	1000	230-300	NASA (1987)
1.1	-	1070	240-350	IUPAC (1989)
1.7(-18)	2.0	479	241-483	Atkinson (1989)

Preferred Values

$k = 1.2 \times 10^{-12} \exp[-(1100 \pm 150)/T]$ cm^3 $molecule^{-1}$ s^{-1} $220 < T < 400$ K

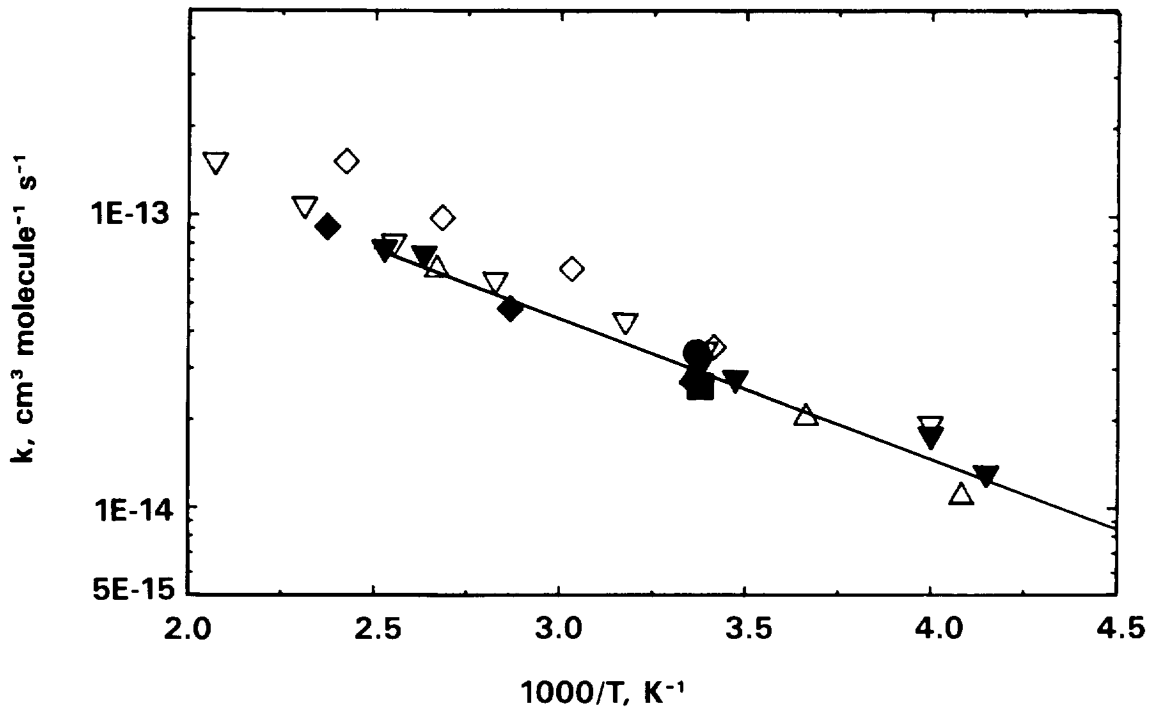
$k_{298} = 3.0 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}

$f_{298} = 1.1$

Comments on Preferred Values

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 rate constants from the latter study are consistently larger than those obtained in all other studies. The expression given here agrees with the recommended expression from NASA (1987) to within about 15% over the stratospheric temperature range.

OH + HCFC-21



$OH + CHF_2Cl$ (HCFC-22) $\rightarrow H_2O + CF_2Cl$

Rate Coefficient Data

Temp. K.	$10^{15} \cdot k$ cm^3 $molecule^{-1}$ s^{-1}	Reference
297	4.75	Atkinson et al. (1975)
348	11.5	
434	27.1	
296	3.4	Howard and Evenson (1976a)
250	1.7	Watson et al. (1977)
273	2.77	
298	4.8	
350	10.1	
253	1.77	Chang and Kaufman (1977)
296	4.25	
358	12.0	
427	24.9	
263	2.0	Handwerk and Zellner (1978)
273	2.7	
283	5.1	
293	4.6	
373	17	
294	3.3	Clyne and Holt (1979b)
321	7.7	
343	12.8	
376	19.7	
391	27.7	
426	39.0	
297	4.58	Paraskevopoulos et al. (1981)
293	4.83	Jeong and Kaufman (1982a)
327	7.68	
360	10.8	
391	17.9	
436	27.5	
482	43.9	

$OH + CHF_2Cl$ (HCFC-22) $\rightarrow H_2O + CF_2Cl$

Derived Arrhenius Parameters

$10^{12} \cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp. K	Reference
1.21	-	1636	297-434	Atkinson et al. (1975)
0.925	-	1575	250-350	Watson et al. (1977)
2.1	-	1780	263-373	Handwerk and Zellner (1978)
9.5	-	2300	294-426	Clyne and Holt (1979b)
1.27	-	1660	293-482	Jeong et al. (1984)
		Reviews and Evaluations		
0.83	-	1550	230-300	NASA (1987)
1.1	-	1620	250-360	IUPAC (1989)
1.51(-18)	2.0	1000	250-482	Atkinson (1989)

Preferred Values

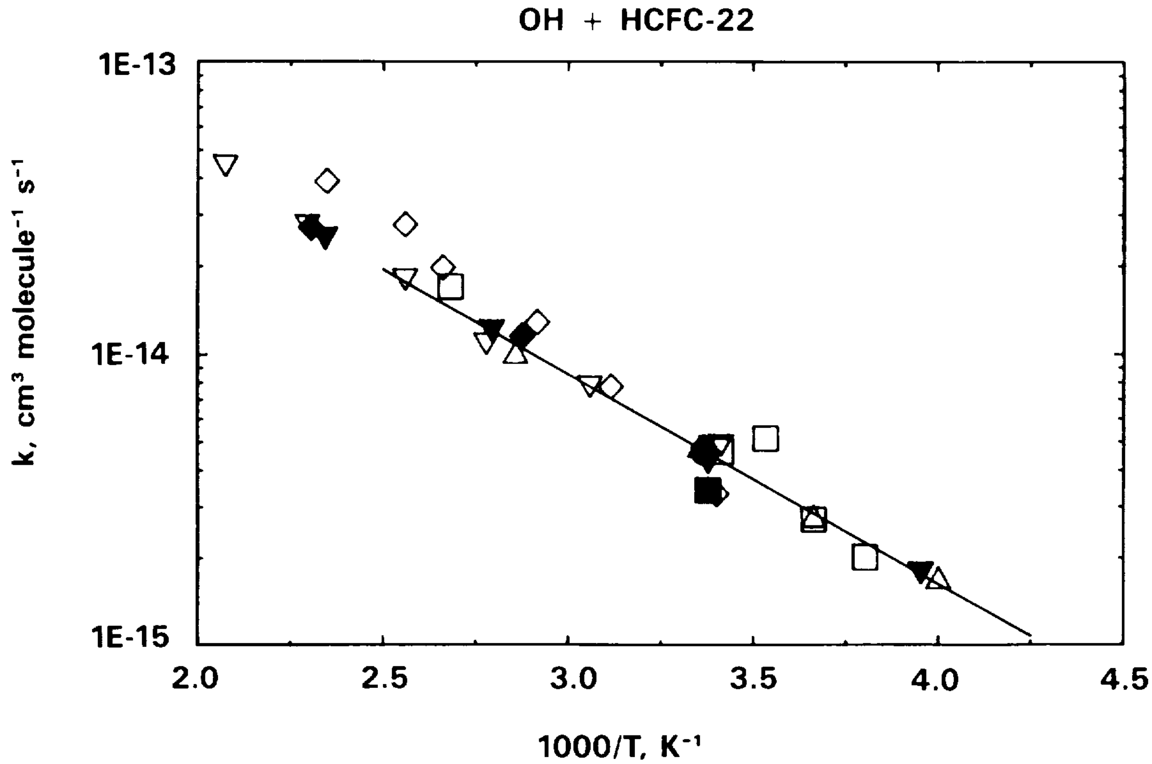
$k = 1.2 \times 10^{-12} \exp[-(1650 \pm 150)/T]$ cm^3 $molecule^{-1}$ s^{-1} $\quad 220 < T < 400$ K

$k_{298} = 4.7 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}

$f_{298} = 1.1$

Comments on Preferred Values

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 expression given here agrees with the recommended expression from NASA (1987) to within about 15% over the stratospheric temperature range.


OH + HCFC-22
1E-13
1E-14
1E-15
k, cm³ molecule⁻¹ s⁻¹
2.0
2.5
3.0
3.5
4.0
4.5
1000/T, K⁻¹

$OH + CHF_3$ (HFC-23) $\rightarrow H_2O + CF_3$

Rate Coefficient Data

Temp. K.	$10^{15}\cdot k$ cm^3 $molecule^{-1}$ s^{-1}	Reference
296	0.2	Howard and Evenson (1976a)
296	1.3	Clyne and Holt (1979b)
430	1.4	
297	0.35	Nip et al. (1979)
387	1.69	Jeong and Kaufman (1982a)
410	2.37	
428	3.31	
447	4.48	
465	5.64	
480	7.19	
1255	550	Ernst et al. (1978)
1320	600	
1345	830	
1395	700	
1400	550	
1445	930	

Derived Arrhenius Parameters

$10^{12}\cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp K	Reference
2.98	-	2910	387-480	Jeong et al. (1984)
Reviews and Evaluations				
1.49(-18)	2.0	1887	387-1445	Atkinson (1989)

$OH + CHF_3$ (HFC-23) $\rightarrow H_2O + CF_3$

Preferred Values

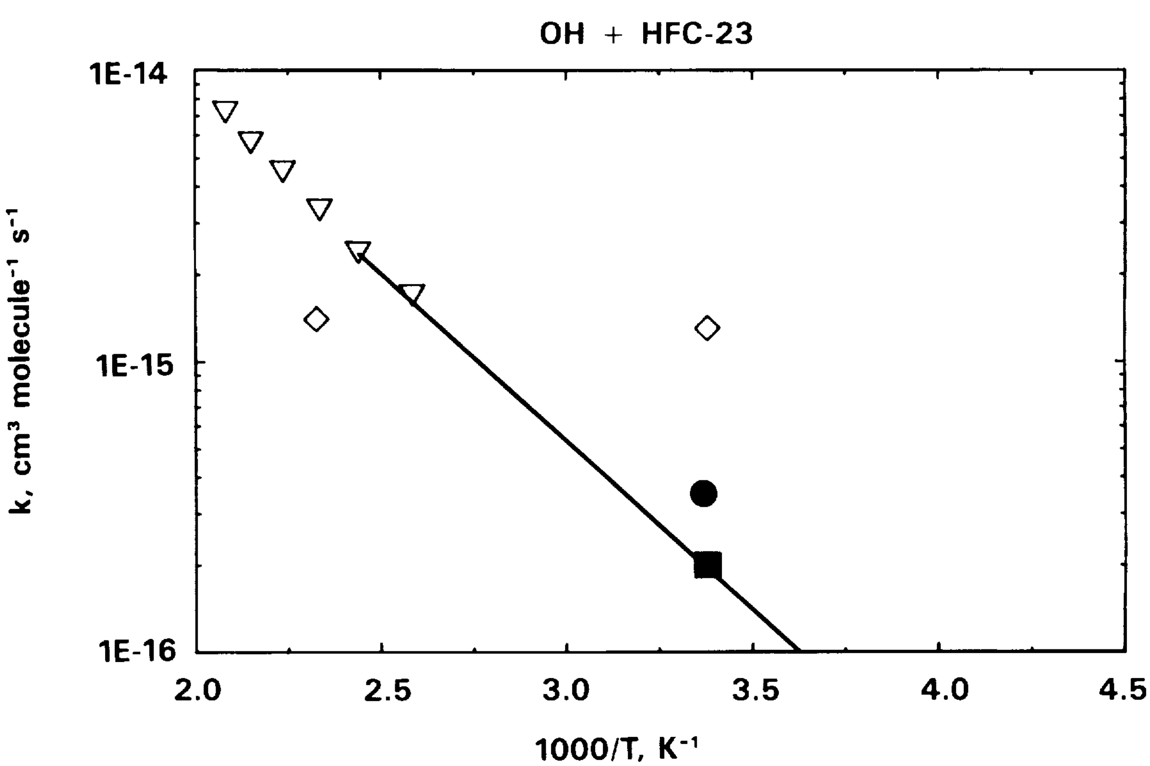
$k = 1.5 \times 10^{-12} \exp[-(2650 \pm 500)/T]$ cm^3 molecule^{-1} s^{-1} $\quad 220 < T < 400$ K

$k_{298} = 2.1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}

$f_{298} = 1.5$

Comments on Preferred Values

The recommendation is based on three data points: the room temperature points of Howard and Evenson (1976a), and the 387 K and 410 K points of Jeong and Kaufman (1982a). The data of Clyne and Holt (1979b) were not considered because of the large disparity with other studies. Because of experimental complications associated with the measurement of rate constants near 10^{-16} cm^3 molecule^{-1} s^{-1}, the k_{298} determinations of Howard and Evenson (1976a) and Nip et al. (1979) should be considered upper limits. The Howard and Evenson value, being the smaller of the two, was therefore used as the basis for the k_{298} recommendation.



$OH + CH_2Cl_2$ (Halocarbon-30) $\rightarrow H_2O + CHCl_2$

Rate Coefficient Data

Temp. K.	$10^{15} \cdot k$ cm^3 $molecule^{-1}$ s^{-1}	Reference
296	155	Howard and Evenson (1976a)
298	145	Perry et al. (1976)
245	47.5	Davis et al. (1976)
298	116	
375	223	
251	95.9	Jeong and Kaufman (1982)
292	153	
323	208	
342	276	
384	352	
415	450	
455	609	

Derived Arrhenius Parameters

$10^{12} \cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp. K	Reference
4.27	-	1094	245-375	Davis et al. (1976)
5.57	-	1042	251-455	Jeong et al. (1984)

Reviews and Evaluations

4.7	-	1050	245-455	NASA (1987)
4.4	-	1030	240-300	IUPAC (1989)
8.54(-18)	2.0	500	245-455	Atkinson (1989)

$OH + CH_2Cl_2$ (Halocarbon-30) $\rightarrow H_2O + CHCl_2$

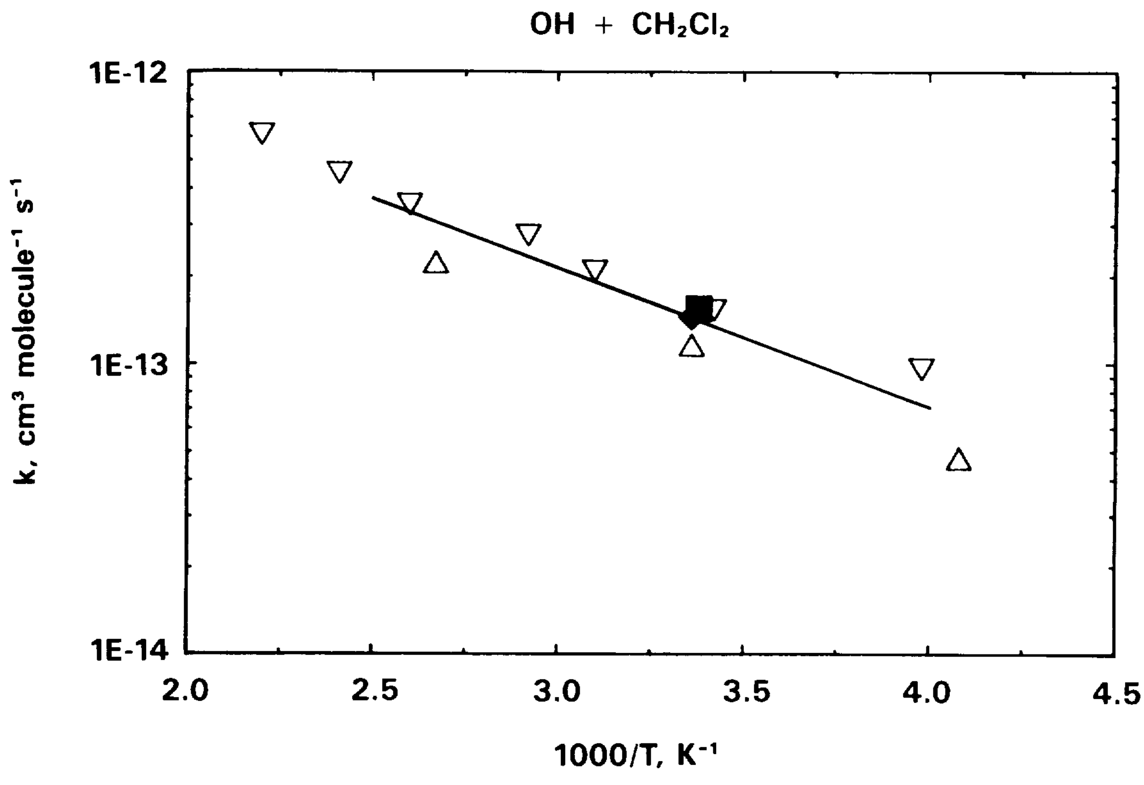
Preferred Values

$k = 5.8 \times 10^{-12} \exp[-(1100 \pm 250)/T]$ cm^3 molecule^{-1} s^{-1} $\quad 220 < T < 400$ K

$k_{298} = 1.4 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}
$f_{298} = 1.2$

Comments on Preferred Values

The data of Howard and Evenson (1976a), Perry et al. (1976), Davis et al. (1976) and Jeong and Kaufman (1982) are in reasonable agreement. The temperature dependence data of Davis et al. tend to somewhat smaller values than Jeong and Kaufman but the resulting activation energies are in good agreement. The preferred Arrhenius expression was derived from a least squares fit to the data below 400 K. The recommended room temperature value was derived from the Arrhenius expression at 298 K.



$OH + CH_2FCl$ (HCFC-31) $\rightarrow H_2O + CHFCl$

Rate Coefficient Data

Temp. K.	$10^{15} \cdot k$ cm^3 molecule^{-1} s^{-1}	Reference
296	37	Howard and Evenson (1976a)
245	16.5	Watson et al. (1977)
298	42.1	
375	98	
273	28	Handwerk and Zellner (1978)
293	35	
373	110	
297	44.5	Paraskevopoulos et al. (1981)
250	27.6	Jeong and Kaufman (1982a)
295	49.4	
323	66.0	
348	88.5	
399	140	
438	172	
486	254	

$OH + CH_2FCl$ (HCFC-31) $\rightarrow H_2O + CHFCl$

Derived Arrhenius Parameters

$10^{12}\cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp. K	Reference
2.84	-	1259	245-375	Watson et al. (1977)
3.1	-	1320	273-373	Handwerk and Zellner (1978)
2.37	-	1137	250-486	Jeong et al. (1984)
		Reviews and Evaluations		
2.1	-	1150	230-300	NASA (1987)
2.6	-	1210	245-350	IUPAC (1989)
3.77(-18)	2.0	604	245-486	Atkinson (1989)

Preferred Values

$k = 3.0 \times 10^{-12} \exp[-(1250 \pm 200)/T]$ cm^3 $molecule^{-1}$ s^{-1} $\quad 220 < T < 400$ K

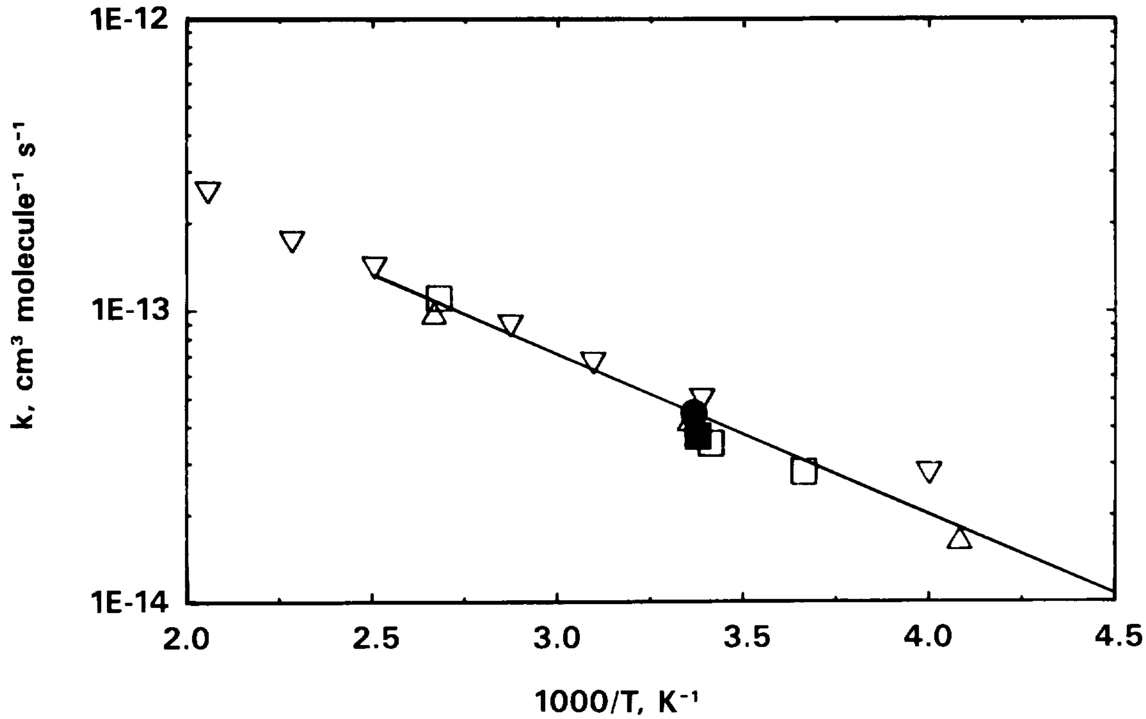
$k_{298} = 4.5 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}

$f_{298} = 1.15$

Comments on Preferred Values

The data for this reaction are in excellent agreement. The recommended Arrhenius expression was derived from the room temperature data of Howard and Evenson (1976a) and Paraskevopoulos et al. (1981), and the temperature dependence data of Watson et al. (1977), Handwerk and Zellner (1978) and Jeong and Kaufman (1982a) below 400 K. The expression given here agrees with the recommended expression from NASA (1987) to within about 15% over the stratospheric temperature range.

OH + HCFC-31



$OH + CH_2F_2$ (HFC-32) $\rightarrow H_2O + CHF_2$

Rate Coefficient Data

Temp. K.	$10^{15}\cdot k$ cm^3 $molecule^{-1}$ s^{-1}	Reference
296	7.8	Howard and Evenson (1976a)
293	5.8	Clyne and Holt (1979b)
327	16.1	
368	24.1	
429	60.3	
297	11.7	Nip et al. (1979)
250	4.29	Jeong and Kaufman (1982a)
298	11.2	
336	21.0	
384	43.4	
432	72.7	
464	95.1	
492	141	

Derived Arrhenius Parameters

$10^{12}\cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp. K	Reference
7.41	-	2100	293-429	Clyne and Holt (1979b)
4.37	-	1766	250-492	Jeong et al. (1984)

Reviews and Evaluations

5.06(-18)	2.0	1107	250-492	Atkinson (1989)

$OH + CH_2F_2$ (HFC-32) $\rightarrow H_2O + CHF_2$

Preferred Values

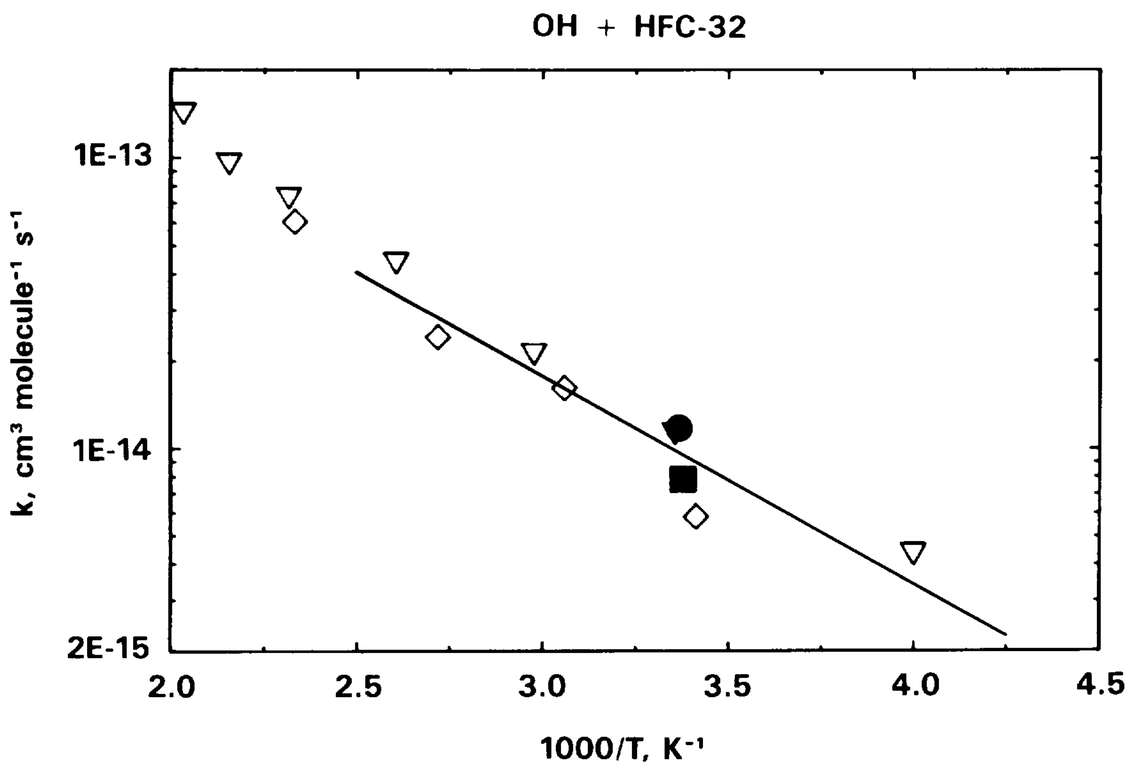
$k = 2.5\times10^{-12}\exp[-(1650\pm200)/T]$ cm^3 molecule^{-1} s^{-1} $\quad$ $220 < T < 400$ K

$k_{298} = 1.0\times10^{-14}$ cm^3 molecule^{-1} s^{-1}

$f_{298} = 1.2$

Comments on Preferred Values

The temperature dependence of the preferred rate expression is derived from the data of Jeong and Kaufman (1982a) below 400 K. The recommendation for k_{298} is derived from the average of the room temperature data of Jeong and Kaufman (1982a), Howard and Evenson (1976a) and Nip et al. (1979). 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.



$OH + CH_3F$ (HFC-41) $\rightarrow H_2O + CH_2F$

Rate Coefficient Data

Temp. K.	$10^{15} \cdot k$ $cm^3\ molecule^{-1}\ s^{-1}$	Reference
296	16	Howard and Evenson (1976a)
297	21.7	Nip et al. (1979)
292	14	Jeong and Kaufman (1982a)
330	25	
356	38.6	
368	47.6	
385	54.8	
416	85.6	
455	131	
480	171	

Derived Arrhenius Parameters

$10^{12} \cdot A$ $cm^3\ molecule^{-1}\ s^{-1}$	n	E/R K	Temp. K	Reference
8.11	-	1887	292-480	Jeong et al. (1984)
Reviews and Evaluations				
5.51(-18)	2.0	1005	292-480	Atkinson (1989)

Preferred Values

$k = 5.4 \times 10^{-12} \exp[-(1700 \pm 300)/T]\ cm^3\ molecule^{-1}\ s^{-1}$ $\quad 220 < T < 400$ K

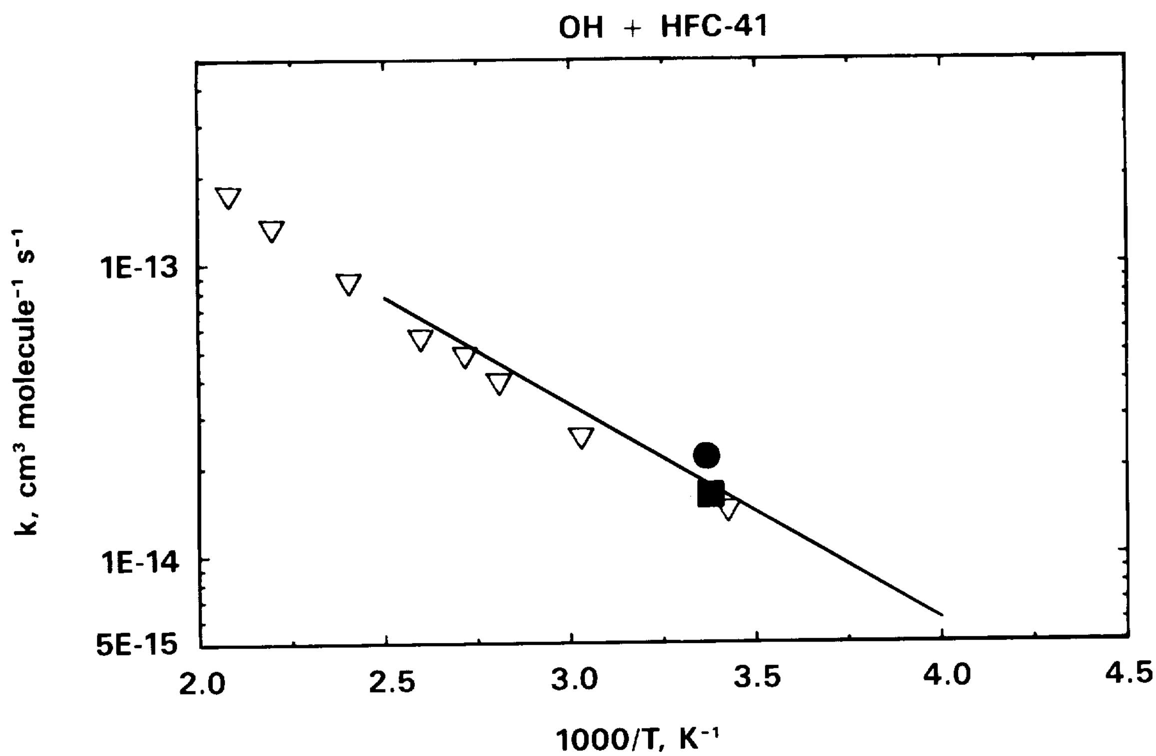
$k_{298} = 1.8 \times 10^{-14}\ cm^3\ molecule^{-1}\ s^{-1}$

$f_{298} = 1.2$

$OH + CH_3F$ (HFC-41) $\rightarrow H_2O + CH_2F$

Comments on Preferred Values

The temperature dependence of the preferred rate expression is derived from the data of Jeong and Kaufman (1982a) below 400 K. The recommendation for k_{298} is derived from the average of the room temperature data of Jeong and Kaufman (1982a), Howard and Evenson (1976a) and Nip et al. (1979).



$OH + CHCl_2CF_3$ (HCFC-123) $\rightarrow H_2O + CCl_2CF_3$

Rate Coefficient Data

Temp. K.	$10^{15} \cdot k$ cm^3 $molecule^{-1}$ s^{-1}	Reference
296	28.4	Howard and Evenson (1976b)
245	16.2	Watson et al. (1979)
298	36	
375	72	
293	38.6	Clyne and Holt (1979b)
329	58.6	
366	80.1	
429	111	
223	15.9	Ravishankara (1989)
229	18.6	
251	22.0	
298	37.5	
322	47.2	
380	71.6	
468	134	
270	25.0	Kurylo (1989)
298	35.2	
330	47.0	
350	49.9	
375	73.6	
400	88.4	

Derived Arrhenius Parameters

$10^{12} \cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp. K	Reference
1.4	-	1102		Watson et al. (1979)
1.12	-	1000		Clyne and Holt (1979b)

$OH + CHCl_2CF_3$ (HCFC-123) $\rightarrow H_2O + CCl_2CF_3$

Reviews and Evaluations

$10^{12} \cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp. K	Reference
1.1	-	1050	245-375	NASA (1987)
1.2	-	1060	245-375	IUPAC (1989)
1.2	-	1060	245-375	Atkinson (1989)

Preferred Values

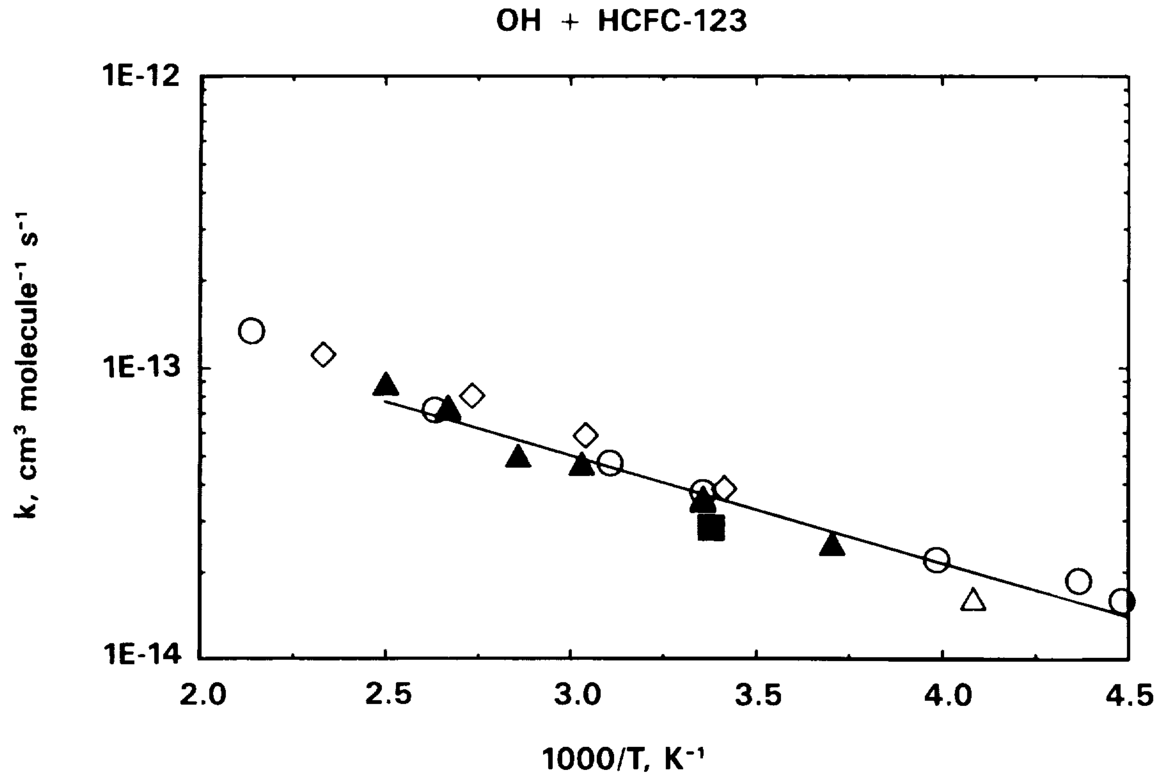
$k = 6.4x10^{-13} \exp[-(850 \pm 250)/T]$ cm^3 $molecule^{-1}$ s^{-1} $\quad$ $220 < T < 400$ K

$k_{298} = 3.7x10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}

$f_{298} = 1.2$

Comments on Preferred Values

The preferred rate expression is derived from the temperature dependence data below 400 K of Ravishankara (1989), Kurylo (1989), 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 Clyne and Holt (1979b) were not considered.


OH + HCFC-123
1E-12
1E-13
1E-14
k, cm³ molecule⁻¹ s⁻¹
2.0
2.5
3.0
3.5
4.0
4.5
1000/T, K⁻¹

$OH + CHFClCF_3$ (HCFC-124) $\rightarrow H_2O + CFClCF_3$

Rate Coefficient Data

Temp. K.	$10^{15}\cdot k$ cm^3 $molecule^{-1}$ s^{-1}	Reference
296	12.4	Howard and Evenson (1976b)
250	4.33	Watson et al. (1979)
301	9.4	
375	22.8	

Derived Arrhenius Parameters

$10^{12}\cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp. K	Reference
0.613	-	1244	298-422	Watson et al. (1979)
Reviews and Evaluations				
0.72		1250	250-375	NASA (1987)
0.64		1240	250-375	IUPAC (1989)
0.64		1233	250-375	Atkinson (1989)

Preferred Values

$k = 6.6x10^{-13} \exp[-(1250 \pm 300)/T]$ cm^3 $molecule^{-1}$ s^{-1} $\quad 220 < T < 400$ K

$k_{298} = 1.0x10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}

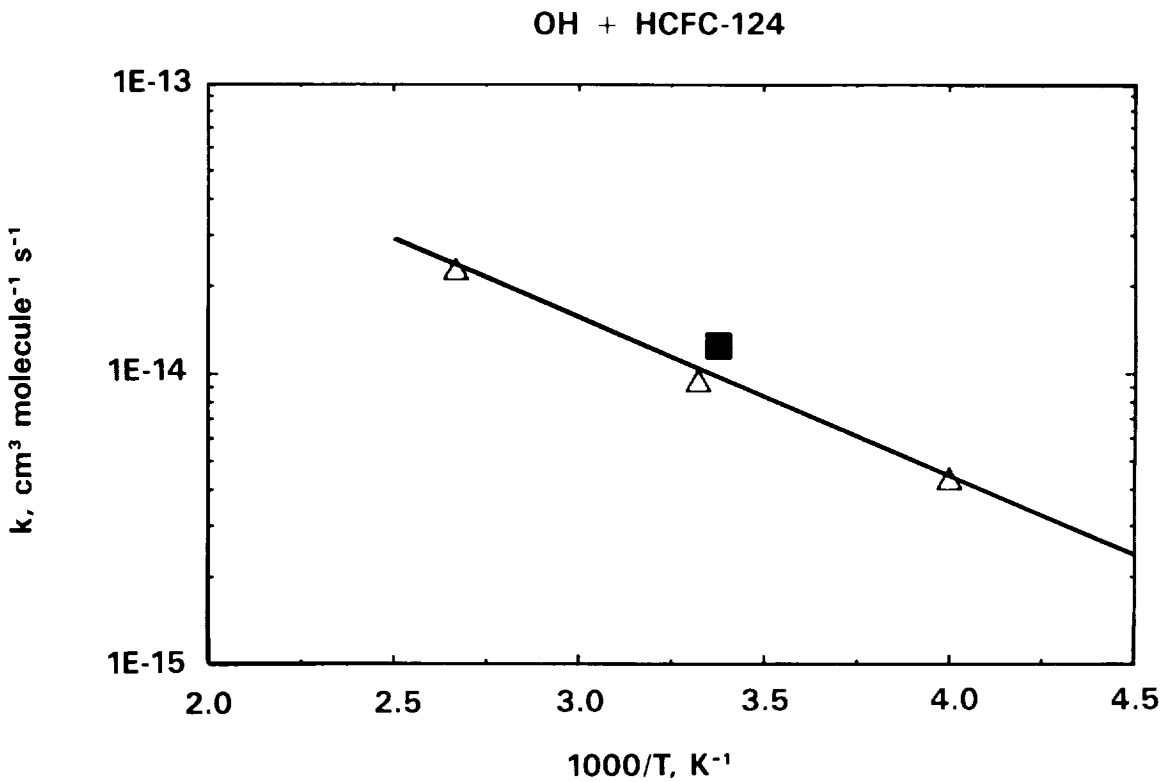
$f_{298} = 1.2$

RATE CONSTANTS

$$OH + CHFClCF_3\ (HCFC\text{-}124) \rightarrow H_2O + CFClCF_3$$

Comments on Preferred Values

The preferred rate expression is derived from the temperature dependence data of 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.



$OH + CHF_2CF_3$ (HFC-125) $\rightarrow H_2O + CF_2CF_3$

Rate Coefficient Data

Temp. K.	$10^{15} \cdot k$ cm^3 molecule^{-1} s^{-1}	Reference
294	5.0	Clyne and Holt (1979b)
294	4.9	
336	6.2	
378	11.3	
441	15.8	
298	2.5	Martin and Paraskevopoulos (1983)

Derived Arrhenius Parameters

$10^{12} \cdot A$ cm^3 molecule^{-1} s^{-1}	n	E/R K	Temp. K	Reference
0.17	-	1100	298-441	Clyne and Holt (1979b)

Reviews and Evaluations

- none -

Preferred Values

$k = 8.9 \times 10^{-13} \exp[-(1750 \pm 500)/T]$ cm^3 molecule^{-1} s^{-1} $\quad 220 < T < 400$ K

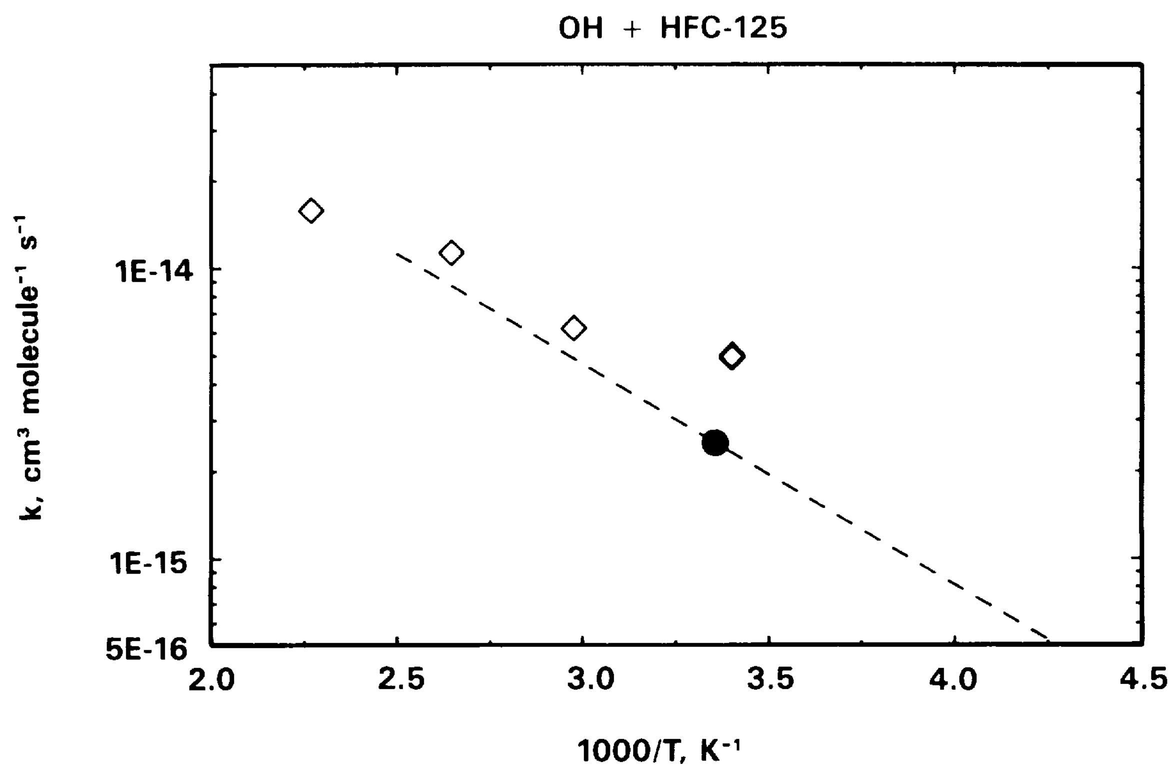
$k_{298} = 2.5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}

$f_{298} = 2.0$

$$OH + CHF_2CF_3 \text{ (HFC-125)} \rightarrow H_2O + CF_2CF_3$$

Comments on Preferred Values

The only temperature dependence data for this reaction are those of 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 agreeement between the Clyne and Holt data and that of other workers for many other halomethanes and haloethanes, the Clyne and Holt data were not used. The preferred value of k_{298} is taken from Martin and Paraskevopoulos (1983). The temperature dependence was estimated by analogy with HFC-134a.



$OH + CH_2ClCF_2Cl$ (HCFC-132b) $\rightarrow H_2O + CHClCF_2Cl$

Rate Coefficient Data

Temp. K.	$10^{15}\cdot k$ cm^3 $molecule^{-1}$ s^{-1}	Reference
250	6.12	Watson et al. (1979)
298	16.7	
350	37.2	
249	14.2	Jeong et al. (1984)
253	16.0	
267	19.1	
295	27.2	
297	24.2	
333	43.1	
365	59.5	
383	80.6	
418	104	
473	160	

Derived Arrhenius Parameters

$10^{12}\cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp. K	Reference
3.0	-	1578	250-350	Watson et al. (1979)
2.02	-	1263	249-473	Jeong et al. (1984)

Reviews and Evaluations

3.4	-	1600	250-350	NASA (1987)
3.0	-	1580	250-350	IUPAC (1989)
2.8(-18)	2.0	672	250-470	Atkinson (1989)

$OH + CH_2ClCF_2Cl$ (HCFC-132b) $\rightarrow H_2O + CHClCF_2Cl$

Preferred Values

$k = 3.6 \times 10^{-12} \exp[-(1600 \pm 400)/T]$ cm^3 molecule^{-1} s^{-1} $220 < T < 400$ K

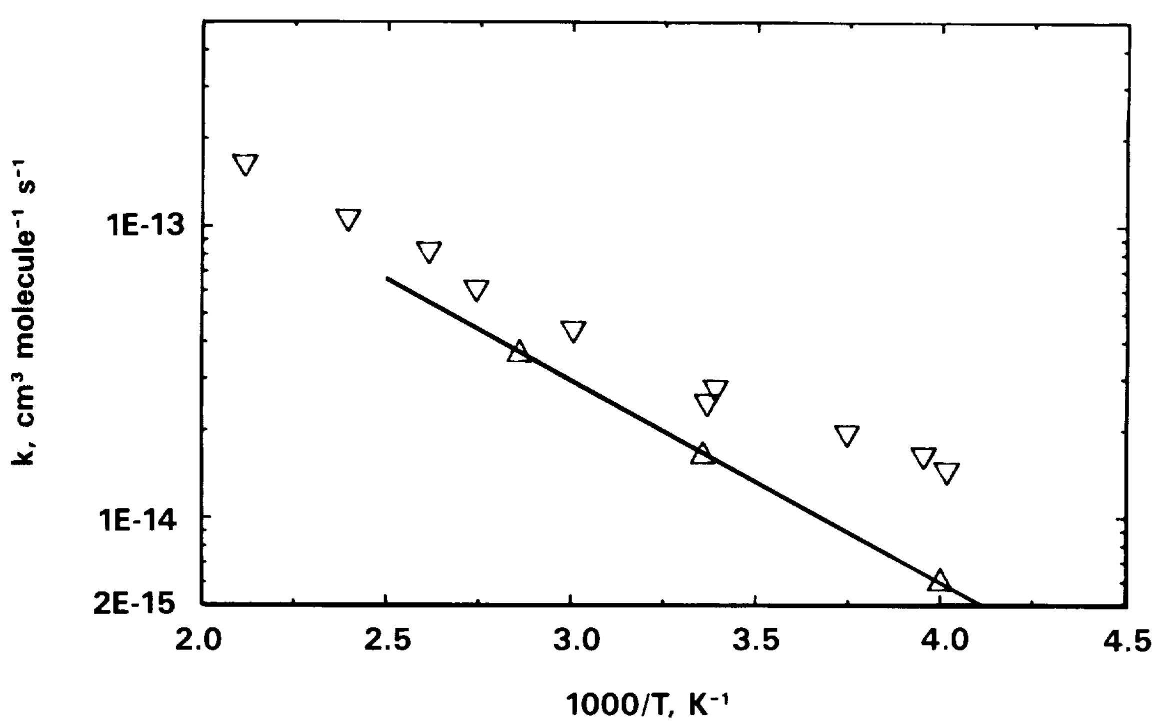
$k_{298} = 1.7 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}

$f_{298} = 2.0$

Comments on Preferred Values

The recommended temperature dependence was derived from the data of Watson et al. (1979) which were corrected by these authors for the presence of alkene impurities. The data of Jeong et al. (1984), indicating substantially faster rate constants may have been affected by such impurities and hence were not included in deriving the recommendation. The preferred value of k_{298} was derived from the recommended Arrhenius expression. This recommendation is essentially identical to the one in NASA (1987).

OH + HCFC-132b



$OH + CH_2ClCF_3$ (HCFC-133a) $\rightarrow H_2O + CHClCF_3$

Rate Coefficient Data

Temp. K.	$10^{15} \cdot k$ cm^3 molecule^{-1} s^{-1}	Reference
296	10.5	Howard and Evenson (1976b)
263	11	Handwerk and Zellner (1978)
268	12	
273	12	
283	15	
293	15	
337	28	
373	36	
294	10.3	Clyne and Holt (1979b)
322	38.3	
344	38.6	
358	69.4	
385	65.8	
407	130	
427	154	

Derived Arrhenius Parameters

$10^{12} \cdot A$ cm^3 molecule^{-1} s^{-1}	n	E/R K	Temp. K	Reference
1.1	-	1260	263-373	Handwerk and Zellner (1978)
38.9	-	2300	294-427	Clyne and Holt (1979b)

Reviews and Evaluations

8.5(-19)	2.0	458	263-373	Atkinson (1989)

$$OH + CH_2ClCF_3 \text{ (HCFC-133a)} \rightarrow H_2O + CHClCF_3$$

Preferred Values

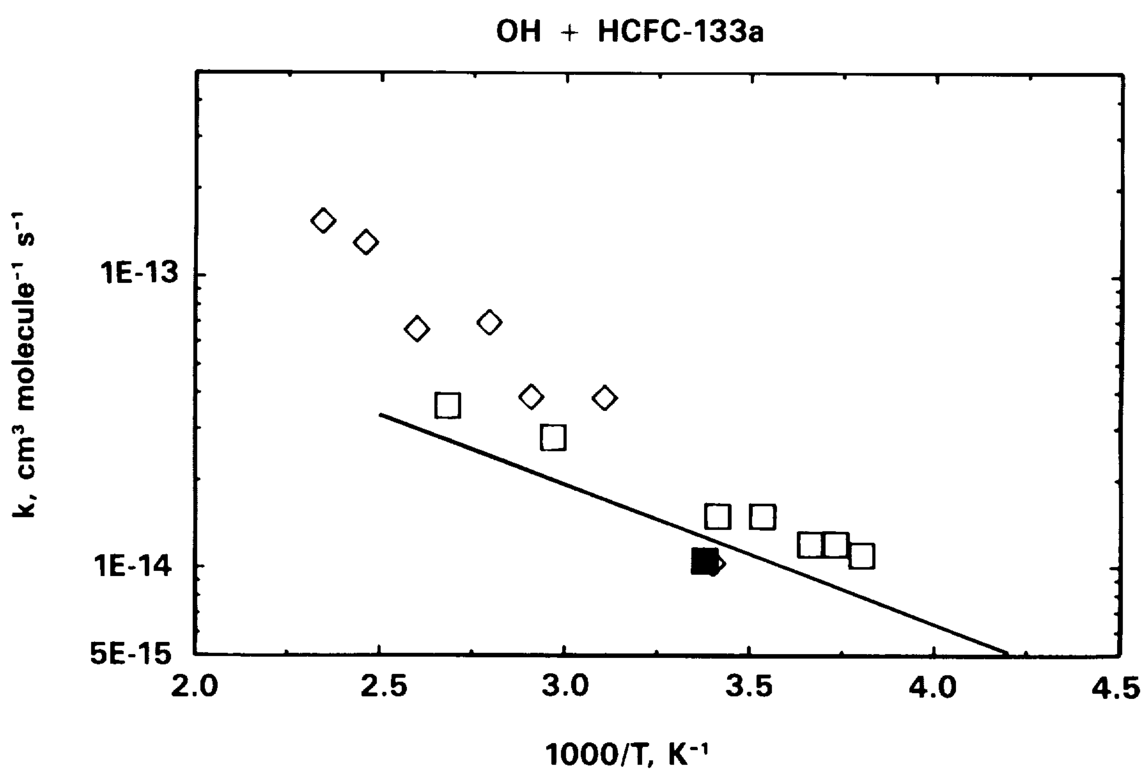
$k = 5.2\text{x}10^{-13} \exp[-(1100 \pm 300)/T]$ cm^3 molecule^{-1} s^{-1} $\quad 220 < T < 400$ K

$k_{298} = 1.3\text{x}10^{-14}$ cm^3 molecule^{-1} s^{-1}

$f_{298} = 1.3$

Comments on Preferred Values

The temperature dependence of the preferred rate expression was derived from the data of Handwerk and Zellner (1978). The recommended value of k_{298} is the average of the values of Howard and Evenson (1976b) and Handwerk and Zellner (1978) adjusted to 298 K. The data of Clyne and Holt (1979b) were not used in deriving this recommendation..



$OH + CHF_2CHF_2$ (HFC-134) $\rightarrow H_2O + CF_2CHF_2$

Rate Coefficient Data

Temp. K.	$10^{15}\cdot k$ cm^3 $molecule^{-1}$ s^{-1}	Reference
294	5.3	Clyne and Holt (1979b)
333	18.8	
389	21.2	
434	48.2	

Derived Arrhenius Parameters

$10^{12}\cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp. K	Reference
2.75	-	1800	294-434	Clyne and Holt (1979b)

Reviews and Evaluations

- none -

Preferred Values

$k = 8.7 \times 10^{-13} \exp[-(1500 \pm 500)/T]$ cm^3 $molecule^{-1}$ s^{-1} $\quad 220 < T < 400$ K

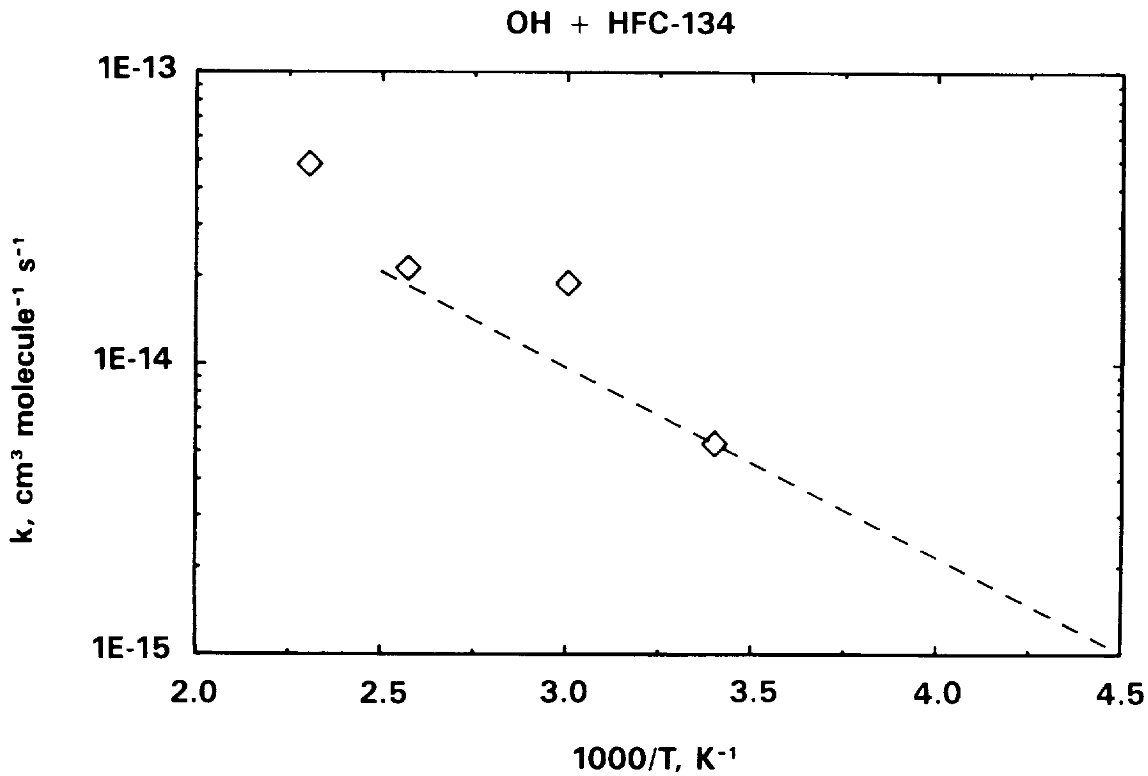
$k_{298} = 5.7 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}

$f_{298} = 2.0$

$$OH + CHF_2CHF_2 \text{ (HFC-134)} \rightarrow H_2O + CF_2CHF_2$$

Comments on Preferred Values

For the preferred rate expression, the data of Clyne and Holt (1979b) were rejected in favor of an estimated temperature dependence. The recommended value of k_{298} was obtained by adjusting the 294 K value of Clyne and Holt (1979b) to 298 K.



$OH + CH_2FCF_3$ (HFC-134a) $\rightarrow H_2O + CHFCF_3$

Rate Coefficient Data

Temp. K.	$10^{15}\cdot k$ cm^3 $molecule^{-1}$ s^{-1}	Reference
294	5.5	Clyne and Holt (1979b)
327	13.2	
344	16.4	
358	19.2	
393	38.3	
424	42.0	
429	36.4	
298	5.2	Martin and Paraskevopoulos (1983)
249	3.9	Jeong et al. (1984)
250	4.4	
268	5.5	
291	7.7	
295	8.2	
298	8.4	
342	15.4	
380	25.4	
430	39.4	
447	45.6	
473	64.4	
298	4.5	Ravishankara (1989)
298	4.3	
294	4.3	
324	7.65	
376	13.9	
425	25.3	
450	32.4	
270	2.63	Kurylo (1989)
298	5.18	
330	8.08	
350	13.1	
375	18.1	
400	27.2	

RATE CONSTANTS

$OH + CH_2FCF_3$ (HFC-134a) $\rightarrow H_2O + CHFCF_3$

Derived Arrhenius Parameters

$10^{12}\cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp. K	Reference
2.75	-	1800	294-429	Clyne and Holt (1979b)
1.10	-	1424	249-473	Jeong et al. (1984)

Reviews and Evaluations

0.66	-	1300	250-440	NASA (1987)
0.66	-	1300	250-440	IUPAC (1989)
1.27(-18)	2.0	769	250-470	Atkinson (1989)

Preferred Values

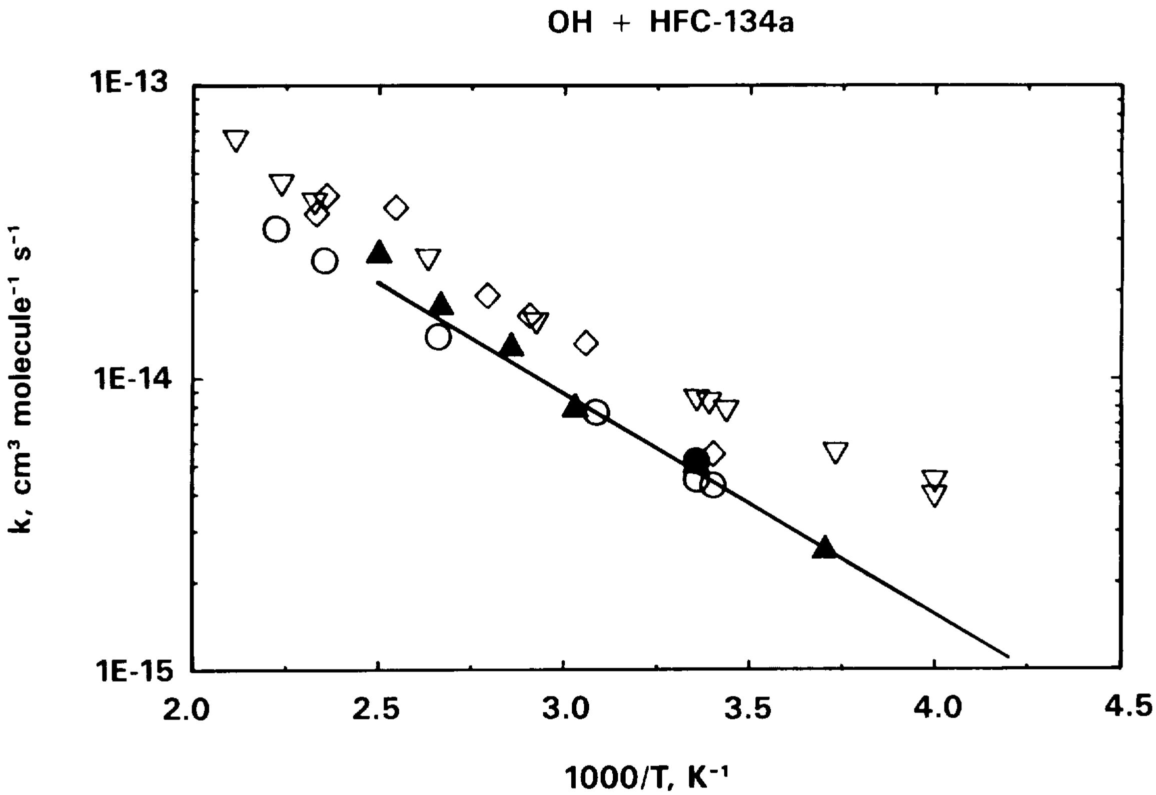
$k = 1.7x10^{-12} \exp[-(1750 \pm 300)/T]$ cm^3 $molecule^{-1}$ s^{-1} $\quad 220 < T < 400$ K

$k_{298} = 4.8x10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}

$f_{298} = 1.2$

Comments on Preferred Values

The preferred rate expression was derived from the data of Ravishankara (1989), Kurylo (1989) and the room temperature data point of Martin and Paraskevopoulos (1983). The recommended value of k_{298} is obtained from the rate expression. The data of Clyne and Holt (1979b) were not used. With the inclusion of the new data of Ravishankara and Kurylo this recommendation is considerably different from that of NASA (1987), which was based primarily on the data of Jeong (1984). The newer data suggest that the latter study may have overestimated the rate constant due to the presence of reactive impurities which can perturb the relatively slow reaction of OH with HFC-134a. This recommendation therefore results in significantly (factor of 2-4) smaller rate constants at stratospheric temperatures.


OH + HFC-134a
1E-13
1E-14
1E-15
k, cm³ molecule⁻¹ s⁻¹
2.0
2.5
3.0
3.5
4.0
4.5
1000/T, K⁻¹

$OH + CH_3CCl_3$ (Halocarbon-140) $\rightarrow H_2O + CH_2CCl_3$

Rate Coefficient Data

Temp. K.	$10^{15} \cdot k$ cm^3 $molecule^{-1}$ s^{-1}	Reference
296	15	Howard and Evenson (1976b)
260	7.1	Watson et al. (1977)
298	15.9	
375	48.5	
278	8.32	Jeong and Kaufman (1979)
293	10.6	
352	29.3	
400	55.2	
457	102	
222	3.18	Kurylo et al. (1979)
253	4.47	
263	5.40	
296	10.8	
363	38.5	
293	18.1	Clyne and Holt (1979a)
310	27.8	
338	45.9	
371	57.3	
399	72.9	
430	86.3	

$OH + CH_3CCl_3$ (Halocarbon-140) $\rightarrow H_2O + CH_2CCl_3$

Derived Arrhenius Parameters

$10^{12} \cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp. K	Reference
3.72	-	1627	260-375	Watson et al. (1977)
5.04	-	1797	278-457	Jeong and Kaufman (1979)
5.4	-	1810	253-363	Kurylo et al. (1979)
2.4	-	1394	293-430	Clyne and Holt (1979a)
		Reviews and Evaluations		
5.0	-	1800	222-457	NASA (1987)
5.1	-	1800	250-460	IUPAC (1989)
5.92(-18)	2.0	1129	253-457	Atkinson (1989)

Preferred Values

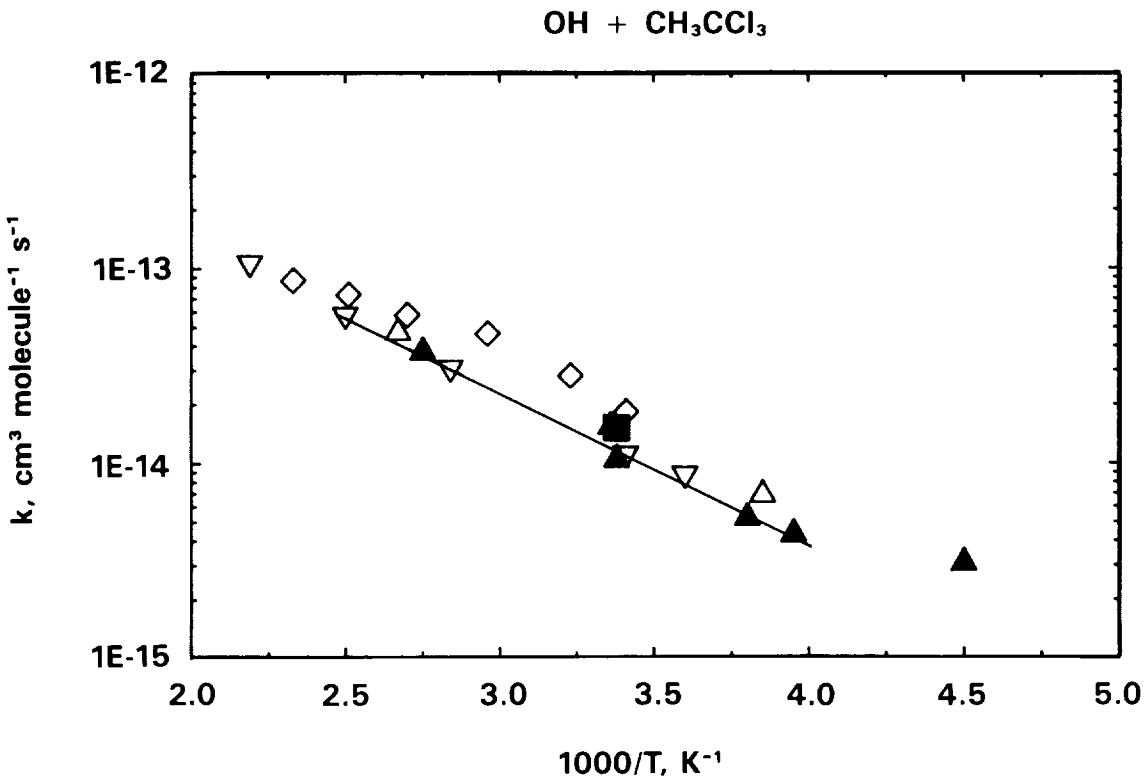
$k = 5.0 \times 10^{-12} \exp[-(1800 \pm 300)/T]$ cm^3 $molecule^{-1}$ s^{-1} $\quad 250 < T < 400$ K

$k_{298} = 1.2 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}

$f_{298} = 1.3$

Comments on Preferred Values

The recommendation is the same as that adopted in NASA (1987). The evaluation is based on the data of Jeong and Kaufman (1979) and Kurylo et al. (1979) excluding the value at 222 K.


OH + CH3CCl3
1E-12
1E-13
1E-14
1E-15
k, cm3 molecule-1 s-1
2.0
2.5
3.0
3.5
4.0
4.5
5.0
1000/T, K-1

$OH + CH_3CFCl_2$ (HCFC-141b) $\rightarrow H_2O + CH_2CFCl_2$

Rate Coefficient Data

Temp. K.	$10^{15}\cdot k$ cm^3 molecule^{-1} s^{-1}	Reference
244	4.13 (FP)	Ravishankara (1989)
277	5.77 (FP)	
293	7.2	
301	7.78 (FP)	
326	10.9	
347	13.9	
390	22.8	
434	36.4	
456	48.1	
243	4.20	Kurylo (1989)
273	5.24	
298	7.01	
330	9.62	
350	13.8	
400	19.4	

Derived Arrhenius Parameters

$10^{12}\cdot A$ cm^3 molecule^{-1} s^{-1}	n	E/R K	Temp.	Reference

- none -

Reviews and Evaluations

3.4	-	1800	270-330	NASA (1987) (Estimated; no data)

$OH + CH_3CFCl_2$ (HCFC-141b) $\rightarrow H_2O + CH_2CFCl_2$

Preferred Values

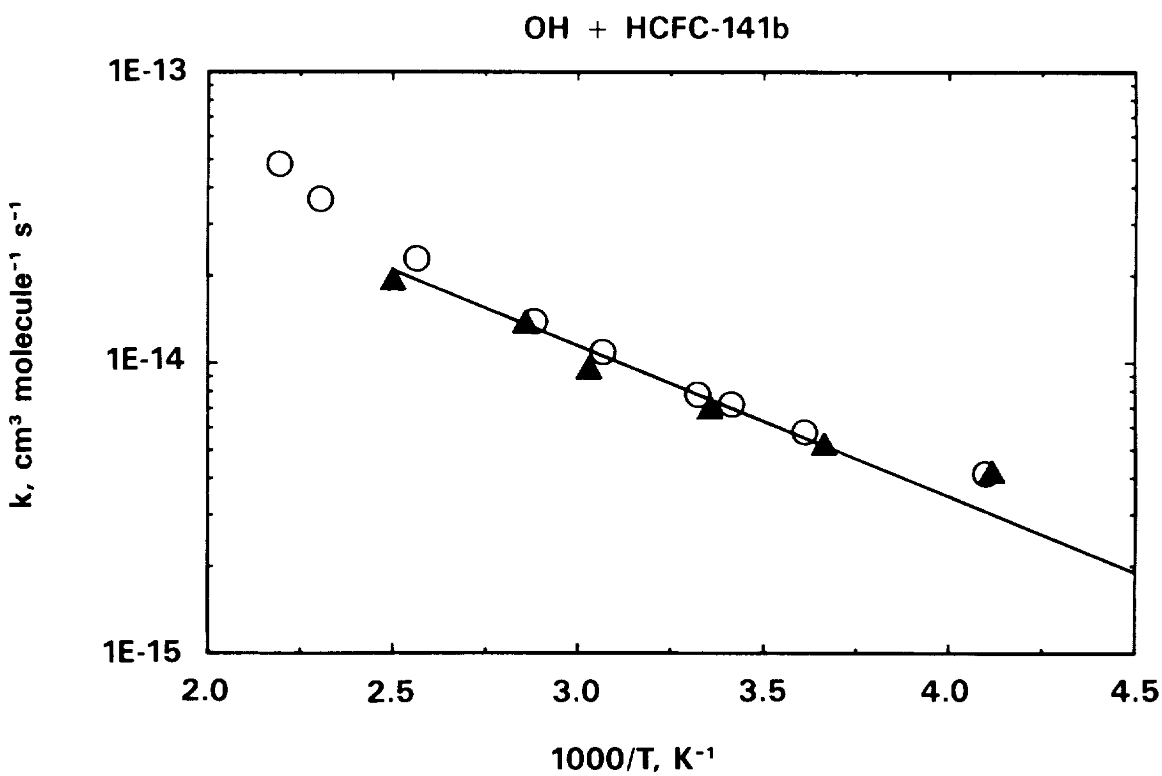
$k = 4.2 \times 10^{-13} \exp[-(1200 \pm 300)/T]$ cm^3 molecule^{-1} s^{-1} $\quad 220 < T < 400$ K

$k_{298} = 7.5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}

$f_{298} = 1.3$

Comments on Preferred Values

The preferred rate expression is significantly different from that estimated in NASA (1987) due to the recent availability of kinetics data from Ravishankara (1989) and Kurylo (1989). There is noticeable curvature in the Arrhenius plots from both studies. While the data can be fit to a reasonably straight line over the temperature range 240 - 400 K, a temperature range for the fit of 273 - 400 K was adopted. The reaction rate at the lowest temperature, being so slow, is most likely to be affected by impurities. In addition, inclusion of the lowest temperature points in the fit results in an unusually small A-factor. Rate constants derived from this recommendation are a factor of 1-3 times larger than those from NASA (1987) at low temperatures.



$OH + CH_3CF_2Cl$ (HCFC-142b) $\rightarrow H_2O + CH_2CF_2Cl$

Rate Coefficient Data

Temp. K.	$10^{15} \cdot k$ cm^3 $molecule^{-1}$ s^{-1}	Reference
296	2.83	Howard and Evenson (1976b)
273	1.92	Watson et al. (1977)
298	3.2	
375	10.9	
293	3.7	Handwerk and Zellner (1978)
373	14	
293	8.4	Clyne and Holt (1979b)
293	6.0	
323	12.0	
363	14.4	
380	30.9	
417	40.6	
297	4.63	Paraskevopoulos et al. (1981)
243	1.22	Ravishankara (1989)
268	2.00	
293	3.48	
352	7.94	
395	14.6	
270	2.14	Kurylo (1989)
298	4.02	
330	6.60	
350	7.97	
375	11.5	
400	17.0	

RATE CONSTANTS

$$OH + CH_3CF_2Cl\ (HCFC\text{-}142b) \rightarrow H_2O + CH_2CF_2Cl$$

Derived Arrhenius Parameters

$10^{12}\cdot A$ cm^3 molecule^{-1} s^{-1}	n	E/R K	Temp.	Reference
1.15	-	1748	273-375	Watson et al. (1977)
1.8	-	1790	293-373	Handwerk and Zellner (1978)
3.3	-	1800	293-417	Clyne and Holt (1979b)

Reviews and Evaluations

1.5	-	1800	270-380	NASA (1987)
1.6	-	1820	270-380	IUPAC (1989)
2.0(-18)	2.0	1170	270-380	Atkinson (1989)

Preferred Values

$k = 9.6\mathrm{x}10^{-13} \exp[-(1650 \pm 250)/T]$ cm^3 molecule^{-1} s^{-1} $220 < T < 400$ K

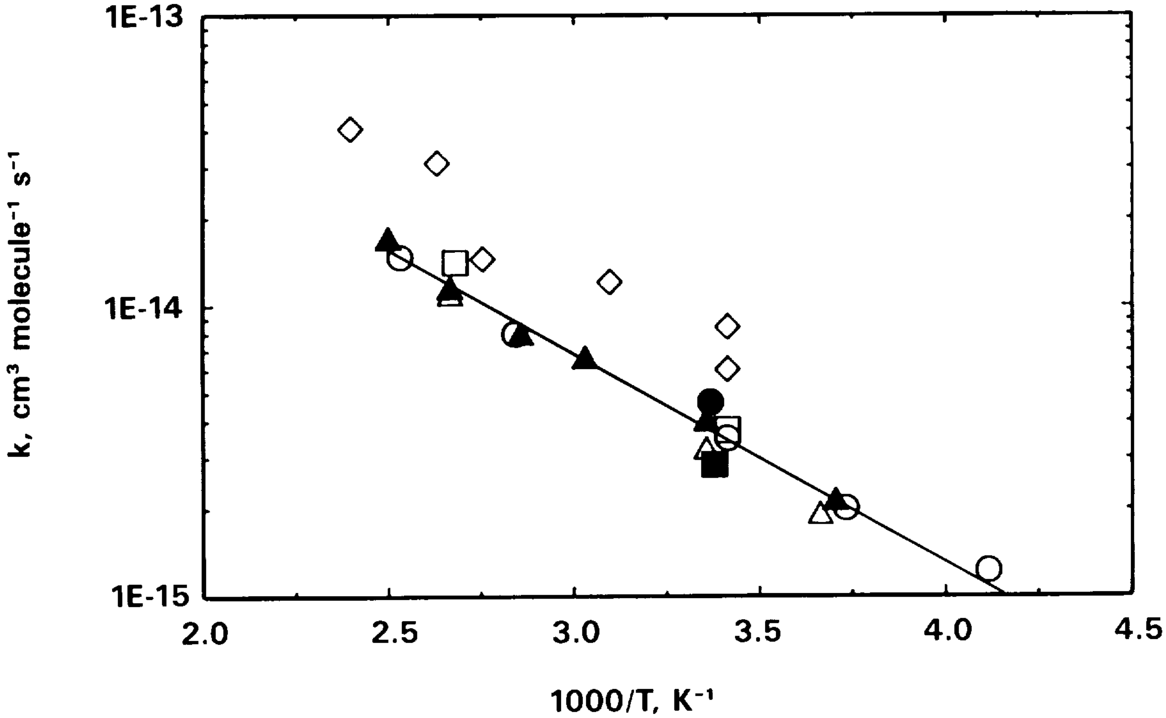
$k_{298} = 3.8\mathrm{x}10^{-15}$ cm^3 molecule^{-1} s^{-1}

$f_{298} = 1.2$

Comments on Preferred Values

The recommended rate expression is derived from a fit to the temperature dependence data of Ravishankara (1989), Kurylo (1989), Watson et al. (1977) and Handwerk and Zellner (1978), and the room temperature data of Howard and Evenson (1976b), and Paraskevopoulos et al. (1981). The value of k_{298} was derived from the rate expression. The preferred rate expression results in rate constants that are up to 25% larger at stratospheric temperatures than those derived from the NASA (1987) recommendation.

OH + HCFC-142b



$OH + CH_2FCHF_2$ (HFC-143) $\rightarrow H_2O$ + products

Rate Coefficient Data

Temp. K.	$10^{15} \cdot k$ cm^3 $molecule^{-1}$ s^{-1}	Reference
293	49.8	Clyne and Holt (1979b)
294	46.8	
335	67.4	
383	90.9	
441	189	
298	18.3	Martin and Paraskevopoulos (1983)

Derived Arrhenius Parameters

$10^{12} \cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp. K	Reference
1.48	-	1000	293-441	Clyne and Holt (1979b)

Reviews and Evaluations

- none -

Preferred Values

$k = 2.8 \times 10^{-12} \exp[-(1500 \pm 500)/T]$ cm^3 $molecule^{-1}$ s^{-1} $\quad 220 < T < 400$ K

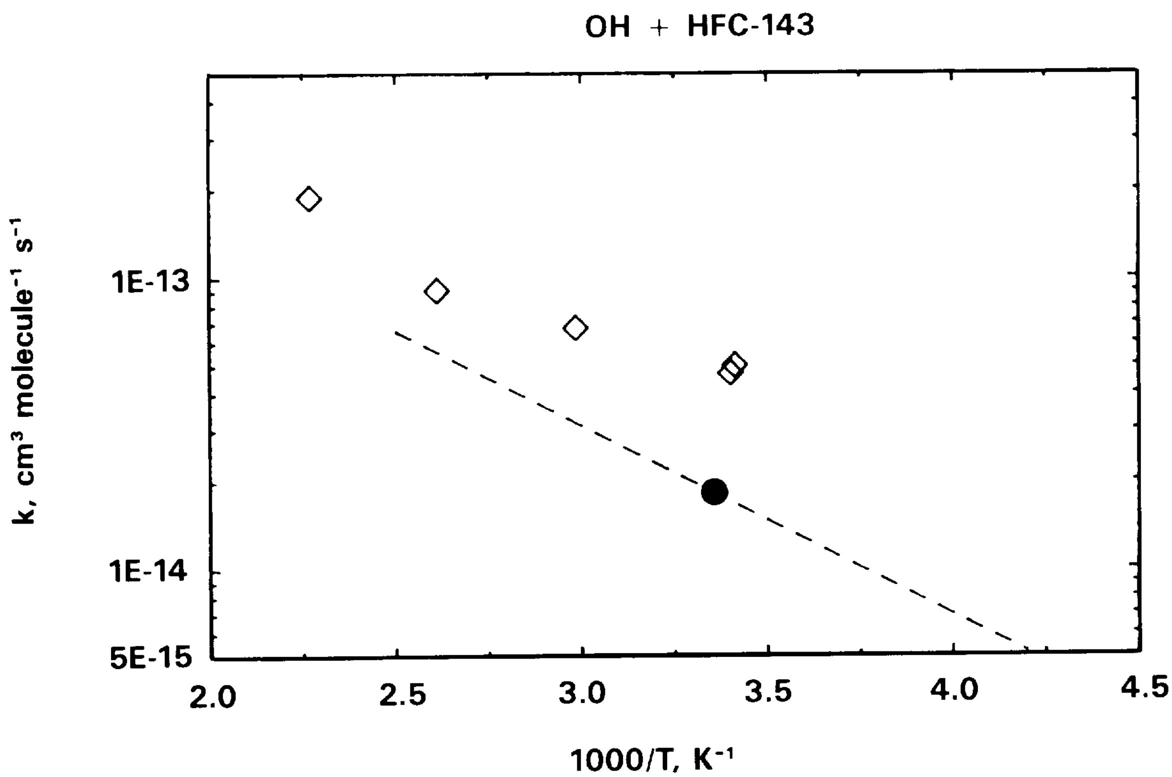
$k_{298} = 1.8 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}

$f_{298} = 2.0$

OH + CH_2FCHF_2 (HFC-143) → H_2O + products

Comments on Preferred Values

The only temperature dependence data for this reaction are those of 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 agreeement between the Clyne and Holt data and that of other workers for several other halomethanes and haloethanes, the Clyne and Holt data were not used in deriving this recommendation. The preferred value of k_{298} is taken from Martin and Paraskevopoulos (1983). The temperature dependence was estimated.



$OH + CH_3CF_3$ **(HFC-143a)** $\rightarrow H_2O + CH_2CF_3$

Rate Coefficient Data

Temp. K.	$10^{15}\cdot k$ cm^3 molecule^{-1} s^{-1}	Reference
293	<1.0	Clyne and Holt (1979b)
333	4.7	
378	12.9	
425	38.4	
298	1.7	Martin and Paraskevopoulos (1983)

Derived Arrhenius Parameters

$10^{12}\cdot A$ cm^3 molecule^{-1} s^{-1}	n	E/R K	Temp. K	Reference
69	-	3200	293-425	Clyne and Holt (1979b)

Reviews and Evaluations

- none -

Preferred Values

$k = 6.0 \times 10^{-13} \exp[-(1750 \pm 500)/T]$ cm^3 molecule^{-1} s^{-1} $220 < T < 400$ K

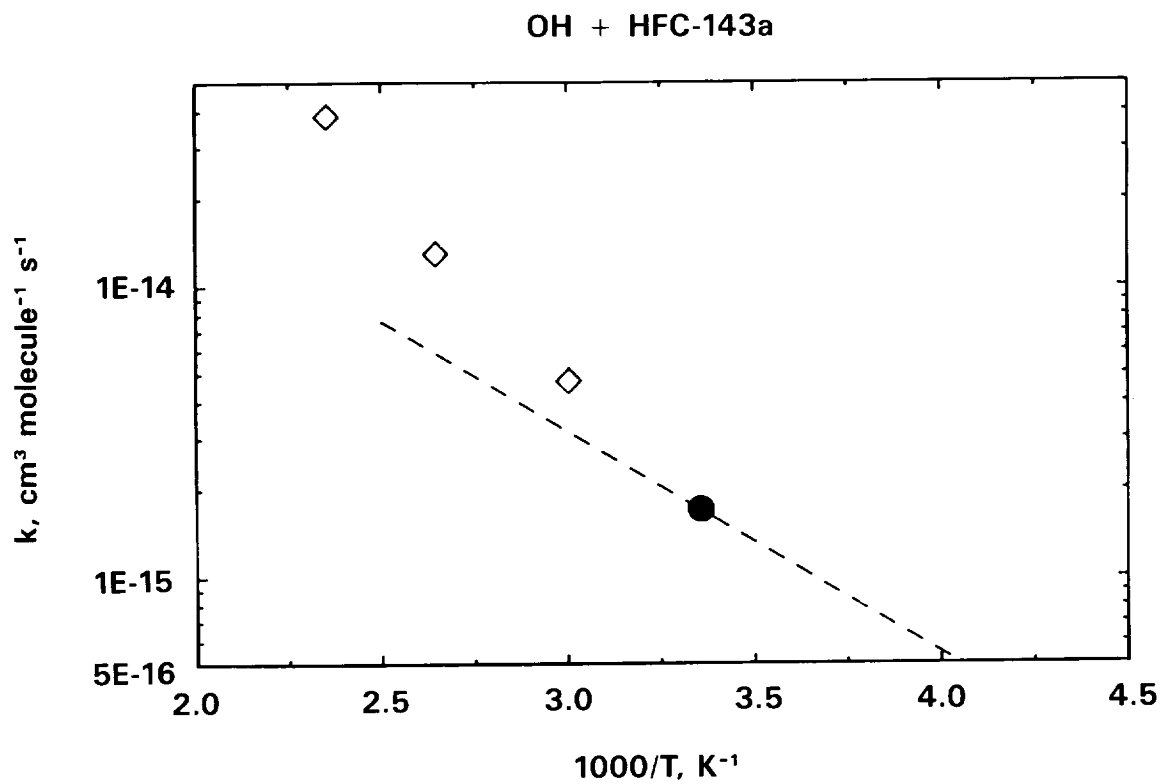
$k_{298} = 1.7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}

$f_{298} = 2.0$

$OH + CH_3CF_3$ (HFC-143a) $\rightarrow H_2O + CH_2CF_3$

Comments on Preferred Values

The only temperature dependence data for this reaction are those of 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 agreeement between the Clyne and Holt data and that of other workers for several other halomethanes and haloethanes, the Clyne and Holt data were not used in deriving this recommendation. The preferred value of k_{298} is taken from Martin and Paraskevopoulos (1983). The temperature dependence was estimated by comparison with HFC 134a.



$OH + CH_2FCH_2F$ (HFC-152) $\rightarrow H_2O + CH_2FCHF$

Rate Coefficient Data

Temp. K.	$10^{15} \cdot k$ cm^3 molecule^{-1} s^{-1}	Reference
298	112	Martin and Paraskevopoulos (1983)

Derived Arrhenius Parameters

$10^{12} \cdot A$ cm^3 molecule^{-1} s^{-1}	n	E/R K	Temp. K	Reference

- none -

Reviews and Evaluations

- none -

Preferred Values

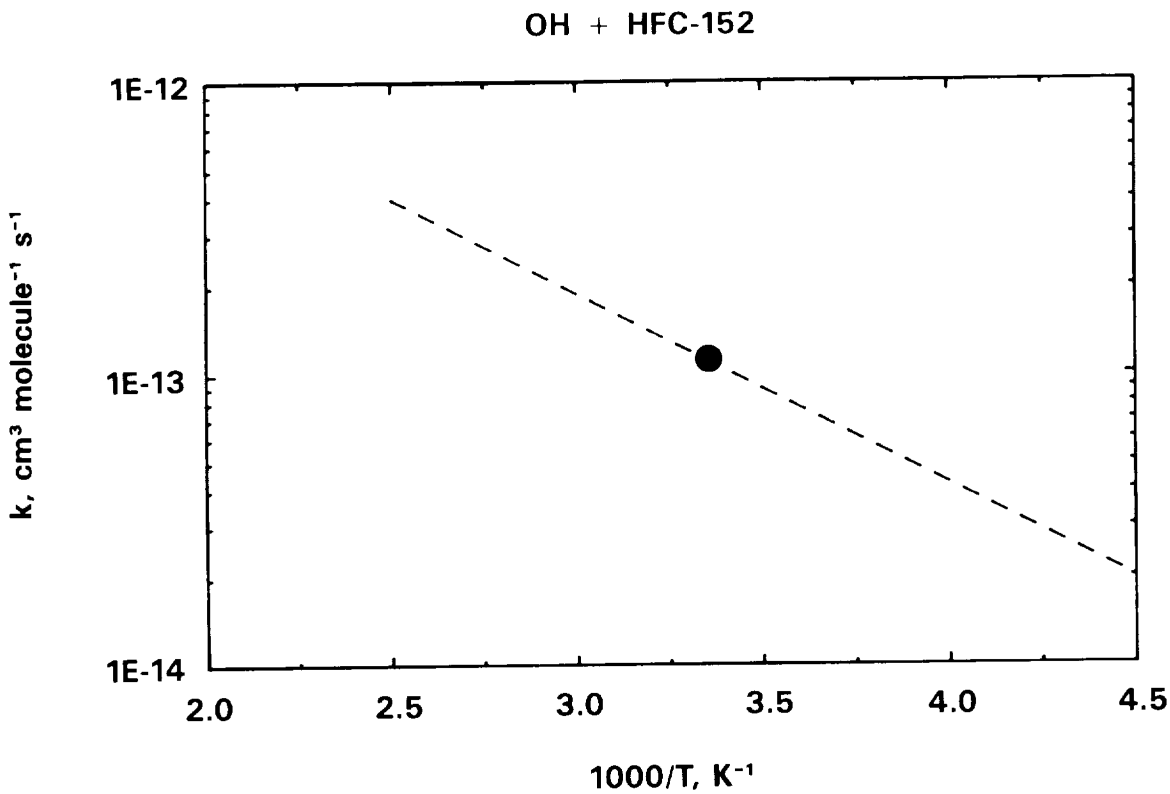
$k = 1.7 \times 10^{-11} \exp[-(1500 \pm 500)/T]$ cm^3 molecule^{-1} s^{-1} $\quad 220 < T < 400$ K

$k_{298} = 1.1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}

$f_{298} = 2.0$

Comments on Preferred Values

The preferred rate expression is derived by fitting an estimated temperature dependence to the room temperature data of Martin and Paraskevopoulos (1983).


OH + HFC-152
1E-12
1E-13
1E-14
k, cm³ molecule⁻¹ s⁻¹
2.0
2.5
3.0
3.5
4.0
4.5
1000/T, K⁻¹

$OH + CH_3CHF_2$ (HFC-152a) $\rightarrow H_2O$ + products

Rate Coefficient Data

Temp. K.	$10^{15} \cdot k$ cm^3 molecule^{-1} s^{-1}	Reference
296	31	Howard and Evenson (1976b)
293	35	Handwerk and Zellner (1978)
297	37	Nip et al. (1979)
293	46.6	Clyne and Holt (1979b)
323	71.6	
363	101	
417	164	
238	15.3	Ravishankara (1989)
258	20.0	
293	34	
349	64	
388	94.3	
402	113	
409	117	
423	132	
270	29.9	Kurylo (1989)
298	42.2	
330	53.2	
350	68.1	
375	73.0	
400	103	

$OH + CH_3CHF_2$ (HFC-152a) $\rightarrow H_2O$ + products

Derived Arrhenius Parameters

$10^{12}\cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp. K	Reference
2.95	-	1200	293-417	Clyne and Holt (1979b)

Reviews and Evaluations

1.9	-	1200	270-330	NASA (1987)

Preferred Values

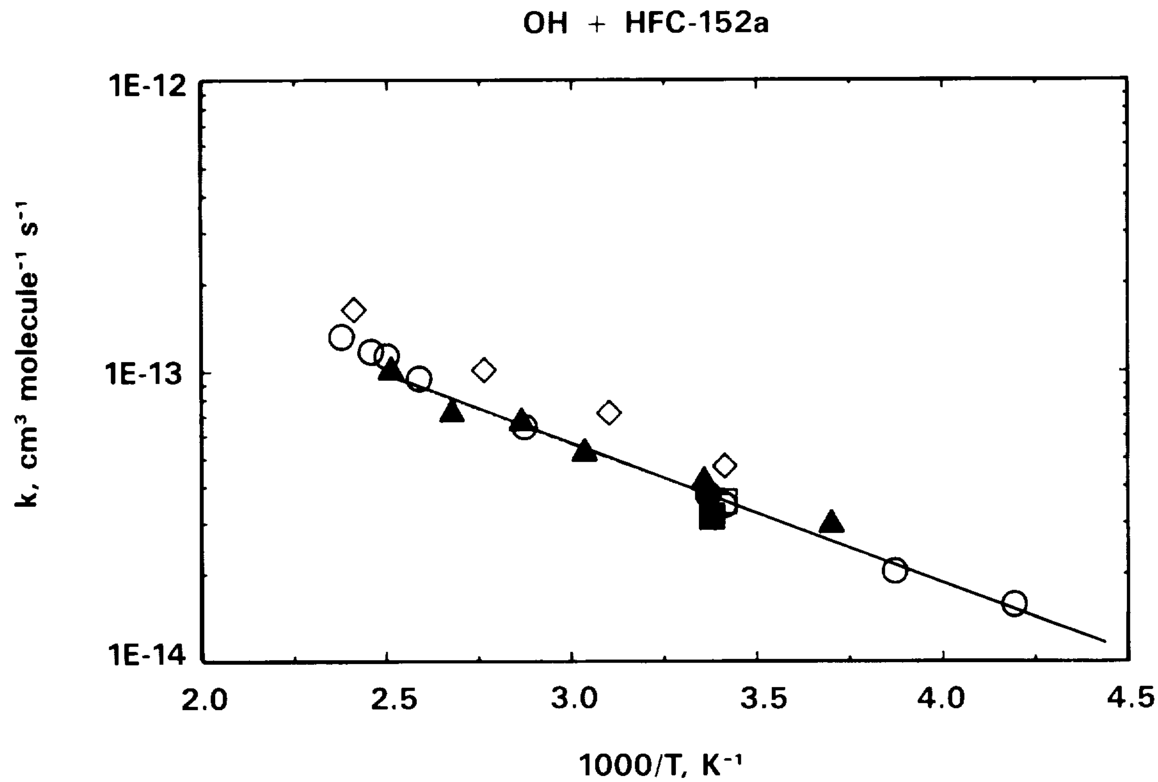
$k = 1.5x10^{-12} \exp[-(1100 \pm 200)/T]$ cm^3 $molecule^{-1}$ s^{-1} $220 < T < 400$ K

$k_{298} = 3.7x10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}

$f_{298} = 1.1$

Comments on Preferred Values

The preferred rate expression is derived from the temperature dependence data of Ravishankara (1989) and Kurylo (1989) and the room temperature data of Howard and Evenson (1976b), Handwerk and Zellner (1978), and Nip et al. (1979). The data of Clyne and Holt (1979b) were not used in this derivation. The value for k_{298} is that calculated from the expression.


OH + HFC-152a
1E-12
1E-13
1E-14
k, cm^3 molecule^{-1} s^{-1}
2.0
2.5
3.0
3.5
4.0
4.5
1000/T, K^{-1}

$OH + CH_3CH_2F$ (HFC-161) $\rightarrow H_2O$ + products

Rate Coefficient Data

Temp. K.	$10^{15}\cdot k$ cm^3 $molecule^{-1}$ s^{-1}	Reference
297	232	Nip et al. (1979)

Derived Arrhenius Parameters

$10^{12}\cdot A$ cm^3 $molecule^{-1}$ s^{-1}	n	E/R K	Temp. K	Reference

- none -

Reviews and Evaluations

- none -

Preferred Values

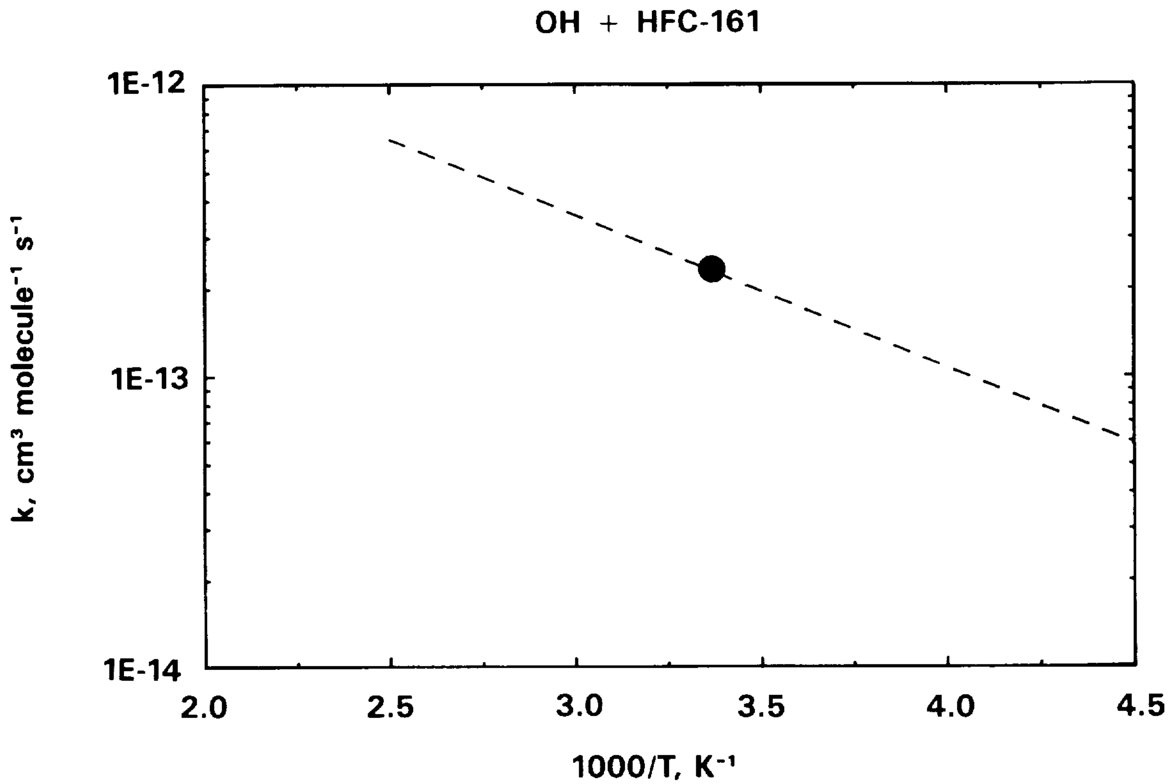
$k = 1.3x10^{-11} \exp[-(1200 \pm 300)/T]$ cm^3 $molecule^{-1}$ s^{-1} $220 < T < 400$ K

$k_{298} = 2.3x10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}

$f_{298} = 2.0$

Comments on Preferred Values

There are no temperature dependence data for this reaction. The temperature dependence of the recommended expression was derived by analogy with members of the homologous series which includes the $OH + C_2H_6$ and $OH + CH_3CHF_2$ (HFC 152a) reactions. The value of k_{298} was taken from the study of Nip et al. (1979). Singleton et al. (1980) determined that 85 ± 3 % of the abstraction by OH is from the fluorine substituted methyl group.


OH + HFC-161
1E-12
1E-13
1E-14
k, cm³ molecule⁻¹ s⁻¹
2.0
2.5
3.0
3.5
4.0
4.5
1000/T, K⁻¹

IV. ABSORPTION CROSS SECTIONS

Review of Ultraviolet Absorption Cross Sections of a Series of Alternative Fluorocarbons

M. J. Molina
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, CA 91109

/06

EXECUTIVE SUMMARY

Solar photolysis is likely to contribute significantly to the stratospheric destruction of those alternative fluorocarbons (HFC's) which have two or more chlorine atoms bonded to the same carbon atom. Two of the eight HFC's considered in this review fall into this category, namely HFC-123 and HFC-141b. For these two species there is good agreement among the various measurements of the ultraviolet cross sections in the wavelength region which is important for atmospheric photodissociation, that is, around 200 nm. There is also good agreement for HFC-124, HFC-22 and HFC 142b; these are the three species which contain one chlorine atom per molecule. The agreement in the measurements is poor for the other species, i.e., those that do not contain chlorine, except in so far as to corroborate that solar photolysis should be negligible relative to destruction by hydroxyl radicals.