# Shock Tube Study on the Thermal Decomposition of Ethanol

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Ⓢ *Supporting Information*

ABSTRACT: The thermal decomposition of C_2H_5OH highly diluted in Ar (1 and 3 ppm) has been studied by monitoring H atoms using the atomic resonance absorption spectrometry (ARAS) technique behind reflected shock waves over the temperature range 1450−1760 K at fixed pressure: 1, 1.45, and 2 atm. The rate constant and the product branching fractions have been determined by analyzing temporal profiles of H atoms; the effect of the secondary reactions on the results has been examined by using a detailed reaction mechanism composed of 103 elementary reactions. The apparent rate constant of ethanol decomposition can be expressed as $k_1/s^{-1} = (5.28 \pm 0.14) \times 10^{10} \exp[-(23\,530 \pm 980)/T]$ $(T = 1450-1670$ K, $P = 1-2$ atm) without a detectable pressure dependence within the tested pressure range of this study. Branching fractions for producing $CH_3 + CH_2OH$ (1a) and $H_2O + C_2H_4$ (1b) have been examined by a quantitative measurement of H atoms

produced in the successive decompositions of the products CH_2OH (1a): the pressure dependence of the branching fraction for channel 1a is obtained by a linear least-squares analysis of the experimental data and can be expressed as $\varphi_{1a} = (0.71 \pm 0.07) - (826 \pm 116)/T$, $(0.92 \pm 0.04) - (1108 \pm 70)/T$, and $(1.02 \pm 0.10) - (1229 \pm 168)/T$ for $T = 1450-1760$ K, at $P = 0.99$, 1.45, and 2.0 atm, respectively. The rate constant obtained in this study is found to be consistent with previous theoretical and experimental results; however, the pressure dependence of the branching fraction obtained in this study is smaller than those of previous theoretical works. Modification of the parameters for the decomposition rate in the falloff region is suggested to be important to improve the practical modeling of the pyrolysis and combustion of ethanol.
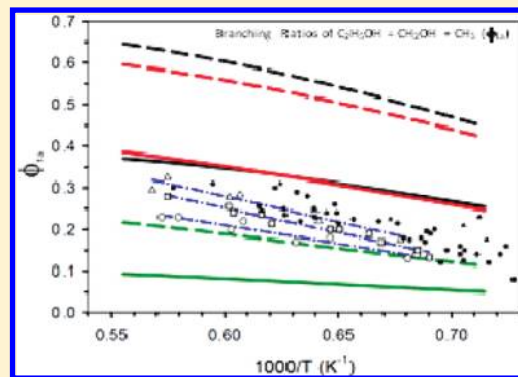
1. INTRODUCTION

Because of the increasing demand for environmentally clean renewable energy sources, the pyrolysis and combustion of alcohol fuels are the targets of investigation both in fundamental kinetic studies and application to practical combustion systems. Ethanol (C_2H_5OH) is one of the most versatile renewable energy sources. It is already being used as a neat fuel, as an oxygenate additive, or as a fuel extender in gasoline. Hence the detailed investigation of ethanol decomposition

$$C_2H_5OH(+ M) \rightarrow \text{products} \qquad (1)$$

has been regarded to be important, and several experimental and theoretical studies have been conducted. Park et al.[1] examined 11 possible decomposition channels in their theoretical calculations based on the potential energies obtained by the G2M method using a microcanonical variational RRKM code.[2] They concluded that the reactions 1a and 1b are predicted to be dominant in a high-temperature and moderate-pressure range

$$C_2H_5OH \rightarrow CH_2OH + CH_3 \qquad (1a)$$
$$\rightarrow C_2H_4 + H_2O \qquad (1b)$$
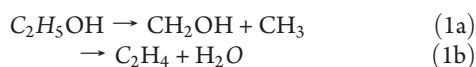
Also a minor but certain contribution from channel 1c is indicated under high-pressure conditions

$$C_2H_5OH \rightarrow C_2H_5 + OH \qquad (1c)$$
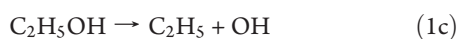
Park et al. also examined the rate constant for 1a and 1b, k_{1a} and k_{1b}, by conducting a pyrolysis experiment in a quartz reactor employing Fourier transform infrared (FTIR) spectrometry for product analyses and the measurement of $[H_2O]_t$ and $[CO]_t$ profiles using cw CO lasers by shock tube study at high temperature.[3] The experimental data displayed good agreement with predicted theoretical calculation and some of the previous experimental results.[4−8]

Marinov constructed a detailed kinetic model of ethanol pyrolysis and oxidation so as to examine experimental results of the shock-induced ignition of rich ethanol mixtures.[8] Tsang examined the rate constants for the three channels 1a−1c based on existing experimental and estimated results.[9] Li et al. supplied experimental data on k_{1b} by monitoring ethanol pyrolysis using a flow reactor at 1.7−3.0 atm and 1045−1080 K.[10] They also conducted calculation based on the multichannel RRKM model to compare with their experimental results. Reaction 1c was not taken into consideration in their calculation. At high temperatures, the calculated k_{1a} agreed well with the value of Park et al.; however, the calculated k_{1b} displayed a higher value than that of Park et al.[1]

Recently, Sivaramakrishnan et al. performed both experiments (shock tube experiments/OH optical absorption and H-ARAS detection) and theoretical calculation (ab initio transition state theory-based master equation) to study the kinetics of ethanol decomposition.[11] They conducted experiments at low concentration of ethanol to reduce the effects of the secondary reactions, and the rate constants k_{1a} and k_{1c} were measured directly by monitoring H and OH concentrations. They concluded that the branchimg fraction of 1c was very small; the main channels of thermal decomposition of C_2H_5OH are 1a and 1b under the experimental conditions of their study; this is consistent with the previous theoretical investigation by Park et al.[1]

As a summary of the previous studies on the thermal decomposition of ethanol, the total rate k_1 is in the falloff region at around 1 atm showing fairly good agreement in the published experimental and theoretical studies, and the contribution of the branching fraction 1c has been concluded to be minor at moderate combustion condition ($T = 1000-2000$ K at around 1 atm). Although the branching fractions of the main channels 1a and 1b are suggested to have fairly large pressure dependence in all the previous theoretical works, they are not consistent with each other and experimental evidence to examine such discrepancies is still insufficient.

The objective of this study is to obtain information on the total rate and the branching fraction of ethanol decomposition by employing very low concentrations (1 and 3 ppm C_2H_5OH diluted in Ar) to minimize the influence from side reactions. Utilizing the advantage of the diaphragmless shock tube, it is possible to achieve measurements at a fixed pressure over a wide temperature range. A special concern in this study is on the examination of the pressure dependence indicated in previous studies. A shock tube/H-ARAS technique is used to monitor H atoms behind reflected shock waves at high temperature (1450−1760 K) under 1, 1.45, and 2 atm Ar pressures.

2. EXPERIMENTS

A diaphragmless shock tube apparatus (length 5.9 m and i.d. 7.6 cm) with an atomic resonance absorption spectrometry (ARAS) detection system has been used to study the kinetics of ethanol decomposition at high temperature. The details of experiments have been described in previous studies.[12,13] For the measurements of temporal profiles of [H], resonant atomic absorption of H atoms corresponding to transition $[^2P-^2S_{1/2}(2p-1s)]$ at 121.6 nm was monitored using a microwave-discharge lamp with a flowing gas mixture of 1% H_2 in He, filtered with a vacuum UV monochromator and detected by a solar-blind photomultiplier tube (PMT). The light passes perpendicularly through the MgF_2 windows at 4 cm upstream of the end plate of the shock tube.

The high sensitivity for H-atom detection technique has been proven to be useful for studies on detailed elementary reactions in our previous report.[13] Before each series of runs, careful baking and pumping of the shock tube and the vacuum lines for a sufficient long period (typically 3−7 days), as well as the blank tests using shock-heated pure Ar, were the essential and routine procedure in this study. The blank tests were repeatedly conducted so as to confirm no detectable trace of H atom (less than 10^{11} atom cm^{-3}) for pure Ar is produced in the reflected shock-wave condition of concern. It is convincing that reliable results can be obtained only by repeating such time-consuming procedures for the kinetic studies conducted in our group using very low concentration of sample gas.

Decomposition of C_2H_5I was used to construct a calibration curve of the concentration of H atoms, as C_2H_5I supplies H atom quickly with $\varphi = 0.90 \pm 0.02$ at high temperature.[14,15] Several mixtures of C_2H_5I in Ar were shock heated over a wide temperature range. For the tests using high concentration of C_2H_5I (above 10^{13} molecules cm^{-3}), temporal absorption intensity shows slow decay due to the secondary reaction: H + HI → H_2 + I. In this case, linear extrapolation of the signal intensity of H atoms back to $t = 0$ (arrival of the reflected shock wave) was employed to cancel the effect. The concentration of H atoms is expressed by the equation

$$[H]/10^{13} \text{atomcm}^{-3} = (0.3816A^3 - 0.0025A^2 + 0.6141A)F(T) \tag{I}$$

in which the absorbance $A = \ln(I_0/I)$, where I_0 and I denote the light intensity before and after production of H atoms, respectively, and $F(T)$ denotes the temperature dependence given as $F(T) = (147.8/T) + 0.931$. The accuracy of this correlation becomes poor for $[H] > 2 \times 10^{13}$ atom cm^{-3} due to the saturation of absorption; therefore, most experiments in this study were carried out below this range.

The experiments were conducted by using sample mixtures of 1 and 3 ppm C_2H_5OH diluted in Ar. The thermal decomposition of C_2H_5OH was carried out under three different pressures (0.99 ± 0.02, 1.45 ± 0.02, and 2.02 ± 0.02 atm) over 1450−1760 K. All the experimental conditions are summarized in Table 1.

He (99.9995%, AGA Specialty Gases), Ar (99.9995%, AGA Specialty Gases), and H_2 (99.999%, BOCLH Industrial Gases) were used without further purification. C_2H_5OH (99.8%, Mallinckrodt, Analytical Reagent grade) was purified by passing the vapor through molecular sieves to remove trace water impurity. C_2H_5I (99%, Sigma-Aldrich, Reagent Plus grade) was purified by repeated degassing by successive freezing and pumping cycles.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Product Branching Fraction. Although a direct channel to produce H atoms in the thermal decomposition of C_2H_5OH is negligible as pointed out by Park et al.,[1] the products of channel 1a (CH_2OH) and 1c (C_2H_5) decompose quickly and supply H atoms through eqs 2 and 3 at elevated temperatures over 1000 K, i.e.

$$CH_2OH + M \rightarrow CH_2O + H + M \tag{2}$$

$$C_2H_5 + M \rightarrow C_2H_4 + H + M \tag{3}$$
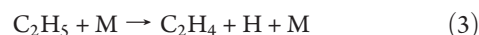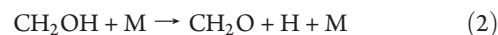
An example of the observed temporal profile produced in the 3 ppm C_2H_5OH in Ar is shown in Figure 1. After the reflected shock waves pass through the detection system, the concentration of H shows exponential rise to the steady level $[H]_\infty$. As already confirmed in the previous studies,[1,11] contribution of 1c to produce H atoms is much smaller than 1a, so 1c is not taken into consideration in the analysis of the present experiment.

If the concentration of C_2H_5OH is sufficiently low, the branching fraction of 1a, φ_{1a}, can be expressed with good accuracy by the simple relation

$$\phi_{1a} = k_{1a}/k_1 = [H]_\infty/[C_2H_5OH]_0 \tag{II}$$

where $[C_2H_5OH]_0$ is the concentration of C_2H_5OH at $t = 0$. By measuring $[H]_\infty$, φ_{1a} can be evaluated in a straightforward manner at high temperatures as shown in Figure 1. The production rate is not fast enough in the low-temperature range to

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Table 1. Summary of the Experimental Conditions for Thermal Decomposition of C_2H_5OH at (A) 0.99 ± 0.02 (B) 1.45 ± 0.02, and (C) 2.02 ± 0.02 atm

	(A)				
C_2H_5OH (ppm)	$\rho_5(C_2H_5OH)/$ 10^{13} [a]	$\rho_5(Ar)/$ 10^{18} [a]	T_5/K	k_1/s[b]	φ_{1a}
1.00	0.41	4.08	1725		0.23
1.00	0.44	4.36	1644	42400 ± 12550	0.22
1.00	0.46	4.59	1547	12900 ± 1800	0.18
1.00	0.51	5.07	1461	4260 ± 535	0.14
3.00	1.23	4.11	1748		0.23
3.00	1.31	4.36	1659	40400 ± 5100	0.20
3.00	1.40	4.65	1584	18800 ± 1000	0.17
3.00	1.53	5.09	1469	5580 ± 2295	0.13

	(B)				
C_2H_5OH (ppm)	$\rho_5(C_2H_5OH)/$ 10^{13}	$\rho_5(Ar)/$ 10^{18}	T_5/K	k_1/s	φ_{1a}
1.00	0.60	5.95	1740		0.28
1.00	0.64	6.39	1662	34600 ± 6850	0.26
1.00	0.67	6.68	1623	27200 ± 4500	0.24
1.00	0.68	6.79	1537	13100 ± 6440	0.20
1.00	0.71	7.06	1507	9870 ± 2315	0.19
1.00	0.74	7.39	1460	6130 ± 555	0.15
3.00	1.91	6.37	1656	30600 ± 9550	0.24
3.00	2.00	6.66	1611	18800 ± 7900	0.21
3.00	2.04	6.79	1547	10700 ± 3315	0.20
3.00	2.11	7.03	1495	6790 ± 1635	0.17
3.00	2.20	7.35	1449	5000 ± 845	0.13

	(C)				
C_2H_5OH (ppm)	$\rho_5(C_2H_5OH)/$ 10^{13}	$\rho_5(Ar)/10^{18}$	T_5/K	k_1/s	φ_{1a}
1.00	0.84	8.43	1760		0.30
1.00	0.90	8.96	1661	43900 ± 16450	0.28
1.00	0.95	9.50	1559	12900 ± 1100	0.22
3.00	2.52	8.38	1740		0.33
3.00	2.68	8.92	1648	33400 ± 12000	0.28
3.00	2.86	9.51	1563	14200 ± 5585	0.25
3.00	3.04	10.1	1476	7490 ± 610	0.18

[a] Unit of molecules per cubic centimeter. [b] Rate coefficient with limit of errors obtained by numerical simulation (see text).

measure directly the steady level of H atom within 500 μs (which is assigned as the upper limit to avoid perturbation caused by the reflected shock wave—contact surface interaction). In such a case, $[H]_\infty$ was evaluated by fitting the observed profile of H atoms to a simple exponential function vs time.

At the beginning of this study, sample gas was prepared with the standard simple procedure: Nominal concentration of C_2H_5OH was determined from pressure measurements by using Baratron capacitance manometers, but it is worthwhile to note that real $[C_2H_5OH]_0$ was found to have a non-negligible deviation from the nominal value. It was found that the evaluated results on φ_{1a} were inconsistent for the different concentration samples with one another. The loss on the wall of the sample cylinders (made of stainless steel) was supposed to be the reason. Therefore, in order to reduce the
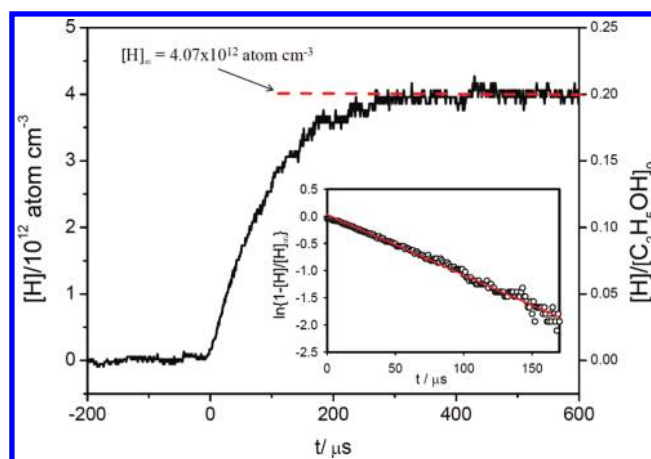

Figure 1. Example of the temporal profile of H atoms observed behind a reflected shock wave for 3 ppm C_2H_5OH in Ar: T = 1547 K, P = 1.45 atm; the inset is the analysis of the first-order rate by using eq II, where the red straight line is the result of analysis given by the linear least-squares fitting of the experimental data.

effect of loss, higher concentration sample gas (1000 ppm C_2H_5OH in Ar) was initially introduced into the sample cylinder to purge the wall for about 30 min and evacuated again to a sufficiently high vacuum level, and then sample gas (1 and 3 ppm C_2H_5OH in Ar) was prepared by the standard procedure of pressure measurement. With this treatment, the magnitude of evaluated φ_{1a} in different concentration samples became stable and consistent with one another.

The result of measured φ_{1a} determined after such treatment is shown in Table 1. The experimental data for T = 1450−1760 K can be summarized by a linear least-squares analysis as

$$\phi_{1a} = (0.71 \pm 0.07) - (826 \pm 116)/T$$
$$(P = 0.99 \pm 0.02 \text{ atm}) \qquad \text{(III-1)}$$

$$\phi_{1a} = (0.92 \pm 0.04) - (1108 \pm 70)/T$$
$$(P = 1.45 \pm 0.02 \text{ atm}) \qquad \text{(III-2)}$$

$$\phi_{1a} = (1.02 \pm 0.10) - (1229 \pm 168)/T$$
$$(P = 2.02 \pm 0.02 \text{ atm}) \qquad \text{(III-3)}$$

The present result is summarized in Figure 2 and compared with previous theoretical and experimental results.[1,10,11] The experimental data on φ_{1a} in this study were found to be noticeably smaller than the theoretical values of Park et al.[1] and Sivaramakrishnan et al.[11] but larger than that of Li et al.[10] Also the present result is slightly smaller than the experimental result of Sivaramakrishnan et al.[11] Although the results for the different concentrations of C_2H_5OH are consistent with each other through the pretreatment of the shock tube with the sample gas, it may not guarantee to have the accurate concentrations. For the case of CH_3OH, the initial concentration could be accurately evaluated by conducting comparative measurements of H atoms for the same CH_3OH sample with excess H_2 (since all the radical products can be converted to H atoms corresponding to two times of the initial concentration of CH_3OH, regardless of the products branching).[13] Such a method cannot be applied to the present case of C_2H_5OH; a possible uncertainty in the initial concentration of C_2H_5OH may be one of the reasons for the slight difference in our result from that of Sivaramakrishnan et al.[11]
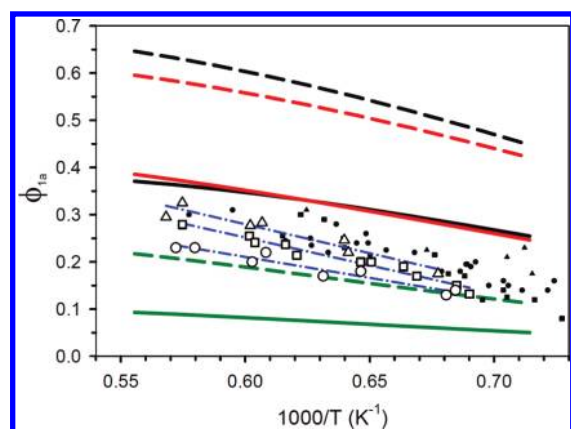
Figure 2. Branching ratios of H-atom production channel 1a obtained by using the first-order analysis at 1450−1760 K compared with previous works. Present work: ○, 1 and 3 ppm C_2H_5OH in Ar at P = 0.99 ± 0.02 atm; □, 1 and 3 ppm C_2H_5OH in Ar at P = 1.45 ± 0.02 atm; Δ, 1 and 3 ppm C_2H_5OH in Ar at P = 2.02 ± 0.02 atm. The blue dash-dot line is the linear least-squares analysis of the present data for the three pressure ranges. Solid and dashed curves (black): Park et al.[1] at P = 1 and 10 atm, respectively; solid and dashed curves (green): Li et al.[10] at P = 1 and 10 atm, respectively; solid and dashed curves (red): Sivaramakrishnan et al.[11] at 1 and 10 atm, respectively; ▲, ■, ●, experimental work of Sivaramakrishnan et al.[11] at P = 0.95−1.29, 0.49−0.79, and 0.2−0.5 atm, respectively.

Pressure dependence of φ_{1a} measured in the present experiment is indicated to be consistent with those theoretical predictions given by Park et al.[1] and Sivaramakrishnan et al.[11] Also, the experimental result on the pressure dependence by Sivaramakrishnan et al.[11] obtained in the lower pressure range (0.2−1.28 atm) seems to be consistent with the present study.

3.2. Thermal Decomposition Rate. For the highly diluted sample gas, the first-order total rate constant k_1 can be approximately given by the equation

$$ln(1 - [H]/[H]_\infty) = -k_1 t \qquad (IV)$$

An example of the first-order analysis is displayed in the inset in Figure 1. As the very low concentration of C_2H_5OH (1 and 3 ppm in Ar) is used in this study, evaluating k_1 by using the simple analysis with IV seems to be a reasonable approximation. However, in order to reduce the uncertainty caused by the secondary reactions, numerical simulation (using a reaction mechanism shown in Table S1 of the Supporting Information) was conducted to determine k_1. Here, the construction of the reaction mechanism was based on the previous kinetic studies on thermal decomposition of C_2H_5OH and simple hydrocarbons.[11,13,16−22]

The empirical correlation III-1−III-3 of φ_{1a} presented in the previous paragraph was retained in the numerical simulation as restricted conditions, i.e., $k_{1a} = \varphi_{1a}k_1$ and $k_{1b} = k_1 - k_{1a} - k_{1c}$, where k_{1c} was given by the theoretical results by Sivaramakrishnan et al.[11] By comparing profiles of H atoms obtained by the numerical simulation with the experiment, the total rate k_1 was determined so that the best fit to the experimental profile was achieved; i.e., the integration of the normalized deviation from experimental profiles of [H] became minimum. The error limit for the estimated rate was evaluated by assuming Gaussian distribution for the integration of the normalized deviation against variation of k_1. The sensitivity analysis for H atoms was
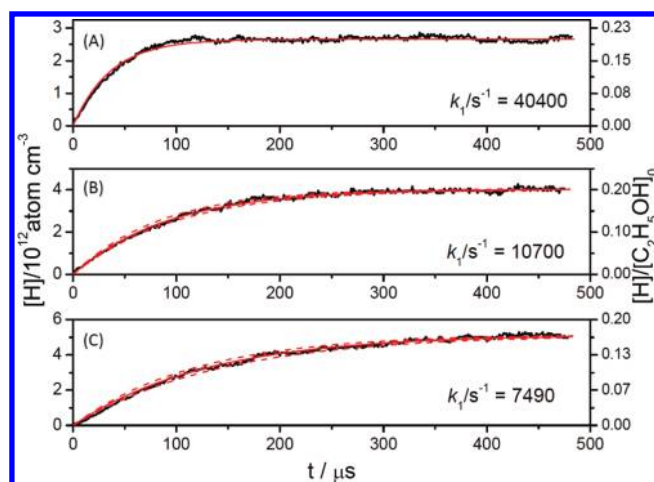

Figure 3. Comparison of observed [H] profiles with those obtained by numerical simulation. (A) 3 ppm C_2H_5OH in Ar at T = 1659 K and P = 0.99 atm, (B) 3 ppm C_2H_5OH in Ar at T = 1547 K and P = 1.44 atm, and (C) 3 ppm C_2H_5OH in Ar at T = 1476 K and P = 2.04 atm. The best fit profiles using the numerical simulation are shown by red solid curves. The results of numerical simulation with ±10% of the center value of k_1 are shown by red dotted lines in (B) and (C).

also performed to examine the effect of the secondary reactions. (An example of such analysis is shown in Figure S1 of the Supporting Information.) Examples of the [H] profiles compared with numerical simulations are shown in Figure 3.

For the experimental data on k_1 at ∼1650 K, the time resolution of the detection system is not sufficiently fast enough to analyze in a straightforward way. Observed profile $h(t)$ in this case should be the convolution of real profile $f(t)$ and the time resolution function of the detection system $g(t)$, i.e., $h(t) = f(t)g(t)$. The latter can be given by measuring the profile of H atoms produced in the thermal decomposition of C_2H_5I in the same detection system, because the reaction to supply H atoms should be very fast (less than 1 μs). From the observed profile of H atoms in C_2H_5I, the time resolution function can be well represented by a simple relation $g(t) = 1 - \exp(-t/\tau)$ with τ = 23 μs. The real profile representing the thermal decomposition of C_2H_5OH, $f(t)$, could be evaluated by deconvoluting the observed profile $h(t)$ with $g(t)$. In Figure 3a, an example at 1659 K is displayed inversely; i.e., the experimental profile of [H] (black solid line) is compared with the convoluted profile of numerical simulation (red solid line).

The present convolution/deconvolution process cannot be applied for the higher temperature data (1700−1750 K) where the time constant of the first-order decomposition becomes much closer to that of the detection system; also such a procedure was not necessary for the data below 1600 K as shown in Figure 3b and 3c, where the raw data of the numerical simulation are directly compared with the experiment. Also numerical simulations assuming ±10% of the center value of k_1 are shown by red dotted lines for comparison.

The rate constant k_1 determined as described above is shown in Table 1 and summarized in Figure 4 compared with previous theoretical and experimental results. It is confirmed that the results obtained by the simple first-order analysis IV shows very small deviation (smaller than the estimated error limit of the individual data point) from those of numerical simulation for the present experimental condition; therefore, the branching fraction
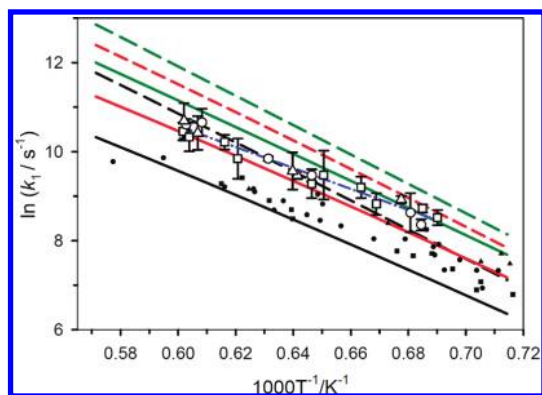
Figure 4. Summary of the experimental and theoretical studies on k_1. Present work: ○, 1 and 3 ppm C_2H_5OH in Ar at $P = 0.99 \pm 0.02$ atm; □, 1 and 3 ppm C_2H_5OH in Ar at $P = 1.45 \pm 0.02$ atm; △, 1 and 3 ppm C_2H_5OH in Ar at $P = 2.02 \pm 0.02$ atm. The blue dash-dot line is the linear least-squares analysis of the present data. Solid and dashed curves (black): Park et al.[1] at $P = 1$ and 10 atm, respectively; solid and dashed curves (green): Li et al.[10] at $P = 1$ and 10 atm, respectively; solid and dashed curves (red): Sivaramakrishnan et al.[11] at 1 and 10 atm, respectively; ▲, ■, ●, experimental work of Sivaramakrishnan et al.[11] at $P = 0.95-1.29$, $0.49-0.79$, and $0.2-0.5$ atm, respectively.

φ_{1a} discussed in the previous paragraph is concluded to have negligibly small error even though the method of extrapolation with a simple relation IV was employed in the low-temperature region.

By applying linear least-squares analysis, the results of this study for the apparent rate constant k_1 can be expressed as

$$k_1/s^{-1} = (5.28 \pm 0.14)$$
$$\times 10^{10} \, exp[-(23\,530 \pm 980)/T](P = 1-2 \text{ atm})$$

$$(V)$$

The experimental result obtained by Sivaramakrishnan et al. in the lower pressure range ($P = 0.20-1.28$ atm)[11] is compared in Figure 4. Their experimental data are slightly smaller than ours. The experimental condition listed in Table 1 is evaluated by using the ideal shock relation in this study. In contrast, the experimental results of Sivaramakrishnan et al. were obtained by including the correction of boundary layer effect for the estimation of the experimental condition; the experimental results can be closer to each other if the same method for evaluation of the experimental condition is employed. The correction for the boundary layer effect in this study is difficult because the condition for applying Mirels' theory is not attained for the diaphragmless shock tube system. Therefore, it is reasonable to regard the present result as having about 2% higher in the evaluated temperature.

The magnitude of k_1 determined in this study is found to be also consistent with the previous theoretical calculations although pressure dependence is not clearly demonstrated within the 1–2 atm pressure.[1,10,11] The uncertainty in the estimated experimental data for k_1 of this study was found to be larger than the pressure dependence predicted by the previous theoretical studies. As the pressure dependence of the branching fraction for 1a shown in Figure 2 is not so large, the uncertainty in k_1 obscures the pressure dependence of k_{1a} and k_{1b} as shown below.

Essentially, k_1 should be expressed as a second-order reaction because thermal decomposition of C_2H_5OH should be apparently in the falloff region. However, it is convenient to summarize k_1 in first-order rate here due to the small pressure dependence at $P = 1-2$ atm.
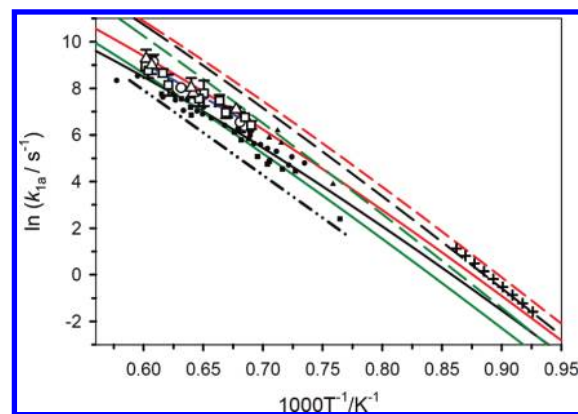

Figure 5. Summary of the experimental and theoretical studies on k_{1a}. Present work: ○, 1 and 3 ppm C_2H_5OH in Ar at $P = 0.99 \pm 0.02$ atm; □, 1 and 3 ppm C_2H_5OH in Ar at $P = 1.45 \pm 0.02$ atm; △, 1 and 3 ppm C_2H_5OH in Ar at $P = 2.02 \pm 0.02$ atm. The blue dash-dot line is the linear least-squares analysis of the present data. Solid and dashed curves (black): Park et al.[1] at $P = 1$ and 10 atm, respectively; solid and dashed curves (green): Li et al.[10] at $P = 1$ and 10 atm, respectively; solid and dashed curves (red): Sivaramakrishnan et al.[11] at 1 and 10 atm, respectively; ▲, ■, ●, experimental work of Sivaramakrishnan et al.[11] at $P = 0.95-1.29$, $0.49-0.79$, and $0.2-0.5$ atm, respectively. Dash-dot-dot (black): experimental data (1 atm) by Natarajan et al.[6] Cross-hair curve (black): experimental data by Tsang et al.[7].
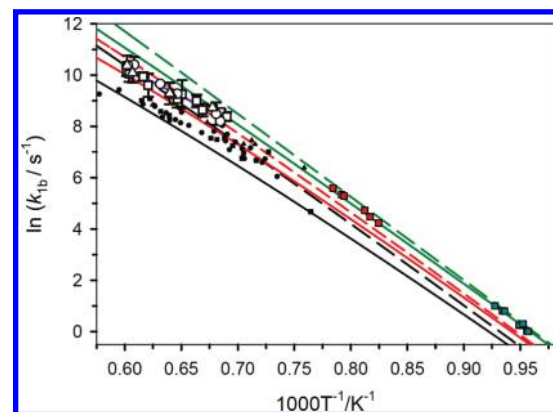

Figure 6. Summary of the experimental and theoretical studies on k_{1b}. Present work: ○, 1 and 3 ppm C_2H_5OH in Ar at $P = 0.99 \pm 0.02$ atm; □, 1 and 3 ppm C_2H_5OH in Ar at $P = 1.45 \pm 0.02$ atm; △, 1 and 3 ppm C_2H_5OH in Ar at $P = 2.02 \pm 0.02$ atm. The blue dash-dot line is the linear least-squares analysis of the present data. Solid and dashed curves (black): Park et al.[1] at $P = 1$ and 10 atm, respectively; solid and dashed curves (green): Li et al.[10] at $P = 1$ and 10 atm, respectively; solid and dashed curves (red): Sivaramakrishnan et al.[11] at 1 and 10 atm; ▲, ■, ●, experimental work of Sivaramakrishnan et al.[11] at $P = 0.95-1.29$, $0.49-0.79$, and $0.2-0.5$ atm, respectively. Blue ■, experimental data by Li et al.;[10] red ■, experimental data by Herzler et al.[23].

By combining the experimental results (III) and (V), k_{1a} is evaluated and shown in Figure 5, compared with previous studies.[1,6,7,10,11] The present result is summarized as

$$k_{1a}/s^{-1} = (4.06 \pm 0.13)$$
$$\times 10^{11} \, exp[-(29\,400 \pm 1350)/T] \quad (VI)$$

This result is consistent with the theoretical prediction by Sivaramakrishnan et al.[11] in the low-temperature range below 1500 K, but it approaches those by Park et al.[1] and Li et al.[10] at

higher temperatures. The pressure dependence of the measured rate is obscured by the scatter of the data on k_1. The experimental result by Sivaramakrishnan et al.[11] is also consistent with the present study.

The experimental result on k_{1b} is shown in Figure 6 for comparison with those of previous studies.[1,10,11,23] The present result is summarized as

$$k_{1b}/s^{-1} = (1.72 \pm 0.05)$$
$$\times 10^{10} \, exp[-(22\,150 \pm 1070)/T](P = 1-2 \text{ atm})$$
$$(VII)$$

This agrees well with the theoretical prediction by Sivaramakrishnan et al. but is substantially larger (about two times at 1600 K) than their experimental values.[11] The difference is caused by the discrepancies in φ_{1a} and k_1 as shown in Figures 2 and 4. It is difficult to speculate why such a difference was introduced, but the uncertainties of the initial concentration of C_2H_5OH and experimental temperature as stated above may result in the deviation in k_{1b}.

4. CONCLUSION

The kinetics of C_2H_5OH thermal decomposition in the temperature range of 1450−1760 K (at $P = 1-2$ atm) was studied by using a shock tube system with atomic resonance absorption spectrometry of H atoms. Pressure dependence of the measured φ_{1a} determined by analyzing evolution of [H] can be expressed by

$$\phi_{1a} = (0.71 \pm 0.07)$$
$$- (826 \pm 116)/T (P = 0.99 \pm 0.02 \text{ atm}) \quad (III-1)$$

$$\phi_{1a} = (0.92 \pm 0.04)$$
$$- (1108 \pm 70)/T (P = 1.45 \pm 0.02 \text{ atm}) \quad (III-2)$$

$$\phi_{1a} = (1.02 \pm 0.10)$$
$$- (1229 \pm 168)/T (P = 2.02 \pm 0.02 \text{ atm}) \quad (III-3)$$

The magnitude of branching ratio of channel 1a is smaller, but the observed pressure dependence is consistent with previous theoretical predictions of Sivaramakrishnan et al.[11] and Park et al.[1] The uncertainty of this result depends on the magnitude of the branching fraction for 1c; the upper limit of the estimated error is less than 10%.[11] It is worth mentioning that the indicated small pressure dependence of III-1−III-3 cannot be determined if the diaphragmless shock tube system was not available.

The apparent total rate constant k_1 for C_2H_5OH thermal decomposition from different concentration mixtures does not exhibit a clear pressure dependence within the 1−2 atm pressure studied; our result can be summarized as

$$k_1/s^{-1} = (5.28 \pm 0.14)$$
$$\times 10^{10} exp[-(23\,530 \pm 980)/T](P = 1-2 \text{ atm})$$
$$(V)$$

As the accurate parameters for the branching fractions and the rate of decomposition in the falloff region are important in practical modeling of the pyrolysis and combustion of ethanol, further experimental information, especially from measurements at an extended higher pressure range, should be very useful.

■ ASSOCIATED CONTENT

⑤ Supporting Information. Mechanism of C_2H_5OH thermal decomposition consisting of 103 elementary reactions for numerical simulation (Table S1); sensitivity analysis of 3 ppm C_2H_5OH at 1547 K and 1.44 atm for H atoms (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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