

# Kinetic Modeling of the Photodecomposition of Ketene.

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Foi modelada a fotodecomposição da cetena a  $310 \pm 10$  nm, usando um conjunto abrangente de equações químicas. Os resultados calculados foram comparados com dados experimentais obtidos previamente. As constantes de velocidade usadas no modelo foram mudados dentro de seis limites de incerteza, a fim de determinar a sua influência nos resultados calculados.

The photodecomposition of ketene at  $310 \pm 10$  nm was modeled using a comprehensive kinetic mechanism. The results of the modeling were compared with experimental results previously obtained. Then, the rate constants were systematically varied between their limits of uncertainty, to determine their influence on the calculated results.

**Key words:** *kinetic modeling; photodecomposition; ketene.*

## Introduction

The photochemistry of ketene has been extensively studied in the near and far ultraviolet, because of its intrinsic interest and importance as a source of methylene. Different photolysis<sup>1,2</sup> techniques have been used, such as flash photolysis pulsed exciplex laser<sup>3</sup> and continuous radiation<sup>4-6</sup>

There remain, however, a number of questions, mainly about the mechanistic differences between steady-state and unsteady-state systems. In the very detailed work of Frey and co-workers<sup>3</sup>, the chemistry initiated by a single pulse of the exciplex laser was largely completed in about  $10^{-2}$ s and since the laser repetition rate was 0.5 Hz, repeated pulses caused no interference with the reaction of the previous pulse. For such times the intermediate species do not reach a stationary state (see below), while for static systems radicals and excited products may reach a stationary concentration, in many cases very different from the initial values. In fact, in another series of experiments in the presence of a continuous electric field, using a static system with irradiation times of 300 s, the experimental results were explained on the basis of the validity of assuming a stationary state for the intermediates and a linear relation between the  $\text{CH}_2(^1\text{A}_1)/\text{CH}_2(^3\text{B}_1)$  and  $[\text{C}_2\text{H}_4]/[\text{C}_2\text{H}_6]$  ratios<sup>4</sup>.

The question about the pertinence of these assumptions remains. Since they are a crucial point in the interpretation of

the electric field results we decided to model the photolysis of ketene at longer times of continuous photolysis in order to confirm the assumptions of this study.

**Reaction Mechanism.** A chemical kinetic reaction mechanism was developed to reproduce experimental results obtained on static photolysis of ketene at  $310 \pm 10$  nm.

The mechanism of Frey and co-workers<sup>3</sup>, proposed to explain the photodecomposition of ketene by 308 nm radiation from a pulsed exciplex laser, was used as the initial set of reactions. Then, the behaviour of the static system, with nonpulsed radiation was analyzed and the pertinence of modifications was considered.

The experimental results indicate that the main condensable products are  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$  at a ratio which depends on pressure, and that the concentration of  $\text{C}_2\text{H}_2$  in the photolysed system is very low. This last fact is very difficult to reconcile with previous experiments. The proposed mechanism should explain these results. The main features concerning the static system are:

(a) Both  $\text{CH}_2(^1\text{A}_1)$  and  $\text{CH}_2(^3\text{B}_1)$  are present in the system. However, it is known that the ultraviolet photolysis of ketene proceeds via a vibronically allowed excitation to the  $\tilde{\text{A}}^1\text{A}_2$  state, followed by fast internal conversion to  $\text{X}^1\text{A}_1$  and/or intersystem crossing to  $\tilde{\text{A}}^3\text{A}_2$  prior to dissociation on the X or  $\tilde{\text{a}}$  potential surface to  $\text{CH}_2(^1\text{A}_1)$  and  $\text{CH}_2(^3\text{B}_1)$ , respectively<sup>5,7-11</sup>. The branching ratio between the two channels

**Table 1** - Simplified reaction mechanism used for the initial calculations (17-step model).

Reactions	Rate Constants ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	Reference
(1) $\text{CH}_2\text{CO} \rightarrow {}^1\text{CH}_2 + \text{CO}$	$1.0 \cdot 10^{-4}$	see text
(2) $\text{CH}_2\text{CO} \rightarrow {}^3\text{CH}_2 + \text{CO}$	0.0	see text
(3) ${}^1\text{CH}_2 + \text{CH}_2\text{CO} \rightarrow \text{C}_2\text{H}_4 + \text{CO}$	$2.5 \cdot 10^{-10}$	15
(4) ${}^1\text{CH}_2 + \text{Ar} \rightarrow {}^3\text{CH}_2 + \text{Ar}$	$6.1 \cdot 10^{-12}$	15, 1c
(5) ${}^3\text{CH}_2 + {}^3\text{CH}_2 \rightarrow \text{C}_2\text{H}_2 + 2\text{H}$	$5.3 \cdot 10^{-11}$	1, 3, 6
(6) ${}^3\text{CH}_2 + \text{H} \rightarrow \text{H}_2 + \text{CH}$	$2.7 \cdot 10^{-10}$	25
(7) $\text{CH}_3 + \text{H} + \text{Ar} \rightarrow \text{CH}_4 + \text{Ar}$	$2.0 \cdot 10^{-10}$	3
(8) $\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$	$4.2 \cdot 10^{-11}$	18
(9) $\text{H} + \text{CH}_2\text{CO} \rightarrow \text{CH}_3 + \text{CO}$	$6.5 \cdot 10^{-14}$	26
(10) ${}^3\text{CH}_2 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_4 + \text{H}$	$5.0 \cdot 10^{-11}$	19
(11) $\text{CH} + \text{CH}_2\text{CO} \rightarrow \text{C}_2\text{H}_3 + \text{CO}$	$5.25 \cdot 10^{-11}$	3
(12) $\text{CH} + \text{CH}_2\text{CO} \rightarrow \text{C}_2\text{H}_2 + \text{H} + \text{CO}$	$1.575 \cdot 10^{-10}$	3
(13) $\text{CH}_3 + \text{C}_2\text{H}_3 \rightarrow \text{C}_3\text{H}_6$	$3.0 \cdot 10^{-11}$	3
(14) ${}^3\text{CH}_2 + \text{C}_2\text{H}_3 \rightarrow \text{C}_3\text{H}_4 + \text{H}$	$1.0 \cdot 10^{-10}$	3
(15) $\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 \rightarrow \text{C}_4\text{H}_6$	$6.0 \cdot 10^{-12}$	3
(16) $\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_2$	$9.0 \cdot 10^{-12}$	3
(17) $\text{H} + \text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_2 + \text{H}_2$	$1.0 \cdot 10^{-11}$	27

depends on the energy. At 308 nm the singlet channel dominates, and it is quite probable that all  $\text{CH}_2({}^3\text{B}_1)$  is formed by collisional induced intersystem crossing of  $\text{CH}_2({}^1\text{A}_1)$ .

(b) At 310 nm none of the radicals or molecules involved in the mechanism absorbs, and so no secondary photolysis need to be considered.

(c) The ratio of the main products  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$  depends on the total pressure.

(d) With O also present during photolysis the yield of ethylene is reduced while the yields of acetylene and ethane are eliminated. It is known<sup>6</sup> that  $\text{CH}_2({}^3\text{B}_1)$  reacts with great selectivity towards  $\text{O}_2$  and, in the presence of small amounts of it, is quantitatively converted in the oxidized carbon products.  $\text{CH}_2({}^1\text{A}_1)$ , on the other hand, is not appreciably affected for small concentrations of  $\text{O}_2$ . Nevertheless, the reaction of  $\text{CH}_2({}^1\text{A}_1)$  with O may simply involve spin conversion to the  $\text{CH}_2({}^3\text{B}_1)$ , followed by a scavenging reaction with another molecule of  $\text{O}_2$ .

(e) In spite of acetylene having been previously observed in the photolysis of ketene<sup>3,5,6</sup>, it was not detected in measurable quantities in the experiments of Ref. 4. It could be due to an experimental failure or to a mechanistic reason. Because of that, this last possibility should be extensively investigated.

Initially, only the set of equations of Table 1 of the paper of Frey and co-workers<sup>3c</sup> was considered (Table 1 of our work). Nevertheless the possibility of secondary reactions of triplet and singlet methylene with ethylene and acetylene should be considered since in a static system the concentration of final products and radicals is high enough to make the velocity of these steps appreciable. So, in a second step all these reactions were considered on the basis of the known reactions of methylene with added  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$ <sup>3c</sup> and the

possibility of another paths of reaction being opened was considered (Table 2).

*Integration of The Rate Equations. Method of Calculation.* In order to provide a quantitative explanation of the product distribution, the kinetic equations for the ketene, intermediates and products were analyzed. We solved the coupled differential equations by numerical integration, avoiding any assumptions about the mechanism.

The computer program used to solve the kinetic equations was written in FORTRAN and run on a PC computer<sup>12</sup>. The integration method is that of Gear's for "stiff" systems, as implemented in LSODE. The details of the method have been extensively discussed elsewhere<sup>13,14</sup>. Briefly, it allows to solve general initial value problems for "stiff" systems of nonlinear ordinary differential equations, using a variable step size and the so-called backward differentiation formula. The step size selection is automatic in order to fit the integration tolerance requested by the user. Subroutines for the differential equations and the Jacobian matrix, were written for the different mechanisms.

In order to gain some appreciation of the sensitivity of the fitting processes and the integration error, many tests were done. First, the relative and absolute tolerance parameters were diminished until repetitive results were obtained. Then the program was run, for the basic mechanism (Table 1), and also considering the secondary reactions of  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_4$ . Finally a rude sensitivity analysis was made by varying the rate constants within their error limits and also the mechanism itself was varied, by omission or addition of steps, to assess the importance of specific reactions. In that manner it was determined that the model of Table 2 leads to a better adjustment to the experimental results.

Table 2 - Complete model for the photodecomposition of ketene.

	Reactions	Rate Constants ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	Reference
(1)	$\text{CH}_2\text{CO} \rightarrow {}^1\text{CH}_2 + \text{CO}$	$1.1 \cdot 10^{-4}$	see text
(2)	$\text{CH}_2\text{CO} \rightarrow {}^3\text{CH}_2 + \text{CO}$	0.0	see text
(3)	${}^1\text{CH}_2 + \text{CH}_2\text{CO} \xrightarrow{1-f} \text{C}_2\text{H}_4 + \text{CO}$	$2.50010^{-10}$	see text
(44)	${}^1\text{CH}_2 + \text{CH}_2\text{CO} \xrightarrow{f} {}^3\text{CH}_2 + \text{CH}_2\text{CO}$	( $F=0.10$ )	
(4)	${}^1\text{CH}_2 + \text{Ar} \rightarrow {}^3\text{CH}_2 + \text{Ar}$	$6.1 \cdot 10^{-12}$	15, 1c
(5)	${}^3\text{CH}_2 + {}^3\text{CH}_2 \rightarrow \text{C}_2\text{H}_2 + 2\text{H}$	$5.3 \cdot 10^{-11}$	1, 3, 6
(6)	${}^3\text{CH}_2 + \text{H} \rightarrow \text{H}_2 + \text{CH}$	$2.7 \cdot 10^{-10}$	25
(7)	$\text{CH}_3 + \text{H} + \text{Ar} \rightarrow \text{CH}_4 + \text{Ar}$	$2.0 \cdot 10^{-10}$	3
(8)	$\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$	$4.2 \cdot 10^{-11}$	18
(9)	$\text{H} + \text{CH}_2\text{CO} \rightarrow \text{CH}_3 + \text{CO}$	$6.5 \cdot 10^{-14}$	25
(10)	${}^3\text{CH}_2 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_4 + \text{H}$	$5.0 \cdot 10^{-11}$	19
(11)	$\text{CH} + \text{CH}_2\text{CO} \rightarrow \text{C}_2\text{H}_3 + \text{CO}$	$5.25 \cdot 10^{-11}$	3
(12)	$\text{CH} + \text{CH}_2\text{CO} \rightarrow \text{C}_2\text{H}_2 + \text{H} + \text{CO}$	$1.575 \cdot 10^{-10}$	3
(13)	$\text{CH}_3 + \text{C}_2\text{H}_3 \rightarrow \text{C}_3\text{H}_6$	$3.0 \cdot 10^{-11}$	3
(14)	${}^3\text{CH}_2 + \text{C}_2\text{H}_3 \rightarrow \text{C}_3\text{H}_4 + \text{H}$	$1.0 \cdot 10^{-10}$	3
(15)	$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 \rightarrow \text{C}_4\text{H}_6$	$6.0 \cdot 10^{-12}$	3
(16)	$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_2$	$9.0 \cdot 10^{-12}$	3
(17)	$\text{H} + \text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_2 + \text{H}_2$	$1.0 \cdot 10^{-11}$	27
(18)	${}^1\text{CH}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_3\text{H}_6$	$2.10 \cdot 10^{-11}$	3
(19)	${}^1\text{CH} + \text{CH}_2 \rightarrow \text{C}_3\text{H}_3$	$1.80 \cdot 10^{-11}$	3
(20)	${}^3\text{CH}_2 + \text{C}_2\text{H}_2 \rightarrow \text{C}_3\text{H}_3 + \text{H}$	$6.50 \cdot 10^{-16}$	3
(21)	${}^3\text{CH}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_3\text{H}_5 + \text{H}$	$6.50 \cdot 10^{-16}$	24
(22)	${}^1\text{CH}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_3\text{H}_5 + \text{H}$	$1.925 \cdot 10^{-11}$	3
(23)	${}^1\text{CH}_2 + \text{C}_2\text{H}_4 \rightarrow {}^3\text{CH}_2 + \text{C}_2\text{H}_4$	$5.75 \cdot 10^{-11}$	3, 28
(24)	$\text{H} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5$	$9.00 \cdot 10^{-13}$	3
(25)	$\text{C}_2\text{H}_5 + {}^3\text{CH}_2 \rightarrow \text{CH}_3 + \text{C}_2\text{H}_4$	$8.00 \cdot 10^{-11}$	3
(26)	$\text{C}_2\text{H}_5 + \text{CH}_3 \rightarrow \text{C}_3\text{H}_8$	$2.50 \cdot 10^{-11}$	3
(27)	$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5 \rightarrow \text{n-C}_4\text{H}_{10}$	$1.118 \cdot 10^{-11}$	3
(28)	$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_4$	$1.820 \cdot 10^{-12}$	3
(29)	$\text{CH} + \text{C}_2\text{H}_4 \rightarrow \text{C}_3\text{H}_4 + \text{H}$	$2.10 \cdot 10^{-10}$	29
(30)	$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_3 \rightarrow \text{1-C}_4\text{H}_8$	$5.00 \cdot 10^{-11}$	3
(31)	$\text{H} + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_6$	$1.00 \cdot 10^{-10}$	3
(32)	$\text{C}_3\text{H}_5 + \text{C}_2\text{H}_5 \rightarrow \text{1-C}_5\text{H}_{10}$	$5.00 \cdot 10^{-11}$	3
(33)	$\text{C}_3\text{H}_5 + \text{CH}_3 \rightarrow \text{1-C}_4\text{H}_8$	$6.70 \cdot 10^{-11}$	3
(34)	$\text{C}_3\text{H}_5 + 3\text{CH}_2 \rightarrow \text{1.3-C}_4\text{H}_6 + \text{M}$	$5.00 \cdot 10^{-11}$	3
(35)	${}^1\text{CH}_2 + \text{C}_2\text{H}_2 \rightarrow \text{C}_3\text{H}_3 + \text{H}$	$1.925 \cdot 10^{-10}$	3
(36)	${}^1\text{CH}_2 + \text{C}_2\text{H}_2 \rightarrow {}^3\text{CH}_2 + \text{C}_2\text{H}_2$	$5.75 \cdot 10^{-11}$	3
(37)	$\text{H} + \text{C}_2\text{H}_2 \rightarrow \text{C}_3\text{H}_3$	$1.00 \cdot 10^{-13}$	3
(38)	$\text{CH} + \text{C}_2\text{H}_2 \rightarrow \text{CH}_2 + \text{H}$	$2.20 \cdot 10^{-10}$	3
(39)	$\text{C}_3\text{H}_3 + {}^3\text{CH}_2 \rightarrow \text{C}_4\text{H}_4 + \text{H}$	$1.20 \cdot 10^{-10}$	3
(40)	$\text{C}_3\text{H}_3 + \text{CH}_3 \rightarrow \text{C}_4\text{H}_6$	$6.70 \cdot 10^{-11}$	3
(41)	$\text{C}_3\text{H}_3 + \text{C}_2\text{H}_3 \rightarrow \text{C}_5\text{H}_6$	$1.00 \cdot 10^{-11}$	3
(42)	$\text{C}_3\text{H}_3 + \text{C}_3\text{H}_3 \rightarrow \text{C}_6\text{H}_6$	$7.00 \cdot 10^{-12}$	3
(43)	${}^3\text{CH}_2 + {}^3\text{CH}_2 \rightarrow \text{C}_2\text{H}_2 + \text{H}_2$	0.0	see text

The rate constant,  $k_1$ , for the initial step was adjusted so as to reproduce the experimental conversion. Changes in this constant affect only the total amount of reacting ketene, but not the relative yield of products, which is the experimental result to be fitted. Note that  $k_1$  and  $k_2$  are pseudo rate constants which incorporate the amount of light absorbed and the primary quantum yields, for example,  $k_1 = \Phi_1 I$ . Since the intensity of the light and the profile of the radiation source are a characteristic of each experimental set, these "constants" should differ from work to work. The other rate constants are discussed later.

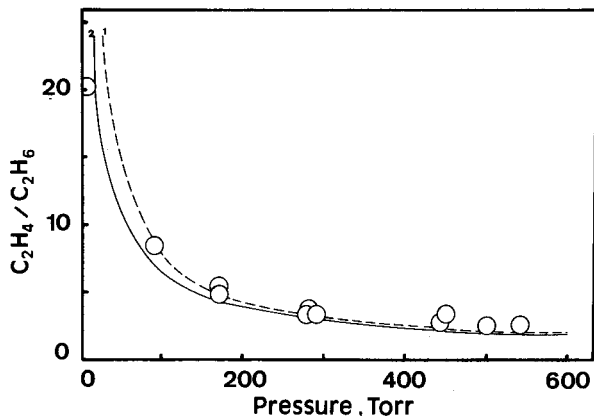
## Results and Discussion of the Mechanism

The results obtained considering only the simplified mechanism of Table 1 are shown in Figure 1. As it is seen, a quite good agreement with the experimental results is obtained. In spite of that this mechanism does not consider the occurrence of secondary reactions and does not take into account the low yield of acetylene.

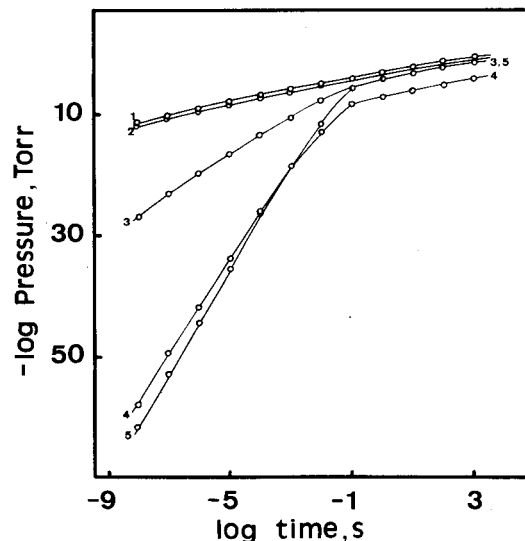
When the further reaction of methylene plus ethylene and acetylene is considered a new curve is obtained (Figure 1). It is worth noting that even the rate constant for the reaction of  $\text{CH}_2(^3\text{B}_1)$  with  $\text{C}_2\text{H}_4$  is about  $6.5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , that is, six orders of magnitude smaller than the rate constant for the addition of  $\text{CH}_2(^1\text{A}_1)$ , the stationary concentration of triplet methylene, at 300 s photolysis, is about five orders of magnitude greater than that of singlet methylene. This fact makes the velocities for both processes comparable. A similar consideration can be made for  $\text{C}_2\text{H}_2$ . This situation is quite different from that of a pulsed-laser system, since at very short times both concentrations are comparable.

The difference between the results for the mechanisms of Table 1 and 2 is about 10-20% depending on the pressure and the species considered. This is certainly within the experimental uncertainties, but it is enough to prove that in a stationary system secondary reactions must be taken into account for a better modeling.

Nevertheless, the concentration of  $\text{C}_2\text{H}_2$  kept comparable to that of  $\text{C}_2\text{H}_6$ . It is worth noting that the products were analyzed by chromatography using a flame ionization detector<sup>4</sup>. Under those conditions the detector response must be significantly lower for acetylene. In spite of that, the time of



**Figure 1.** Comparison of experimental data with calculated points for the  $[\text{C}_2\text{H}_4]/[\text{C}_2\text{H}_6]$  ratio as a function of total pressure, for 300 s of photolysis.  $\circ$  experimental points, curve 1: calculations using the 17-step model (Table 1), curve 2: calculations with the complete model (Table 2).

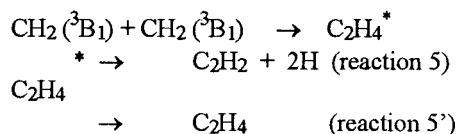


**Figure 2.** Calculated pressures (Torr) for some final products as a function of time (seconds): 1: CO, 2:  $\text{C}_2\text{H}_4$ , 3:  $\text{C}_2\text{H}_2$ , 4:  $\text{CH}_4$ , 5:  $\text{C}_2\text{H}_2$ . The modeling, at 116 Torr total pressure, was done using the complete model.

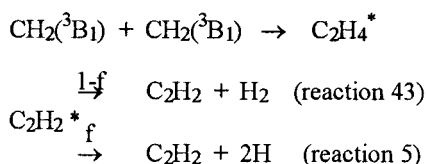
elution of  $\text{C}_2\text{H}_2$  was determined with a known sample, and during the reaction analysis, there was no evidence of even a smaller peak at that time.

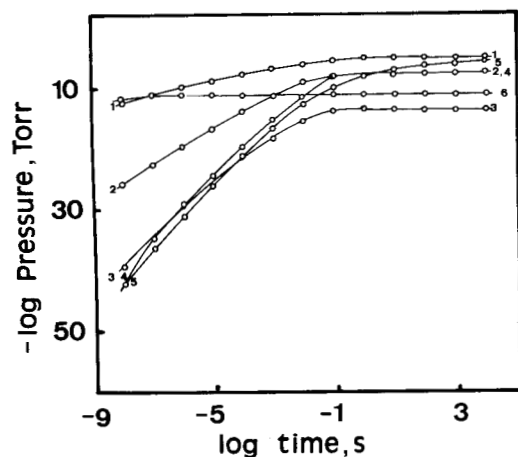
We concluded that two possibilities remain: first, the acetylene could be irreversibly absorbed on the column when injected in small amounts; second, the  $\text{C}_2\text{H}_2$  is further reacting with methylene. From these modeling results this second possibility can be discarded and so more experimental work should be done in order to elucidate this point.

The triplet methylene recombination has been the subject of previous controversies<sup>1,3,6</sup>. We have no experimental evidences to decide between the formation of atomic and molecular hydrogen, then, we initially adopted the first approach. In addition, the formation of  $\text{C}_2\text{H}_4$  is a highly exothermic reaction (about 175 kcal/mol) and so a vibrationally excited product is formed,



Pilling and co-workers<sup>1</sup> found that in the flash photolysis of ketene, triplet methylene reacted almost entirely by bimolecular reaction to form acetylene. Nevertheless, we consider the possibility of  $\text{C}_2\text{H}_4^*$  being stabilized by collisions. If so, the amount of reaction proceeding via 5' must be very small in order to fit satisfactorily the experimental results. The same situation arises when considering the possibility of molecular hydrogen formation<sup>3b</sup>, that is:

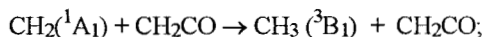




**Figure 3.** Calculated pressures (Torr) for some intermediates as a function of time (seconds): 1:  $^3\text{CH}_2$ , 2: H, 3: CH, 4:  $\text{C}_2\text{H}_3$ , 5:  $\text{C}_2\text{H}_5$ , 6:  $\text{CH}_2$ . The modeling, at 116 Torr total pressures, was done using the complete model.

By varying  $f$  we found, for example, that if  $\text{C}_2\text{H}_4^*$  decomposes, giving nearly 75%  $\text{H}_2$  and 25%  $2\text{H}$  the concentration of  $\text{C}_2\text{H}_4$  changes by approximately 1% at low pressures and 10% at high pressures. By contrast, the concentration of  $\text{C}_2\text{H}_6$  and  $\text{C}_2\text{H}_2$  changes by approximately 60% and 20% respectively, and then the fit to experimental results is bad. Certainly, atomic hydrogen plays an important role in controlling the velocity of formation of  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_6$  (via CH and  $\text{CH}_3$  radicals). Also, the results of Ref. 27 show that the reaction:  $\text{H} + \text{CH}_2(^3\text{B}_1) \rightarrow \text{CH} + \text{H}_2$  is very fast, and so we believe that the formation of molecular hydrogen (reaction 43) is not an important path of the system. We believe that the impossibility of distinguish between these two paths of reactions in the experiments of Ref. 3c was due to the conditions of the pulsed experiment (i.e. the low concentration of atoms and radicals when compared with the stationary system).

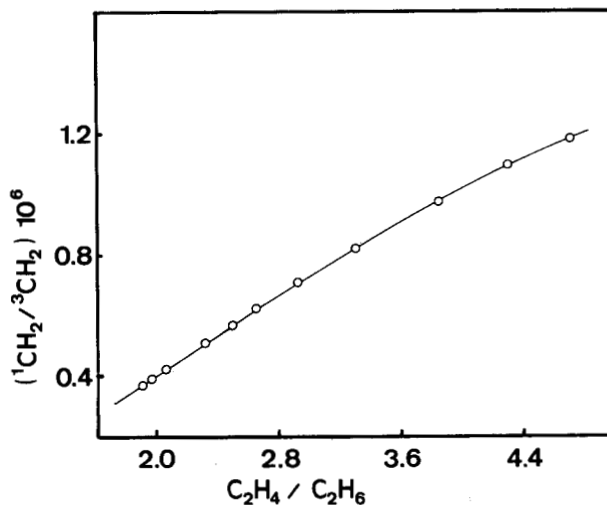
The possibility of intersystem crossing:



$$k \leq 2.7 \cdot 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

was also tested (reaction 44). Considering this last reaction the results at high pressure are quite similar. Nevertheless, at pressures lower than 200 Torr the ratio  $[\text{C}_2\text{H}_4]/[\text{C}_2\text{H}_6]$  is appreciably smaller and it seems in better agreement with the experimental results.

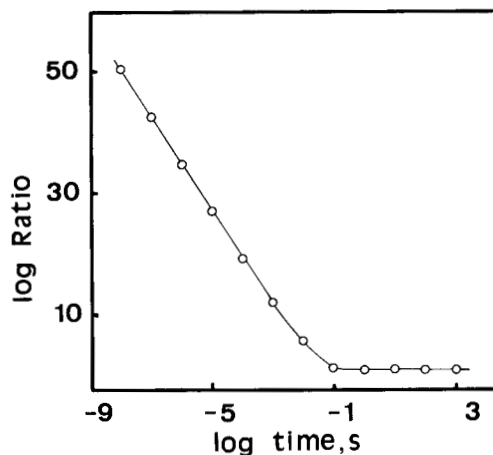
**Sensitivity analysis.** This set of coupled equations involves a large number of parameters and so is important to know to what extent the results of the simulation depend on the values of the parameters. One approach to the problem is to calculate the derivatives of the concentrations  $y_i$  with



**Figure 4.**  $[\text{C}_2\text{H}_4]/[\text{C}_2\text{H}_6]$  and methylene ratios for 300 s photolysis. The calculations were done using the complete model. Each point corresponds to a different total pressure.

respect to the parameters (here, the rate constants,  $k_j$ ). The other possibility is to systematically vary each of the constants between their limits of uncertainty.

We adopted the second method. In that way we found that  $\text{C}_2\text{H}_4$  is formed mainly via reaction 3, and the results for this product are quite insensitive to the rate constants for the other paths and to the amount of the radicals involved. The rate constant of reaction 3 has been experimentally determined<sup>15</sup> as  $(2.7 \pm 0.2) \times 10$  cm molecule s which leads to an uncertainty of about  $\pm 5\%$  in the concentration of  $\text{C}_2\text{H}_4$ . This is also the most important channel in the reaction of singlet methylene with ketene, with possible contributions ( $<10\%$ )



**Figure 5.**  $[\text{C}_2\text{H}_4]/[\text{C}_2\text{H}_6]$  ratio as a function of time (seconds). The calculations were done using the complete model and a total pressure of 116 Torr.

**Table 3.** Most sensitive rate constants for the photodecomposition of ketene. Reaction numbers are given in Table 2. Reactions are listed in order of decreasing sensitivity from left to right. The results were obtained by calculating the  $S_{ij}$  for 300s. See text for explanations.

Component	Most sensitive rate constants									
	3	1	9	4	24	5	37	44	21	
CH <sub>2</sub> CO	3	1	9	4	24	5	37	44	21	
<sup>1</sup> CH <sub>2</sub>	1	4	9	3	44	24	37	5	23	
<sup>3</sup> CH <sub>2</sub>	1	4	5	9	44	3	21	20	24	
C <sub>2</sub> H <sub>4</sub>	1	9	4	24	37	44	3	5	28	
C <sub>2</sub> H <sub>2</sub>	1	4	9	37	44	3	20	21	24	
C <sub>2</sub> H <sub>6</sub>	1	9	24	4	5	37	44	21	20	

from intersystem crossing. In fact, there is no evidence that singlet methylene and ketene react by others channels<sup>17</sup>.

The change in the concentration of final products with a change of 15% in  $k_5$ , is also about  $\pm 4\%$ , while the ratio  $[C_2H_4]/[C_2H_6]$  changes by 10%.

The rate constant for reaction 4, that is removal of CH<sub>2</sub>(<sup>1</sup>A<sub>1</sub>) by Ar, by inducing intersystem crossing to the triplet ground state, was also varied within its experimental uncertainty<sup>15</sup>:  $(5.8 \pm 0.5) \times 10^{-2} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . This uncertainty results in a change of about  $\pm 3\%$  for C<sub>2</sub>H<sub>4</sub>,  $\pm 5\%$  for C<sub>2</sub>H<sub>4</sub> and  $\pm 7\%$  for C<sub>2</sub>H<sub>2</sub>.

The rate constant  $k_7$  for recombination of CH<sub>3</sub> and H was varied within the errors given in the literature<sup>18,19</sup>, but no significant differences in the results were observed.

By varying the rate constants for reactions 9, 12, 16, 17, 28 in 10%, the species concentrations were modified by less than 1%.

We concluded from these results that the error in the determination of the individual rate constants affects the modeling within the uncertainty of the experimental  $[C_2H_4]/[C_2H_6]$  ratio, and therefore no more work in this sense is necessary.

In a second step we analyzed the contribution of each individual step. The computer program used was Kinal<sup>20</sup>, a program package for kinetic analysis of reaction mechanisms. This program solves the stiff differential equations, computes the local concentration sensitivity matrix and the contribution of reaction steps to the production rate of species.

The solution of the differential equations in Kinal is based on a fourth-order semi-implicit Runge-Kutta method. As expected, using this program the calculated ratio  $[C_2H_4]/[C_2H_6]$  differs by less than 5% from the LSODE values, showing that numerical errors due to the method of integration do not affect the results of the modeling.

When treating the importance of the parameters, it may be necessary to distinguish between two kinds of approaches. Tuning importance give a picture about the effectiveness of parameter changes around their nominal values for the inspected measure (concentration) and is obtained by calculating the  $S_{ij} = \partial c / \partial k$  which are referred to as the concentration sensitivity coefficients and are a measure of the response of the species concentrations to a perturbation in the parameters. This kind of results are difficult to interpret and, also, it is known that if a parameter has a small tuning

**Table 4.** Elimination analysis for each individual step. The entries in the Table are the deviation (%) in the calculated product concentration for 300 s of photolysis when setting the rate constant equal to zero.

Product	$k_3$	$k_{10}$	$k_{12}$	$k_{16}$	$k_{17}$	$k_{28}$
C <sub>2</sub> H <sub>4</sub>	69.61	0.13	11.93	0.13	11.93	12.46
C <sub>2</sub> H <sub>6</sub>	135.22	7.47	79.96	7.47	79.96	22.53
C <sub>2</sub> H <sub>2</sub>	146.39	1.17	43.30	1.17	43.30	30.36
CH <sub>4</sub>	115.21	47.82	53.69	47.82	43.69	48.83
CO	18.5	0.51	8.78	0.51	8.78	3.28
H <sub>2</sub>	154.19	1.16	97.56	1.16	97.56	30.37

importance with respect to the important species or features, this parameter may not be necessarily eliminated. One of the reasons is that the calculated  $S_{ij}$  can correctly give a quantitative characterization of the rate constants for differential variations and considering that only one concentration (that which is being analyzed) is affected at a time. That is, the study of a normalized sensitivity matrix allows determination of the rank order of the parameters on the basis of the effect on each  $c_i$  of a small parameter change for a certain time. This is not the case when rate constant are greatly changed, as it has been done in our previous analysis. Here the significance of the individual elementary stages may change, introducing a qualitative modification in the mechanism. The same situation arises when analyzing the reduction importance of a parameter which can be determined by setting the parameter to zero and rerunning the model. The rank order of reduction importance obtained may be quite different from that of tuning importance and from the results of varying the rate constants within their limits of error. This is shown by our calculations: In Table 3 we show the most sensitive rate constants, for the main products, obtained by calculating the sensitivity coefficients,  $S_{ij}$  (tuning importance), that is the local partial derivatives of each concentration with each rate constant. In Table 4, we show the reduction importance results for the main products and relative importance of each path of reaction, obtained by setting the rate constants equal to zero. These calculations may involve a substantial change in the mechanism since they eliminate a elementary reaction from the model.

## Conclusions

The interpretation of the results of Ref. 4 was done on the basis of the applicability of the steady state assumption for a static system with a photolysis time of 300s, and the proportionality between the  $[C_2H_2(^1A_1)]/[CH_2(^3B_1)]$  and the  $[C_2H_4]/[C_2H_6]$  ratios. The pertinence of these considerations was confirmed, as it is shown in Figures 2-4.

It can be seen from Figures 2-3 that the behavior of the system is quite different for times shorter than  $10^{-2}$  s and for longer times (i.e. 300s). In particular, radical concentrations are several orders of magnitude smaller in the first case and the system is clearly in a nonstationary state. Also, Figure 5 shows that the ratio  $[C_2H_4]/[C_2H_6]$  is strongly dependent of time. Because of that the results of the pulsed and continu-

ous radiation experiments are not directly comparable. Nevertheless, a complete mechanism, such as the one used in this work, can explain both kind of experiments: the difference is that the relative importance of the reaction steps is different since it is a function of time. Finally, it must be pointed out that the results of Frey et. al. for  $10^{-2}$ s are not necessarily directly comparable with the ones of our model (for the same time) since  $k_1$  is a pseudo-rate constant which depend on the conditions of the radiation source.

The proposed mechanism satisfactorily explains the experimental results. The only serious discrepancy arises when considering the low experimental yield of  $C_2H_2$ . Since we believe that it is due to a analytical error, new experiments are needed in order to gain a better knowledge of this system. Also, only new, careful experiments may be able to distinguish between mechanisms of Tables 1 and 2. We think that this system is a good illustration of the interaction between theory and experiment, within the philosophy of new gas-kinetics works. The sensitivity analysis shows that the uncertainty in the rate constants does not affect our conclusions since the error in the calculated and experimental  $[C_2H_4]/[C_2H_6]$  ratio is comparable. The values of the  $S_{ij}$  and the results from the reduction analysis show that reactions such as number 24, 28 and 37, involving radicals  $C_2H_3$ ,  $C_2H_5$ , may be important for longer time of reactions when the concentration of these species becomes larger (see Figure 3).

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