KINETIC MEASUREMENTS ON ELEMENTARY FOSSIL FUEL COMBUSTION
REACTIONS OVER WIDE TEMPERATURE RANGES

Progress Report

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INTRODUCTION AND METHOD

The goals of this work are to provide accurate data on the temperature dependence of the kinetics of elementary combustion reactions (i) for use by combustion modelers, and (ii) to gain a better fundamental understanding of, and hence predictive ability for, the chemistry involved. Experimental measurements are made using the pseudo-static HTP (high-temperature photochemistry) technique. This approach allows observations on single reactions in the 300 to 1800 K temperature range to be made. Typical total (bath gas) pressures are in the 100 to 1000 mbar range. Ground-state O atoms are produced by flash photolysis of O₂ or CO₂ or ArF excimer laser-photolysis of SO₂. The relative atom concentrations are monitored by resonance fluorescence pumped by a cw microwave discharge flow lamp. The molecular reactant-in-excess is introduced through a cooled inlet. Adequate time for mixing, 0.1 to 10 s, between this inlet and the photolysis/observation zone is achieved by using slow flows (typically less than 20 cm s⁻¹).

PROGRESS

In the reporting period our work on the O + HCl reaction was published,¹ experimental work on the O + benzene and O + 1-butene reactions was completed, and measurements on the O + isobutene reaction were initiated.

The O-Atom Benzene Reaction

Fig. 1 summarizes the present measurements and compares them to those of earlier workers²⁻⁴ and Wagner's shock tube study,⁵ which appeared while our work was in progress. All the measurements are in excellent agreement. The present work, which has covered the 600-1310 K regime, has bridged the gap between the lower temperature work ($T < 870$ K) and the 1200 to 1450 K shock tube study. While Wagner and coworkers flow tube work below 680 K had a hint of curvature (which they thought might be an experimental artifact), their shock tube and the combined

work shows no such trend. A simple Arrhenius expression $k(T) = 3.9 \times 10^{-11} \exp(-2364 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ best represents all the data from 300 to 1450 K. At low temperatures the reaction is known to proceed by O-atom addition to the aromatic ring.^{2,3} While an abstraction reaction is likely to be of importance above some temperature, Fig. 1 clearly indicates that such is not yet the case in the 1400 K range. This is in agreement with the 61.5 kJ/mol activation energy estimated from BEBO calculations.³

A publication based on these results is in preparation.

The O-Atom 1-Butene Reaction

We have made measurements on this reaction from 340 to 1110 K. The data are best represented by the expression $k(T) = 2.3 \times 10^{-17} (T/\text{K})^{1.95} \exp(330 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. As may be seen from Fig. 2, this result is in good agreement with previously reported low temperature ($T < 500 \text{ K}$) data,⁶⁻⁹ as well as with the best fit expression for the 260-860 K range given in an abstract by Perry.¹⁰ It has been postulated that the reaction proceeds by addition at low temperatures, while hydrogen-atom abstraction will become increasingly important at elevated temperatures.^{6,7} Apparent confirmation for abstraction comes from the detection of OH in molecular beam experiments with LIF¹¹ and mass spectrometer¹² detection.

To establish to what extent the abstraction channel could be the cause of the sharp upward curvature in the Arrhenius plot, Fig. 2, we have performed a Transition State Theory (TST) calculation for it and added the resulting rate data to those for the addition channel from the TST calculation by Singleton and Cvetanovic.⁷ Their calculation involved fitting to experimental $k(T)$ data. For the abstraction channel we used the 8.0 kJ mol⁻¹ energy barrier from one of the beam studies,¹¹ combined with the usual partition functions. The resulting sum of the rate coefficients is shown in Fig. 2 as "Theory" and can be seen to give pronounced curvature, but to fall increasingly below the experimental curve with increasing T . Further calculations are in progress, which will be included in the manuscript in preparation.

The O-Atom Isobutene Reaction

Fig. 3 gives the Arrhenius plots for the O-atom reactions of all four butenes taken from the expressions in Perry's abstract.¹⁰ His 1-butene expression is as noted above, in excellent agreement with ours. However, our first observations in the 350-1050 K range are in qualitative agreement only with his measurements, and suggest a much flatter plot. If confirmed, this also casts some doubt on his cis- and trans-2-butene observations.

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Figure 1. Summary of Rate Coefficients of the $\text{O} + \text{C}_6\text{H}_6$ Reaction.

Figure 2. Summary of Rate Coefficients of the O + 1-Butene Reaction.

Figure 3. Comparison of the Arrhenius Plots of the O-Atom Reactions With the Four Butenes, as given by Perry.¹⁰

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