

## QUENCHING OF DIACETYLENE FORMATION DURING THE REACTION OF OXYGEN ATOMS WITH ACETYLENE AT 300 K

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**KEYWORDS:** diacetylene, acetylene, oxygen atoms

### ABSTRACT

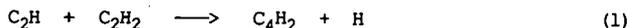
The production of diacetylene in the low pressure reaction of oxygen atoms with acetylene was monitored with a photoionization mass spectrometer. The addition of methane, nitrous oxide or molecular hydrogen quenched the formation of diacetylene. Stern-Volmer kinetics were observed, which implies that both acetylene and the quenching gas compete for a single reactive intermediate. This quenching appears to be closely connected with the quenching of chemi-ionization reported previously (*Chem. Phys. Lett.* **164**, 625 (1989)). Quantitative comparisons of quenching rates with known rate constants suggest that  $\text{CH}(X^2\pi)$  is the intermediate involved. Application of an electric field to this system had no effect on the diacetylene concentration, showing that chemi-ions are not involved in  $\text{C}_4\text{H}_2$  formation.

### INTRODUCTION

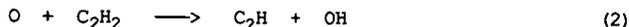
Diacetylene ( $\text{C}_4\text{H}_2$ ) is an important intermediate in the combustion of acetylene and other hydrocarbons, especially for fuel-rich conditions [1-5]. As much as 35% of the acetylene consumed in a flame may pass through  $\text{C}_4\text{H}_2$  [4]. It has been argued that diacetylene and heavier polyacetylenes are precursors of soot [1,4], although others do not support this proposal.

The atomic oxygen-acetylene system has been studied extensively and there is agreement that the mechanism of diacetylene formation is complex [6-8]. The initial rate of formation of  $\text{C}_4\text{H}_2$  is proportional to the product of concentrations  $[\text{O}][\text{C}_2\text{H}_2]$ , and this rate can be accelerated by adding hydrogen atoms or inhibited by adding  $\text{O}_2$  or  $\text{H}_2$ .

The reaction that forms diacetylene in flames has not been clearly established. The reaction usually proposed is,



and this reaction is known to be fast [9]. However, a reasonable source of  $\text{C}_2\text{H}$  radicals in flames is not known. The direct abstraction, favored in the past,



is now known to be endoergic by 30 kcal mol<sup>-1</sup> [10], and thus can be ignored except for very high temperature combustion.

We have extended earlier quenching studies [11] in an attempt to clarify the mechanism by which diacetylene is formed during acetylene combustion.

## EXPERIMENTS

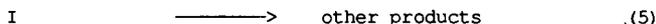
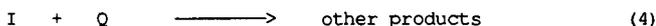
Oxygen atoms were made by discharging a flowing mixture of 0.5% CO<sub>2</sub> in He in a microwave discharge (2450 MHz). Titration with NO<sub>2</sub> showed that the typical [O] was 3 mTorr. Acetylene, also diluted in He, and other quenching gases were added upstream of the pinhole to a photoionization mass spectrometer. The diacetylene was photoionized by Lyman  $\alpha$  radiation (10.2 eV) and detected at mass 50. The total pressure was kept constant at 3 Torr as the quenching gases were added by varying the He flow. Further experimental details are given elsewhere [12].

## RESULTS and DISCUSSION

We have observed that adding methane, nitrous oxide or molecular hydrogen to the O + C<sub>2</sub>H<sub>2</sub> system quenches the formation of diacetylene. These quenching molecules are relatively inert to attack by oxygen atoms at 300 K for the short contact times (<15 ms) used in this study.

For methane and nitrous oxide the quenching followed a simple Stern-Volmer law, as can be seen in Figure 1. The quenching efficiency depends on the partial pressure of acetylene present. The original data are recorded elsewhere [12].

Simple Stern-Volmer plots suggest that both acetylene and the quencher molecule are competing for the same intermediate. If the intermediate, I, reacts with acetylene, a molecule of diacetylene is formed (not necessarily in a single step).



Reaction between I and quencher molecule Q does not result in diacetylene formation. Reaction (5) is included to allow loss of I by other reactions, on the walls, etc.

If it is assumed that the addition of Q does not affect the rate of formation of I, then reactions 3, 4 and 5 lead to the steady state expression,

$$\frac{[C_4H_2]_0}{[C_4H_2]} = 1 + \frac{k_4[Q]}{k_3[C_2H_2] + k_5} \quad (A)$$

where [C<sub>4</sub>H<sub>2</sub>]<sub>0</sub> refers to the diacetylene signal when no quencher gas is present. The quenching data for methane and nitrous oxide have been fit to Equation A using least squares.

If Equation A is valid, the inverse of the slopes of the Stern-Volmer plots should depend linearly on the acetylene concentration. A test of this relationship is shown in Figure 2. For this simple model, the slopes of the lines in Figure 2 then give the ratios for k<sub>3</sub>/k<sub>4</sub> and the intercepts give k<sub>5</sub>/k<sub>4</sub>. Values for these k<sub>3</sub>/k<sub>4</sub>

ratios are collected in Table I.

Molecular hydrogen was a less efficient quencher than methane or nitrous oxide and so more of it was necessary to give significant quenching. The resulting Stern-Volmer plots were slightly concave downward. It is not clear if this indicates that a more complex quenching mechanism is needed, or that some other effect resulting from the large concentrations of  $H_2$  is involved. It is known that hydrogen atoms promote the formation of diacetylene [8], and it is possible that the large  $H_2$  concentrations could result in hydrogen atoms being produced (e.g. by collisional dissociation of  $H_2$  by  $CO(a^3\pi)$ , which is produced in this system [13], or by radical attack on  $H_2$ ). The hydrogen quenching curves could be fit to equations of the form,

$$\frac{[C_4H_2]_0}{[C_4H_2]} = 1 + \beta[H_2] + \gamma[H_2]^2 \quad (B)$$

By analogy to Eqn. A, the reciprocal of  $\beta$  was plotted against the acetylene concentration, and the resulting points are consistent with a straight line (Fig. 2). The slope of this line is entered in Table 1 under  $k_3/k_4$  for hydrogen with the understanding that this assignment is tentative.

The second column of numbers in Table 1 gives the ratio of  $k_3/k_4$  if the intermediate I is the ground state  $C_2H$  radical. According to the present study, the precursor to diacetylene reacts with methane only 2.7 times slower than it does with acetylene, while  $C_2H$  reacts 50 times slower. The tentative ratio for hydrogen is also not compatible with the intermediate being  $C_2H$ . Unfortunately, the rate constant for  $C_2H$  reacting with  $N_2O$  has not been measured yet. From the comparison of the first two columns of Table I, we conclude that the intermediate I is not the  $C_2H$  radical.

The CH radical has been proposed by Homann and Schweinfurth as one of the precursors leading to diacetylene [8]. The third column of Table I gives the ratios of  $k_3/k_4$  for  $CH(X^2\pi)$ . In comparing the first and third columns of Table I, better agreement is seen, although the values for hydrogen still differ significantly.

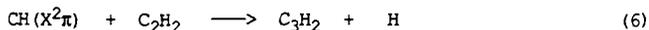
A more impressive comparison can be made between the quenching of chemi-ionization reported previously for this system [11] and the quenching of diacetylene. The fraction of the chemi-ionization that can be quenched follows a Stern-Volmer law, and a plot of the reciprocal of the Stern-Volmer slopes vs. acetylene looks very similar to the present Figure 2. In particular, for methane quenching, the lines show identical slopes, i.e. identical values for  $k_3/k_4$ . Quenching by  $N_2O$  also agrees closely ( $k_3/k_4 = 3.5$  for chemi-ionization quenching, compared to 4.8 in Table I). Since the quenching of the chemi-ionization almost certainly involves reaction with the  $CH(X^2\pi)$  radical, this strengthens the case for CH being a precursor to diacetylene.

The similarity of quenching of chemi-ions and diacetylene raises the possibility that chemi-ions might be precursors to diacetylene. This possibility was tested in a radial electric field reactor, with a pinhole leading to the photoionization mass spectrometer. The diacetylene signals with and without an electric field (4.8 Townsend)

were carefully compared; no change in intensity could be observed (<5%). The smaller peak at mass 52 (C<sub>4</sub>H<sub>4</sub>) also did not change. Since this electric field will reduce the residence time of the chemi-ions by approximately a factor of 100, we must conclude that chemi-ions are not precursors to the observed diacetylene in this system.

In the Homann and Schweinfurth mechanism [8], the CH radical reacts with acetylene to form C<sub>3</sub>H<sub>2</sub>, which subsequently reacts with an oxygen atom to form C<sub>2</sub>H. The diacetylene is then formed when C<sub>2</sub>H reacts with another acetylene (Reaction 1). If this were the correct mechanism, then adding a quenching molecule that could react with both CH and C<sub>2</sub>H should give Stern-Volmer plots that curve upward. The magnitude of this effect can be seen in Figure 3, where the solid curves show the expected behavior for methane quenching using known rate constants for C<sub>2</sub>H and a linear term that fits the initial slope. The lack of curvature in the experimental points suggests that sequential quenching of two precursors is not important for this system.

If CH(X<sup>2</sup>π) is the radical that is being intercepted by the various quenching molecules, then it is very likely that the reaction,



is the next step in forming diacetylene. Reaction 6 is sufficiently exoergic to form any one of the three isomers of C<sub>3</sub>H<sub>2</sub>. Direct sampling and trapping studies have shown evidence for C<sub>3</sub>H<sub>2</sub> in flames [3,14]. However, very little is known about the kinetic behavior of any of these isomers. The mechanism leading from C<sub>3</sub>H<sub>2</sub> to diacetylene can only be speculative at this time. However, it should be noted that any of the following intermediates that are known to be present in this system could donate a carbon atom to C<sub>3</sub>H<sub>2</sub> to give diacetylene in an exoergic reaction: C; C<sub>2</sub>O; CH; vinylidene; CH<sub>2</sub>; HC<sub>2</sub>O; or C<sub>3</sub>H<sub>2</sub> itself.

#### CONCLUSIONS

The present quenching studies, especially the results with methane which are the most extensive, do not support C<sub>2</sub>H as the precursor to diacetylene in the oxygen atom-acetylene system. Combining the present results with those from a previous chemi-ion quenching study suggests that CH(X<sup>2</sup>π) is the intermediate that is being quenched. Quenching by molecular hydrogen is anomalous and is not understood. Clearly chemi-ions do not participate in the formation of diacetylene. Kinetic studies need to be done on the C<sub>3</sub>H<sub>2</sub> isomers to understand the next step in the formation of diacetylene in this system.

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**Table I: Comparison of Experimental Ratios of  $k_3/k_4$  with Ratios of Known Rate Constants.** Rate constants for  $C_2H$  were taken from [9] and from Lander et al. (*J. Phys. Chem.* **94**, 7759 (1990)). Rate constants for  $CH(X^2\pi)$  were taken from the review by Sanders and Lim (*Chemical Kinetics of Small Organic Radicals*, Vol. 3, ed. Z. Alfassi, CRC Press, Boca Raton, 1986, p. 103). 95% confidence limits for  $k_3/k_4$  are shown.

Quencher	Experimental $k_3/k_4$	If intermediate is	
		$C_2H$	$CH(X^2\pi)$
$CH_4$	$2.7 \pm 0.5$	50	4.1
$N_2O$	$4.8 \pm 0.9$	?	5.4
$H_2$	$17 \pm 7$	340	>400

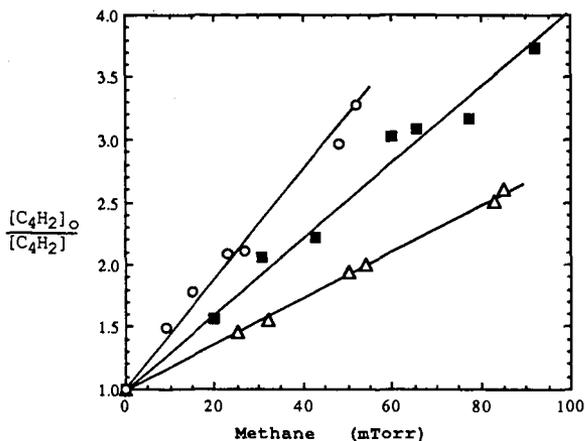


Figure 1: Stern-Volmer Plot of Diacetylene Quenching by Methane. The different symbols represent different partial pressures of acetylene: circles 3.9 mTorr; squares 8.4 mTorr; triangles 14 mTorr. All runs had  $[O]$  of 2.7 mTorr and 3 Torr total pressure. The least squares lines were forced through unity at zero methane.

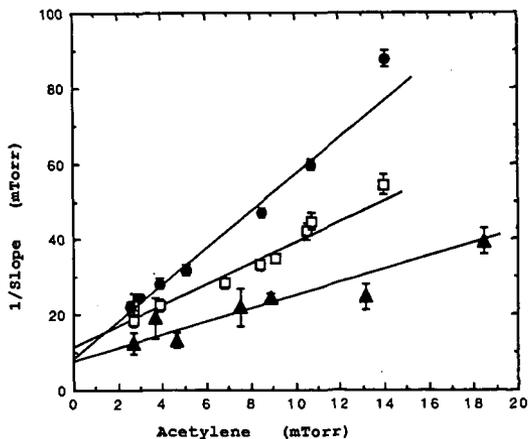


Figure 2: Reciprocal of the Stern-Volmer Slopes as a Function of Acetylene. The solid circles represent quenching by methane and the open squares quenching by nitrous oxide. For hydrogen the values of  $\beta^{-1}$  have been divided by 10 before being plotted. The straight lines represent weighted least squares calculations. The slopes of these lines are entered in the first column of Table I.

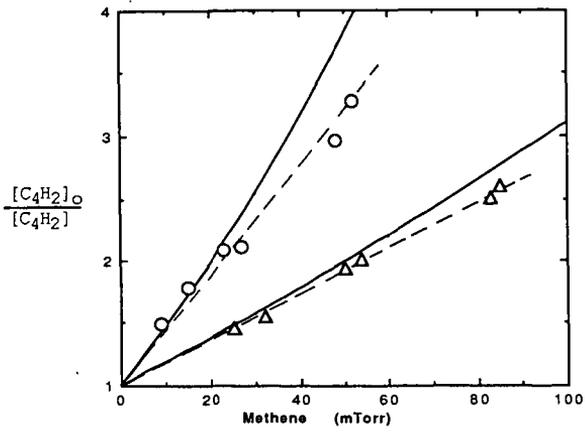


Figure 3: Comparison of Observed Quenching Data with Model for Sequential Quenching. Data are the same as in Figure 1.