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A SHOCK TUBE STUDY OF THE REACTIONS OF THE HYDROXYL RADICAL WITH COMBUSTION SPECIES AND POLLUTANTS

Final Report

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ABSTRACT

Shock heating t-butyl hydroperoxide behind a reflected shock wave has proved to be as a convenient source of hydroxyl radicals at temperatures near 1000 K. We applied this technique to the measurement of reaction rate coefficients of OH with several species of interest in combustion chemistry, and developed a thermochemical kinetics/transition state theory (TK-TST) model for predicting the temperature dependence of OH rate coefficients.

I. INTRODUCTION: PROJECT OVERVIEW

The reactions of OH radicals with hydrocarbons have received a great deal of attention in recent years because of these processes are principal steps in the oxidation of organic fuels--whether occurring in combustion/propulsion systems, in the atmosphere, or elsewhere. Of the various radicals capable of attacking hydrocarbons, OH radicals are generally the most reactive. In the atmosphere, the combined effects of the OH radical's reactivity and concentration make it the single species that determines the atmospheric lifetime of an organic substance. In many combustion systems, the OH radical plays a similar rate-determining role in the kinetics of fuel oxidation.

The principal goals of the kineticist in the field of oxidation chemistry are (1) to measure as many elementary reaction rate coefficients as are conveniently studied in the laboratory; and (2) to develop theoretical and/or semiempirical tools for extrapolating from measured rate coefficients to unmeasured ones. The latter step is necessary because of the sheer number of reactions of possible interest. *Ab initio* theoretical studies provide the most refined nonexperimental procedures for the completion of part (2) of the above program, but again, the large number of reactions (and the considerable cost of computer time) renders impractical detailed theoretical evaluation of every one. To this end, Benson and coworkers[1] developed the procedures of the thermochemical kinetics (TK) approach to transition state theory (TST): a collection of recipes and simple techniques for predicting reaction rate coefficients with reasonable accuracy. The method is most reliable when used simply to extrapolate rate coefficients from one temperature range to other temperatures, but a single temperature measurement can provide the basis for extrapolation. The procedure is further sharpened when applied to a family of homologous reactions for which a set of experimental measurements places more stringent constraints on the structural parameters of the activated complex that are required for the calculations. (It is assumed that the activated complexes for a homologous series of reactions are very similar to one another.) Studies of OH radicals with a series of alkanes have provided a wealth of experimental data that constitute an ideal test case for the application of thermochemical kinetics to predicting reaction rate coefficients.

To extend the semi-empirical techniques of Benson and coworkers, and to extend the database of reliable high temperature measurements of OH radicals with hydrocarbons and other fuels and their decomposition products, we undertook, with DOE support, a research program with both experimental and computational tasks. The experimental goal was to design a procedure for measuring, at combustion temperatures, the reaction rate coefficients of OH radicals with fuels and other species of importance in combustion or propulsion systems. The computational effort was intended to refine the semi-empirical thermochemical kinetics/ transition-state-theory (TK-TST) procedures for extrapolating rate coefficients of reactions of OH with combustion species of interest, for predicting rate coefficients for species not studied in the laboratory, and to examine the ability of the theory to predict rate coefficients for different pathways in cases where the reagent possessed nonequivalent H atoms.

These scientific goals can contribute to DOE's broad mission to improve the efficiency of combustion processes while minimizing undesirable effects such as production of pollutants. Both aims require a detailed knowledge of the mechanisms of the combustion processes and the kinetics of each individual step. As noted above, OH radicals are a key species in oxidation and combustion of any fuel (or other molecule) containing abstractable H atoms--which includes all but the most exotic fuels. A series of measurements for a carefully selected array of species can provide the basis for a semi-empirical formulation to estimate rates for any arbitrary molecule of interest--information that engineers, scientists, and other modelers will need in studying combustion problems, predicting fuel efficiency, or minimizing undesired pollutant products.

This project complemented, without duplicating, several other DoE-funded research programs. F. P. Tully (Sandia National Laboratories, Combustion Research Facility) has been measuring OH reactions with alcohols and chlorinated hydrocarbons at temperatures below 700 K. R. K. Hanson and C. T. Bowman (Stanford University) have been developing new experimental techniques to couple with shock tube kinetics studies. W. Tsang and J. T. Herron (National Institute of Standards and Technology) have been compiling an evaluated kinetics database for combustion chemistry; they rely on experimental studies such as ours. Similarly, C. K. Westbrook and W. J. Pitz (Lawrence Livermore National Laboratory) have pioneered in developing complex, detailed kinetic models for pyrolysis and oxidation of a variety of practical hydrocarbon fuels. They depend on experimentally measured data wherever available.

The work on the hydrocarbons provided the incentive for revising an earlier model[2] used to carry out thermochemical kinetics/transition state theory (TK-TST) calculations for the reaction rate coefficients of OH with alkanes. In a careful review of the application of TK-TST to OH + alkane reactions we concluded that there are good theoretical reasons for expecting different primary, secondary, or tertiary H atoms (distinguished on the basis of number of nearest neighboring C atoms) to have different rate parameters.[3]

In order to obtain the maximum benefit from experimental data and the TK-TST calculations, it is necessary to know equilibrium constants for the abstraction reactions. An extensive examination of methods for the estimation of enthalpies, entropies, and heat capacities for alkanes and alkyl radicals resulted in two publications.[4,5]

II. EXPERIMENTAL PROCEDURE

The experiments were performed in our shock tube facility. The stainless steel shock tube has a 10-m-long, 16.2-cm-diam test section with a 3-m-long, 7.5-cm-diam driver section. The shock tube, the gas-handling equipment, and the optical configuration as originally configured were described in detail by Bott and Cohen[9]. During 1993 an extensive renovation of the shock tube facility was undertaken. This was prompted by the irreproducibility of recent calibration runs and the fact that the shock tube had not been completely cleaned in several years. In addition to the physical disassembly and part-by-part manual cleaning of the 30-foot shock tube, the mechanical pumps and diffusion pumps have been refurbished and new oil baffles installed to protect the shock tube itself from any exposure to pump oil or other contaminants. The old gas handling system was completely replaced using new components. All mechanical pressure gauges were replaced with capacitance manometers (Baratron 0-10 torr, 0-100 torr, 0-1000 torrr, and 0-5000 torr) so that more accurate mixtures and pressure measurements could be made. The antiquated system used to measure shock front velocities was rebuilt replacing analog recording equipment (heat transfer gauges, raster generator, and oscilloscopes) with digital. The outputs of Endevco model 8530C-50 high speed piezoresitive pressure transducers were amplified and processed using three HP54201A digitizing oscilloscopes. Shock velocities accurate to better than $\pm 0.3\%$ can be obtained from the digitized data. Calibration experiments were carried out to establish new system characteristics--in particular, the exponent ν defined in eq. (1) below. Details of the rebuilt system were reported by Koffend and Cohen.[10]

In most of the experiments OH resonance radiation in the (A - X) system was obtained from a microwave-powered discharge through a mixture of helium and water vapor flowing at 70 torr through 12 mm-external-diam quartz tubing fitted with a quartz window. Flow rates of dry helium and wet helium were adjusted to maximize the output intensity. The high intensity and stability of the lamp enabled us to measure decay rates of OH at initial concentrations of 5×10^{-10} mol cm^{-3} (with a nominal 40 ppm TBH at 1200 K and 1.25 atm), for which the absorption is 12%. In the rebuilt system [OH] was detected using a frequency doubled Coherent Radiation 699-21 ring dye laser. Rhodamine 640 dye was used and frequency-doubled intracavity to obtain single mode laser radiation in the region of the OH A 2S+ - X 2P transition near 310 nm. The $^{Q}Q_{11}(4.5)$ in line of the A-X system was probed since the $J'' = 4.5$ level has the highest population at the shock tube temperatures near 1100 K. Part of the laser beam was split with a quartz flat and passed through a Bunsen burner flame in order to use the OH in the flame to tune the laser frequency to the OH transition. The beam intensity was detected with a 1P28 photomultiplier and minimum transmitted laser intensity indicated when line center was reached. Another portion of the laser beam was sent through the shock tube to detect OH behind the reflected shock wave. Since the laser was operated in a different room than the shock tube facility, a 120-foot-long quartz fiber optic was used to carry the laser radiation into the room containing the shock tube. The laser intensity was monitored with a Thorn EMI 9789QA photomultiplier tube. The time response of the PMT was determined to be 2 μsec when terminated with a 2000W resistor. The PMT output was recorded with an HP54201A digitizing oscilloscope.

The HP54201A was controlled using LABVIEW 3.1 data acquisition software installed on a Mac IIfx computer. Since this electronic transition is discrete and strong (t_{rad} = 700 nsec), peak absorption cross sections are extremely large, making this method of OH detection much more sensitive than OH resonance absorption using a microwave discharge.

Gas mixtures containing a concentration of 40 ppm of TBH are used. They are prepared by injecting the reagent substrate to be studied into a Teflon-coated mix tank containing 1.2 torr of TBH. The resulting mixture is diluted with argon through a supersonic injection sting to insure rapid, thorough mixing. A fraction of the mixture is diluted further to the required concentration. The gases include TBH (with impurities of 5% t-butyl alcohol and 5% water) and argon (Matheson UHP, 99.999%).

The operating procedure begins by filling the evacuated shock tube with the test gas to a pressure of typically 50 torr. The gas is allowed to remain in the tube for 10 minutes, after which the tube is again evacuated to a pressure less than 0.04 torr. The test section is then filled with fresh test gas to 50 torr and a shock wave is generated. The time interval between the final filling and shock wave production is kept as short as possible, on the order of 1-2 minutes. This procedure helps flush out impurities and tends to passivate the shock tube wall with the experimental mixture. Reproducible levels of absorption are obtained with this procedure, and no absorption is measured without the TBH in the gas mixture.

At our typical shock speeds of 0.65 mm/μsec in Ar, our $\pm 0.3\%$ uncertainty in the velocity leads to a possible uncertainty of 6 K in the temperature. Since the rate constants of OH for these types of reactions vary approximately as T_2, this temperature error results in about a 5% uncertainty in the rate coefficients. The velocity uncertainty also results in about a 1% uncertainty in the density and thus to the rate constants. Because of small estimated deviations from ideal due to boundary layer effects, we place a ± 16 K temperature uncertainty upon the data reported here.

III. CHEMISTRY BEHIND THE SHOCK WAVE AND OH CALIBRATION

t-butyl hydroperoxide (TBH) dissociates rapidly at our temperatures (near 1200 K) to produce t-butoxy and OH radicals:

$$(CH_3)_3COOH \rightarrow (CH_3)_3CO\cdot + OH \qquad k_a = 6.6 \times 10^7 \text{ sec}^{-1}$$

the t-butoxy radicals in turn very rapidly dissociate to give CH_3 radicals and acetone:

$$(CH_3)_3CO\cdot \rightarrow \cdot CH_3 + CH_3COCH_3 \qquad k_b \approx 3 \times 10^{10} \text{ sec}^{-1}$$

The acetone then decomposes--but, unfortunately, not very fast on our time scale--to give $\cdot CH_3$ and $CH_3CO\cdot$ radicals:

$$CH_3COCH_3 \rightarrow CH_3CO\cdot + \cdot CH_3 \qquad k_c = 40 \text{ sec}^{-1}$$

And the $CH_3CO\cdot$ radicals will rapidly fall apart to give $\cdot CH_3$ and CO:

$$CH_3CO\cdot \rightarrow \cdot CH_3 + CO \qquad k_d \approx 4 \times 10^{10} \text{ sec}^{-1}$$

The net result of these four reactions is:

$$(CH_3)_3COOH \rightarrow \cdot OH + 3\ \cdot CH_3 + CO$$

If the third reaction were sufficiently fast, then the analysis of the measurements would be considerably simplified, because we would then be looking at an instantaneously produced concentration of OH radicals, CH_3 radicals, and CO. The fact that this is not so forces us to model [OH] as a function of time and deduce reaction rates of the OH with added substrates by computer modeling.

The OH radical then undergo several reactions in the absence of any other reagents, and have a characteristic half-life. When another reagent with an abstractable H atom is present, it too can react with the OH. From the disappearance rate of OH as a function of the added reagent RH concentration, the reaction rate coefficient for the process, OH + RH → products, is calculated.

The OH concentration can be related to its uv absorption. However, because of the large spectral band width (Δlambda = 4.8 nm) of the detected emission, the OH absorption is not expected to obey Beer-Lambert's law, but can be described approximately by

$$\ln(I_0/I) = e_{eff}\,([OH] \times l)^{v} \qquad (1)$$

where I is the light signal seen by a detector, l = optical path length and e_{eff} = effective extinction coefficient. e_{eff} and v are functions of the gas temperature and pressure, the slit width, and the operating characteristics of the lamp.

The difficulty of calibrating UV sources for detection of OH is treated in earlier references.[11,12,13,14] The absorption due to the OH can be determined from the spectral characteristics of the lamp for a given set of experimental conditions.[15] Previously, our OH detection system was calibrated using shock-heated mixtures of O_2, H_2, and Ar. However, the mixtures must be heated to about 1900 K in order to obtain any significant amount of OH. When we originally did this, we obtained a value of 0.91 for the parameter v. Bradley *et al.* found $v = 0.58$, while Ernst, Wagner, and Zellner[13] found $v = 0.74$ for temperatures between 1200 and 2000 K. Our lamp is similar to that of Ernst *et al.*, except that they used argon instead of helium as the carrier gas and operated at 1 torr instead of 70 torr. Details of our calibration procedure were given by Bott and Cohen.[9] When we repeated the calibration procedure after rebuilding the shock facility we obtained considerably smaller values for v (variously 0.53 and 0.36, depending inexplicably on unknown conditions). Hence, we decided to calibrate our detection system by recording OH absorption signals from shock heated t-BuOOH/Ar mixtures so that the calibration temperature is the same as the temperature under which we studied the OH + RH reactions. The calibration data for this work are shown in Fig. 1. We obtained a value of $v = 0.91$ from this graph. Also displayed in Fig. 1. are the results of shock heating an $H_2/O_2/Ar$ mixture to 1900 K, which yielded $v = 0.36$.

If OH is removed by reaction with reagent RH, the rate law for its disappearance is

$$d[OH]/dt = -k[OH][RH], \tag{2}$$

or

$$\ln([OH]_t/[OH]_o) = -k[RH]t \tag{3}$$

or

$$[OH]_t/[OH]_o = \exp(-k[RH]t) \tag{4}$$

From eq (1),

$$\ln[OH]_t = (1/v)\ \ln[\ln(1-I_t/I_i)] - C \tag{5}$$

where I_i and I_t are the transmitted light with no OH present (*i.e.,* the incident beam) and at time t after generation of the OH, respectively; C is a constant that depends on l, v, and e.

From the last equation,

$$\ln([OH]_t/[OH]_o) = \{\ln[\ln(I_i/I_t)] - \ln[\ln(I_i/I_o)]\}/v \tag{6}$$

Hence, it is not necessary to know the absolute OH concentrations to deduce the rate coefficient for the OH + RH reaction; a plot of the right hand side of eq (6) *vs.* t gives k[RH]. The decay rates are measured for different concentrations of the reagent RH being studied, and the rate coefficient for OH removal is determined from the slope of the decay rate plotted *vs.* [RH]. However, the calibration data are needed to confirm that the dependence of the absorption on [OH] can be described by Eq. 1 and to establish the value of v. For small levels of absorption, it can be shown that the exponential decay rate of [OH] is approximately equal to the exponential decay rate of the OH absorption divided by v, the absorption parameter of Eq. 1.

The computed [OH] profiles in the presence of an added reactant, say, propane, could be described accurately with an exponential removal rate. However, in addition to the reaction of OH with the propane itself, other chemical reactions remove some OH. These include reactions with OH itself; with CH_3, CO, and CH_3COCH_3, all formed by the decomposition of the TBH; and with C_2H_6 and C_2H_4, both formed by subsequent reactions of the CH_3 radicals. At initial times, the reaction with CH_3 is the fastest removal process. In order to determine the relationship of the empirical OH removal rate to the rate coefficient of the reaction with the principal reagent (in this case, propane), computer calculations were carried out with NEST, a chemical kinetics code, using the experimental conditions of the study. Literature values were used for rate coefficient where possible, and best estimates were used for the others. The calculated exponential decay rates of [OH] were plotted *vs.*

[RH], and fell along a straight line with a slope within a few percent of the input value for the rate coefficient of the OH + propane reaction. This result justified the method of deducing the rate coefficient from the slope of the measured decay rates plotted *vs.* RH concentrations. In some of the other cases studied previously, there was the possibility of the OH reacting with other decomposition products of the reagent being studied if the latter underwent substantial thermal decomposition. To guard against misinterpretation of the experimental data, computer simulations were carried out wherever appropriate.

Several factors contribute to the total uncertainty in the rate coefficient determination. The scatter in measured rate coefficients is typically about 10%, slightly more than the uncertainty in the determination of the exponential decay rate of an individual absorption profile. Our calibration factor, ν, has a 10% uncertainty. Other sources of error include uncertainties in the concentration of the RH reagent in the mixtures (2%), the initial pressure (1%), the shock-compressed density ratio (0.35%), the oscilloscope time-sweep calibration (2%), and the approximate nature of relating absorption decay to concentration decay (4%). The 0.3% uncertainty in the shock velocity determination translates into a 6.5 K temperature uncertainty. Considering these sources of uncertainty, we calculate the total RMS uncertainty in the rate coefficients to be about 15%, and the uncertainty in the temperature to be about 15 K.

IV. RESULTS

During the course of this contract, we completed[9,10,16,17,18] shock tube measurements of reactions of OH radicals with 30 species of interest in combustion or pollution chemistry. The results, all near 1000 K and 1 atm, are summarized in Table I. The last column of the table lists the reference for those results that have already been published.

Table 1. Rate Coefficients Measured for OH Reactions

Reactant	Method (OH detection)	Temp. (K)	Rate Coeff. (10^9 L/mol-s)	Reference
CH_3	Resonance lamp	1200	11	17
H_2	Resonance lamp	1212	2.7	16
CH_4	Resonance lamp	1234	2.6	16
C_2H_6	Resonance lamp	1200	5.3	17
	Resonance lamp	970	5.0	10
C_3H_8	Resonance lamp	1220	15.8	9
C_6H_{14}	Resonance lamp	962	13.1	10
C_7H_{16}	Resonance lamp	1186	20.1	10
C_8H_{18}	Resonance lamp	1078	26.6	10
C_9H_{20}	Resonance lamp	1097	27.4	10
$C_{10}H_{22}$	Resonance lamp	1109	34.0	10
i-C_4H_{10}	Resonance lamp	1146	12.6	16
c-C_5H_{10}	Resonance lamp	1194	28.0	16
	Laser	1101	13.4	
c-C_6H_{12}	Laser	1102	21.3	
c-C_7H_{14}	Resonance lamp	1117	16.3	
	Laser	896	24.7	
c-C_8H_{16}	Laser	1132	53.8	
neo-C_8H_{18}	Resonance lamp	1180	18.0	18
i-C_8H_{18}	Resonance lamp	1186	22.4	18
2,3-dimethylbutane	Resonance lamp	1220	20.8	18
2-methylpentane	Resonance lamp	997	13.5	
2-methylpentane	Laser	1095	13.6	
3-methylpentane	Resonance lamp	1124	17.5	
3-methylpentane	Laser	975	11.3	
2,3,4-trimethylpentane	Resonance lamp	955	7.7	
2,3,4-trimethylpentane	Resonance lamp	1116	14.3	
2,3,4-trimethylpentane	Laser	1110	13.9	
C_2H_2	Resonance lamp	1208	0.28	18
C_2H_4	Resonance lamp	1197	2.64	18
C_3H_6	Resonance lamp	1204	9.6	18
HCHO	Resonance lamp	1200	11.7	18
CH_3COCH_3	Resonance lamp	1200	9.0	17
CH_3OH	Resonance lamp	1205	5.2	18
C_2H_5OH	Resonance lamp	1204	5.3	18
CH_3CHO	Resonance lamp	1071	12.4	
CH_3OCH_3	Laser	1119	11.4	
CH_3CCl_2F	Laser	1084	0.39	

The reaction of OH with CH_3 radicals followed a different procedure.[17] This process is always occuring in our system because CH_3 radicals are produced in the decomposition of the TBH via reactions b, c, and d. Overall, three CH_3 radicals are produced for every OH radical in the pyrolysis of the tBOOH. In order to vary the ratio of $[OH]:[CH_3]$, varying quantities of di-t-butyl-peroxide [$(tBuO)_2$] were added to the tBOOH. Like tBuOOH, $(tBuO)_2$ decomposes rapidly at the temperatures behind the reflected shock tube, but produces only CH_3 and CO:

$(CH_3)_3COOC(CH_3)_3 \rightarrow 2\,(CH_3)_3CO\cdot$ $\quad k_e = 7 \times 10^8\ sec^{-1}$

$(CH_3)_3CO\cdot \rightarrow \cdot CH_3 + CH_3COCH_3$ $\quad k_f = ?\ 3 \times 10^{10}\ sec^{-1}$

$CH_3COCH_3 \rightarrow \cdot CH_3CO + \cdot CH_3$ $\quad k_c = 40\ sec^{-1}$

$\cdot CH_3CO \rightarrow \cdot CH_3 + CO$ $\quad k_d = ?\ 4 \times 10^{10}\ sec^{-1}$

For a net overall reaction of:

$$(CH_3)_3COOC(CH_3)_3 \rightarrow 4\ \cdot CH_3 + 2\ CO$$

Extraction of the OH + $\cdot CH_3$ reaction rate coefficient of $1.1 \times 10^{11}\ L\ mol^{-1}\ s^{-1}$ required the utilization of a detailed computer model. Although we did not directly measure the products of the reaction, we believe that the primary mechanism for OH removal of $\cdot CH_3$ near 1200 K and 1 atm is by their combination to form CH_3OH.

V. TRANSITION-STATE THEORY CALCULATIONS

Ultimately it could be of great utility to chemists, engineers, and modelers to know the relative rates of the individual pathways in reactions such as those of OH radicals with alkanes larger than ethane, in which not all the abstractable hydrogen atoms are equivalent.

To a first approximation, the H atoms of 2-methyl pentane and 3-methyl pentane can be categorized as 9 primary, 4 secondary, and 1 tertiary, where the designation indicates whether the carbon atom to which the H atom is attached is bound to one, two, or three other carbon atoms. Similarly, 2,3,4-trimethyl pentane has 15 primary and 3 tertiary H atoms. A more detailed examination takes into account more precisely the nature of the ligands of the carbon atom from which the H atom is being abstracted: for example, a primary carbon attached to a secondary carbon is different from a primary carbon attached to a tertiary carbon atom. Cohen and Benson[19] used a notation P(i), S(ij), T(ijk), where the i, j, and k are 1, 2, or 3 if a ligand is a primary, secondary, or tertiary C, respectively. With this notation, 2-methyl pentane consists of 2 P(3), 1 P(2), 1 S(12), 1 S(23), and 1 T(112) groups; 3-methyl pentane consists of 2 P(2), 1 P(3), 2 S(13), and 1 T(122) groups; and 2,3,4-trimethyl pentane consists of 5 P(3), 1 T(133), and 2 T(113) groups. (Each P group has 3 primary H atoms, each S group has 2 secondary H atoms, and each T group has one tertiary H atom.) As Cohen3 discussed, there are good reasons for expecting differences in rate parameters at this level of detail for the different H atom abstractions. At the time of that study, however, available experimental evidence was just barely sufficient to discern differences among different classes of primary, secondary, or tertiary H atom abstractions.

Atkinson[20] has taken a slightly different approach and derived a set of rate coefficient expressions to predict H abstraction rates by OH radicals as follows:

$$k(CH_3\text{-}X) = k_{prim}\, F(X) \tag{7}$$

$$k(CH_2\text{-}X,Y) = k_{sec}\, F(X)F(Y) \tag{8}$$

$$k(CH\text{-}X,Y,Z) = k_{tert}\, F(X)F(Y)F(Z), \tag{9}$$

where $F(\text{-}CH_3) = 1$ and $F(\text{-}CH_2\text{-})$, $F(>CH\text{-})$, and $F(>C<) = \exp(76/T)$ and

$$k_{prim} = 4.5 \times 10^{-18}\, T^2 \exp(-303/T), \tag{10}$$

$$k_{sec} = 4.3 \times 10^{-18}\, T^2 \exp(233/T), \text{ and} \tag{11}$$

$$k_{tert} = 1.9 \times 10^{-18}\, T^2 \exp(711/T)\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}. \tag{12}$$

This model allows for differences between the various types of H atoms as characterized in the previous paragraph, but at present does not distinguish numerically between the S(12) and S(13) groups or between the T(122) and T(133) groups (*i.e.*, it treats the indices > 1 as identical). This model can easily be applied to the three branched alkanes under consideration in this paper to predict overall rate coefficients under the experimental conditions of the shock tube. It can also predict the relative contributions of the separate primary, secondary, and tertiary abstraction pathways to that total rate, for which we have no direct experimental data.

The transition state theory model of Cohen[3] can also be used (though not so conveniently as Atkinson's model) to predict the shock tube measurements, channel by channel, provided that an experimental rate coefficient is available at some other temperature (generally, but not necessarily, 298 K). Since only total rate coefficients are available at 298 K, one needs some scheme to apportion the overall rate coefficients among the various channels. For this purpose we use eqs. 7-12 to calculate relative rates by each pathway and normalize to the experimental total rate at 298 K. The results predicted by Atkinson's and Cohen's models for the individual pathways and total rates under shock tube conditions are shown in Table 2.

Table 2: Comparison of calculated and experimental rate coefficients for reactions of OH with branched alkanes

Compound and channels	Rate Coefficients (units of 10^{10} L/mol-s)		
	k(298)[a]	k(shock)[b]	k(shock)[c]
2-Methylpentane (T_{shock} = 997 K)			
Calculated relative rates			
1 P(2) + 2 P(3)	0.08	0.38	0.54
1 S(12) + 1 S(23)	0.47	0.47	0.24
1 T(112)	0.45	0.16	0.21
Calculated total rate		1.6	1.5
Experimental rate	0.34	1.4	
3-Methylpentane (T_{shock} = 1124 K)			
Calculated relative rates			
2 P(2) + 1 P(3)	0.08	0.40	0.46
2 S(13)	0.38	0.44	0.11
1 T(122)	0.54	0.16	0.42
Calculated total rate		2.0	1.8
Experimental rate	0.34	1.7	
2,3,4-Trimethylpentane (T_{shock} = 955 K)			
Calculated relative rates			
5 P(3)	0.09	0.55	0.67
2 T(112) + 1 T(133)	0.92	0.45	0.33
Calculated total rate		1.6	1.1
Experimental rate	0.42	1.1	

[a] Relative rates calculated from eqs. 1-6 and normalized to experimental total rate. [b] Calculated by eqs. 1-6.
[c] Calculated by Transition State Theory using procedure of Ref 3.

The molecular properties of the transition state necessary to carry out the TST calculations (bond lengths and angles, vibrational frequencies, internal rotation barriers and moments of inertia, imaginary frequency of reaction coordinate, electronic spin degeneracy) were the same as identified in Ref. 3. Recently, Martell *et al.*[21] have carried out calculations for the OH + C_2H_6 reaction that resulted in a set of vibrational frequencies and geometric properties that could be applied to the present calculations as well, assuming that the portions of the reagent alkane more than 2 atoms removed from the reaction site are unchanged in the transition state (an assumption that is probably no worse than other assumptions of the method of Ref. 3). These vibrational frequencies result in a significantly larger entropy of activation, in turn leading to rate coefficients at shock tube temperatures about a factor of 2 larger than the experimental results or than the other calculated results of Table 2.

It is interesting to compare the calculated results by the models of Atkinson and Cohen, shown in Table 2. It is inappropriate, however, to rush to conclusions regarding the relative merits of the two predictive schemes. Atkinson's equations require no experimental input; the TST calculations, on the other hand, make use of $k(298)_{expt}$ and the assumed branching ratios at 298 K as calculated by Atkinson's model. While the calculated total rate coefficients agree with the experimental values--within the combined experimental and computational uncertainties--there are significant differences in the relative rates by different pathways. This reflects the fact that there are so few definitive data on detailed reaction probabilities for OH + alkane reactions that there is considerable uncertainty in the assumed parameters of the two models. It is still not possible to state which of the two sets of calculated branching ratios at shock tube temperatures is the more accurate. This highlights the necessity for accurate data on separate reaction channels, so that computational models can be refined accordingly.

In preparation for our experiments on reactions of OH with halocarbons, we carried out TST calculations for several reactions that have been studied elsewhere at low temperatures (250-400 K), but not higher.[22] (As it turned out, time permitted the study of only one of these compounds in the shock tube.) The calculations predict the range of rate coefficients that we should be prepared to expect; the experiments will then verify the assumptions of the calculations. The predicted rate coefficients, which require an assumed value of k(298) (taken from published experimental data), are fitted to three-parameter expressions, $k(T) = A\,T^{n} \exp(-E/RT)$. Table 3 lists the compounds, the log k(298), and values for the rate coefficient parameters (for $200 < T/K < 2000$):

Table 3. Calculated Rate Coefficients for Reactions of OH with Haloalkanes

Compound	log k(298)	log A (L/mol-s)	n	E/R
CH_3CHCl_2F	6.56	5.17	1.3	1255
$CHClFCF_2CClF_2$	6.73	3.05	1.9	700
$CH_3CF_2CFCl_2$	6.15	5.74	1.2	1765
CF_3CHFCF_3	5.98	2.40	2.1	1105
$CHCl_2CF_2CF_3$	7.18	2.93	1.9	325
CHF_2Br	6.76	2.94	2.0	780
CH_3CH_2Br	8.28	4.73	1.7	450
CH_2BrCH_2Br	8.08	4.26	1.7	180
CF_3CH_2Br	6.95	3.35	1.9	765
CF_3CHFBr	7.00	3.06	1.9	520
$CF_3CHClBr$	7.54	1.57	2.3	-190
$CH_2BrCHBrCH_2Cl$	8.40	2.44	2.2	-365

An integral part of this research program was the development and use of Transition State Theory calculations to predict and extrapolate reaction rate coefficients for H abstraction reactions, particularly by OH radicals. In this connection, it is interesting to note a recent series of publications that provides support for our longstanding contention that these computational techniques can often provide rate coefficient estimations more reliable than experimental measurements. The story begins with our publication in 1987 of a paper reporting our thermochemical kinetic transition state theory calculations for a series of reactions of OH radicals with halogenated alkanes.[23] In almost all cases except one where there were experimental data for comparison, the agreement between calculations and measurements was very good. The single puzzling exception was the reaction of OH with $CHCl_3$, chloroform. We argued that there was no reasonable explanation for this single anomalous result, and suggested that the experimental data were in error.

In 1989, Taylor *et al.*[24] published the results of another measurement of the same reaction extending to higher temperatures; their results were in very good agreement with the earlier measurements, and consequently shifted the probable source of error in the calculations, rather than the measurements.

Therefore, when we published our data sheet[25] for the OH + $CHCl_3$ reaction, we recommended a rate expression in agreement with the two measurements, noting the disagreement between experiments and calculations: "Notwithstanding the very good agreement among the different experimental studies, the failure of the calculations to predict the same temperature dependence is disconcerting. (Failure of the model to give results in agreement with the data is so puzzling only because the same model gives good agreement in the cases of 18 other halomethanes and haloethanes.) Consequently, we recommend with caution the expression of [Taylor *et al.*]."

Some time later, Taylor and coworkers published a new study of this and other OH reactions. They found that high photolysis intensities measurably increased the apparent rate coefficients, with the effect increasing with temperature.[26] The result was to give a spuriously larger temperature effect than is actually the case. When this anomaly was taken into account and the experimental procedure modified accordingly, the new results were in excellent agreement with the theoretical calculations. More recently, DeMore[27], prompted by us to re-examine this system, presented experimental measurements confirming the revised results of Taylor and coworkers.

This sequence of events is an interesting vindication of the theoretical procedures we have been using, and also a confirmation of what we once termed the "persistence of literature values"--the tendency of experimentalists to be overly influenced by previously published results in analyzing and interpreting their data.[28]

OH + Acetaldehyde. This study appears to provide the first reported measurement of the reaction of OH + CH_3CHO at temperatures above 528 K, and as such deserves some comment. The three experimental studies at lower temperatures agree on a negative temperature dependence between 244 and 528 K.[29,30,31] In the absence of additional data, Warnatz[32] proposed a temperature-independent rate coefficient at combustion temperatures. Baulch *et al.* combined the low-temperature negative dependence with the assumed high temperature independence and proposed $k = 2.3 \times 10^7\ T^{-0.73} \exp(+560/T)$ L/mol-s, which, extrapolated to the temperature of these experiments, predicts a rate coefficient of 6.4×10^9 L/mol-s, about a factor of 2 lower than we report. It is tempting to explain the increase in rate at higher temperature as due to the opening up of a second reaction pathway: the CH_3CO--H bond strength is 89.3 kcal/mol, while that of H-CH_2CHO is 94.8 kcal/mol. Thus one would expect that abstraction of the methylic hydrogens to proceed with a slightly higher activation energy (1-2 kcal/mol) than that for the lone aldehydic hydrogen. The low temperature negative temperature dependence suggests not the simple and direct bimolecular collision mechanism that occurs between OH and the alkanes, but rather a process via a long-lived intermediate, as suggested by Semmes *et al.*[28]

OH + Ethane, Acetone, and Dimethyl ether. The reaction of OH with C_2H_6 has been well characterized and studied over a wide temperature range.[33] The reactions with CH_3OCH_3 and CH_3COCH_3[34] have been studied only over the temperature range of 240 - 440K. These three reactions are similar in that OH abstracts one of six hydrogen atoms from two methyl groups at either end of a symmetrical molecule. The principal difference between the three molecules as far as H abstraction is concerned is the differing strengths of the C--H bonds: 100.5 kcal/mol in ethane, 98.3 in acetone, and 93.0 in dimethyl ether. The activation energies (near room temperature) should scale approximately as the bond strengths, so that ethane and acetone would be expected to have activation energies that differ by at most a half kcal/mol (approximately 2 kcal/mol), while that for the ether should be close to zero or negative (an Evans-Polanyi correlation plot for OH + hydrocarbon reactions suggests that the apparent activation energy approaches zero as the bond dissociation energy approaches 94 kcal/mol). The experimental activation energies are consistent with these expectations: they are approximately 2.7, 1.2, and 0.6 kcal/mol for ethane, acetone, and dimethyl ether, respectively.

However, the absolute experimental values for acetone reported over 240-440 K are not so reasonable.[35] Note that acetone and ethane have almost identical room temperature rate coefficients (log k(298) = 8.11 and

8.13, respectively), but the apparent activation energies differ by 1.5 kcal/mol. This would imply an unusually small entropy of activation in order to match both slope and absolute values of the rate coefficient over the experimental range of temperatures (240-440 and 1200 K). Furthermore, even if one could select transition state parameters that matched the slope over 240-440 K, it would be very difficult to match simultaneously the experimental value at 1200 K. Thus, unless the transition state is very different from that for OH + C_2H_6, which seems unlikely, there must be an error in either (1) the shock tube value, (2) the absolute values at 240-440 K (by some constant factor), or (3) the temperature dependence over 240-440 K. The absolute value at room temperature is supported by a measurement by Kerr and Stocker[36], whose own result was only about 25% larger than that of Wallington and Kurylo, but not by Chiorboli *et al.*,[37] who reported a value larger by a factor of almost 3. The latter result, however, could be in error because the possibility of acetone photolysis was apparently not taken into account [according to Atkinson *et al.*].

With such small activation energies (0.6 to 2.7 kcal/mol) the shock tube results are primarily sensitive to the preexponential factors. The activation energies of 0.6, 1.2, and 2.7 kcal/mol reduce the rate coefficients by factors of 1.35, 1.8, and 3.9 from the pre exponential factor. That is to say, we would expect ethane and acetone to be factors of 2.9 and 1.3, respectively, slower than the ether. In fact, they are slower by almost exactly these factors (ignoring the slight differences in temperatures).

VI. THERMOCHEMICAL DATA

In order to obtain the maximum benefit from experimental data and the TK-TST calculations, it is necessary to know equilibrium constants for the abstraction reactions. This requires thermochemical parameters for various organic molecules and radicals, which may not be available from experimental measurements. In order to generate our own equilibrium constant data, we made an extensive examination of methods for the estimation of enthalpies, entropies, and heat capacities for alkanes and alkyl radicals. This study resulted in five publications: one focusing on the alkanes[4]; a second, on the alkyl radicals themselves;[5] and two others, on additivity methods in general for the estimation of enthalpies of formation of organic species.[6,7] Another paper reviewing the thermochemistry of C-H-O compounds was intended for application to later phases of this project that never were completed.[8]

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VII. PUBLICATIONS RELATED TO THIS GRANT

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