

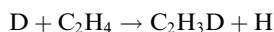
Rate constants for $D + C_2H_4 \rightarrow C_2H_3D + H$ at high temperature: implications to the high pressure rate constant for $H + C_2H_4 \rightarrow C_2H_5$

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Abstract

The shock tube technique with H- and D-atom atomic resonance absorption spectrometry detection has been used to study the reaction,



over the temperature range, 1153–1616 K. The rate constants for this reaction were found to be temperature dependent with $k = (2.56 \pm 0.46) \times 10^{-10} \exp(-2797 \pm 239K/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ with the errors being at the one standard deviation level. The present data have been combined with earlier lower temperature determinations, and the joint database has been examined with theory that includes both an ab initio determination of the potential energy surface and an evaluation of the rate constants using the RRKM theory. Similar calculations have been made for the analogous all-H reaction. For both isotopic combinations, the agreement between theory and experiment is good, allowing a new estimate from theory for the high-pressure limit for $H + C_2H_4 \rightarrow C_2H_5$ of $0.420 \times 10^{-15} T^{1.75} \exp(-604.9 K/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for 200–2000 K. Since the $D + C_2H_4$ measurements reported here are the only high temperature measurements for either isotopic combination, the new high-pressure limiting estimate should be the best available at high temperatures.

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Keywords: Rate constants; Shock tube; RRKM theory; High-pressure limit; Isotopic ratio

1. Introduction

The $H + C_2H_4$ reaction has been the subject of numerous investigations for over 50 years [1], with three studies [2–4], covering a particularly broad

temperature and pressure range. At low temperatures, the reaction mechanism is totally dominated by the energy transfer mechanism and follows the RRKM theory:



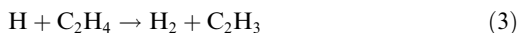
However, if temperature is increased then H-atom abstraction can occur

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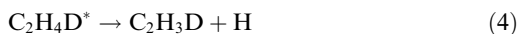
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The reverse of this latter process has also been directly studied [5], allowing reliable rate constants to be determined for reaction (3) through the known equilibrium constants.

In the present work, the isotopic modification of the $\text{H} + \text{C}_2\text{H}_4$ reaction, $\text{D} + \text{C}_2\text{H}_4$, has been studied. Two potential reaction pathways are then possible, addition and/or abstraction. Using an estimate from the previous work [5], on the analogous all-H case at the highest temperature of the present study, 1616 K, the abstraction process is <4% of the measured rate constant. At all temperatures, abstraction is then negligible within experimental error. Hence, the present study simply relates only to the energy transfer mechanism. By analogy with reactions (1), (-1) and (2), the mechanism then becomes:



where reaction (4) leads to isotopic exchange through the vibrational excited species. Using the RRKM theory, the rate constant based on D-atom depletion, k_{D} , is

$$k_{\text{D}} = k_{\text{D}\infty} \int_{\varepsilon_0}^{\infty} ((k_{\text{f}\varepsilon} + \beta\omega)/(k_{\text{f}\varepsilon} + k_{\text{b}\varepsilon} + \beta\omega))f(\varepsilon) d\varepsilon. \quad (5)$$

$k_{\text{D}\infty}$ is the high-pressure rate constant for reaction (1D), $k_{\text{f}\varepsilon}$ is the specific RRKM rate constant for forward dissociation from $\text{C}_2\text{H}_4\text{D}^*$, reaction (4), $k_{\text{b}\varepsilon}$ is the specific RRKM rate constant for backward dissociation of $\text{C}_2\text{H}_4\text{D}^*$, reaction (-1D), to give reactants at the threshold energy, ε_0 , β is the collisional deactivation efficiency, ω is the collision rate constant, reaction (2D), and $f(\varepsilon)$ is the normalized chemical activation distribution function originating at ε_0 for a given temperature. In the present case, the pressure is relatively low and the temperature is high, suggesting that stabilization will be slow in comparison with either forward or back dissociation. Hence, the rate constant becomes, $k_{\text{D}} = k_{\text{D}\infty} \langle k_{\text{f}\varepsilon}/(k_{\text{f}\varepsilon} + k_{\text{b}\varepsilon}) \rangle$, where the average is taken over the distribution function, $f(\varepsilon)$, and this then becomes the rate constant for the title reaction. If H-atom formation is used to determine the rate behavior, then the rate constant, k_{H} , becomes

$$k_{\text{H}} = k_{\text{D}\infty} \int_{\varepsilon_0}^{\infty} (k_{\text{f}\varepsilon}/(k_{\text{f}\varepsilon} + k_{\text{b}\varepsilon} + \beta\omega))f(\varepsilon) d\varepsilon. \quad (6)$$

If pressure stabilization is not competitive with dissociations, then $k_{\text{D}} = k_{\text{H}} = k_{\text{D}\infty} \langle k_{\text{f}\varepsilon}/(k_{\text{f}\varepsilon} + k_{\text{b}\varepsilon}) \rangle$.

There have been many RRKM [1–4,6–8], TST [9,10], trajectory [11], and purely electronic structure [12,13] calculations on the kinetics and reaction barrier of the $\text{H} + \text{C}_2\text{H}_4$ reaction. Several of these studies [6,9,10] have theoretically considered the isotopic modifications that involve deuterium and even muonium substitutions. Although there will be more detailed discussions of these previous studies in later sections, in general this theoretical work is based on electronic structure calculations with relatively small basis sets and/or restricted correlation. With increasing computer power, more computationally intensive electronic structure calculations can be carried out to remedy these deficiencies. As demonstrated recently in our analogous paper on $\text{H} + \text{C}_2\text{H}_2$ addition [14], high temperature deuterium addition measurements combined with computationally rigorous calculations can connect D and H addition measurements over the entire temperature range. The goal then of this present work was to develop models that can be used to explain the present data but also data that exist on analogous all-H modifications of the reaction.

In the present study, rate constants were measured using the thermal dissociation of $\text{C}_2\text{D}_5\text{I}$ as the source of D-atoms [15]. Both D-depletion and H-formation experiments were performed, and the experiments were carried out with a large excess of C_2H_4 so that the decay of D-atoms and the formation of H-atoms would be approximately pseudo-first-order.

2. Experimental

The present experiments, in Kr diluent, were performed with the reflected shock tube technique using atomic resonance absorption spectrometric (ARAS) detection. The method and the apparatus currently being used have been previously described [16,17]. Therefore, only a brief description of the experiment will be presented here.

The apparatus consists of a 7-m (4-in. o.d.) 304 stainless steel tube separated from the He driver chamber by a 4-mil unscored 1100-H18 aluminum diaphragm. The tube was routinely pumped between experiments to $<10^{-8}$ Torr by an Edwards Vacuum Products Model CR100P packaged pumping system. The velocity of the shock wave was measured with eight equally spaced pressure transducers (PCB Piezotronics, Model 113A21) mounted along the end portion of the shock tube, and temperature and density in the reflected shock wave regime were calculated from this velocity and include corrections for boundary layer perturbations [18–20]. The 4094C Nicolet digital oscilloscope was triggered by delayed pulses that derive from the last velocity gauge signal.

D- and H-atom ARAS detection was used to follow $[\text{D}]_{\text{t}}$ and $[\text{H}]_{\text{t}}$ quantitatively as described

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