289al The Thermal Dissociation of H2o

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Because it is important in H2/O2 flame chemistry, the thermal decomposition of water

$$H_2O + M \rightarrow OH + H + M \quad (1)$$

has been studied five times. The direct studies, either by observing H2O depletion or by OH-radical formation, have been confined to temperatures above ~2700 K because the sensitivity for detection has been relatively low. We have recently described a multi-pass optical system that allows for the detection of OH-radicals in concentrations between 2×10^{12} and 2×10^{13} molecules cm-3. Hence, rate constants can be measured at lower temperatures, and this study now extends the OH-radical profile database to 500 K below the previous studies. Thirty-eight experiments were performed on the thermal decomposition in reflected shock waves over the T-range, 2200-2800 K, using three reaction mixtures, 0.3%, 0.5% and 1% H2O, diluted in Kr. The temporal concentration build up of the product, $[OH]_t$, was determined from measured absorbance, through an earlier determination of the absorption cross section at 308 nm. Considering all previous studies, the experiments of Homer and Hurle appear to be the most thorough even though the delayed flash absorption of OH required extraordinary control over the shock strengths in succeeding experiments. These authors varied [H2O]/[Ar] by about a factor of ten and directly documented a strong increase in the rate constant due to H2O with H2O collisional activation. At 2930 K, they report $k_{1,H_2O} = (20 \pm 7) k_{1,Ar}$. This enhancement was previously suggested in H2/O2 shock tube studies. Combining the present results with those of Homer and Hurle, the composite Arrhenius expression describing the data in either Ar or Kr bath gas is

$$k_{1,Kr,(or\ Ar)} = (2.43 \pm 0.57) \times 10^{-10} \exp(-47117 \pm 633\ K/T)\ cm^3\ molecule^{-1}\ s^{-1} \quad (2)$$

We have applied the Troe factorization method to understatnd the present data and those at lower-T for the back reaction. To within $<\pm18\%$ over the T-range, 300-3400 K, we suggest the three parameter expression

$$k_{1,Ar} = 1.00702 \times 10^4\ T^{-3.312} \exp(-60782\ K/T)\ cm^3\ molecule^{-1}\ s^{-1} \quad (3)$$

as the best representation for use in flame modeling.