J. Phys. Chem. A **1999,** *103,* 2649−2654

Rate Constants for the Reactions of Hydroxyl Radical with Several Alkanes, Cycloalkanes, and Dimethyl Ether

W. B. DeMore* and K. D. Bayes

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109

Received: August 4, 1998; In Final Form: January 28, 1999

Relative rate experiments were used to measure ratios of rate constants as a function of temperature for the reactions of OH with propane, *n*-butane, *n*-pentane, *n*-hexane, cyclopropane, cyclobutane, cyclopentane, cyclohexane, and dimethyl ether. To assure internal consistency, ratios were measured for seventeen reactant pairs among these reactants. All of the derived rate constants are based on an absolute rate constant of the $OH + C_2H_6$ reaction using $k(\text{ethane}) = 1.0 \times 10^{-11} \exp(-1094/T)$ cm^3/molecule s. The rate constants obtained are as follows. propane: $1.29 \times 10^{-11} \exp(-730/T)$, $k(298\text{ K}) = 1.11 \times 10^{-12}$. *n*-butane: $1.68 \times 10^{-11} \exp(-584/T)$, $k(298\text{ K}) = 2.37 \times 10^{-12}$. *n*-pentane: $1.94 \times 10^{-11} \exp(-494/T)$, $k(298\text{ K}) = 3.70 \times 10^{-12}$. *n*-hexane: $2.60 \times 10^{-11} \exp(-480/T)$, $k(298\text{ K}) = 5.19 \times 10^{-12}$. cyclopropane: $5.15 \times 10^{-12} \exp(-1255/T)$, $k(298\text{ K}) = 7.64 \times 10^{-14}$. cyclobutane: $1.62 \times 10^{-11} \exp(-611/T)$, $k(298\text{ K}) = 2.08 \times 10^{-12}$. cyclopentane: $2.57 \times 10^{-11} \exp(-498/T)$, $k(298\text{ K}) = 4.83 \times 10^{-12}$. cyclohexane: $3.58 \times 10^{-11} \exp(-500/T)$, $k(298\text{ K}) = 6.69 \times 10^{-12}$. dimethyl ether: $1.51 \times 10^{-11} \exp(-496/T)$, $k(298\text{ K}) = 2.86 \times 10^{-12}$. These results are compared with previous literature data and are discussed in terms of trends in preexponential factors and activation energies. Also, rate constants and Arrhenius parameters are derived for methylene groups in the alkanes and cycloalkanes. In the low temperature regime, the present data illustrate a persistent discrepancy between absolute and relative rate measurements. The relative data show less curvature at low temperatures, and can be adequately fit with two-parameter Arrhenius expressions.

Introduction

Reactions of OH with simple alkanes and cycloalkanes are among the most important processes in chemical kinetics, especially for atmospheric and combustion chemistry. Recent publications suggest that rate constant data for these reactions are for the most part well-known.[11,26,19] Nevertheless, trends in parameters such as Arrhenius activation energies and preexponential factors are not well-established, and in a few cases, such as cyclopropane and cyclohexane, there are serious discrepancies in the literature reports for the rates.

In the present work we have conducted a number of temperature-dependent relative rate measurements among ethane, propane, *n*-butane, *n*-pentane, *n*-hexane, cyclopropane, cyclobutane, cyclopentane, and cyclohexane. The precision of this technique provides a clearer picture of the rate constant trends among these reactants and offers some improvement in the reliability of the rate constant data. Dimethyl ether was included because of its intrinsic importance and because it serves as a convenient reference reaction for intercomparison of the alkanes.

Methods

Relative Rate Measurements. The technique used in this work has been described in several recent publications.[8,17,16] The method involves measurement of the fractional loss of the reactant compound, compared to a reference compound, in the presence of OH. The OH radicals are produced by direct photolysis of H_2O at 185 nm, or, for those cases such as dimethyl ether which absorb at 185 nm, by 254 nm photolysis of O_3 ($(5-10) \times 10^{16}$ cm^{-3}) in the presence of water vapor ($(1-5) \times 10^{17}$ cm^{-3}). For experiments significantly below 273 K, the water vapor pressure is too low for the foregoing methods. In those experiments, we photolyzed a mixture of N_2O (4×10^{16} cm^{-3}) and H_2 (1.5×10^{18} cm^{-3}) at 185 nm.

$$N_2O + h\nu \rightarrow N_2 + O(^1D) \tag{1}$$

$$O(^1D) + H_2 \rightarrow OH + H \tag{2}$$

Under the low-temperature conditions, the $OH + H_2$ reaction is sufficiently slow so that some of the OH reacts with the added hydrocarbons (7×10^{14} cm^{-3}). For all measurements, small concentrations of O_2 were maintained to remove H-atoms and alkyl radicals.

Measurements were made using the stopped-flow method, for which the rate constant ratio is given by the equation,

$$k_{\text{reactant}}/k_{\text{reference}} = \ln(\text{DF})_{\text{reactant}}/\ln(\text{DF})_{\text{reference}} \tag{3}$$

where the quantity DF is the depletion factor, i.e., the ratio of initial concentration to final concentration. In the present experiments the concentration measurements were made with an SRI 8610 or HP 5890 gas chromatograph, using flame ionization detectors. Concentrations were measured by expanding the cell contents into a sample loop. Silica gel and Porapak Q columns were used for most of the measurements. At each temperature at which a rate constant ratio was measured, depletion factors were varied over a sufficient range to test for linearity in the plot of $\ln(\text{DF})_{\text{reactant}}$ vs $\ln(\text{DF})_{\text{reference}}$, to verify adherence to eq 3.

10.1021/jp983273d CCC: $18.00

Temperatures were determined using a platinum resistance thermometer traceable to a NIST calibration. All measurements were done at atmospheric pressure using argon as the carrier gas.

All the relative rate constants were placed on an absolute basis by reference to ethane, taking the Atkinson recommendation[2] for the rate constant (fitted to a two-parameter Arrhenius expression at 298 K):

$$k(\text{ethane}) = 1.00 \times 10^{-11} \exp(-1094/T) \text{ cm}^3/\text{molecule s} \quad (4)$$

This recommendation is in excellent agreement with the data of Talukdar et al.,[26] Donahue et al.,[11] and Clarke et al.[7] at temperatures above 230 K. To test for effects of non-Arrhenius behavior in the ethane data, we used a three-parameter expression, as suggested by Talukdar et al., which also fits the Donahue et al. and Clarke et al. data:

$$k(\text{ethane}) = 1.53 \times 10^{-17} \text{ T}^2 \exp(-512/T) \text{ cm}^3/\text{molecule s} \quad (5)$$

However, in the temperature range of the bulk of our experiments (230−400 K), the difference is not significant (3% or less).

The relative rate method is usually not sensitive to impurities, but in any case either research grade or minimum 99% pure chemicals were used except in the case of cyclobutane. Cyclobutane was prepared from cyclobutyl bromide (Sigma-Aldrich) via a Grignard reagent,[6] and the purity was not as high as the purities for the other reactants. For that reason special tests for impurity effects were made, as discussed in the Results section.

Results

Table 1 shows the results of the ratio measurements at different temperatures for the various reaction pairs. Rate constants calculated from these ratios are shown in Figures 1−9, which include data from other laboratories for comparison. Arrhenius fits to the data are given in Tables 2−4.

Propane. Figure 1. As shown in Figure 1 and in **Table 2**, our derived rate expression for propane is in excellent agreement with the absolute rate constants of Talukdar et al.,[26] Donahue et al.,[11] and Clarke et al.[7] At 298 K the agreement is within 3% or better. There are small differences in the Arrhenius parameters, which are related to the fact that at low temperatures the relative rate data show somewhat lower propane rate constants than the absolute measurements, as seen in Figure 1. This is true regardless of whether the linear (eq 4) or T^n expression (eq 5) is used for the reference ethane rate constant. Over the temperature range of this study (227−428 K), there is no significant deviation from linearity in the Arrhenius plot.

n-Butane. Figure 2. As in the propane case, the derived rate constant for *n*-butane is in excellent agreement (4% or better at 298 K) with both the Talukdar et al. and Donahue et al. data.

n-Pentane. (Figure 3). Pentane was measured relative to both propane and butane, and the results are in good agreement. Curiously, however, our results are about 8% lower than those of Donahue et al.[11] and Talukdar et al.,[26] which are in good agreement with each other. We note that our pentane-to-butane ratio measurement at 298 K, 1.57, is in excellent agreement with the Atkinson et al.[4] value at 299 K of 1.60. Our ratio data are also in good agreement with the results of Harris and Kerr.[15] Further, pentane was used along with propane and butane as a reference for hexane and cyclohexane, and the results showed no discrepancy when using our derived rate for pentane. It appears therefore that the absolute measurements for pentane are slightly high.

TABLE 1: Experimental Results for the Rate Constant Ratios

propane vs ethane		*n*-butane vs propane		*n*-pentane vs propane		*n*-pentane vs *n*-butane	
T(K)	ratio	*T*(K)	ratio	*T*(K)	ratio	*T*(K)	ratio
227	6.333	235	2.422	308	3.189	233	1.711
237	5.988	251	2.359	345	2.942	253	1.649
246	5.640	264	2.300			273	1.585
265	5.081	275	2.156			298	1.570
273	4.907	293	2.133			326	1.520
283	4.687	298	2.142			351	1.500
287	4.625	328	1.985			364	1.500
298	4.394	336	2.057				
323	4.079	358	1.950				
343	3.715	361	1.966				
349	3.722						
383	3.295						
428	2.965						

n-hexane vs propane		*n*-hexane vs *n*-butane		*n*-hexane vs *n*-pentane		cyclopropane vs ethane		cyclobutane vs propane	
T(K)	ratio	*T*(K)	ratio	*T*(K)	ratio	*T*(K)	ratio	*T*(K)	ratio
292	4.860	294	2.165	303	1.387	298	0.299	272	1.957
298	4.696	310	2.116			276	0.289	288	1.908
307	4.665	329	2.041			300	0.301	293	1.855
315	4.618	354	2.023			316	0.310	298	1.740
321	4.417	367	1.988			348	0.325	303	1.859
337	4.300					363	0.337	309	1.882
339	4.064					383	0.333	343	1.749
353	4.247					403	0.346	366	1.758
357	4.045					421	0.353		
366	4.236								

cyclopentane vs *n*-butane		cyclopentane vs *n*-hexane		cyclohexane vs propane		cyclohexane vs *n*-butane	
T(K)	ratio	*T*(K)	ratio	*T*(K)	ratio	*T*(K)	ratio
273	2.119	277	0.933	301	5.946	298	2.862
292	2.054	318	0.963	301	5.888	326	2.846
310	1.953	338	0.972			350	2.765
326	1.915	360	0.956			363	2.733
348	1.972						
354	1.913						
373	1.916						
398	1.910						
423	1.855						

cyclohexane vs *n*-pentane		dimethyl ether vs *n*-butane		dimethyl ether vs *n*-pentane		dimethyl ether vs cyclohexane	
T(K)	ratio	*T*(K)	ratio	*T*(K)	ratio	*T*(K)	ratio
298	1.798	263	1.250	295	0.811	306	0.4423
312	1.816	273	1.205	305	0.824	324	0.4331
338	1.786	293	1.180	318	0.754	351	0.4270
368	1.765	298	1.151	328	0.778	361	0.4350
		313	1.187	336	0.838		
		333	1.140	345	0.764		
		351	1.096	364	0.750		

***n*-Hexane. (Figure 4).** Hexane was measured relative to propane, butane, and pentane, and as seen in the figure the results are in good agreement with each other and with the absolute data of Donahue et al.[11]

Cyclopropane. (Figure 5). Cyclopropane was measured relative to ethane. The results are in fair agreement with the absolute data of Dobe et al.,[10] at high temperatures, but somewhat poorer agreement with data of Clarke et al.[7] and Jolly et al.[18]

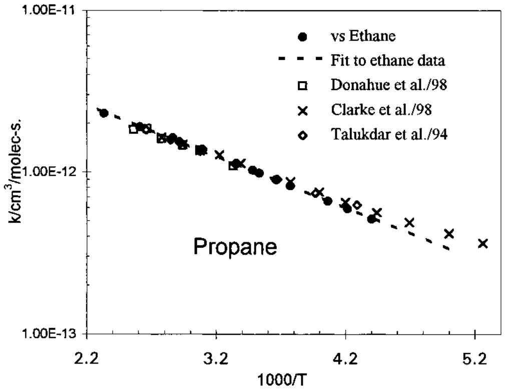

Figure 1. Rate constant data for propane.

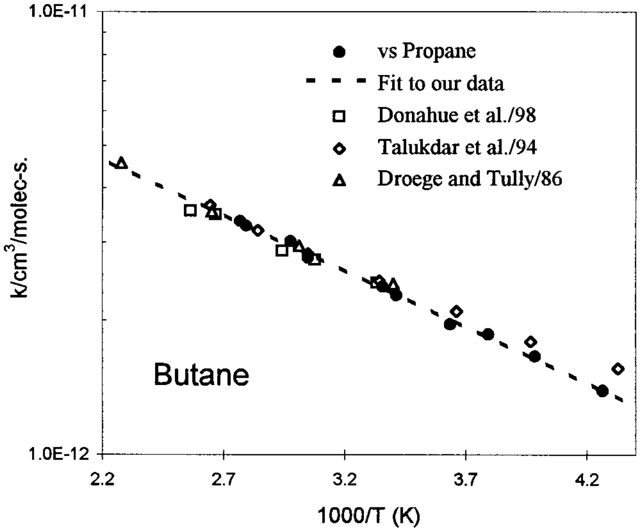

Figure 2. Rate constant data for *n*-butane.

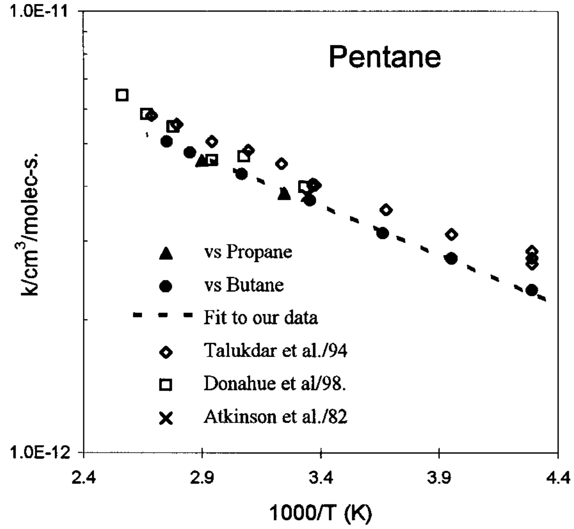

Figure 3. Rate constant data for *n*-pentane. The Atkinson et al./82 rate constant is from their relative rate measurement and is calculated from our *k*(butane).

Cyclobutane. ***(*****Figure 6).** Our rate constants are in fair agreement (about 20% higher) than those of Dobe et al.[10] We tested for possible complications due to impurities that might not be resolved in the GC analysis of the cyclobutane sample by conducting experiments at very large conversions and also by (in one case) simultaneous IR analysis of cyclobutane via its strong C−H band near 2985 cm^{-1}.[20] No evidence of significant impurity effects was found.

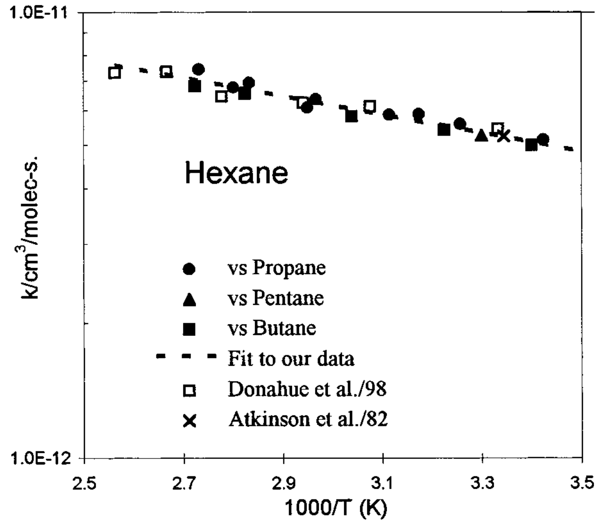

Figure 4. Rate constant data for *n*-hexane. The Atkinson et al./82 rate constant is from their relative rate measurement and is calculated from our *k*(propane).

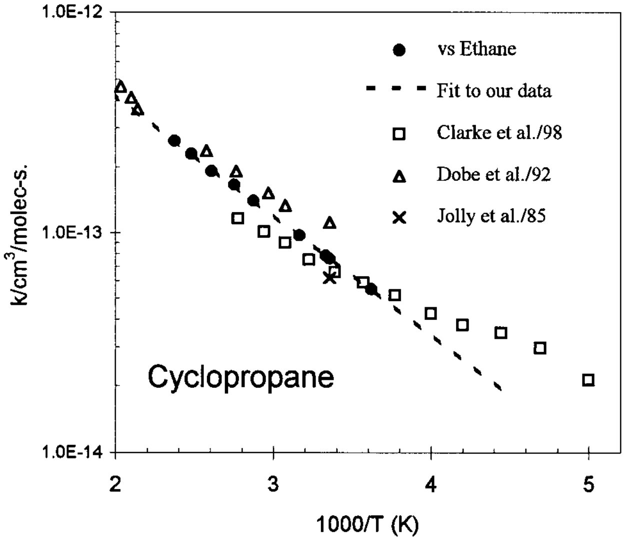

Figure 5. Rate constant data for cyclopropane.

Cyclopentane. (Figure 7). Cyclopentane was measured relative to butane and hexane, and the results are in excellent agreement with each other and with the absolute data of Droege and Tully[14] and Jolly et al.[18] A relative rate measurement by Atkinson et al.[5] at 299 K is in perfect agreement with our data. The absolute data of Donahue et al.[11] are slightly higher and show lower Arrhenius parameters (see Table 3).

Cyclohexane. (Figure 8). Cyclohexane was measured relative to propane, butane, and pentane, with excellent agreement among the results. Absolute data by Droege and Tully,[14] Saunders et al.,[24] and Donahue et al.[11] are in good agreement, although the absolute data tend to yield a slightly higher *k*(298 K) (about 7%). Relative rate data by Sommerlade et al.[25] vs hexane are in excellent agreement with our data.

Dimethyl Ether. (Figure 9). Our relative rate measurements vs butane, pentane, and cyclohexane are in good agreement (7% or better). Among the absolute data, our results agree best with Tully and Droege.[27] Absolute data of Mellouki et al.,[21] Wallington et al., [28] and Arif et al.[1] are in approximate agreement.

Discussion

Rate Constants for the Alkanes, Cycloalkanes, and Dimethyl ether. Our relative rate data, referenced ultimately to

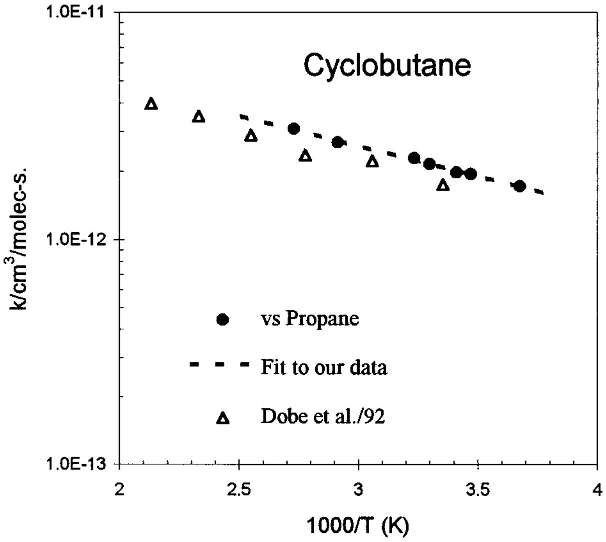

Figure 6. Rate constant data for cyclobutane.

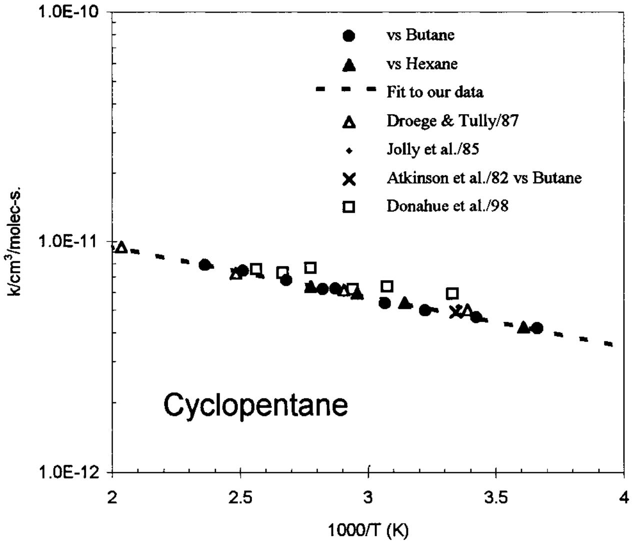

Figure 7. Rate constant data for cyclopentane.

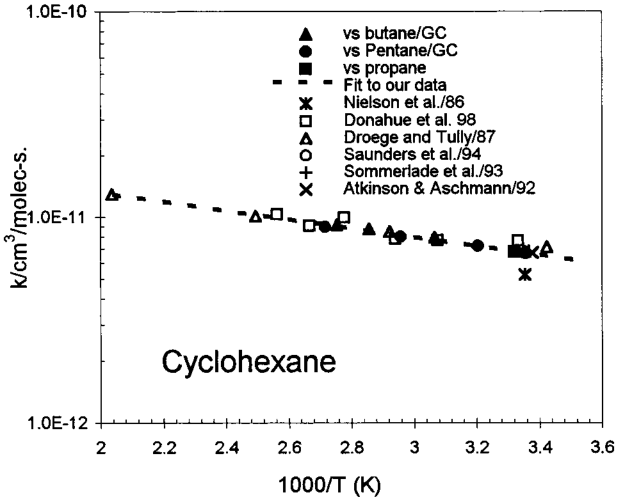

Figure 8. Rate constant data for cyclohexane.

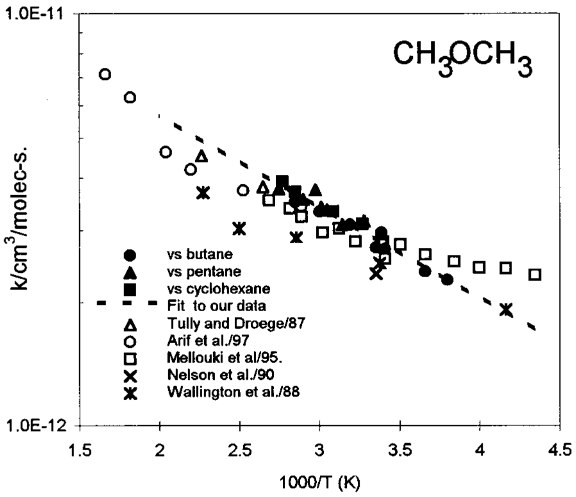

Figure 9. Rate constant data for dimethyl ether.

TABLE 2: Derived Rate Constants for Alkanes and Comparison with Recent Work[a]

compound	*A* factor[b]	*E*/*R*[c]	*k*(298 K)	ref
ethane	1.00×10^{-11}	1094	2.54×10^{-13}	Atkinson [2]
propane	$(1.29 \pm 0.03) \times 10^{-11}$	730 ± 6	1.11×10^{-12}	this work[d]
	1.03×10^{-11}	660	1.12×10^{-12}	Talukdar et al.[26]
	1.12×10^{-11}	693	1.09×10^{-12}	Donahue et al.[11]
	9.25×10^{-12}	624	1.14×10^{-12}	Clarke et al.[7]
	1.02×10^{-11}	657	1.12×10^{-12}	Atkinson[2]
n-butane	$(1.68 \pm 0.10) \times 10^{-11}$	584 ± 11	2.37×10^{-12}	this work[d]
	1.34×10^{-11}	503	2.48×10^{-12}	Talukdar et al.[26]
	1.34×10^{-11}	514	2.39×10^{-12}	Donahue et al.[11]
	1.11×10^{-11}	451	2.44×10^{-12}	Atkinson[2]
	1.59×10^{-11}	558	2.45×10^{-12}	Droege and Tully[13]
n-pentane	$(1.94 \pm 0.05) \times 10^{-11}$	494 ± 7	3.70×10^{-12}	this work[d]
	1.92×10^{-11}	454	4.18×10^{-12}	Talukdar et al.[26]
	2.97×10^{-11}	609	3.85×10^{-12}	Donahue et al.[11]
	1.60×10^{-11}	413	4.00×10^{-12}	Atkinson[2]
n-hexane	$(2.60 \pm 0.26) \times 10^{-11}$	480 ± 33	5.19×10^{-12}	this work[d]
	1.96×10^{-11}	384	5.40×10^{-12}	Donahue et al.[11]
	1.00×10^{-11}	182	5.43×10^{-12}	Atkinson[2]

[a] Arrhenius parameters shown for previous work are our fits to the authors' data. [b] Units are cm³/molecule s. [c] Units K. [d] Errors shown are standard deviations of the least-squares fit and do not reflect uncertainties in the reference rate constant.

ethane using the Atkinson recommendation, have proven to be in good agreement among themselves and with recent absolute data. Cross correlations among different reaction pairs tend to substantiate the accuracy of the data. The best agreement with absolute data was for propane, butane, hexane, cyclopentane, and cyclohexane. Poorest agreement was for pentane and cyclopropane. For dimethyl ether, the absolute data are in approximate agreement with our derived rate constant. We believe that all the rate constants reported here can be used with confidence with an uncertainty of about 5% at room temperature and with an uncertainty in the *E*/*R* values of the order of 100 K. The latter value comes mainly from uncertainty in the temperature dependence of the reference reaction, with some small additional uncertainty arising from error in the relative rate measurements.

Some trends in Arrhenius parameters for *n*-alkanes and cycloalkanes are evident in Tables 2 and 3. The *A* factors increase monotonically as the number of carbon atoms increases, and the *E*/*R* values decrease, approaching in both cases a value in the range of 450−500 K.

Reactivity of $-CH_2-$ Groups in *n*-Alkanes and Cycloalkanes. There are some significant trends in the rate behavior of methylene groups in the *n*-alkanes and also some striking similarities with methylene groups in the cycloalkanes. These effects can be seen by removing the contribution of the CH_3

TABLE 3: Derived Rate Constants for Cycloalkanes and Comparison with Recent Work

compound	A factor[a]	E/R[c]	k(298 K)	ref
cyclopropane	$(5.15 \pm 0.12) \times 10^{-12}$	1255 ± 8	7.64×10^{-14}	this work[c]
	8.11×10^{-13}	723	7.17×10^{-14}	Clarke et al.[7]
	3.96×10^{-12}	1089	1.02×10^{-13}	Dobe et al.[10]
cyclobutane	$(1.62 \pm 0.1) \times 10^{-11}$	611 ± 18	2.08×10^{-12}	this work[c]
	1.17×10^{-11}	561	1.77×10^{-12}	Dobe et al.[10]
cyclopentane	$(2.57 \pm 0.13) \times 10^{-11}$	498 ± 17	4.83×10^{-12}	this work[c]
	2.40×10^{-11}	460	5.13×10^{-12}	Droege and Tully[14]
	1.88×10^{-11}	352	5.77×10^{-12}	Donahue et al.[11]
			5.18×10^{-12}	Jolly et al.[18]
cyclohexane	$(3.58 \pm 0.29) \times 10^{-11}$	500 ± 26	6.69×10^{-12}	this work[c]
	2.83×10^{-11}	408	7.20×10^{-12}	Donahue et al.[11]
	2.98×10^{-11}	423	7.21×10^{-12}	Droege and Tully[14]
			6.8×10^{-12} [d]	Sommerlade et al.[25]
			6.7×10^{-12}	Saunders et al.[24]
	1.89×10^{-11}	287	7.21×10^{-12}	Atkinson[2]

[a] Units are cm^3/molecule s. [b] Units K. [c] Errors shown are standard deviations of the fit, and do not reflect uncertainties in the reference rate constant. [d] Relative to *n*-hexane, using our *k* from Table 3.

TABLE 4. Results for Dimethyl Ether and Comparison with Recent Work

A factor[a]	E/R[b]	k(298 K)	ref
$(1.51 \pm 0.15) \times 10^{-11}$	496 ± 31	2.86×10^{-12}	this work
7.1×10^{-12}	315	2.47×10^{-12}	Wallington et al.[28]
8.6×10^{-12}	318	2.95×10^{-12}	Arif et al.[1]
1.04×10^{-11}	373	2.98×10^{-12}	Tully and Droege[27]
		2.35×10^{-12}	Nelson et al.[22]
		2.86×10^{-12} [c]	Nelson et al.[22]

[a] Units are cm^3/molecule s. [b] Units K. [c] Relative to cyclohexane, using our *k* from Table 3.

TABLE 5: Contributions per Methylene Group to the Overall Rate Constant (298 K) and *A* Factor in *n*-Alkanes and the Effective Activation Temperature[a]

$(CH_2)_n$	k(298K) per CH_2 (cm^3/molecule s)	A factor per CH_2 group (cm^3/molecule s)	E/R (K)
$-CH_2-$	8.0×10^{-13}	5.63×10^{-12}	583
$-CH_2CH_2-$	9.9×10^{-13}	5.91×10^{-12}	531
$-CH_2CH_2CH_2-$	1.11×10^{-12}	5.20×10^{-12}	461
$-CH_2CH_2CH_2CH_2-$	1.21×10^{-12}	5.25×10^{-12}	437

[a] See text for method of calculation of these quantities.

groups from the *n*-alkane rates. To do this one can assume that the contribution is equal to the ethane rate, so that the net rate constant of the residual methylene groups would be given by

$$k(CH_2)_n = (k_{\text{alkane}} - k_{\text{ethane}}) \tag{6}$$

However, experiments by Droege and Tully[12,13] show enhanced reactivity for the methyl groups in propane and butane, compared to ethane. We therefore used their data from propane to make the correction in that molecule, and their butane data to make the correction for the remaining alkanes, butane, pentane, and hexane. (The results are not very sensitive to the choice of a correction for the methyl contributions, since in most of the alkanes the reaction is dominated by attack of OH at the methylene sites.) We then performed an Arrhenius plot of the net methylene rate constants over the temperature range of the present experiments to determine the methylene Arrhenius parameters. The resulting *A* factor and *E*/*R* values are shown in Table 5, from which several results may be noted. The *A* factors for all the methylene groups are nearly identical, whereas the *E*/*R* values decrease monotonically from propane to *n*-hexane. The rate constants increase in this order, due to the decreasing *E*/*R* values. As previously noted by Droege and Tully[12,13] and by Talukdar et al.,[26] the methylene environment changes only slightly as the chain length of the alkane increases. Our results for the methylene rate constants for propane and butane are nearly identical to those obtained by Droege and Tully, although our Arrhenius parameters are slightly lower.

TABLE 6: Contributions per Methylene Group to the Overall Rate Constant (298 K) and *A* Factor in Cycloalkanes, and the Overall Activation Temperature

compound	k per CH_2 group (cm^3/molecule s)	A factor per CH_2 group (cm^3/molecule s)	E/R (K)
cyclopropane	2.55×10^{-14}	1.72×10^{-12}	1255
cyclobutane	5.20×10^{-13}	4.05×10^{-12}	611
cyclopentane	9.66×10^{-13}	5.14×10^{-12}	498
cyclohexane	1.12×10^{-12}	5.97×10^{-12}	500

Table 6 shows the analogous methylene contributions in the cycloalkanes, and the rate constant per methylene group approaches essentially the same value as was seen in the alkane case, as the ring size increases. Similarly, the preexponential factors (per CH_2) and *E*/*R* values for the higher cycloalkanes are nearly the same as those for the alkanes. The diminished reactivity of methylene groups seen in cyclopropane, due to increased C−H bond energies in that molecule, is largely but not entirely gone in cyclobutane. The lower reactivity of cyclopropane is due in part to a lower preexponential factor, following the general dependence of *A* factors on rate constant that is observed in a large number of OH abstraction reactions.[9] According to our rate constant data, the *A* factor for cyclopropane is not anomalously low, and fits well with the general trends as discussed in ref 9. However, the data of Clarke et al.[7] correspond to an *A* factor which cannot be accommodated by this general behavior, and would require a different explanation, as put forward in their paper. This disagreement cannot be resolved until the disparity in data is removed.

Rate Constant Behavior at Low Temperatures. It is well-known that strictly Arrhenius behavior of rate constants is not expected over a wide range of temperature, especially high temperatures. Here we are concerned with temperatures between 430 and 230 K, where the situation is less clear. A reaction such as OH with propane should show some curvature, since there are two reactive sites with different temperature dependences. However, the degree of curvature to be expected is not known. Absolute measurements show noticeable curvature, and this is usually attributed to nonlinear Arrhenius behavior. However, the relative rate data do not reproduce the low-temperature curvature. This is seen in Figures 1 and 2 for propane and butane, respectively. The amount of curvature in our derived rate constants is of course based on the amount of curvature taken for the reference rate constant *k*(ethane). However, as stated previously (Methods section), the absolute data for ethane do not show significant curvature in the relevant temperature regime. The discrepancy is best illustrated by comparison of the actual ratio data, as taken in our experiments, vs that calculated from the absolute measurements. Figure 10 shows percent deviations of the individual ratio points from the least-squares line for our propane vs ethane Arrhenius fit, along with points from the absolute data of Talukdar et al.[26] and Clarke et al.[7] (To obtain absolute data at the same temperatures for propane and ethane, the propane data points were corrected to the temperatures of the ethane experiments using the authors' own temperature dependence. These were small extrapolations). Agreement between the relative and absolute measurements of the observed ratios is within about 5% above 270 K, but at

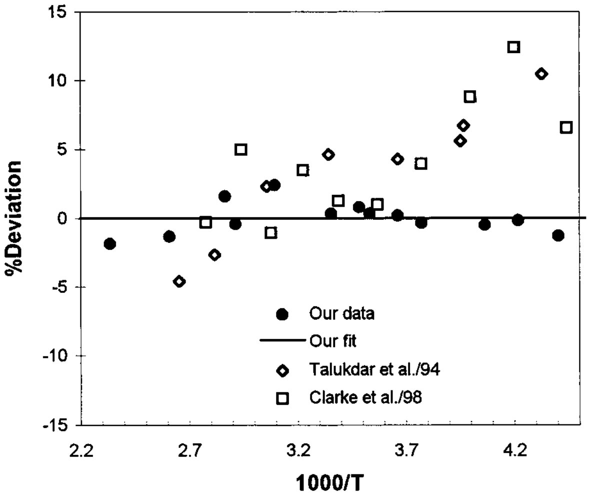

Figure 10. Deviations of the ratio k(propane)/k(ethane) from absolute measurements from the least-squares fit to the relative rate measurements: k(propane)/k(ethane) = 1.29 exp(364/T).

lower temperatures there is a clear divergence, with the absolute measurements giving larger ratios. Apparently some systematic error in either the absolute or the relative rate measurements increases as the temperature decreases. Since loss of OH by reaction with impurities and with radicals becomes more important as the temperature decreases, and interferes with the absolute measurements but not the relative measurements, we favor the simple Arrhenius expression derived from the relative data.

Acknowledgment. We have benefited greatly from frequent discussions with members of the JPL Kinetics and Photochemistry group. We are especially grateful to Dr. Robert Hampson of NIST for many comments and suggestions during the course of this work. A referee's comments were also very constructive. This research was carried out by the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration.

References and Notes

(1) Arif, M.; Dellinger, B.; Taylor, P. H. *J. Phys. Chem. A* **1997**, *101*, 2436−2441.

(2) Atkinson, R. *J. Phys. Chem. Ref. Data* **1997**, *26*, 215−290.

(3) Atkinson, R.; Aschmann, S. M. *Int. J. Chem. Kinet.* **1992**, *24*, 983.

(4) Atkinson, R.; Aschmann, S. M.; Carter, W. P. L.; Winer, A. M.; Pitts, J. N., Jr. *Int. J. Chem. Kinet.* **1982**, *14*, 781.

(5) Atkinson, R.; Aschmann, S. M.; Winer, A. M.; Pitts, J. N., Jr. *Int. J. Chem. Kinet.* **1982**, *14*, 507.

(6) Cason, J.; Way, R. L. *J. Org. Chem.* **1949**, *14*, 31.

(7) Clarke, J. S.; Kroll, J. H.; Donahue, N. M.; Anderson, J. G. *J. Phys. Chem. A* **1998**, *102*, 9847−9857.

(8) DeMore, W. B. *J. Phys. Chem.* **1996**, *100*, 5813−5820.

(9) DeMore, W. B.; Edmond W. Wilson, J. *J. Phys. Chem. A* **1999**, *103*, 573−576.

(10) Dobe, S.; Turanyi, T.; Ioganson, A. A.; Berces, T. *Int. J. Chem. Kinet.* **1992**, *24*, 191−198.

(11) Donahue, N. M.; Anderson, J. G.; Demerjian, K. L. *J. Phys. Chem. A* **1998**, *102*, 3121−3126.

(12) Droege, A. T.; Tully, F. P. *J. Phys. Chem.* **1986**, *90*, 1949−1954.

(13) Droege, A. T.; Tully, F. P. *J. Phys. Chem.* **1986**, *90*, 5937−5941.

(14) Droege, A. T.; Tully, F. P. *J. Phys. Chem.* **1987**, *91*, 1222−1225.

(15) Harris, S. J.; Kerr, J. A. *Int. J. Chem. Kinet.* **1988**, *20*, 939−955.

(16) Hsu, K. J.; DeMore, W. B. *J. Phys. Chem.* **1995**, *99*, 1235−1244.

(17) Hsu, K. J.; DeMore, W. B. *J. Phys. Chem.* **1995**, *99*, 11141−11146.

(18) Jolly, G. S.; Paraskevopoulos, G.; Singleton, D. L. *Int. J. Chem. Kinet.* **1985**, *17*, 1.

(19) Kramp, F.; Paulson, S. E. *J. Phys. Chem. A* **1998**, *102*, 2685−2690.

(20) Li, H.; Miller, C.; Philips, L. A. *J. Chem. Phys.* **1994**, *100*, 8590−8601.

(21) Mellouki, A.; Teton, S.; LeBras, G. *Int. J. Chem. Kinet.* **1995**, *27*, 791−805.

(22) Nelson, L.; Rattigan, O.; Neavyn, R.; Sidebottom, H.; Treacy, J.; Nielson, O. J. *Int. J. Chem. Kinet.* **1990**, *22*, 1111−1126.

(23) Nielsen, O. J.; Munk, J.; Pagsberg, P.; Silleson, A. *Chem. Phys. Lett.* **1986**, *128*, 168−171.

(24) Saunders: S. M.; Baulch, D. L.; Cooke, K. M.; Pilling, M. J.; Smurthwaite, P. I. *Int. J. Chem. Kinet.* **1994**, *26*, 113.

(25) Sommerlade, R.; Parlar, H.; Wrobel, D.; Kochs, P. *Environ. Sci. Technol.* **1993**, *27*, 113.

(26) Talukdar, R. K.; Mellouki, A.; Gierczak, T.; Barone, S.; Chiang, S.-Y.; Ravishankara, A. R. *Int. J. Chem. Kinet.* **1994**, *26*, 973−990.

(27) Tully, F. P.; Droege, A. T. *Int. J. Chem. Kinet.* **1987**, *19*, 251−259.

(28) Wallington, T. J.; Liu, R.; Dagaut, P.; Kurylo, M. J. *Int. J. Chem. Kinet.* **1988**, *20*, 41.