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# Shock Tube Measurements of Growth Constants in the Branched-Chain Ethane-Carbon Monoxide-Oxygen System

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# SHOCK TUBE MEASUREMENTS OF GROWTH CONSTANTS IN THE BRANCHED-CHAIN ETHANE-CARBON MONOXIDE-OXYGEN SYSTEM

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## SUMMARY

Exponential free-radical growth constants have been measured for ethane-carbon monoxide-oxygen mixtures by monitoring the growth of oxygen atom concentration as manifested by CO flame-band emission. Data were obtained over the temperature range of 1200 to 1700 K.

The data were analyzed using an ethane oxidation mechanism involving seven elementary reaction steps. Calculated growth constants were close to experimental values at lower temperatures, up to about 1400 K, but at higher temperatures computed growth constants were considerably smaller than experiment. In attempts to explain these results additional branching reactions were added to the mechanism. However, these additional reactions did not appreciably change calculated growth constants.

## INTRODUCTION

Ethane is a simple hydrocarbon and is also an intermediate in the rich combustion of other hydrocarbons. Thus, in order to obtain a complete set of chemical reactions and rates for modeling hydrocarbon combustion it is desirable to know the pathways by which ethane reacts.

The shock tube has proved useful for obtaining elementary reaction rates from growth constants in the $H_2$-CO-$0_2$ (ref. 1) and $CH_4$-CO-$0_2$ (ref. 2) systems. Consequently an analogous study of the $C_2H_6$-C0-$0_2$ system was initiated in hopes of extracting elementary reaction rates for ethane oxidation.

### Ethane Oxidation Scheme

When a mixture containing carbon monoxide, oxygen, and a small amount of ethane is subjected to a temperature and pressure pulse in a shock tube, small concentrations of atoms and free radicals may first be formed by processes such as

$$CO + 0_2 \; 4CO_2 + O$$

$$C_2H6 + 0_2 + C_2H5 + H0_2$$

and

$$C_2H_6 + M \rightarrow 2CH_3 + M$$

followed by

$$CH_3 + O_2 \rightarrow CH_3O + O \rightarrow CH_2O + O + H$$

These atoms and free radical concentrations may then grow exponentially via the branched chain scheme

$$H + O_2 \xrightarrow{k_2} OH + O \tag{2}$$

$$OH + CO \xrightarrow{k_5} CO_2 + H \tag{5}$$

$$OH + C_2H_6 \xrightarrow{k_6} H_2O + C_2H_5 \tag{6}$$

$$H + C_2H_6 \xrightarrow{k_7} H_2 + C_2H_5 \tag{7}$$

$$O + C_2H_6 \xrightarrow{k_8} OH + C_2H_5 \tag{8}$$

$$C_2H_5 + O_2 \xrightarrow{k_9} C_2H_4 + HO_2 \tag{9}$$

$$C_2H_5 + M \xrightarrow{k_{10}} C_2H_4 + H + M \tag{10}$$

Reactions have been numbered to be compatible with notation used in the study of the $H_2$-$O_2$-CO system (ref. 1)

Theory shows (refs. 1 to 5) that in such chain branched systems when depletion of reactants is negligible and temperature and pressure are constant, the atom and radical concentrations increase proportional to $\exp(\lambda t)$ (except very early in the reaction). The growth constant $\lambda$ depends on the rate constants of the elementary chemical reactions and the concentrations of stable reactants - in this case CO, $O_2$, and $C_2H_6$.

This report presents experimental growth constants measured behind incident shocks for a range of pressures, temperatures, and gas compositions. These experimental growth constants are compared with values computed using rate constants from the literature. Calculated growth constants are close to experimental values at temperature below 1400 K, but at higher temperatures

computed growth constants are considerably smaller than the experimental values. Attempts to explain this result using additional chain branching reactions have not been successful.

## EXPERIMENTAL ASPECTS

Growth constants were obtained by measuring the blue CO flame band emission behind incident shocks. The intensity of this radiation is proportional to the product of carbon monoxide and oxygen atom concentrations (ref. 6), and since little CO is consumed the light measures the increase of oxygen atom concentration with time. Details of the shock tube and associated optical and electronic equipment have been described elsewhere (ref. 7). Flame band radiation centered at 4100 Å was isolated by a high precision ultraviolet interference filter having a 100 Å band pass.

Gas mixtures contained small amounts of $C_2H_6$ with varying amounts of CO, $O_2$, and $CO_2$ diluted with argon. (Carbon dioxide was added to ensure vibrational relaxation of CO in mixtures with a large CO concentration.) Oxygen, carbon dioxide, ethane, carbon monoxide, and argon were high purity tank gases and were used without further purification.

It has been shown (refs. 7 and 8) that boundary-layer effects must be considered in analyzing data obtained behind incident shocks. Conditions behind the shocks, in the region of the experimental measurements, were obtained from a computer program (ref. 9) which integrates the equations of chemical change for a shocked gas accounting for the effects of boundary-layer buildup. The procedure has been described for both turbulent (ref. 7) and laminar (ref. 8) boundary layers. The data in this report were obtained with laminar boundary layers.

Exponential growth constants were obtained from plots of logarithm of observed light intensity versus gas time. The relation between gas and laboratory times was obtained from the computer calculations.

## THEORETICAL CONSIDERATIONS

The analytic solutions of the differential equations describing the ignition kinetics in chain-branched systems involving hydrogen, oxygen, and carbon monoxide have been discussed in detail previously (refs. 3 to 5) and the solution has been presented for the methane-carbon monoxide-oxygen system (ref. 2). The solution for the system of reactions presented in the introduction is quite analogous and will merely be outlined here.

To obtain the analytic solution, the atom and radical concentrations - H, OH, O, and $C_2H_5$ - are assumed to be small in comparison to the concentrations of reactants $C_2H_6$, CO, and $O_2$ so that the reactant concentrations may be considered constant and reactions between chain carriers are unimportant. In addition, the temperature and pressure must be nearly constant over the time range of the experimental observations.

Subject to these assumptions, the chemical kinetics are described by a system of simultaneous first-order linear differential equations, one for each chain carrier. The solution of these equations shows that during the growth

period the chain-carrier concentrations grow as $\exp(\lambda t)$ (except very early in the reaction). During the growth period only reactions (2) to (10) are important. The growth constant $\lambda$ is the positive root of a polynomial of a degree equal to the number of chain carriers. Thus with H, OH, O, and $C_2H_5$ as chain carriers, the following quartic equation is obtained:

$$\begin{vmatrix} -(v_9 + v_{10} + \lambda) & v_8 & v_6 & v_7 \\ 0 & -(v_8 + \lambda) & 0 & v_2 \\ 0 & v_8 & -(v_5 + v_6 + \lambda) & v_2 \\ v_{10} & 0 & v_5 & -(v_2 + v_7 + \lambda) \end{vmatrix} = 0 \qquad (1)$$

where $v_2 \equiv k_2[O_2]$, $v_5 \equiv k_5[CO]$, $v_6 \equiv k_6[C_2H_6]$, $v_7 \equiv k_7[C_2H_6]$, $v_8 \equiv k_8[C_2H_6]$, $v_9 \equiv k_9[O_2]$, and $v_{10} \equiv k_{10}[M]$. The rows in this equation derive from the differential equations for the rates of formation of $C_2H_5$, O, OH, and H, respectively. The columns derive from the rates of formation or destruction of $C_2H_5$, O, OH, and H in the elementary chemical reactions.

This equation was used to calculate growth constants corresponding to the experimental conditions using rate constants taken from the literature. The rate constants and sources are listed in the appendix. Equation (1) was numerically differentiated to obtain the sensitivities of the calculated rate constants to the various reaction rates.

## RESULTS AND DISCUSSION

The compositions of the three gas mixtures investigated are given in table I. Also shown are the sensitivities, $\partial \ln\lambda/\partial \ln v_i$ for the various reaction rates. The range of sensitivities shown is for the temperature range of the data for each composition. Mixture 1 shows sensitivity to the rates of reactions 2, 5, 6, and 8 while mixtures 2 and 3 are sensitive mainly to reactions 2 and 8.

The experimental results are set forth in table II and plotted in figures 1 to 3. Because the reactions in the ethane oxidation scheme are all bimolecular, the growth constant at a given temperature should be proportional to the pressure. Consequently, in figures 1 to 3 the experimental data are plotted as the logarithm of $\lambda/P$ versus reciprocal temperature. Also shown as solid lines are values computed from equation (1) using rate constants taken from the literature, and set forth in the appendix.

For mixture 1 calculated growth constants are 25 to 50 percent lower than experimental values, with the larger discrepancies at the higher temperatures. For mixtures 2 and 3 calculation and experiment are in better agreement, particularly at temperatures below about 1400 K; but at the highest temperatures calculated values are 20 to 50 percent below experiment.

The agreement between theory and experiment can be improved by upward adjustments in $k_5$ and $k_8$. However, the rate of reaction 5 is quite well established, and the increases required - fivefold or more - cannot be justified.

Other reactions were added to the scheme in hopes of improving the agreement between calculated and experimental growth constants. Additional reactions considered included

$$\text{A.}\quad HO_2 + CO \rightarrow CO_2 + OH$$

$$\text{B.}\quad \begin{cases} C_2H_5 + CO \rightarrow C_2H_4 + HCO \\ HCO + M \rightarrow CO + M + H \end{cases}$$

$$\text{C.}\quad HO_2 + M \rightarrow H + O_2 + M$$

$$\text{D.}\quad HO_2 + C_2H_6 \rightarrow H_2O_2 + C_2H_5$$

$$\text{E.}\quad \begin{cases} C_2H_5 + O_2 \rightarrow C_2H_5O + O \\ C_2H_5O + M \rightarrow CH_3CHO + M + H \end{cases}$$

The introduction of another chain carrier - $HO_2$ or HCO - in schemes A to D increased mathematical complexity by transforming equation (1) to a quintic. However, these schemes had negligible affect on calculated growth constants.

Finally another reaction between atomic oxygen and ethane was added to the basic oxidation scheme:

$$O + C_2H_6 \rightarrow CH_3O + CH_3 \qquad (8a)$$

$$CH_3 + O_2 \rightarrow CH_3O + O$$

$$CH_3O + M \rightarrow CH_2O + H + M$$

Growth constants calculated assuming equal rate for reactions 8 and 8(a) were 23 to 24 percent larger for mixture 1 over the experimental temperature range. Although this is an improvement, it is not nearly large enough at the higher temperatures. If a larger activation energy were assumed for reaction 8(a) so as to increase the rate of change of growth constant with temperature, the rate constants for reaction 8(a) would be smaller and the increases in calculated growth constants would be less than 24 percent.

Thus a completely satisfactory theoretical analysis of the experimental growth constants has not been achieved. Perhaps the assumptions of the linearized analysis - negligible depletion of reactants, negligible heat release, negligible radical-radical reactions - are not valid at the higher temperatures.

## APPENDIX

## SPECIFIC REACTION RATE CONSTANTS

This appendix lists individual reactions used in calculations and indicates values and sources of the assumed rate constants. Bimolecular rate constants are expressed in $cm^3 mole^{-1} sec^{-1}$. Temperatures are in degrees Kelvin and activation temperatures, E/R, are in degrees Kelvin.

$$H + O_2 \rightarrow OH + O \qquad k_2 = 1.38\times10^{14} \exp\left(\frac{-8253}{T}\right) \tag{2}$$

This rate constant, from reference 8, was measured in the shock tube used in this investigation.

$$OH + CO \rightarrow CO_2 + H \qquad k_5 = 10^{12} \exp\left(\frac{-1862}{T}\right) \tag{5}$$

This rate constant (ref. 1) was determined in the shock tube used in this investigation.

$$OH + C_2H_6 \rightarrow H_2O + C_2H_5 \qquad k_6 = 8.7\times10^{13} \exp\left(\frac{-1771}{T}\right) \tag{6}$$

Rate constant from reference 10.

$$H + C_2H_6 \rightarrow H_2 + C_2H_5 \qquad k_7 = 1.32\times10^{14} \exp\left(\frac{-4881}{T}\right) \tag{7}$$

Rate constant from reference 10.

$$O + C_2H_6 \rightarrow OH + C_2H_5 \qquad k_8 = 1.13\times10^{14} \exp\left(\frac{-3950}{T}\right) \tag{8}$$

Rate constant from reference 11.

$$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2 \qquad k_9 = 1.5\times10^{12} \exp\left(\frac{-2445}{T}\right) \tag{9}$$

Rate constant from reference 12.

$$C_2H_5 + M \rightarrow C_2H_4 + M + H \qquad k_{10} = 10^{16} \exp\left(\frac{-15\ 097}{T}\right) \tag{10}$$

Rate constant from reference 13.

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TABLE I. - MIXTURE COMPOSITION AND GROWTH CONSTANT SENSITIVITIES

| Composition, mole percent | Gas mixture | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| $C_2H_6$ | 0.0215 | 0.0190 | 0.0204 |
| CO | 3.04 | 10.33 | 10.08 |
| $O_2$ | 9.90 | 2.87 | 1.034 |
| $CO_2$ | 2.74 | 5.05 | 5.04 |
| Calculated sensitivities, reaction i | | | |
| 2 | 0.19 to 0.11 | 0.50 to 0.37 | 0.56 to 0.49 |
| 5 | .25 to .26 | .10 to .17 | .06 to .10 |
| 6 | .09 to .15 | .02 to .03 | .005 to .02 |
| 7 | -.005 to -.001 | -.02 to -.001 | -.008 to -.001 |
| 8 | .46 to .47 | .41 to .43 | .38 to .40 |
| 9 | -.10 to .02 | -.07 to -.006 | -.015 to -.003 |
| 10 | .12 to .03 | .09 to .011 | .025 to .006 |

TABLE II. - EXPERIMENTAL RESULTS

| Temperature, K | Pressure, atm | Growth constant $\lambda$, $sec^{-1}$ |
|---|---|---|
| Mixture 1 | | |
| 1699 | 0.1642 | $17.11 \times 10^3$ |
| 1683 | .1421 | 17.02 |
| 1677 | .1485 | 17.41 |
| 1644 | .1590 | 18.48 |
| 1617 | .1584 | 16.28 |
| 1605 | .1292 | 13.28 |
| 1603 | .1340 | 12.06 |
| 1580 | .1343 | 10.01 |
| 1483 | .1347 | 9.29 |
| 1472 | .1260 | 6.73 |
| 1409 | .1160 | 7.63 |
| 1390 | .1092 | 4.64 |
| Mixture 2 | | |
| 1602 | 0.1328 | $8.82 \times 10^3$ |
| 1558 | .1292 | 8.20 |
| 1535 | .1417 | 10.52 |
| 1529 | .1510 | 9.32 |
| 1498 | .1225 | 5.91 |
| 1477 | .1310 | 7.15 |
| 1447 | .1229 | 5.06 |
| 1438 | .1252 | 4.31 |
| 1409 | .1366 | 3.79 |
| 1377 | .1188 | 3.91 |
| 1359 | .1244 | 3.07 |
| 1337 | .1152 | 3.45 |
| 1315 | .1170 | 3.18 |
| 1287 | .1136 | 2.46 |
| 1221 | .1064 | 1.759 |
| 1208 | .1035 | 1.918 |

TABLE II. - CONCLUDED

| Temperature, K | Pressure, atm | Growth constant $\lambda$, $sec^{-1}$ |
|---|---|---|
| Mixture 3 | | |
| 1605 | 0.1323 | $8.59 \times 10^3$ |
| 1565 | .1396 | 8.25 |
| 1536 | .1603 | 7.68 |
| 1529 | .1278 | 4.94 |
| 1501 | .1501 | 6.03 |
| 1463 | .1173 | 2.92 |
| 1443 | .1272 | 4.01 |
| 1438 | .1591 | 4.91 |
| 1432 | .1270 | 3.15 |
| 1416 | .1406 | 3.90 |
| 1408 | .1363 | 3.07 |
| 1388 | .1459 | 2.69 |
| 1355 | .1157 | 1.803 |
| 1342 | .1338 | 2.12 |
| 1321 | .1301 | 2.39 |
| 1320 | .1201 | 2.34 |

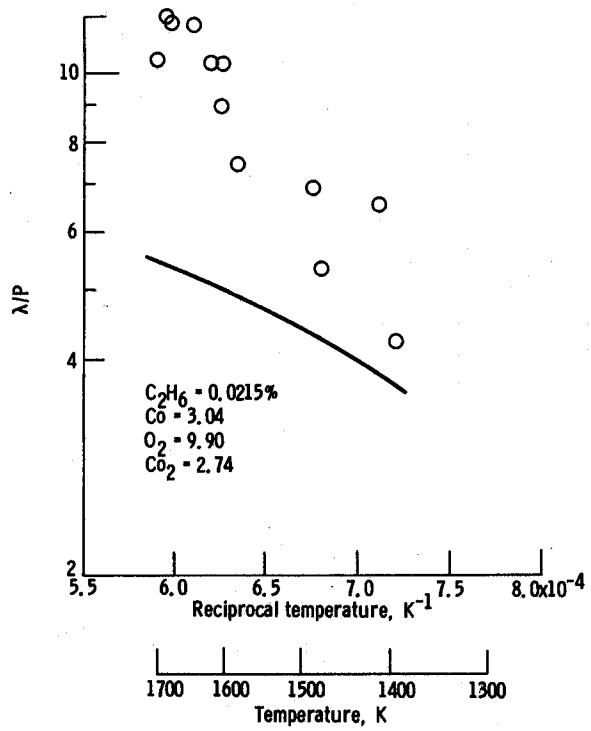


Figure 1. - Experimental and computed growth constants as a function of temperature. Mixture 1.

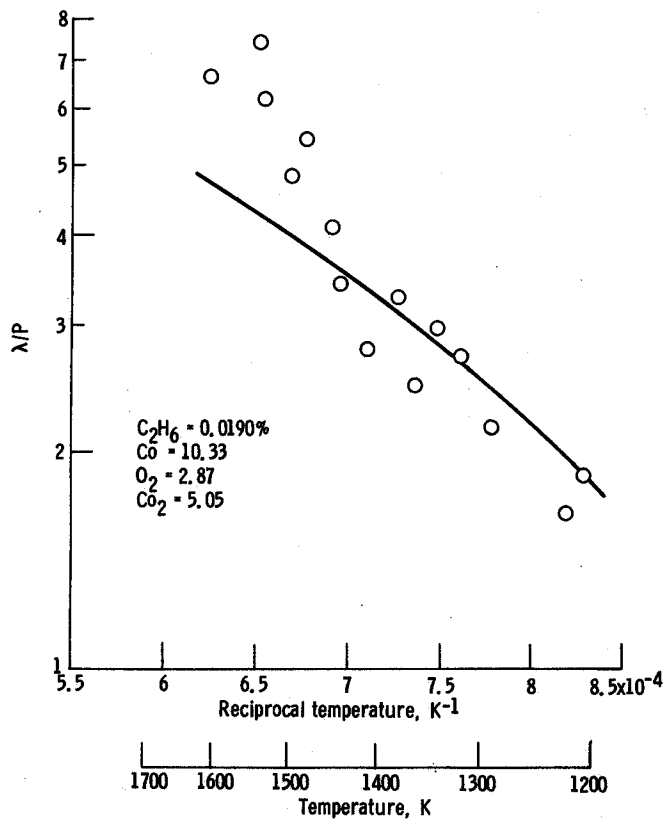


Figure 2. - Experimental and computed growth constants as a function of temperature. Mixture 2.

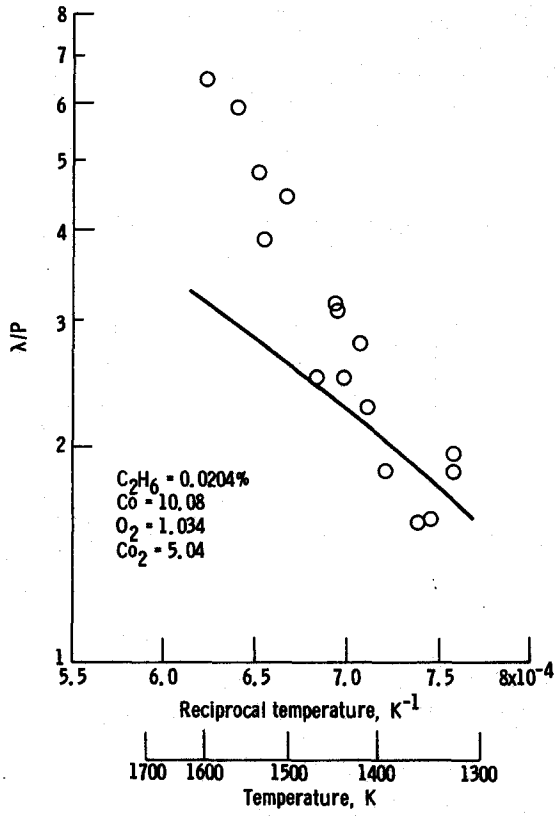


Figure 3. - Experimental and computed growth constants as a function of temperature. Mixture 3.

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15. Supplementary Notes

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16. Abstract

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