RATE CONSTANTS FOR THE REACTIONS OF OH WITH CH_3Cl, CH_2Cl_2, $CHCl_3$, and CH_3Br

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Abstract. Rate constants for the reactions of OH with CH_3Cl, CH_2Cl_2, $CHCl_3$, and CH_3Br have been measured by a relative rate technique in which the reaction rate of each compound was compared to that of HFC-152a (CH_3CHF_2) and, for CH_2Cl_2, HFC-161 (CH_3CH_2F). Using absolute rate constants for HFC-152a which we have determined relative to those for CH_4 and CH_3CCl_3, and for HFC-161 as determined relative to C_2H_6 [Hsu and DeMore, 1994], temperature dependent rate constants of both compounds were derived. The derived rate constant for CH_3Br is in good agreement with recent absolute measurements [Mellouki et al, 1992; Zhang et al., 1992]. However, for the chloromethanes all the rate constants are lower at atmospheric temperatures than previous estimates [JPL 92-20], especially for CH_2Cl_2 where the present rate constant is about a factor of 1.6 below the JPL 92-20 value. The new rate constant appears to resolve contradictions between observed atmospheric concentrations and estimated release rates for that compound [Koppmann et al., 1993].

Introduction

The compounds CH_3Cl, CH_2Cl_2, $CHCl_3$, and CH_3Br are significant atmospheric species which are present at concentrations of about 600 ppt for CH_3Cl and about an order of magnitude less for the other three compounds. [See WMO, 1985; Koppmann et al., 1993; and previous references quoted therein]. Methyl chloride, which is mainly of natural origin, is a significant source of stratospheric chlorine. Methylene chloride has largely industrial sources in the Northern hemisphere, and has a latitudinal gradient which makes it useful as an atmospheric tracer. Sources of $CHCl_3$ are not well understood, but are probably both industrial and

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natural. CH_3Br has both man made and natural sources, and is especially significant as a source of atmospheric bromine. The principal fate of all three compounds is destruction by OH attack. To determine the atmospheric lifetimes, it is necessary to have accurate temperature dependent rate constants for the OH abstraction reactions. Measurements of rate constants relative to that for CH_3CCl_3 are especially useful because global distributions of that compound are used to calculate average tropospheric OH concentrations. [Singh, 1977; Prinn et al., 1992]. Global distributions of CH_3CCl_3, combined with the known emission rates [Midgely, 1989], have been used to calculate the CH_3CCl_3 lifetime in the atmosphere. Therefore, atmospheric lifetimes relative to that of methyl chloroform may be calculated from the inverse dependence on the ratio of rate constants [Prather and Spivakovsky, 1990]. The derived lifetimes are thus independent of the absolute CH_3CCl_3 rate constant.

Experimental Method

The experimental method was similar to that previously described [DeMore, 1992 and 1993]. The major advantage of this method is that it is not sensitive to reactant impurities, secondary reactions of OH, or wall loss of OH. The OH radicals are produced by UV photolysis of O_3 in the presence of water vapor in a slow-flow, temperature-controlled photochemical reactor. All experiments were at atmospheric pressure. Each reactant is depleted by the OH reaction in a manner similar to that of the atmosphere. The rate constant ratio is obtained from the relation:

$$k_{reactant}/k_{reference} = \ln(DF)_{reactant}/\ln(DF)_{reference} \qquad (I)$$

The quantity DF (depletion factor) is given by:

$$DF = (\text{Initial Conc.})/(\text{Final Conc.}) \qquad (II)$$

HFCs 152a and 161 were used as reference compounds because their infrared spectra are resolved from those of the chloromethanes, and they have strong, well-defined C-F bands which are suitable for the relative concentration measurements. We have separately measured the rate constant for HFC-152a with reference to both CH_4 and

CH_3CCl_3 [Hsu and DeMore, 1994], using the currently recommended rate constants for those compounds [JPL 92-20]. Although 152a was the principal reference compound used for all four compounds in the present work, CH_2Cl_2 was also measured against HFC-161 as a check on the HFC-152a results. This was considered necessary in view of the fact that our derived rate constant for CH_2Cl_2 is much lower than previous measurements have indicated. The reference rate constants used were k(152a) = 2.3E-12 exp(-1275/T) and k(161) = 1.0E-12 exp(-1228/T), in units of cm^3/molec-s. The 152a rate constant is an average of calibrations versus CH_4 and CH_3CCl_3: $k(152a)^{CH4}$ = 1.87E-12exp(-1221/T) and $k(152a)^{CH3CCl3}$ = 2.76E-12 exp(-1330/T). These two results are in excellent agreement and give k(298 K) for 152a = 3.1E-14 and 3.2E-14 cm^3/molec-s, respectively. This result is similar to our previous experience with HFC-134a [DeMore,1993], in which similarly identical results for the 134a rate constant were obtained from CH_4 and CH_3CCl_3 as references. The implication is that the JPL 92-20 rate constants for CH_4 and CH_3CCl_3 are accurate, at least on a relative basis.

Initial reactant concentrations were in the range 10^{14} to 10^{15} cm^{-3}, and depletion factors were normally about 1.1 to 1.5. Concentrations were monitored with a Nicolet 20SX FTIR operated at 0.5 cm^{-1} resolution in the absorbance mode using a White cell with a three-meter path length. The photolysis cell was quartz with a water jacket for temperature control. The light source was a low pressure Hg lamp.

Results

Table 1 summarizes the ratios measured, and Figures 1(a)-(e) are graphs of the ratio data in Arrhenius form. The Arrhenius expressions as derived from linear least squares fits of these data are listed in Table 2. Table 3 gives the calculated rate constants, based on the reference rate constants as indicated in the footnotes. Figures 2-4 show a graphical comparison of the present results compared to other recent work.

Discussion

The rate constants reported in this work are based on those of CH_4, CH_3CCl_3, and (to a lesser extent) C_2H_6. CH_4 and CH_3CCl_3 are useful as references because their OH rate

constants appear to be very accurately known, and CH_3CCl_3 is used to calibrate OH concentrations in the troposphere, as previously mentioned. When compared to a common reference such as HCFC-141b, HFC-134a, or HFC-152a. [DeMore, 1993; Huder and DeMore, 1993; and Hsu and DeMore, 1994], the CH_4 and CH_3CCl_3 rate constants as recommended in JPL 92-20 are mutually consistent within 3% or better at 298 K. This consistency also shows that little propagation of error is introduced through the use of a transfer standard such as HFC-152a. The C_2H_6 rate constant, which we used to obtain the HFC-161 rate constant, also appears to be accurate on an absolute basis, although a direct comparison with CH_4 and CH_3CCl_3 is difficult because of the large difference in magnitude of the rate constants.

The three chloromethane rate constants derived in this work are substantially lower than those of the JPL 92-20 evaluation.This is in keeping with the general trend of recently measured OH abstraction rate constants to be lower than those of earlier work.

Our CH_3Cl rate constant is 40% lower at 298 K than the JPL 92-20 recommendation (see Table 3). Agreement with the Taylor et al. [1993] results is good at higher temperatures (around 370 K), but less satisfactory at 298 K (see Figure 2).

The results for CH_2Cl_2 are the most surprising, being about a factor of 1.6 lower than previous absolute measurements, which are in good agreement with each other. Because of this discrepancy, we tested our results by additional experiments relative to HFC-161, which in turn was referenced to C_2H_6. The resulting consistency (within 12%) argues against any large error in our ratio measurements or in our rate constant for the reference compound HFC-152a. We thus believe that the CH_2Cl_2 rate constant is indeed much lower than previously reported. This conclusion is consistent with atmospheric measurements of CH_2Cl_2 [Koppmann et al., 1993], which showed higher concentrations of that compound (by about the same factor) than expected on the basis of estimated release rates and the previous rate constant.

Our result for $CHCl_3$ is in reasonable agreement with earlier measurements (Table 3 and Figure 4), although again somewhat lower. Previous problems with the reported Arrhenius parameters for this compound [Cohen and Westberg, 1991], which were revealed by transition state

theory (TST) calculations, appear to have been resolved both by our work and by the recent data of Taylor et al. (1993). The new results yield much lower rate constants at high temperature than previous measurements from that laboratory, and are now consistent with the TST predictions.

Our rate constant for CH_3Br is in good agreement with the JPL 92-20 recommendation, both in terms of the absolute value (6% lower at 298 K) and the Arrhenius parameters. A recent absolute measurement by Chichinin et al. (1993) is also in good agreement at 298 K with the previous results, although the Arrhenius parameters are slightly lower.

Acknowledgements

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Fig. 1. Arrhenius plots of the rate constant ratio data from Table 1.

Fig. 2. Arrhenius plot of the data for CH_3Cl and comparison with previous results.

Fig. 3. Arrhenius plot of the data for CH_2Cl_2 and comparison with previous results.

Fig. 4. Arrhenius plot of the data for $CHCl_3$ and comparison with previous results.

Fig. 5. Arrhenius plot of the data for CH_3Br and comparison with previous results.

Table 1. Experimental Data for Ratios Measured vs. HFC-152a and HFC-161

CH_3Cl		CH_2Cl_2				$CHCl_3$		CH_3Br	
T(K)	Ratio/152a	T(K)	Ratio/152a	T(K)	Ratio/161	T(K)	Ratio/152a	T(K)	Ratio/152a
293	0.958	293	2.562	298	0.565	288	2.904	298	0.833
298	0.934	293	2.652	298	0.563	293	3.002	298	0.925
298	1.028	298	2.594	298	0.565	293	3.103	303	0.922
301	0.998	308	2.535	310	0.550	298	2.645	308	0.934
308	1.072	318	2.472	319	0.539	298	2.544	313	0.919
308	0.974	331	2.453	328	0.518	298	2.618	323	0.890
313	1.059	343	2.239	341	0.530	308	2.639	328	0.978
323	1.104	349	2.229	353	0.508	318	2.565	338	1.025
333	1.118	354	2.158	368	0.511	328	2.307	343	1.010
345	1.025	360	2.241			338	2.313	351	0.945
358	1.090	360	2.162			351	2.147	359	0.995
						357	2.095	360	1.045

Table 2. Ratios Measured and Their Temperature Dependences

Ratio	Arrhenius Expression[a]	Ratio at 298 K
$k(CH_3Cl) / k(152a)$	$(1.91 \pm 0.45) \exp((-195 \pm 74)/T)$	0.99
$k(CH_2Cl_2) / k(152a)$	$(0.97 \pm 0.09) \exp((294 \pm 29)/T)$	2.60
$k(CH_2Cl_2) / k(161)$	$(0.32 \pm 0.02) \exp((171 \pm 20)/T)$	0.57
$k(CHCl_3) / k(152a)$	$(0.52 \pm 0.11) \exp((495 \pm 64)/T)$	2.74
$k(CH_3Br) / k(152a)$	$(1.94 \pm 0.28) \exp((-232 \pm 46)/T)$	0.89

Units of A and k are cm^3/molec-s.

(a) Errors shown are standard deviations. Actual uncertainties are approximately a factor of 1.3 in the A-factor ratios and 75-125 K in the E/R values.

Table 3. Derived Rate Constants and Comparisons with Other Work.

Reactant	A-Factor	E/R (K)	k(298 K)	Source
CH_3Cl	4.4E-12	1470	3.1E-14	This work[a]
	2.1E-12	1150	4.4E-14	JPL 92-20
	1.1E-11	1712	3.5E-14	Taylor et al. (1993)
CH_2Cl_2	2.2E-12	981	8.2E-14	This work[a]
	3.2E-12	1057	9.2E-14	This work[b]
	5.8E-12	1100	1.4E-13	JPL 92-20
	6.0E-12	1096	1.5E-13	Taylor et al. (1993)
$CHCl_3$	1.2E-12	780	8.8E-14	This work[a]
	4.3E-12	1100	1.1E-13	JPL 92-20
	1.2E-12	714	1.1E-13	Taylor et al. (1993)
CH_3Br	4.4E-12	1507	2.8E-14	This work[a]
	1.9E-12	1230	3.0E-14	Chichinin et al. (1993)
	2.4E-12	1300	3.0E-14	Mellouki et al. (1992)
	5.8E-12	1560	3.1E-14	Zhang et al. (1992)

Units of A and k are cm^3/molec-s.

(a) Using k(HFC-152a) = 2.3E-12exp(-1275/T). See text.

(b) Using k(HFC-161) = 1.0E-11exp(-1228/T). See text.

Figure 1a

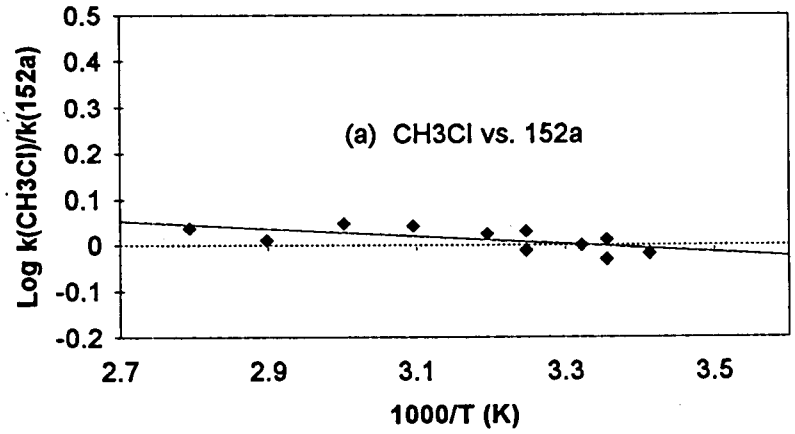

0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
Log k(CH3Cl)/k(152a)
(a) CH3Cl vs. 152a
2.7
2.9
3.1
3.3
3.5
1000/T (K)

Figure 1b

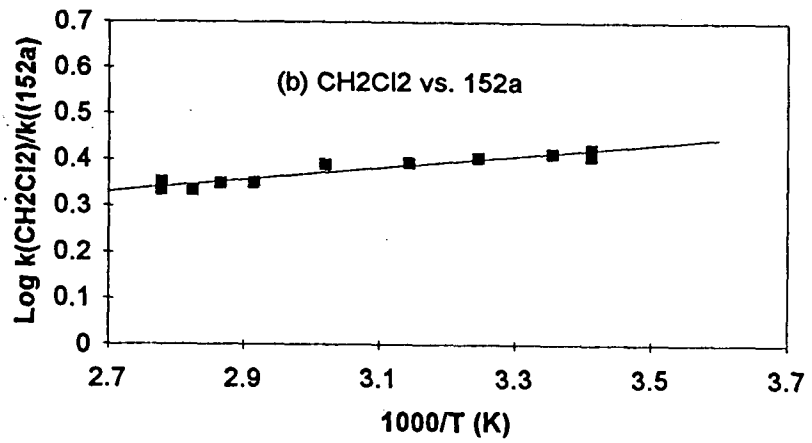

(b) CH2Cl2 vs. 152a
Log k(CH2Cl2)/k((152a)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
2.7
2.9
3.1
3.3
3.5
3.7
1000/T (K)

Figure 1c

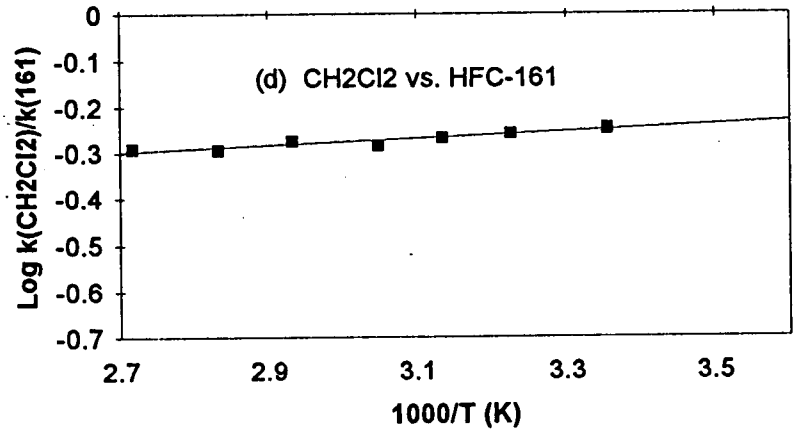

(d) CH2Cl2 vs. HFC-161
Log k(CH2Cl2)/k(161)
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
2.7
2.9
3.1
3.3
3.5
1000/T (K)

Figure 1d

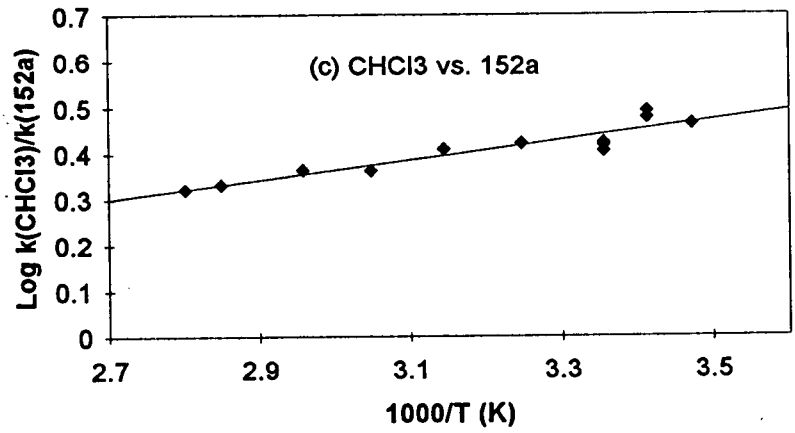

(c) CHCl3 vs. 152a
Log k(CHCl3)/k(152a)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
2.7
2.9
3.1
3.3
3.5
1000/T (K)

Figure 1e

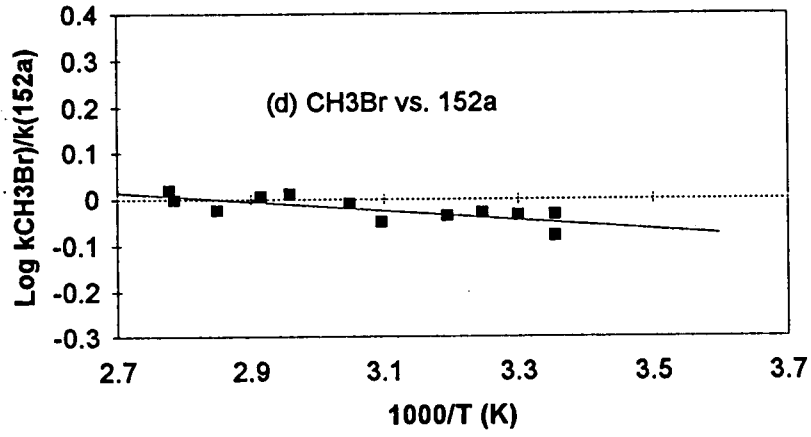

(d) CH3Br vs. 152a
Log kCH3Br)/k(152a)
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
2.7
2.9
3.1
3.3
3.5
3.7
1000/T (K)

Figure 2

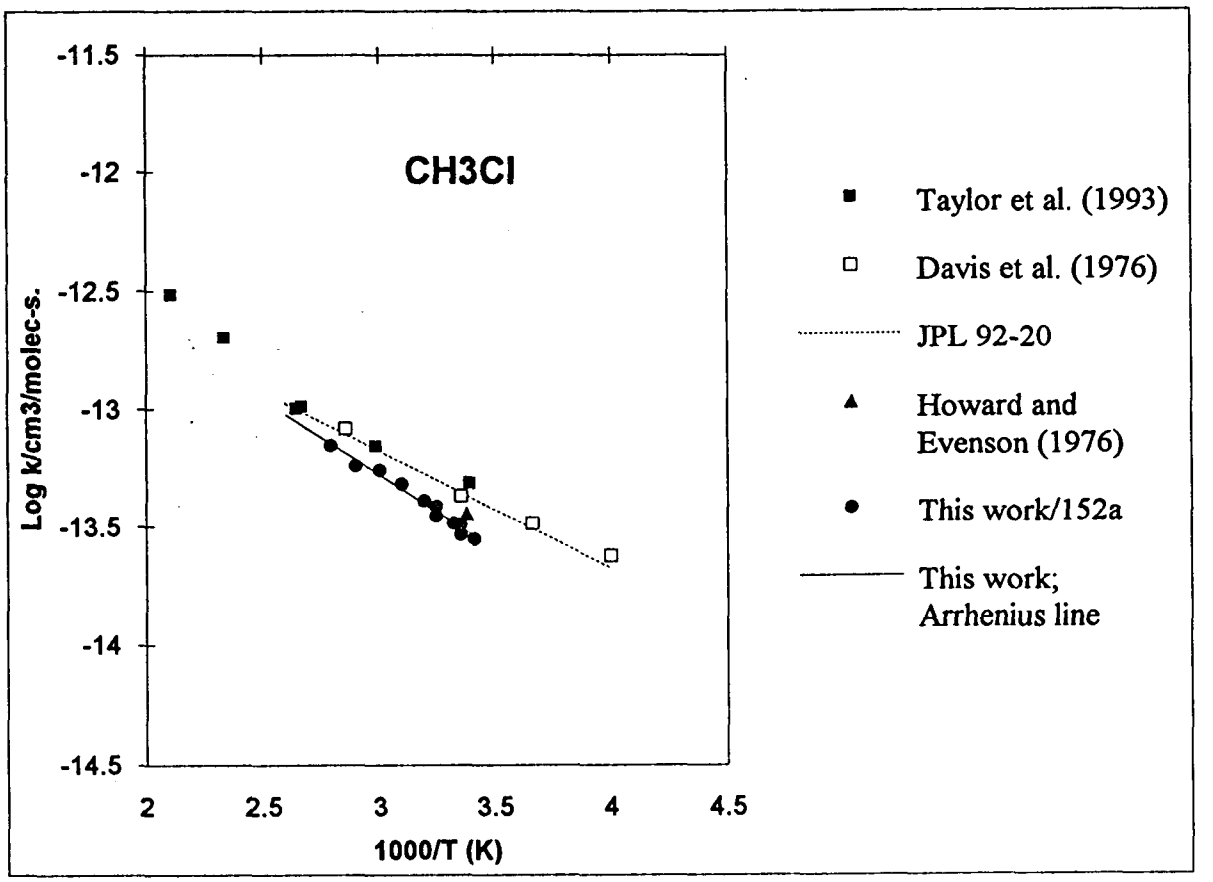

CH3Cl
-11.5
-12
-12.5
-13
-13.5
-14
-14.5
Log k/cm3/molec-s.
2
2.5
3
3.5
4
4.5
1000/T (K)
Taylor et al. (1993)
Davis et al. (1976)
JPL 92-20
Howard and Evenson (1976)
This work/152a
This work; Arrhenius line

Figure 3

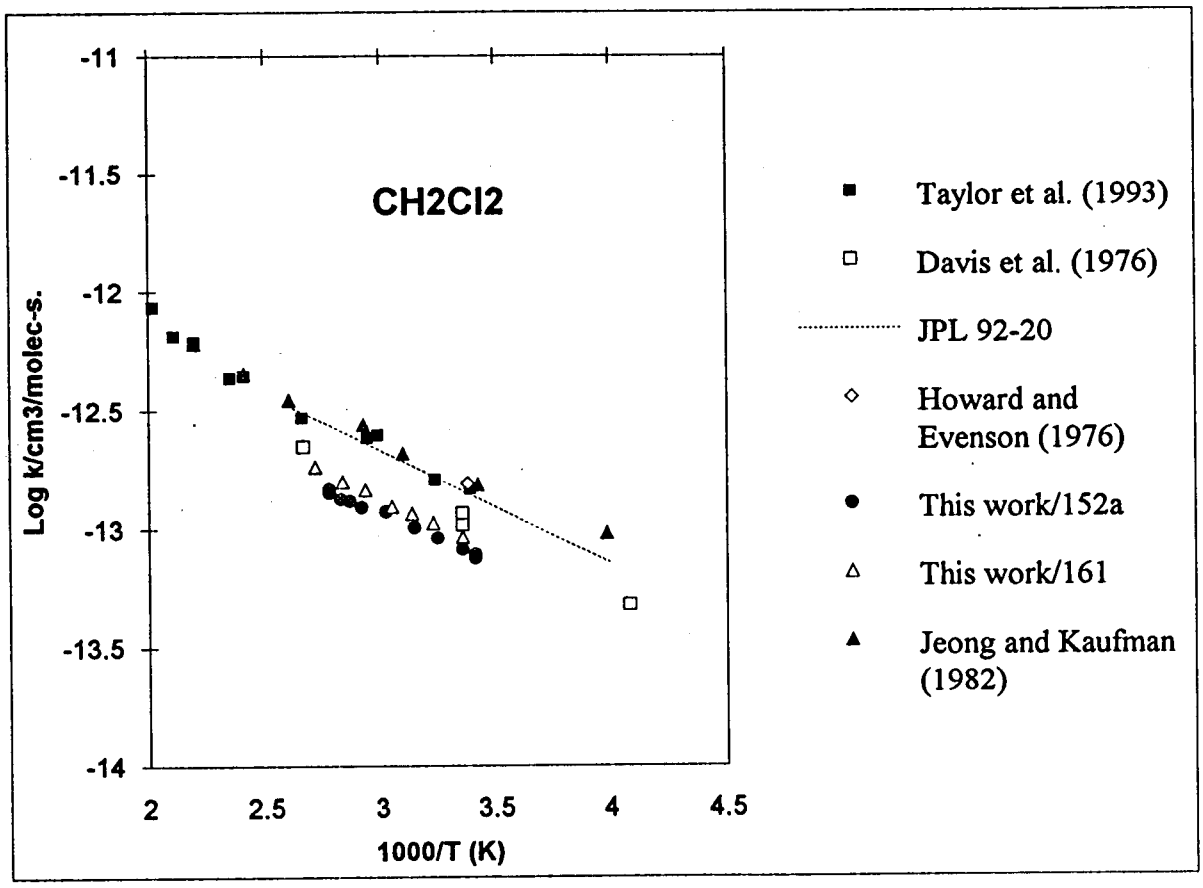

CH2Cl2
Log k/cm3/molec-s.
-11
-11.5
-12
-12.5
-13
-13.5
-14
2
2.5
3
3.5
4
4.5
1000/T (K)
Taylor et al. (1993)
Davis et al. (1976)
JPL 92-20
Howard and Evenson (1976)
This work/152a
This work/161
Jeong and Kaufman (1982)

Figure 4

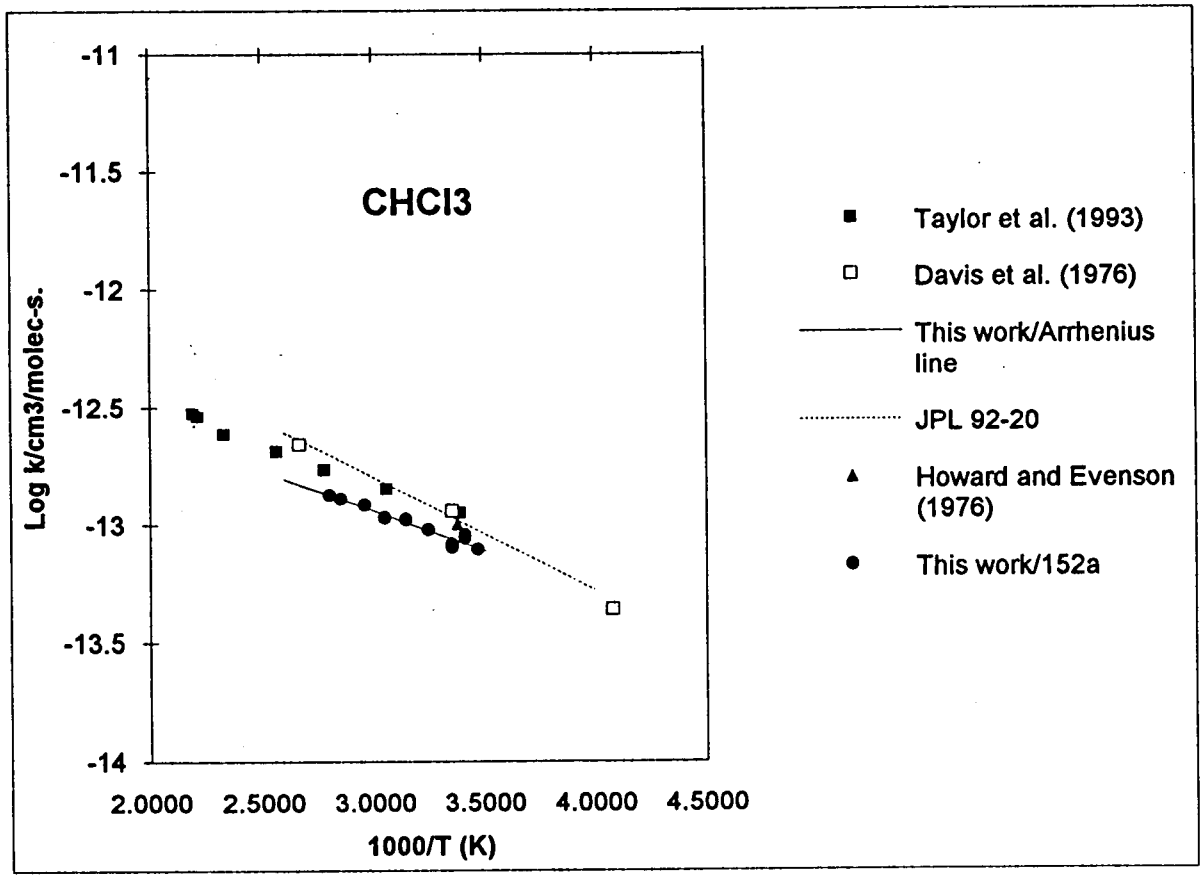
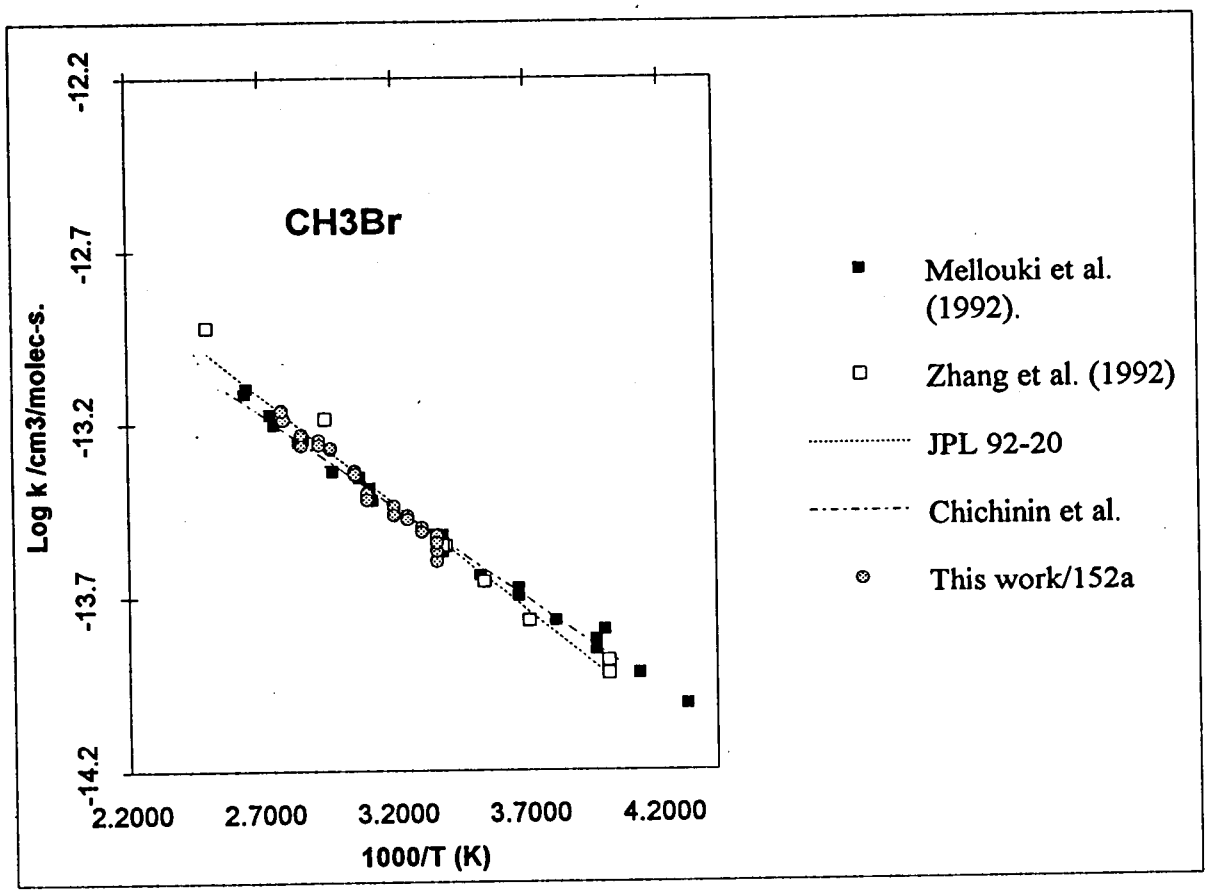

CHCl3
Log k/cm3/molec-s.
-11
-11.5
-12
-12.5
-13
-13.5
-14
2.0000
2.5000
3.0000
3.5000
4.0000
4.5000
1000/T (K)
Taylor et al. (1993)
Davis et al. (1976)
This work/Arrhenius line
JPL 92-20
Howard and Evenson (1976)
This work/152a

Figure 5


CH3Br
Log k /cm3/molec-s.
-12.2
-12.7
-13.2
-13.7
-14.2
2.2000
2.7000
3.2000
3.7000
4.2000
1000/T (K)
Mellouki et al. (1992).
Zhang et al. (1992)
JPL 92-20
Chichinin et al.
This work/152a