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High-temperature kinetics of propyne and allene: Decomposition vs. isomerization

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Abstract

The kinetics of the unimolecular dissociation of propyne and allene, $C_3H_4 + M \rightarrow C_3H_3 + H + M$, was investigated behind reflected shock waves at temperatures between 1400 and 2150 K and at pressures near 0.3, 1.3, 2.6 (propyne only), and 4.0 bar with argon as bath gas. Rate coefficients were obtained from the initial slope of the hydrogen-atom concentration–time profiles monitored with atomic resonance absorption spectroscopy at the Lyman α wavelength (121.6 nm). Within the experimental uncertainty (±30%), identical rate coefficients for propyne and allene decomposition were obtained, indicating a fast mutual isomerization. The dissociation reactions are shown to be in the low-pressure limit with a bimolecular rate coefficient $k^{\mathrm{bim}}(T) = (3.4 \pm 1.0) \times 10^{12} \exp[-(36,300 \pm 400)\ \mathrm{K}/T]\ \mathrm{bar}^{-1}\ \mathrm{s}^{-1}$. From a combination of our experimental results with kinetic data from the literature, we infer the following temperature and pressure dependence of the rate coefficient, which reproduces most of the experimental data at temperatures between 1200 and 2400 K and pressures between 0.1 and 5 bar better than within a factor of two: $k(T,P) = 2.58 \times 10^{41} (T/\mathrm{K})^{-7.81} \exp(-50,590\ \mathrm{K}/T)(P/\mathrm{bar})\ \mathrm{s}^{-1}$. This corresponds to a bimolecular rate coefficient in concentration units of $k^{\mathrm{bim}}(T) = 3.56 \times 10^{19} (T/\mathrm{K})^{-6.81} \exp(-50,590\ \mathrm{K}/T)\ \mathrm{cm}^3\ \mathrm{s}^{-1}$.
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1. Introduction

Propyne ($H_3C\text{–}C{\equiv}CH$, pC_3H_4) and allene ($H_2C{=}C{=}CH_2$, aC_3H_4) are important species in hydrocarbon combustion and pyrolysis, because they are precursors for the propargyl radical (C_3H_3), which is considered a critical intermediate in the formation of the first aromatic ring from aliphatic fuels [1–5]. The propargyl radical can be formed from propyne and allene in bimolecular hydrogen-abstraction steps (which requires a sufficiently high radical concentration) and by thermal unimolecular decomposition:

$$pC_3H_4 + M \rightarrow C_3H_3 + H + M \tag{1}$$

$$aC_3H_4 + M \rightarrow C_3H_3 + H + M \tag{2}$$

The kinetics of these reactions at higher temperatures is influenced, however, by a mutual thermal unimolecular isomerization

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$$pC_3H_4 + M \rightleftharpoons aC_3H_4 + M \qquad (3)$$

and/or a bimolecular hydrogen atom-assisted isomerization [6–8]

$$pC_3H_4 + H \rightleftharpoons aC_3H_4 + H \qquad (4)$$

Again, the latter reaction is only important, if hydrogen atoms are present in a sufficiently high concentration. Different aspects of the competition between the thermal unimolecular reactions (1)–(3) have attracted considerable attention over the years [1,6,7,9–21].

In a recent work of Miller and Klippenstein [21], the different experimental results are reviewed and analyzed in terms of a time-dependent, multiple-well master equation. The authors conclude from an eigenvector–eigenvalue analysis that at temperatures $T > 1800$ K (for pressures around 1 bar) a distinction between reactions (1) and (2) in kinetic experiments becomes increasingly difficult due to rapid interconversion of the reactants in reaction (3). This is in accord with conclusions from earlier works [1,6,7,9–11,13–18]. Convenient expressions for the rate coefficient of reaction (3) are given in [7], e.g., for a pressure of $P = 1.013$ bar: $k_3(T, P = 1.013\ \text{bar}) = 5.2 \times 10^{60}(T/\text{K})^{-13.93} \exp(-45,800\ \text{K}/T)\ \text{s}^{-1}$, and an analogous equation for the reverse reaction (−3) can be found in [21]: $k_{-3}(T, P = 1.013\ \text{bar}) = 7.8 \times 10^{39}(T/\text{K})^{-7.80} \exp(-39,478\ \text{K}/T)\ \text{s}^{-1}$. Both parameterizations reproduce most of the earlier experimental results with reasonable accuracy [7,21]. For example, for a temperature of $T = 2000$ K, one obtains $k_3 = 6.1 \times 10^4\ \text{s}^{-1}$ and $k_{-3} = 3.7 \times 10^5\ \text{s}^{-1}$, which results in a relaxation time of $(k_3 + k_{-3})^{-1} \sim 2\ \mu\text{s}$, being short compared to the timescale of typical shock-tube experiments in the order of 100–1000 μs.

In contrast to the large number of works on reaction (3), experimentally determined rate coefficients for reactions (1) and (2) are scarce [1,6,15,20]. In a most early work in 1987, Wu and Kern [1] from a shock-tube study of allene pyrolysis ($T = 1300$–2000 K, $P = 0.2$–0.5 bar, bath gas: Ne) inferred rate coefficients by modeling concentration–time profiles of different reaction products in terms of a complex mechanism consisting of 80 reactions. Identical Arrhenius expressions $k_1^{\text{bim}} = k_2^{\text{bim}} = 1.0 \times 10^{17} \exp(-35,200\ \text{K}/T)\ \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ were employed, resulting in pseudo-first-order rate coefficients at $T = 2000$ K and $P = 1$ bar of $k_1 = k_2 = 1.4 \times 10^4\ \text{s}^{-1}$ considerably smaller than $(k_3 + k_{-3})$ given above.

Two years later, Hidaka et al. [15] studied propyne and allene pyrolysis in a shock tube ($T = 1200$–1570 K, $P = 1.7$ and 2.6 bar, bath gas: Ar) with time-resolved detection of the educts by IR emission and gas-chromatographic product analysis. Again a complex mechanism (34 reactions) was used for modeling, and the following temperature dependencies for the rate coefficients of reactions (1) and (2) were obtained from the fits: $k_1^{\text{bim}} = 4.7 \times 10^{18} \exp(-40,000\ \text{K}/T)\ \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ and $k_2^{\text{bim}} = 2.0 \times 10^{18} \exp(-40,000\ \text{K}/T)\ \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$. This results in pseudo-first-order rate coefficients at $T = 2000$ K and $P = 1$ bar of $k_1 = 5.8 \times 10^4\ \text{s}^{-1}$ and $k_2 = 2.4 \times 10^4\ \text{s}^{-1}$, again smaller than $(k_3 + k_{-3})$ given above and with $k_1 > k_2$.

In a combined experimental and theoretical study, Kiefer et al. [6] determined rate coefficients for reactions (1) and (2) from shock-tube studies ($T = 1800$–2500 K, $P = 90$–900 mbar, bath gas: Kr or Ne) with laser-schlieren and time-of-flight mass spectrometric detection and performed a RRKM analysis. These authors obtained rate coefficients $k_1(T, P)$ and $k_2(T, P)$ very close to each other but with k_1 slightly larger than k_2 and with surprisingly little pressure dependence (i.e., close to first-order). The latter was ascribed to a comparatively high density of states of pC_3H_4/aC_3H_4 due to extensive isomerization-hindered internal rotation [6] (see also the discussions in [18]). Unfortunately, no compact parameterizations of k_1 and k_2 are given in [6]. For the sake of comparison, we derived the following approximate expressions from Figs. 8 and 9 of [6] (neglecting the weak pressure dependence): $k_1^{\text{bim}} = 7.3 \times 10^{16} \exp(-31,800\ \text{K}/T)\ \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ and $k_2^{\text{bim}} = 1.1 \times 10^{17} \exp(-33,100\ \text{K}/T)\ \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$. From these Arrhenius expressions, we obtain for $T = 2000$ K and $P = 1$ bar: $k_1 = 5.5 \times 10^4\ \text{s}^{-1}$ and $k_2 = 4.3 \times 10^4\ \text{s}^{-1}$.

Finally, Scherer et al. [20] performed a shock-tube study ($T = 1300$–1700 K, $P = 1.7$–1.9 bar, bath gas: Ar), using atom resonance absorption spectroscopy to detect hydrogen atoms as a product of reactions (1) and (2). The following Arrhenius expressions were obtained: $k_1 = 1.34 \times 10^{12} \exp(-35,200\ \text{K}/T)\ \text{s}^{-1}$ and $k_2 = 2.3 \times 10^{12} \exp(-35,070\ \text{K}/T)\ \text{s}^{-1}$. From extrapolation to $T = 2000$ K and $P = 1$ bar, by assuming first-order pressure dependence, it follows: $k_1 = 1.7 \times 10^4\ \text{s}^{-1}$ and $k_2 = 3.1 \times 10^4\ \text{s}^{-1}$ with $k_2 > k_1$ in contrast to the results of [6,15].

As can be seen from our extrapolations to uniform conditions ($T = 2000$ K and $P = 1$ bar), all four experimental studies on reactions (1) and (2) appear to give grossly consistent kinetic data. However, it remains unclear whether reaction (1) or reaction (2) is faster, or if the isomerization reaction (3) is fast enough for both reactions to occur with virtually identical rates at least on practically relevant timescales. Since also no systematic study of the pressure dependence is available (apart from the study of Kiefer et al. for $T > 1800$ K and $P < 1$ bar [6]), and k_1 and k_2 were mostly obtained from complex modeling, we performed a shock-tube study over a comparatively broad pressure range and used direct detection of H atoms by atomic resonance absorption

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