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Laser Photolysis/Laser Induced Fluorescence Study of OH–C_2H_5Cl Rate Constants from 294 to 789 K

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Absolute rate coefficients for the reaction of hydroxyl radical (OH) with ethyl chloride (C_2H_5Cl) were measured over the temperature range 294–789 K, at atmospheric pressure, by using a laser photolysis/laser induced fluorescence technique. Hydroxyl (OH) was generated via photodissociation of N_2O and the subsequent reaction of $O(^1D)$ with H_2O. Relative radical concentration was monitored versus reaction time by using laser-induced fluorescence. The data were fit to the modified Arrhenius expression $k(T) = (2.96 \pm 2.94) \times 10^{-13}(T/300)^{2.59\pm0.666} \exp(229 \pm 624 \text{ cal mol}^{-1}/RT)$, where k is in units of cm^3 molecule^{-1} s^{-1}. Random errors in the measured rate data, as determined by a propagation of error analysis, were typically 10–20% ($\pm 2\sigma$). Agreement with available room-temperature literature data and proposed methods of rate constant estimation, over extended temperature ranges, are shown.

Introduction

High-temperature incineration has emerged as an attractive method of disposal for hazardous organic wastes. It has been estimated that ~20% of this waste is in the form of chlorinated hydrocarbons (CHCs).[1] Experimental[2] and modeling[3] studies have shown that hydroxyl radicals (OH) are an important species in hydrocarbon oxidation. The successful modeling of high-temperature systems presumes reliable kinetic data for radical species, such as OH, approaching temperatures found in incinerators (1073–2000 K). We have recently reported H atom metathesis rate constant measurements for the reaction of OH with methyl chloride (CH_3Cl), methylene chloride (CH_2Cl_2), and chloroform ($CHCl_3$) over an extended temperature range (295–800 K) using a single apparatus.[4] This article reports similar measurements for the following reaction

$$C_2H_5Cl + OH \xrightarrow{k_1} C_2H_4Cl + H_2O \qquad \Delta H^\circ_{298} = -35.1 \text{ kcal mol}^{-1}$$

over a temperature range of 294–789 K at a total pressure of 740 ± 10 Torr.

Room-temperature rate constants for k_1 have been reported, as well as empirical and semiempirical estimations. Using a discharge-flow system to generate OH, and laser magnetic resonance to probe the relative OH concentration, Howard and Evenson[5] reported a value of $(3.9 \pm 0.72) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} for k_1 at 296 K. Paraskevopoulos et al.[6] reported a value of k_1, $(3.94 \pm 0.53) \times 10^{13}$ cm^3 molecule^{-1} s^{-1}, at 297 K using a flash photolysis, resonance absorption technique. This value is in excellent agreement with that reported by Howard and Evenson. Several estimation techniques have been employed to produce modified Arrhenius parameters for this reaction. From transition-state theory, Cohen and Benson[7] determined a modified Arrhenius expression for k_1, $k_1(T) = 9.56 \times 10^{-17}T^{1.6} \exp(-250/T)$ cm^3 molecule^{-1} s^{-1}. Utilizing an empirical relationship, Cohen and Benson[8] determined a second expression for this rate constant, $k_1(T) = 1.63 \times 10^{-16}T^{1.5} \exp(-180/T)$ cm^3 molecule^{-1} s^{-1}. This relationship considers abstraction of α-H only and uses the number of abstractable H atoms as well as molecular weight as input parameters. The structure–activity relationship (SAR) proposed by Atkinson[9] yields the following equation, $k_1(T) = 4.47 \times 10^{-18}T^2 \exp(-471/T) + 4.32 \times 10^{-18}T^2 \exp(-55/T)$ cm^3 molecule^{-1} s^{-1}, where the first term represents β-H abstraction and the second term accounts for α-H abstraction. All three estimations of k_1 are in good agreement (±16%) with the literature room-temperature rate measurements.

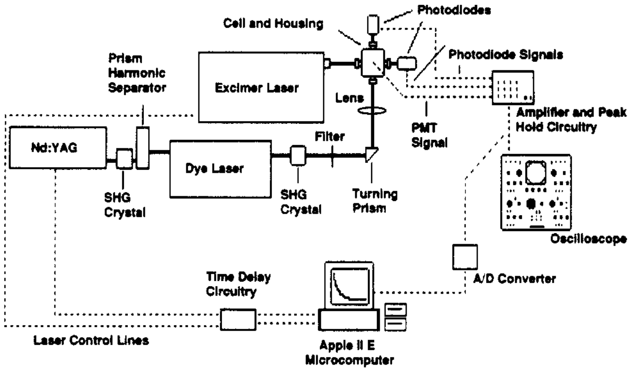

Figure 1. Schematic of OH radical creation and detection system.

The primary objective of this work is to report atmospheric pressure rate constants for k_1, obtained with a single experimental apparatus, spanning an extended temperature range. This data augments previously published results obtained with this device.[4] Comparison with transition-state and other methods of rate constant estimation will be presented to determine which methods predict the high-temperature behavior and curvature observed in the Arrhenius plots. The predictive ability of these techniques significantly affects the viability of CHC combustion modeling efforts. Since all possible reactants cannot be studied, the accuracy of estimation methods is important and must be verified by comparison with high-temperature experimental data.

Experimental Section

To obtain OH–chlorohydrocarbon kinetics data over extended temperature ranges, a modified laser photolysis/laser induced fluorescence system was developed (see Figure 1). The apparatus provides a clean source of OH radicals and the capability of atmospheric pressure measurements. This device was described recently in detail;[4] an abbreviated description of the experimental technique follows.

A resistively heated, quartz optical test cell permits data to be acquired from room temperature to 1000 K. The gas transport time, from the onset of heating until the reaction volume was reached, was ~0.875 s. Mutually perpendicular axes of the quartz cell permitted irradiation of the reaction volume by the photolysis and probe lasers and detection of the laser-induced OH fluorescence. Data were taken at a 10-Hz rate coinciding with the firing of the lasers. A linear gas velocity of 4 cm s^{-1} was maintained through the cell to ensure that each photolysis/probe pulse pair encountered a fresh reaction volume, thus reducing the buildup

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of reaction products. The cell temperature was constantly monitored by a thermocouple placed 5 mm below the reaction zone. A temperature controller was used to maintain the desired cell temperature (within 2 K) during experiments. Measurements from a second retractable thermocouple inserted into the gas flow indicated no more than a ±2 K temperature variation across the reaction volume.

Hydroxyl radicals were generated by the photolysis of nitrous oxide (N_2O) in the presence of water vapor (H_2O). The photolysis laser was an ArF excimer laser (Lumonics, TE-430) which operated at 193 nm. This N_2O photolysis produced excited O atoms which quickly reacted with H_2O to generate OH

$$N_2O + h\nu\ (193\ \text{nm}) \rightarrow N_2 + O(^1D)$$

$$O(^1D) + H_2O \rightarrow 2OH$$

To ensure complete conversion of O atoms to OH, the ratio of H_2O to N_2O was typically 15:1. Once created, the relative OH population was monitored by laser-induced fluorescence. A frequency-doubled, Nd:YAG pumped dye laser (Quanta-Ray, DCR-2 and PDL-2) was used to produce 2–3-mJ pulses at 282.08 nm. This light was used to excite the ($X^2\Pi$, $\nu = 0$, $J = {}^5/_2 \rightarrow A^2\Sigma^+$, $\nu = 1$, $J = 6^1/_2$) transition of the OH radical. Hydroxyl fluorescence was collected at 309 nm, corresponding to the 0–0 vibronic transition.

Helium was used as a carrier gas for the OH precursors and the reactant. Each gas was separately metered by differential flow controllers (Porter Instrument; VCD-1000) and thoroughly mixed in a Pyrex manifold. Ethyl chloride was introduced downstream of the manifold by means of a syringe pump (Sage Instruments, 341B). The flow controllers and syringe pump were periodically calibrated by using the soap bubble meter method. With this procedure, flow rates may be measured within ±0.3%. The repeatability of the flow controller and syringe pump calibrations is ±2%. Variation of the syringe pump injection rate was used to control the concentration of C_2H_5Cl in the reaction volume.

Hydroxyl fluorescence was collected by a quartz lens mounted on top of the test cell and focused on the photocathode of a photomultiplier tube (RCA, 31034A) which has been calibrated for linearity. To aid in discrimination of the fluorescence signal, a band-pass filter (Acton Research, 308.5 nm, 11 nm fwhm) and two colored glass filters (Schott, UG-11 and WG-305) were employed. The output current from the PMT was fed into a custom-built, peak-hold circuit and stored until sampled and digitized by a microcomputer. The quartz reactor apparently acted as a conduit for scattered laser radiation which the three filters were not able to fully remove. Time delays before 2 ms were inaccessible due to interference by the initial photolysis pulse which is stretched out by the time constant of the peak-hold circuitry.

All experiments were performed under pseudo-first-order kinetic conditions with $[C_2H_5Cl] \gg [OH]$. Typical OH concentrations were estimated by a three-level laser-induced fluorescence model[10] to be 7×10^{10}–3×10^{11} molecules cm^{-3}. Ethyl chloride concentrations ranged from 2×10^{13} to 8×10^{14} molecules cm^{-3}. OH decays were obtained over 2–3 decay times by signal-averaging 500–1500 pump and probe laser shots. Over the entire temperature range, OH decay profiles exhibited exponential behavior (see Figure 2a,b) and were fit by the following nonlinear expression

$$[OH] = [OH]_0 \exp(-k't) + c$$

where $k' = k[C_2H_5Cl] + k_d$ and c is an additional term accounting for background light levels. This expression was fitted by using the Levenberg–Marquardt[11] method, an iterative χ^2 minimization technique (least squares). The bimolecular rate constant, k, was separated from the diffusive rate constant, k_d, by fitting a weighted least-squares line ($\omega_k = 1/\sigma_{k'}{}^2$) through the ($[C_2H_5Cl]$, k') data points (see Figure 3). Observed pseudo-first-order OH decay rates, in the absence of C_2H_5Cl, were 80 ± 20 s^{-1}.

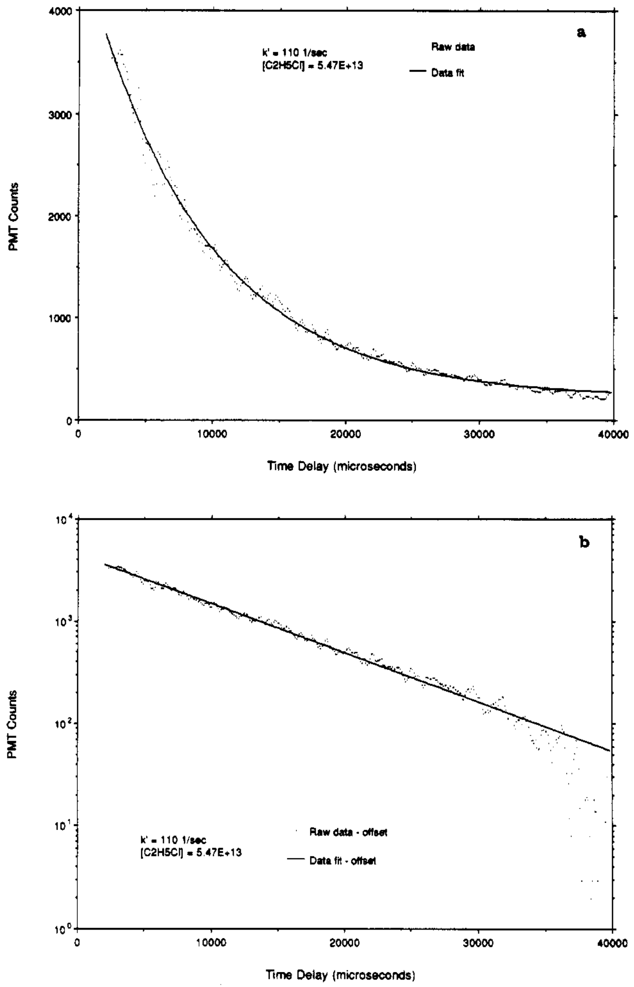

Figure 2. (a) Fitted raw data showing typical OH decay profile versus probe laser delay time. (b) Natural logarithm of OH decay profile (background offset subtracted).

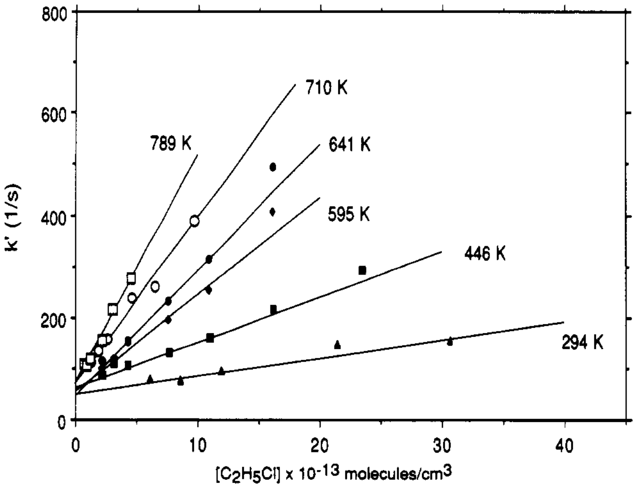

Figure 3. First-order decay constant k' as a function of $[C_2H_5Cl]$ at various experimental temperatures.

All gases used in this experiment were of high purity. The stated minimum purities were as follows: He, 99.9999%; N_2O, 99.0%; H_2O, 99.9999%; C_2H_5Cl, 99.9% (analyzed by GC/MS).

Results and Discussion

Atmospheric pressure absolute rate constants for k_1 are given in Table I. A propagation of error analysis was performed, and the total rate constant error (including all sources of experimental

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TABLE I: $C_2H_5Cl + OH$ Rate Coefficients

temp, K	k, 10^{13} cm^3 molcule^{-1} s^{-1}	no. of measurements
294.8	4.08 ± 0.31[a]	6
330.5	5.62 ± 0.51	2
381.9	7.98 ± 0.70	4
421.3	9.46 ± 0.43	3
447.4	10.1 ± 0.69	3
490.0	12.4 ± 1.61	1
548.0	16.0 ± 3.93	1
595.0	19.3 ± 2.51	2
600.0	23.1 ± 1.10	6
641.0	24.3 ± 2.88	2
687.0	27.5 ± 3.95	1
710.0	32.7 ± 3.27	2
714.0	32.4 ± 2.22	2
733.0	35.1 ± 6.81	1
769.2	39.7 ± 4.05	5
788.7	42.9 ± 5.96	3

[a] 95% confidence intervals.

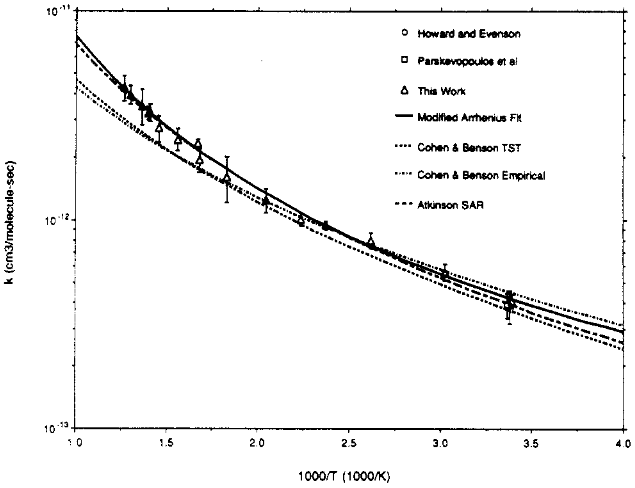

Figure 4. Comparison of Arrhenius plots of rate constant (k_1) determinations for the reaction $C_2H_5Cl + OH \rightarrow C_2H_4Cl + H_2O$.

error) is estimated at 20%. Due to the curvature observed in the data (see Figure 4), the following modified Arrhenius equation was used, $k = A(T/300)^n \exp(E/T)$. The weighted version of the Levenberg–Marquardt method[11] was used to fit the bimolecular rate data, with each measurement being weighted by $1/\sigma_k^2$. The resulting least-squares fit for C_2H_5Cl, in units of cm^3 molecule^{-1} s^{-1} (all limits are 95% confidence intervals), is

$$k(T) = (2.96 \pm 2.94) \times 10^{-13}(T/300)^{2.59 \pm 0.666} \exp(229 \pm 624 \text{ cal mol}^{-1}/RT) \quad (1)$$

To ensure that secondary reactions which might lead to the disappearance of OH were minimized, experimental parameters were varied and rate measurements compared. Changes in the ratio of H_2O/N_2O (by a factor of 3) showed no influence on rate measurements, indicating that unreacted O atoms were not affecting observed decays. The use of high-purity reactants and comparison of rate coefficients to literature values at room temperature indicate no potential interference from olefinic (worst case) contaminants. Studies were also performed to determine the possibility of interference by photolysis products (due to 193-nm irradiation from the excimer laser). If photolytic products reacting with OH were affecting the observed rate constants, then changes in photolysis energy flux would directly affect reactant concentration and the observed rate constant. All rate constant measurements were made at or below 12 mJ cm^{-2} photolysis energy flux. Variation in the photolysis beam flux by a factor of 2 resulted in changes in the measured rate constants which were within experimental precision.

Thermal decomposition of C_2H_5Cl was also of concern. Shock tube studies under pyrolytic conditions have shown that C_2H_5Cl decomposes by four-center HCl elimination to form ethylene (C_2H_4) with a rate constant of $k(T) = 1.45 \times 10^{13} \exp(-56460/RT)$ s^{-1}.[12] The most recent high-temperature rate expressions for reaction of OH with these reaction products are $k_{C_2H_4+OH}$ (651–900)[13] = $(3.36 \pm 0.64) \times 10^{-11} \exp[(-5955 \pm 287)/RT]$ cm^3 molecule^{-1} s^{-1} and k_{HCl+OH} (210–460)[14] = $3.0 \times 10^{-12} \exp[(-844/RT]$ cm^3 molecule^{-1} s^{-1}. Under experimental conditions at 789 K (0.5% decomposition), the ratio of k_1 to the reaction rate of OH with C_2H_5Cl decomposition products is computed to be 115. At temperatures above 825 K, our measured rate constants decreased significantly and became more erratic as the cell temperature was increased. The reaction rate of OH with C_2H_5Cl decomposition products, calculated by using the reported rate constant expressions, approaches 10% of k_1 at ~850 K, which is in approximate agreement with our experimental observations.

Since reaction products were not monitored in this study, we offer the following argument that the reported measurements for k_1 describe the kinetics for H atom transfer reactions to OH. The hard-sphere collision frequency at 300 K between OH[15] and C_2H_5Cl[16] is 3.2×10^{-10} cm^3 molecule^{-1} s^{-1}. Using group additivity and C_2H_4ClOH as a model transition state for both α- and β-H abstraction, one can readily obtain an estimate of the minimum A_{300} of 1.4×10^{-13} cm^3 molecule^{-1} s^{-1}. The A factor determined from the experimental data (2.96×10^{-13} cm^3 molecule^{-1} s^{-1}) falls between these two limits and is consistent with H atom transfer processes.

Figure 4 compares the rate measurements of this study with that of Howard and Evenson[5] and Paraskevopoulos et al.[6] The rate constant estimations of Cohen and Benson[7,8] and Atkinson[9] are also plotted for comparison. Agreement with previous experimental measurements at room temperature is excellent (±5%). Atkinson's[9] estimation is in excellent agreement with the data obtained in this study (within 7% for all temperatures). The transition-state theory[7] and empirical[8] approaches of Cohen and Benson are also in agreement throughout the experimental temperature range (±30%).

From Figure 4 it appears that the SAR approach of Atkinson[9] yields the best fit to the experimental data of the various estimation techniques.[7-9] The methods proposed by Cohen and Benson[7,8] have somewhat underestimated the A factor and activation energy of k_1. Increasing both quantities will translate these curves upward and rotate them clockwise, resulting in a better match to the experimental data. The curvature present in the experimental data ($n = 2.59$) is greater than that predicted by any estimation technique.[7-9] Previous work conducted on this apparatus[4] showed curvature in the chloromethanes to increase with the level of chlorine substitution. Subsequent experimentation is being conducted on the remaining chlorinated ethanes to determine whether this trend continues.

No attempts were made to determine the rate constant of α-H versus β-H abstraction; the reported data reflects the sum of both. Relative C–H bond strengths suggest that β-H abstraction may be significantly slower than α-H abstraction at room temperature. Jeong and Kaufman[17] have measured the rate constants for the reaction of OH with 1,1,1- and 1,1,2-trichloroethane (CH_3CCl_3 and $CH_2ClCHCl_2$), the former containing only β-H's while the latter contains only α-H's. Their findings indicate that the room-temperature rate constant for hydrogen atom abstraction from $CH_2ClCHCl_2$ (($3.18 \pm 0.06) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 295 K) is a factor of 30 greater than that of CH_3CCl_3 (($1.06 \pm 0.09) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 293 K). This suggests that α-H abstraction should dominate k_1 at low temperatures. Ex-

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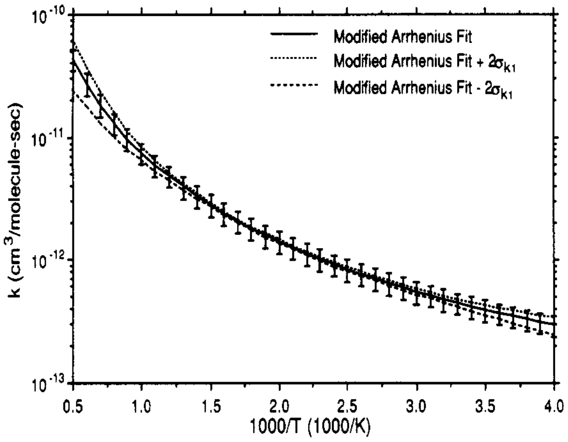

Figure 5. 95% confidence intervals for k_1. Vertical error bars represent ±20% limits.

trapolation of Jeong and Kaufman's data to 800 K yields rate constants for $CH_2ClCHCl_2$ and CH_3CCl_3 of 8.8×10^{-13} and 9.9×10^{-13} cm^3 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 C_2H_5Cl.

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] 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 $(1.37 \pm 0.310) \times 10^{-11}$ cm^3 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 C_2H_5Cl 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 C_3H_3Cl.[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 show[4] 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.

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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 $CH_3CHO + H \rightarrow CH_3CO + H_2$ (1) of $(11 \pm 2) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} was obtained. The branching fractions for the subsequent reactions (2a) $CH_3CO + H \rightarrow CH_3 + HCO$ and (2b) $CH_3CO + H \rightarrow CH_2CO + H_2$ 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 Wagner[1] as follows:

$$CH_3CHO + H \rightarrow CH_3CO + H_2 \qquad (1)$$

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

$$\rightarrow CH_2CO + H_2 \qquad (2b)$$

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

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

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