A Shock Tube Study of the Reaction of the Hydroxyl Radical with H_2, CH_4, $c\text{-}C_5H_{10}$, and $i\text{-}C_4H_{10}$

J. F. BOTT and N. COHEN

Aerophysics Laboratory, The Aerospace Corporation, P.O. Box 92957, Los Angeles, California 90009

Abstract

Reactions of the hydroxyl radical, OH, with several reactants have been studied near 1200 K in shock tube experiments in which UV absorption was used to monitor the OH concentration. The values of the rate coefficients were found to be 2.7×10^{12}, 2.6×10^{12}, 2.8×10^{13}, and 1.26×10^{13} cm^3/mol-s for the reactions of OH with hydrogen, methane, cyclopentane, and isobutane, respectively. These measured values are compared with previous experimental results and transition-state theory calculations.

Introduction

An important elementary reaction in any oxidation process, whether it be hydrocarbon combustion or photochemical smog, is often OH + fuel molecule. The hydroxyl radical plays an important role because it is the most reactive oxidizing species present and because its reactions lead directly to the formation of water, one of the final products. It is of particular importance in the lean mixtures [1] used to obtain efficient and nonpolluting combustion. An understanding of these reactions and their rate coefficients is necessary for predicting intermediate and final product species that will affect air pollution and combustion efficiencies.

A number of OH reactions with hydrocarbons have been studied between room temperature and 700 K, a convenient temperature range for heated flow tubes. Until a few years ago, it was customary to use two-parameter, Arrhenius expressions [2–4] ($k = A \exp(-B/T)$) to extrapolate these rate coefficients for OH + RH to the higher temperatures important in combustion. Indeed, data below 700 K do not provide strong justification for nonArrhenius expressions (i.e., $k = AT^n \exp(-B/T)$, for $n \neq 0$) for many of the OH + RH reactions. In some cases the data are limited to even narrower temperature ranges.

One of us [5] has calculated temperature-dependent rate coefficients for OH reacting with a number of alkanes using conventional transition-state theory (TST) and an experimental rate coefficient below 700 K. The calculations show pronounced curvature in the Arrhenius (i.e., ln k vs. $1/T$) plots. For OH + C_3H_8, for example, the calculated rate coefficient near 2000 K is an order of magnitude larger than predicted by a linear extrapolation based on data between 300 and 500 K. Although the calculations require experimental data to anchor them, they could eliminate the need for experimental data over the whole range of temperatures of interest if they could be proven accurate. Cohen[5] has proposed a model with rate coefficient parameters for primary, secondary, and tertiary hydrogen abstration abstraction by OH from alkanes. If those parameters can be verified for representative reactions of each type, then their credibility will be greatly increased. The object of the present study is to obtain data at combustion temperatures to validate the predictions so that the theoretical model can be used with confidence.

In our previous shock tube study [6], we reported results for the OH + propane reaction, in which the abstraction of both primary and secondary H atoms occur. The measured rate coefficients were found to agree with TST calculations within 5%. Two molecules, H_2 and CH_4, were chosen for the present study to validate the experimental technique because their rate coefficients are well-established near 1200 K [7]. The present results for OH + H_2 are, however, the first direct measurements of this rate coefficient above 1020 K. Cyclopentane, c-C_5H_{10}, was chosen to allow refinement of the theoretical treatment for secondary H abstraction. At the time of the study reported in ref. [5], there were no reacton rate data for OH + cycloalkanes for temperatures above 500 K, and H atom abstractions from linear and cyclic species were treated similarly. This simplification ignored the fact that cyclic compounds have ring deformation modes whose frequencies will be altered in the activated complex. (The treatment of ref. [5] did not take into account the effect of the OH adduct on internal rotations in the alkane; this would introduce another difference between H abstractions from linear carbons and from cyclic carbons because there are no internal rotations in cycloalkanes.)

Excluding such esoteric molecules as cubane, there are no alkanes with only tertiary H atoms. Isobutane, i-C_4H_{10}, has one tertiary and nine primary H atoms. Prior to the commencement of this study there were no accurate measurements of its reaction rate with OH radicals above 500 K. Since there were no other alkanes with tertiary H atoms for which the OH reaction rates had been studied above room temperature, we expected an accurate higher temperature measurement for OH with isobutane to be of great help in improving the semiempirical model for OH + tertiary H reactions.

We have performed the present experiments at temperatures near 1200 K; t-butyl hydroperoxide was chosen as the OH source because it dissociates rapidly at this temperature [8] and has proven easy to handle in existing equipment.

Experimental Procedure

The experiments were performed behind reflected shock waves in a 16.2-cm-diam stainless steel shock tube. The shock tube, gas-handling facility, and optical diagnostics have been described previously [6]. The OH concentration behind the reflected shock wave was followed by UV absorption using OH resonance radiation at 309 nm. The resonance radiation was produced by a microwave discharge through a mixture of helium and water vapor flowing at 70 torr. The optical configuration was unchanged from that of Ref. 6 except that for some of the runs, a 2-$k\Omega$ load resistor was used in the 1P28 photomultiplier, giving it a time response of 2 μs instead of 5 μs.

The OH concentration can be related to its UV absorption. However, because of the large spectral band width ($\Delta\lambda \cong 4.8$ nm) of the resonance lamp/monochromator, the OH absorption is not expected to obey the Beer-Lambert law but can be described approximately by

(1) $$\ln(I_0/I) = E_{\text{eff}}([\text{OH}] \times \ell)^{\nu}$$

where ℓ = optical path length and E_{eff} = effective extinction coefficient. E_{eff} and ν are functions of the gas temperature and pressure, the slit width, and the operating characteristics of the lamp. (Beer-Lambert's law results if $\nu \equiv 1$). A method of calibrating OH emission sources for the detection of OH has been described by Schott and Getzinger [9]: The OH absorption can be calculated for given temperature and pressure conditions from the measured spectral characteristics of the lamp. However, it has proven more practical to calibrate directly by shock-heating mixtures of H_2, O_2, and Ar and recording the absorption by OH, the concentration of which can be calculated for the partially equilibrated gas mixture [9,10,11]. In the previous study [6], we calibrated the lamp and detection system in this way and obtained a value of 0.91 $\pm$ 0.09 for ν in the temperature and pressure range of this study. Further details of the calibration are given in ref. [6]. The lamp was not recalibrated in this study; a value for E_{eff} is not needed in the data analysis.

The photomultiplier signal for each run was recorded with a Biomation 805 transient recorder, stored in a Nicolet 1072 signal averager, and then transferred to a DEC 11/23 computer for data reduction. The OH absorption profiles were fitted to exponential functions, and their exponential decay times were determined. For small levels of absorption, it can be shown that the exponential decay rate of the

OH concentration, $-d(\ln[\text{OH}])/dt$, is approximately equal to the OH absorption decay rate, $-d(\ln[I_0 - I])/dt$, divided by ν, the absorption parameter in eq. (1).

The temperatures and pressures behind the reflected shock waves were calculated from the incident shock speeds and the initial conditions. The estimated uncertainties in the incident shock speeds are approximately 0.3%. No boundary layer corrections were made since the exponential decay times were 120 μs or shorter.

The tube has an apparent leak rate of 2×10^{-5} torr/h after being pumped down to about 2×10^{-5} torr pressure with a 4-inch-diam diffusion pump backed up by a mechanical forepump. The gas mixtures were made manometrically in a 10-liter, Teflon-coated mix tank. The gases included t-butyl hydroperoxide (with impurities of 5% t-butyl alcohol and 5% water), argon (Matheson, ultra high purity, 99.999%), methane (Matheson, ultra high purity 99.97%), cyclopentane (Phillips, research grade, 99.99%), 10.14% hydrogen in argon (Matheson, analyzed gas mixture), and isobutane (Matheson, instrument grade, 99.5%).

The operating procedure included filling the evacuated shock tube with the test mixture to a pressure of 40 torr. The test mixtures contained 50 ppm of t-butyl hydroperoxide, which resulted in an initial OH absorption of about 12% behind the reflected shock wave. Some experiments were performed with 40 ppm t-butyl hydroperoxide at 50 torr initial pressure. The test gas was flowed through the tube and exhausted through the end wall until about 25 to 30% of the gas had been replaced. This procedure flushed out impurities pushed toward the end wall during the fill. Fresh gas replaced the slug of test gas at the end of the tube, from which some of the t-butyl hydroperoxide may have been lost to the wall. Reproducible levels of absorption were obtained with this procedure and no absorption was measured without the t-butyl hydroperoxide in the gas mixture.

Results

Experiments were performed in which gas mixtures were shock-heated to temperatures near 1200 K and pressures of 1.1 to 1.3 atm. The absorption records obtained with gas mixtures of argon and 50 ppm of t-butyl hydroperoxide could be fitted with a function having an exponential decay time of about 100 μs. About 12% absorption was obtained from the dissociation of the nominal concentration of 50 ppm (5.4×10^{-10} mols/cm^3) of t-butyl hydroperoxide. Shorter decay times were obtained when the reactant gases were added to the mixtures. The measured decay rates (i.e., the reciprocal decay times) are listed along with shock velocities, temperatures, density ratios, and total densities in Tables I–IV. The decay rates are plotted versus ad-

TABLE I. OH Reaction with hydrogen[a].

Run	Velocity mm/μs	T_5[b] K	ρ_5/ρ_1[c]	$[\rho_5] \times 10^5$ mol/cm^3	H$_2$ ppm	$[H_2] \times 10^8$ mol/cm^3	$(1/\tau) \times 10^{-4}$ 1/sec
168	0.719	1249	5.027	1.35	1963	2.66	7.06
169	0.709	1218	4.944	1.33	1963	2.62	6.90
170	0.703	1200	4.895	1.32	1963	0.59	6.84
171	0.706	1209	4.920	1.32	0	0.00	0.97
172	0.727	1274	5.093	1.27	0	0.00	0.87
173	0.657	1058	4.518	1.22	0	0.00	1.03
174	0.673	1107	4.647	1.25	0	0.00	0.73
175	0.673	1107	4.647	1.25	0	0.00	0.89
176	0.709	1218	4.944	1.06	1600	1.71	4.74
177	0.703	1200	4.895	1.05	1600	1.69	5.44
178	0.703	1200	4.895	1.05	1600	1.69	5.46
179	0.708	1215	4.936	1.06	1600	0.71	4.81
180	0.697	1181	4.845	1.04	800	0.84	2.99
181	0.706	1209	4.920	1.06	800	0.85	2.86
182	0.697	1181	4.845	1.04	800	0.84	3.05
183	0.713	1231	4.977	1.07	800	2.86	3.25
184	0.716	1240	5.002	1.08	2663	2.88	8.03
185	0.714	1234	4.986	1.07	2663	2.87	7.63
186	0.711	1225	4.961	1.07	2400	2.57	8.19
187	0.709	1218	4.944	1.06	2400	2.56	7.46
188	0.710	1222	4.953	1.07	2400	2.57	6.89
189	0.713	1231	4.977	1.07	2400	2.58	6.46

[a]P_1 = 50 torr and 40 ppm of t-butyl hydroperoxide for Runs #168–175; P_1 = 40 torr and 50 ppm of t-butyl hydroperoxide for Runs #176–189.

[b]T_5 = Temperature behind the reflected shock.

[c]ρ_1 = Initial density; ρ_5 = density behind reflected shock.

ditive concentrations in Figures 1–4. It should be noted that the decay rates listed in Tables I–IV and plotted in Figures 1–4 are the decay rates of the absorption signal and not the decay rates of the OH concentrations. The slopes of the decay rates divided by our calibration factor of $\nu = 0.91 \pm 0.09$ give the rate coefficients for the removal of OH by the additives. We have chosen to apply the calibration factor corrections to the slopes of the measured data instead of applying it to each individual decay rate.

The rate coefficients obtained for the additives are listed in Table V along with the average temperatures of the measurements and previously measured or calculated values. The temperatures of the

TABLE II.   OH reaction with methane.

Run	Velocity mm/μs	T_5 K	ρ_5/ρ_1	$[\rho_5] \times 10^5$ mol/cm³	CH_4 ppm	$[CH_4] \times 10^8$ mol/cm³	$(1/\tau) \times 10^{-4}$ 1/sec
154	0.714	1235	4.986	1.35	640	0.86	3.00
155	0.709	1220	4.944	1.34	640	0.85	3.01
156	0.718	1248	5.019	1.36	640	0.87	3.03
157	0.714	1235	4.986	1.35	640	0.86	3.03
159	0.714	1235	4.986	1.35	960	1.29	4.15
160	0.713	1232	4.977	1.34	960	1.29	3.82
161	0.711	1226	4.961	1.34	960	1.29	4.33
162	0.714	1235	4.986	1.35	960	1.29	3.94

P_1 = 50 torr, 40 ppm t-butyl hydroperoxide.

$OH - H_2$ measurements ranged between 1181 and 1231 K, with the average being 1212 K. Within the accuracy of the data, no dependence on temperature was discernible over this small range.

Several factors contribute to the total uncertainty in the rate coefficients. The scatter in the data shown in Figure 1 amounts to about 15%, somewhat more than the uncertainty in the determination of the exponential decay rate of an individual absorption profile. We have estimated an uncertainty of 10% in the value of ν, our calibration factor. Other sources of error include uncertainties in the concentration of the additive in the mixtures (2%), the initial pressure of 40.0 torr (1%), the shock-compressed density ratio (0.35%), the oscilloscope time sweep calibration (2%), and the approximate nature of the

TABLE III.   OH reaction with cyclopentane.

Run	Velocity mm/μs	T_5 K	ρ_5/ρ_1	$[\rho_5] \times 10^5$ mol/cm³	CP ppm	$[CP] \times 10^8$ mol/cm³	$(1/\tau) \times 10^4$ 1/sec
192	0.700	1192	4.870	1.05	247	0.260	7.44
193	0.700	1192	4.870	1.05	247	0.260	8.10
194	0.700	1192	4.870	1.05	247	0.260	8.87
195	0.700	1192	4.870	1.05	237	0.249	5.96
196	0.701	1195	4.878	1.05	237	0.250	7.64
197	0.703	1201	4.895	1.05	237	0.251	7.55
198	0.701	1195	4.878	1.05	237	0.250	6.47

CP = Cyclopentane, P_1 = 40 torr, and 50 ppm t-butyl hydroperoxide.

TABLE IV. OH reaction with isobutane.

Run	Velocity mm/μs	T_5 K	ρ_5/ρ_1	$[\rho_5] \times 10^5$ mol/cm^3	I-B ppm	$[I\text{-}B] \times 10^9$ mol/cm^3	$(1/\tau) \times 10^{-4}$ 1/sec
215	0.688	1155	4.771	1.03	207	2.13	3.63
216	0.683	1139	4.730	1.02	207	2.11	3.03
217	0.682	1136	4.722	1.02	207	2.11	3.07
218	0.684	1142	4.738	1.02	207	2.12	3.36
219	0.684	1142	4.738	1.02	283	2.90	4.27
220	0.687	1152	4.763	1.03	283	2.91	4.88
221	0.687	1152	4.763	1.03	283	2.91	4.57
223	0.686	1149	4.755	1.03	0	0.00	0.90
224	0.678	1124	4.689	1.01	0	0.00	0.88
226	0.687	1152	4.763	1.03	0	0.00	0.88
227	0.687	1152	4.763	1.029	263	2.71	3.80
228	0.688	1155	4.771	1.031	263	2.71	3.80
229	0.682	1136	4.722	1.020	263	2.68	3.80

P_1 = 40 torr, 50 ppm t-butyl hydroperoxide, I-B = isobutane.

expression relating absorption decay to concentration decay (4%). The 0.3% uncertainty in the velocity determination translates into a 6.5 K temperature uncertainty. Considering these sources of uncertainty, we estimate the total uncertainty in the rate coefficients to be about ±20% on the basis of the root-mean-square of the individual uncertainties, with an uncertainty of about ±15 K in the median temperatures. However, we make this claim knowing that history's judgement of experimental uncertainties is usually a good deal less optimistic than that of the authors.

Discussion

OH + H_2. The present results include the first direct measurement of the OH + H_2 rate coefficient above 1020 K [12]. Previous determinations of k_1 above 1020 K were deduced from systems where several reactions were occurring concurrently, and the value derived for the OH + H_2 rate coefficient depends on the values that were assigned to the rate coefficients of these concurrent reactions. The indirect nature of this kind of determination may account for the considerable scatter in the previous data above 1020 K.

Cohen and Westberg [7] reviewed the data for this reaction published prior to 1983 and recommended an expression for the rate coefficient, based on what were then considered the most reliable published measurements, of $k_1 = 6.3 \times 10^6\, T^2 \exp(-1490/T)$ cm^3/mol-s.
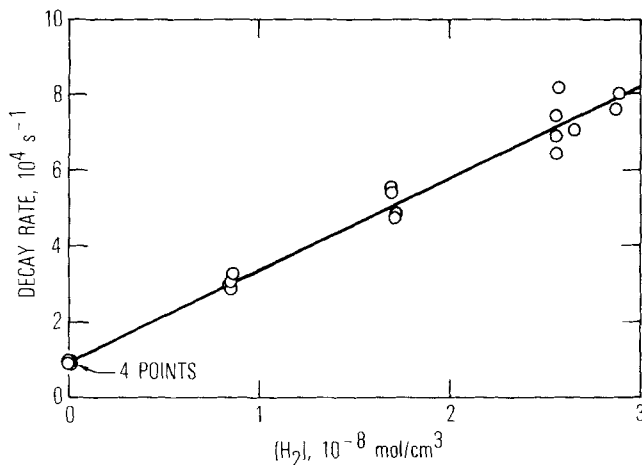
Figure 1.   Measured decay rates vs. hydrogen concentration.

Although their recommended rate coefficient expression is heavily weighted by the data below 1000 K, it yields a value for k_1 of 2.7 × 10^{12} at 1212 K, in excellent agreement with the value of (2.7 ± 0.5) × 10^{12} obtained in the present study. Since the review of ref. [7], two more studies have been reported. One, by Madronich and Felder [13], was a measurement of k_{-1}, the rate coefficient for the reverse reaction, $H + H_2O \rightarrow OH + H_2$, at 1160 to 1390 K. It yielded results in good agreement with the recommendation of ref. [7]. The other, by Bera and Hanrahan [14], was a pulse radiolysis-absorption spectroscopy experiment at room temperature. The data, which required computer modeling to permit extraction of rate coefficients, gave values
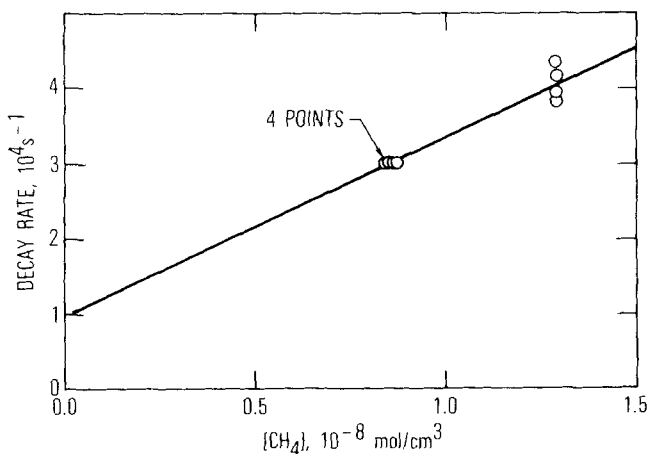
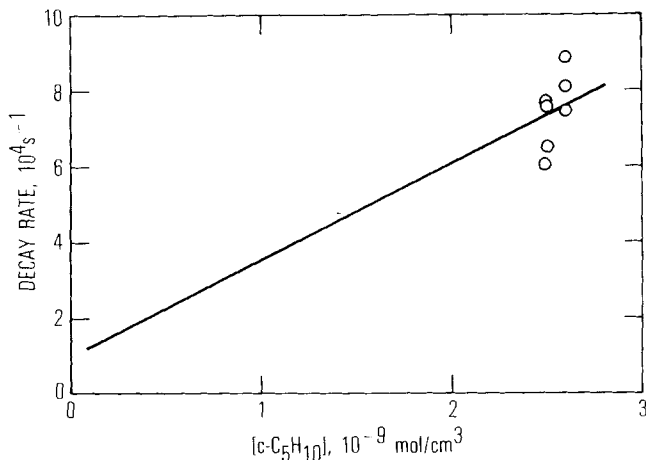Figure 2.   Measured decay rates vs. methane concentration.

Figure 3. Measured decay rates vs. cyclopentane concentration.

about 50% lower than most other, more direct, studies. We conclude that there is no reason at present to modify the recommended rate expression of Ref. 7.

OH + CH$_4$. Figure 5 shows the previous and present data for the OH + CH$_4$ reaction. After reviewing all the studies published through 1982, Cohen and Westberg [7] recommended the expression $k_2 = 1.90 \times 10^5 \, T^{2.4} \exp(-1060/T)$, based on a fit to selected data at high, intermediate, and low temperatures. The value of $(2.6 \pm 0.5) \times 10^{12}$ cm^3/mol-s obtained in the present study is greater than their recommended value of 2.1×10^{12} at 1234 K by a factor of 1.24. A least-squares fit to all the experimental data reviewed in ref. [7] gives a rate
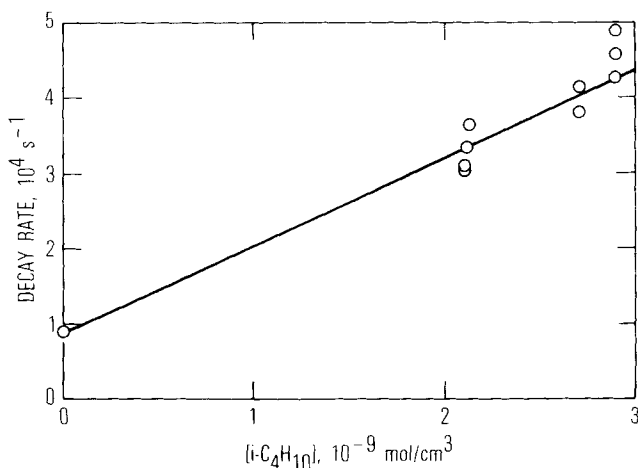

Figure 4. Measured decay rates vs. isobutane concentration.

TABLE V. Reaction rate coefficients for H-atom abstraction by OH.

Reactant	T, K	Present Study	Previous Work Calculated	Previous Work Measured
H_2	1212	2.7×10^{12}		2.7×10^{12}
CH_4	1234	2.6×10^{12}	2.7×10^{12} [b]	2.5×10^{12}
$c-C_5H_{10}$	1194	2.8×10^{13}	1.9×10^{13} [d]	
$i-C_4H_{10}$	1146	1.26×10^{13}	7.4×10^{12} [d]	

[a] Literature review of Ref. 7. All rate coefficients are in units of $cm^3/mol \cdot s$.
[b] Ref. 29.
[c] Present least squares fit to literature review of Ref. 7.
[d] Ref. 5.

coefficient expression $k_2 = 3.34 \times 10^6 \, T^{2.05} \exp(-1305/T)$, which has a value of 2.52×10^{12} at 1234 K and is within 3% of the present value. It is plotted as the solid curve in Figure 5.

Recently, Madronich and Felder [27] studied the OH + CH$_4$ reaction with a flash-photolysis/resonance-fluorescence technique in a high temperature reactor. Their measured rate coefficients, between 298 and 1512 K, could be fitted by $k_2 = 1.55 \times 10^7 \, T^{1.83} \exp(-1369/T)$ cm^3/mol·s. Their results agree with our least squares fit to all the data to
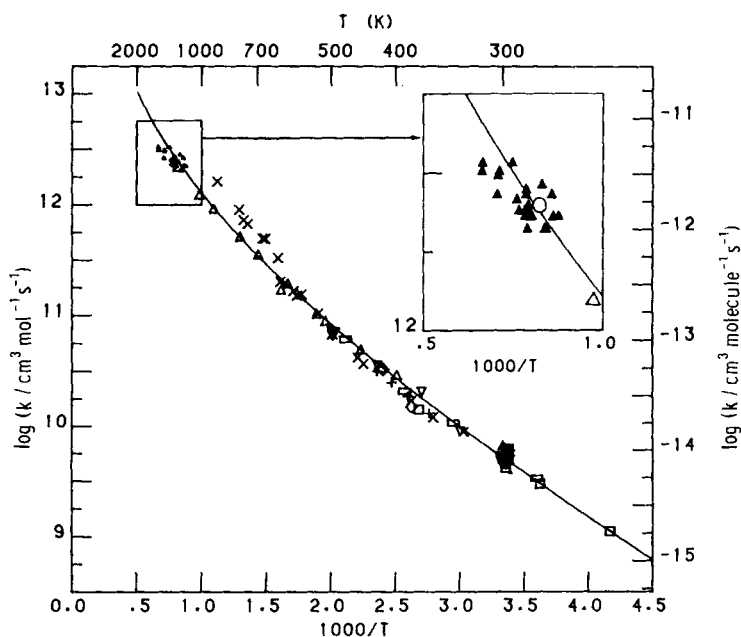

Figure 5. OH + Methane rate coefficients. Solid curve-least squares fit to the data. Experimental data: ▲-[15]; ▽-[16]; + -[17]; ☐-[18]; ●-[19]; ■-[20]; ▼-[21]; ×-[22]; △-[23]; ☐-[24]; ◇-[25]; ▲-[26]; and ○-present results.

within 1% at 400 K and 15% at 1500 K, and cannot be distinguished from the solid curve plotted in Figure 5. Their fitted rate coefficient expression yields a value of 2.3×10^{12} at 1234 K, which differs from the present value by only 13%.

Jonah, Mulac, and Zeblinski [28] measured k_2 over the temperature range of 340 to 1250 K using pulse radiolysis as an OH source. The disappearance of OH was monitored by absorption of resonance radiation from a microwave discharge through an H_2O-He mixture. They obtained $k_2 = 2.2 \times 10^{13} \exp(-2550/T)$, which gives a value at 1234 K of 2.8×10^{12}, also in good agreement with our result.

Cohen's previously reported[5] transition-state theory (TST) calculations of the OH + CH_4 rate coefficients give a value of 3.9×10^{12} at 1234 K. With a more recent calculation [29], designed to optimize agreement with experiments of ref. [27], he obtained values fitted by the expression $k_2 = 5.1 \times 10^8 \ T^{1.4} \exp(-1710/T)$, which agrees with the above least-squares expression within 20% over the temperature range of 298 to 2400 K. This expression yields a value of 2.7×10^{12} at 1234 K, in agreement with our result within the accuracies of the experiment. Thus, taking all the evidence, experimental and theoretical, into account, either the least squares fit, above, or the TST calculation of Ref. 29 provides an adequate representation of the best rate coefficient data at present.

OH + *c-C_5H_{10}*. There are four previous measurements for OH + *c-C_5H_{10}* near room temperature [30–33], the most recent two of which are in excellent agreement. After our experiments were completed, Droege and Tully [34] published the first temperature-dependent measurements. Over the range of 295 to 602 K, they fitted their data by $k_3 = 3.64 \times 10^8 \ T^{1.52} \exp(111/T)$ cm^3/mol-s, which extrapolates to 1.9×10^{13} at 1194 K. This compares to the value of 2.8×10^{13} cm^3/mol-s measured in the present study.

Cohen [5] used TST to extrapolate the room temperature rate coefficients to higher temperatures and obtained $k_3 = 4.8 \times 10^6 \ T^{2.1} \exp(430/T)$, which gives a value at 1194 K of 2.0×10^{13} cm^3/mol-s. This is in agreement with the extrapolation of Droege and Tully's results, but somewhat lower than our measured value of 2.8×10^{13}. His model for reactions of OH radicals with alkanes treated all secondary hydrogen atoms on alkanes as equivalent, regardless of whether the alkane is cyclic or acyclic. That model neglected two second-order complications: the effect of the OH adduct on the internal rotations of the acyclic alkane reagents, and its effect on the ring deformation vibrational frequencies of cyclic alkanes.

A revised TST model is being developed but awaits completion of more shock tube measurements for further refinement.

OH + *i-C_4H_{10}*. Cohen and Westberg [7] reviewed the experimental work (between 293 and 753 K) on this reaction through 1982 and rec-

ommended $k_4 = 2.6 \times 10^5 \, T^{2.4} \exp(590/T) \, cm^3/mol$-s. At 1146 K, this expression gives 9.6×10^{12}, approximately 25% smaller than our experimental value of 1.26×10^{13}. Since the completion of our experiments, three more studies have been published, two at room temperature [35,36] and one over the range 293 to 864 K [37]. In the latter study, the results were fitted by the expression, $k_4 = 2.59 \times 10^7 \, T^{1.8} \exp(175/T) \, cm^3/mol$-s, which extrapolates to a value at 1146 K of 9.7×10^{12}. Using TST, Cohen [5] calculated a value of 7.4×10^{12} at 1150 K. Both of these results are smaller than the present value of 1.26×10^{13} by factors of approximately 1.3 to 1.7.

Isobutane has one tertiary and nine primary H atoms whereas propane has two secondary and six primary H atoms. In our previous study [5] of the OH reaction with propane we obtained good agreement (within 5%) between the measured data and the TST calculations. The results of ref. [5] suggested that near 1200 K, 70% of the reaction of OH with propane represents attack on the primary H atoms, compared to 83% in the case of isobutane. (Other empirical correlation schemes suggest slightly smaller contributions from the tertiary H atom in isobutane [38,39].) If the assumption is valid that all the primary, secondary, or tertiary H atoms can be treated as kinetically equivalent (an assumption that has been questioned [40], particularly as the size of the alkane increases), then in order to obtain agreement between these isobutane experiments and theory without upsetting the agreement for propane, it would be necessary to increase the rate of attack of OH on the tertiary H atoms.

However, k_4 (1200) is not very sensitive to the value of tertiary attack at 298 K, $k_t(298)$: according to the present model, an increase in $k_4(1200)$ of a factor of 1.25 by increasing the contribution from tertiary attack would require an increase in $k_t(298)$ of a factor of nearly 40 provided that other parameters remained the same. Therefore, it would seem that the other parameters of the model, in particular, the assumed vibrational frequencies in the activated complex for the tertiary H abstraction path, may be in need of adjustment.

We plan to obtain a high-temperature measurement of 2,3-dimethylbutane, which has two tertiary H atoms, to check for the consistency of this conclusion, the theoretical implications of which are currently being examined. In the meantime, the recommendation of Cohen and Westberg [7] agrees with our data as well as those of Tully et al. [35] within 25% and provides an adequate overall representation of all the experimental data.

The very pronounced curvature in the temperature dependence of the OH reactions mandates combustion-temperature verification of theoretical or extrapolated rate coefficients. Traditional Arrhenius fits to the low temperature data would underpredict the rate coefficients at combustion temperatures. Comparisons of experimental

data and calculated values at high temperatures are good tests of theoretical calculations because the transition-state calculations are less sensitive at elevated temperatures to the choice of the room temperature rate coefficient used to anchor them.

The present transition-state-theory calculations predict curvature of the Arrhenius plots (log k vs. $1/T$) of the rate coefficients, but still underpredict the values as compared to the present experiments for isobutane and cyclopentane. We are inclined to believe that this discrepancy can be remedied by modifying the assumed properties of the transition state, and in particular by adjusting the assumptions regarding relative contributions of primary vs. secondary or tertiary H abstraction in molecules containing more than one kind of H atom. We would thereby improve the predictive powers of the method for other, as yet unmeasured hydrocarbons. However, we are awaiting the completion of shock tube experiments on other molecules before completing the revisions in the calculations.

The excellent agreement of the present results for the OH + H_2 and OH + CH_4 reactions with the extrapolated values of the data below 1050 K gives us confidence in the technique of using t-butyl hydroperoxide as a source of OH radicals. We shall extend these studies to other hydrocarbons in the near future.

Acknowledgment

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