Rate Coefficients and Products of Ethyl and Vinyl Cross-Radical Reactions

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Rate constants and products for cross-radical reactions of vinyl (C_2H_3) and ethyl (C_2H_5) radicals have been determined at $T = 298$ K and a total pressure (predominately helium) of 93.3 kPa (700 Torr). C_2H_3 and C_2H_5 were produced simultaneously through the 193-nm excimer laser photolysis of dilute mixtures of $C_2H_5COC_2H_3$ (EVK)/He. This is the first report of direct rate determination for the $C_2H_5 + C_2H_5$ reaction and using the photolysis of EVK as a precursor for producing a nearly 1:1 ratio of C_2H_5/C_2H_3. Time-resolved UV absorption spectroscopy and gas chromatographic/mass spectroscopic (GC/MS) product analysis methods were employed for kinetics and product studies. Major reaction products consisted of *n*-butane, 1,3-butadiene, and 1-butene which are formed, respectively, through the combination reactions: $C_2H_5 + C_2H_5 \rightarrow$ *n*-butane (1c), $C_2H_3 + C_2H_3 \rightarrow$ 1,3-butadiene (2c,) and $C_2H_5 + C_2H_3 \rightarrow$ 1-butene (3c). Minor products, ethane, ethylene, and acetylene, result from disproportionation reactions. Analysis of the temporal absorptions at 230 and 235 nm through kinetic modeling of the reaction system resulted in an overall rate constant of $k_3 = 9.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for the $C_2H_5 + C_2H_3$ cross-radical reaction. A detailed error analysis with estimates of both random error and systematic errors for each parameter in the model was performed; the resulting combined uncertainty on the rate constant k_3 is $\pm 1.9 \times 10^{-11}$ cm^3 molecular^{-1} s^{-1}. Using previously published rate constants for the combination reactions 1c and 2c [2.0×10^{-11} and 9.3×10^{-11} cm^3 molecule^{-1} s^{-1}, respectively], and relative yields of the combination products the rate constant for the cross-combination reaction k_{3c} [$C_2H_3 + C_2H_5$] calculated to be $(6.5 \pm 1) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

I. Introduction

Knowledge of the termination rates together with the yield and nature of the termination products for reactions of hydrocarbon radicals are of great importance in understanding and modeling of hydrocarbon combustion[1−3] as well as planetary atmospheric reactions.[4−6] The role of small unsaturated hydrocarbon radicals are particularly significant. Despite their suspected importance, little is known about the kinetics and reaction mechanism of unsaturated radicals. It is also known that both vinyl and ethyl radicals are observed in hydrocarbon combustion and photochemical processes. The self-reactions of ethyl and vinyl radicals have, directly and indirectly, been studied in a number of laboratories.[7−10] Nonetheless, no experimentally determined rate coefficient for ethyl−vinyl cross-radical reaction has previously been reported. Thus one of the objectives of this paper is to measure the rate constant for the bimolecular reaction of vinyl and ethyl radicals. In addition, the contribution of the combination (c) and disproportionation (d) channels for the vinyl−ethyl cross-radical reaction will be determined.

Baulch et al.[7] have critically reviewed the published data on the self-reaction of ethyl radicals and recommended a high-pressure rate constant value of $k_{1c} = (1.9 \pm 0.3) \times 10^{-11}$

$$C_2H_5 + C_2H_5 \xrightarrow{M} C_4H_{10} \quad (1c)$$

$$C_2H_5 + C_2H_5 \xrightarrow{M} C_2H_4 + C_2H_6 \quad (1d)$$

cm^3 molecule^{-1} s^{-1} for the combination channel and a branching ratio of $k_{1c}/k_{1d} = 7.9$

The reaction $C_2H_3 + C_2H_3$ has previously been studied in our laboratory using a number of methods and radical precursors.[8−10] The first direct and absolute kinetic measurement of vinyl self-reaction employed vacuum−UV flash photolysis in conjunction with vacuum−UV absorption detection of vinyl radicals and GC product analysis. In later studies excimer laser photolysis−UV kinetic absorption spectroscopy and GC/MS product analysis methods were used to determine the rate constant and product channels for the vinyl self-reaction.[8,9]

$$C_2H_3 + C_2H_3 \xrightarrow{M} C_4H_6 \text{ (1,3-butadiene)} \quad (2c)$$

$$C_2H_3 + C_2H_3 \xrightarrow{M} C_2H_4 + C_2H_2 \quad (2d)$$

These studies established an overall rate constant of $k_2 = (12 \pm 2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at ambient temperature and the pressure range of about 6.6−53 kPa. In addition, the product yield determinations indicated that the combination channel 2c producing 1,3-butadiene is the dominant channel at pressures higher than about 6.6 kPa with relative rates $k_{2c}/k_{2d} = 3.0$.[8,9]

In a later study, Thorn et al.[10] employing a flow discharge and direct mass spectroscopic detection of vinyl radicals determined, at a nominal pressure of 0.13 kPa and $T = 298$ K, a total rate constant of $(14 \pm 6) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for vinyl self-reaction, which is in good agreement with the total rate constant value $(12 \pm 2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} determined in our laboratory at higher pressures. But under the

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experimental conditions of Thorn et al., the major products are reported to be ethylene and acetylene rather than 1,3-butadiene, i.e., no combination products were observed. Thus high pressures are required to measure contributions of both combination and disproportionation reactions.

Here we report the rate constants and products of the vinyl−ethyl cross-radical reactions, determined at relatively high pressures (93.3 kPa or 700 Torr) and at a temperature of 298 K. Excimer laser photolysis, UV-kinetic absorption spectroscopy, and quantitative GC/MS product analysis have been used for these studies. We also report on the photolysis of ethylvinyl ketone (EVK) as a simultaneous source for producing ethyl and vinyl radicals. Our preliminary results on the pressure dependence of the product channels and rate coefficients for the C_2H_5 and C_2H_3 mixed radical system suggest very complex and interesting behavior. The complexity is the result of the large exoergicity for the combination process and the competition of collisional quenching with unimolecular decomposition and isomerization. The detailed results of the pressure effect on C_2H_5 and C_2H_3 mixed radical reactions will be reported soon.

II. Experimental Procedures

Ethyl and vinyl radicals were produced by the 193-nm photolysis of EVK. Time-resolved UV absorptions of both ethyl and vinyl radicals were monitored and used for kinetic determinations. The final products of the ethyl−vinyl mixed radical reactions were identified and quantified through gas-chromatographic and mass-spectroscopic (GC/MS) analysis of the reaction products.

A summary of our methods is presented here. More detailed descriptions of the procedures can be found in previous publications from our laboratory.[12] The output radiation of an excimer laser is expanded uniformly by a cylindrical lens and fills the reaction cell side-on through a Suprasil[11] flat window over the cell length ($l = 10$ cm). For optical determinations, a monitoring light from a 75-W xenon arc lamp is rendered nearly parallel using a condenser and two long-focal-length lenses. An interposed fast electromechanical shutter, normally closed, is located between the xenon lamp and the reaction cell. The shutter is electronically opened shortly before the photolysis laser pulse and closed at a preset time following the photolysis event. Thus photolysis by the monitoring light is minimized. The monitoring light traverses the cell four times, is deflected by a prism, and then focused on the slit of a monochromator. The signal from the photomultiplier is fed into a multi-time base waveform digitizer through a differential comparator. The transient signal is recorded by the digitizer and then transferred to a computer for storage and signal averaging. A self-enclosed gas circulating pump was used to flow the gas mixture through the reaction cell so that the cell contents were replaced between the photolysis pulses of 0.5-Hz repetition rate. A total system volume of about 2000 times that of the active photolysis volume was used. Because of the significant product dilution, secondary reactions due to product photolysis is unimportant. The effect of photodissociation energy on the kinetics was examined by varying the excimer laser output energies between about 200 and 70 mJ (as monitored at the source).

Identification and quantification of final reaction products were performed using an on-line HP-4890 gas chromatograph equipped with a flame ionization detector (FID), and a HP-5973 mass-selective detector (MSD).[11] In most experiments ethyl and vinyl radicals were simultaneously produced from the 193-nm photolysis of EVK. Ethyl and vinyl radicals were also produced, in a limited number of test experiments, from the 193-nm photolysis of dilute mixtures of diethyl ketone (C_2H_5-COC_2H_5) and divinyl ketone ($C_2H_3COC_2H_3$) in He. The photolysis samples consisted of a small amount of the radical precursor, typically in the range of about $(6-13) \times 10^{15}$ molecule cm^{-3}, in an excess amount of He (93 kPa). The photolyzed sample was admitted to an evacuated injection loop and directly injected onto two separate Al_2O_3-coated capillary columns (HP-19095P) by admitting the carrier gas into the collection loop. Temperature programming of the oven was required to separate the products. The retention times and response of the FID and MS were calibrated by injection of standard samples with concentrations similar to those produced from the laser photolysis. The uncertainty of our quantitative GC analysis, determined from repetitive measurements of known samples, is typically 15% or less for C_2-C_6 hydrocarbons. Radical precursor molecules were obtained commercially, at the highest purity available (99.5%) and were used after successive freeze−pump−thaw cycles. Ultrahigh purity He (99.999%) was used for sample preparations and as carrier gas for GC/MS.

III. Results and Discussion

Production of C_2H_5 and C_2H_3 Radicals. Ethyl and vinyl radicals were produced from the 193-nm photolysis of dilute mixtures of EVK in He. Although there are no previously reported studies on the photolysis of EVK, it appeared to be a worthwhile choice since the primary decomposition channel for small ketones is C−C rupture. For example, the 193-nm photolysis of methylvinyl ketone ($CH_3COC_2H_3$), diethyl ketone ($C_2H_5COC_2H_5$), and acetone have been used, in our and a number of other laboratories, as photolytic sources of methyl, vinyl, and ethyl radicals.[8−10,12−14] In the present studies the formation of ethyl and vinyl radicals from the193-nm photolysis of EVK are confirmed through product analysis determinations and also direct optical detection.

Product Analysis. The reaction mixtures following photolysis of the radical precursor in He were analyzed employing an on-line gas chromatograph coupled to a flame ionization detector and a quadrupole mass spectrometer. The nature and yields of the final reaction products, at a total pressure of about 93.3 kPa (700 Torr) and at ambient temperature, were determined. The major final reaction products consisted of *n*-butane, 1,3-butadiene, and 1-butene (products of combination reactions) and ethane, ethylene, and acetylene (products of disproportionation reactions). A major photolytic product, CO, is not detectable by FID method, and the corresponding MSD peak overlapped with a background air peak thus could not be quantified. No oxygenated hydrocarbon products were detected suggesting that the 193-nm photolysis of EVK primarily produces CO and ethyl and vinyl radicals.

Two isomers of C_4H_8 (1-butene and 2-butene), with a relative yield of [2-butene]/[1-butene] $\simeq$ 0.04, were identified. In addition to 1,3-butadiene, a small quantity of 1,2-butadiene was also detected ([1,2-butadiene]/[1,3-butadiene] $\simeq$ 0.05); also, several C_3, C_5, and C_6 hydrocarbon products were identified. The yield of these later products appear to increase when the total reaction pressure was decreased. The preliminary results on the pressure dependence of the product channels for the C_2H_5 and C_2H_3 mixed radicals system suggest very complex mechanistic behavior involving reactions of the chemically activated combination adducts. The pressure dependence of the C_6 products is an indicator of sequential reaction of the energetic combination adduct. Similarly, significant pressure effects on product channels of the reaction $CH_3 + C_2H_3$ have been recently reported by Fahr et al.[12] Thorn et al.[13] and Stoliarov et al.[14]

TABLE 1: Experimental Conditions and Yields of the Major Final Products (10^{13} molecule cm^{-3}) Following the 193-nm Photolysis of Mixtures of EVK in He at $T = 298$ K and a Total Pressure of 93.3 KPa

[EVK][a]	laser energy[b]	[C_2H_2][a]	[C_2H_4][a]	[C_2H_6][a]	[C_4H_6][a]	[C_4H_8][a]	[C_4H_{10}][a]
6.5×10^{15}	~200	1.31	2.54	0.89	2.77	3.72	3.62
8.0×10^{15}	~130	0.82	2.08	0.78	2.14	2.80	2.75
6.5×10^{15}	~70	0.54	1.0	0.46	1.13	1.40	1.28
13×10^{15}	~75	1.21	1.87	0.82	2.30	3.36	2.98

[a] Concentration unit in molecule cm^{-3}. [b] ArF laser pulse energy (mJ) as monitored at the source.

The pressure dependent studies of the C_2H_5 and C_2H_3 mixed-radicals reactions are currently in progress in our laboratory and the results will be reported soon.[15]

Table 1 lists a number of experimental conditions and the absolute yield of the major final products at a pressure of 93.3 kPa as derived from the calibrated GC/MS product analysis.

Based on the previous studies of the self-reactions of ethyl radicals, $C_2H_5 + C_2H_5$, and vinyl radicals, $C_2H_3 + C_2H_3$, and in conjunction with the results of the present final product analysis, for the mixed C_2H_5 and C_2H_3 reactions, the following reaction sequences at high-pressure conditions are expected upon the 193-nm photolysis of EVK:

$$C_2H_5COC_2H_3 \xrightarrow{193\text{ nm}} C_2H_5 + C_2H_3 + CO$$

$$C_2H_5 + C_2H_5 \xrightarrow{M} C_4H_{10} \tag{1c}$$

$$C_2H_5 + C_2H_5 \xrightarrow{M} C_2H_4 + C_2H_6 \tag{1d}$$

$$C_2H_3 + C_2H_3 \xrightarrow{M} C_4H_6\ (\text{1,3-butadiene}) \tag{2c}$$

$$C_2H_3 + C_2H_3 \xrightarrow{M} C_2H_4 + C_2H_2 \tag{2d}$$

$$C_2H_5 + C_2H_3 \xrightarrow{M} C_4H_8\ (\text{1-butene}) \tag{3c}$$

$$C_2H_5 + C_2H_3 \xrightarrow{M} C_2H_4 + C_2H_4 \tag{3d1}$$

$$C_2H_5 + C_2H_3 \xrightarrow{M} C_2H_6 + C_2H_2 \tag{3d2}$$

Each of the final disproportionation products, ethane, ethylene and acetylene, are formed through multichannel reactions. To assess the relative rates of the combination and disproportionation channels for the $C_2H_5 + C_2H_3$ reaction, it is necessary to determine the contribution of each reaction channel to the production of the final disproportionation products.

The contribution of the disproportionation channels involving self-reactions of ethyl radicals and vinyl radicals (channels 1d and 2d), on the formation of ethane, ethylene and acetylene, can be determined from the known ratios of the combination/disproportionation for these reactions.[8−10]

$$[C_2H_6]_{1d} = [C_2H_4]_{1d} = [C_4H_{10}]/8 \tag{1}$$

$$[C_2H_4]_{2d} = [C_2H_2]_{2d} = [C_4H_6]/3.0 \tag{2}$$

The contribution of the cross-radical reaction $C_2H_5 + C_2H_3$ on the formation of ethane, ethylene, and acetylene can be assessed as follows:

$$[C_2H_4]_{3d1} = [C_2H_4]_{total} - [C_2H_4]_{1d} - [C_2H_4]_{2d} = [C_2H_4]_{total} - [C_4H_{10}]/8\text{-}[C_4H_6]/3.0 \tag{3}$$

$$[C_2H_6]_{3d2} = [C_2H_2]_{3d2} = [C_2H_6]_{total} - [C_2H_6]_{1d} = [C_2H_6]_{total} - [C_4H_{10}]/8 \tag{4}$$

Thus the ratios of disproportionation/combination channels for ethyl−vinyl cross-radical reactions can be determined from the product ratios

$$k_{3d1}/k_{3c} = [C_2H_4]_{3d1}/2[C_4H_8] = \{[C_2H_4]_{total} - [C_4H_{10}]/8\text{-}[C_4H_6]/3.0\ \}/2[C_4H_8] \tag{5}$$

$$k_{3d2}/k_{3c} = [C_2H_6]_{3d2}/[C_4H_8] = \{[C_2H_6]_{total} - [C_4H_{10}]/8\}/[C_4H_8] \tag{6}$$

It should be noted that the values of k_{3d1}/k_{3c} and k_{3d2}/k_{3c} derived from eqs 5 and 6 are expected to have large uncertainties due to the propagation of measurement uncertainties on various parameters affecting the ratios. Estimates of the ratio of the combination/disproportionation channels derived from eqs 5 and 6 suggest the disproportionation channels, at conditions of $P = 93.3$ kPa and $T = 298$ K, are about 10% to 20% of the combination channel.

Kinetic Absorption Spectroscopy at 230 and 235 nm. Time-resolved absorption spectroscopy of the mixed ethyl and vinyl radical reaction system was performed by monitoring absorptions at wavelengths of 230 and 235 nm. Analysis of the time-resolved absorption data requires knowledge of the absorption characteristics of the transient radical species and the stable reaction products and their absorption cross sections at the monitoring wavelength(s). The UV absorption spectrum and cross sections for vinyl radicals, in the spectral range of 225−238 nm, have previously been determined in our laboratory.[16] The vinyl UV absorption exhibits a relatively broad feature with cross sections of $\sigma_{C_2H_3} = 5.3 \times 10^{-18}$ cm^2 molecule^{-1} at 230 nm and $\sigma_{C_2H_3} = 3.1 \times 10^{-18}$ cm^2 molecule^{-1} at 235 nm.[16]

Ethyl radicals also have a broad absorption feature between about 200−260 nm[17,18] due to a number of transitions; some structures develop further into the UV. Absorption cross sections for ethyl radicals in the spectral range 200−260 nm have been reported by Munk et al.[17] At the monitoring wavelengths of this study, the cross sections are $\sigma_{C_2H_5} = 1.7 \times 10^{-18}$ cm^2 molecule^{-1} at 230 nm and $\sigma_{C_2H_5} = 2.5 \times 10^{-18}$ cm^2 molecule^{-1} at 235 nm.

Among the reaction products, only 1,3-butadiene has a significant absorption at the monitoring wavelengths of this study.[19] All other final reaction products have appreciable absorptions at considerably shorter wavelengths.[20] To confirm the absorption characteristics of the reaction products, known samples of the expected products of the mixed ethyl−vinyl radical reactions (excluding 1,3-butadiene) with concentrations similar to those expected in experiments were introduced into the reaction cell. The monitoring light intensity was monitored before and after the introduction of the sample. No detectable variations of the monitoring light level were observed.

The temporal UV absorption traces, following the 193-nm photolysis of EVK samples, were averaged and recorded at the selected monitoring wavelengths. Figure 1 displays one such trace obtained at 235 nm. No variations of the monitoring light intensity were detected when the cell containing only He was irradiated by ArF laser pulses. Thus the observed signal is a result of the photolysis and not of optical or electrical interferences.

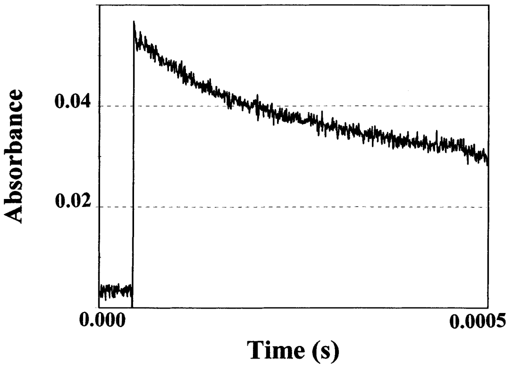

Figure 1. Time-resolved absorption trace at 235 nm after the 193-nm photolysis of a mixture of 1.3 × 10^{16} molecule cm^3 of $C_2H_5COC_2H_3$ in 93 kPa He. The trace is an average of 1000 sweeps.

TABLE 2: Rate Constants Used in the Analysis of the Time-Resolved Absorption Data

reaction	parameter	ref
$C_2H_5 + C_2H_5 \rightarrow$ products	$k_1 = 2.2 \times 10^{-11}$ (fixed)	7
$C_2H_3 + C_2H_3 \rightarrow C_4H_6$	$k_{2c} = 9.3 \times 10^{-11}$ (fixed)	8, 9
$C_2H_3 + C_2H_3 \rightarrow C_2H_4 + C_2H_2$	$k_{2d} = 3.1 \times 10^{-11}$ (fixed)	8, 9
$C_2H_5 + C_2H_3 \rightarrow$ products	k_3 = adjusted	
$[C_2H_5]^0$ and $[C_2H_3]^0$	adjusted	

The trace in Figure 1 shows an instant absorption rise due to nascent vinyl and ethyl radicals produced from the EVK photolysis. The contribution of each radical to this absorption is proportional to its corresponding absorption cross section and concentration. The second absorption component is a decay to a nonzero baseline which is a composite absorption due to loss of vinyl and ethyl radicals and the absorption rise due to formation of the 1,3-butadiene product. The third absorption component at long observation times (the "absorption tail") is primarily due to the product 1,3-butadiene. The absorbance at any time A_t can be related, by the Beer–Lambert law (eq 7), to concentrations of the absorbing species n_i, absorption cross section σ_i, and the absorption path length l_{abs}

$$A_t = \Sigma n_i \sigma_i (l_{abs}) \tag{7}$$

Data Analysis. Kinetic modeling and simulation were used for analysis of the time-resolved absorption data and deriving the overall rate constant for the $C_2H_5 + C_2H_3$ reaction. Acuchem and Acufit packages of modeling and analysis programs[11,21,22] were used here.

The reaction sequences 1–3 were modeled at high-pressure conditions. A listing of the reactions and rate constants is provided in Table 2. The following absorption coefficients (σ, 10^{-18} cm^2 $molecule^{-1}$) were fixed in the modeling calculation:

At 230 nm: $\sigma_{C_2H_3} = 5.3$,[16] $\sigma_{C_2H_5} = 1.7$ [17], and $\sigma_{1,3-C_4H_6} = 11.0$.[19]

At 235 nm: $\sigma_{C_2H_3} = 3.1$,[16] $\sigma_{C_2H_5} = 2.5$ [17], and $\sigma_{1,3-C_4H_6} = 3.7$.[19]

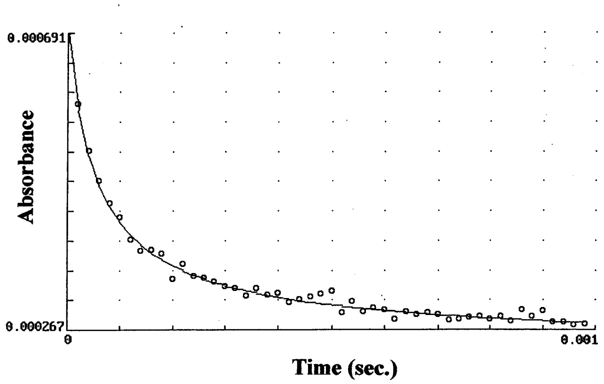

Figure 2. Time-resolved absorbance at 235 nm determined experimentally (circles) and from fitting (solid line) using modeling parameters in Table 2 and with derived values of $k_3 = (9.5 \pm 0.4) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, $[C_2H_5] = (10.5 \pm 0.5) \times 10^{13}$ molecule cm^{-3}, and $[C_2H_3] = (11.1 \pm 0.4) \times 10^{13}$ molecule cm^{-3}.

The time-resolved absorption data cannot distinguish various product channels which lead to nonabsorbing products such as those for the reactions $C_2H_5 + C_2H_5$ and $C_2H_5 + C_2H_3$. Thus, the overall k_1 rate constant ($k_1 = k_{1c} + k_{1d}$) was used as a fixed parameter and the overall k_3 rate constant ($k_3 = k_{3c} + k_{3d}$) was evaluated through the modeling and fitting procedures.

The Acufit kinetic simulation program is specifically designed for analysis of time-resolved absorption data; it uses the experimental data file, the model information generated by Acuchem and user selected values for input parameters. Known parameters are held at their input values. An iterative procedure is used to adjust the values of parameter(s) of interest until the "best" fit of the experimental data to the assumed model is achieved. The initial ethyl and vinyl radical concentrations is calculated from the Beer–Lambert law by using the absorbance immediately following the photolysis event, the known absorption cross sections for the ethyl and vinyl radicals and the optical path length of the absorption cell. However, the values for the initial radical concentrations along with the k_3 value were determined from the fitting procedures. In this way the relative and absolute values for the initial radical concentrations were allowed to vary until best fit was obtained. The quality of the fit and adequacy of the mechanism was assessed using the chi square (ψ^2) statistic.[22] The Acufit iterative least-squares procedure, through the ψ^2 minimization, returns the value of the searched parameters, their error estimates and ψ^2 value for the fit. The error estimates of the searched parameter(s) depend on the signal/noise ratio of the experimental trace and the number of the searched parameters.

Table 3 lists the experimental conditions and the values for the measured parameters from such fits of the modeled signals to different time-resolved absorption signals at $\lambda = 230$ nm and $\lambda = 235$ nm.

These results suggest an overall rate constant of about 9.6 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} for the $C_2H_5 + C_2H_3$ cross-radical

TABLE 3: The Overall Rate Constant, k_3, for the $C_2H_5 + C_2H_3$ Reaction and the Initial Radical Concentrations Derived from the Modeling of Time-Resolved Absorption Data

EVK/He, molecule cm^{-3}/kPa	laser energy,[a] mJ	monitoring λ, nm	k_3,[b] 10^{-11} cm^3 $molecule^{-1}$ s^{-1}	$[C_2H_5]_0$,[b] 10^{13} molecule cm^{-3}	$[C_2H_3]_0$,[b] 10^{13} molecule cm^{-3}	% dissociation
13 × 10^{15}/93	~70	230	9.3 ± 0.3	11.1 ± 0.3	10.5 ± 0.3	~0.9
6.5 × 10^{15}/93	~130	230	10.1 ± 0.3	10.1 ± 0.2	9.6 ± 0.3	~1.4
13 × 10^{15}/93	~75	235	10.9 ± 0.4	16.2 ± 0.4	15.4 ± 0.4	~1.2
6.5 × 10^{15}/93	~200	235	8.0 ± 0.6	12.3 ± 0.3	10.9 ± 0.3	~1.9
8.0 × 10^{15}/93	~140	235	9.5 ± 0.4	11.1± 0.4	10.5 ± 0.5	~1.3

[a] ArF excimer laser energy as read at the source. [b] Error estimates derived from modeling fits.

TABLE 4: Biases on Measured k_3 Due to Uncertainties of the Known Parameters Used in Analysis of Absorption Data[a]

parameter:	$k_{1c} + k_{1d}$	k_{2c}	k_{2d}	$\sigma_{C_2H_3}$	$\sigma_{C_2H_5}$	$\sigma_{C_4H_6}$	measured k_3	bias on k_3
central value:	2.2[b]	9.3[c]	3.1[c]	3.1[d]	2.5[e]	3.7[f]	9.6 ± 0.4[g]	0.0
3	+0.3						9.1	0.5
	−0.3						9.8	0.2
4		+1.5					1 0.6	1.0
		−1.5					8.4	1.2
5			+0.5				9.0	0.6
			−0.5				10.0	0.4
6				+0.7			10.6	1.0
				−0.7			8.5	1.1
7					+0.1		10.1	0.5
					−0.1		8.9	0.7
8						+0.2	10.2	0.6
						−0.2	8.7	0.9

[a] The units are $\sigma \times 10^{18}$ cm^2 molecule and $k \times 10^{11}$ cm^3 molecule^{-1} s^{-1}. [b] Rate constant value and error from ref 7. [c] From ref 8. [d] From ref 16. [e] From ref 17. [f] From ref 19. [g] Measurement (random) error.

reaction. The results of the analysis, within the measurement uncertainties, agree with a one-to-one production of ethyl and vinyl radicals through the 193-nm photolysis of EVK. The calculated initial radical concentrations relative to the radical precursor concentrations at various experimental conditions suggest a photodissociation efficiency of about 1% to 2% depending upon the photolysis energy.

As unknown parameters are extracted from a relatively complex, multicomponent reaction scheme, it is essential to quantify a realistic uncertainty for the derived parameter(s). In general, both systematic (inaccurate value for known parameter(s) or faulty calibration) and random (unpredictable variations in the measurement) errors must be included. Systematic errors are often called *biases* in the measurement.[22,23] In the present work we have assessed the contribution of uncertainties of each known parameter used in the modeling of the ethyl−vinyl reaction system toward the combined uncertainty of the measured k_3 rate constant.

Table 4 lists the parameters used in the data analysis (first row), their central values (second row) and corresponding error limits (rows 3−8). By using the central values for known parameters a rate constant value of $k_3 = 9.6 \times 10^{-11}$ has been determined from analysis of an absorption trace obtained at 235 nm. The random error for determining k_3, derived by the analysis program, is ±0.4 (listed in the second row). The random error primarily is due to the level of signal/noise on the data and also depend on the number of measured parameters.

In developing rows 3−8 of Table 4, the known parameters are fixed either at their best known (central) values, as given on the second row of the Table 4, or at the upper or lower limits of values as dictated by the corresponding uncertainties. If a cell is blank the central value for that parameter is employed. The k_3 value is then derived for the corresponding set of known parameters. All rows involve the analysis of the same absorption trace obtained at 235 nm. The biases on k_3, listed in the last column of Table 4, are the difference of the k_3 values when the central and noncentral values for known parameters are used.

The results of the error analysis suggest that biases on k_3 are largest (∼10%) when k_{2c} and $\sigma_{C_2H_3}$ are fixed at "noncentral" values. Variations of other parameters, within their corresponding uncertainties, each result in about a 5% bias on k_3 value. The combined uncertainty on the measured k_3 value can be estimated through the vector addition of the biases (systematic errors) and the random error.[22, 23]

$$\delta^2 k_3 = (0.35)^2 + (1.1)^2 + (0.5)^2 + (1.0)^2 + (0.55)^2 + (0.8)^2 + (0.4)^2 = (1.9)^2 \quad (8)$$

TABLE 5: Product Yields Derived from Modeling of the C_2H_5 and C_2H_3 Mixed Radical System for Various k_{3c} Values and by Using the Rate Parameters Listed in Table 2[a]

k_3	$[C_2H_2]$[b]	$[C_2H_4]$[b]	$[C_2H_6]$[b]	$[C_4H_6]$[b]	$[C_4H_8]$[b]	$[C_4H_{10}]$[b]
2.0×10^{-11}	2.2	6.3	1.6	2.7	1.0	3.2
4.0×10^{-11}	1.8	4.9	1.3	2.7	2.1	3.2
6.5×10^{-11}	1.4	3.2	0.9	2.7	3.4	3.2
8.0×10^{-11}	1.1	2.2	0.6	2.7	4.1	3.2

[a] $[C_2H_5]^0 = [C_2H_3]^0 = 1.2 \times 10^{14}$ molecule cm^{-3}, $k_3 = 9.6$ cm^3 molecule^{-1} s^{-1}, and $k_{3D1}/k_{3D2} = 2$. [b] Concentrations in units of 10^{13} molecule cm^{-3}.

The contribution of the biases from each fixed parameter is taken as the average of the upper and lower biases determined at the uncertainty limits of each known parameter.

The vector addition (eq 8) assumes that the errors in the fixed parameters are not correlated. Since values of known parameters are obtained from independent experiments, they are thus uncorrelated errorwise and they are as likely to have a positive as a negative error associated with them.

Therefore, the overall rate constant value for the ethyl and vinyl cross-radical reaction, with a combined uncertainty as derived from these measurements can best be presented as: $k_3 = (9.6 \pm 1.9) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

Evaluation of the Combination Rate Constant k_{3c} Using Comparative Methods. In mixed radical systems, the major product yields and the known rate coefficients can be used to determine an unknown radical−radical rate coefficient. Here, through use of the kinetic modeling and comparison of the experimental product yields with the numerical simulations, we have determined the k_{3c} rate constant for the combination reaction $C_2H_5 + C_2H_3 \rightarrow C_4H_8$. The reaction sequences 1−3 were modeled, at high-pressure conditions, using known rate coefficients for the self-reactions of ethyl radicals and vinyl radicals as given in Table 2. The kinetic modeling was performed using the Acuchem[21,22] numerical integration routine. Initial radical concentrations similar to those of the experimental conditions were used. The product yields determined experimentally were compared with the modeling results for a range of k_{3c} values between 1×10^{-11} and 9.6×10^{-11} cm^3 molecule^{-1} s^{-1}. The total k_3 value ($k_3 = k_{3c} + k_{3d}$) was kept constant at 9.6×10^{-11} cm^3 molecule^{-1} s^{-1}, and a ratio of $k_{3d1}/k_{3d2} = 2$ was used. Table 5 lists the product concentrations derived when $[C_2H_5]^0 = [C_2H_3]^0 = 1.2 \times 10^{14}$ molecule cm^{-3} was used.

The best agreement between the yield of the products determined experimentally and through the modeling was achieved when $k_{3c} = 6.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. A 20%

variation of the k_{3c} from the central value, $(6.5 \pm 1.3) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, resulted in variations of the simulated product yields which were within about the 15% uncertainties of the experimental product analysis measurements.

The rate constant of $k_{3c} = 6.5 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} for the combination reaction $C_2H_5 + C_2H_3 \rightarrow C_4H_8$ is nearly a factor of 2 slower than a previously reported rate constant of 12×10^{-11} cm^3 $molecule^{-1}$ s^{-1} for the combination reaction $CH_3 + C_2H_3 \rightarrow C_3H_6$.[9,14] The difference in collision cross sections of the ethyl and methyl radicals account for about 25% reduction in rate constant for $C_2H_5 + C_2H_3$. However, additional factors such as energetics of the reactions and products may also play significant roles in the efficiency of the radical−radical combination reactions. Deviations from hard sphere collision rate constants have recently been presented.[25]

The geometric mean rule[24] $k_{AB} = 2(k_{AA}k_{BB})^{0.5}$ also has often been used to estimate rate constants for cross-radical combination reactions k_{AB} when rate constants for the radical self-combination reactions k_{AA} and k_{BB} are known. Using $k_{1c} = 2.0 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} and $k_{2c} = 9.3 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, a value of $k_{3c} = 8.6 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} is calculated from the geometric mean rule. This value is about 30% higher than the k_{3c} value derived through kinetic modeling but within the uncertainties of two measurements.

IV. Conclusions

The cross-radical reactions of ethyl and vinyl radicals have been investigated, for the first time, employing excimer laser photolysis in conjunction with time-resolved UV-absorption spectroscopy, quantitative GC/MS product analysis, and detailed kinetic modeling. Ethyl and vinyl radicals were simultaneously produced through the 193-nm photolysis of EVK in a helium bath. Analysis of the time-resolved UV absorption data, collected at $T = 298$ K and $P = 93.3$ kPa, resulted in an overall rate constant of $(9.6 \pm 1.9) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} for the $C_2H_5 + C_2H_3$ cross-radical reaction. The reported uncertainty was calculated from contributions of both random and systematic errors for each parameter used in the model calculation.

The final products of the mixed ethyl−vinyl radical system were identified and quantified using GC/MS analysis. The combination channel, yielding 1-butene, appears to be dominant at high-pressure conditions with a rate constant of about 6.5×10^{-11} cm^3 $molecule^{-1}$ s^{-1} The analysis of the time-resolved absorption data and product analysis agree with the 1:1 production of ethyl and vinyl radicals upon 193-nm photolysis of EVK. Under the experimental conditions of this study a photodissociation yield of about 1% to 2% for EVK has been achieved.

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