Rate Constant and a Detailed Error Analysis for $C_2H_3 + H$ Reaction

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Abstract

The production and reactions of vinyl radicals and hydrogen atoms from the photolysis of vinyl iodide (C_2H_3I) at 193 nm have been examined employing laser photolysis coupled to kinetic-absorption spectroscopic and gas chromatographic product analysis techniques. The time history of vinyl radicals in the presence of hydrogen atoms was monitored using the 1,3-butadiene (the vinyl radical combination product) absorption at 210 nm. By employing kinetic modeling procedures a rate constant of 1.8×10^{-10} cm² molecule⁻¹ s⁻¹ for the reaction $C_2H_3 + H$ has been determined at 298 K and 27 KPa (200 torr) pressure. A detailed error analysis for determination of the $C_2H_3 + H$ reaction rate constant, the initial C_2H_3 and H concentrations are performed. A combined uncertainty of $\pm 0.43 \times 10^{-10}$ cm² molecule⁻¹ s⁻¹ for the above measured rate constant has been evaluated by combining the contribution of the random errors and the systematic errors (biases) due to uncertainties of each known parameter used in the modeling. (© 1995 John Wiley & Sons, Inc.

Introduction

Reactions of vinyl radicals are expected to play an important role at both the low temperatures of planetary atmospheres and the high temperatures involved in hydrocarbon pyrolysis and combustion. Despite their importance, relatively little is known about the chemistry of vinyl radicals. This has been due to difficulties in generating these radicals cleanly, monitoring them directly, and also difficulties in analyzing their complex reaction kinetic data. Only in recent years has there been considerable progress in understanding some aspects of the spectroscopy [1,2] and gas-phase chemistry of vinyl radicals [2–9]. There are only a few measurements of the rate constant for vinyl radical reactions with hydrogen atoms. Two recent kinetic studies of these reactions have employed discharge flow systems coupled with low energy electron impact mass spectrometry to monitor C_2H_3 [6,9]. These studies were performed at low pressures (about 1 Pa or less). A rate constant of $(1.1 \pm 0.3) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ has been determined by Monks et al. [9] for reactions of vinyl radicals with hydrogen atoms, yielding acetylene and ethylene;

(1a)
$$C_2H_3 + H \cdots \gg C_2H_2 + H_2$$

$$C_2H_3 + H \cdots > C_2H_4$$

Certain commercial instruments are identified in this article to adequately specify the procedure. In no case does such identification imply recommendation or endorsement by National Institute of Standards and Technology, nor does it imply that the products identified are necessarily the best available for the purpose.

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On the other hand, a rate constant of $(0.5 \pm 0.3) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ has been reported by Heinemann et al. [6] determined at very low pressures, for the channel yielding acetylene (1a). In addition, in previous work from this laboratory, UV laser photolysis has been used to generate vinyl radicals and hydrogen atoms and their reaction kinetics was briefly examined [5]. An approximate value, in the order of 2×10^{-10} cm³ molecule⁻¹ s⁻¹, for $k_{1a} + k_{1b}$ was derived from those studies [5].

In this article, through a detailed examination of the photochemical processes involving the 193 nm photolysis of C_2H_3I , the production and subsequent reactions of vinyl radicals and H-atoms have been reexamined. The rate constant for the reaction of $C_2H_3 + H$ has been derived employing results of the gas chromatographic analysis of the reaction products and kinetic modeling of the time dependent UV kinetic absorption data.

As unknown parameters are extracted from a relatively complex, multicomponent chemical reaction system, it is essential to quantify a realistic uncertainty for the derived parameter(s). In general, a measurement procedure has imperfections that gives rise to the measurement error. Errors may be random or systematic. A random error arises from unpredictable variations in measurements. A systematic error is introduced by faulty calibration, an imperfect knowledge of the values for known parameters or uncertainty of a technique. These systematic errors are often called biases in the measurement [10]. One objective of this article is to asses the contribution of uncertainties of each known parameter used in the modeling of the vinyl-hydrogen reaction system towards the uncertainty of the measured parameters. The ACUCHEM/ACUFIT programs are employed here to evaluate optimum values and realistic uncertainties for measured parameters. Detailed operational descriptions of these programs and procedures for assessment of errors are demonstrated in earlier articles from this laboratory [11–14] and will not be repeated here.

Experimental and Results

Experiments were performed using excimer laser photolysis coupled with UV kinetic-absorption spectroscopy and gas chromatographic (GC) product analysis techniques. These methods have previously been described in detail [5]. Briefly, vinyl radicals and H-atoms were produced from the photolysis of vinyl iodide at 193.3 nm using an ArF excimer laser. A CW Xe analysis light, perpendicular to the laser radiation, was used for optical detection. The continuum radiation was passed through the photolysis cell and then focused onto the entrance slit of a 0.25-m vacuum UV monochromator. The repetitive photon signals were averaged, stored, and subsequently analyzed by computer. A self enclosed gas circulating pump operational up to about 30 KPa was used to flow the gas mixture through the reaction cell. The active volume of the photolysis cell was 4 cm^3 , about 1/1000 of the total sample volume.

Gas Chromatographic Product Analysis

An on-line gas chromatograph was used for product identification and absolute yield measurements. Measurements of end products serve to define the overall chemistry. A nonreactive tracer gas, cyclopropane, was added in known amounts to the gas mixtures to provide a calibrant of sample size. In this way each product, relative to the tracer, provided absolute product yields. The precursor was mixed with ultrahigh purity He (99.9999%) plus added cyclopropane tracer and experiments were conducted with various sample mixtures.

The 193 nm photolysis of mixtures of vinyl iodide in helium yielded acetylene, ethylene, and 1,3-butadiene with acetylene being the major product. Results of the gas chromatographic measurements for various sample mixtures are presented in Table I.

From these determinations a photolysis yield of $22.6\% \pm 2.2\%$ is determined with a relative yield of acetylene/butadiene ≈ 40 . As will be shown later, an approximate relative yield of acetylene/vinyl ≈ 3.6 could be derived from these results. Within the pressure range of these experiments, no detectable pressure dependencies for the dissociation or product yields were observed.

Kinetic Absorption Spectroscopy at 210 nm

The strong absorption of 1,3-butadiene (the product of the vinyl radical combination reaction) at 210 nm ($\epsilon = 9.7 \times 10^{-17}$ cm² molecule⁻¹) [5,15] has been used as a measure of the butadiene concentration and hence as a temporal monitor of the vinyl radical concentration. Figure 1 shows a typical real-time absorption signal, monitored at 210 nm, following the 193 nm photolysis of 20 Pa (150 m torr) vinyl iodide in 27 KPa (200 torr) He. At 210 nm, in addition to butadiene, the vinyl iodide radical precursor also absorbs [5] with a cross section of 1.2×10^{-17} cm² molecule⁻¹. Other reaction products do not have significant absorptions at this monitoring wavelength. Therefore, the observed composite absorption signal at 210 nm can be attributed to the instantaneous decrease in absorption, following the laser pulse, due to the loss of vinyl iodide precursor and the increase in absorption due to build up of the butadiene product. The analysis of the results from kinetic absorption spectroscopic experiments requires accurate knowledge of the absorption coefficients of the precursor and reaction products. The UV absorption spectrum of vinyl iodide and the predicted stable products of the photolysis were independently measured using a 1m vacuum monochromator. Some of these data have previously been reported [5,15]. The real-time absorption data are analyzed through modeling procedures as described below.

Reaction Mechanism

The photofragmentation process, following the 193 nm photolysis of vinyl iodide, and subsequent reactions as evidenced by photometric detection and chromatographic

Mixture, VI	(Pa) He _(KPa)	$[C_2H_2]^a$	$[C_2H_4]^a$	$[C_4H_6]^{a}$	%Dissociation	$[C_2H_2]/[C_2H_3]^b$
14.3	33	6.67	0.87	0.19	20.9	3.1
14.3	33	6.10	0.78	0.18	19.1	3.2
13.3	13	6.91	0.73	0.22	22.3	3.6
14.3	27	8.22	0.82	0.16	24.7	4.2
20.0	27	11.08	1.18	0.26	24.1	3.8
26.6	30	15.06	1.52	0.37	24.5	4.0
Average					22.6 ± 2.2 ^c	$3.6\pm0.4^{ m c}$

TABLE I. Product yields, derived from the GC analysis, following the 193 nm photolysis of vinyl iodide (VI) mixtures.

^a Concentrations in molecule cm⁻³ \times 10¹⁴.

 $^{b}[C_{2}H_{3}]\approx\,2([C_{4}H_{6}]_{\infty}\,+\,[C_{2}H_{4}]_{\infty})$ as described in the text.

^c Measurement (random) error, 1σ



Figure 1. Temporal absorption signal at 210 nm following 193 nm photolysis of 20 Pa vinyl iodide (VI) in 27 KPa He.

product analysis are described by the following reaction sequence.

(2a)
$$C_2H_3I \xrightarrow{\hbar} C_2H_3^* + I$$

(2b)
$$C_2H_3^* \xrightarrow{M} C_2H_3$$

$$(2c) C_2 H_3^* \longrightarrow C_2 H_2 + H_3$$

3)
$$C_2H_3 + C_2H_3 \xrightarrow{M} C_4H_6$$
 (1, 3-butadiene)

(4)
$$C_2H_3 + C_2H_3 \longrightarrow C_2H_2 + C_2H_4$$

(5)
$$C_2H_2 + H \xrightarrow{M} C_2H_3$$

$$(1b) C_2H_3 + H \longrightarrow C_2H_4$$

Acetylene is the major product which is formed, in part, from the disproportionation reaction of vinyl radicals (4) but mainly through dissociation of excited vinyl radicals (2c).

The dissociation of vinyl iodide requires the addition of about 260 kJ/mol energy [16]. The 193 nm photon of ArF excimer laser carries about 620 kJ/mol which leaves about 360 kJ/mol excess energy to be distributed in the vinyl iodide photofragments. The vinyl iodide photofragmentation studies at 248 nm have shown that iodine atoms are produced primarily in the excited $I^{*}(^{2}P_{1/2})$ state consuming about 96 kJ/mol [16]. Thus the photolysis at 193 nm can leave about 264 kJ/mol in the $C_{2}H_{3}$ fragment. The dissociation of $C_{2}H_{3} \rightarrow C_{2}H_{2} + H$, on the other hand, requires about 155 kJ/mol. Therefore sufficient energy is available to permit the production of acetylene and H-atoms. This agrees with the results of the GC analysis which suggest a significant fraction of the initial excited vinyl radicals dissociate to yield acetylene. The remainder of the vinyl radical concentration could be estimated from: $[C_{2}H_{3}] \approx 2([C_{4}H_{6}]_{\infty} + [C_{2}H_{4}]_{\infty})$. The butadiene concentration accounts for the vinyl radicals consumed by the combination reaction (3) and the ethylene approximately accounts for the radicals

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consumed through the disproportionation reaction (4) and reaction with H-atoms. Analysis of the results listed in Table I yield a ratio of $[C_2H_2]_{\alpha}/[C_2H_3] \approx 3.6 \pm 0.4$.

The reaction of vinyl radicals with hydrogen atoms to yield acetylene (1b) is the dominant channel at low pressures [6] with a reported rate constant in the order of 0.5×10^{-10} cm³ molecule⁻¹ s⁻¹. The branching ratio for channels (1a) and (1b) could not, in our experiments, be accurately determined chromatographically since acetylene and ethylene are produced from multiple sources.

The reaction of vinyl radical and acetylene is relatively slow, at ambient temperature [7], with a rate constant of about 10^{-15} cm³ molecule⁻¹ s⁻¹ and is not expected to contribute appreciably to vinyl radical loss and hence is not included in the mechanism. The addition reaction of acetylene and hydrogen atoms to yield vinyl radicals (5) is included in the mechanism with a rate constant of 2×10^{-13} cm³ molecule⁻¹ s⁻¹ at ambient temperature [17].

All the parameters that are needed for the kinetic modeling and analysis of the time dependent absorption data are known or determined from independent measurements, except for k_1 , [C₂H₃], and [H] which will be determined here. The technique requires an initial estimate for the parameters to be measured. The initial estimates for the vinyl radical and hydrogen atom concentrations are derived here from the GC product analysis as described earlier and for k_1 an initial value of 2×10^{-10} cm³ molecule⁻¹ s⁻¹ was assigned. However, any initial estimated values within a reasonable range for the measured parameters would yield an identical result if a unique solution for the system could be derived through the kinetic modeling procedures.

The analysis program, ACUFIT, used here reads the actual laboratory data file followed by the model data file (as generated by ACUCHEM and using the input values). By employing an iterative adjustment procedure the analysis yields the best fit of the model data file to the laboratory data file [12,14] and the best values for the measured parameters based on these fits.

Figure 2 displays the fit of the modeled curve to the temporal absorption at 210 nm for 193 nm photolysis of 20 Pa vinyl iodide in 27 KPa He. Table II lists the values of the measured parameters from such fits of the modeled signals to different time dependent absorption signals at 210 nm. All parameters that affect the fit of the modeled curve to absorption data are listed in row 1 of Table III. The central values for the known parameters used in the modeling are also listed (row 2).

Table III, in addition, is constructed to illustrate the biases on the derived parameters due to uncertainty in the known parameters used in the modeling. We usually do not know the exact values for the known parameters, but only an average value with a plus and minus uncertainty. In developing rows 3 through 8 of Table III the known parameters are fixed either at their best known (central) values or within the uncertainties of the known values as given. Values of the known parameters were chosen to the fullest extent, so that the evaluation of the biases are based on the available data. If a cell is blank the central value for that parameter is employed. All rows involve the analysis of the same real-time absorption signal. The values for the derived parameters, with their uncertainties and biases on k_1 , are listed.

The uncertainties (random) of the measured parameters are derived by the analysis program and primarily are due to the level of signal/noise on the data as well as the number of measured parameters. In addition, when noncentral values for known parameters are used, biases on the measured parameters are produced. These biases are due to the "imperfect" knowledge of the values for known parameters.



Figure 2. Fit of the temporal absorption at 210 nm (20 Pa vinyl iodide in 27 KPa He) and the modeled signal (solid line).

Relatively small biases on the vinyl radical and hydrogen atom concentrations are developed regardless of which parameter is individually fixed at a "noncentral value. Biases on k_1 are also mostly small except when k_5 and $[C_2H_2]$ are fixed at "noncentral" values. A 50% uncertainty in k_5 and 10% uncertainty in $[C_2H_2]$ (this level of uncertainty is typical for our GC analysis) each result in a bias of about $0.1 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in k_1 . These results also indicate that the mechanism is more sensitive to the values of these two known parameters, and that the evaluation of a more accurate value for k_1 will require values for k_5 and $[C_2H_2]$ that have been determined with less uncertainty.

Only when biases determined for measured parameters are added to random errors is there an appreciation of the real error in such determinations. The combined standard uncertainty on measured parameters may be approximated through the vector addition of the random and systematic errors (biases) engendered by fixing a parameter at a noncentral value [10]. We assume, for evaluation of the combined error

Mixture	VI(Pa)	He(KPa)	$[C_2H_3]^a$	$[H]^{a}$	k_1	
1	14	33	1.9	5.6	1.9 ^b	
2	14	33	1.2	4.9	1.5	
3	20	13	2.5	8.0	2.2	
4	20	27	2.2	7.3	1.8	
5	25	27	2.7	7.7	1.9	
6	25	27	3.4	9.8	1.7	
Average					$(1.8 \pm 0.3)^{\circ}$	

TABLE II. Summary of the derived parameters from fits of the model signal to the absorption signals at 210 nm.

^a Concentrations in molecule ${
m cm}^{-3}$ imes 10¹⁴.

^b Rate constants in cm³ molecule⁻¹ s⁻¹ \times 10⁻¹⁰.

^c Measurement (random) error, 1σ .

Known parameters fixed at their central values (blank) or fixed at values within expected errors as given					Measured parameters					
Parameter Central Value	$\epsilon_{ m bd}$ 9.7	$\epsilon_{ m VI}$ 1.2	$k_3 \\ 0.94$	k_4 0.31	k_5 0.002	[C ₂ H ₂] 6.0	$\frac{k_1}{1.80\pm0.24}$	Bias on <i>k</i> ₁ 0.00	$[{\rm C_2H_3}] \\ 2.2\pm0.3$	[H] 7.3 ± 0.4
	+5%						1.73	0.07	2.0	7.4
3	-5%						1.85	0.05	2.3	7.3
		+5%					1.83	0.03	2.2	7.4
4		-5%					1.74	0.06	2.0	7.2
			+20%				1.76	0.04	2.1	7.3
5			-20%				1.83	0.03	2.2	7.5
				+20%			1.76	0.04	2.1	7.4
6				-20%			1.82	0.02	2.2	7.1
					+50%		1.89	0.09	2.4	7.6
7					-50%		1.67	0.13	2.0	7.1
						+10%	1.94	0.14	2.3	7.5
8						-10%	1.70	0.10	1.9	6.9

TABLE III. The biases on the derived parameters due to uncertainty of the known parameters.

The units are $\epsilon \times 10^{17}$ cm², [concentration] $\times 10^{-15}$ molecules and rate constants are $k \times 10^{10}$ cm³ molecule⁻¹ s⁻¹, respectively.

^a Random errors due to noise.

on the determination of k_1 , the contribution of the biases for each "fixed" parameter as the average of the upper and lower biases determined at the uncertainty limits of each known parameter. Thus the total combined uncertainty due to the random and systematic errors, would be:

$$\sigma^{2}(k_{1}) = (0.30)^{2} + (0.24)^{2} + (0.06)^{2} + (0.045)^{2} + (0.035)^{2} + (0.03)^{2} + (0.11)^{2} + (0.12)^{2} = (0.43)^{2}$$

Therefore, a more realistic value for the H-atoms and vinyl radical reaction rate constant, derived from these measurements is;

 $(k_{1a} + k_{1b}) = (1.80 \pm 0.43) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

In conclusion, a rate constant of 1.8×10^{-10} cm³ molecule⁻¹ s⁻¹ for the reaction of C₂H₃ + H, at 298 K and in the 13–33 KPa pressure range, has been derived through modeling of the kinetic system following 193 nm photolysis of vinyl iodide. This value is slightly higher than the value of 1.1×10^{-10} cm³ molecule⁻¹ s⁻¹ recently determined by Monks et al. [9] using discharge flow coupled with mass spectrometric detection. The higher overall rate constant determined here could be due to significantly higher pressures used in our experiments. The branching ratio for these two channels could not, in our experiments, be accurately determined since acetylene and ethylene are produced from multiple sources. Assuming a rate constant of 0.5×10^{-10} cm³ molecule⁻¹ s⁻¹, as determined by Heinemann et al., for the channel yielding acetylene, a rate constant of about 1.3×10^{-10} cm³ molecule⁻¹ s⁻¹ can be assigned for the channel producing ethylene.

The contribution of uncertainties of each known parameter, used in the modeling of the reaction system, towards the uncertainty of the derived parameters have been assessed. A more realistic estimate of errors for determination of the $C_2H_3 + H$ reaction rate constant is determined by vector addition of the random and systematic errors.

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