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Unimolecular decomposition of formic and acetic acids: A shock tube/laser absorption study

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Abstract

The thermal decomposition of formic acid (HCOOH) and acetic acid (CH_3COOH), two carboxylic acids which play an important role in oxygenate combustion chemistry, were investigated behind reflected shock waves using laser absorption. The rate constants of the primary decomposition pathways of these acids:

$$HCOOH \rightarrow CO + H_2O \quad (R1)$$
$$HCOOH \rightarrow CO_2 + H_2 \quad (R2)$$
$$CH_3COOH \rightarrow CH_4 + CO_2 \quad (R3)$$
$$CH_3COOH \rightarrow CH_2CO + H_2O \quad (R4)$$

were measured using simultaneous infrared laser absorption of CO, CO_2 and H_2O at wavelengths of 4.56, 4.18 and 2.93 microns, respectively. Reaction test conditions covered temperatures from 1230 to 1821 K and pressures from 1.0 to 6.5 atm for dilute mixtures of acids (0.25–0.6%) in argon. The rate constants of dehydration (R1) and decarboxylation (R2) reactions of formic acid were calculated by fitting exponential functions to the measured CO, CO_2 and H_2O time-history profiles. These two decomposition channels were found to be in the fall-off region and have a branching ratio, k_1/k_2, of approximately 20 over the range of pressures studied here. The best-fit Arrhenius expressions of the first-order rates of R1 and R2 were found to be:

$$k_1(1\ \text{atm}) = 1.03 \times 10^{11}\ \exp(-25651/T)\ \text{s}^{-1}(\pm 37\%)$$
$$k_1(6.5\ \text{atm}) = 9.12 \times 10^{12}\ \exp(-30275/T)\ \text{s}^{-1}(\pm 32\%)$$
$$k_2(1\ \text{atm}) = 1.79 \times 10^{8}\ \exp(-21133/T)\ \text{s}^{-1}(\pm 41\%)$$
$$k_2(6.5\ \text{atm}) = 2.73 \times 10^{8}\ \exp(-20074/T)\ \text{s}^{-1}(\pm 37\%)$$

The rate constants for acetic acid decomposition were obtained by fitting simulated profiles, using an acetic acid pyrolysis mechanism, to the measured species time-histories. The branching ratio, k_4/k_3, was

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found to be approximately 2. The decarboxylation and dehydration reactions of acetic acid appear to be in the falloff region over the tested pressure range:

$k_3(1\ \text{atm}) = 3.18 \times 10^{11}\ \exp(-28679/T)\ \text{s}^{-1}(\pm 30\%)$

$k_3(6\ \text{atm}) = 3.51 \times 10^{12}\ \exp(-31330/T)\ \text{s}^{-1}(\pm 26\%)$

$k_4(1\ \text{atm}) = 7.9 \times 10^{11}\ \exp(-29056/T)\ \text{s}^{-1}(\pm 34\%)$

$k_4(6\ \text{atm}) = 6.34 \times 10^{12}\ \exp(-31330/T)\ \text{s}^{-1}(\pm 31\%)$.

Keywords: Formic acid; Acetic acid; Shock tube; Laser absorption; Rate constants

1. Introduction

Carboxylic acids are compounds which contain one or more carboxyl groups (COOH). They are readily formed during the pyrolysis and oxidation of large oxygenated species. This is particularly important in the modelling of ester-based bio-diesel fuels as carboxylic acids and ketenes are the main products of the pyrolysis of esters [1]. Formic acid (HCOOH) has been shown to be the main product of ethyl formate pyrolysis [2] and acetic acid (CH_3COOH) was observed to be a primary product of ethyl acetate decomposition [2,3]. Formic acid is also an important intermediate during the oxidation of dimethyl ether at low and intermediate temperatures [1] and acetic acid is the major product of acetic anhydride pyrolysis [4,5]. Accurate rate constant data describing the pyrolysis of formic and acetic acids are needed to build reliable kinetic mechanisms for large oxygenated fuels.

There are two main pathways for the decomposition of formic acid [6]; dehydration (R1), and decarboxylation (R2):

$$HCOOH \rightarrow CO + H_2O \quad (R1)$$

$$HCOOH \rightarrow CO_2 + H_2 \quad (R2)$$

A number of experimental [6–11] and theoretical [12–15] studies have been carried out on the decomposition of formic acid, including three shock tube studies. Hsu et al. [6] studied the decomposition of formic acid using infrared (IR) laser absorption of CO. They determined the rate constants of both reactions R1 and R2 using a non-linear least square fitting of the measured CO profiles. They found that the branching ratio, k_1/k_2, was ~10 at low temperatures and approaches 1 at 2000 K. Saito et al. [7] studied the thermal decomposition of formic acid in a shock tube using formic acid emission near 3.4 μm, CO emission near 4.6 μm and CO_2 emission near 4.23 μm. Their measurements found that the branching ratio, k_1/k_2, was of order 100 over the entire temperature range (1300–2000 K). The observed rate constant behaviour agreed with their calculations using the Rice–Ramsperger–Kassel–Marcus (RRKM) weak collision theory. In 2005, Saito et al. [8] reinvestigated the decomposition of the formic acid by monitoring the IR emission of formic acid monomer (5.66 μm), CO (4.63 μm) and CO_2 (4.23 μm). They noted that 10–20% of gaseous formic acid is converted to formic acid dimer, $(HCOOH)_2$, at room temperature and this concentration cannot be neglected. Rate constant results obtained from this study were in reasonable agreement with their previous study [7].

Similar to formic acid, there are two main pathways for the decomposition of acetic acid; decarboxylation (R3) and dehydration (R4):

$$CH_3COOH \rightarrow CH_4 + CO_2 \quad (R3)$$

$$CH_3COOH \rightarrow CH_2CO + H_2O \quad (R4)$$

Blake and Jackson [16,17] studied the acetic acid pyrolysis using static and flow systems at temperatures of 733–1053 K and pressures near 1 atm. They concluded that the decarboxylation reaction is first order while the dehydration reaction is second order below 873 K and it exhibits first order behaviour for higher temperatures. Mackie and Doolan [18] studied the thermal decomposition of acetic acid in a single-pulse shock tube. Using gas chromatograph and IR cell analysis of the product gases, they found that the acetic acid decomposed through the two competing pathways, R3 and R4, at approximately equal rates and both rates were first order. Saito et al. [3] used a shock tube to study the thermal decomposition of ethyl acetate which produces acetic acid and ethylene. The branching ratio, k_4/k_3, was measured by comparing the monitored IR emissions from CO_2 (4.23 μm) and H_2O (2.68 μm) and was found to be approximately unity. Another study by Butkovskaya et al. [19] used a flow reactor and IR emission of CO_2 and H_2O to study acetic acid decomposition. They concluded that the k_4/k_3 ratio was two and in agreement with the *ab initio* calculations of Nguyen et al. [20] and Duan and Page [21].