

Regularities in Arrhenius parameters for rate constants of abstraction reactions of hydroxyl radical with C–H bonds

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Abstract

For compounds with a single type of C–H bond, it is shown that the Arrhenius parameters E/R and the A -factor for OH abstraction reactions can be reliably predicted from $k(298\text{ K})$, based on relationships derived from selected literature data. The principal criterion for selection is that the data shall have been verified by both absolute and relative rate measurements. Predictions are compared to tabulated data in recent NASA data evaluations, showing for the most part good agreement. In two of the cases where discrepancies exist, the OH reactions with CH_3CN and $\text{CF}_3\text{CH}_2\text{Cl}$ (HCFC-133a), new relative rate data are presented which show improved agreement with predictions.

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1. Introduction

There is now an extensive body of data for the rates of abstraction reactions by OH from hydrocarbons and halocarbons. From these data, two types of useful correlations can be made. The first is the effect of different substituent groups on the magnitudes of the rate constants. This approach, sometimes referred to as the structure–additivity–relationships (SAR) method [1], can often predict $k(298\text{ K})$ for the OH reactions within a factor of about 1.5–2, depending on the accuracy of the database used for calibration and other factors such as the number and type of groups attached to a given carbon atom in the molecule. The second, which is the main subject of this paper, is a correlation between $k(298\text{ K})$ and the quantities A and E/R in the two-parameter Arrhenius equation, $k(T) = Ae^{-E/RT}$. The pre-exponential factor A is normally given in units of $\text{cm}^3/(\text{mol s})$, and the activation temperature E/R has the unit K. The quantity R is the gas constant, with the value $1.987\text{ cal K}^{-1}\text{ mol}^{-1}$. The two-parameter Arrhenius equation is appropriate only in the temperature range below about 450 K. At higher temperatures, a more complex temperature dependence becomes apparent, and

a three-parameter expression such as $k(T) = A'T^n e^{(-E'/RT)}$ must be used. However, the bulk of reported kinetics data fall in the lower temperature region, and the two-parameter Arrhenius expression is an adequate representation of the data. At very low temperatures, other factors such as different reaction sites, possible tunneling, or experimental error may lead to appreciable curvature in a two-parameter Arrhenius plot.

Correlations of Arrhenius parameters with $k(298\text{ K})$ have been discussed previously [2,3], based on an observed dependence of the pre-exponential factors for OH reactions on the magnitude of $k(298\text{ K})$. Inclusion of the dependence of A -factors on the magnitude of the rate constant is an improvement over earlier rate constant estimates [4] in which a constant A -factor (per C–H) bond was assumed. Such an approximation is acceptable when the rate constants are of similar magnitude, but fails when they differ by a factor of ten or more. The present paper emphasizes the relationship between E/R values and $k(298\text{ K})$, an approach which further demonstrates that pre-exponential factors per C–H bond increase systematically with increasing $k(298\text{ K})$. The correlation between $k(298\text{ K})$ and the Arrhenius parameters is sufficiently accurate that temperature dependence studies below about 450 K for reactions with compounds having only one type of C–H bond are unnecessary

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Table 1
Selected data for OH abstraction reactions for calibration of the relationship between E/R values and $k(298\text{ K})$

Compound	Temperature range (K) ^a	A -factor ($\text{cm}^3/(\text{mol s})$)	E/R (K)	$k(298\text{ K})$ ($\text{cm}^3/(\text{mol s})$)	Reference
CH_3CFCl_2 (141b)	287–393	1.71×10^{-12}	1699	5.71×10^{-15}	Talukdar et al. [20]
CHF_2Br (22B)	233–432	1.11×10^{-12}	1405	9.98×10^{-15}	Talukdar et al. [21]
CHF_2Cl (22)	298–460	7.76×10^{-13}	1495	5.14×10^{-15}	Orkin and Khamaganov [22]
CH_2F_2 (32)	222–381	1.66×10^{-12}	1487	1.13×10^{-14}	Talukdar et al. [20]
CF_3CH_3 (143a)	296–374	1.2×10^{-12}	2024	1.34×10^{-15}	Talukdar et al. [20]
$\text{CF}_3\text{CH}_2\text{F}$ (134a)	273–450	1.34×10^{-12}	1690	4.60×10^{-15}	Gierczak et al. [23]
$\text{CF}_2\text{ClCCl}_2\text{H}$ (122)	298–460	1.21×10^{-12}	942	5.14×10^{-14}	Orkin and Khamaganov [22]
CH_3Br	273–379	2.38×10^{-12}	1310	2.93×10^{-14}	Mellouki et al. [24]
CH_3OCH_3	263–364	1.51×10^{-11}	496	2.86×10^{-12}	DeMore and Bayes [25]
$c\text{-C}_6\text{H}_{12}$	225–408	3.10×10^{-11}	471	6.38×10^{-12}	Wilson et al. [26]
$c\text{-C}_5\text{H}_{10}$	209–407	2.67×10^{-11}	509	4.84×10^{-12}	Wilson et al. [26]
$c\text{-C}_3\text{H}_6$	272–463	7.28×10^{-12}	1356	7.68×10^{-14}	Wilson et al. [26]
$c\text{-C}_4\text{H}_8$	272–366	1.62×10^{-11}	611	2.09×10^{-12}	DeMore and Bayes [25]
CH_4	n/a	2.45×10^{-12}	1775	6.34×10^{-15}	JPL 97-4 [5]
CH_3CH_3	n/a	8.70×10^{-12}	1070	2.40×10^{-13}	JPL 97-4 [5]

^a Temperature range in which data were fit.

in most cases, a single measurement at 298 K being sufficient.

Rate constant evaluations such as NASA/JPL 97-4 [5] and 02-25 [6] are averages or fits to all reported data which are not clearly erroneous, without compelling regard for estimations or expected Arrhenius parameters. It is shown in the present analysis that such recommendations are generally accurate, although in a few cases errors are apparent. For two such cases, the OH abstraction reactions with CH_3CN and $\text{CF}_3\text{CH}_2\text{Cl}$ (HFC-133a), previously unpublished data are presented which show better agreement with expectations.

2. Methods

2.1. Calibration of the relationship between $k(298\text{ K})$ and the Arrhenius parameters

Table 1 shows a selection of rate constant data for OH abstraction reactions covering three orders of magnitude in $k(298\text{ K})$. It is important to note that each compound has C–H bonds of only one type. This requirement avoids ambiguity arising from the presence of different reaction sites with different rate parameters. The data are taken from several laboratories and were chosen for the most part by the requirement that they have been verified by both absolute and relative rate measurements. The set is not unique, but inclusion of other data meeting the same criteria would not change the result significantly.

Table 2
Rate constants for the reference compounds used in this work for relative rate studies^a

Reference compound	A -factor ($\text{cm}^3/(\text{mol s})$)	E/R (K)	$k(298\text{ K})$ ($\text{cm}^3/(\text{mol s})$)	Source
Methane	$(2.45 \pm 0.25) \times 10^{-12}$	1775 ± 50	6.34×10^{-15}	JPL 97-4 [5]
Methyl chloroform	$(2.02 \pm 0.25) \times 10^{-12}$	1608 ± 50	9.15×10^{-15}	Talukdar et al. [27] ^b

^a Uncertainties in the Arrhenius parameters are our estimates (1 sigma).

^b Rate parameters derived from fit to data at 295–379 K.

2.2. Relative rate measurements for CH_3CN and $\text{CF}_3\text{CH}_2\text{Cl}$

The method used here for the relative rate measurements has been described in detail previously [3]. It consists of a slow-flow photolysis apparatus in which OH is produced by photolysis of ozone in the presence of water vapor, and in which reactant concentrations and losses are measured by FTIR spectroscopy.

The reference gases for CH_3CN and $\text{CF}_3\text{CH}_2\text{Cl}$ were methane and methyl chloroform, respectively. The reference rate constants are shown in Table 2.

3. Results

3.1. Relationship between $k(298\text{ K})$ and the Arrhenius parameters

The rate constants $k(298\text{ K})$ must be normalized to a per-hydrogen basis in order to account for the fact that many compounds have more than one C–H bond. Fig. 1 is a graph of such data from Table 1, showing a linear relationship between the E/R values and $k(298\text{ K})/n$ for both hydrocarbons and halocarbons, where n is the number of H-atoms. From a fit to the data,

$$\frac{E}{R} (\text{K}) = (-509.05 \pm 8.65) \log_{10} \left(\frac{k_{298\text{ K}}}{n} \right) - (5771.2 \pm 119.2) \quad (1)$$

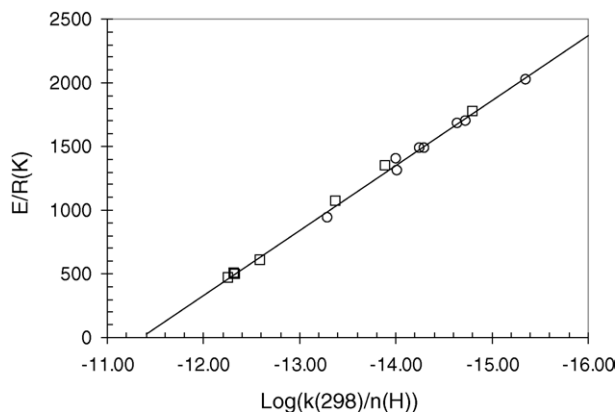


Fig. 1. Dependence of E/R on $k(298\text{ K})$ for selected abstraction reactions of OH. Squares are hydrocarbons and circles are halocarbons. The line is a least squares fit to all data in Table 1 and is given by Eq. (1).

The precision of this fit demonstrates regularities among the pre-exponential factors for the reactions. It shows that they are essentially equal (per C–H bond), except for a dependence on the magnitude of $k(298\text{ K})$. If the normalized A -factors were independent of k_{298} , but otherwise the same for all C–H bonds regardless of the nature of the compound, then the slope of E/R versus $\log_{10}(k_{298})$ would be equal to $-\ln(10) \times 298 = -686$, rather than the observed -509 . The decreased negative slope is a reflection of the decreasing A -factors for slower reactions.

The corresponding value of the A -factor (per C–H bond), in units of $\text{cm}^3/(\text{mol s})$, can be obtained from Eq. (2), which was derived by substitution of Eq. (1) in the Arrhenius equation $\log_{10}(k_{298}/n) = \log_{10}(A/n) - (E/R)/\ln(10) \times 298$.

$$\log_{10}\left(\frac{A}{n}\right) = (0.2581 \pm 0.0290) \log_{10}\left(\frac{k_{298\text{ K}}}{n}\right) - (8.411 \pm 0.400) \quad (2)$$

3.2. Comparison of results with JPL 97-4 and 02-25

Eq. (1) can be used as a consistency check on E/R values for rate constant data such as those tabulated in JPL 97-4 and 02-25. Table 3 compares the recommended E/R values with predictions. Figs. 2 and 3 show the results graphically. In most cases, the recommendations are in good agreement with the calculated values, well within the uncertainties given for the recommendations. However, some severe discrepancies are revealed, in which the predicted E/R differs by more than 200 K from the recommendation.

3.3. Relative rate constant data for CH_3CN and $\text{CF}_3\text{CH}_2\text{Cl}$

The experimental rate constant ratios are shown in Table 4. Combining data from Table 4 with the reference rate

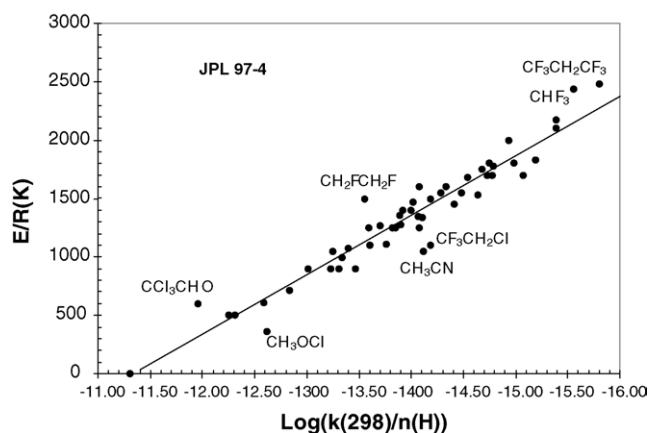


Fig. 2. Comparison of recommended E/R values from JPL 97-4 with predictions. The line is a fit to Eq. (1), which was derived from the most reliable data. The reactions represented are OH abstractions from compounds containing only a single type of C–H bond. Labeled points are those differing by more than 200 K from the expected value and, therefore, believed to be in error.

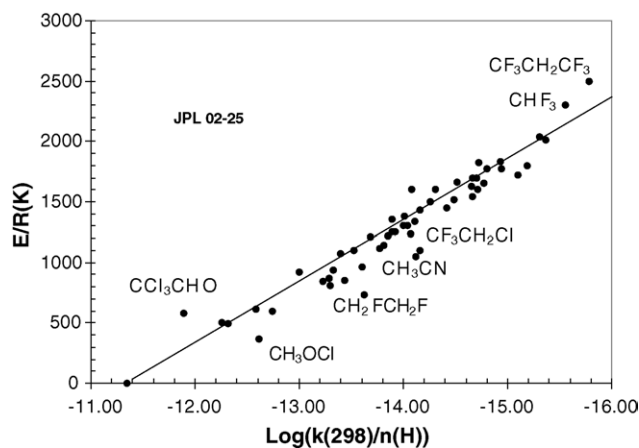


Fig. 3. Comparison of recommended E/R values from JPL 02-25 with predictions. The line is a fit to Eq. (1), which was derived from the most reliable data. The reactions represented are OH abstractions from compounds containing only a single type of C–H bond. Labeled points are those differing by more than 200 K from the expected value and, therefore, believed to be in error.

constants of Table 2, the results for CH_3CN and $\text{CF}_3\text{CH}_2\text{Cl}$ were calculated at each temperature. Arrhenius plots of the results are illustrated graphically in Figs. 4 and 5, and are compared with previous literature data. The derived rate constants, Arrhenius A -factors and activation energies are listed in Table 5, along with the JPL 97-4 and 02-25 recommendations.

4. Discussion

The present results demonstrate that the Arrhenius A -factor and E/R for OH abstraction reactions appropriate for the temperature region around 298 K are predictable when $k(298\text{ K})$ is accurately known. It is also further confirmed

Table 3
Comparison of *E/R* values in JPL 97-4 and 02-25 with those predicted from Eq. (1)

Compound	From JPL 97-4				From JPL 02-25			
	A-factor	<i>E/R</i>	<i>k</i> (298 K)	<i>E/R</i> difference ^a	A-factor	<i>E/R</i>	<i>k</i> (298 K)	<i>E/R</i> difference ^a
CH ₃ F	3.00E-12	1500	1.95E-14	50	2.50E-12	1430	2.06E-14	-9
CH ₂ F ₂	1.90E-12	1550	1.05E-14	51	1.70E-12	1500	1.11E-14	14
CHF ₃	1.00E-12	2440	2.78E-16	292	6.30E-13	2300	2.80E-16	154
CH ₂ FCH ₂ F	1.7E-11	1500	1.11E-13	370	1.10E-12	730	9.50E-14	-434
CF ₃ CH ₃	1.80E-12	2170	1.24E-15	110	1.10E-12	2010	1.29E-15	-40
CF ₃ CH ₂ F	1.50E-12	1750	4.22E-15	51	1.05E-12	1630	4.42E-15	-59
CHF ₂ CHF ₂	1.60E-12	1680	5.70E-15	47	1.60E-12	1660	6.09E-15	42
CF ₃ CHF ₂ (125)	5.60E-13	1700	1.86E-15	-27	6.00E-13	1700	2.00E-15	-11
CF ₃ OCH ₃	1.50E-12	1450	1.16E-14	-116	1.50E-12	1450	1.16E-14	-116
CF ₂ HOCF ₂ H	1.90E-12	2000	2.31E-15	168	1.10E-12	1830	2.37E-15	3
CF ₃ OCHF ₂	4.70E-13	2100	4.09E-16	38	4.60E-13	2040	4.89E-16	18
CF ₃ CF ₂ CH ₂ F	1.50E-12	1750	4.22E-15	51	1.30E-12	1700	4.33E-15	6
CF ₃ CH ₂ CF ₃	1.30E-12	2480	3.16E-16	208	1.45E-12	2500	3.30E-16	237
CF ₃ CHF ₂ CF ₃	5.00E-13	1700	1.67E-15	-52	4.30E-13	1650	1.69E-15	-98
CF ₃ CH ₂ CH ₂ CF ₃	3.00E-12	1800	7.14E-15	64	3.40E-12	1820	7.57E-15	96
CHF ₂ CF ₂ CF ₂ CF ₂ H	7.80E-13	1530	4.60E-15	-151	7.70E-13	1540	4.39E-15	-151
CF ₃ CH ₂ CF ₂ CH ₂ CF ₃	1.20E-12	1830	2.58E-15	-131	1.10E-12	1800	2.62E-15	-158
CH ₂ ClF	2.80E-12	1270	3.95E-14	65	2.40E-12	1210	4.14E-14	15
CHFCl ₂	1.70E-12	1250	2.56E-14	103	1.20E-12	1100	2.99E-14	-13
CHF ₂ Cl	1.00E-12	1600	4.66E-15	76	1.05E-12	1600	4.89E-15	86
CH ₃ CFCl ₂	1.70E-12	1700	5.66E-15	-24	1.25E-12	1600	5.82E-15	-118
CH ₃ CF ₂ Cl	1.30E-12	1800	3.10E-15	-58	1.30E-12	1770	3.42E-15	-65
CH ₂ ClCF ₂ Cl (132b)	3.60E-12	1600	1.68E-14	206	3.60E-12	1600	1.68E-14	206
CHCl ₂ CF ₂ Cl	1.00E-12	900	4.88E-14	-105	7.70E-13	810	5.08E-14	-186
CHFClCFCl ₂	1.00E-12	1250	1.51E-14	-15	7.10E-13	1140	1.55E-14	-119
CH ₂ ClCF ₃ (133a)	5.20E-13	1100	1.30E-14	-351	5.60E-13	1100	1.40E-14	-335
CHCl ₂ CF ₃ (123)	7.00E-13	900	3.42E-14	-184	6.30E-13	850	3.64E-14	-220
CHFClCF ₂ Cl	9.20E-13	1280	1.25E-14	-25	8.60E-13	1250	1.30E-14	-48
CHFClCF ₃	8.00E-13	1350	8.62E-15	-38	7.10E-13	1300	9.05E-15	-78
CH ₃ CF ₂ CFCl ₂	7.70E-13	1700	2.56E-15	-199	7.70E-13	1720	2.40E-15	-194
CF ₃ CF ₂ CHCl ₂	1.00E-12	1100	2.49E-14	-53	6.30E-13	960	2.51E-14	-192
CF ₂ ClCF ₂ CHFCl	5.50E-13	1250	8.29E-15	-147	5.50E-13	1230	8.60E-15	-150
CH ₃ Cl	4.00E-12	1400	3.65E-14	88	2.40E-12	1250	3.62E-14	-64
CH ₂ Cl ₂	3.80E-12	1050	1.12E-13	76	1.90E-12	870	1.03E-13	-124
CHCl ₃	2.00E-12	900	9.76E-14	48	2.20E-12	920	1.00E-13	74
CH ₃ OCl	2.40E-12	360	7.17E-13	-294	2.5E-12	370	7.1E-13	-282
CH ₃ CCl ₃	1.80E-12	1550	9.92E-15	-50	1.60E-12	1520	9.75E-15	-84
CCl ₃ CHO	8.20E-12	600	1.09E-12	283	9.1E-12	580	1.3E-12	301
CHF ₂ Br	1.10E-12	1400	1.00E-14	45	1.00E-12	1380	9.75E-15	19
CH ₂ BrCF ₃	1.40E-12	1340	1.56E-14	-70	1.40E-12	1340	1.56E-14	-70
CHFBrCF ₃	7.20E-13	1110	1.74E-14	-123	7.30E-13	1120	1.70E-14	-118
CHClBrCF ₃	1.30E-12	995	4.61E-14	-23	1.10E-12	940	4.69E-14	-74
CHFClCF ₂ Br	9.30E-13	1250	1.40E-14	-31	8.40E-13	1220	1.40E-14	-61
CH ₃ Br	4.00E-12	1470	2.88E-14	106	2.35E-12	1300	3.00E-14	-56
CH ₂ Br ₂	2.40E-12	900	1.17E-13	-65	2.00E-12	840	1.19E-13	-121
CHBr ₃	1.60E-12	710	1.48E-13	-50	1.35E-12	600	1.80E-13	-116
CH ₄	2.50E-12	1775	6.47E-15	17	2.45E-12	1775	6.34E-15	12
H ₂ CO	1.00E-11	0	1.00E-11	18	9.00E-12	0	9.00E-12	-5
C ₂ H ₆	8.70E-12	1070	2.40E-13	21	8.70E-12	1070	2.40E-13	21
CH ₃ CN	7.80E-13	1050	2.30E-14	-364	7.80E-13	1050	2.30E-14	-364

Units of *E/R* are (K) and units of *A* and *k*(298) are cm³/(mol s).

^a The *E/R* difference is the recommended *E/R* minus the *E/R* predicted by Eq. (1).

that pre-exponential factors increase with *k*(298 K), but otherwise are independent of the nature of the substrate. That is, they are the same for hydrocarbons, halocarbons, fluoroethers, etc., provided that account is taken of the number of C–H bonds in the molecule. Each C–H bond behaves as a separate reaction site. The fact that the pre-exponential

factor increases for the faster reactions is, in retrospect, not surprising since for these cases the looser transition state will have a higher entropy and, therefore, a higher *A*-factor [7]. It is evident that the entropy change for formation of the transition state is essentially independent of the nature of the substrate, aside from those factors (mainly the

Table 4
Rate constant ratios measured for CH₃CN and CF₃CH₂Cl

<i>T</i> (K)	<i>k</i> (CH ₃ CN)/ <i>k</i> (CH ₄)	<i>T</i> (K)	<i>k</i> (CF ₃ CH ₂ Cl)/ <i>k</i> (CH ₃ CCl ₃)
306	2.868	298	0.950
308	2.713	309	1.033
323	2.605	326	0.967
355	2.110	345	0.867
368	2.364	351	0.991
383	2.106	360	0.980
388	2.113		
393	2.132		

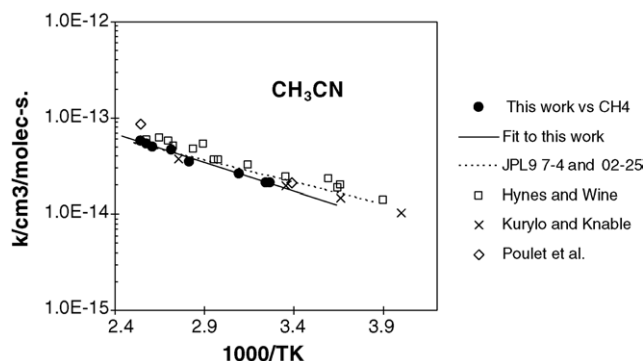


Fig. 4. Arrhenius plot of the present results for the CH₃CN abstraction rate constant, and comparison with previous data of Hynes and Wine [9], Kurylo and Knable [8], and Poulet et al. [19].

strength of the C–H bond) which make the reaction fast or slow.

The criteria developed in this paper can be used as an aid in the evaluation of rate constant data, especially in those cases where several measurements exist which are in approximate but not perfect agreement. Rather than averaging all such data, preference can be given to those in best agreement with the correlation. This approach can be illustrated by considering some examples discussed below.

Table 3 and Figs. 2 and 3 show that most of the recommendations in JPL 97-4 and 02-25 are in reasonable agreement with the correlation between *k*(298 K) and *E/R* as expressed by Eq. (1). While recommendations not in accord with the correlation are probably in error, agreement does not necessarily prove accuracy, because fortuitous combinations of *E/R* and *k*₂₉₈ are possible. As seen in the figures, some large discrepancies exist, most of which are common to both evaluations. These include CH₃CN, CF₃CH₂Cl (133a), CCl₃CHO,

Table 5
Derived experimental rate constants for the reactions of OH with CH₃CN and CF₃CH₂Cl (HFC-133a), and comparison with JPL evaluations

Compound	<i>A</i> -factor (cm ³ /(mol s))	<i>E/R</i> ^a (K)	<i>k</i> (298 K) (cm ³ /(mol s))	Reference
CH ₃ CN	(1.85 ± 0.33) × 10 ⁻¹²	1377 ± 62	1.82 × 10 ⁻¹⁴	This work vs. methane
	7.8 × 10 ⁻¹³	1050	2.3 × 10 ⁻¹⁴	JPL 97-4
	7.8 × 10 ⁻¹³	1050	2.3 × 10 ⁻¹⁴	JPL 02-25
CF ₃ CH ₂ Cl (133a)	(1.64 ± 0.62) × 10 ⁻¹²	1553 ± 125	8.94 × 10 ⁻¹⁵	This work vs. CH ₃ CCl ₃
	5.2 × 10 ⁻¹³	1100	1.3 × 10 ⁻¹⁴	JPL 97-4
	5.6 × 10 ⁻¹³	1100	1.4 × 10 ⁻¹⁴	JPL 02-25

^a Errors are standard deviations of the least squares fit.

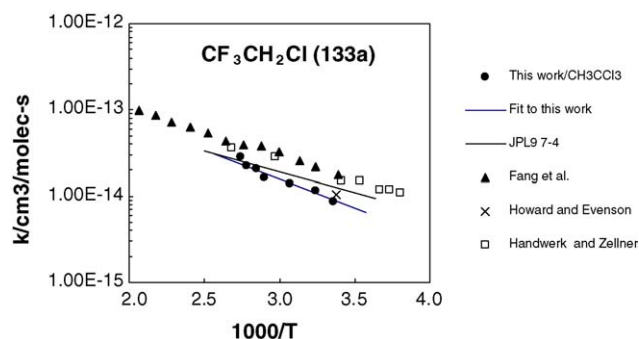


Fig. 5. Arrhenius plot of the present results for the CF₃CH₂Cl (133a) abstraction rate constant. The highest temperature point was considered an outlier and was not used in the fit to the data. Previous data of Howard and Evenson [12], Fang et al. [11], and Handwerk and Zellner [10] are shown for comparison. Fang et al. have higher temperature data not shown in this graph.

CH₃OCl, CH₂ClCF₂Cl (132b), CF₃H, CF₃CH₂CF₃ (236fa), CH₂FCH₂F (152), and CHCl₂CF₃ (123), in which cases the recommended *E/R* differs by more than about 200 K from the predicted value. Such discrepancies do not indicate that the error is solely in *E/R*. It is more often true that both *k*(298 K) and *E/R* are in error. This is evidently the case for both CH₃CN and CF₃CH₂Cl.

For CH₃CN, the new relative rate data are in reasonable agreement with some of the earlier absolute data, especially that of Kurylo and Knable [8], but differ somewhat from the JPL recommendations, which encompass other data (see Fig. 4). Fig. 6 shows that the new data for both *E/R* and *k*(298 K) are in good agreement with the correlation. In connection with CH₃CN, it has been suggested [9] that the reaction with OH is not a normal abstraction reaction, but may involve an addition complex. If this were the case, a correlation with true abstraction reactions would not necessarily be expected. While the possibility of an addition mechanism cannot be ruled out, the present results show that the Arrhenius parameters are consistent with those expected for an abstraction mechanism.

The present CF₃CH₂Cl results shown in Fig. 5 are not in good agreement with earlier data of Handwerk and Zellner [10] or Fang et al. [11], but do agree well with the single data point of Howard and Evenson [12] at 296 K. Also, Fig. 6 shows that the present results are consistent with the correlation.

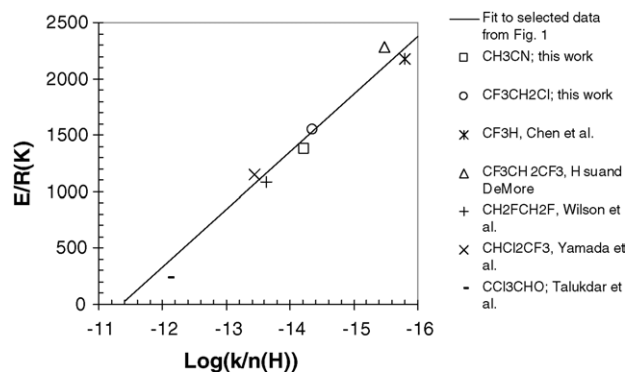


Fig. 6. Comparison of possible new recommendations for CH_3CN , $\text{CF}_3\text{CH}_2\text{Cl}$, CF_3H , $\text{CF}_3\text{CH}_2\text{CF}_3$, and CHCl_2CF_3 with the correlations represented by Eq. (1). See Section 4 for basis of the recommendations.

In both JPL evaluations, the compounds CCl_3CHO and CH_3OCl are severe outliers. The reasons are unclear, but more recent work by Talukdar et al. [13] for CCl_3CHO (not available at the time of the evaluations) gives $E/R = 240\text{ K}$ and $k_{298} = 8.0 \times 10^{-13}\text{ cm}^3/(\text{mol s})$, where E/R differs by only 147 K from the correlation (see Fig. 6).

The $\text{CH}_2\text{ClCF}_2\text{Cl}$ (132b) recommendation in both evaluations suffers from older and limited data, and this reaction needs further work.

For CF_3H , recent relative rate studies by Chen et al. [14] yield a lower E/R (2180 K) and higher k_{298} ($3.2 \times 10^{-16}\text{ cm}^3/(\text{mol s})$) than those in the present evaluations, in better agreement with the correlation (see Fig. 6). These new data are to be preferred.

For $\text{CF}_3\text{CH}_2\text{CF}_3$ (236fa), the previous results reported by Hsu and DeMore [15] ($E/R = 2280\text{ K}$ and $k_{298} = 3.3 \times 10^{-16}\text{ cm}^3/(\text{mol s})$) are in better agreement with the correlation, but still deviate somewhat, as seen in Fig. 6. Further work is needed for this reaction.

For $\text{CH}_2\text{FCH}_2\text{F}$ (152), both recommendations disagree with the correlation. The JPL 97-4 value for E/R was only an estimate, since no temperature dependence data were available, and was clearly too high. In JPL 02-25, the recommendation is based on newer data, but is in disagreement (too low) with the correlation because it was obtained from a fit to data below 298 K, which show unexpectedly different Arrhenius behavior compared to data at higher temperatures. As shown in Fig. 6, data of Wilson et al. [16] ($E/R = 1084\text{ K}$ and $k_{298} = 9.4 \times 10^{-14}\text{ cm}^3/(\text{mol s})$), as well as that of Kozlov et al. [17] above room temperature, are in good agreement with the correlation.

There is a tendency, especially evident in Fig. 3, for deviations from the correlation to be more negative than positive. The reason for this is that absolute rate constant measurements frequently have positive errors due to impurity effects and other unrecognized sources of OH loss, and the relative contributions of these errors tend to increase with decreasing temperature. The result is that the derived E/R values (as well as the A -factors) are too low.

The recent results of Yamada et al. [18] for the compound CHCl_2CF_3 (HCFC-123) ($E/R = 1146\text{ K}$ and $k_{298} = 3.7 \times 10^{-14}\text{ cm}^3/(\text{mol s})$; derived from our fit to their data below 450 K) are in somewhat better agreement with the correlation (see Fig. 6) than the fit to earlier measurements that were used in the recommendations (see the notes in the JPL evaluations). The earlier data are in approximate agreement on an absolute scale, but nevertheless show a different temperature dependence. Thus the data of Yamada et al. should be given more weight.

For compounds with more than one type of C–H bond, for example, CH_3CHF_2 (152a), it is necessary to treat each reaction site separately. The relative contributions to $k(298\text{ K})$ can usually be estimated with sufficient accuracy by the group additivity approach, as demonstrated previously for the 152a [16]. It was shown, as is often the case, that one group (here CHF_2) dominates $k(298\text{ K})$, with the CH_3 group contributing only about 10% of the overall reaction. Thus, it was possible to accurately reproduce the slight curvature in the Arrhenius plot resulting from the two reaction sites with different parameters.

Although the treatment discussed in this paper relates primarily to the temperature region of about 298–450 K, the implications with regard to Arrhenius parameters are for the most part applicable to lower temperatures, such as those of the troposphere and stratosphere. However, extrapolated data are sometimes in disagreement with experimental measurements, such as those for $\text{CH}_2\text{FCH}_2\text{F}$ (152) [16].

Regularities similar to those shown in the present paper for OH can be demonstrated for abstraction reactions of other species, such as atomic chlorine. However, for Cl insufficient verified data are available to establish a completely reliable correlation.

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