Experimental and Estimated Rate Constants for the Reactions of Hydroxyl Radicals with Several Halocarbons

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Abstract

Relative rate experimental data are used to derive rate constants and temperature dependencies of the reactions of OH with CH_3F (41), CH_2FCl (31), CH_2BrCl (30B1), CH_2Br_2 (30B2), $CHBr_3$ (20B3), $CF_2BrCHFCl$ (123aB 1α), and $CF_2ClCHCl_2$ (122). Rate constants for additional compounds of these types are estimated using an empirical rate constant estimation method, which is based on measured rate constants for a wide range of halocarbons. The experimental data are combined with the estimated and previously reported rate constants to illustrate the effects of F, Cl, and Br substitution on OH rate constants for a series of 19 halomethanes and 25 haloethanes. Application of the estimation technique is further illustrated for some higher HFCs, including $CHF_2CF_2CF_2CF_2H$ (338pcc), $CF_3CHFCHFCF_2CF_3$ (43-10mee), $CF_3CH_2CH_2CF_3$ (356ffa), $CF_3CH_2CF_2CH_2CF_3$ (458mfcf), $CF_3CH_2CHF_2$ (245fa), and $CF_3CH_2CF_2CH_3$ (365mfc). The predictions are compared with literature data for these compounds.

introduction

Many halocarbons containing at least one hydrogen atom are currently of interest as possible chlorofluorocarbon replacements for refrigerants, lubricants, solvents, fire suppressants, and other applications. The tropospheric lifetime of these compounds, which is an important measure of their potential environmental impact, is determined primarily by the rate of reaction with the OH radical. Owing to the large number of possible isomeric compounds of these types, laboratory measurement of every one is very time-consuming.. It is therefore desirable to use empirical methods to extrapolate the data whenever possible. In the present work a combination of experimental and estimated rate constants are presented for all possible F, Cl, and Br compounds of methane which contain at least one H atom, and also for a set of 25 compounds of ethane. Methods are shown which permit extension of the results to other isomers.

Methods

Relative Rate Measurements. The technique used in this work has been described in several recent publications. [1-6] The method involves measurement of the fractional loss of the reactant compound compared to a reference compound, in the presence of OH. In the present work we have used the reference compounds which are shown in **Table 1.** The OH radicals are produced by 254 nm photolysis of O_3 (5- 10 x 10^{16} cm^{-3}) in the presence of water vapor (3-5 x 10^{17} cm^{-3}) or by direct photolysis of H_2O at 185 nm. The experiments are done in a temperature-controlled cylindrical quartz cell, operated either in a slow-flow or stopped-flow mode. The cylindrical cell is 10 cm in length and 5 cm in diameter, and is either water-jacketed (for the 0_3 photolysis experiments) or wrapped with heating tape and insulating material for the H_2O photolysis experiments. Residence times in the cell for the slow-flow mode are about one minute. Concentrations are 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. Other details of the experimental procedure are described in the papers referenced above.

Rate Constant Estimation Method. A simple group additivity approach has been used for the estimation of OH abstraction rate constants. It is basically an extension of existing data, and is similar in principle to that described by Atkinson,[7] but somewhat different in detail. In this method the logarithm (base 10) of the rate constant (per H-atom) is given by the following equation :

$$\log k = \log k(CH_4) + G \qquad \text{(I)}$$

The total rate constant is given by the sum of the contributions from each C-H bond present in the molecule. The quantity G is the contribution for the various groups, such as Cl, Br, CH3, CF3, etc. The group contributions are determined from the data of **Table. 2** by an optimization procedure such as that in the Excel spreadsheet program. In this procedure the cumulative difference between log k(experimental) and log k(estimated) is minimized by varying the group contributions to obtain the best fit,

Significant parameterization is necessary to account for interactions between groups when more than one group is present on the carbon atom. Two approaches have been used, one for two groups and one for three groups, When the two groups are atoms, the interactions are accounted for by treating them as a single group, and the best value of the net contribution is determined in the fitting procedure. Most two-atom combinations could actually be treated as the sum of the corresponding single group contributions. However, this is not the case for two fluorine atoms, for which the group contribution is not even approximately additive. The group contribution for two F-atoms is less than that for a single F-atom. For all other two-group combinations (i. e., those not involving two atoms), the assumption of group additivity is made. When three groups are present, a multiplier (determined in the fitting procedure) is applied to reduce the contribution of the third group. An alternative procedure would be to apply a multiplier to all three groups. However, a better fit is obtained by the adopted procedure. To decide which is to be the third group, atoms are always considered as first and second groups, and radicals (such as CCl_3, for example) are taken as the third group. When ambiguity exists (as when all three groups are atoms), the rate constant is calculated for all possible combinations, and the average is taken. The results for different assumptions usually do not differ more than 20-300A, except when one or two of the atoms are F, in which case the difference may be a factor of two or more.

In the fitting procedure the maximum allowed error factor between estimated and experimental rate constants was set at 1.35. That value was chosen because the experimental rate data are believed to be in error by no more than this factor. A smaller factor cannot be fit by the program, which may be due in part to small variations in the pre-exponential factors for different reactions, which are not accounted for by the group approach. See further evaluation below (Discussion section) on possible A-factor differences among the OH abstraction reactions.

When more than one reactive site is present, the total rate constant is calculated as the sum of the separate contributions. This calculation gives a good estimate of the relative rates of attack at different sites in the molecule.

The fitted group contributions and the third-group multiplier are listed in **Table** 3. The range of group contributions can be extended by taking them as equal to those of similar groups. For example, the group contribution for C_2F_5 is taken to be identical to that of CF_3. The experimental data of **Table** 2 were fit with an average error of 15%. The estimated rate constants are usually reliable to within a factor of 1.3 to 1.5. For the most part the accuracy is comparable to that of absolute rate constant measurements, which often are high due to impurity effects. When combined with estimated A-factors, the temperature dependence of the rate constants can be deduced. Thus the entire Arrhenius expression can be obtained quickly and reliably.

The estimated A-factors are based on the previously reported observation that ratios of A-factors as determined in relative rate experiments are very closely proportional to the number of H-atoms in the molecule (i. e., for reactive sites within the molecule where the H-atoms are equivalent). The value A/n= 8.013-13 cm3/molec.-s, where n is the number of H-atoms, is found to adequately represent the bulk of the reliable experimental data.

The compound $CF_3CH_2CHF_2$ (HFC-245fa), with two reactive carbon atom sites, can be used as an example of the rate constant estimation method, using the fitted parameters from **Table** 3. (Units are cm^3/molec-s.).

$-CH_2-$ site: log k = -14.79+- $G(CF_3)$ + $G(CH_2F)$ + log 2. = -14.55
k= 2.8E-15

$-CHF_2$ site: log k = -14.79 + G(2F) + 0.37 $G(CH_2F)$ = -14.22
k = 5.2E-15

The total rate constant is 8.OE-15, which compares well with the experimental value of 6.8 E-15. In this example it may be noted that CH2F was used as a surrogate for the CF3CH2 group. The calculation shows that the CHF_2 group is the major reaction site in the molecule, despite the fact that there is only one H atom at that site. This is a consequence of the strongly deactivating effect of the CF3 group adjacent to the CH2 site.

Results

Experimental Measurements.

The rate constant ratio measurements at different temperatures arc shown in **Table** 4 for the five halomethanes studied in this work. The corresponding results for the two haloethanes, $CF_2BrCHFCl$ (123aB *la)* and $CF_2ClCHCl_2$ (122), are shown in **Table** 5. Linear least squares fits to these data in Arrhenius form are listed in **Table 6.** Using the reference rate constant expressions from **Table 1,** the ratio expressions from **Table 6** were converted to absolute rate constants, and the resulting data are plotted in **Figures 1-7.** The figures include data from other laboratories for comparison.

Tables 7 and 8 summarize the experimental rate constants from the present work, along with estimated rate constants for additional compounds in the series.

CH_3F (41). The magnitude of the 298 K rate constant obtained in the present work with reference to CH_3Cl agrees to within 5°/0 with the value obtained previously with I WC-152a as the references *See* **Figure 1**.The data are also in excellent agreement with the earlier results of Jeong and Kaufman[8] and Howard and Evenson.[9] The Schmoltner ct al. data[10] are in good agreement in the upper temperature range, but are slightly higher at low temperatures. Our ncw data, covering a wider

temperature range than our previous data, yield a higher A-factor than that obtained in our earlier work. As seen in **Table** 6, the A-factor ratio for CH3F and CH_3Cl is close to unity. This tends to resolve the discrepancy based on our earlier result for CH_3F relative to HFC-152a, which seemed to indicate a lower A-factor (factor of 2) for CH_3F. Our combined data for CH3F (both HFC- 152a and CH_3Cl as references) correspond to a least squares rate constant of k = 4.41{-12 exp(-1655/T). This result is probably accurate at 298 K to within 10%, based on the agreement between the two experiments with different reference gases.. The uncertainty in E/R is about 150 K.

CH_2FCl (31). The database for this reaction was previously thought to be well-established. [11] However, our results are about a factor of 1.6 lower (at all temperatures) than the earlier data of Jeong and Kaufman, on which the JPL 94 recommendation is largely based. See **Figure 2.** A similar discrepancy occurred previously with the CH_2Cl_2 rate constant, for which Jeong and Kaufman obtained a higher value by about the same factor. The results near 298 K of Handwerk and Zellner[12] and Howard and Evenson[9] for CH_2FCl are about 20°/0 higher than ours. The uncertainty in our derived rate constant at 298 K is estimated to be about 15%, and the uncertainty in E/R is about 150 K. The A-factor **(Table** 7) is nearly identical to those of CH_2BrCl, CH_2Br_2, and CH_2Cl_2, as expected.

CH_2BrCl (30B1). **(Figure 3).** There are ***no*** previous data for this reactant. Our data indicate a rate constant essentially equal to that for CH_2Cl_2, although with a slightly lower E/R. At lower temperatures (below about 315 K), the experiment was affected by apparent aerosol formation, which interfered with the infrared analysis. This accounts for the increased scatter of data at these temperatures. The uncertainties in k(298 K) and E/R are about 20°/0 and 200 K, respectively.

CH_2Br_2 (30B2). **(Figure 4).** Our data and those of Mellouki et al. [13] are in essentially perfect agreement. No other measurements are known. This rate constant appears to be well-established, with an uncertainty of about 10°/0 at 298 K and about 100 K in E/R.

$CHBr_3$ (20B3). (Figure 5). There are no other published data for this reaction. The low temperature data are scattered somewhat because of aerosol formation, as with CH_2BrCl Also, this compound photolyzes at 254 nm, and therefore there was some loss (about 20°/0) when the lamp was turned on. A constant first order loss of reactant would not affect the rate constant ratio measurement. Therefore the experiments were conducted with the lamp always on, and the OH reaction was turned on and off by means of adding or withholding ozone. The steady-state ozone concentrations were small enough to avoid significant change in the J-value for $CHBr_3$ due to the added ozone. However, because of aerosol formation and the photolysis problem, we assign an uncertainty of 25% in k(298 K) and an uncertainty of 200 K in E/R. It may be noted that the derived A-factor of 1.6E-12 is anomalously high for a compound with only one H atom. This is probably a reflection of experimental error.

CF2BrCHFCl (123aB1 a). **(Figure** 6). There are no previous data for this compound. As seen in **Table** 8, the rate constant and the Arrhenius parameters are very similar to those for $CF_2ClCHFCl$ (123a) and CCl_2CHFCl (122a). At temperatures below 45 oC, them was some aerosol interference. The infrared spectrum of this sample is complex, due to the presence of the three halogen atoms. Also, there was some evidence that the $CF_2BrCHFCl$ sample had significant impurities, based on the presence of some IR bands which did not change by the same amount as the majority. This would not affect the measured rate constant ratio, since those bands were not used to measure the changes in concentration of the $CF_2BrCHFCl$. The estimated uncertainty of this rate constant is about 20% at 298 K and about 200 K in E/R.

$CF_2ClCHCl_2$ (122). **(Figure 7).** Initial experiments with CH_2Cl_2 as the reference gas showed a dependence on the extent of reactant conversion, which is a certain indication of error. However, at

higher 03 concentrations the data were well-behaved. Apparently there is significant release of atomic chlorine in secondary chemistry, and most of the Cl reacts with CH_2Cl_2 because of the relatively rapid rate constant for that reaction. The rate of reaction of Cl with HCFC- 122 is not known, but is probably an order of magnitude slower than with CH_2Cl_2. Provided that the 03 is not allowed to be completely depleted, the Cl is scavenged by reaction with 03, which is much faster than the reaction with CH_2Cl_2. Additional experiments were conducted with CF_3CHCl_2 (HCFC-1 23) as a reference gas. The results were in excellent agreement with those obtained with CH_2Cl_2 at high 03 concentrations, as shown in the figure. This compound reacts about 30 times slower with Cl than does CH_2Cl_2. No complications were observed, even at low 03 concentrations. It is desirable, nevertheless, to avoid experiments with near-zero final 03 concentrations, in which there is a possibility of Cl formation. The only known previous data for IICFC-122 are those of Orkin et al.,[14] shown in the figure. Their data are about 25% higher than ours, at all temperatures. Their rate constant is k = 1.1 E-12 exp(-9 18/T). This is to be compared with our expression, k = 8.3 E-13 exp(-893/T). Thus the principal difference is in the A-factor. The estimated uncertainty of our rate constant is about 15% in k(298 K) and about 150 K in E/R.

Rate Constant Estimations.

Halomethanes. The estimation method has been used in **Table** 7 to expand the rate constant set to include all possible isomers of F, Cl, and Br for the halogen-substituted methanes containing at least one H atom. The predictions are based on the entire database as represented by Table 2, not just the halomethanes. Some compounds in **Table** 7 for which experimental data exist were not included in the calibration database. These include CHF3 (23), CHF_2Br (22B 1), $CHCl_2F$ (21), and CHBr3 (20B3). The compound CHF3 represents an extreme case of the third group interaction, and would require a negative multiplier which would be unique to this case and have no general applicability. For the other three compounds, the estimated rate constants are within a factor of 1.35 of the experimental values.

Haloethanes. In Table 8 rate constants for compounds of the type CX3CH3, CX3CH2X, and CX_3CHX_2 are estimated, where X represents either F or Cl and the tabulated compounds include every possible combination of these two atoms. When combined with the experimental database (which includes one Br-containing isomer), these rate constants illustrate the effect of progressive replacement of F by Cl in the CF3 group, and also the effect of halogenation of the CH_3 group. The only estimated rate constant in **Table** 8 for which experimental data have been reported is CCl_3CHCl_2. For this compound Qiu et al.[15] report k(298 K) = 2.3E-13 cm^3/molec-s. This result is five times higher than the predicted value, and is inconsistent with trends of other data in the table. It must therefore be regarded as suspect.

Higher HFCs. To show the applicability of the estimation method to more complex halocarbons, rate constants were estimated for six higher 1 IFCs for which experimental data exist. None were used in the calibration of the method. The results are shown in **Table** 9. All the predictions are in satisfactory agreement with experiment, especially when possible experimental errors are considered , which often are a factor in the range of 1.3-1.5.

Discussion

Trends in Rate Constants. **Table 7** shows that OH rate constants for halogenated methanes increase steadily as F is replaced by Cl or Br. For the haloform compounds, the increase from CHF3 to $CHBr_3$ is nearly three orders of magnitude. For the methylene halides, it is one order of magnitude, and for the methyl halides only a factor of about two. This is primarily due to the severe interaction between F atoms; the rate constants (per abstractable H-atom) for the Cl and Br compounds are much less affected by multiple substitution. In general, the brominated derivative is slightly more reactive than the corresponding Cl compound. However, one curious exception exists. The CH_3Cl rate constant appears to be slightly higher than that of CH_3Br. This difference, which appears not to be experimental error, may be the result of small A-factor differences between the two reactions. This is not revealed in the experimental measurements of those A-factors, but is within the possible errors of the A-factor measurements.

Two general effects are seen in the haloethane data of **Table** 8. One, as with the halomethanes, is the increase in rate constant as F is replaced by either Cl or Br. Once again Cl and Br have approximately the same effect. The second observation is related to the multiple-group interactions which were noted in the rate constant estimation method, When CX_3 is progressively changed from CF_3 to CCl_3 in the CX3CH3 series (all of which are single group compounds), the rate constant increases by nearly an order of magnitude. However, when multiple groups are present, as in CX3CH2X or CX_3CHX_2, the dependence on the substitution in CX3 is significantly reduced. This is a manifestation of the reduced third group effect.

Rate Constant Estimation Method for Halocarbons. Experience with the method indicates that it rarely is in error by more than a factor of 1.5. The predictions are relatively insensitive to minor changes in the method, such as the occasional addition of a new calibration reaction to the database, Experimental measurements which differ greatly (more than a factor of two) from the prediction are probably incorrect. Normally when this happens (as in the case of CCl_3CHCl_2 discussed above), the experimental rate constant is too high, which is the case when impurity effects are not adequately dealt with.

Inspection of **Table *3*** reveals several general features of the group contributions. The fact that most group contributions are positive indicates that the majority of groups increase the C-H reactivity when substituted for an H atom in CH_4. Only a few groups, notably CF_3, decrease the reactivity and therefore have negative group contributions. As Cl (or Br) is substituted for F in CF3, the group contribution increases steadily and reaches a positive value for $CFCl_2$. The CH3 group is the most enhancing of those included in the table. The CH_3 contribution is diminished by substitution of H by any halogen atom, especially F. Br and Cl have approximately the same effect on rate constants, although the Br effect is in general slightly more enhancing. (The CH_3Br exception was discussed above).

The assumption of group additivity fails most significantly in the case of fluorine atoms, especially in the case of CHF_3. It should be noted that the behavior of CHF_3 is not directly related to the CF3 group itself. The CF3 group behaves in an additive manner, and the rate constant for HFC-236fa, which contains two CF3 groups, is accurately predicted by the assumption of additivity. At least one other example of severe non-additivity exists. In our earlier study of fluoro-ethers,[6] it was shown that the CF30 group behaves in much the same way as an F atom, and its effect on rate constants cannot be treated in a general way by a single group contribution.

A-factors. For the most part the pre-exponential factors found in the present work are consistent with the previous observations that a standard A-factor of 8. 0E- 13 cm^3/molec-s. per H-atom is a good approximation for all OH abstraction rate constants. The high A-factor measured in the present work for $CHBr_3$ is probably a result of experimental error, due to difficulties in dealing with that compound. Otherwise, the haloform and methylene halide A-factors are close to the standard value. The most striking exception is the case of the methyl halides, which seem to have A-factors per H-atom that are about twice the standard value. Further experiments, such as direct ratio measurements between methyl and methylene halides, are required to resolve this question.

As mentioned in previous work,[5] some of the haloethanes of the CX_3CH_3 type seem to have A-factors on the low side of the standard value. This can be seen in Table 8. Also, our earlier data for HFC-236fa[5] gave an A-factor per H-atom of 3.5]3-13., significantly below the more typical value. This is due in part to the fact that these measurements were relative to HFC- 125, for which the reference A-factor is already low, i. e., 5.6E-1 3. It is not unlikely that this experimental A-factor, based on absolute rate constant measurements, is too low. Thus, when allowance is made for possible error in the A-factor of the reference rate constant, plus additional error in the relative rate measurement, the apparently low A-factors can be seen to be possible artifacts.

Other Applications of the Estimation Method. Since the OH abstraction rate constants depend primarily on the corresponding C-H bond energies, and correlate very well with D(C-H) (see, for example, Hsu and DeMore[6]), the estimated rate constants are equivalent to estimated C-H bond energies. Thus the strength of any C-H bond in halocarbons of these types can be obtained to a good approximation. Also, the OH abstraction rate constants which have been placed on an accurate and self-consistent basis by means of the relative rate measurements are found to correlate with excellent precision with the corresponding abstraction reactions of Br and I. Previously, correlations were obscured by errors in the OH database. Thus, measurement of one reaction rate constant is equivalent to several. Abstraction reactions by other groups, such as radicals, may also correlate as well,

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Tables

Table 1. Rate Constants of the Reference Compounds Used in This Work.

Reference Compound	Arrhenius Rate Constant[a]	k(298 K)(a)
CH_3Cl	4.4E-12 exp(-1470/T)	3.2E-14
CH_2Cl_2	2.2E-12 exp(-981/T)	8.2E-14
CH_3CCl_3	1.8E-12 exp(-1550/T)	1.0E-14
CF_3CCl_2H (123)	6.4E-13 exp(-910/T)	3.0E-14

(a). Units are cm^3/molec-s.

Table 2. Database for Calibration of the Rate Constant Estimation Method

Compound	log k(est)	log k(ex)	k(298K)ex	Reference
CH2F2 (32)	-14.14	-14.01	9.8E-15	Hsu & DeMore[5]
CH'2FC1(31)	-13.51	-13.49	3.2E-14	This work
CH_2ClBr	-13.05	-13.06	8.8E-14	This work
CH3F(41)	-13.75	-13.77	1.7E-14	This work
CHF_2CHF_2 (1 34)	-14.17	-14.24	5.8E-15	DeMore[2]
CH_2FCF_3 (134a)	-14.43	-14.42	3.8E-15	DeMore[2]
CH_2FCHF_2 (1 43)	-13.82	-13.82	1.5E-14	Sidebottom et al. [16]
CH3CH3 my unpub	-12.80	-12.67	2.1E-13	DeMore, unpublished
CH3CH2CH3	-11.99	-11.96	1.1E-12	JPL 94-26
CH3CF3 (143a)	-14.81	-14.90	1.3E-15	Hsu & DeMore[5]
CH3CHF2 (1 52a)	-13.40	-13.50	3.2E-14	Hsu & DeMore5
CH_3CH_2F (161)	-12.69	-12.82	1.5E-13	Hsu & DeMore[5]
CH_3Cl	-13.57	-13.51	3.1E-14	Hsu & DeMore[4]
CH_2Cl_2	-13.03	-13.09	8.1E-14	Hsu & DeMore[4]
$CHCl_3$	-13.06	-13.06	8.7E-14	Hsu & DeMore[4]
CH3Br	-13.48	-13.55	2.8E-14	Hsu & DeMore[4]
Cl13CFC12(14 lb)	-14.23	-14.23	5.9E-15	Huder & DeMore[3]
CH_3CF_2Cl (142b)	-14.50	-14.50	3.2E-15	JPL 94-26
CH_3CCl_3 (1 40)	-14.02	-14.02	9.5E-15	JPL 94-26
CHF_2Cl (22)	-14.17	-14.30	5.0E-15	Hsu & DeMore[5]
CHF2Br (2211)	-14.13	-14.00	1.0E-14	Hsu & DeMore5
CF_3CHFCF_3 (227ea)	-14.92	-14.80	1.6E-15	Hsu & DeMore5
$CF_3CHFCHF2$ (236ea)	-14.29	-14.29	5.1E-15	Hsu & DeMore[5]
$CF_3CH_2CF_3$ (236fa)	-15.49	-15.49	3.2E-16	Hsu & DeMore5
$CHF_2CF_2CH_2F$ (245ca)	-14.22	-14.12	7.5E-15	Hsu & DeMore[5]
$CHFClCF_3$ (124)	-14.00	-14.13	7.4E-15	Hsu & DeMore5
$CHCl_2CF_2Cl$ (122)	-13.40	-13.39	4.1E-14	This work
$CHFClCCl_2F$ (1 22a)	-13.78	-13.75	1.8E-14	Hsu & DeMore[5]
$CHCl_2CF_3$ (123)	-13.52	-13.52	3.0E-14	Hsu & DeMore5
$CF_2ClCHFCl$ (1 23a)	-13.88	-13.90	1.3E-14	Orkin et al.[14]
CHF2CF3 (125)	-14.63	-14.72	1.9E-15	JPL 94-26
CH2Br2	-12.95	-12.95	1.1E-13	This work

Table 3. Derived Group Contributions and Third-Group Multiplier for ***OH*** Rate Constant Estimations.

Group	G
F	0.56
2F	0.35
CF_3	-0.50
CH_2F	0.44
CHF_2	-0.08
CH_3	1.21
Cl	0.73
2Cl	1.46
CH_2Cl	0.77
$CHCl_2$	0.60
CHFCl	0.05
CF_2Cl	-0.19
F,Cl	0.98
CCl_3	0.29
$CFCl_2$	0.08
Br	0.83
2Br	1.54
Br,Cl	1.43
F,Br	1.1*
3rd Group Multiplier ‘	0.37

* This group contribution was estimated.

Table 4. Experimental results for rate constant ratios, k/k_{ref}, for the halogen-substituted methanes.

CH_3F		CH_2FCl		CH_2BrCl		CH_2Br_2		$CHBr_3$	
T(K)	k/k_{ref} [(a)]	T(K)	k/k_{ref} [(b)]	T(K)	k/k_{ref} [(b)]	T(K)	k/k_{ref} [(b)]	T(K)	k/k_{ref} [(b)]
308	0.562	293	0.388	293	1.035	293	1.319	298	1.976
333	0.610	300	0.402	298	1.136	298	1.383	298	1.724
343	0.620	313	0.397	298	0.987	298	1.42.0	312	1,783
363	0.641	323	0.408	303	1.124	303	1.328	323	1.631
378	0.654	333	0.436	308	1.067	313	1.385	333	1,667
393	0.657	343	0.426	318	1.026	333	1.258	342	1.650
		358	0.446	328	1.089	355	1.253	357	1.595
		369	0.453	335	1.072	366	1.285	366	1.538
		371	0.452	344	1.029	375	1.218		
				358	1.004				
				371	0.991				
				376	1.031				

(a) Reference compound was CH_3Cl.

(b) Reference compound was CH_2Cl_2.

Table 5. Experimental results for rate constant ratios, k/k_{ref}, for the halogen-substituted ethanes.

$CF_2BrCHFCl$ (123aB1α)		$CF_2ClCHCl_2$ (122)			
T(K)	k/k_{ref} (a)	T(K)	k/k_{ref} (b)	T(K)	k/k_{ref} (c)
315	1.240	313	1.357	303	.488
318	1.210	333	1.414	343	.493
323	1.379	358	1.292	343	.483
323	1.428	371	1.314	343	.498
328	1.245			363	.489
336	1.349				
353	1.190				
363	1.195				
367	1.142				
372	1.111				

(a) CH_3CCl_3 was the reference compound.
(b) CF_3CCl_2H (123) was the reference compound.
(c) CH_2Cl_2 was the reference compound.

Table 6. Arrhenius Expressions for the Rate Constant Ratio Data

Reactant	Reference	k/k_{ref} (a)
CH_3F	CH_3Cl	(0.97 ± 0.23) exp(-156 ± 82) /T)
c112FC1 (31)	CH_2Cl_2	(0.81 ± 0.06) exp(-216 ± 24)/T
CH_2BrCl	CH_2Cl_2	(0.83 ± O. 13) exp(75 ± 49)/T
CH_2Br_2	CH_2Cl_2	(0,84 ± 0.11) exp(145 ± 39)/T
$CHBr_3$	CH_2Cl_2	(0.73 ± 0. 16) exp(276 ± 71)/T
CF2BrCHFCl(123B let)	CH_3CCl_3	(0.52 ± O. 18) exp(298 ± 115)/T
$CF_2ClCHCl_2$ (1 22)	CH_2Cl_2	(0.50 ± 0.05) exp(-8 ± 32)/T
$CF_2ClCHCl_2$ (1 22)	CF_3CCl_2H	(0.96 ± 0.28) exp(1 14 ± 98)/T

(a). Errors shown are standard deviations.

Table 7. Measured and Estimated Rate Constants for Halomethanes.

Compound	A-Factor	E/R	k(298 K)	Source
CHX_3				
CHF3 (23)	6.4E-13	2354	2.4E-16	Hsu & DeMore[5]
CHF_2Cl (22)	7.1E-13	1478	5.0E-15	Hsu & DeMore[5]
CHF_2Br (22131)	9.6E-13	1360	1.0E-14	Hsu & DeMore[5]
$CHCl_2F$ (21)	1.2E-12	1100	3.0E-14	JPL 94-26
CHBrClF (21B1)	8.0E-13	794	5.6E-14	estim.
$CHBr_2F$ (21B2)	8.0E-13	679	8.2E-14	estim.
$CHCl_3$ (20)	1.2E-12	780	8.8E-14	Hsu & DeMore[4]
$CHCl_2Br$ (20B 1)	8.0E-13	631	9.6E-14	estim.
$CHBr_2Cl$ (20B2)	8.0E-13	571	1.2E-13	estim.
$CHBr_3$ (20B3)	1.6E-12	711	1.5E-13	This work
CH_2X_2				
CH_2F_2 (32)	1.8E-12	1552	9.9E-15	Hsu & DeMore[5]
CH2FCI(31)	1.8E-12	1197	3.2 E-14	This work
CH2FBr (3 1B1)	1.6E-12	1093	4.1 E-14	est im.
CH_2Cl_2 (30)	2.2E-12	981	8.2E-14	Hsu & DeMore[4]
CH_2BrCl (30B 1)	1.8E-12	906	8.8E-14	This work
CH2Br2 (30B2)	1.9E-12	836	1.1E-13	This work
CH3X				
CH3F (41)	4.4E-12	1655	1.7E-14	This work
CH_3Br (40B1)	4.4E-12	1507	2.8E-14	Hsu & DeMore[4]
CH_3Cl (40)	4.4E-12	1470	3.2E-14	Hsu & DeMore[4]

Table 8. Measured and Estimated Rate Constants for Some Haloethanes.

Compound	A-Factor	E/R	k(298 K)	Source
CX_3CH_3				
CF_3CH_3 (143a)	1.213-12	2055	1.2E-15	I Isu & DeMore[5]
CF_2ClCH_3 (142b)	1.3E-12	1800	3.1E-15	JPL 94-26
$CFCl_2CH_3$ (14 lb)	1.413-12	1630	5.9E-15	Huder & DeMore[3]
CCl_3CH_3 (140)	1.8E-12	1550	9.911-15	JPL 94-26
CX_3CH_2F				
CF_3CH_2F (1 34a)	1.3E-12	1740	3.8E-15	DeMore[2]
CF_2ClCH_2F (133b)	1.6E-12	1593	7.6E-15	estim.
$CFCl_2CH_2F$ (132c)	1.6E-12	1408	1.411-14	estim.
CCl_3CH_2F (13 lb)	1.613-12	1264	2.311-14	est im.
CX3CHF2				
CF_3CHF_2 (125)	5.6E-13	1700	1.9E-15	JPL 94-26
CF_2ClCHF_2 (124a)	8.013-13	1657	3.1E-15	estim.
$CFCl_2CHF_2$ (123b)	8.013-13	1588	3.9E-15	estim.
CCl_3CHF_2 (122b)	8. 0E-13	1534	4.7E-15	estim.
CX_3CHFCl				
CF_3CHFCl (124)	9.7E-13	1459	7.311-15	1 Isu & DeMore[5]
$CF_2ClCHFCl$ (123a)	9.213-13	1281	1.2E-14	Orkin[14]
$CF_2BrCHFCl$ (123aB 1)	9.3E-13	1252	1.4E-14	This work
$CCl_2FCHFCl$ (122a)	7.1E-13	1158	1.5E-14	1 Isu & DeMore[5]
CCl_3CHFCl (121a)	8. 0E-13	1103	2.0E-14	estim.
CX_3CH_2Cl				
CF_3CH_2Cl (133a)	1.613-12	1691	5.511-15	estim.
CF_2ClCH_2Cl (132b)	1.613-12	1476	1.111-14	estim.
$CFCl_2CH_2Cl$ (131a)	1.6E-12	1291	2.1E-14	estim.
CCl_3CH_2Cl (1 30)	1.6E-12	1147	3.411-14	estim.
CX_3CHCl_2				
CF_3CHCl_2 (123)	6.4E-13	910	3.0E-14	1 Isu & DeMore[5]
$CF_2ClCHCl_2$ (122)	8.3E-13	893	4.1}1-14	This work
$CFCl_2CHCl_2$ (121)	8. 0E-13	827	5.0E-14	estim.
CCl_3CHCl_2 (120)	8.013-13	774	6.0E-14	estim.

Table 9. Rate Constant Estimations for Some Higher HFCs.

Compound	log k(pr)	log k(ex)	k(298)ex	Error*	Source
$CHF_2CF_2CF_2CF_2H$ (338pcc)	-14.33	-14.34	4.6E-15	1.03	NIST[17]/NOAA[10]
$CF_3CHFCHFCF_2CF_3$ (43-10 mee)	-14.46	-14.47	3.4E-15	1.02	NIST[17]/NOAA[10]
CF3CH2CH2CF3 (356ffa)	-14.24	-14.06	8.7E-15	1.53	NIST[17]
$CF_3CH_2CF_2CH_2CF_3$ (458mfcf)	-14.76	-14.56	2.8E-15	1.60	Nelson et al. [18]
CF3CH2CHF2 (245fa)	-14.09	-14.17	6.8E-15	1.21	Nelson et al. [18]
$CF_3CH_2CF_2CH_3$ (365mfc)	-14.31	-14.06	8.7E-15	1.76	Mellouki et al. [19]

* The absolute factor by which prediction and experiment differ, regardless of which is greater.

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Figure Captions

Figure 1. Summary of Rate Constant Data for CH_3F (HFC-41).
Figure 2. Summary of Rate Constant Data for CH_2FCl (HCFC-31).
Figure 3. Summary of Rate Constant Data for CH_2BrCl (HCBC-30B1).
Figure 4. Summary of Rate Constant Data for CH_2Br_2 (HBC-30B2).
Figure 5. Summary of Rate Constant Data for $CHBr_3$ (HBC-20B3).
Figure 6. Summary of Rate Constant Data for $CF_2BrCCFClH$ (HFCBC-123aB1 α).
Figure 7. Summary of Rate Constant Data for CClF2CCl2H (HCFC-122).

Fig. 1
DeMore

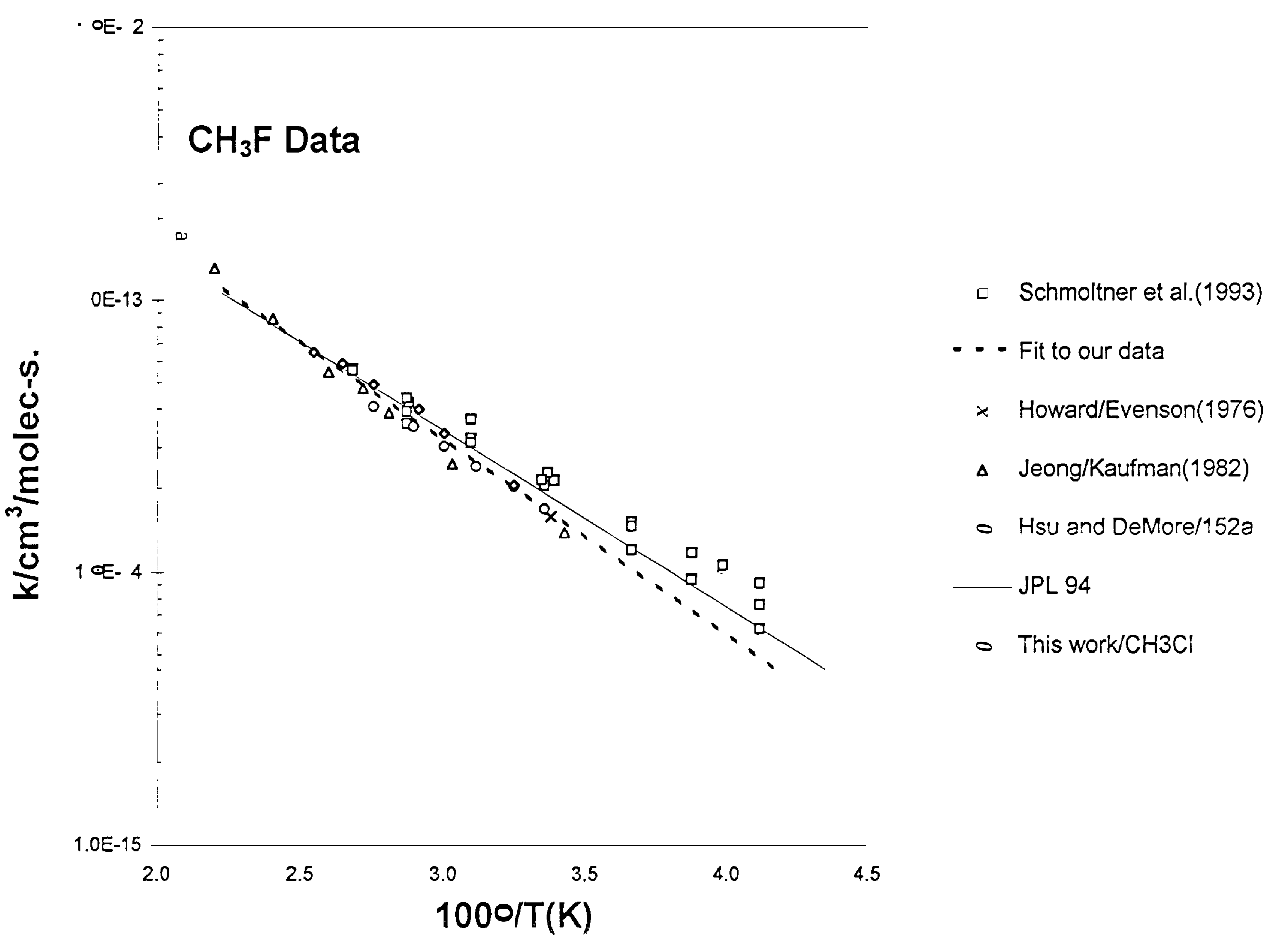

CH3F Data
k/cm3/molec-s.
100o/T(K)
oE- 2
0E-13
1 oE- 4
1.0E-15
2.0
2.5
3.0
3.5
4.0
4.5
Schmoltner et al.(1993)
Fit to our data
Howard/Evenson(1976)
Jeong/Kaufman(1982)
Hsu and DeMore/152a
JPL 94
This work/CH3Cl

Fig. 2
DeMore

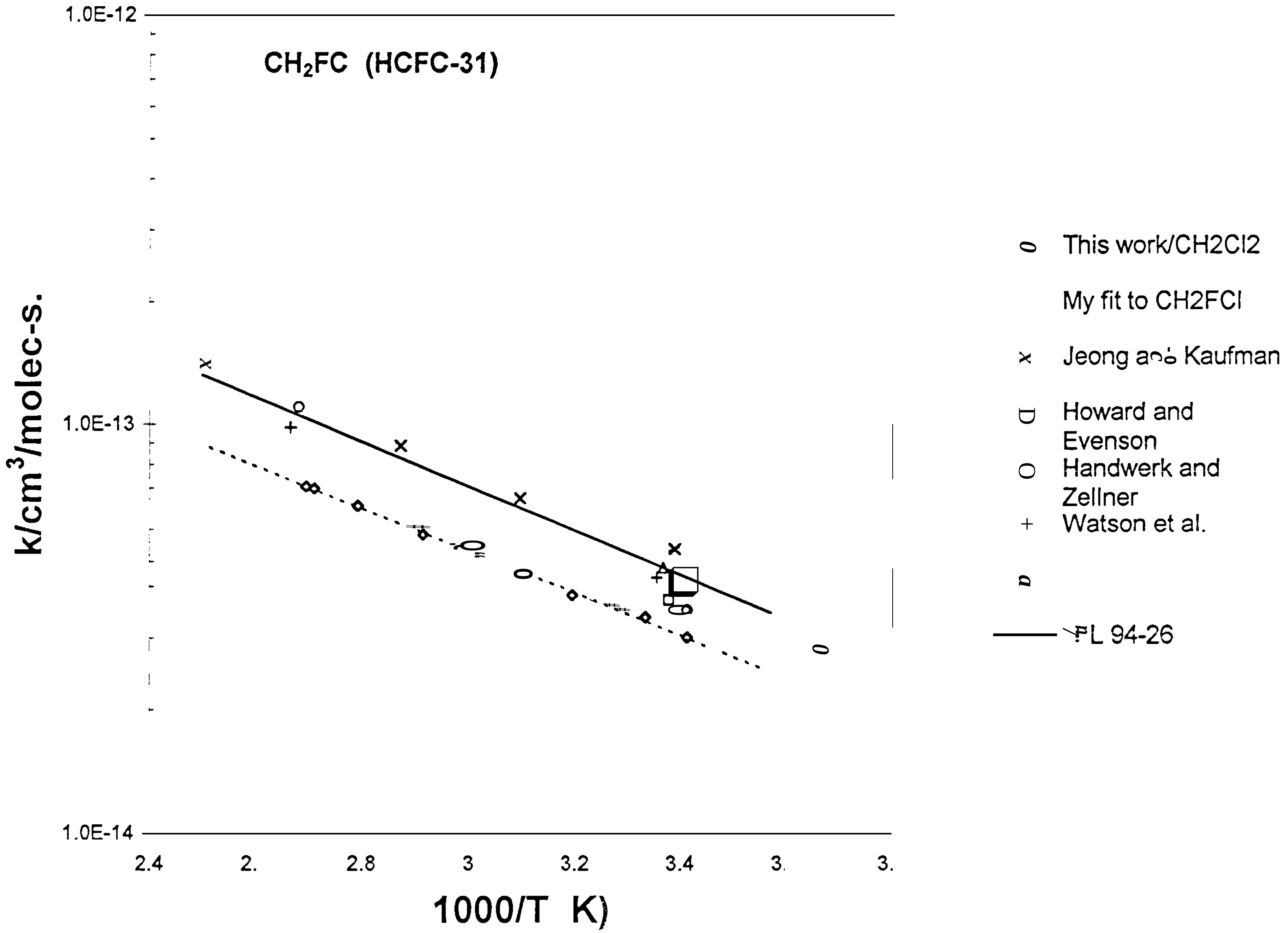
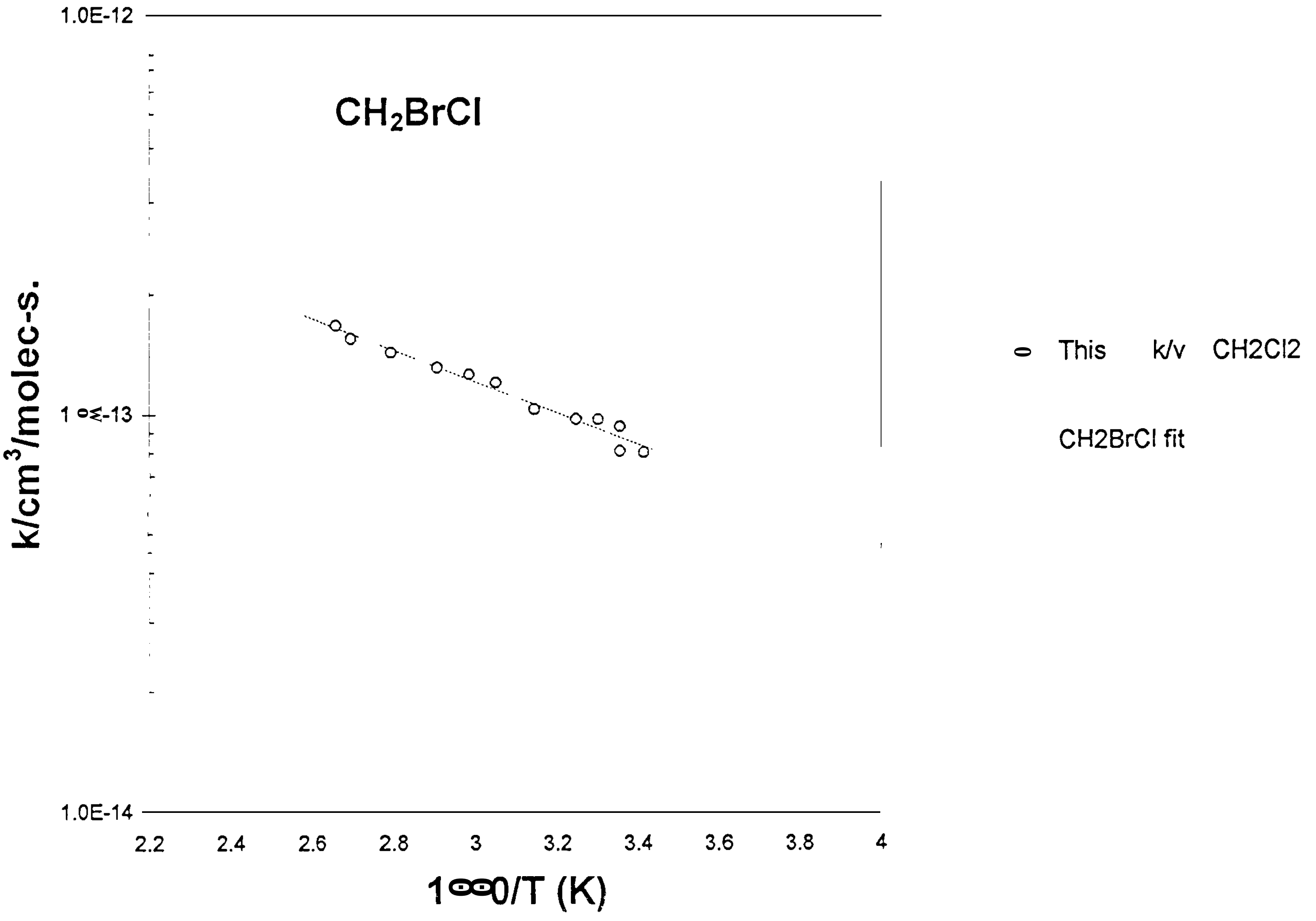
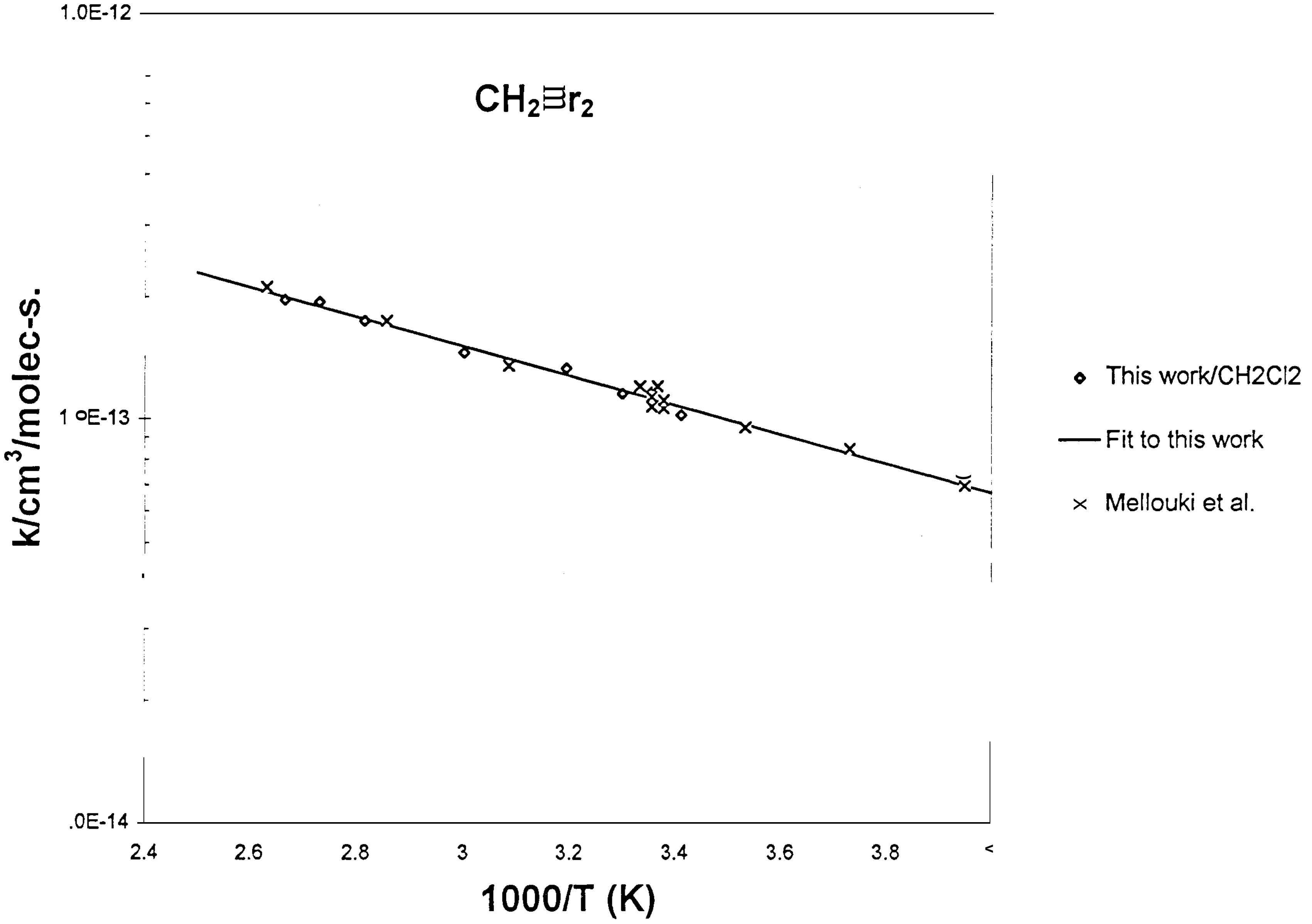

CH₂FC (HCFC-31)
k/cm³/molec-s.
1.0E-12
1.0E-13
1.0E-14
2.4
2.
2.8
3
3.2
3.4
3.
3.
1000/T K)
This work/CH2Cl2
My fit to CH2FCl
Jeong and Kaufman
Howard and Evenson
Handwerk and Zellner
Watson et al.
JPL 94-26

Fig. 3
DeMore



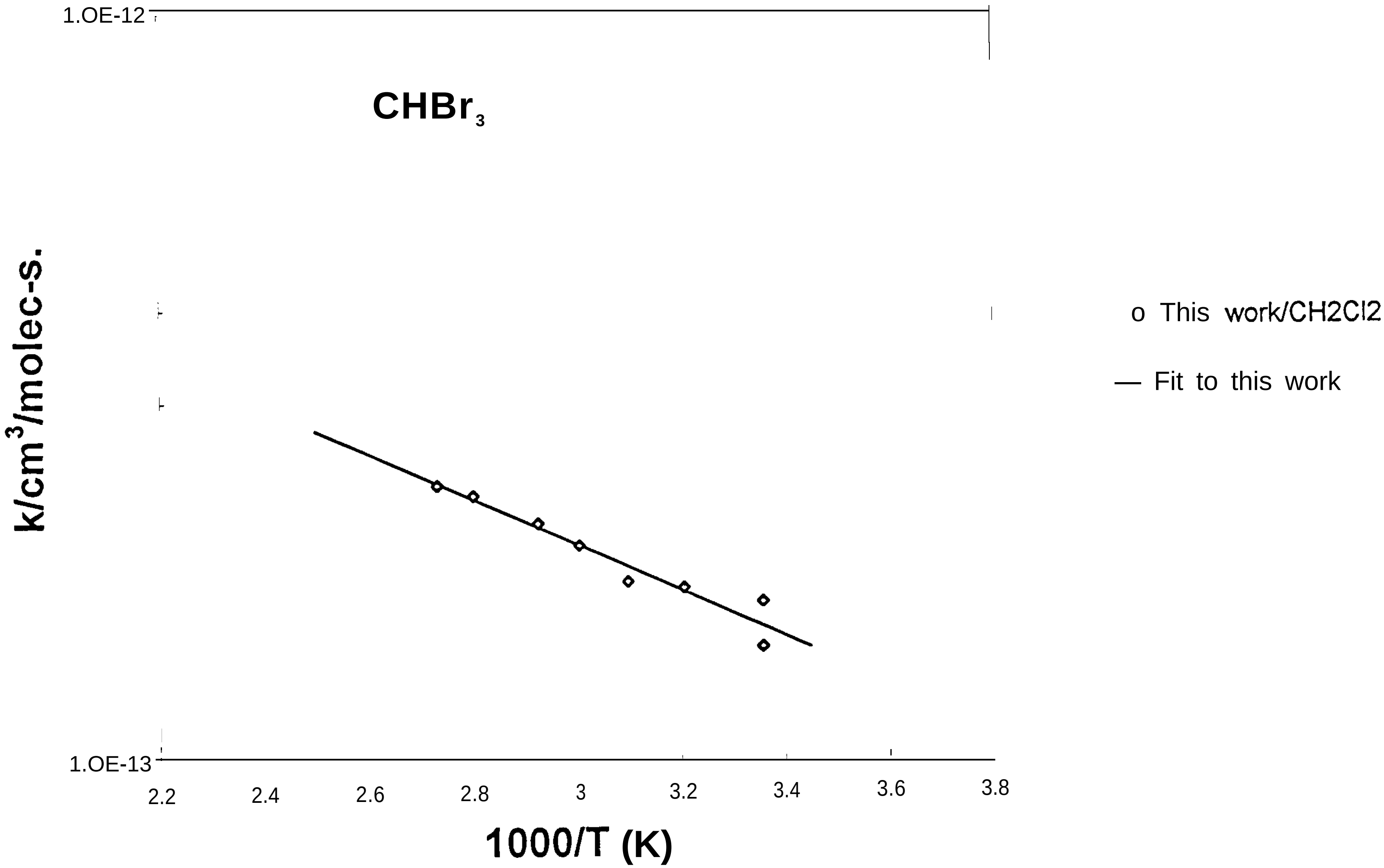
CH2BrCl
1.0E-12
1.0E-14
k/cm3/molec-s.
2.2
2.4
2.6
2.8
3
3.2
3.4
3.6
3.8
4
0/T (K)
This k/v CH2Cl2
CH2BrCl fit

Fig. 4
DeMore



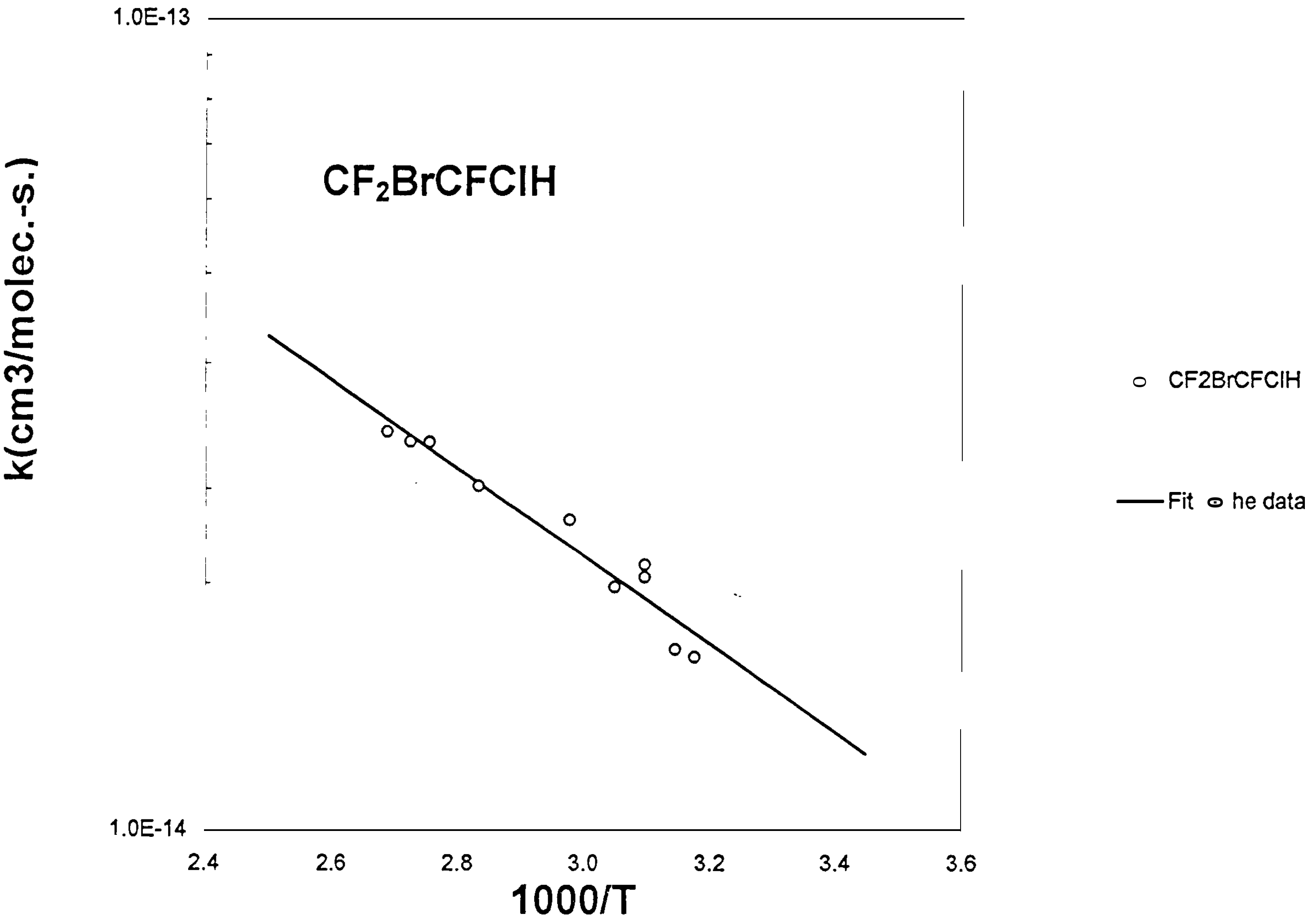
1.0E-12
1 oE-13
.0E-14
CH_2Br_2
k/cm³/molec-s.
2.4
2.6
2.8
3
3.2
3.4
3.6
3.8
1000/T (K)
This work/CH2Cl2
Fit to this work
Mellouki et al.

Fig. 5
DeMore



1.OE-12
CHBr3
k/cm3/molec-s.
o This work/CH2Cl2
— Fit to this work
1.OE-13
2.2
2.4
2.6
2.8
3
3.2
3.4
3.6
3.8
1000/T (K)

Fig. 6
DeMore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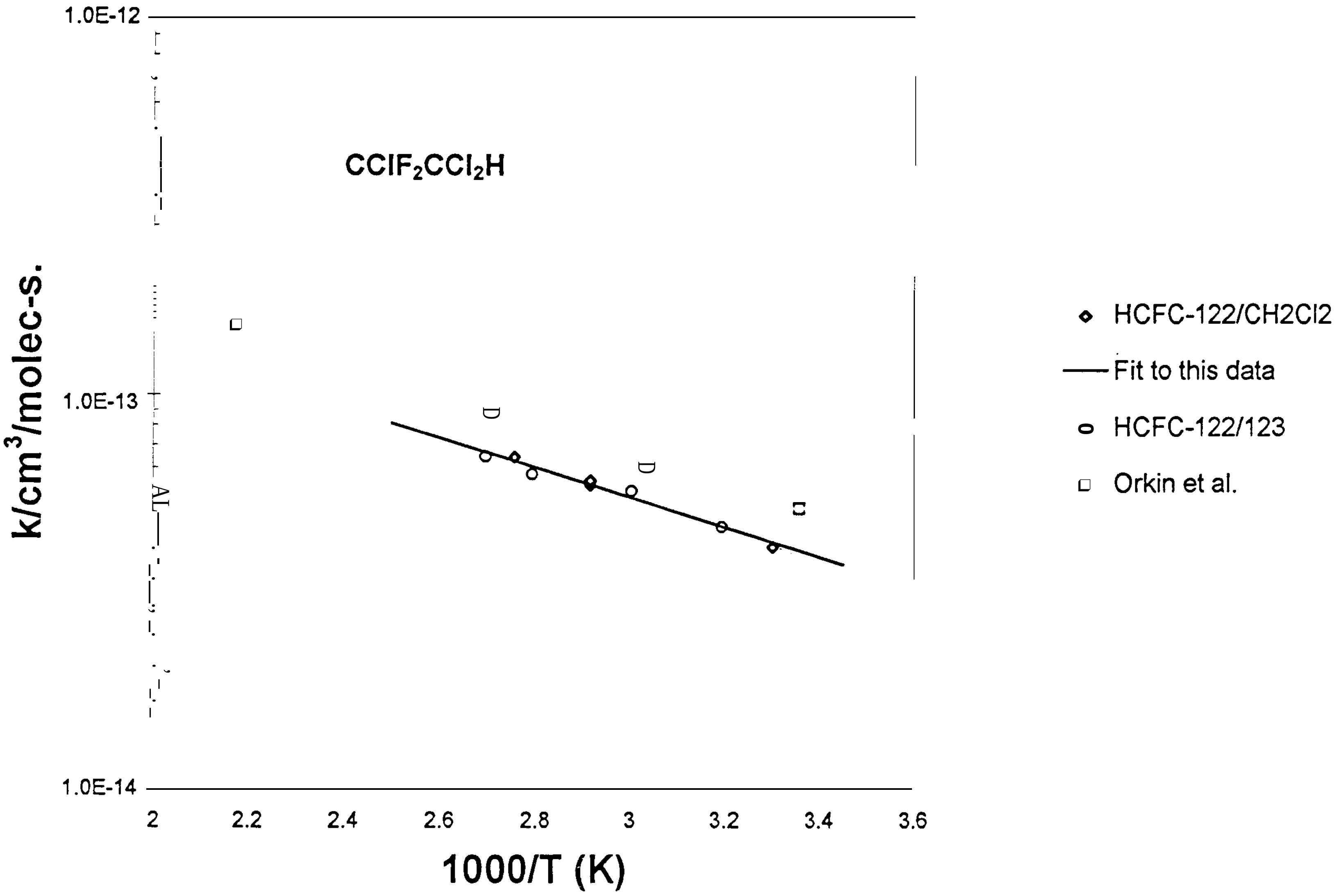
1.0E-14
k(cm3/molec.-s.)
CF2BrCFClH
2.4
2.6
2.8
3.0
3.2
3.4
3.6
1000/T
CF2BrCFClH
Fit he data

Fig. 7
DeMore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k/cm^3/molec-s.
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1.0E-13
1.0E-14
2
2.2
2.4
2.6
2.8
3
3.2
3.4
3.6
1000/T (K)
HCFC-122/CH2Cl2
Fit to this data
HCFC-122/123
Orkin et al.