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Elementary Reaction Rate Measurements at High Temperatures

by Tunable-Laser Flash-Absorption*

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Elementary Reaction Rate Measurements at High Temperatures by Tunable-Laser Flash-Absorption

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The major objective of this program is to measure thermal rate coefficients and branching ratios of elementary reactions. To perform these measurements, we have constructed an ultrahigh-purity shock tube to generate temperatures between 1000 and 5500 K. The tunable-laser flash-absorption technique is used to measure the rate of change of the concentration of species which absorb below 50,000 cm^{-1} *e.g.*: OH, CH, and CH_3. This technique is being extended into the vacuum-ultraviolet spectral region where we can measure atomic species *e.g.*: H, D, C, O, and N; and diatomic species *e.g.*: O_2, CO, and OH.

Correlation Analysis While evaluating our high-temperature measurements of the kinetic behavior of hydroxyl to determine the rate coefficient for H + O_2 → O + OH we noticed that sensitivity coefficients did not quantitatively predict the relative importance of different reactions nor did they provide any information about the correlation between the rates of the reactions. Rates of reactions are correlated if a change in one rate coefficient may be accompanied by a correlated change in another rate coefficient such that a calculation of an experimental observation would remain essentially the same. To establish a new quantitative scheme for utilizing sensitivity coefficients we have combined concepts from non-linear least-squares analysis with the definition of sensitivity coefficients to devise a scheme which determines (1) the relative importance of reactions for predicting the behavior of a specific observable over a given interval, and (2) the degree to which the reactions are correlated. This scheme may be used to design experiments, to calculate the propagation of uncertainties when rate coefficients have been determined, and to compare the relative accuracy of different experiments. This scheme uses a standard code for evaluating sensitivity coefficients[1] and represents a relatively simple addition to any sensitivity analysis.

Methyl Chemistry Since the reaction of methyl with molecular oxygen is the main branching process in any hydrocarbon oxidation system and because methyl is the simplest alkyl radical, we begin with methyl chemistry. We have used the correlation analysis scheme discussed above to shown why azomethane is the best pyrolytic source of methyl radicals for chemical studies at high temperatures. At combustion temperatures there are two main channels for the reaction of methyl radicals with molecular oxygen

$$CH_3 + O_2 \rightarrow CH_3O_2^* \quad \begin{array}{ll} \rightarrow CH_3O + O \rightarrow CH_2O + O + H & \text{(Rxn. 51 + 156)} \\ \rightarrow CH_2OOH \rightarrow CH_2O + OH & \text{(Rxn. 52)} \end{array}$$

Reactions 51 and 156 are endothermic whereas reaction 52 is exothermic. The energy difference between these two channels is just the dissociation energy

of hydroxyl, $D_0^0/k = 50970$ K. Because of this large energy difference, the branching ratio between these channels will control the ignition rate of hydrocarbon/oxygen mixtures.

We have used the above correlation analysis to show that in very lean mixtures, $[O_2]_0/[C_2H_6N_2]_0 > 4000$, the hydroxyl radical may be monitored to measure the rate of reaction 52 without any significant interference from other hydrocarbon reactions. To illustrate this we show, in figure 1, the fractional sensitivity for the measurement of hydroxyl with initial mole fractions of azomethane, oxygen, and argon at 0.01%, 42%, and 58% respectively and at a temperature of 1544 K and a pressure of 151.4 kPa.

6   O+H2<=>OH+H
10 2OH<=>H2O+O
52 CH3+O2<=>CH2O+OH
165 CH2O+M<=>CO+H2+M
169 CH2O+OH<=>HCO+H2O
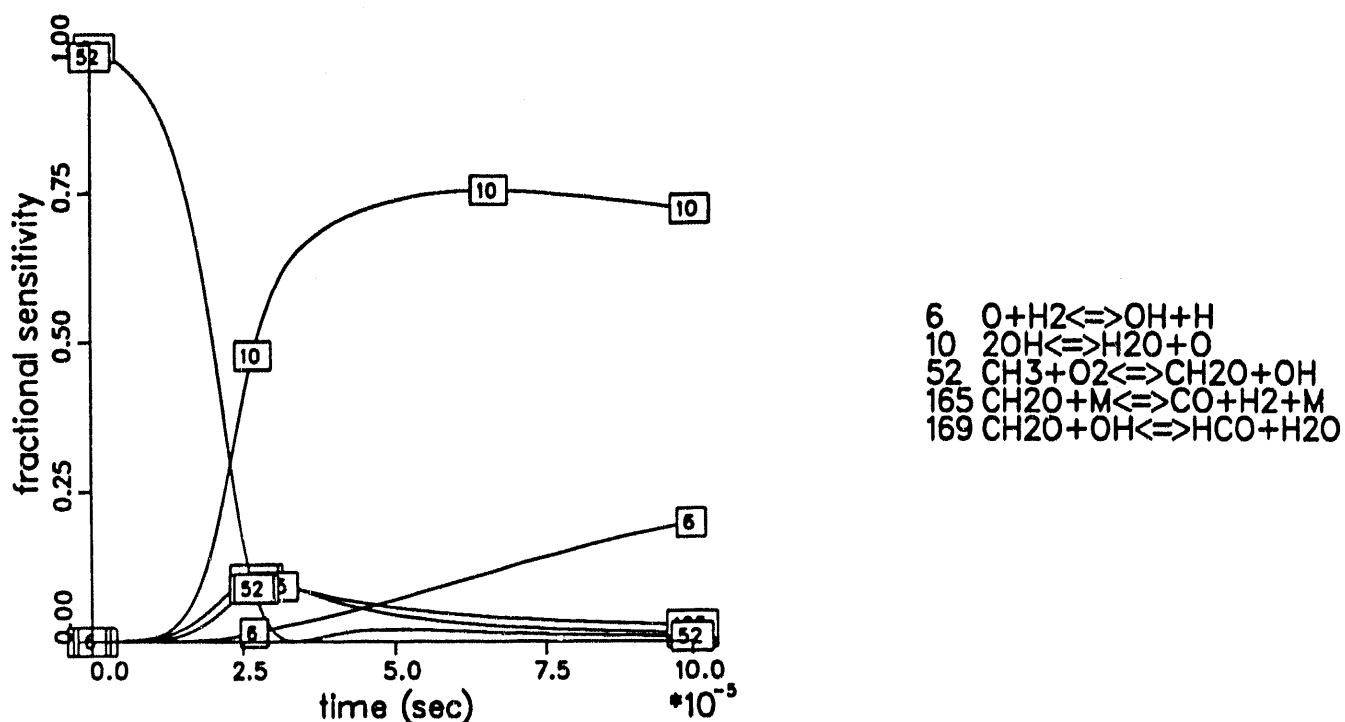
Figure 1. Fractional sensitivities for measurement of hydroxyl.

In figure 2, we show the measured absorption profile for hydroxyl and the results of the non-linear least-squares analysis used to determine the rate coefficient of reaction 52. A preliminary analysis of our results gives

$$k(CH_3 + O_2 \rightarrow CH_2O + OH) = 5.1 \times 10^{-12} \exp(-8700/T(K)) \quad cm^3 s^{-1}.$$

The above activation energy is significantly higher than the most recent measurement[2] and calculation.[3]

Parallel Computations for Least-Squares Analysis   The complete reaction mechanism used to describe the oxidation of methyl contains over one-hundred-fifty reactions. Even a "core" mechanism, which may be used to describe shock tube experiments at very early times is relatively large. To perform a multi-dimensional least-squares analysis of experimental data with large mechanisms we employ parallel processing at the time consuming step of numerically evaluating derivatives. We have implemented a code for such processing on our

Alliant Concentrix 2800. The CPU time and, more importantly, the human time required for data analysis is significantly reduced by the use of a parallel computer architecture.
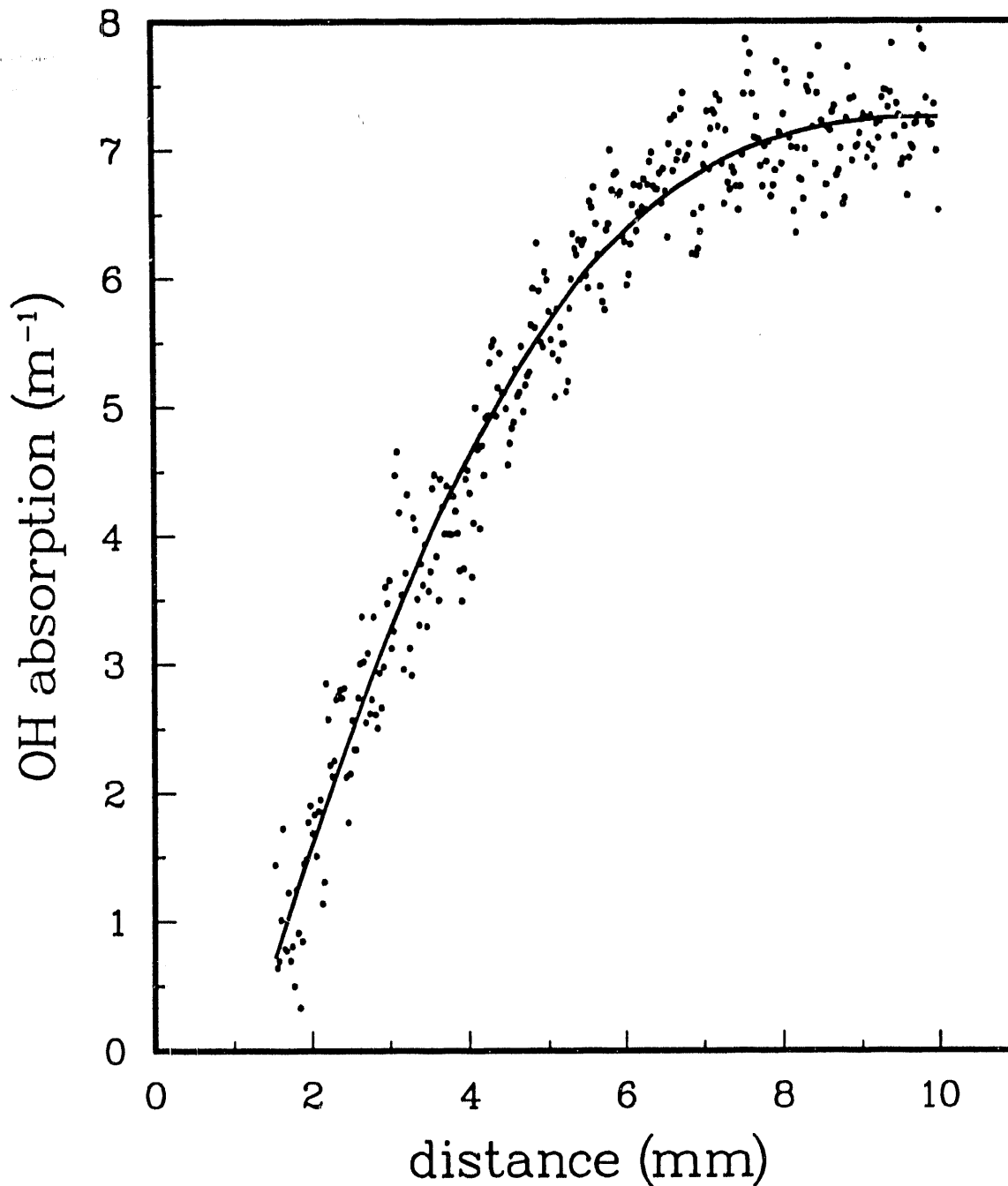

Figure 2. Hydroxyl absorption profile obtained with initial mole fractions given in the text. Shock parameters: Mach No. 4.354, T_2(K) 1544, and P_2(kPa) 151.4.

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