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

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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, and their reactions directly yield water molecules, one of the major final oxidation products. In the atmosphere, the combined effect of the OH radical's reactivity and concentration make it the single species that determines the atmospheric lifetime of an organic substance.

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 renders impractical detailed theoretical evaluation of every one. To this end, Benson and coworkers¹ developed the procedures of thermochemical kinetics: 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.

In the experimental portion of this program we have carried out shock tube measurements of the reactions of OH radicals with several species. The experiments were performed behind reflected shock waves in a stainless steel shock tube. The tube has a 10-m-long, 16.2-cm-diameter test section with a 3-m-long-7.5 cm-diameter driver section. OH radicals were produced in most cases by shock-heating t-butyl hydroperoxide (TBH) diluted in argon. TBH dissociates rapidly at our temperatures (near 1200 K) to produce t-butoxy and OH radicals. The t-butoxy radicals in turn rapidly pyrolyze to give CH₃ radicals and acetone; the acetone then decomposes to give CH₃ + CO. The overall process is thus

Thin-film heat transfer gauges mounted in the tube wall signal the passage of the shock wave. The speed of the shock wave is calculated from the distance between the gauges and the time between the heat transfer gauge signals. From the shock speed, the pressure and temperature behind the reflected shock are calculated.

The OH radicals then undergo several reactions in the absence of any other reagents, and have a characteristic half-life. When another reagent is present, it too can react with the OH. The disappearance rate of OH as a function of the concentration of the added reagent RH gives the reaction rate coefficient for the process, $\text{OH} + \text{RH} \rightarrow \text{products}$. The OH concentration behind the reflected shock wave was monitored by uv absorption using OH resonance radiation at 309 nm, produced by a microwave discharge through a mixture of helium and water vapor flowing at 70 torr.

To date we have completed and published^{2,3}--or have submitted for publication⁴--shock tube measurements of the reactions of OH radicals with several species: H_2 , CH_4 , C_2H_6 , $\text{c-C}_5\text{H}_{10}$, $\text{i-C}_4\text{H}_{10}$, $\text{i-C}_6\text{H}_{18}$, $\text{neo-C}_5\text{H}_{18}$, 2,3-dimethylbutane, C_2H_2 , C_2H_4 , C_3H_6 , H_2CO , CH_3COCH_3 , CH_3OH , and $\text{C}_2\text{H}_5\text{OH}$. The results, all near 1200 K and 1 atm, are summarized below.

Reagent	Rate Coefficient (10^9 L/mol-s)
H_2	2.7
CH_4	2.6
C_2H_6	9.0
$\text{c-C}_5\text{H}_{10}$	28.0
$\text{i-C}_4\text{H}_{10}$	12.6
$\text{neo-C}_5\text{H}_{18}$	18.0
$\text{i-C}_6\text{H}_{18}$	22.0
2,3-dimethylbutane	21.0
C_2H_2	0.28
C_2H_4	2.6
C_3H_6	9.6
H_2CO	12.0
CH_3COCH_3	5.3
CH_3OH	5.2
$\text{C}_2\text{H}_5\text{OH}$	5.3

In addition, in a separate set of experiments, the reaction rate of OH with CH_3 was measured. This process is always occurring in our system because CH_3 radicals are produced in the decomposition of the TBH. As eq. (1) above shows, 3 CH_3 radicals are produced for every OH radical in the pyrolysis of TBH. In order to vary the ratio of $[\text{OH}]:[\text{CH}_3]$, varying quantities of di-t-butyl-peroxide (TBP) were added to the TBH. Like TBH, TBP decomposes rapidly at the temperatures behind the reflected shock tube, but produces only CH_3 and CO :

Extraction of the $\text{OH} + \text{CH}_3$ reaction rate coefficient of $1.1 \times 10^{10} \text{ L/mol-s}$ 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 by CH_3 near 1200 K and 1 atm is by their combination to form CH_3OH .

The work on the hydrocarbons provided the incentive for revising an earlier model⁵ used to carry out thermochemical transition state theory (TST) calculations for the reaction rate coefficients of OH with alkanes. In a careful review of the application of 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. If true, this invalidates the usual procedure of treating the total rate coefficient for $\text{OH} + \text{RH}$ as

abstraction processes as the sum of invariant primary, secondary, and tertiary rates multiplied by the respective number of such H atoms in the molecule. A separate question is whether there is really sufficient experimental evidence to justify distinguishing among different types of primary (or secondary, or tertiary) H atoms, or whether, given experimental and theoretical uncertainties, it is adequate to treat them all as equivalent. We concluded that there are measurable differences among various primary and possibly secondary H atom abstractions, but the scant experimental record needs corroboration. The database cannot as yet distinguish among tertiary H atoms.

In our experimental work next year we intend to extend our measurements to other reagents. Additionally, we plan to incorporate the necessary analytical apparatus to permit measurements on some of the expected reaction products, thus allowing us to say more about the mechanisms of those reactions where more than one pathway is possible. The untimely demise last year of Jerry Bott, who was in charge of the experimental portion of this program, has delayed our work somewhat, but we are currently reconstructing and improving the shock tube facility.

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