

# A kinetics study of the reaction of OH radicals with two C<sub>2</sub> hydrocarbons: C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub>

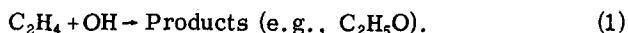
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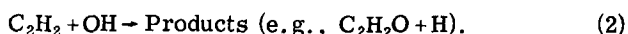
The flash photolysis-resonance fluorescence technique has been utilized to study the kinetics of hydroxyl radical reactions with ethylene and acetylene at 300 K over a wide range of experimental conditions. (1)  $\text{OH} + \text{C}_2\text{H}_4 \xrightarrow{k_1} \text{Products}$  (e.g., C<sub>2</sub>H<sub>5</sub>O), (2)  $\text{OH} + \text{C}_2\text{H}_2 \xrightarrow{k_2} \text{Products}$  (e.g., C<sub>2</sub>H<sub>2</sub>O + H). The bimolecular rate constant for Reaction (1) was observed to increase from (2.24 to 5.33) × 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> · sec<sup>-1</sup> as the total pressure varied from (3–300) torr of helium. The rate constant for Reaction (2) was invariant with total pressure, and at 300°K its value was found to be (1.65 ± 0.15) × 10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> · sec<sup>-1</sup>. The observed pressure dependency of Reaction (1) brings nearly all existing literature values for *k*<sub>1</sub> into reasonable agreement. Reaction (2) has been shown to be particularly sensitive to secondary processes the details of which are discussed.

## I. INTRODUCTION

Hydroxyl radical reactions have been the subject of considerable interest in recent years due to their importance in combustion processes and in the chemistry of the atmosphere. Ethylene is thought to be a minor, but significant constituent of the effluents emitted from automobile exhausts,<sup>1</sup> and its presence in urban atmospheres has been shown to increase the rate of conversion of NO to NO<sub>2</sub>, which is the precursor for the formation of ozone.<sup>2</sup> The reaction of hydroxyl radicals with ethylene is now thought to be an important step in this process.



The reaction of hydroxyl radicals with acetylene is of importance in the degradation of acetylene to CO<sub>2</sub>, both in the atmosphere and in diffusion controlled flames.



As a result of the importance of Reactions (1) and (2) there have been numerous studies of these chemical systems.<sup>3–10</sup> In the case of Reaction (1), the values reported by different workers for the rate constant at ambient temperatures (~300 °K) are at variance by as much as a factor of 3.<sup>3–8</sup> Most of these previous studies, which were performed in both flow and static systems using a wide variety of detection techniques, were carried out at total pressures lower than 20 torr. In none of these investigations was a systematic variation in pressure performed.

Morris *et al.*<sup>3</sup> qualitatively observed mass spectrometric adduct peaks in their study of Reaction (1), and proposed the primary process to be

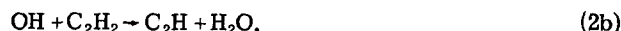


Bradley *et al.*<sup>4</sup> also reported observing the adduct peak, but in addition observed peaks indicating that ethanol also plays a role in the overall mechanism.

Of the studies on Reaction (2) documented in the literature, only four were performed at room temperature<sup>7–10</sup>; and the rate constants reported varied by as much as a factor of 5. Those studies carried out in flow systems<sup>8–10</sup>

used low initial stoichiometries ( $[\text{C}_2\text{H}_2]_0/[\text{OH}]_0$ , ranging from 2.3 to 120), which resulted in stoichiometric corrections being required for most of the rate constant data. However, only one study<sup>9</sup> actually measured the stoichiometric correction factor, *n*, while other workers reported either *k*<sub>2</sub>/*n* or used the single value of *n* which had been previously published. A more recent study performed,<sup>7</sup> using the flash photolysis-resonance absorption technique, employed moderately high initial stoichiometries, e.g.,  $[\text{C}_2\text{H}_2]_0/[\text{OH}]_0 \sim 10^2$ . That study reported that corrections to the rate data due to secondary processes were not required.

Breen and Glass<sup>9</sup> used mass spectrometric product analysis to obtain a value for the stoichiometry of Reaction (2). From this it was argued that the following two reaction channels were consistent with the data:



while the following was not:



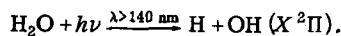
However, evidence obtained from a crossed molecular beam experiment (Gehring *et al.*)<sup>11</sup> supported Reaction (2c) as being the dominant primary process. Kanofsky *et al.*,<sup>12</sup> on the other hand, proposed that the primary process was not (2a), (2b), or (2c), but rather



## II. EXPERIMENTAL

The flash photolysis-resonance fluorescence technique has been described in great detail in previous publications<sup>13</sup> and only a summary description will therefore be presented in this text.

As in an earlier study involving reactions of the hydroxyl radical,<sup>13</sup> photolysis of H<sub>2</sub>O was used as the source of OH:



In the present study, reaction mixtures consisted of

50–300 mtorr of H<sub>2</sub>O, 20–500 torr of He, and either 1–7 mtorr of C<sub>2</sub>H<sub>4</sub> or 2–30 mtorr of C<sub>2</sub>H<sub>2</sub>. These mixtures were photolyzed using a N<sub>2</sub> spark flash lamp equipped with either a CaF<sub>2</sub> or Suprasil quartz window. CaF<sub>2</sub> was used in the study of Reaction (1) almost exclusively to reduce the photolysis of C<sub>2</sub>H<sub>4</sub>. Similarly in the case of Reaction (2), Suprasil windows were normally used to minimize photolysis of C<sub>2</sub>H<sub>2</sub>. Based upon the known absorption spectrum of H<sub>2</sub>O and previously conducted actinometry on the flash lamp using ethylene as the actinic gas, it was determined that within the spectral range 105–200 nm on the order of  $1.5\text{--}36 \times 10^{11}$  OH radicals/cm<sup>3</sup> were typically produced per flash in the reaction cell (the precise flash energy, the spectral bandwidth, and the H<sub>2</sub>O concentration defined the actual concentration).

Excitation of OH was accomplished via the use of an OH resonance lamp. This lamp primarily produced the emission characteristic of the ( $A\Sigma^{2+}; v'=0$ ) → ( $X^2\Pi; v''=0$ ) transition of OH. A small fraction of the OH, produced by the photolysis of H<sub>2</sub>O, was continuously excited by the emission from this lamp. Fluorescence from excited OH was measured using a photomultiplier tube located at right angles to the lamp. The intensity of this fluorescent emission was found to be directly proportional to the amount of OH present in the mixture. The fluorescence signal from the photomultiplier tube was then stored as a function of time in a multichannel analyzer, operated in the multiscaling mode.

Since the C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub> pressures were adjusted to make Reactions (1) and (2) kinetically pseudo-first order with respect to OH, the observed rate of OH disappearance was always exponential. Because the OH concentrations utilized in the two studies was low ( $[\text{OH}]_0 \leq 3.6 \times 10^{12}$  molecule cm<sup>-3</sup>), the observed signal levels were also low. Thus, multiple flashes on a single gas mixture were required to produce a single smooth kinetic decay curve. However, the number of flashes per gas mixture was always restricted to minimize the decomposition of C<sub>2</sub>H<sub>2</sub> or C<sub>2</sub>H<sub>4</sub> to less than 3%. Thus, several fillings of an identical gas mixture were used for the development of a single experimental decay curve. The initial hydroxyl radical concentration was kept low in order to ensure that the bimolecular disproportionation reaction of hydroxyl radicals could be neglected, and to obtain high initial stoichiometries, typically ( $[\text{C}_2\text{H}_2]_0/[\text{OH}]_0 \geq 500$ ), so that the importance of secondary reactions could be minimized. Even with high initial stoichiometries, however, secondary reactions were not always eliminated (to be discussed later).

Since the observed kinetics were pseudo-first order, the first order rate constants could be obtained from a plot of the logarithm of the count rate in each channel of the analyzer (after the background was subtracted) versus time. The slope of the line in each case was established by a least squares treatment of the data. This treatment was extended out to two and in some cases three 1/e times of the decay. Bimolecular rate constants were obtained from a least squares treatment of the slope of the line obtained from a plot of the pseudo-first order rate constants versus C<sub>2</sub>H<sub>2</sub> or C<sub>2</sub>H<sub>4</sub> pressure. Each bimolecular rate constant, therefore, represents

an average of more than ten individual experiments.

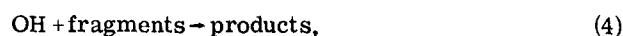
Gas pressures of less than 3 torr were measured using an MKS Baratron pressure gauge which was periodically checked against a dibutyl phthalate manometer. The high pressure measurements (10–800 torr) were made with a two-turn Bourdon gauge (Wallace and Tierman type FA-145). The precision to which gas mixtures could be made, with the exception of H<sub>2</sub>O, was estimated to be ~3% or better. The H<sub>2</sub>O pressure could not be metered so precisely due to adsorption effects on the surfaces of the reaction cell.

The C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> used in these experiments were from Matheson Co. and had stated purities of 99.6% and 99.98%. Both gases were degassed in liquid nitrogen prior to use. Matheson "Gold Label Ultra-High Purity" helium was used without further purification. The H<sub>2</sub>O used in all experiments was distilled and then degassed using liquid N<sub>2</sub> prior to its introduction into the gas handling system.

### III. RESULTS AND DISCUSSION

#### A. OH + C<sub>2</sub>H<sub>4</sub> → products

The results for Reaction (1) are presented in Table I. It can be seen that a wide variation in experimental conditions was performed in an effort to show that kinetic complications were not affecting the observed rate constants. These variations included using H<sub>2</sub>O pressures of 50 to 300 mtorr, flash energies of 45–~500 J, and ethylene pressures of 1–7 mtorr. Under these widely differing conditions the pseudo-first order rate constants were found to be invariant (for any given C<sub>2</sub>H<sub>4</sub> pressure) within the assigned experimental uncertainties of the measurements. The indications are, therefore, that OH reactions of the following type were not significant:



In addition, the reaction of OH with the products of (1) could not be important. In all the above cases, the rate of removal of OH would depend upon the square power of the flash intensity since the radical concentration in these rate expressions depends directly upon the flash energy. If these reactions had been significant, then there would have been an observed dependence of  $k_1$  upon the flash intensity. Finally, since the products of ethylene photolysis consist chiefly of H<sub>2</sub> and C<sub>2</sub>H<sub>2</sub>,<sup>14,15</sup> experiments were performed in which the number of flashes per gas filling was varied. The range of this variation was 10 to 100. Reactions of possible importance here would include the following:



The results of this test were that within the experimental

TABLE I. OH + C<sub>2</sub>H<sub>4</sub> → products.

Diluent (torr)	H <sub>2</sub> O (mtorr)	C <sub>2</sub> H <sub>4</sub> (mtorr)	Flash energy (Joules)	K <sub>1</sub> (sec <sup>-1</sup> )	K <sub>bimolecular</sub> × 10 <sup>12</sup> (cc/molecule · sec <sup>-1</sup> )
3 (N <sub>2</sub> )	100	0	~320	83	
3	100	1	~320	220	
3	100	2	~500	325	
3	100	3	~500	420	3.64 ± 0.20
3 (He)	100	0	88	205	
3	100	1	88	290	
3	100	1	~500	295	
3	100	2	88	370	
3	100	2	~500	365	
3	100	3	~500	430	
3	100	5	88	525	
3	100	5	~500	575	2.24 ± 0.22
5 (He)	100	0	88	140	
5	100	5	~320	585	2.79 ± 0.37
6 (He)	100	0	88	120	
6	100	1	88	230	
6	100	2	88	330	
6	100	3	88	445	3.32 ± 0.43
10 (He)	100	0	88	105	
10	100	2	88	340	3.63 ± 0.50
20 (He)	100	0	88	70	
20	100	1	88	215	
20	100	2	45	350	
20	100	2	88	365	
20	100	2	~500	380	
20	100	3	88	500	
20	100	5	88	700	4.06 ± 0.38
100 (He)	100	0	88	40	
100	100	1	88	204	
100	100	2	88	350	
100	100	3	88	510	
100	100	5	~320	650	4.72 ± 0.60
300 (He)	100	0	88	28	
		0.5		140	
300	100	1	88	210	
		1.5		267	
300	100	2	88	362	5.33 ± 0.65

error of the measurements ( $\pm 6\%$ ) no variation in the observed first-order rate constants was noted. Even though secondary Reactions (2)–(8) were found to be insignificant under our experimental conditions, a CaF<sub>2</sub> window ( $\lambda > 120$  nm) was used over the flash lamp to limit the extent to which C<sub>2</sub>H<sub>4</sub> was photolyzed.

A possible source of systematic error in the above measurements could involve rotationally or vibrationally excited OH species produced by the flash pulse. Previous experiments<sup>13</sup> utilizing 307 nm and 345 nm interference filters over the resonance lamps indicated that vibrationally excited OH, if present, was not directly detected by the system. If there was a significant initial population of OH in the  $v''=1$  level, which was subsequently quenched into the  $v''=0$  level, then an apparent underestimate in the pseudo-first-order rate constants would be noted due to the slow production of ground state OH. However, previous experiments<sup>13</sup> utilizing 40 mtorr of CO, 20–100 torr of He or 20 torr of N<sub>2</sub>, and 50–300 mtorr of H<sub>2</sub>O for the study of Reaction (10)



showed no evidence for quenching of excited OH outside

of the experimental uncertainty. If there had been a significant population of excited OH, then the observed rate constant would have varied with total pressure due to quenching, and the decay plots would not be logarithmic as observed. Thus, at the pressures utilized in this study, excited OH does not appear to have been a problem in defining a value for either  $k_1$  or  $k_2$ .

The only experimental parameter which caused deviations in  $k_1$  outside the experimental uncertainty were variations in total pressure. Within the experimental range of pressure 3–300 torr of He, a variation of a factor of 3 in the experimentally determined value of  $k_1$  was observed. Experiments utilizing 3 torr of N<sub>2</sub> were also performed. The He pressure data are presented in Fig. 1 as the logarithm of the bimolecular rate constant versus the logarithm of the total pressure. The observed results indicate that Reaction (1) is intermediate between second and third order in the pressure range examined in this study.

The present results indicate that within the pressure range 3–300 torr of He, the bimolecular rate constant varies from 2.24 to  $5.33 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> · sec<sup>-1</sup>. The estimated uncertainty in all first-order rate constants was judged to be  $\pm 6\%$ . The uncertainties in the bimolecular rate constants represent two standard deviations of the mean, as determined from a linear least-squares-curve fitting technique. In general, these uncertainties ranged in value from 10 to 13%.

## B. OH + C<sub>2</sub>H<sub>2</sub> → products

Table II summarizes the data used to compute the bimolecular rate constant for Reaction (2) at 300 °K. As in the case of Reaction (1), wide variations in experimental conditions were performed. The H<sub>2</sub>O pressure was reduced from 300 mtorr by a factor of 6, the total pressure (He) was varied by a factor of 25 (20–500 torr), and the acetylene pressure ranged from 2 to 30 mtorr. For a constant acetylene pressure, no significant variations of the pseudo-first-order rate constant outside of the experimental error were observed for the above changes. Variation of the flash intensity by a factor of

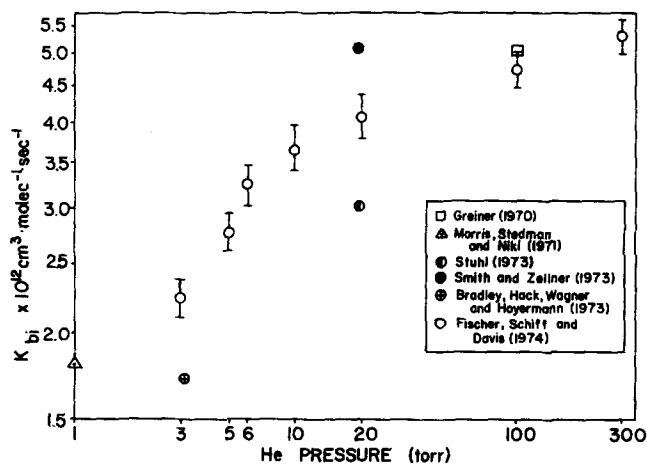


FIG. 1. A plot of  $\log k_2$  (the bimolecular rate constant) vs  $\log P$  (He) for the reaction of OH with ethylene.

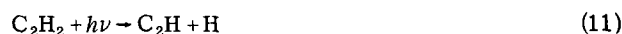
TABLE II. OH + C<sub>2</sub>H<sub>2</sub> → products.

Helium (torr)	H <sub>2</sub> O (mtorr)	C <sub>2</sub> H <sub>2</sub> (mtorr)	Flash energy (Joules)	K <sub>1</sub> (sec <sup>-1</sup> )	K <sub>bi</sub> <sup>bimolecular</sup> × 10 <sup>13</sup> cm <sup>3</sup> · molecule <sup>-1</sup> · sec <sup>-1</sup>	
20	100	0	88	45		
	100	2	88	58		
	100	10	88	105		
	100	10	88	97		
	100	10	45	103		
	100	20	88	155		
	150	20	88	155		
	150	20	88	160		
	150	30	88	205	1.68 ± 0.12	
	50	300	0	45	43	
50	300	5	45	69		
50	300	10	45	99		
50	300	15	45	125	1.73 ± 0.13	
100	300	0	88	25		
	300	2	45	33		
	300	5	20	45		
	300	5	45	48		
	300	10	20	72		
	50	10	45	76 (av)		
	300	20	20	135 (av)		
	300	20	45	125		
	300	20	320	225 (av)		
	300	20	500	340 (av)		
	300	30	45	185	1.61 ± 0.17	
	500	300	0	45	22	
		300	5	45	48	
300		10	20	72		
300		10	45	71	1.55 ± 0.18	
					Av = 1.65 ± 0.15	

~ 25 (20–~ 500 J) did show significant perturbations in the first-order rate constants.

Figure 2 shows the variation in the pseudo-first-order rate constant as a function of acetylene pressure for several flash energies. The dependence of the pseudo-first-order rate constant with flash intensity was thoroughly investigated at a fixed total pressure (100 torr) and fixed acetylene pressure (20 mtorr). For flash energies of 320 J the observed first order rate constants were nearly a factor of 2 faster than those obtained at energies ≤ 45 J. The data collected using flash energies > 45 J were prone to scatter and the individual logarithmic decay plots were not always strictly linear, indicating the importance of secondary processes. These high flash energy experiments were particularly sensitive to changes in the transmission characteristics of the flash lamp window, as this governed the photon flux entering the cell. Changes in transmission properties were due to material being deposited upon the window from the electrodes, and to F-center formation in the window. When the flash energy was varied below 88 J there was no perceptible deviation in the observed rate constants outside of the bounds of the experimental error.

There are numerous possible explanations for the above observations some of which will now be explored in greater detail. The experimental data suggest that the flash decomposition product of acetylene, C<sub>2</sub>H, should not be important as its concentration can be calculated to be ~ $\frac{1}{30}$ [OH]<sub>0</sub> (this is based upon the relevant absorption cross-section data of H<sub>2</sub>O<sup>16</sup> and C<sub>2</sub>H<sub>2</sub>,<sup>17,18</sup> and the concentrations of these species in the reaction cell).

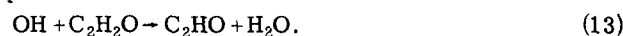


Therefore, even if C<sub>2</sub>H reacted on every collision with OH radicals, this should not cause a significant increase in the net rate of removal of OH. The H atoms formed in the photolysis of H<sub>2</sub>O are initially produced with a concentration equal to that of the hydroxyl radicals, and can react with acetylene to form C<sub>2</sub>H<sub>3</sub>:



The rate constant data for Reaction (12) published by different workers are not in good agreement<sup>19–22</sup>; and consequently, the equivalent bimolecular rate constant at 100 torr total pressure is not well established. It could be as high as 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> · sec<sup>-1</sup>. The product, C<sub>2</sub>H<sub>3</sub>, is expected to be highly reactive towards OH radicals.

A further process which could be important in the removal of OH radicals is that involving OH radicals reacting with the primary product of Reaction (2). For example,



Again the rate constant for this process could be expected to be rapid. The overall rate of removal of OH can now be expressed as:

$$-d[\text{OH}]/dt = k_2[\text{OH}][\text{C}_2\text{H}_2] + k'[\text{OH}][\text{C}_2\text{H}] + k''[\text{OH}][\text{C}_2\text{H}_3] + k'''[\text{OH}][\text{C}_2\text{H}_2\text{O}].$$

It can be seen that all processes, except for (2), depend upon the square power of the flash intensity. It has been shown by these authors, using the above kinetic scheme, that when [OH]<sub>0</sub> = (1.5–3.5) × 10<sup>11</sup> radical cm<sup>-3</sup> there appears to be no significant perturbation due to secondary processes; whereas, when [OH]<sub>0</sub> = (2.3–3.6) × 10<sup>12</sup> radical cm<sup>-3</sup>, the experimental data and computer model calculations show the presence of significant secondary reaction processes.

Other reactions of possible significance could involve electronically excited C<sub>2</sub>H<sub>2</sub><sup>\*</sup>,

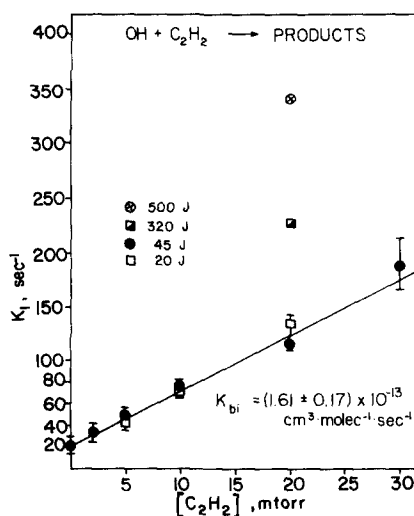


FIG. 2. Kinetics of the OH + C<sub>2</sub>H<sub>2</sub> reaction. A plot of the pseudo-first-order rate constant as a function of both acetylene pressure and flash energy.



These species are thought to be long-lived enough to participate in reactions with OH.<sup>23</sup> Also, since excited C<sub>2</sub>H<sub>2</sub><sup>\*</sup> is formed at long wavelengths where the light flux from the flash lamp is more intense, these reactions could have been of significant importance to the observed flash dependence of the first-order rate constants.

At flash energies  $\leq 45$  J and for total pressures ranging from 20 to 500 torr of He, the bimolecular rate constant  $k_2$  was found to be  $1.65 \pm 0.15 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> · sec<sup>-1</sup> independent of the total pressure.

#### IV. DISCUSSION OF PREVIOUS WORK

##### A. OH + C<sub>2</sub>H<sub>4</sub> → products

There have been six room-temperature studies of Reaction (1).<sup>3-8</sup> The earliest study was performed by Wilson and Westenberg<sup>8</sup> using a discharge-flow system coupled with ESR detection of OH. They reported a value for  $k_1$  of  $5 \times 10^{-12}/n$  cm<sup>3</sup> molecule<sup>-1</sup> · sec<sup>-1</sup>; where  $n$  is a stoichiometric correction factor which represents the number of OH radicals that react for each initial C<sub>2</sub>H<sub>4</sub> that reacts (i. e.,  $n > 1$  due to OH reacting with species produced in the primary and subsequent processes). Considering the low pressures utilized in flow systems, the value of  $n$  which is required in order to bring their results into agreement with the present study would have to be approximately 2.

Greiner,<sup>5</sup> utilizing kinetic absorption spectroscopy, reported a value for  $k_1$  of  $5 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> · sec<sup>-1</sup>. No mention was made of the total pressure used in his system. The experimental data was corrected in order to allow for secondary reactions caused by reaction products. However, it was assumed that the photolysis products of ethylene would not cause any appreciable increase in the rate of removal of OH radicals. This assumption appears to be valid in that the photolysis products of C<sub>2</sub>H<sub>4</sub> are probably C<sub>2</sub>H<sub>2</sub> and H<sub>2</sub>, and these both react slower with OH radicals than does C<sub>2</sub>H<sub>4</sub>. Also, if the total pressure in his system was 100 torr, as was used in previous studies,<sup>24</sup> then the results obtained are in substantial agreement with those obtained in the present study at 100 torr total pressure of He.

Morris, Stedman, and Niki<sup>3</sup> used a discharge-flow system at 1 torr total pressure of He coupled with mass spectrometric detection of OH under both ethylene-rich and OH-rich conditions. Their value of  $k_1 = 1.8 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> · sec<sup>-1</sup>, obtained by monitoring C<sub>2</sub>H<sub>4</sub> in the presence of an excess concentration of OH radicals, is in substantial agreement with our experimental value of  $k_1$  at 3 torr total He pressure. This study did not require a stoichiometric correction factor, as the primary products of Reaction (1) would preferentially react with the excess concentration of OH radicals and not with the C<sub>2</sub>H<sub>4</sub> which was being monitored. The value reported for the ethylene-rich system, where OH radicals were monitored, was  $2.5/n \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> · sec<sup>-1</sup>. No value was reported for  $n$ .

Stuhl,<sup>6</sup> utilized the resonance fluorescence technique

to monitor hydroxyl radicals in the presence of an excess concentration ( $> 100$ ) of C<sub>2</sub>H<sub>4</sub> and obtained a value for  $k_1$  of  $3 \pm 1 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> · sec<sup>-1</sup> at 300 °K and 20 torr total pressure of He. This value is slightly lower than that obtained in the present study at the same total pressure,  $k_1 = 4.1 \pm 0.2 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> · sec<sup>-1</sup>. However, it can be seen that the two values are in agreement within the expressed uncertainties. Secondary reactions were shown to be unimportant under their experimental conditions. No mention of any pressure dependence was noted by Stuhl.

Smith and Zellner<sup>7</sup> used the flash photolysis-resonance absorption technique to study Reaction (1) in a static cell at either, (a) 10–20 torr total pressure of He or, (b) 10 torr of H<sub>2</sub> and 10 torr of N<sub>2</sub>O. High initial concentrations of hydroxyl radicals were used ( $[\text{OH}]_0 \leq 3 \times 10^{13}$  radical cm<sup>-3</sup>), but the authors reported that this did not lead to the presence of complicating secondary reactions. They found a value for  $k_1$  of  $5.2 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> · sec<sup>-1</sup> which was invariant with total pressure or diluent gas. Although the value obtained in the present study with 20 torr of He ( $k_1 = 4.2 \pm 0.2 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> · sec<sup>-1</sup>) is within 25% of their value, it is felt that the two studies are not in particularly good agreement as N<sub>2</sub>O would be expected to be a more efficient third body than He.

Bradley *et al.*<sup>4</sup> studied Reaction (1) in a discharge flow system at 3 torr total pressure (He), using ESR detection of hydroxyl radicals. Low initial stoichiometries, ( $[\text{C}_2\text{H}_4]_0/[\text{OH}]_0 = 5.5 = 13.1$ ) were used, which resulted in a stoichiometric correction factor,  $n$ , being required to allow for secondary removal of hydroxyl radicals. A mass spectrometric end product analysis yielded a value of 2.6 for  $n$ , which when combined with the experimental value of  $k_1/n$ , produced a value of  $1.67 \pm 0.5 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> · sec<sup>-1</sup> for  $k_1$ . This value is slightly lower than that obtained in the present study at 3 torr of He, but within the reported experimental uncertainties of the two studies.

In summary, from an examination of all the previous data on  $k_1$  it is seen that when the pressure dependence of Reaction (1) is considered, the previously published results are in reasonably close agreement.

##### B. OH + C<sub>2</sub>H<sub>2</sub> → products

Of the room temperature studies of Reaction (2) that have been reported, the earliest work was done by Wilson and Westenberg<sup>8</sup> utilizing ESR detection of OH generated by the reaction  $\text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}$  in a fast flow system. They obtained the result that  $k_2 = 1.0 \times 10^{-12}/n$  cm<sup>3</sup> molecule<sup>-1</sup> · sec<sup>-1</sup>, where  $n$  is a stoichiometric correction factor. For there to be substantial agreement between the present work and that of Wilson and Westenberg, a stoichiometric correction factor of 5–6 would have to be employed. This correction appears to be too large and does not fully account for the differences between the two measurements.

A measurement by Breen and Glass<sup>9</sup> is in better agreement with the present work. They used a dis-

charge-flow system coupled with ESR detection of OH which was again produced from the H/NO<sub>2</sub> reaction. A stoichiometry correction factor of 2 was required for OH consumption via secondary reactions. This was obtained from a mass spectrometric analysis of the end products of the reaction. The rate of consumption of OH radicals in the presence of an excess concentration of C<sub>2</sub>H<sub>2</sub> ( $[C_2H_2]_0/[OH]_0$ , 3.7–57.0) was monitored via ESR detection, and the decay curve was modeled with an assumed kinetic scheme to calculate  $k_2(\text{eff}) = k_2/n$  ( $n$  = stoichiometric correction factor). From the values of  $k_2(\text{eff})$  and  $n$ , a value of  $1.9 \pm 0.6 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> · sec<sup>-1</sup> was obtained. This value is in good agreement with that obtained from the present study.

A study of Reaction (2) was performed by Smith and Zellner utilizing the flash photolysis–resonance absorption technique. They obtained a bimolecular rate constant of  $8.7 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> · sec<sup>-1</sup>, a result which is approximately a factor of 5 higher than that obtained in the present work. High flash energies on the order of 180–500 J were used, producing initial hydroxyl radical and hydrogen atom concentrations of  $\leq 3 \times 10^{13}$  radical cm<sup>-3</sup>. This could have resulted in secondary processes becoming a highly significant perturbation in their system even though their initial  $[C_2H_2]_0/[OH]_0$  ratio was typically 100 (estimated from the experimental data given in their paper). Thus, the stoichiometric correction factor could have been quite large. This line of argument presupposes that the secondary reactions of C<sub>2</sub>H<sub>3</sub> (from reaction of H and C<sub>2</sub>H<sub>2</sub>) and C<sub>2</sub>H<sub>2</sub>O with OH radicals are rapid.

Recently Pastrana and Carr<sup>10</sup> studied Reaction (2) in a flow system utilizing resonance line absorption detection of OH. Acetylene to OH ratios of (a) 2.3–13.2 and (b) 14–125 were used in two separate studies. The values obtained for the bimolecular rate constant  $k_2$  were  $(2.9 \pm 0.3)/n \times 10^{-13}$  and  $(2.1 \pm 0.6)/n \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> · sec<sup>-1</sup>, respectively, where  $n$  is the stoichiometric correction factor. They assumed that  $n$  had a value of 2.1 (as measured by Breen and Glass<sup>9</sup>) in series (a), yielding a bimolecular rate constant of  $(1.4 \pm 0.3) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> · sec<sup>-1</sup>. In series (b) they assumed that experimental conditions were such that secondary processes would be of less significance and that  $n$  would have a value close to unity. Although secondary reactions may not be so important in series (b), it is quite conceivable that  $n$  could be significantly greater than unity. The overall value reported for  $k_2$  was  $(2.0 \pm 0.6) \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> · sec<sup>-1</sup>. It can be seen that this value is in good agreement with that obtained in the present study.

In summary, the present study has shown that there is no pressure dependency for the rate of Reaction (2).

However, the rate of removal of hydroxyl radicals is extremely sensitive to secondary reactions. The species most likely to participate in secondary removal of OH are: (a) the primary product of Reaction (2), e.g., C<sub>2</sub>H<sub>2</sub>O and (b) the C<sub>2</sub>H<sub>3</sub> radical formed in the H+acetylene reaction. The value reported for  $k_2$  in the present study was obtained using low flash energies and therefore should be free of any significant perturbation due to secondary processes.

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