# Photolysis of Methyl Vinyl Ketone at 193.3 nm: Quantum Yield Determinations of Methyl and Vinyl Radicals

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The primary dissociation processes in the photolysis of methyl vinyl ketone (MVK) at 193.3 nm have been investigated. A quantum yield of close to unity for the formation of both CH<sub>3</sub> and C<sub>2</sub>H<sub>3</sub> radicals has been determined using real-time absorption data in conjunction with gas chromatographic analysis of final products. Detailed kinetic modeling of the system indicates a rate constant of  $(1.5 \pm 0.3) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for the cross-combination of methyl with vinyl radicals. A combination/disproportionation ratio for the vinyl-vinyl system of  $3.2 \pm 0.7$  was obtained. The ultraviolet absorption spectrum and absorption cross-sections of methyl vinyl ketone over the wavelength range from 160 to 200 nm were measured.

#### Introduction

The photolysis of ketones, in the gas phase, has been used extensively as a convenient source of hydrocarbon radicals.<sup>1</sup> In continuation of our efforts to identify a convenient and clean source of vinyl radicals we have investigated the photodissociation of methyl vinyl ketone (MVK) at 193.3 nm. We are particularly interested in the quantum yield of vinyl radical formation and, necessarily, an understanding of the chemistry of this system. To our knowledge, the photodissociation of this molecule has not been investigated previously.

The simplest ketone, acetone, has long been used as a photolytic source of methyl radicals<sup>1</sup> and has been extensively studied under various photolysis conditions as a function of incident wavelength and pressure. Early "prelaser" experiments have been reviewed by Lee and Lewis<sup>1</sup> and reveal that the primary photochemical dissociation event, at low photolysis energies and  $\lambda > 200$  nm, generally results in the cleavage of a single C-C bond to produce a methyl and acetyl radical followed by a temperature dependent decomposition of the CH<sub>3</sub>CO into yet another CH<sub>3</sub> plus CO. At higher incident photon energies, from photolysis at 193 nm, the excitation into the 3s-n Rydberg transition leads to both C-C bonds broken in a two step fragmentation, producing a CO molecule and two methyl radicals with a near unity quantum yield.<sup>2</sup> The dynamics of the chemical bond breaking sequence in acetone has been the subject of a number of investigations. Of particular interest is the sequence of events that takes place on the excited potential surface(s). For example, do the two C-C bonds rupture sequentially or simultaneously? Does the dissociation proceed directly on the initially excited surface, or does the system predissociate by crossing from a quasi-bound surface to a lower un-bound surface? Also, what is the nascent distribution of the internal energy of the fragments? Leone and co-workers<sup>3</sup> have performed a series of experiments in order to determine the distribution of translation and internal energy between the CO and CH<sub>3</sub> fragments following the photolysis of acetone at 193 nm.<sup>3</sup> They have observed rapid vibrational relaxation of CH<sub>3</sub> in agreement with earlier results of Callear<sup>4</sup> and also reported a rotational temperature distribution of the fragments. Houston and co-workers<sup>5</sup> also have studied the dynamics and energetics of the photofragmentation of acetone at 193 nm. They found no evidence for two distinct CH<sub>3</sub> populations, as might be characteristic of a stepwise photolysis mechanism. They suggested the available energy is partitioned equally between the two dissociating C-C bonds with two bonds cleaving in rapid succession on a time scale short enough to allow little redistribution of energy into the methyl degrees of freedom. More recently, Hall et al.<sup>6</sup> have examined the photodissociation of acetone- $d_6$ . Applying the analysis of Strauss and Houston,<sup>5b</sup> they showed that the interpretation of the acetone dissociation is consistent with a fully stepwise dissociation but in which the lifetime of the acetyl fragment is sufficiently long to permit formation of rotationally averaged methyl radicals from the secondary fragmentation.

In contrast to extensive studies of acetone photochemistry no work of which we are aware has been reported on the photochemistry of methyl vinyl ketone. In the work reported here we have investigated the photolysis of this unsaturated ketone at 193 nm. Two independent actinometric techniques, optical absorption spectroscopy and gas chromatographic analysis of products, were employed to measure the quantum yield of methyl vinyl ketone photodissociation, quantum yields of radical formation, and product distributions. In addition, UV absorption cross sections for methyl vinyl ketone between 160 and 260 nm have been determined. We have also reexamined the reaction kinetics of the methyl-vinyl system using a detailed kinetic modeling program and have utilized a new approach to measure, more accurately, the rate parameters of this important kinetic system.

## **Experimental Section**

Several experimental procedures which have been described previously<sup>7</sup> were utilized for these studies and only a brief summary is presented here.

(A) Absorption Spectra. The analysis of the experimental results requires accurate knowledge of the absorption coefficients of precursor and product molecules. The optical ultraviolet absorption spectra of methyl vinyl ketone is reported here for the first time. The absorption measurements were made using a 1-m McPherson,<sup>16</sup> normal incidence, vacuum monochromator provided with interchangeable vacuum uv and uv photomultipliers, analog to digital circuitry, computer controlled wavelength stepping motor drive, and computerized data acquisition. Absorption data were recorded digitally and presented graphically. The absorption measurements were recorded at 0.2 nm intervals. Adherence to the Beer-Lambert absorption law was assured through variation of the sample pressure. The resulting extinction coefficients were quite reproducible with a precision of better than 5%. Wavelengths were calibrated using both the 253.7 nm Hg line and the 121.6 nm Lyman- $\alpha$  line. The UV absorption spectrum of acetone, 1,3-butadiene, propylene and other predicted stable products of

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methyl vinyl ketone photolysis were also measured using this apparatus. Some of these data have been reported previously in papers from this laboratory<sup>7</sup> and the present results agree quantitatively with earlier data. The strong absorption of 1,3-butadiene, the product of the vinyl radical combination reaction, in the spectral region about 164 nm has been used previously as a probe of the vinyl radical concentration.<sup>7a</sup>

(B) UV Kinetic Absorption Spectroscopy. The laser photolysiskinetic absorption spectroscopy apparatus used for both the optical quantum yield and real-time kinetic measurements has been described earlier.<sup>7</sup> Briefly, the photolysis source of the apparatus consists of a Lambda Physik (EMG 201) excimer laser with a CW Xe light source for optical detection. The photolysis laser pulse was incident upon a Suprasil cell perpendicular to the Xe probe radiation. The continuum radiation was passed through the photolysis cell and then focused onto the entrance slit of a 0.25-m Czerny-Turner mount vacuum UV monochromator. The dispersed light was monitored using Hamamatsu photomultipliers. A self-enclosed Watson gas circulating pump,<sup>8</sup> operational up to about 40 kPa (300 Torr), was used to flow the gas mixture through the reaction cell so that the cell contents were replaced several times each second. The laser pulse repetition was chosen not to exceed the sample replacement rate. The active volume of the photolysis cell was 4 cm<sup>3</sup>, about 0.001 of the total sample volume. The total cell length, 11 cm, was restricted by a mask to a photolysis length of about 4 cm with a sample thickness of about 1 cm. Product yields were normalized with respect to the parent concentration, laser energy and number of laser pulses.

(C) Gas Chromatographic Analysis. Provisions for sampling into an on-line gas chromatograph provided additional means of absolute quantum yield and product yield measurements. The photolyzed sample was admitted to an evacuated injection loop that was subsequently pressurized and the sample directly injected onto an appropriate column. A nonreactive tracer gas, cyclopropane, was added in known amounts to the gas mixture to provide a calibrant of sample size. In this way each product, relative to the tracer, and normalized to the number of laser pulses, provided absolute product yields. Gas chromatographic separation and identification of photolysis products were carried out using Poropak R and N columns and a flame ionization detector. Temperature programming of the oven was required to separate the products. The retention times and response of the gas chromatograph were calibrated by injection of standard samples with concentrations similar to those produced by the laser photolysis.

(D) Chemicals. The methyl vinyl ketone was obtained commercially from Columbia Organic Chemical Co. and used after successive freeze-pump-thaw cycles at 77 K. Chromatographic analysis of the sample, before photolysis, showed no impurity on a detectable level. The parent molecule was mixed with excess helium (99.99% purity) or argon (99.95% purity) and uniformly distributed throughout the system.

### **Results and Discussion**

(A) System Calibration: 193 nm Photolysis of Acetone. The photolysis of acetone at 193.3 nm was performed in order to test and calibrate the photometric techniques that would be employed in the methyl vinyl ketone studies. The dissociation of acetone following photolysis was determined, by photometric detection, through reduction of its absorption at 195 nm. The decrease in absorption by acetone was converted to the percent dissociation per pulse using the absorption cross section of acetone at 195 nm ( $\sigma = 2.1 \times 10^{-17}$  cm<sup>2</sup> molecule<sup>-1</sup>, base e) and the Beer-Lambert law. Several measurements for photolysis of mixtures with acetone concentration of 16 × 10<sup>15</sup> molecule cm<sup>-3</sup> in 13 kPa (100 Torr) He indicated that  $3.7 \pm 0.4\%$  of parent CH<sub>3</sub>COC<sub>2</sub>H<sub>3</sub> was dissociated per pulse in the photoactive region. In these experiments the formation of CH<sub>3</sub> was monitored through its strong absorption at 216.4 nm. The absorption decreased with



Figure 1. Absorption coefficients for methyl vinyl ketone.

time due to the methyl combination reaction. The initial methyl concentration was obtained by extrapolating the measured methyl radical absorption at 216.4 nm to zero time. The yield of ethane, the methyl radical combination product determined chromatographically, provided additional means of testing the accuracy of the optical measurements. Within the experimental error, the initial CH<sub>3</sub> concentrations determined independently, from (1) the loss of acetone, (2) direct optical detection of CH<sub>3</sub>, and (3) the ethane yield, were all in good agreement. These determinations also lead to an absorption cross section of  $4.3 \times 10^{-17}$  cm<sup>2</sup> molecule<sup>-1</sup> for CH<sub>3</sub> at 216.4 nm and a recombination rate constant of  $5.0 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, in accord with previously reported values from this laboratory and those reported by Pilling et al.<sup>7,9</sup>

The photolysis of acetone at 193 nm also provided means for determinations by chemical actinometry of the laser energy deposition using the yield of methyl radical formation and yield of ethane. The measured laser fluence inside the cell, when the laser was at optimum operating energy, was about  $10 \text{ mJ/cm}^2$  per pulse.

(B) MVK Dissociation Yield and Optical Actinometry at 190 nm. The photodissociation of the methyl vinyl ketone was determined actinometrically employing the techniques used for calibration of the system with acetone: first, the absolute quantity of methyl vinyl ketone photolyzed by the laser pulse was determined spectroscopically; second, the absolute yield of stable products were determined chromatographically; third, the absolute yield of methyl and vinyl radicals were determined using realtime absorption spectroscopy in conjunction with detailed computer modeling of the experimental absorption data at 216.4 nm.

The real-time absorption data at 216.4 nm were modeled using a reasonable reaction sequence to describe the system and employing an improved version of the Acuchem kinetics modeling program.<sup>10</sup> The program was modified to provide output rate constants, absorption coefficients of experimentally monitored species and the temporal profiles of radical and product concentrations via a least squares iterative procedure. Details of this program, its capabilities and applications for analysis of complex kinetic systems will be presented in the near future.

Mass balance requires the number of methyl vinyl ketone molecules dissociated be in quantitative agreement with the yield of reaction products. As mentioned above, the dissociation of  $CH_3COC_2H_3$  was obtained from the reduction in absorption by the ketone upon photolysis. This measurement requires an accurate value of the absorption cross section at the probe wavelength used for the spectroscopic analysis. The ultraviolet spectrum for MVK, between 160 and 260 nm, shown in Figure 1, is seen to be largely unstructured with a threshold at 240 nm. It is dominated by a strong continuum with maxima at about 195 and 170 nm. Absorption bands at the same energies have been observed by electron-loss spectroscopy and both have been assigned.<sup>11</sup> At 193 nm dissociation of methyl vinyl ketone is probably from a 3s Rydberg state which is analogous to dissociation of other ketones at 193 nm. The value of the absorption cross section is relatively constant over a broad



Figure 2. Increase in transmission, at 190 nm, due to the reduction of MVK concentration following photolysis of a mixture with MVK concentration of  $26 \times 10^{14}$  molecule cm<sup>-3</sup> in 13.3 kPa (100 Torr) He.

TABLE I: Spectroscopic Determinations for Loss of MVK, following the Laser Photolysis at 193 nm (See Also Figure 1)

п	nixtu	re	laser energy			$\Delta[MVK]/$ [MVK] <sup>0</sup> (% reaction)	
[MVK]ª	М	P <sub>M</sub> (kPa)	(mJ)	$-\ln(I/I_0)$	$\Delta[MVK]^b$		
16.2	He	9.3	≈8.5	0.0537	3.66	22.6	
16.2	He	9.3	≈8.5	0.0510	3.49	21.5	
25.9	He	13.3	≈8.5	0.0800	6.37	24.6	
25.9	He	13.3	≈8.5	0.0793	6.31	24.4	
25.9	He	13.3	≈10.4	0.0766	6.11	23.6	
25.9	He	13.3	≈10.4	0.0820	6.47	25.0	
25.9	He	26.6	≈10.0	0.0778	6.11	23.5	
25.9	Ar	26.6	≈10.5	0.0792	6.31	24.3	
25.9	Ar	26.6	≈10.4	0.0754	6.02	23.2	
					ave	23.6 ● 1.1°	

<sup>a</sup> Concentrations in units of (molecule cm<sup>-3</sup>) × 10<sup>-14</sup>. <sup>b</sup>  $\sigma_{MVK}$  = (3.2 ± 0.2) × 10<sup>-17</sup>, cm<sup>2</sup> molecule<sup>-1</sup>, at 193 nm. <sup>c</sup> Systematic error.

wavelength region and at 193 nm is  $\sigma_{MVK} = (3.2 \pm 0.2) \times 10^{-17}$  cm<sup>2</sup> molecule<sup>-1</sup> (base e).

The strong absorption of CH<sub>3</sub>COC<sub>2</sub>H<sub>3</sub> facilitated the direct spectroscopic determination of its loss following photolysis. Figure 2 shows the increase in transmission (downward direction in the figure) at an analyzing wavelength of 190 nm following photolysis of a mixture with MVK concentration of  $2.6 \times 10^{15}$  molecule cm<sup>-3</sup> in 13.3 kPa (100 Torr) He. The traces are the result of averaging 40 pulses. The prompt increase in transmission per pulse is clearly the result of a reduction in concentration of the starting material which can be converted to the percent photolyzed in the photoactive region. The photolysis yield, determined optically, at various pressures and compositions are given in Table I. The reproducibility of the measurements particularly at He pressures higher than 9.6 kPa (70 Torr) are very good and resulted in 23.6  $\pm$  1.1% photodissociation of MVK per pulse. The decomposition is locally large so as to enhance the probability of radical-radical reactions.

(C) Product Yields by End-Product Analysis. The yields of final products have been determined quantitatively under a variety of conditions, including the effect of initial ketone concentration, the diluent buffer gas pressure and the laser fluence. The results of the chromatographic determinations are presented in Table II. The product yields are absolute and normalized to the number of laser pulses, laser fluence, and the initial concentration of the parent molecule. For these experimental runs, the laser fluence was varied by a factor of 2 from about 10 mJ/cm<sup>2</sup> per pulse to about 5 mJ/cm<sup>2</sup> per pulse. No significant change in the product distribution was observed and the yield, over this range of incident intensities, was linear with fluence indicating the absence of multiphoton processes.

In earlier work from this laboratory, divinylmercury was used as a photolytic source of vinyl radicals.<sup>7a,12</sup> Experimentally difficult to handle, the divinylmercury exhibited slow but steady decomposition on the gas handling surface. In comparison methyl vinyl ketone has proven to be a clean precursor for vinyl and methyl radicals and exhibits no "dark" reactions resulting from surface decomposition. All the products listed in Table II, therefore, are the result of either the initial photolysis or subsequent reactions between methyl and vinyl radicals or their dissociation products. As will be discussed later small amount of hydrogen atoms, estimated to be less than 10% that of the total methyl radical yield, are also produced. The importance of determining end products such as ethane, butadiene and propylene are most significant and strictly define the overall chemistry. The final product yields place strict boundary conditions on any computer model of the system.

(D) Mechanism. The photofragmentation processes, following the 193 nm photolysis of methyl vinyl ketone, and subsequent reactions of the photofragments as evidenced by photometric detection and chromatographic product analysis may be described by the following reaction sequence. The photodissociation is written as a composite of probable sequential bond ruptures:

$$CH_{3}COC_{2}H_{3} \xrightarrow{h\nu} CH_{3} + C_{2}H_{3}^{*} + C_{0}$$

$$C_{2}H_{3}^{*} + M \rightarrow C_{2}H_{3} + M \qquad (1)$$

$$C_2 H_3^* \to C_2 H_2 + H \tag{2}$$

$$CH_3 + CH_3 \rightarrow C_2H_6$$
 (3)

$$C_2H_3 + C_2H_3 \rightarrow C_4H_6 (1,3-butadiene)$$
(4)

$$C_2H_3 + C_2H_3 \rightarrow C_2H_2 + C_2H_4$$
 (5)

$$CH_3 + C_2H_3 \rightarrow C_3H_6 \text{ (propylene)}$$
 (6)

$$CH_3 + C_2H_3 \rightarrow CH_4 + C_2H_2 \tag{7}$$

$$C_2H_3 + H + M \rightarrow C_2H_4 + M$$
 (8)

$$CH_3 + H + M \rightarrow CH_4 + M \tag{9}$$

On the time scale of these experiments, the photodissociation produces both  $CH_3$  and  $C_2H_3$  radicals plus a CO molecule in a time short compared to the kinetic measurement. For the purposes of these experiments the dissociation dynamics are not an important factor.

All of the stable products, indicated above, except CO can be detected and their yield determined through chromatographic analysis. Intermediates and final products that are monitored spectroscopically consist of MVK, CH<sub>3</sub> and 1,3-butadiene. The formation of excited vinyl radicals which can decompose as shown in reaction 2 may be deduced from the thermochemistry of the dissociation. The sequential dissociation of methyl vinyl ketone requires the addition of 426 kJ/mol<sup>13</sup>. The absorption of a 193 nm photon (620 kJ/mol) leaves about 194 kJ/mol to be distributed in rotational, vibrational and translational energy in the photofragments. If the CH<sub>3</sub> radical formed is the "primary" process and it has as much internal energy as the first CH<sub>3</sub> radical from the photodissociation of acetone at 193 nm, 35 kJ/mol, than at least 158 kJ/mol remain in the  $C_2H_3$  and CO fragments. The dissociation of  $C_2H_3$ , reaction 2, requires about 155 kJ/mol. Therefore, sufficient energy is barely available to permit the dissociation. As will be shown later, the production of  $C_2H_2$  + H from  $C_2H_3^*$  represents a minor fraction of the  $C_2H_3$  yield. The dissociation of excited vinyl radicals has been observed previously in the broad-band  $vuv^{14}$  and 193 nm<sup>15</sup> photolysis of  $C_2H_4$ . Alternatively, the initial process may form  $C_2H_3 + CH_3CO$ , a process that may be more endothermic, by about 18 kJ/mol, than initial CH<sub>3</sub> formation. Here, it is assumed the  $C_2H_3$ -CO bond is about 8-9 kJ/mol stronger than the C-C bond in acetyl due to enhanced resonance energy.

Propylene is a major product of MVK photolysis and is formed through the cross-combination reaction between methyl and vinyl radicals (reaction 6). The yield of propylene has a small pressure dependence that is most noticeable at low added inert gas pressure. Detailed studies of the pressure dependencies of the product yields are currently under investigation.

TABLE II: Gas Chromatographic Determination of Methyl and Vinyl Radical Yields, Normalized with Respect to the MVK Concentration and the Laser Energy (Concentrations in Units of (molecule  $cm^{-3}$ ) × 10<sup>-14</sup>)

mixu	ure	laser										
[MVK]	P <sub>He</sub> (kPa)	energy (mJ)	[CH₄]	[C <sub>2</sub> H <sub>4</sub> ]	[C <sub>2</sub> H <sub>4</sub> ]	[C <sub>2</sub> H <sub>2</sub> ]	[C <sub>2</sub> H <sub>4</sub> ]	[C₄H₄]	Σ[CH₃]/ [MVK]	$\frac{\Sigma[C_2H_3]}{[MVK]}$	Σ[C <sub>2</sub> H <sub>n</sub> ]/ [MVK]	k4/k5
32	0.7	≈8.1	0.35	0.42	1.49	1.84	2.88	1.29	6.24	6.24	7.63	2.9
129	0.8	≈8.5	$0.42 \pm 0.06$	$0.58 \pm 0.03$	1.39 ± 0.07	1.91 ± 0.20	$2.59 \pm 0.32$	$1.36 \pm 0.11$	5.76 ± 0.49	$6.47 \pm 0.18$	7. <b>79</b>	2.5
65	1.3	≈8.8	0.39	0.42	1.36	1.75	$2.85 \pm 0.23$	$1.49 \pm 0.32$	6.05	6.77	8.06	3.2
194	2.6	≈8.5	0.48	0.45	1.29	2.39	3.04	2.10	6.08	8.44	10.25	3.7
194	2.6	≈8.5	0.48	0.61	1.30	1.68	3.43	2.17	6.57	9.03	10.10	3.5
32	13.3	≈9.2	0.42	0.42	0.94	1.23	4.85	1.23	7.57	8.15	8.96	3.1
32	13.3	≈5.4	0.48	0.29	0.71	0.71	4.30	1.16	6.24	7.15	7.54	3.7
64	13.3	≈10.0	0.55	0.48	1.36	1.71	4.53	1.33	7.86	8.22	9.41	2.5
32	26.6	≈10.0	0.61	0.68	1.55	1.84	3.30	1.58	7.02	7.70	9.54	2.3
26	26.6	≈10.0	$0.36 \pm 0.07$	0.39 ± 0.06	0.94	1.65 ± 0.23	$3.59 \pm 0.39$	$1.16 \pm 0.19$	$5.86 \pm 0.65$	$6.31 \pm 0.84$	7.51	2.6
64	26.6	≈8.5	0.61	0.48	1.07	1.58	4.75	2.07	7.34	9.67	10.71	4.4
129	26.6	≈8.5	0.47	0.45	1. <b>49</b>	1.55	4.17	1.75	7.63	8.57	9.70	3.9
av			$0.45 \pm 0.09$	$0.48 \pm 0.10$	$1.23 \pm 0.26$	1.65 ± 0.39		1.55 ± 0.39	6.70 ± 0.77	7.73 ± 1.13	8.93 ± 1.20	$3.2 \pm 0.7$



Figure 3. Temporal absorption at 216.4 nm (from 193.3 nm photolysis of a mixture with MVK concentration of  $45.3 \times 10^{14}$  molecule cm<sup>-3</sup> in 13.3 kPa (100 Torr) He. Solid line modeled using parameters in Table III.

 TABLE III: Reactions and Parameters Used in the Modeling of the Experimental Data

reaction no.	reaction, $\epsilon^a$	parameter <sup>b</sup>		
	$MVK \rightarrow xCH_1 + yC_2H_1 + zH$	x, $y = (adjusted), z = x - y$		
3	$CH_3 + CH_3 \rightarrow C_2H_6$	$k_3 = 0.5E - 10^{\circ}$ (fixed)		
4	$C_2H_3 + C_2H_3 \rightarrow C_4H_6$	$k_4 + k_5 = 1.25 E - 10$ (fixed)		
5	$C_2H_3 + C_2H_3 \rightarrow C_2H_2 + C_2H_4$	$k_4/k_5 = 3 \pm 1 \text{ (ranged)}$		
6	$CH_3 + C_2H_3 \rightarrow C_3H_6$	$k_6 + k_7 = (adjusted)$		
7	$CH_3 + C_2H_3 \rightarrow C_2H_2 + CH_4$	· · · · · ·		
8	$CH_3 + H \rightarrow CH_4$	$k_8 = 0.65 \text{E} - 10 \text{ (fixed)}$		
9	$C_2H_3 + H \rightarrow C_2H_4$	$k_9 = 2.0E - 10$ (fixed)		
	$\sigma_{MVK}$ , at 216.4 nm	0.53E-17 (fixed)		
	σ <sub>CH<sub>1</sub></sub> , 216.4 nm	4.3E-17 (fixed)		
	$\sigma_{C,H_{\rm el}}$ , at 216.4 nm	6.5E-17 (fixed)		

<sup>a</sup> Absorption cross sections ( $\sigma$ ) in units of cm<sup>2</sup> molecule<sup>-1</sup>. <sup>b</sup> Rate constants in units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. <sup>c</sup> Read as 0.5 × 10<sup>-10</sup>.

Another major product is 1,3-butadiene, which is formed by combination of vinyl radicals (reaction 4). The yield of 1,3butadiene relative to that of ethylene, is equal to the ratio of the vinyl radical combination/disproportionation rate constants  $(k_4/k_5 \approx [C_4H_6]/[C_2H_4])$ . An average value of  $k_4/k_5 = 3.2 \pm 0.7$ is obtained from these experiments. This ratio was found previously to be 4.7,<sup>7a</sup> which is in good agreement with the present value when reported errors are considered. The present value is preferred since the previous measurements from this laboratory used divinylmercury as the photolytic source of vinyl radicals. As already noted the presence of surface-induced "dark" reactions introduced an error in determination of the product yield particularly that of C<sub>2</sub>H<sub>4</sub>.

The yield of ethane, the methyl-methyl recombination product, is independent of total pressure and scaled linearly with laser intensity. The primary source of ethylene in this system is the vinyl radical disproportionation reaction which will also yield an identical amount of acetylene<sup>6</sup> (reaction 5). It is seen in Table II, however, that the yield of acetylene is higher than that of ethylene. Additional  $C_2H_2$  could conceivably be formed from two processes: (1) dissociation of excited vinyl radicals (reaction 2), a process that also forms an H atom and, (2) the disproportionation reaction between vinyl and methyl which has been determined to be about 0.3 that of the combination reaction.<sup>7a</sup> These two secondary processes account, qualitatively, for the "extra"  $C_2H_2$ . The yield of H atoms could not be determined directly. The yield of CH<sub>4</sub>, in part, is affected by the H atom concentration (reaction 9). A computer model that fits not only the final product distribution but the composite temporal profile at 216.4 nm (MVK, CH<sub>3</sub> radical and butadiene temporal absorptions) requires as input or derived parameter, a concentration of H atoms that will remove CH<sub>3</sub> radicals through reaction 9. The best fit to the temporal absorption data at 216.4 nm, discussed below, required an H atom concentration that is about 10% that of the CH<sub>3</sub> concentration. The H atom concentration, derived from modeling of the optical data, is equivalent to the "extra" acetylene yield from the gas chromatographic end-product analysis.

Methane is formed primarily from the disproportionation reaction between methyl and vinyl radicals (reaction 7). A small fraction of the methane could result from the reaction between methyl radical and H-atoms formed through reaction 2, the dissociation of excited vinyl radicals.

The total yield of radicals is determined simply from

$$\sum [CH_3] = 2[C_2H_6]_{\infty} + [C_3H_6]_{\infty} + [CH_4]_{\infty} = [CH_3]_0$$
$$\sum [C_2H_3] = 2[C_4H_6]_{\infty} + 2[C_2H_4]_{\infty} + [C_3H_6]_{\infty} = [C_2H_3]_0$$

The total yields of the initial methyl and vinyl radicals (expressed as a percentage of parent photodissociated) which contribute to the formation of the final products are  $\Sigma$ [CH<sub>3</sub>] = 20.7 ± 2.4% and  $\sum [C_2H_3] = 23.9 \pm 3.5\%$ . These yields are in good agreement within the experimental error of the measurement. The evaluation of these data suggests that the primary photodecomposition process generates equal quantities of methyl and vinyl radicals. The relative quantum yields of methyl and vinyl radicals are independent of the initial methyl vinyl ketone concentration, the total pressure and the laser fluence. The yield of methyl and vinyl radicals in Table II determined via end-product analysis agrees very well with the optical actinometric determinations of methyl vinyl ketone loss  $(23.6 \pm 1.1\%)$  shown in Table I. These results yield a quantum yield of nearly unity for production of both methyl and vinyl radicals from the 193 nm photolysis of methyl vinyl ketone. Further, the equivalent quantum yields suggest that no process, other than those postulated here, makes a significant contribution to the overall photochemistry of methyl vinyl ketone at this wavelength.

(E) Actinometry by Real-Time Optical Detection of Products. The temporal absorption obtained at 216.4 nm following the 193

TABLE IV: Cross Radical Reaction Rate Constant,  $k_6 + k_7$ , the Percent Yields of Methyl and Vinyl Radicals and the Percent Reaction As Derived from Modeling of the Real-Time Absorption Data at 216.4 nm, following Photolysis of MVK at 193.3 nm (Concentrations in Units of (molecule cm<sup>-3</sup>) × 10<sup>-14</sup>)

mixture		laser								
[MVK]	P <sub>He</sub> , (kPa)	energy (mJ)	$(k_6 + k_7) \times 10^{10}$ (cm <sup>3</sup> molecule <sup>4</sup> s <sup>4</sup> )	[CH <sub>3</sub> ] <sub>0</sub>	[C <sub>2</sub> H <sub>3</sub> ] <sub>0</sub>	[CH <sub>3</sub> ] <sub>0</sub> /[MVK] (% reaction)	[C <sub>2</sub> H <sub>3</sub> ] <sub>0</sub> /[MVK]	[CH <sub>3</sub> ] <sub>0</sub> /[C <sub>2</sub> H <sub>3</sub> ] <sub>0</sub>		
48.5	13.3	≈9.2	1.7	9.35	8.77	19.3	18.1	1.06		
45.2	26.6	≈10.0	1.9	10.87	10.20	24.0	22.5	1.07		
35.6	13.3	≈9.2	$1.8 \pm 0.4^{a}$	8.93	7.96	25.1	22.4	$1.12 \pm 0.06^{a}$		
32.4	13.3	≈10.0	1.4	7.15	6.47	22.1	20.0	1.10		
32.4	13.3	≈8.5	$1.7 \pm 0.3^{a}$	7.41	6.89	25.0	23.3	$1.08 \pm 0.06^{a}$		
32.4	13.3	≈9.2	2.0	9.48	8.22	29.3	25.5	1.15		
32.4	39.9	≈10.0	$1.6 \pm 0.3^{a}$	6.89	6.34	21.3	19.6	$1.09 \pm 0.05^{a}$		
32.4	13.3	≈5.4	$1.3 \pm 0.3^{a}$	6.73	6.02	20.8	18.6	1.12		
32.4	13.3	≈5.4	1.2	6.37	5.66	19.7	17.5	1.13		
97.0	13.3	≈6.5	1.0	19.77	16.7	20.4	17.2	1.18		
16.2	13.3	≈9.2	$1.0 \pm 0.4^{a}$	3.45	3.1	21.6	19.3	1.12		
av			$1.5 \pm 0.3^{b}$			$22.8 \pm 3.3^{\circ}$	$20.4 \pm 2.7^{\circ}$	$1.11 \pm 0.04^{b}$		

<sup>a</sup> Systematic error when  $k_4/k_5$  ranges from 2 to 4 (3 ± 1). <sup>b</sup> An estimate of random error on data ( $k_4/k_5$  centered at 3.0). <sup>c</sup> Normalized with respect to the MVK concentration and laser energy (10.0 mJ).

nm photolysis of a mixture with MVK concentration of  $45 \times 10^{14}$ molecule cm<sup>-3</sup>, in 13.3 kPa (100 Torr) He is shown in the insert of Figure 3. A sharp increase in the absorption signal, following the laser pulse, is observed which decays to a nonzero baseline. At 216.4 nm where the methyl radical absorbs strongly, 1,3butadiene and parent MVK also absorb with cross sections of 4.3  $\times 10^{-17}$ , 6.5  $\times 10^{-17}$ , and 0.53  $\times 10^{-17}$  cm<sup>2</sup> molecule<sup>-1</sup>, respectively. The vinyl radical and other products do not absorb at this analysis wavelength. Therefore, the composite absorption signal at 216.4 nm can be attributed to the time history of three species: (i) The instantaneous loss of precursor following the laser pulse. This segment of the absorption remains constant through the time span after the laser pulse as shown in Figure 2. (ii) The rapid increase in absorption following the laser pulse due to photolytic production of methyl radicals. The CH<sub>3</sub> absorption decreases with time due to reaction. (iii) An increase in absorption resulting from the formation of butadiene by vinyl radical combination (reaction 4). The contribution of the butadiene absorption becomes more evident when absorption due to methyl radicals decays to an apparent nonzero baseline.

The observed complex temporal profile at 216.4 nm is treated by modeling the system using the rate constants and the absorption cross sections of the methyl-vinyl system as shown in Table III. Since all parameters cannot be adjusted simultaneously, the best strategy is to fix those whose values are well known or can be determined from independent experiments. The adjusted (calculated) parameters, chosen here, were the initial methyl and vinyl concentrations and the total methyl-vinyl cross combination rate constant ( $k_6 + k_7$ ).

Initial input values of  $CH_3$  or  $C_2H_3$  concentrations were derived from the chromatographic results. The calculation optimized their values, via an iterative procedure, to best fit the synthesized temporal profile to the experimental absorption data at 216.4 nm. In comparison, the absorption cross sections for  $CH_3COC_2H_3$ ,  $CH_3$ , and butadiene and all other rate constants were *fixed* at their best known values as given in Table III.

Table IV lists the derived values for the adjusted parameters,  $k_{6+7}$ ,  $[CH_3]_0$  and  $[C_2H_3]_0$  for a series of real-time absorption data measured at 216.4 nm. The best fit to the data was obtained with the values given in Table IV.

The quantum yields of  $CH_3$  and  $C_2H_3$  radicals derived from optical actinometry at 216.4 nm and those determined by chromatographic actinometry are in good agreement as is the percent dissociation of the precursor as determined via three independent actinometric methods. These determinations indicate that the photolysis of methyl vinyl ketone is an efficacious source of vinyl radicals where each photolyzed molecule yields nearly one vinyl and one methyl radicals, or the quantum yield for radical production is one.

The total methyl-vinyl cross combination rate constant determined in this work,  $(1.5 \pm 0.3) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, is in excellent agreement with our previous determination of this rate constant, using different sources of methyl and vinyl radicals. The combination/disproportionation ratio for vinyl-vinyl radical reactions,  $k_4/k_5 \approx [C_4H_6]/[C_2H_4]$  was found to be 3.2 ± 0.7.

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(16) Certain commercial instruments and materials are identified in this paper to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by NIST, nor does it imply that the instruments or materials identified are necessarily the best available for the purpose.