Measurement and Estimation of Rate Constants for the Reactions of Hydroxyl Radical with Several Alkanes and Cycloalkanes

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Relative rate experiments were used to measure ratios of chemical kinetics rate constants as a function of temperature for the reactions of OH with isobutane, isopentane, 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane, 2,3-dimethylpentane, 2,4-dimethylpentane, 2,3,4-trimethylpentane, *n*-heptane, *n*-octane, cyclopentane, cyclohexane, and cycloheptane. The results have been used to calibrate a structure−reactivity rate constant estimation method for *k*(298 K) which, when combined with previously determined relationships between *k*(298 K) and the Arrhenius parameters, is capable of determining the temperature dependence accurately. The estimation method reproduces most of the observed rate data within experimental accuracy but appears to fail for 2,3-dimethylbutane, which has an anomalously high rate constant. Curvature in the Arrhenius plots at low temperatures is not present for compounds with a single type of C−H bond and, for compounds with different C−H bonds, is shown to be consistent with effects due to different group sites on the molecule.

Introduction

Reaction with hydroxyl radicals is the major pathway by which most organic compounds are removed from the atmosphere. It is imperative that accurate values of chemical rate constants be obtained for these reactions. Atmospheric modelers use these values to understand the current and future state of the atmosphere. However, despite the importance of straight and branched chain alkanes, relatively few rate constants for OH abstraction are well established for these compounds, especially with regard to the temperature dependence. Lack of reliable data severely hampers the calibration of empirical rate constant estimation methods, such as structure−reactivity relationships.[1] It is for these reasons that we have undertaken to measure the rates of reaction of several alkanes reacting with hydroxyl radicals, with particular emphasis on low temperatures. In addition, we have used the results to calibrate and apply a rate constant estimation method for alkanes, including temperature dependence.

In the relative method for rate constant determinations, both sample and reference gases experience the same conditions during the measurement process. Impurities, which often affect absolute measurements of OH loss, do not affect relative rate results, provided that the analytical technique properly monitors the concentration changes of the reactants. Although relative rate measurements can be subject to error, the measurements are intrinsically simple and capable of great accuracy depending on the analytical method used.

The present work extends earlier relative rate studies of DeMore and Bayes,[2] who measured temperature-dependent rate constants for propane, *n*-butane, *n*-pentane, *n*-hexane, cyclopropane, cyclobutane, cyclopentane, cyclohexane, and dimethyl ether. All rate constants derived were ultimately traceable to that of OH + C_2H_6, which has a well-established rate constant over a wide temperature range. To avoid possible propagation of errors, multiple intercomparisons using different reference gases were conducted. All the reference rate constants were shown to be self-consistent within a few percent.

The present study measured temperature-dependent rate constants for 13 linear, branched-chain, and cyclic alkanes. To demonstrate consistency, some of these were the same as those measured in the DeMore and Bayes study. The process of using multiple intercomparisons was again followed. The present work includes 2-methylpropane, 2-methylbutane, 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane, 2,3-dimethylpentane, 2,4-dimethylpentane, 2,3,4-trimethypentane, *n*-heptane, *n*-octane, cyclopentane, cyclohexane, and cycloheptane.

Methods

Relative Rate Measurements. The technique used in this work has been described in several recent publications.[2−4] A schematic of the apparatus is given in Figure 1. Rate constants and temperature dependencies for hydrocarbons reacting with OH radicals according to eq 1 were measured by a relative method.

$$R{-}H + {}^{\bullet}OH \rightarrow R^{\bullet} + HOH \qquad (1)$$

Measurements were made in the range 203−423 K. Each hydrocarbon studied was measured relative to at least two reference standards whose rate constants were traceable to pub-

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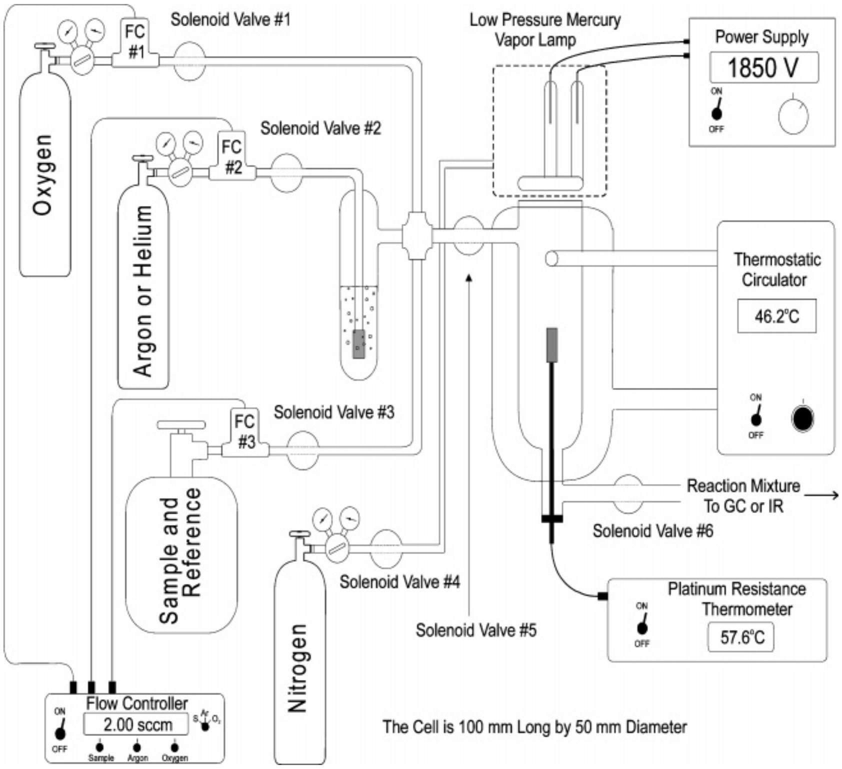

Figure 1. Experimental apparatus used in this work. Reprinted with permission from ref 30. Copyright 2000 Arkansas Academy of Science.

lished values of absolute rates. Equation 2 defines the relationship that exists between the rates of sample and reference.

$$k_{\text{sample}}/k_{\text{reference}} = [\ln(C_0/C_{\text{final}})_{\text{sample}}]/[\ln(C_0/C_{\text{final}})_{\text{reference}}] \qquad (2)$$

Concentrations before and after reaction, C_o and C_{final}, were measured by means of a GC/MS, using single ion monitoring. For each temperature, the reaction times were adjusted so that sample depletions were between 80% and 20%. Sample and reference gases (each $\sim 7 \times 10^{14}$ molecules per cm^3) were mixed together in cylindrical quartz cells, 5 cm diameter by 10 cm long. Helium was added to the reaction mixture to dilute the samples and maintain the pressure at 1 atm. The cells were jacketed and a thermostatic circulator filled with low viscosity silicon oil was attached to the cell and adjusted to the desired temperature. For temperatures below 10 °C, the temperature was controlled by circulating cold nitrogen gas obtained by boiling a dewar of liquid nitrogen. The boil-off gas was channeled through the cell's thermostatic jacket. A Variac controlled the rate of boiling and was periodically adjusted to maintain a constant temperature.

The butane and isobutane were obtained from Scott Specialty Gases, Inc. All other sample and reference compounds were obtained from Sigma-Aldrich Co. The purity of all compounds was 98% or better.

For most measurements above 0 °C, the hydroxyl radicals were generated by photolysis of water vapor ($(1-5) \times 10^{17}$ cm^{-3}), using a low-pressure mercury vapor lamp.

$$H_2O + h\nu\ (185\ \text{nm}) \rightarrow H + OH \qquad (3)$$

For all the low-temperature measurements, and some above ambient temperature, hydroxyl radicals were generated by photolysis of N_2O/H_2 mixtures ($N_2O = 4 \times 10^{16}$ cm^{-3}, $H_2 = 1.5 \times 10^{18}$ cm^{-3}).

$$N_2O + h\nu\ (185\ \text{nm}) \rightarrow N_2 + O(^1D) \qquad (4)$$

$$O(^1D) + H_2 \rightarrow H + OH \qquad (5)$$

A small amount of O_2 ($(2-5) \times 10^{17}$ molecules cm^{-3}) was added to remove H atoms and the resulting alkyl radicals. The latter is important in order to avoid possible reactant reformation by radical−radical reactions. In every case, it was verified that rate constant ratios calculated from eq 2 were independent of the sample depletions. Results obtained by this method were in good agreement with those from the H_2O photolysis method in the overlap region near room temperature. However, in several cases, it was noted that above room temperature the apparent rate constants obtained by the N_2O-H_2 technique were higher than those from the H_2O method and showed increasing upward deviation as the temperature increased. The reason for this problem is not known with certainty but may be due to direct reaction of one reactant with the N_2O. For that reason data above room temperature from the N_2O-H_2 method was not used.

Reference rate constants used in these studies are summarized in Table 1.

Rate Constant Estimations. There are two components of the rate constant estimation method. The first is prediction of a rate constant at one temperature, usually 298 K, and the second is prediction of the temperature dependence, or E/R value. These are discussed below.

Estimation of the Rate Constant at 298 K. Structure−reactivity relationships for estimation of rate constants such as those for OH abstraction are based on the assumption that groups attached to a given C−H bond affect the reactivity of that C−H bond in a reproducible manner in different molecules. The widely used approach of Kwok and Atkinson[1] has shown the power of this method for many classes of organic compounds. The principal requirement for calibration of the method is

TABLE 1: Reference Rate Constants Used in This Study[a]

compound	*A* factor	E/*R*	*k*(298 K)	reference
n-butane	1.68×10^{-11}	584	2.37×10^{-12}	DeMore and Bayes[2]
n-hexane	2.60×10^{-11}	480	5.19×10^{-12}	DeMore and Bayes[2]
n-heptane	3.38×10^{-11}	497	6.38×10^{-12}	this work
cyclopentane	2.57×10^{-11}	498	4.83×10^{-12}	DeMore and Bayes[2]
cyclohexane	3.58×10^{-11}	500	6.69×10^{-12}	DeMore and Bayes[2]
isobutane	$5.24 \times 10^{-15}T^{1.125}e^{-122/T}$		2.11×10^{-12}	this work
2,3-dimethylbutane	$7.54 \times 10^{-13}T^{0.418}e^{-90/T}$		6.03×10^{-12}	this work

[a] Units are cm^3 molecule^{-1} s^{-1} for *k* and *A*, and deg K for *E*/*R*.

accurate data with which to establish the proper group effects. Reliable measurements of temperature dependence, especially in the range below room temperature, are also necessary in order to establish temperature coefficients. Lack of such data has hampered the development of estimation methods which are reliable at low temperatures.

An advantage of the rate constant estimation is that it gives a measure of the rates of attack at different sites in the molecule, which is then useful in predicting the overall temperature dependence.

An important question for hydrocarbon estimations is the effect of different alkyl group sizes and structure on the reactivity of adjacent C−H bonds. Here it is necessary to distinguish between groups as reactive sites, such as CH_3, CH_2, and CH, as opposed to attached groups which affect the reactivity of those sites. The latter may be alkyl groups, halogens or a wide variety of other moieties. However, for the present, we are dealing only with alkyl groups. A single value cannot accurately represent all such groups. For example, it has been shown by Tully and co-workers[5−8] that reactivity of the CH_3 group increases in the series ethane, propane, and butane. Furthermore, previous results of DeMore and Bayes,[2] as well as those of the Tully group[5−8] and Talukdar et al.,[9] show that methylene reactivity increases with the size of the alkane. Thus, the CH_2 group in propane is less reactive than a CH_2 group in butane, and the central CH_2 in *n*-pentane is more reactive than the other two CH_2 groups. A successful estimation method must account for these differences.

In the present work we have found it sufficiently accurate to fit the data with two attached group sizes, as in the Kwok and Atkinson method.[1] Thus, CH_3 is one group and all other alkyl radicals, regardless of structure or size, are represented by the second group. The two group sizes are designated as $n = 1$ or 2.

With this approach it is possible to generate a concise table of rate constant contributions for the three reactive sites, CH_3, CH_2, and CH, wherein the contributions to each site depend on the size (i.e., $n = 1$ or 2) of the groups attached to it. Table 2 provides the parameters to estimate the 298 K rate constant for any linear or branched chain alkane. The entries in Table 2 were determined by fitting the combined data of the present experiments and that of DeMore and Bayes.[2] Only experimental rate constants for linear alkanes and branched chain alkanes containing a single CH group were used in the fitting procedure.

Table 2 also compares the results with those of Kwok and Atkinson[1] and it is seen that the values are similar but not identical. The principal reason is that different rate constants were used for the calibrations.

To illustrate the use of Table 2, the 298 K rate constant for isobutane is estimated. To each of the three CH_3 groups is attached an isopropyl group ($n = 2$). The sum of three CH_3 ($n = 2$) contributions ($3 \times 1.81 \times 10^{-13}$) and one CH (1,1,1) contribution (1.60×10^{-12}) yields a rate constant, *k*(298 K) of 2.14×10^{-12} cm^3 molecule^{-1} s^{-1}.

TABLE 2: Group Contributions for the Estimation of Alkane Rate Constants at 298 K with Comparison to the Previous Results of Kwok and Atkinson[1]

n	this work	Kwok and Atkinson
	CH_3	
1	1.26×10^{-13}	1.36×10^{-13}
2	1.81×10^{-13}	1.68×10^{-13}
	CH_2	
1,1	7.41×10^{-13}	9.34×10^{-13}
1,2	1.00×10^{-12}	1.15×10^{-12}
2,2	1.36×10^{-12}	1.41×10^{-12}
	CH	
1,1,1	1.60×10^{-12}	1.94×10^{-12}
1,1,2	2.06×10^{-12}	2.39×10^{-12}
1,2,2	2.67×10^{-12}	2.94×10^{-12}
2,2,2	3.45×10^{-12}	3.62×10^{-12}

Temperature Dependence. In this discussion we are primarily concerned with the temperature region of about 220−450 K, in which the bulk of the kinetics data is taken. In the first version of our approach,[10] used primarily for halocarbons, estimation of the temperature dependence was based on the assumption of a constant value (8×10^{-13} cm^3 molecule^{-1} s^{-1}) for the preexponential factor in the Arrhenius equation, $k = Ae^{-E/RT}$. This constant value, when combined with a value of *k*(298 K), permitted the calculation of *E*/*R*. Further data showed a clear dependence of the *A* factor on the magnitude of the rate constant,[11,12] and it became necessary to take this into account when calculating Arrhenius parameters. The assumption of a constant *A* factor is not satisfactory when there are large differences in the magnitude of *k*(298 K) values. A further development of this approach improved expressions for the Arrhenius parameters, *E*/*R* and *A*.[13] The improvements were derived using a selected set of rate constant data. The principal criterion for selection was that the data had been verified by both absolute and relative rate measurements. In that work by DeMore, it was further confirmed that preexponential factors increase with *k*(298 K) and are the same for hydrocarbons, halocarbons, fluoroethers, etc, provided that account is taken of the number of C−H bonds in the molecule. Equations 6 and 7, which apply to halocarbons as well as hydrocarbons, are taken from the DeMore paper:[13]

$$\mathrm{E/R/(K)} = (-509.05 \pm 8.65) \log (k_{298}/n) - (5771.2 \pm 119.2) \quad (6)$$

$$\log (A/n) = (0.2581 \pm 0.0290) \log (k_{298}/n) - (8.411 \pm 0.400) \quad (7)$$

In this paper we show that the estimation of *k*(298 K), combined with these equations, accurately reproduces the temperature dependence for hydrocarbons studied in this work.

TABLE 3: Experimental Results for the Rate Constant Ratios

isobutane vs *n*-butane/H_2O		isobutane vs *n*-butane/N_2O-H_2		isopentane vs *n*-butane/H_2O		isopentane vs *n*-butane/N_2O-H_2		isopentane vs isobutane/H_2O		isopentane vs isobutane/N_2O-H_2		2-methylpentane vs cyclohexane/H_2O	
T (K)	ratio	T (K)	ratio	T (K)	ratio	T (K)	ratio	T (K)	ratio	T (K)	ratio	T (K)	ratio
276	0.927	229	1.054	296	1.517	213	2.210	283	1.724	242	1.883	283	0.786
283	0.912	234	1.039	323	1.476	222	2.108	310	1.672	264	1.829	292	0.799
298	0.892	240	1.020	364	1.405	254	1.776	323	1.676	292	1.749	312	0.749
313	0.881	249	0.995	407	1.360	266	1.712	338	1.655	313	1.676	332	0.750
328	0.868	266	0.955			288	1.610	352	1.645			355	0.738
343	0.860	292	0.913			304	1.558	370	1.623			387	0.733
358	0.849	307	0.902			347	1.514	381	1.600				
373	0.843	322	0.900			382	1.517	399	1.587				
403	0.834	347	0.901										

2-methylpentane vs *n*-heptane/H_2O		3-methylpentane vs cyclohexane/H_2O		3-methylpentane vs *n*-heptane/H_2O		2,3-dimethylbutane vs *n*-hexane/H_2O		2,3-dimethylbutane vs *n*-hexane/N_2O-H_2		2,3-dimethylbutane vs *n*-heptane/H_2O	
T (K)	ratio	T (K)	ratio	T (K)	ratio	T (K)	ratio	T (K)	ratio	T (K)	ratio
285	0.875	284	0.825	284	1.000	285	1.179	220	1.711	288	1.007
293	0.907	303	0.830	292	0.981	293	1.199	227	1.591	300	1.012
302	0.860	323	0.802	312	0.918	299	1.130	231	1.545	322	0.932
303	0.908	342	0.772	331	0.913	311	1.164	239	1.501	333	0.888
317	0.856	370	0.763	353	0.899	324	1.076	253	1.377	346	0.868
327	0.797	400	0.752	381	0.900	348	1.030	261	1.340	371	0.856
333	0.821					372	0.990			398	0.803
347	0.809					407	0.943				
359	0.817										
372	0.762										
377	0.789										
398	0.808										

2,3-dimethylbutane vs *n*-heptane/N_2O-H_2		2,3-dimethylbutane vs cyclohexane/H_2O		2,3-dimethylbutane vs cyclohexane/N_2O-H_2		2,3-dimethylpentane vs *n*-hexane/H_2O		2,3-dimethylpentane vs cyclohexane/H_2O		2,3-dimethylpentane vs *n*-heptane/H_2O	
T (K)	ratio	T (K)	ratio	T (K)	ratio	T (K)	ratio	T (K)	ratio	T (K)	ratio
245	1.169	302	5.97E−12	271	0.998	287	1.279	292	0.983	283	0.872
251	1.121	328	6.28E−12			299	1.260	314	0.960	294	0.985
266	1.065	355	6.92E−12			308	1.150	332	0.934	312	0.952
274	1.031	378	7.51E−12			311	1.223	342	0.917	331	1.060
		318	6.26E−12			323	1.197	369	0.884	354	0.988
		342	6.83E−12			333	1.114	395	0.860	388	1.012
		403	7.82E−12			344	1.240				
						365	1.129				
						376	1.104				
						403	1.050				

2,3-dimethylpentane vs 2,3-dimethylbutane/H_2O		2,3,4-trimethylpentane vs *n*-heptane/N_2O-H_2		2,3,4-trimethylpentane vs *n*-hexane/N_2O-H_2		2,3,4-trimethylpentane vs *n*-hexane/H_2O		*n*-heptane vs *n*-hexane/N_2O-H_2		*n*-heptane vs *n*-hexane/H_2O	
T (K)	ratio	T (K)	ratio	T (K)	ratio	T (K)	ratio	T (K)	ratio	T (K)	ratio
272	0.829	244	1.286	246	1.647	287	1.225	241	1.227	299	1.282
299	1.006	251	1.268	259	1.546	325	1.127	250	1.225	314	1.273
320	1.117	255	1.261	269	1.467	348	1.046	261	1.225	324	1.175
334	0.988	264	1.196			373	0.999	271	1.243	326	1.282
348	0.971	270	1.192							362	1.297
365	1.017									373	1.170
386	1.063									389	1.314
410	1.134										

n-heptane vs cyclohexane/H_2O		*n*-heptane vs cyclopentane/H_2O		*n*-octane vs *n*-heptane/H_2O		*n*-octane vs cyclohexane/H_2O		cyclopentane vs cyclohexane/H_2O		cyclopentane vs cyclohexane/N_2O-H_2	
T (K)	ratio	T (K)	ratio	T (K)	ratio	T (K)	ratio	T (K)	ratio	T (K)	ratio
284	0.922	279	1.395	284	1.215	296	1.092	280	0.724	222	0.728
293	0.924	288	1.332	295	1.176	314	1.148	294	0.744	240	0.702
296	0.939	302	1.230	304	1.173	334	1.137	308	0.731	264	0.702
305	0.911	310	1.297	323	1.218	353	1.188	323	0.720	292	0.713
322	0.911	317	1.293	344	1.177	373	1.201	337	0.720	317	0.721
331	0.993	342	1.364	362	1.205	393	1.104	353	0.721		
338	0.996	359	1.276	384	1.204			367	0.725		
346	0.977	406	1.345					382	0.729		
355	0.924							395	0.730		
368	0.926										
379	1.013										
384	0.927										
397	0.924										
288	1.960	209	2.255	288	2.563	225	3.058	274	2.021	291	1.566

TABLE 3: Continued

cyclopentane vs n-butane/H_2O		cyclopentane vs n-butane/N_2O-H_2		cyclohexane vs n-butane/H_2O		cyclohexane vs n-butane/N_2O-H_2		cycloheptane vs n-hexane/H_2O		cycloheptane vs cyclohexane/H_2O	
T (K)	ratio	T (K)	ratio	T (K)	ratio	T (K)	ratio	T (K)	ratio	T (K)	ratio
323	1.953	228	2.248	323	2.572	253	2.917	300	1.971	312	1.542
367	1.891	253	2.134	369	2.438	267	2.870	326	1.956	336	1.548
407	1.853	267	2.096	408	2.402	304	2.668	351	1.948	361	1.538
		310	2.011			344	2.704	373	1.924	386	1.586
		345	1.990			386	2.531	404	1.880	408	1.505
		386	1.988								

Results

Rate Constant Measurements. Table 3 shows the results of the ratio measurements at different temperatures for the various reaction pairs. Table 4 summarizes results from each reference compound, including the reference rate constant used, the temperature range, the method of OH generation, and the calculated rate constant for that particular reference gas. Table 5 lists the rate constants derived as the best fit to combined data from all references, and compares the rate constants either with the Atkinson recommendations[14] or with other previous work. Figures 2−14 show results graphically, along with selected results from earlier studies. To maintain clarity in the graphs, inclusion of previous results is limited to recent or otherwise relevant reports. A comprehensive summary of all literature data may be found in the Atkinson review.[14]

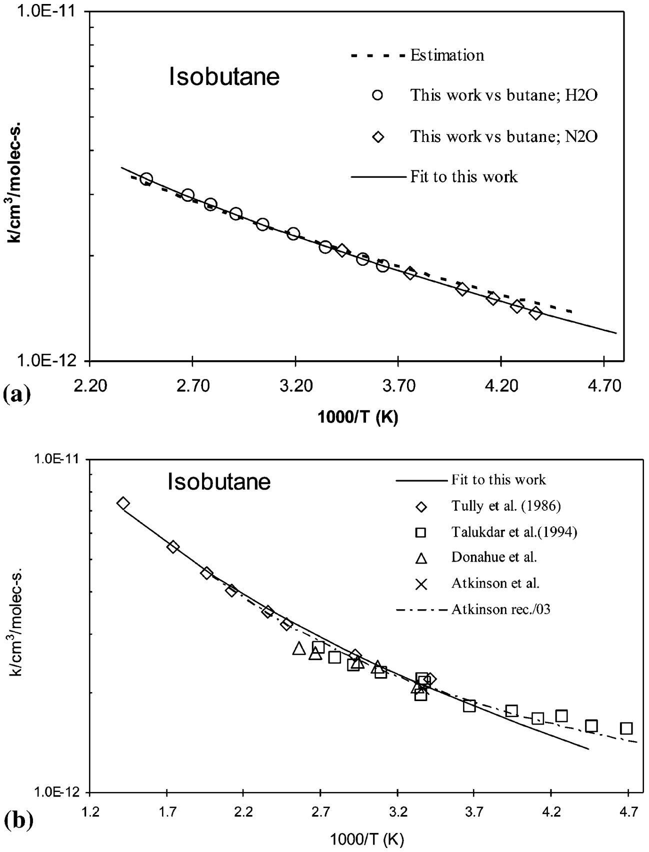

Figure 2. (a) Experimental and estimated rate constants for isobutane. (b) Comparison of the fit to present results for isobutane with previous work.

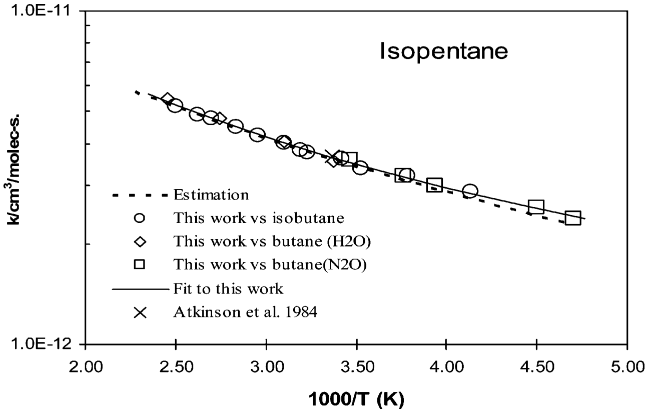

Figure 3. Experimental and estimated rate constants for isopentane and comparison with the previous work of Atkinson et al.[15]

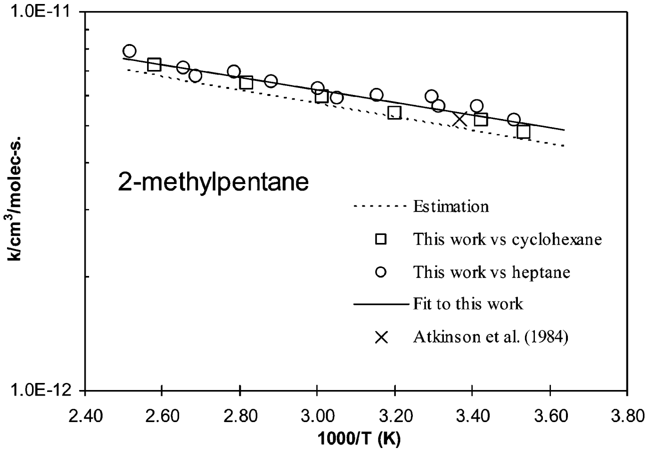

Figure 4. Experimental and estimated rate constants for 2-methylpentane and comparison with the previous work of Atkinson et al.[15]

2-Methylpropane (Isobutane) (Figure 2, parts a and b). This compound was studied vs n-butane over the temperature ranges 276−403 K with the H_2O photolysis technique and 229−347 K with the N_2O-H_2 method. However, only data below 298 K were used from the latter series, for reasons discussed in the Experimental Section. In the overlap region near room temperature, the results from the two methods of OH production are in excellent agreement. Figure 2b shows good agreement of the present results (in the region of data overlap and also extrapolated to higher temperatures by means of the fitted equation given in Table 4) with those of Tully et al.[8] and in fair agreement with those of Talukdar et al.[9] However, as is often the case when comparing absolute data to relative rate data, the relative rate data show less upward curvature in the Arrhenius plot at low temperatures. Arrhenius plots of the results for isobutane do show noticeable curvature, owing to the presence of different reaction sites in the molecule, each with different Arrhenius parameters depending on the number and nature of the C−H bonds attacked. The estimation method gives the rate constant $k = 3.5 \times 10^{-12}e^{-234/T}$ for reaction with the C−H bond (small A factor since there is only one H atom and low E/R because it is a weak C−H bond) and $k = 1.35 \times 10^{-11}e^{-958/T}$ for the nine methyl C−H bonds (larger A factor because of the nine H atoms and high E/R because of the

TABLE 4: Compounds Studied and Rate Constant Results from Each Reference Compound

	reference *k*				result		
reference	*A* factor (cm^3 molecule^{-1} s^{-1})	*E*/*R* (K)	method	temp (K)	*A* factor (cm^3 molecule^{-1} s^{-1})	*E*/*R* (K)	*k*(298) (cm^3 molecule^{-1} s^{-1})
			2-Methylpropane				
n-butane	1.68×10^{-11}	584	H_2O	276−403	1.11×10^{-11}	493	2.12×10^{-12}
n-butane	1.68×10^{-11}	584	N_2O/H_2	229−347	1.05×10^{-11}	468	2.19×10^{-12}
			T^n fit to all data		$5.24 \times 10^{-15}\ T^{1.125}e^{-121.8/T}$		
			2-Methylbutane				
n-butane	1.68×10^{-11}	584	H_2O	296−407	1.69×10^{-11}	462	3.59×10^{-12}
n-butane	1.68×10^{-11}	584	N_2O/H_2	213−382	1.12×10^{-11}	329	3.69×10^{-12}
2-methylpropane	$5.24 \times 10^{-15} \times \mathrm{T}^{1.125}$	122	H_2O	283−399	1.48×10^{-11}	421	3.60×10^{-12}
2-methylpropane	$5.24 \times 10^{-15} \times \mathrm{T}^{1.125}$	122	N_2O/H_2	242−313	1.03×10^{-11}	309	3.66×10^{-12}
			T^n fit to all data		$2.54 \times 10^{-15}\ \mathrm{T}^{1.267}\ e^{15.7/T}$		
			2-Methylpentane				
cyclohexane	3.58×10^{-11}	500	H_2O	283−387	2.07×10^{-11}	413	5.19×10^{-12}
n-heptane	3.38×10^{-11}	497	H_2O	285−398	1.82×10^{-11}	352	5.57×10^{-12}
			Arrhenius fit to all data		1.96×10^{-11}	383	5.42×10^{-12}
			3-Methylpentane				
cyclohexane	3.58×10^{-11}	500	H_2O	284−400	2.06×10^{-11}	395	5.48×10^{-12}
n-heptane	3.38×10^{-11}	497	H_2O	284−381	2.16×10^{-11}	375	6.14×10^{-12}
			Arrhenius fit to all data		1.77×10^{-11}	330	5.85×10^{-12}
			2,3-Dimethylbutane				
n-hexane	2.60×10^{-11}	480	H_2O	285−407	1.39×10^{-11}	250	6.01×10^{-12}
n-hexane	2.60×10^{-11}	480	H_2O	292−394	1.47×10^{-11}	280	5.72×10^{-12}
n-hexane	2.60×10^{-11}	480	N_2O/H_2	220−261	9.64×10^{-12}	147	5.89×10^{-12}
n-heptane	3.38×10^{-11}	497	H_2O	288−398	1.45×10^{-11}	249	6.31×10^{-12}
n-heptane	3.38×10^{-11}	497	N_2O/H_2	245−274	1.22×10^{-11}	211	6.03×10^{-12}
cyclohexane	3.58×10^{-11}	500	H_2O	302−403	1.85×10^{-11}	345	5.80×10^{-12}
cyclohexane	3.58×10^{-11}	500	N_2O/H_2	271			5.66×10^{-12}
			T^n fit to all data		$7.54 \times 10^{-13}T^{0.418}e^{-90/T}$		
			2,3-Dimethylpentane				
n-hexane	2.60×10^{-11}	480	H_2O	287−403	1.84×10^{-11}	313	6.44×10^{-12}
cyclohexane	3.58×10^{-11}	500	H_2O	292−395	2.09×10^{-11}	345	6.55×10^{-12}
			Arrhenius fit to all data		1.95×10^{-11}	329	6.47×10^{-12}
			2,4-Dimethylpentane				
n-heptane	3.38×10^{-11}	497	H_2O	283−388	4.81×10^{-11}	619	6.03×10^{-12}
cyclohexane	3.58×10^{-11}	500	H_2O	304−343	3.15×10^{-11}	601	4.19×10^{-12}
2,3-dimethyl-butane	$7.54 \times 10^{-13}T^{0.418}$	90	H_2O	272−410	2.25×10^{-11}	408	5.72×10^{-12}
			Arrhenius fit to all data		2.49×10^{-11}	443	5.64×10^{-12}
			2,3,4-Trimethylpentane				
n-hexane	2.60×10^{-11}	480	H_2O	287−373	1.30×10^{-11}	221	6.20×10^{-12}
n-hexane	2.60×10^{-11}	480	N_2O/H_2	246−269	1.09×10^{-11}	144	6.75×10^{-12}
n-heptane	3.38×10^{-11}	497	N_2O/H_2	244−270	1.82×10^{-11}	283	7.04×10^{-12}
			Arrhenius fit to all data		9.85×10^{-12}	124	6.49×10^{-12}
			n-Heptane				
n-hexane	2.60×10^{-11}	480	N_2O/H_2	241−271	3.54×10^{-11}	506	6.48×10^{-12}
n-hexane	2.60×10^{-11}	480	H_2O	299−389	3.26×10^{-11}	480	6.52×10^{-12}
cyclohexane	3.58×10^{-11}	500	H_2O	284−397	3.71×10^{-11}	531	6.24×10^{-12}
cyclopentane	2.57×10^{-11}	498	H_2O	279−406	3.32×10^{-11}	492	6.36×10^{-12}
			Arrhenius fit to all data		3.38×10^{-11}	497	6.38×10^{-12}
			n-Octane				
n-heptane	3.38×10^{-11}	497	H_2O	284−384	4.19×10^{-11}	517	7.39×10^{-12}
cyclohexane	3.58×10^{-11}	500	H_2O	296−393	4.67×10^{-11}	545	7.51×10^{-12}
			Arrhenius fit to all data		4.52×10^{-11}	538	7.43×10^{-12}
			Cyclopentane				
cyclohexane	3.58×10^{-11}	500	H_2O	28−395	2.55×10^{-11}	493	4.87×10^{-12}
cyclohexane	3.58×10^{-11}	500	N_2O/H_2	222−317	2.54×10^{-11}	499	4.76×10^{-12}
n-butane	1.68×10^{-11}	584	H_2O	288−407	2.71×10^{-11}	526	4.64×10^{-12}
n-butane	1.68×10^{-11}	584	N_2O/H_2	209−386	2.77×10^{-11}	518	4.87×10^{-12}
			Arrhenius fit to all data		2.67×10^{-11}	509	4.84×10^{-12}
			Cyclohexane				
n-butane	1.68×10^{-11}	584	H_2O	288−408	3.40×10^{-11}	513	6.08×10^{-12}
n-butane	1.68×10^{-11}	584	N_2O/H_2	225−386	3.34×10^{-11}	488	6.51×10^{-12}
			Arrhenius fit to all data		3.10×10^{-11}	471	6.37×10^{-12}
			Cycloheptane				
n-hexane	2.60×10^{-11}	480	H_2O	274−404	4.31×10^{-11}	426	1.03×10^{-11}
cyclohexane	3.58×10^{-11}	500	H_2O	291−408	5.29×10^{-11}	484	1.04×10^{-11}
			Arrhenius fit to all data		4.81×10^{-11}	457	1.04×10^{-11}

TABLE 5: Derived Rate Constant Expressions for Alkanes and Cycloalkanes Studied in This Work and Comparison with Recent Recommendations of Atkinson[14] or with Other Work[a,b,c]

compound	A (cm^3 molecule^{-1} s^{-1})	n	E/R (K)	k(298 K) (cm^3 molecule^{-1} s^{-1})	source
2-methylpropane	5.24×10^{-15}	1.125	121.8	2.12×10^{-12}	this work
	1.17×10^{-17}	2.0	213	2.12×10^{-12}	Atkinson
2-methylbutane	2.54×10^{-15}	1.267	−15.7	3.65×10^{-12}	this work
				3.6×10^{-12}	Atkinson
2-methylpentane	$(1.96 \pm 0.17) \times 10^{-11}$		383 ± 29	5.42×10^{-12}	this work
				5.2×10^{-12}	Atkinson
3-methylpentane	$(1.77\pm0.29) \times 10^{-11}$		330 ± 53	5.85×10^{-12}	this work
				5.2×10^{-12}	Atkinson
2,3-dimethylbutane	7.54×10^{-13}	0.418	90.0	6.05×10^{-12}	this work
	1.66×10^{-17}	2.0	−407	5.78×10^{-12}	Atkinson
2,3-dimethylpentane	$(1.95 \pm 0.16) \times 10^{-11}$		(329 ± 28)	6.47×10^{-12}	this work
					no previous data
2,4-dimethylpentane	$(2.49 \pm 0.73) \times 10^{-11}$		(443 ± 97)	5.64×10^{-12}	this work
				4.77×10^{-12}	Atkinson
2,3,4-trimethylpentane	$(9.85 \pm 0.71) \times 10^{-12}$		(124 ± 20)	6.50×10^{-12}	this work
	$(5.57 \pm 1.3) \times 10^{-12}$		(-57 ± 65)	6.74×10^{-12}	Harris and Kerr[16]
n-heptane	$(3.38 \pm 0.17) \times 10^{-11}$		(497 ± 16)	6.38×10^{-12}	this work
	1.28×10^{-11}		190	6.76×10^{-12}	Atkinson
n-octane	$(4.52 \pm 0.37) \times 10^{-11}$		(538 ± 27)	7.43×10^{-12}	this work
	1.78×10^{-11}		235	8.11×10^{-12}	Atkinson
cyclopentane	$(2.67 \pm 0.56) \times 10^{-11}$		(509 ± 6)	4.84×10^{-12}	this work
	1.79×10^{-11}		382	4.97×10^{-12}	Atkinson
cyclohexane	$(3.10 \pm 0.18) \times 10^{-11}$		(471 ± 18)	6.37×10^{-12}	this work
	2.14×10^{-11}		334	6.97×10^{-12}	Atkinson
cycloheptane	$(4.81 \pm 0.28) \times 10^{-11}$		(457 ± 19)	1.04×10^{-11}	this work
	2.62×10^{-11}		223	1.24×10^{-11}	Atkinson

[a] Fit of all data to either a two-parameter Arrhenius equation ($k = Ae^{-E/RT}$) or, where the temperature range is sufficient to show curvature, a three-parameter Arrhenius equation ($k = AT^n e^{-E/RT}$). [b] Errors shown are 1 standard deviation of the least-squares fit, and they do not reflect uncertainties in the reference rate constant or other possible systematic errors. [c] In some cases the Atkinson three-parameter recommendations have been converted to two-parameter formats at 298 K for comparison with the present work.

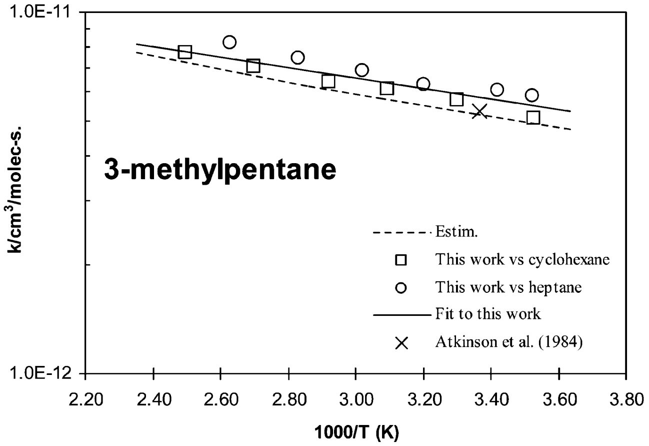

Figure 5. Experimental and estimated rate constants for 3-methylpentane and comparison with the previous work of Atkinson et al.[15] at room temperature.

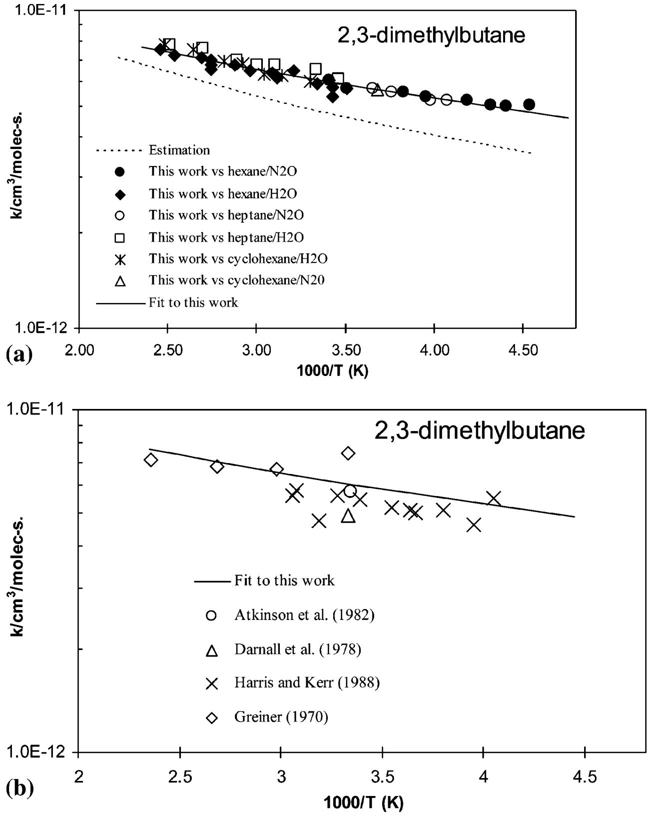

Figure 6. (a) Experimental and estimated rate constants for 2,3-dimethylbutane. (b) Comparison of the fit to present results for 2,3-dimethylbutane with previous work.

stronger bonds). Figure 2a shows that the sum of these two rates is a reasonable fit to the data, although the data points fall about 6% below the prediction at the lowest temperature. This contrasts with the results for isopentane (discussed in the next section) where the low temperature data fall slightly above the estimation. In either case the discrepancies are within experimental error.

2-Methylbutane (Isopentane) (Figure 3). This compound was studied vs *n*-butane and isobutane as references over the temperature region 213−407 K, using both the H_2O and N_2O-H_2 methods of OH generation. As shown in Figure 3 results from both reference compounds are in excellent agreement among themselves and with the previous room-temperature measurement of Atkinson et al.[15] There are no previous measurements of the temperature dependence. As with isobutane, the estimated rate constants are in good agreement with the experimental data, although in this case the predicted curvature at low temperatures is slightly less than observed.

2-Methylpentane (Figure 4). This compound was studied over the temperature range 283−398 K by the H_2O technique

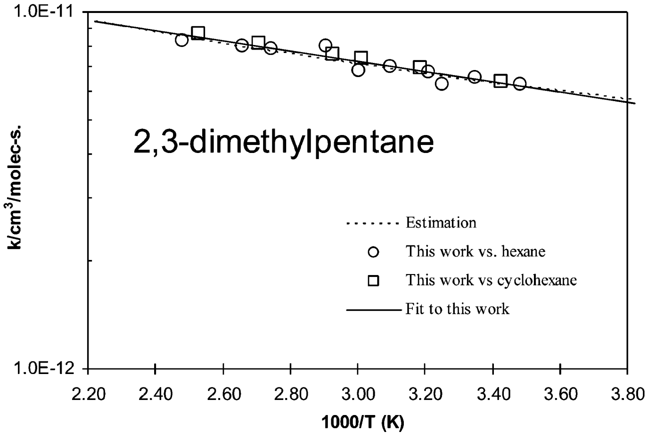

Figure 7. Experimental and estimated rate constants for 2,3-dimethylpentane.

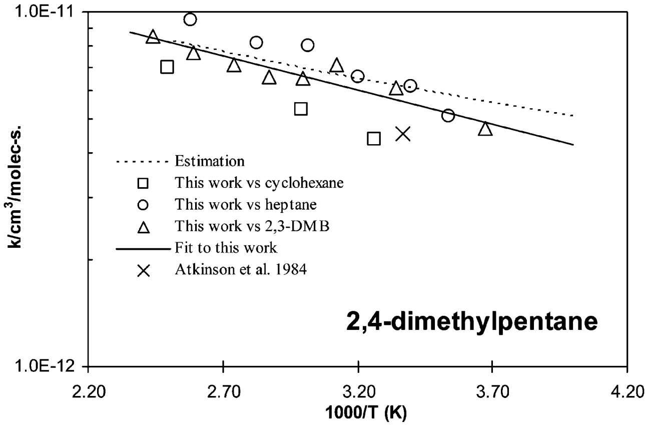

Figure 8. Experimental and estimated rate constants for 2,4-dimethylpentane and comparison with the previous work of Atkinson et al.[15] at room temperature.

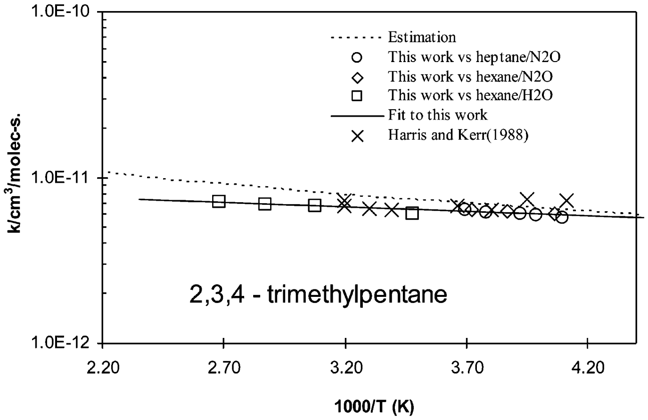

Figure 9. Experimental and estimated rate constants for 2,3,4-trimethylpentane and comparison with previous work.

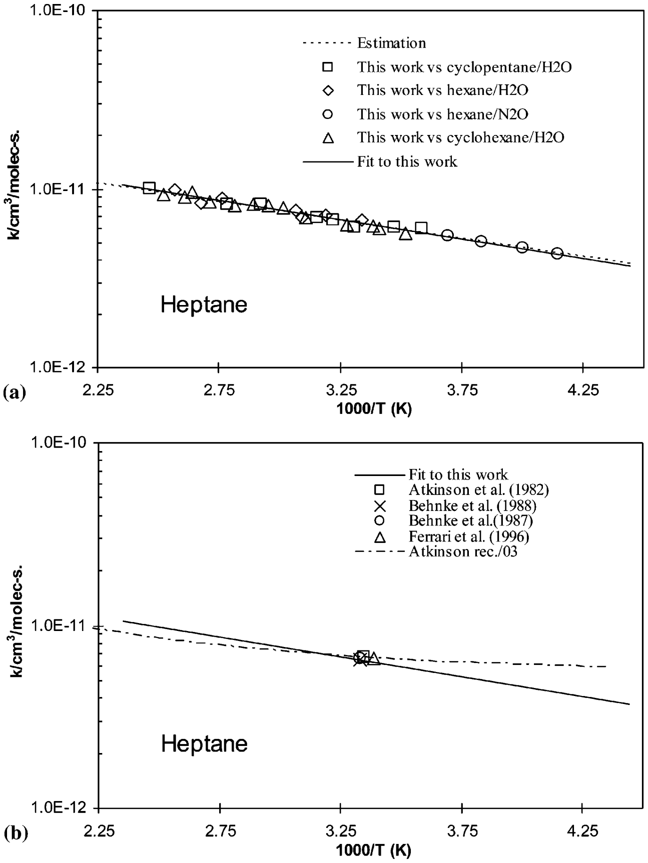

Figure 10. (a) Experimental and estimated rate constants for heptane. (b) Comparison of the fit to present results for heptane with previous work.

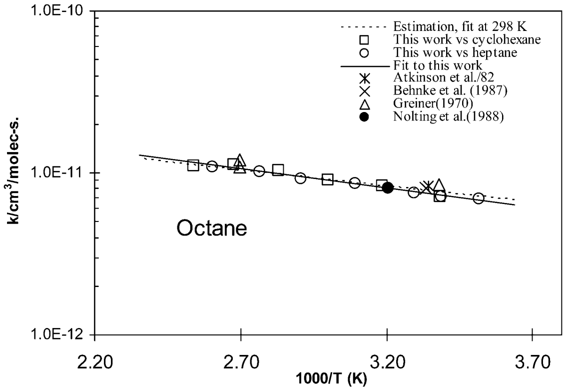

Figure 11. Experimental and estimated rate constants for octane and comparison with previous work.

using cyclohexane and heptane as references. As shown in Figure 4, the results are in good agreement at all temperatures for the two reference compounds and with the estimation. The previous result of Atkinson et al.[15] at 297 K is also in excellent agreement. The temperature range of this study was not sufficient to reveal curvature in the Arrhenius plot.

3-Methylpentane (Figure 5). The temperature range for these experiments was 284−400 K, using the H_2O technique with cyclohexane and heptane as references. As expected, because of group size effects and as predicted by the estimation (Table 6), the rate constant is similar to but slightly higher than that for 2-methylpentane. As in the previous case of 2-methylpentane, data with heptane as the reference are a few percent higher (in this case 12% at 298 K) than those obtained using cyclohexane as the reference. Also, the cyclohexane data are in better agreement with the Atkinson et al. result at 297 K,[15] as well as with the estimation for 3-methylpentane. While this might suggest that the heptane reference rate constant is slightly high, there is no indication either from the heptane experiments (see below) or from the estimation prediction for heptane (see Table 6) that this is the case. It is more likely that the difference is due to experimental error in the present experiment.

2,3-Dimethylbutane (Figure 6, Parts a and b). This compound was extensively studied over a substantial temperature range (220−407 K), using hexane, heptane, and cyclohexane as references. It was also measured against 2,4-dimethylpentane as a further test of the rate constant. The reason

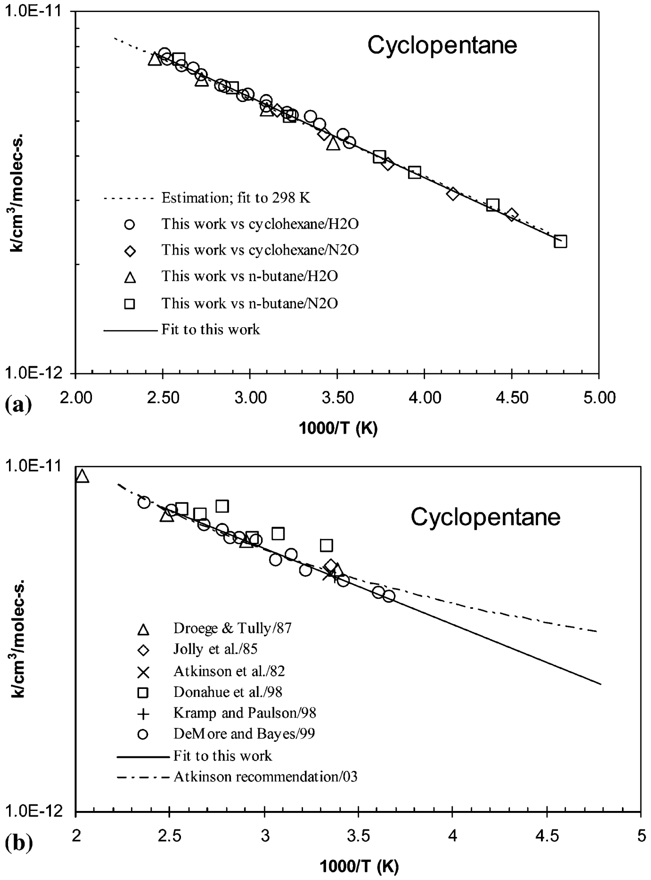

Figure 12. (a) Experimental and estimated results for cyclopentane. (b) Comparison of the fit to present work for cyclopentane with previous work.

for the repeated measurements was that the rate constant is anomalously high, and it cannot be accounted for by any application of group additivity that is consistent with other branched alkanes containing one or two C−H reactive sites. One demonstration of the anomaly can be seen by noting that 2,3-dimethylbutane should, to a first approximation, be about twice as fast as isobutane. However, it is about 2.8 times faster (at 298 K). Figure 6a and Table 6 show that the disagreement with the estimation is much greater than that observed for any other compound measured in this work. The principal factor responsible for the high rate constant is a low activation energy, and not a high preexponential factor, since the observed *A* factor (fit to the region near 298 K) is nearly identical to the predicted value (see Table 6). This compound seems to represent a violation of group additivity for hydrocarbons, but the reason is not apparent. Previous studies on this compound, shown in Figure 6b, are somewhat scattered but generally support the present results.

2,3-Dimethylpentane (Figure 7). There are no previous data on this compound. The present experiments cover the temperature range 287−403 K. The reference compounds were hexane and cyclohexane. Results from the two references are in good agreement and also, in contrast to the case of 2,3-dimethylbutane, agree very well with the estimation both in terms of absolute value and temperature dependence.

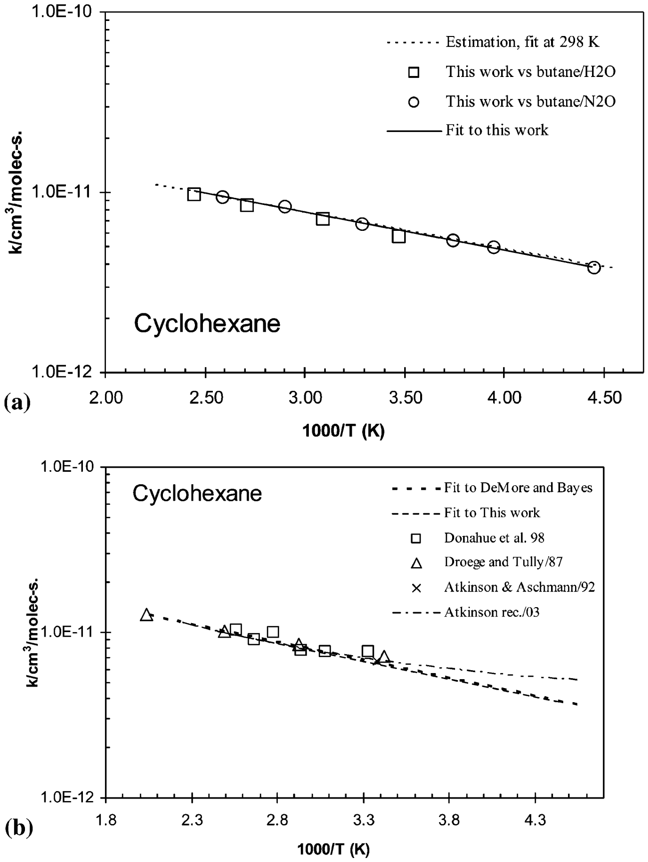

Figure 13. (a) Experimental and estimated results for cyclohexane. (b) Comparison of the fit to present results for cyclohexane with previous work.

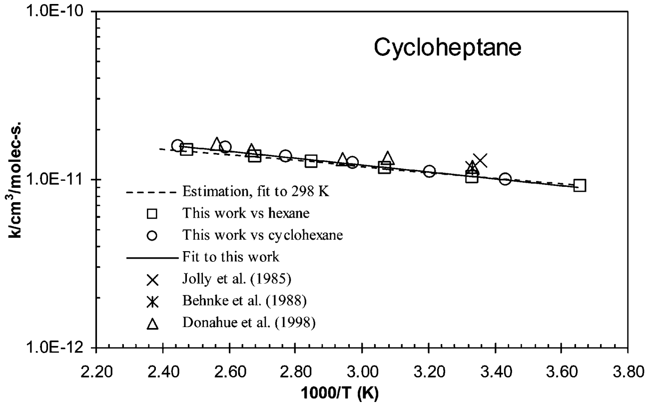

Figure 14. Experimental and estimated results for cycloheptane and comparison with previous work. Estimation was fit to the experimental *k*(298 K).

2,4-Dimethylpentane (Figure 8). This compound was studied in the temperature range 272−410 K with heptane, cyclohexane, and 2,3-dimethylbutane as references. The latter reference was used to verify that 2,3-dimethylbutane has nearly the same rate constant as 2,4-dimethylpentane, despite the fact that group additivity would predict a higher rate for the latter. It has an additional CH_2 group which, from entries in Table 2, should result in an increment of more than 1×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. As seen in Table 3, the rate constant ratios are in fact near unity. This is a further demonstration of the anomalous behavior of 2,3-dimethylbutane. The 2,4-dimethylpentane rate is reasonably well predicted by the estimation, and as expected is similar to 2,3-dimethylpentane.

Our results for this compound are somewhat scattered, and data with cyclohexane as the reference do not agree well with those from the other two references, although the results relative to cyclohexane seem to agree with the previous report of Atkinson et al.[15] Some additional work may be required in this case.

TABLE 6: Comparison of Experimental and Estimated Alkane Rate Constants Based on the Present SAR Calculations

compound	*A* factor (cm^3 molecule^{-1} s^{-1})	*E*/*R* (K)	*k*(298 K) (cm^3 molecule^{-1} s^{-1})	ratio exp/est	source
ethane	9.78×10^{-12}	1095	2.48×10^{-13}	0.98	Atkinson[14]
	8.21×10^{-12}	1038	2.52×10^{-13}		estimated
propane	1.29×10^{-11}	730	1.11×10^{-12}	1.00	DeMore and Bayes[2]
	1.10×10^{-11}	686	1.11×10^{-12}		estimated
n-butane	1.68×10^{-11}	584	2.37×10^{-12}	1.00	DeMore and Bayes[2]
	1.65×10^{-11}	580	2.36×10^{-12}		estimated
n-pentane	1.94×10^{-11}	494	3.69×10^{-12}	0.99	DeMore and Bayes[2]
	2.11×10^{-11}	516	3.73×10^{-12}		estimated
n-hexane	2.60×10^{-11}	480	5.20×10^{-12}	1.02	DeMore and Bayes[2]
	2.71×10^{-11}	499	5.07×10^{-12}		estimated
n-heptane	3.38×10^{-11}	497	6.38×10^{-12}	0.99	this work
	3.26×10^{-11}	483	6.43×10^{-12}		estimated
n-octane	4.52×10^{-11}	538	7.43×10^{-12}	0.96	this work
	3.69×10^{-11}	464	7.78×10^{-12}		estimated
n-nonane	1.66×10^{-11}	160	9.70×10^{-12}	1.06	Atkinson[14]
	4.37×10^{-11}	466	9.15×10^{-12}		estimated
n-decane	2.08×10^{-11}	190	1.10×10^{-11}	1.05	Atkinson[14]
	4.93×10^{-11}	461	1.05×10^{-11}		estimated
2-methylpropane	9.80×10^{-12}	457	2.11×10^{-12}	0.99	this work
(isobutane)	1.01×10^{-11}	462	2.14×10^{-12}		estimated
2,2-dimethylpropane	1.22×10^{-11}	803	8.24×10^{-13}	1.14	Atkinson[14]
(neopentane)	1.80×10^{-11}	958	7.24×10^{-13}		estimated
2-methylbutane	1.23×10^{-11}	362	3.65×10^{-12}	1.02	this work
(isopentane)	1.52×10^{-11}	432	3.58×10^{-12}		estimated
2-methylpentane	1.96×10^{-11}	383	5.42×10^{-12}	1.10	this work
	2.07×10^{-11}	427	4.94×10^{-12}		estimated
3-methylpentane	1.77×10^{-11}	330	5.85×10^{-12}	1.13	this work
	1.96×10^{-11}	396	5.18×10^{-12}		estimated
2,2-dimethylbutane	3.37×10^{-11}	809	2.23×10^{-12}	1.30	Atkinson[14]
	1.89×10^{-11}	714	1.72×10^{-12}		estimated
2,3-dimethylbutane	1.24×10^{-11}	215	6.03×10^{-12}	1.25	this work
	1.54×10^{-11}	347	4.81×10^{-12}		estimated
2,3-dimethylpentane	1.95×10^{-11}	329	6.47×10^{-12}	1.00	this work
	1.93×10^{-11}	325	6.46×10^{-12}		estimated
2,4-dimethylpentane	2.49×10^{-11}	443	5.64×10^{-12}	0.92	this work
	2.09×10^{-11}	364	6.16×10^{-12}		estimated
2,3,4-trimethylpentane	9.85×10^{-11}	124	6.49×10^{-12}	0.85	this work
	2.07×10^{-11}	297	7.64×10^{-12}		estimated
2,2,3,3-tetramethylbutane	1.31×10^{-11}	774	9.76×10^{-13}	0.90	Atkinson[14]
	2.71×10^{-11}	958	1.09×10^{-12}		estimated
2,2,3-trimethylbutane	6.04×10^{-11}	137	3.81×10^{-12}	0.97	Atkinson[14]
	2.06×10^{-11}	494	3.93×10^{-12}		estimated
2,2,4-trimethylpentane	1.54×10^{-11}	456	3.33×10^{-12}	0.78	Atkinson[14]
	2.09×10^{-11}	473	4.29×10^{-12}		estimated

2,3,4-Trimethylpentane (Figure 9). This compound was studied with reference to hexane and heptane, using both the H_2O and N_2O-H_2 methods for OH generation. The temperature range was 244−373 K. The value of the rate constant near 298 K is 15% lower than the estimation, and both the *A* factor and *E*/*R* are much lower than predicted (see Table 6 and Figure 9). This compound may represent another failure of the estimation method (the other being 2,3-dimethylbutane), or there may be a problem with the data, especially the data points above room temperature. Although those results are in fair agreement with earlier relative rate data of Harris and Kerr,[16] additional work on this compound is needed.

***n*-Heptane (Figure 10, Parts a and b).** This compound was studied with reference to hexane and cyclohexane, using both the H_2O and N_2O-H_2 methods for OH generation, over the temperature range 241−406 K. The results, shown in Figure 10a, are in good agreement for both references and both methods of OH generation. Rate constant values near room temperature are well-established in previous work of Atkinson et al.,[17] Behnke et al.,[18,19] and Ferrari et al.[20] (Figure 10b), and are in good agreement with the present work. However, the temperature dependence does not show the curvature represented in the Atkinson recommendation[14] shown in Figure 10b. The estimation result shown in Figure 10a is in perfect agreement with the data.

***n*-Octane (Figure 11).** The reference compounds for this study were heptane and cyclohexane, and the temperature range was 284−393 K. The H_2O method for OH production was used. Results from the two references are in good agreement with each other and with the data point of Nolting et al.[21] at 312 K, but are slightly lower near room temperature than previous measurements by Atkinson et al.,[17] Behnke et al.,[19] and Greiner[22] and also compared to the estimation. Although the difference is small, it is possible that the estimation rate constant (Table 6) is preferable to the experimental value because the experimental value of *E*/*R* (546 K) is too high to be consistent with the trend of *E*/*R* values for the other straight chain alkanes. (see Figure 15.)

Cyclopentane (Figure 12, Parts a and b). This compound was studied vs butane and cyclohexane over the temperature range 222−407 K, using both the H_2O and N_2O-H_2 methods of OH generation. As seen in Table 4 and Figure 12a, the results of all the present experiments are in good agreement, and are consistent with previous measurements of Droege and Tully,[23] Jolly et al.,[24] Atkinson et al.,[25] and DeMore and Bayes[2], but they are slightly lower than those of Donahue et al.[26] These are the first measurements below 277 K, and as expected for a compound with only one type of C−H bond, there is no evidence of curvature in the Arrhenius plot down to 222 K. This contrasts with the recommended temperature dependence

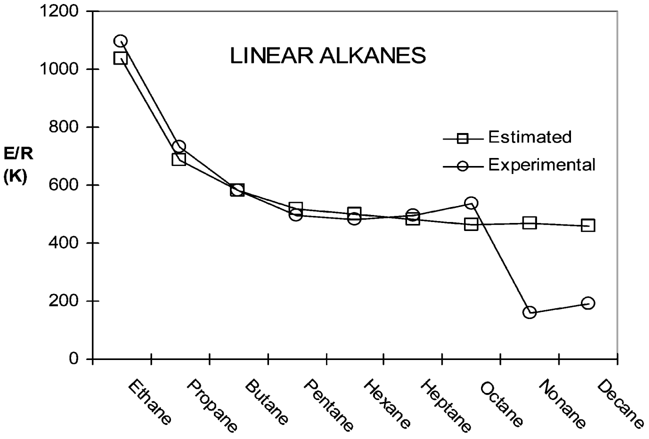

Figure 15. Comparison of estimated and experimental values of E/R for n-alkanes. The E/R values for nonane and decane are the Atkinson recommendations,[14] fit to a two-parameter Arrhenius equation at 298 K.

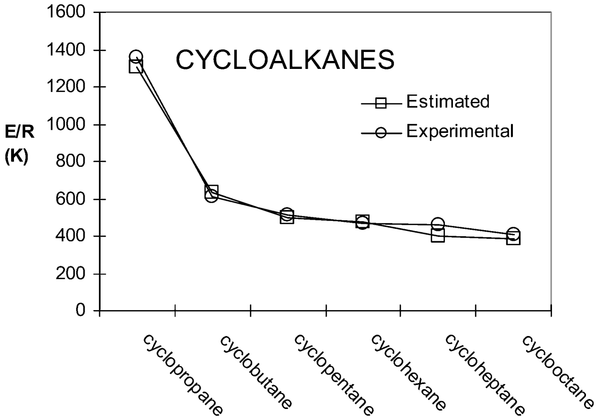

Figure 16. Comparison of estimated and experimental values of E/R for cycloalkanes.

for cyclopentane given in the Atkinson review,[14] which shows pronounced curvature below room temperature. Our estimation, fit to 298 K, reproduces our experimental temperature dependence very well.

Cyclohexane (Figure 13, Part a and b). As with cyclopentane, this compound has been studied in the temperature range near room temperature and up to about 500 K, but otherwise not at lower temperatures. The present results cover the temperature range 225−406 K, using both the H_2O and N_2O-H_2 methods of OH generation. The reference gas was n-butane. Results of the present work from the two experiment types are in agreement, and are in excellent agreement with the previous data of DeMore and Bayes.[2] Absolute data of Droege and Tully[23] agree well, except possibly at the lowest temperature of their measurements, where there is an apparent onset of upward curvature. Data of Donahue et al.[26] are in approximate agreement, although somewhat scattered. A relative rate measurement at 296 K by Atkinson and Aschmann[27] is in essentially perfect agreement. A number of additional measurements have been made on this compound, and are summarized in the review by Atkinson.[14] However, the recommended temperature dependence in that review, shown in Figure 13b, does not agree with the data. As with cyclopentane, the estimation, fit to 298 K, reproduces our experimental temperature dependence accurately.

Cycloheptane (Figure 14). This compound was studied vs the references n-hexane and cyclohexane using the H_2O method of OH production, in the temperature range 274−408 K. The only previous temperature dependence study is that of Donahue et al.,[26] (300−390 K), the results of which are in approximate agreement with the present. Room-temperature measurements by Behnke et al.[18] (relative rate) and Jolly et al.[24] (absolute) are in reasonable agreement, although slightly higher. The estimation method reproduces the temperature dependence well.

Rate Constant Estimations. Table 6 compares the estimated values for k(298 K) and the Arrhenius parameters A and E/R for all compounds studied in this work or the previous series,[2] along with selected additional compounds for which data are summarized in the Atkinson review.[14] For the linear alkanes (which were used in the data fit for estimation of k(298 K)), all the experimental results for k(298 K) in the present and earlier work can be reproduced to within 2%, with the exception of octane, which is high by 5%. Furthermore, the predicted Arrhenius parameters using eqs 6 and 7 are in essentially perfect agreement with the experimental values for the linear alkanes propane through heptane, although none of these temperature dependence data were used in the derivation of those equations. Figure 15 illustrates this agreement, and shows that (as mentioned before) our experimental value for E/R of the octane reaction may be slightly high. Also, Figure 15 suggests that the E/R values recommended in the Atkinson review[14] for n-nonane and n-decane are too low. In these cases, the estimated Arrhenius parameters are to be preferred.

The average error for the singly branched alkanes studied in this work and shown in Table 6 is about 6%, most of which arises from 3-methylpentane. As suggested above in the discussion of 3-methylpentane results, our data for that compound may be slightly high.

For those alkanes with two or more C−H groups, the average error is 13%, again with most of the error being in one compound, the anomalous 2,3-dimethylbutane. In this case error in the experimental data seems unlikely, considering the large number of measurements conducted against several references, as well as previous work from other laboratories. This discrepancy appears to be a failure of the estimation method. It may be noted, however, that if the estimated rate constants for the two components of the reaction (abstraction from the four CH_3 groups and the two CH groups) are arbitrarily scaled up by the same factor to match the experimental k(298 K), then the predicted temperature dependence closely reproduces the experimental. However, the reason this adjustment is necessary remains unknown.

A large discrepancy of 30% is shown in Table 6 for the case of 2,2-dimethylbutane. In this case the experimental database is limited and it is probable that the estimated rate constant is more accurate. Similarly, the estimation is likely better for 2,2-dimethylpropane, for which the experimental data are scattered.[14] The discrepancy here is, however, only 14%. The estimation is also probably more accurate than the experimental data for 2,2,4-trimethylpentane, since, as may be seen in Table 6, the reported measurements seem too low when compared to those for 2,2,3-trimethylbutane.

For the cycloalkanes, a priori estimates of k(298 K) cannot be made because of the effects of ring strain. For cycloheptane, in which ring strain is presumably minimal, the experimental rate constant at 298 K corresponds to a rate constant per CH_2 group of 1.48×10^{-12} cm^3 molecule^{-1} s^{-1}, which is to be compared to the value 1.36×10^{-12} cm^3 molecule^{-1} s^{-1} predicted for an open chain compound from Table 2.

With regard to the temperature dependence for cycloalkanes, the predicted values calculated from the experimental values of k(298 K) using eq 6 are in excellent agreement with the experimental results, as shown in Figure 16. The experimental data shown in this figure for cyclooctane are from Donahue et al. [26]

Conclusions

(1) The present work shows further evidence of a discrepancy between low-temperature rate constant behavior for alkanes as determined by absolute methods and relative methods.[2,28,29] Evidently there are errors in one or both of the experimental approaches. At low temperatures absolute methods often show upward curvature in rate constant data which is not reproduced in relative rate experiments. (see, for example, Figure 2b). If our relative rate data are correct, then it is apparent from the low-temperature rate constant behavior of reactants such as cyclopentane and cyclohexane that compounds with a single type of C−H bond do not depart significantly from linearity in Arrhenius fits below room temperature, at least in the present temperature range down to approximately 220 K. Similarly, compounds such as *n*-heptane, in which reaction at low temperatures is dominated by the CH_2 groups, no curvature is evident below room temperature. Thus, three parameter fits with a T^2 dependence are unsuitable for representation of data in the low-temperature range, since they over-predict the curvature. There is no a priori reason to assume that a T^n fit that is appropriate at high temperatures will also be correct at low temperatures.

(2) The structure−additivity method for rate constant estimation is usually successful for the prediction of k(298 K) for alkanes, but it appears to fail in the case of 2,3-dimethylbutane for unknown reasons. No change in methodology or adjustment of the estimation parameters can account for this inconsistency without introducing errors for other compounds. Evidently some additional factor is missing from the method.

(3) Without exception, temperature dependence of OH abstraction reactions can be accurately calculated from knowledge of the rate constant at 298 K, using empirical relations represented by eqs 6 and 7. Adherence to these equations can be used as a criterion for the accuracy of rate constant data, not only for hydrocarbons but also for halocarbons as well.[13]

(4) Reaction of OH with compounds with more than one type of C−H bond can be represented as the sum of the individual reaction rates, using two-parameter Arrhenius expressions, and the curvature predicted is a good match to experimental results.

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