A kinetic study on the decay of formic acid produced by the thermal decomposition of ethyl formate

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Abstract. The thermal decomposition of ethyl formate diluted in argon has been investigated behind reflected shock waves over the temperature range 1220–1710 K, with a total density of $\sim 1.2 \times 10^{-5}$ mol/cm^3. Production and decay processes of formic acid were monitored by means of the time-resolved IR emission at 5.7 μm. The emission profiles were analyzed by utilizing the integrated profiles method developed by Yamasaki et al. The resultant first-order decay rate constant is expressed as $k = 10^{9.10} \exp(-40.7 \text{ kcal mol}^{-1}/RT)$ s^{-1}, which is in proper agreement with that for the pyrolysis of formic acid obtained by Blades at lower temperatures, but slightly lower than the estimated expression suggested by Benson and O'Neal. The formation rate for carbon dioxide, however, is found to be greatly accelerated compared to that with formic acid as a starting material, which attributes to the chemical activation of the intermediary produced formic acid.

1 Introduction

The thermal decomposition of esters with a β-hydrogen in the alkyl group provides the corresponding carboxylic acid and olefin through a six-centered cyclic transition structure [1]. For the decomposition of ethyl formate at elevated temperatures, the formic acid produced decays through two competing elimination channels, i.e., dehydration and decarboxylation:

$$\mathrm{HCOOC_2H_5} \rightarrow \mathrm{HCOOH} + \mathrm{C_2H_4} \tag{1}$$

$$\mathrm{HCOOH} \rightarrow \mathrm{CO} + \mathrm{H_2O} \tag{2}$$

$$\mathrm{HCOOH} \rightarrow \mathrm{CO_2} + \mathrm{H_2}\ . \tag{3}$$

In our previous study [2] we clearly observed chemical activation effect of the intermediary produced formic acid on the branching fraction of the successive two channels. It was found that the formic acid produced by the decomposition (1) has a tendency to react by the decarboxylation (3) as compared to the reaction of formic acid in thermal equilibrium. The tendency is remarkable as the initial pressure decreases.

The observed results were interpreted with ab initio molecular orbital calculations [2]: they were attributed to the displacement of a β-hydrogen along the reaction coordinate in the vicinity of the transition state for the initial step (1). The geometry and vibrational modes played a crucial role in selection of the successive competing reaction. Formic acid has two forms as to the conformation of the hydrogen atoms: *trans*- and *cis*-conformers. Dehydration (2) occurs from *trans*-HCOOH through a three-centered transition structure, while decarboxylation (2) takes place from *cis*-HCOOH through a four-centered transition structure. At the transition state of (1) the hydrogen forming the cyclic structure (β-hydrogen) has a large displacement vector. This large velocity can

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[⋆] Deceased.

induce hydrogen inversion after the C–H bond rupture to give a *cis*-form and the channel (3) proceeds.

The decay rate constant of ethyl formate was reported in the temperature range of 1000–1300 K from the time-resolved absorption of ethylene at 174.5 nm as [2]

$$k_1 = 10^{12.70} \exp(-48.5\,\mathrm{kcal\ mol^{-1}}/RT)\,\mathrm{s^{-1}},$$

which gives about 1.8 times larger values than the values suggested by Benson and O'Neal [3]. No kinetic studies on the decay of the produced formic acid, however, have been reported yet, except the branching fraction of CO_2 to CO formation [2]. Practical difficulty exists in the evaluation of the respective rate constants. A conventional way of the kinetic analysis is a nonlinear method or an approximate graphical method [4] for a consecutive reaction consisting of two first-order processes. Unfortunately, as often is the case when the growth and decay rate constants are not sufficiently different, the analysis fails to derive correct values, as demonstrated by Yamasaki and Watanabe [5] for evaluation of the rate constants for state-to-state vibrational energy transfer. An alternative new method, called integrated profiles method [5,6], was proposed and proved useful to obtain kinetic parameters properly. In the present study, in order to have more insight into the thermal decomposition of ethyl formate, we focus on the kinetic behavior of the intermediary produced formic acid and evaluate its decay rate constants by the application of the integrated profiles method.

2 Experimental

The experiments were performed in a pressure-driven shock tube made of stainless steel. Apparatus and procedures employed in the present study were basically the same as those described previously [7,8]. The driven section is 3.67 m long with a 9.4-cm i.d. and is evacuated by a 6-inch oil-diffusion pump to less than 1×10^{-4} Pa before each run. It is separated from the driver section by a polyester diaphragm. Shock waves are generated by bursting the diaphragm with a needle. Three pressure transducers are mounted flush with the inside wall 160 mm apart near the end of the driven section. One of them is used as a trigger of the recording system, and the others are for the measurement of the incident shock speed which is determined by counting the time intervals of shock-arrival signals with a universal counter (Iwatsu, SC-7201).

All experiments were employed behind reflected shock waves. Reflected shock conditions for each run were calculated from the measured incident shock speed by use of the shock relations for the ideal gas. Production and decay processes of formic acid were monitored by means of the time-resolved IR emission through an MgF_2 window mounted on the tube walls 2 cm upstream from the end plate. The IR radiation was passed through a band-pass interference filter and was detected by a photoconductive HgCdTe element cooled at 77 K. The output signal was amplified (Iwatsu, DA-2A) and fed into a digital storage oscilloscope (Kawasaki Electronica, KDS-103) controlled by a personal computer. The obtained emission profile was saved in a disk and analyzed to obtain kinetic parameters.

Ethyl formate for the experiments was purchased from Wako Pure Chemical Industries, Ltd. and was carefully degassed under vacuum by repeated freeze–pump–thaw cycles. After the first fraction was pumped off, the sample was expanded into an evacuated glass flask, diluted with Ar (99.9995 % purity) to 0.10–0.20 mol % and stored.

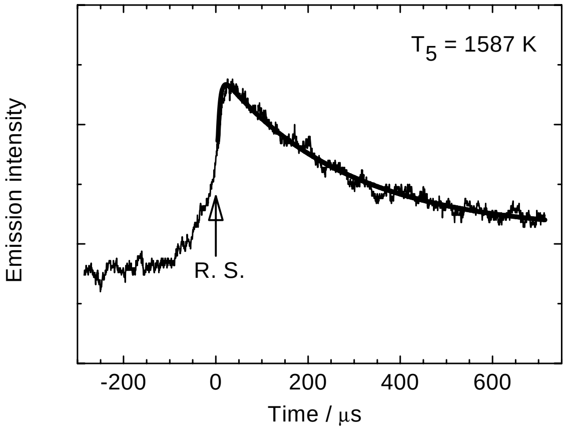

Fig. 1. A typical IR emission profile at 5.7 μm. A thick line drawn from the reflected shock arrival is a fitting result to the measured profile (thin line) analyzed by the integrated profiles method.

3 Analysis Method

Two types of temporal profiles were observed in the present study. In lower temperature regime below 1350 K, the emission intensity increases exponentially with time behind the reflected shock front. The profile is typical for the first-order formation of a product. Evaluation of the rate constant is straightforward in this regime, although we can see some contribution from decomposition by the incident shock heat. At higher temperatures, on the other hand, the emission intensity increases fast and then gradually decreases with time. The profile corresponds to the temporal change of concentration of an intermediate in a consecutive reaction. Figure 1 shows a typical IR emission profile at 1587 K.

The first-order rate constant for the second step can be accurately evaluated from the profile by the application of the integrated profiles method suggested recently by Yamasaki and Watanabe [5]. It is noted at the present point that the emission intensity does not go to zero but to a certain constant value towards the end of the shock heating time. This is due to the contribution from the emission from H_2O (R-branch of ν_2) formed by the decomposition of the intermediate formic acid. This factor was taken into account in the analysis to incorporate into the original equation, and a modified equation for the present analysis was obtained as described below.

The equation to analyze the observed profiles is formulated as follows. We can set up the following equations with respect to the signal intensity of each species:

$$I_{\mathrm{HCOOH}}(t) = I_{\mathrm{HCOOH}}(0) + \beta k_1 \int_0^t [\mathrm{HCOOEt}]dt - (k_2 + k_3) \int_0^t I_{\mathrm{HCOOH}}(t)dt \ , \quad (4)$$

$$I_{\mathrm{H_2O}}(t) = \frac{\gamma}{\beta} k_2 \int_0^t I_{\mathrm{HCOOH}}(t)dt \ , \quad (5)$$

where β and γ are proportionality constants to relate the signal intensities to the concentrations of HCOOH and H_2O, respectively, and k_i is the rate constant for reaction

(i). The emission profile at 5.7 µm is expressed as the sum of (4) and (5):

$$I_{5.7\mu}(t) = I_{\mathrm{HCOOH}}(t) + I_{\mathrm{H_2O}}(t)\ . \tag{6}$$

Equation (6) is an integral equation and contains $I_{\mathrm{HCOOH}}(t)$ which cannot be obtained in the present measurements. Thus, $I_{\mathrm{HCOOH}}(t)$ is expressed here as a function of $I_{5.7\mu}(t)$ by differentiating Eq. (6). The result is

$$I_{\mathrm{HCOOH}}(t) = I_{5.7\mu}(t) - \frac{\gamma}{\beta}k_2 \exp\left(-\frac{\gamma}{\beta}k_2 t\right)\int_0^t \exp\left(\frac{\gamma}{\beta}k_2 t'\right) I_{5.7\mu}(t')dt'\ .$$

The emission profiles can be therefore analyzed to evaluate the rate constants for the decay of formic acid according to the following equation:

$$\begin{aligned} &I_{5.7\mu}(t) \\ &= I_{5.7\mu}(0) + \beta k_1 \int_0^t [\mathrm{HCOOEt}]dt' - \left\{\left(1-\frac{\gamma}{\beta}\right)k_2 + k_3\right\}\int_0^t I_{5.7\mu}(t')dt' \\ &+ \left\{\left(1-\frac{\gamma}{\beta}\right)k_2 + k_3\right\}\frac{\gamma}{\beta}k_2 \int_0^t \exp\left(-\frac{\gamma}{\beta}k_2 t'\right)\int_0^{t'} \exp\left(\frac{\gamma}{\beta}k_2 t''\right) I_{5.7\mu}(t'')dt''dt'\ . \end{aligned} \tag{7}$$

Unknown parameters are β, k_2, and k_3 here. We employed a nonlinear regression analysis to the profiles and determine these parameters. The fitted result for the typical example is also shown in Fig. 1 as a thick line.

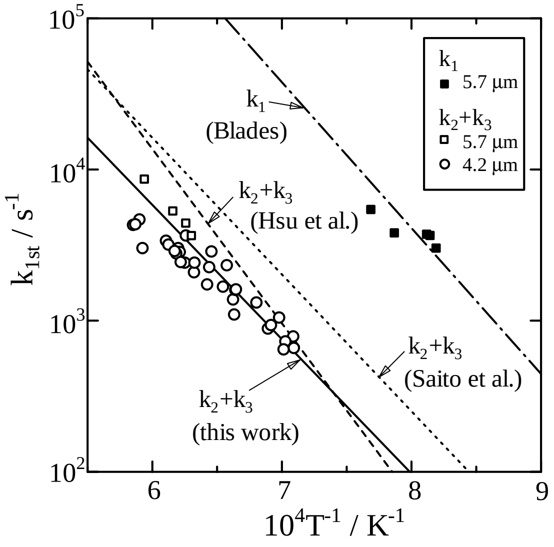

Fig. 2. Arrhenius plot of the rate constants for the production (k_1) and decay (k_2+k_3) of formic acid. Lines for k_2+k_3 except this work indicate the pyrolysis rate constants with formic acid as a starting material.

4 Results and Discussion

The kinetic parameters were obtained from the runs in the temperature range of 1220–1710 K, with a total density of $\sim 1.2 \times 10^{-5}$ mol/cm^3. Figure 2 shows the Arrhenius plot of the first-order rate constants for the production and decay of formic acid. Also shown in Fig. 2 are the data obtained from CO_2 emission profiles at 4.2 µm. In lower temperature regime below 1350 K, the obtained first-order rate constants agree with the extrapolation of the experimental data reported by Blades at lower temperatures [9] and slightly lower than the estimated value suggested by Benson and O'Neal [3]. At higher temperatures, the total decay rate constant of the formic acid produced by the thermal decomposition of ethyl formate, $k_2 + k_3$, obtained in this study is expressed as

$$k_2 + k_3 = 10^{9.10} \exp(-40.7\,\mathrm{kcal\,mol^{-1}}/RT)\,\mathrm{s^{-1}}.$$

The activation energy is lower than the value reported by Hsu et al. in the study on the pyrolysis of formic acid [10] by about 10 kcal/mol, but the rate constants are similar each other. The present rate constant is about three times slower than that for the pyrolysis of formic acid obtained by Saito et al. [11]. We feel that the data in Ref. [11] have a tendency to give slightly faster rates. There is a possibility of having an error in the present data arising from the estimation of contribution from water in the measured profiles. However, the $k_2 + k_3$ data obtained with the 5.7-µm profiles agree well with the 4.2-µm emission data (CO_2 production) in a series, demonstrating the acuracy of the integrated profiles method and our data points. It is worth noticing that in the present analysis we can evaluate the rate constants for the respective decay channels (2) and (3) from the profiles without knowing absolute concentrations of the final products. The

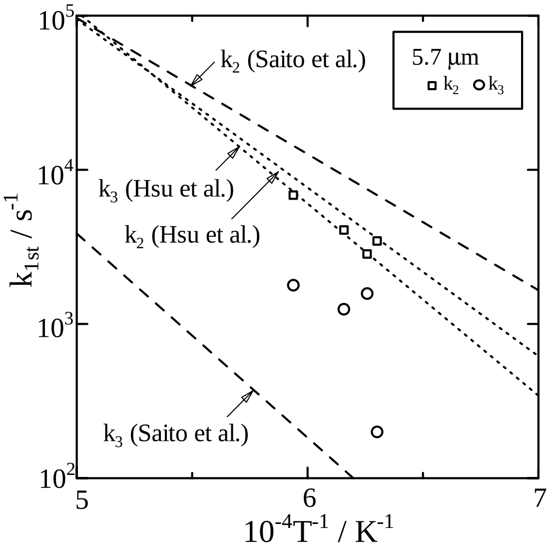

Fig. 3. Arrhenius plot of the rate constants for the each decay channel of the intermediary produced formic acid. Lines indicate the pyrolysis rate constants with formic acid as a starting material.

$k_2 + k_3$ data are simply calculated as the sum of k_2 and k_3 obtained from the analysis of the 5.7-µm profiles.

Figure 3 displays the Arrhenius plot of k_2 and k_3 for the decay of formic acid. The lines in Fig. 3 indicate the rate constants with formic acid as a reactant. They are different between two groups, especially in the k_3 values. Hsu et al. [10] obtained the rate constant k_3 indirectly from the CO concentration profiles, because in their measurement system they could not monitor the CO_2 production. We infer that their k_3 is less accurate due to error propagation. Saito et al. [11] found that the amount of the CO_2 production by the pyrolysis of formic acid was not more than a few percent of the CO production.

The present data for the smaller rate constant k_3 scatter, but the data are about an order of magnitude larger in the reaction from the ester than in the reaction starting from formic acid. This illustrates further evidence about chemical activation of the formic acid produced from ethyl formate.

In summary, we obtained the total decay rate constant of the formic acid produced by the thermal decomposition of ethyl formate by means of the time-resolved measurement of the IR emission at 5.7 µm, followed by the analysis with the integrated profiles method. The data together with the emission data from CO_2 were summarized as the Arrhenius expression, $k_2 + k_3 = 10^{9.10} \exp(-40.7\ \mathrm{kcal\ mol^{-1}}/RT)\ \mathrm{s^{-1}}$. The CO_2 production rate is found to be about an order of magnitude accelerated, compared to that of the reaction initiating from formic acid. This evidence endorses our statement suggested in Ref. [2].

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