

Figure 5. 95% confidence intervals for k_1 . Vertical error bars represent $\pm 20\%$ limits.

trapolation of Jeong and Kaufman's data to 800 K yields rate constants for CH₂ClCHCl₂ and CH₃CCl₃ of 8.8 × 10⁻¹³ and 9.9 × 10⁻¹³ cm³ molecule⁻¹ s⁻¹, respectively. This result suggests that an increasingly larger portion of k_1 is due to β -H abstraction as temperature rises. This effect could contribute to the curvature observed in our rate measurements for C₂H₅Cl.

A major application of this data is the testing of CHC combustion models. Postflame reactions at 1273 K or lower are believed to be important in determining combustion emissions.^{4,18-20}

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Modeling of CHC destruction in this temperature regime requires accurate rate data and/or reliable estimation techniques if pollutant emissions are to be reliably predicted. The data obtained in this study do not extend beyond 789 K. However, given the variance/covariance values for the fitted rate constant parameters, $COV_{An} = -4.87 \times 10^{-14}, COV_{AB} = -2.30 \times 10^{-11}, COV_{nB} = 5.17$ $\times 10^{1}$, the uncertainty in extrapolating outside of the experimental temperature range may be determined (cf. Figure 5).²¹ Extrapolation of eq 1 to 1273 K yields a bimolecular rate constant of $(1.37 \pm 0.310) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ (95% confidence intervals). To compute the predicted fraction remaining, $f_r =$ $[C_2H_5Cl]/[C_2H_5Cl]_0$, in the postflame zone of an incinerator, we have assumed that H abstraction by OH is the dominant pathway for destruction of C₂H₅Cl at 1273 K. The OH concentration has been estimated from an equilibrium calculation for the fuel-lean combustion of a waste mixture (in 50% excess air) with an elemental composition of C₃H₃Cl.⁴ Assuming a reaction time of 1 s, our data suggests $f_r = 0.66 \pm 0.74\%$. Similar calculations using the rate constants predicted by refs 7–9 suggest $f_r = 6.94\%$, 9.54%, and 1.38%, respectively. These calculations again show⁴ that reasonably accurate estimation techniques based on lower temperature data can still result in significant differences (as high as a factor of 10) in the predicted destruction of C_2H_5Cl versus that obtained from higher temperature rate data. Experimental data over extended temperature ranges, as well as improved estimation techniques, are necessary to reduce the uncertainty in the modeling of high-temperature oxidation of CHCs.

Acknowledgment. The authors acknowledge S. Heneghan for assistance with transition-state calculations and R. Striebich for assistance with aspects of data analysis. This project is supported by the National Science Foundation under Grant CBT 8900750.

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Studies on the Reaction of Acetaldehyde and Acetyl Radicals with Atomic Hydrogen

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The reaction of acetaldehyde and acetyl radical with atomic hydrogen was studied with a discharge flow tube equipped with an electron-impact mass spectrometer. Experiments were performed under the condition of excess atomic hydrogen at 299 • 5 K. A rate constant for the reaction CH₃CHO + H \rightarrow CH₃CO + H₂ (1) of (11 ± 2) × 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹ was obtained. The branching fractions for the subsequent reactions (2a) CH₃CO + H \rightarrow CH₃ + HCO and (2b) CH₃CO + H \rightarrow CH₂CO + H₂ are found to be 65 ± 4% and 35 ± 2%, respectively.

Introduction

The reactions of acetaldehyde and acetyl radical with atomic hydrogen are important in low-temperature combustion such as cool flames and combustion of hydrocarbons in the induction period; also they are believed to be important key species in photochemical smog formation.

The reaction mechanism for $CH_3CHO + H$ system under the condition of excess atomic hydrogen has been established by von

Aders and Wagner¹ as follows:

 $CH_{3}CHO + H \rightarrow CH_{3}CO + H_{2}$ (1)

 $CH_3CO + H \rightarrow CH_3 + HCO$ (2a)

 $\rightarrow CH_2CO + H_2$ (2b)

 $CH_3 + H + M \rightarrow CH_4 + M$ (3)

 $HCO + H \rightarrow CO + H_2$ (4)

$$CH_2CO + H \rightarrow CH_3 + CO$$
 (5)

$$CH_3 + CH_3 + M \rightarrow C_2H_6 + M \tag{6}$$

While several studies have been performed on the rate constant for reaction $1, 1^{-4}$ and the branching fractions for (2a) and (2b) have been measured by two groups,^{1,2} there appears to be a large discrepancy in these values.

In the present study, the branching fractions for (2a) and (2b) as well as the rate constant for reaction 1 were obtained by measuring the absolute formation rate of methane and ketene. A discussion on the discrepancy between the previous measurement of the branching fractions for (2a) and (2b) and a comparison with analogous systems are presented.

Experimental Section

A discharge-flow system coupled with an electron-impact mass spectrometer was used in the present experiments. H atoms were prepared by a microwave discharge of H_2/He mixture. The initial concentration of H atoms was determined by using the well-known titration reaction

$$H + NO_2 \rightarrow NO + OH$$
 (7)

and monitoring NO₂ signals. Some corrections were made for the subsequent reactions 8-13.

$$OH + OH \rightarrow O + H_2O$$
 (8)

$$O + OH \rightarrow H + O_2 \tag{9}$$

$$O + NO_2 \rightarrow O_2 + NO$$
 (10)

$$H \rightarrow \text{wall loss}$$
 (11)

$$H + H + M \rightarrow H_2 + M \tag{12}$$

$$H + OH + M \rightarrow H_2O + M \tag{13}$$

The tube has a 19-mm i.d., and the inlet has a 6-mm o.d. The inner surface of the flow tube and the outer one of the movable inlet were coated with Teflon (FEP 856-200). The wall removal rate constant of hydrogen atoms could be reduced to 9.5 ± 8.3 s^{-1} by this coating. Acetaldehyde was added to the main flow through a movable inlet. Reactants and products were introduced to the electron-impact mass spectrometer through a pinhole with a 0.1-mm i.d. at the end of the flow tube. Flow rates of all gases were measured by capillary flow meters, which were calibrated by pressure drop of calibrated volume.

He (Nippon Sanso, 99.9999%) and H₂ (Takachiho Kagaku Kogyo, 99.999%) were used without further purification. CH₃-CHO (Koso Chemical, 81%) was purified by trap-to-trap distillation. NO2 was prepared by mixing NO (Matheson, 99%) and O₂ (Nippon Sanso, 99.99%) and then purified by the trap-to-trap distillation. Ketene was prepared by a pyrolysis of diketene⁵ and purified by trap-to-trap distillation.

All the experiments were performed under the condition of excess atomic hydrogen at room temperature (299 \pm 5 K) and a pressure of 2.4 ± 0.1 Torr of He. All indicated error limits represent 2 standard deviations.

Results

The branching fractions for (2a) and (2b) are determined by measuring the absolute formation rate of methane and ketene with an electron-impact mass spectrometer under the condition of excess atomic hydrogen. The detection sensitivities of CH4 and CH2CO were determined by measuring signal intensities of m/e = 16 and 42 flowing CH₄-He and CH₂CO-He mixtures, respectively. The product CH₃ of reaction 2a reacts with excess atomic hydrogen rapidly and was converted quantitatively to methane by reaction 3. The contribution of reaction 6 can be neglected under the

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Figure 1. Absolute formation rates of methane and ketene. Conditions: total pressure, 2.52 Torr; flow rate, 1932 cm s⁻¹; $[H]_0 = 4.99 \times 10^{13}$ molecule cm⁻³; [CH₃CHO]₀ = 3.85×10^{12} molecule cm⁻³.

TABLE I: Comparison of the Present and Previous Branching Fractions for Reactions 2a and 2b and k_1 at Room Temperature

fractions			$10^{14}k_{1}$ cm ³		
2a	2b	2b (corr) ^a	molecule ⁻¹ s ⁻¹	methods	ref
0.82	0.18	0.19	5.5%	DF-MS ^d	1
(0.37)	0.63	0.45	5.3	DF-PIMS ^e	2
			8.9 ± 0.7	FP-RF⁄	3
			9.8 ± 0.8	DF-RF [#]	4
0.65	0.35	0.35	11 ± 2	DF-MS	this work [*]
			7 ± 5	DF-MS	this work ⁱ

^aCorrected branching fractions for 2b (see text). ^bMeasured at 388.7 K. Calculated from the Arrhenius expression for k_1 . ^d Discharge flow mass spectrometry. ^e Discharge flow photoionization mass spectrometry. ¹Flash photolysis resonance fluorescence. ^g Discharge flow resonance fluorescence. ^h Determined by the formation rates of CH₄ and CH₂CO. ¹Determined by the decrease of acetaldehvde.

present conditions. On the other hand, the product CH₂CO of reaction 2b is consumed by the subsequent reaction 5 and converted to methyl radical. Therefore, a correction for this subsequent reaction was made [though this correction was small in the present experimental condition (<4%)]. Also corrections for the decrease of the concentration of acetaldehyde with reaction time and heterogeneous removal of atomic hydrogen were also taken into account. An example of the time dependence of the concentrations of the products CH₄ and CH₂CO is shown in Figure 1. Assuming that reactions 2 and 3 are much faster than reaction 1, the formation rates of methane and ketene are described by eq 14 and 15, where [H]₀ and [CH₃CHO]₀ represent the initial

$$d[CH_4]/dt = (k_{2a}/k_2)k_1[H]_0[CH_3CHO]_0$$
(14)

$$d[CH_2CO]/dt = (k_{2b}/k_2)k_1[H]_0[CH_3CHO]_0$$
(15)

concentrations of atomic hydrogen and acetaldehyde, respectively. From eqs 14 and 15 and the slope of the lines such as those given in Figure 1 and assuming that (2a) and (2b) are only pathways of reaction 2, the branching fractions for (2a) and (2b), as well as the rate constant k_1 for reaction 1 are determined to be

$$k_{2a}/k_2 = 0.65 \pm 0.04$$

 $k_{2b}/k_2 = 0.35 \pm 0.02$

$$k_1 = (11 \pm 2) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

which are compared with previous works¹⁻⁴ in Table I. These branching fractions are weighted averages of two measurements.

The direct measurement of k_1 from the pseudo-first-order decay of the concentration of acetaldehyde was also tried. k_1 was determined to be $(7 \pm 5) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ in this measurement. This experiment, however, exhibited larger uncertainties in the rate constant result mainly because of the heterogeneous

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removal of atomic hydrogen, since reaction 1 is very slow and the experiment required long reaction time.

Discussion

Comparison with Previous Works. There appears to be a large discrepancy in the branching fractions for (2a) and (2b); von Aders and Wagner¹ neglected the consumption of ketene by reaction 5; the analysis in the experiment performed by Slemr and Warneck² included a large correction for reaction 5. However the rate constant they used for reaction 5 was about twice as large as the recent measurement. Thus we reanalyzed the values of previous measurements using the recent rate constant for reaction 5. The results are also shown in Table I. Better agreement with the present work is thereby obtained.

The present rate constant for reaction 1 agrees with those of the previous measurements,^{3,4} though it contains large uncertainty.

Comparison with Analogous Systems. Analogous product branching of radical atom reactions with reaction 2 is known for several systems. The reaction of CH_3CO with atomic oxygen proceeds via two pathways:

$$CH_3CO + O \rightarrow CH_1 + CO_2 \tag{16a}$$

$$\rightarrow CH_2CO + OH$$
 (16b)

and the branching fractions have been determined to be $76 \pm 24\%$ and $22 \pm 5\%$, respectively.⁷ Reaction of a smaller carbonyl radical, HCO, with hydrogen atoms has been investigated theoretically⁸ and revealed to proceed via two pathways (an addition-elimination pathway, (17a), and a direct abstraction pathway, (17b)):

$$HCO + H \rightarrow (H_2CO)^* \rightarrow H_2 + CO$$
(17a)

$$\rightarrow$$
 H₂ + CO (17b)

with almost equal branching fractions (45% and 55% for (17a) and (17b), respectively).

Although no theoretical information on the reaction dynamics has been available for reactions 2 and 16, reactions 2a and 16a will be addition-elimination processes similar to reaction 17a and reactions 2b and 16b will be direct abstractions similar to reaction 17b. Though one might consider that reactions 2b and 16b are addition-elimination processes, the elimination processes will be entropically unfavorable because the methyl group intramolecular rotation is restricted at the transition state. This effect has been quantitatively discussed on $C_2H_5 + O$ system.⁹ Therefore, reactions 2b and 16b will be direct abstractions. This type of reaction (one bond breaks and two bonds are formed via reaction) usually has no (or a very small) barrier on potential energy surfaces and easily occur even at room temperature. For more reliable discussion on the reaction dynamics, an ab initio calculation of the potential energy surfaces of these reactions are needed.

Registry No. CH₃CHO, 75-07-0; CH₃CO, 3170-69-2; H, 12385-13-6; CH₄, 74-82-8; CH₂CO, 463-51-4.

Heterogeneous Reactions on Model Polar Stratospheric Cloud Surfaces: Reaction of N_2O_5 on Ice and Nitric Acid Trihydrate

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A Knudsen cell flow reactor was used to study the heterogeneous reaction of N_2O_5 on laboratory ice surfaces and nitric acid trihydrate (NAT) surfaces representative of polar stratospheric clouds (PSCs). N_2O_5 was quantitatively converted to HNO₃ on ice surfaces at 188 K. On initially pure ice surfaces, a gradual increase in the N_2O_5 uptake efficiency was observed up to a maximum value near 0.03. The slow rise in reactivity with time is consistent with an acid-catalyzed surface reaction. With increasing initial nitric acid concentrations, the maximum reactivity occurred more rapidly although the overall reactivity was depressed. The uptake efficiency for N_2O_5 on NAT at 188 K was found to be 0.015 \pm 0.006.

Introduction

Heterogeneous reactions on the surfaces of polar stratospheric clouds (PSCs) over Antarctica are now recognized to play a central role in the photochemical mechanism responsible for the dramatic yearly occurrence of the Antarctic "ozone hole".¹ Laboratory studies²⁻⁶ have confirmed that heterogeneous reactions can occur on ice surfaces thought to be representative of type II PSCs found in the cold Antarctic stratosphere. For example, reactions 1–3 involving reactive chlorine have been shown to occur readily on laboratory ice surfaces. These reactions convert the stable chlorine reservoir species (ClONO₂ and HCl) into more active forms (HOC1, Cl₂, ClNO₂) which photolyze readily to provide Cl for catalytic ozone destruction cycles.⁷

$$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$$
 (1)

$$CIONO_2 + H_2O \rightarrow HOCI + HNO_3$$
 (2)

$$N_2O_5 + HCl \rightarrow CINO_2 + HNO_3$$
(3)

The fate of odd nitrogen in the Antarctic stratosphere is also of key importance in understanding the ozone losses observed there. All of the above reactions plus reaction 4 result in the formation $N_2O_5 + H_2O \rightarrow 2HNO_3$ (4)

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