

High-T Measurements in Reflected Shock Waves of Rate Constants for $D + CH_3$ and $D + H_2$: Comparisons with Theory

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The 17th Symposium on Gas Kinetics, University of Essen
Essen, Germany, August 24-28, 2002

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D-atom atomic resonance absorption spectrometric (ARAS) detection has been used to study the thermal decomposition of C_2D_5I to give C_2D_5 -radicals in $\sim 70\%$ yield (924-1370 K). C_2D_5 then decomposes to give $C_2D_4 + D$ effectively instantaneously on the time scale of the bimolecular kinetics experiments.

The concurrent thermal decompositions of both C_2D_5I and CH_3I can then be used to prepare well-defined initial concentrations of both D-atoms and CH_3 -radicals. Experiments were performed by observing absolute $[D]$ depletion and $[H]$ formation. The results were initially modeled with a 33 step mechanism; however, because of the high sensitivity for H- and/or D-detection, the mechanism could be reduced to four reactions, all of which are known except the exchange reaction, $D + CH_3 \rightarrow CH_2D + H$. The rate constants were found to be temperature independent with $k = (2.20 \pm 0.22) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $1294 \leq T \leq 1753 \text{ K}$. The present data have been combined with earlier lower temperature determinations, and the resultant database has been compared with unimolecular rate theory results. From theory, $k = k_\infty \langle k_{fe} / (k_{fe} + k_{be}) \rangle = k_\infty F$. Using the frequencies and structures given in Seakins et al. and Sutherland et al., we find $F(300 \text{ K})$ is 0.928 (in good agreement with Seakins et al.), and at higher-T, $F(1800 \text{ K}) = 0.857$. Klippenstein, Goergievski, and Harding find, from recent extensive theoretical calculations, values for F varying from 0.92 to 0.79 over the same T-range. Reliable values for the high-pressure limiting rate constant for methane dissociation at high-T can now be inferred from the present study.

With the C_2D_5I method for preparing $[D]$, new experiments have been performed on the $D + H_2$ reaction. Flash Photolysis-Shock Tube (FP-ST) measurements from this laboratory were made on this reaction over a decade ago, and the results agreed, within experimental error, with the best available theoretical calculations at that time. However, theoretical development continues (as recently reviewed by Mielke et al.) primarily on determining and describing a more precise potential energy surface. The precision of these new results suggests with some confidence that the experimental high-T results could be high by ~ 25 to 50% . Since our new method for D-atom production is simpler and our detection of H- and/or D-atoms is ~ 4 times more sensitive, we decided to re-

examine this reaction. Experiments were performed by observing absolute [D] depletion and [H] formation. Our present results can be summarized by the Arrhenius expression, $k = 2.70 \times 10^{-10} \exp(-4934 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ($1100 \leq T \leq 2100 \text{ K}$), which can be compared to our earlier FP-ST result, $k = 3.76 \times 10^{-10} \exp(-4985 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The new results are consistently lower than our previous results by ~25%. But it should be noted that the one standard deviation errors of the two studies overlap. We also note that the new results agree much better with the new quantum scattering thermal rate constant calculations by Mielke, Schwenke, Truhlar, Garrett, and Peterson whose tentative data can be represented over the same T-range by $k = 3.00 \times 10^{-10} \exp(-5051 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

This work was supported by the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract No. W-31-109-ENG-38.