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

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

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SUMMARY

Exponential free-radical growth constants have been measured for formaldehyde-carbon monoxide-oxygen systems 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 2000 K.

The data have been analyzed using a formaldehyde oxidation mechanism involving 12 elementary reaction steps. The computed growth constants are roughly in accord with experimental values, but are much more temperature dependent. The data have also been analyzed assuming formaldehyde is rapidly decomposed to carbon monoxide and hydrogen. Growth constants computed for the resulting carbon monoxide-hydrogen-oxygen mixtures have a temperature dependence similar to experiment; however, for most mixtures, the computed growth constants were larger than experimental values.

INTRODUCTION

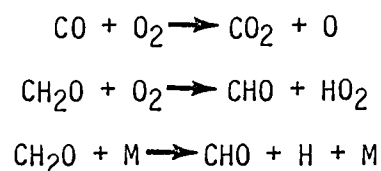
Formaldehyde is an important intermediate in the oxidation of hydrocarbons to carbon dioxide and water. Thus, in order to obtain a complete set of chemical reactions and rates for modeling hydrocarbon combustion it is desirable to know the pathways by which formaldehyde reacts to form carbon monoxide, hydrogen, water, and carbon dioxide.

The shock tube has proved useful for obtaining elementary reaction rates from growth constants in the  $H_2-CO-O_2$  (ref. 1) and  $CH_4-CO-O_2$  (ref. 2) systems. Consequently an analogous study of the  $CH_2O-CO-O_2$  system was initiated in hopes of extracting elementary reaction rates for formaldehyde oxidation.

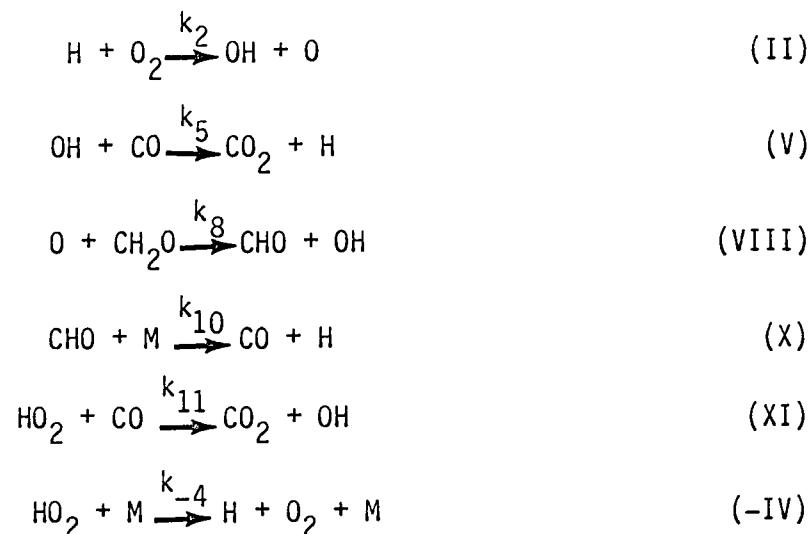
Formaldehyde Oxidation Scheme

When a mixture containing carbon monoxide, oxygen, and a small amount of formaldehyde is subject 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

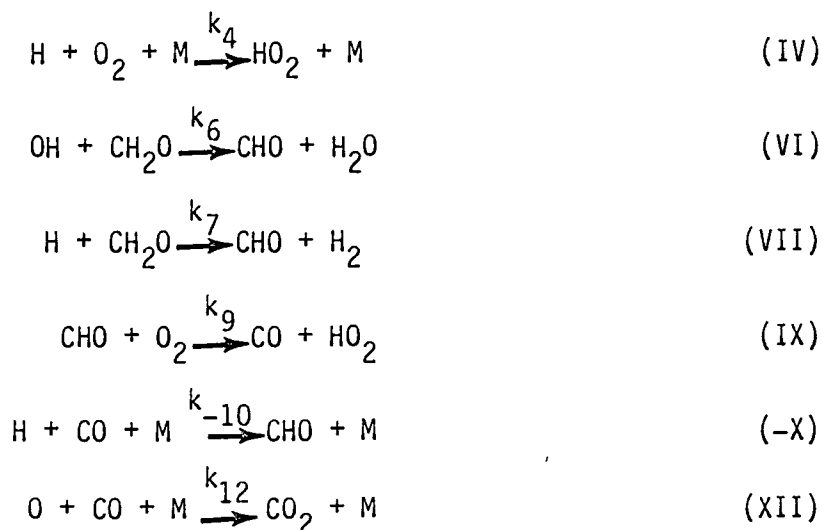
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These atom and free-radical concentrations may then grow exponentially via the branched-chain scheme



Chainbranching is inhibited by the reactions



The chain carriers H, OH, and O are more reactive than CHO, which in turn is more reactive than HO<sub>2</sub>. Numerical integration of this kinetic scheme for the experimental conditions indicates that the rate of reaction (-IV) is greater than reaction (IV) and that there may be some reversal of reaction (V). Reactions have been numbered to be compatible with notation used in the study of the H<sub>2</sub>-O<sub>2</sub>-CO system (ref. 1).

Theory shows (refs. 2 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

( $\lambda t$ ) increases (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<sub>2</sub>, and CH<sub>2</sub>O.

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 from theory. Agreement between theory and experiment is only semiquantitative.

Inasmuch as the analysis of the data is not definitive, the experimental conditions for each datum - gas time interval, temperature range, and pressure, are recorded for the benefit of others who may wish to reevaluate the data.

### 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 or no 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).

Gas mixtures contained small amounts of CH<sub>2</sub>O with varying amounts of CO, O<sub>2</sub>, and CO<sub>2</sub> diluted with argon. (Carbon dioxide was added to ensure vibrational relaxation of carbon monoxide.) Oxygen and argon were high-purity tank gases and were used without further purification. Carbon monoxide was condensed at liquid nitrogen temperature; about a fourth of the condensate was pumped off and discarded. Dry ice served as a convenient source of carbon dioxide. It was purified by subliming three quarters of a sample into a liquid nitrogen cooled trap. The first quarter of this trapped fraction was discarded and the middle half used for mixture preparation.

Formaldehyde was prepared from trioxane, a cyclic trimer of formaldehyde which contains no combined water. This is important, since traces of water catalyze the polymerization of formaldehyde to paraformaldehyde. On the other hand, pure dry formaldehyde gas shows no visible signs of polymerization when stored in glass vessels at 80 to 100° C.

Trioxane was depolymerized by passing a nitrogen-trioxane mixture over an acid catalyst at 200 to 240° C. Formaldehyde was collected in a trap cooled by liquid nitrogen and purified by two bulb-to-bulb transfers in a glass-vacuum system. A 5 percent formaldehyde mixture in argon was prepared from the purified liquid and was stored in a glass bulb maintained at 110° C.

Test mixtures were prepared in a large glass vessel by introducing first the formaldehyde argon mixture and then adding an appropriate CO-O<sub>2</sub>-CO<sub>2</sub> argon mixture from a high pressure storage tank.

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 boundary layers (ref. 7) and laminar boundary layers (ref. 8). Data were obtained with both laminar and turbulent boundary layers in this report.

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 equations discussed 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, HO<sub>2</sub>, and CHO are assumed to be small in comparison to the concentrations of reactants CH<sub>2</sub>O, CO, and O<sub>2</sub> 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 the chain-carrier concentrations grow as exp(λt) (except very early in the reaction). The growth constant λ is the positive root of a polynomial of a degree equal to the number of chain carriers. Thus, with H, OH, O, HO<sub>2</sub>, and CHO as chain carriers, the following quintic equation is obtained:

$$0 = \begin{vmatrix} -(v_8 + v_{12} + \lambda) & v_2 & 0 & 0 & 0 \\ 0 & -(v_2 + v_4 + v_{-5} + v_7 + v_{-10} + \lambda) & v_5 & v_{-4} & v_{10} \\ v_8 & (v_2 + v_{-5}) & -(v_5 + v_6 + g) & v_{11} & 0 \\ 0 & v_4 & 0 & -(v_{-4} + v_{11} + \lambda) & v_9 \\ v_8 & (v_7 + v_{-10}) & v_6 & 0 & -(v_9 + v_{10} + \lambda) \end{vmatrix} \quad (1)$$

where  $v_2 \equiv k_2[O_2]$ ,  $v_4 \equiv k_4[O_2][M]$ ,  $v_{-4} \equiv k_{-4}[M]$

$v_5 \equiv k_5[CO]$ ,  $v_{-5} \equiv k_{-5}[CO_2]$ ,  $v_6 \equiv k_6[CH_2O]$ ,  $v_7 \equiv k_7[CH_2O]$

$v_8 \equiv k_8[CH_2O]$ ,  $v_9 \equiv k_9[O_2]$ ,  $v_{10} \equiv k_{10}[M]$ ,  $v_{10} \equiv k_{-10}[CO][M]$

$v_{11} \equiv k_{11}[CO]$ , and  $v_{12} \equiv k_{12}[CO][M]$

The rows in this equation derive from the differential equations for the rates of formation of H, OH, O, HO<sub>2</sub>, and CHO, respectively. The columns derive from the rates of formation or destruction of H, OH, O, HO<sub>2</sub> and CHO 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. Also, Equation (1) was numerically differentiated to obtain the sensitivities of the calculated growth constants to the various reaction rates.

## RESULTS AND DISCUSSION

The compositions of the four gas mixtures are given in table I. For mixture 1 there were slightly different compositions, designated as a, b, and c. 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. On the basis of low sensitivities several reactions might be eliminated from the scheme reactions (IV), (-V), (-X), (XII), and perhaps (-IV).

The experimental results are set forth in table II and Figures 1 to 4. The data for mixtures 1 and 2 were obtained at pressures (1 to 1.5 atm) where the boundary layers were turbulent. The data for mixtures 3 and 4 were at lower pressures (0.12 to .25 atm) where boundary layers were laminar. The data for mixtures 1 and 2 range from about 1400K to 1600K; the data for mixtures 3 and 4 cover a wider temperature range, from about 1200K to over 2000K.

Because the most important reactions in the formaldehyde oxidation scheme are all bimolecular [only reactions (IV), (-X), and (XII) are not], the growth constant at a given temperature should be proportional to the pressure. Consequently, in figures 1 to 4 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.

The calculated growth constants are generally smaller than experimental values, except for mixtures 3 and 4 at the higher temperatures. Indeed, at the lowest temperatures, computed growth constants for mixtures 3 and 4 are about one seventh of the experimental values.

Attempts were made to reconcile theory and experiment by changing the rates of several of the important reactions. From the sensitivities in table I, the important reactions are (II), (V), (VI), (VII), (VIII), (IX), (X), and (XI). The rates of reactions (II) and (V) are well-established and are not candidates for tinkering. Values of  $k_9$  were computed from mixture 3 using equation (1) together with the experimental growth constants. Although a good correlation was obtained, when the rate constant was fitted to the Arrhenius equation the pre-exponential factor was  $8 \times 10^{16}$  which is three orders of magnitude too large for such a bimolecular abstraction reaction. In another attempt to fit the data  $k_{10}$  was computed from mixture 3; these calculations yielded rate constants which were larger at low temperatures than at high temperatures, which is absurd. In still another attempt to fix the data  $k_7$  was computed from mixtures 1 and 2.

When these rate constants were fitted to the Arrhenius equation, the pre-exponential factor was about four orders of magnitude too large.

The pattern which seems to emerge is the following: to fit the data, reactions that promote branching such as (II), (V), (VIII), (X), or (XI), must be assigned small or negative temperature dependences; or inhibiting reactions such as (VI), (VII), and (IX) must be assigned very strongly positive temperature dependence. Neither alternative is reasonable.

Perhaps the formaldehyde is rapidly decomposed to hydrogen and carbon monoxide so that the growth constants are really those of the  $H_2-CO-O_2$  system. To explore this possibility, growth constants were calculated for the  $H_2-CO-O_2$  system, assuming the formaldehyde present decomposed instantaneously to hydrogen and carbon monoxide. Results are shown as dashed curves on figures 1 to 4. For mixtures 3 and 4 (figs. 3 and 4), which span a wide range of temperature, growth constants computed for the  $H_2-CO-O_2$  system show a temperature dependence similar to that of the experimental data; indeed, for mixture 3, calculated and experimental growth constants are in agreement. For mixture 4, calculated growth constants are perhaps 60 percent to 90 percent larger than experiment. For mixture 1, experimental growth constants lie between values calculated for the  $CH_2O-CO-O_2$  and  $H_2-CO-O_2$  systems, while for mixture 2, calculated growth constants for both schemes are lower than experimental values.

The analyses reported here suggest there may be substantial but incomplete decomposition of formaldehyde to carbon monoxide and hydrogen prior to the exponential growth of chain carriers. To model this situation, numerical chemical kinetic calculations would be required. It is not clear that such calculations would accomplish more than a rationalization of the experimental data; it is uncertain as to whether rates of elementary reactions could be established with confidence.

#### CONCLUDING REMARKS

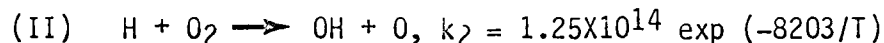
Exponential free-radical growth constants have been measured for formaldehyde-carbon monoxide-oxygen systems by monitoring the growth of oxygen atom concentration as manifested by CO flame band emission. Data were obtained over the temperature range of 1200 to 2000 K.

The data have been analyzed using a formaldehyde oxidation mechanism involving 12 elementary reaction steps. The computed growth constants are roughly in accord with experimental values, but are much more temperature dependent. The data have also been analyzed assuming formaldehyde is rapidly decomposed to carbon monoxide and hydrogen. Growth constants computed for the resulting carbon monoxide-hydrogen-oxygen mixtures have a temperature dependence similar to experiment; however, for most mixtures, the computed growth constants were larger than experimental values.

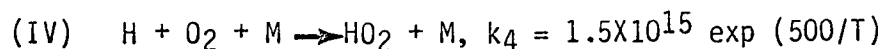
## APPENDIX

### SPECIFIC REACTION RATE CONSTANTS

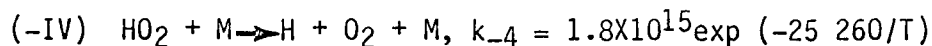
This appendix lists individual reactions used in the calculations and indicates values and sources of the assumed rate constants. Bimolecular rate constants are expressed in  $\text{cm}^3\text{mole}^{-1}\text{sec}^{-1}$  and the molecular rate constants are in  $\text{cm}^6\text{mole}^{-2}\text{sec}^{-1}$ . Temperatures are in degrees Kelvin and activation temperatures, E/R, are in degrees Kelvin.



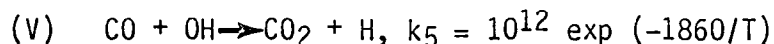
This rate constant, from reference 1, was measured in the shock tube used in this investigation.



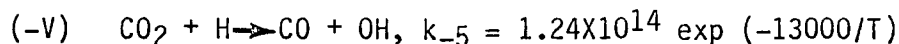
This rate constant (ref. 10) is for argon as the third body. Other third-body factors used (Ar = 1) were  $\text{O}_2$  and  $\text{CO} = 1.3$ ,  $\text{CO}_2 = 5$ , and  $\text{CH}_2\text{O} = 1$ .



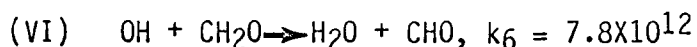
This rate constant is obtained from the rate of reaction (IV) and the equilibrium constant for reaction (IV), from reference 11. Chaperon efficiencies are the same as in reaction (IV).



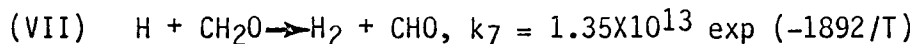
This rate constant (ref. 1) was obtained from the shock tube used in this investigation.



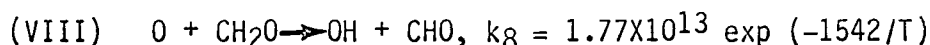
This rate constant is obtained from the rate of reaction (V) and the equilibrium constant for reaction (V) from reference 11.



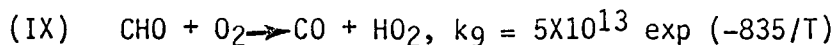
Recommendation of reference 12.



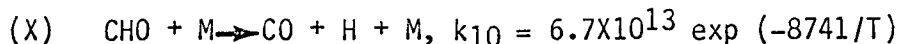
From reference 13.



From reference 14.

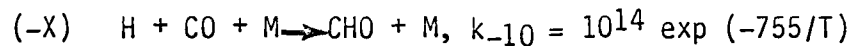


This rate constant is obtained by fitting the Arrhenius equation to the room temperature recommendation of reference 12 with the 1600K value of reference 15.

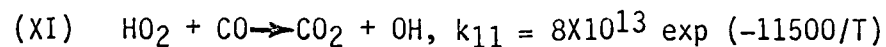




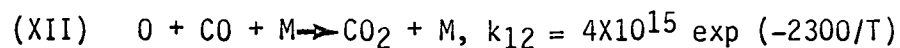
This rate constant is obtained from the rate of reaction (-X), and the equilibrium constant for reaction (X). The equilibrium constant was calculated from the thermodynamic data of reference 11, with an adjustment to account for the heat of formation of CHO recommended in reference 12. The rate shown is for M = Argon. Other chaperon efficiencies were taken to be those of reaction (IV).



This rate is 0.2 of that suggested in reference 16 with hydrogen as a third body and was assumed appropriate for M = Argon. Other chaperon efficiencies were assumed the same as reaction (IV).



Recommendation of reference 16.



Recommendation of reference 16.

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TABLE I. - MIXTURE COMPOSITION AND GROWTH CONSTANT SENSITIVITIES

Compositions, mole %	Gas mixture					
	1			2	3	4
	a	b	c			
CH <sub>2</sub> O	0.481	0.530	0.474	0.117	0.175	0.170
CO	4.91	4.96	4.92	5.36	4.73	3.32
O <sub>2</sub>	.520	.525	.474	.567	1.88	15.30
CO <sub>2</sub>	4.96	5.01	4.97	5.42	.964	1.16

Sensitivities, reaction i	Gas mixture			
	1	2	3	4
II	1.12 to 1.05	0.92 to 0.70	0.96 to 0.35	0.49 to 0.07
IV	-.02 to -0.01	-.04 to -0.01	-.01 to 0	-.04 to 0
-IV	.05 to 0.06	.01 to 0.02	.01 to 0.05	.02 to 0.19
V	.14 to 0.11	.21 to 0.17	.65 to 0.23	.82 to 0.40
-V	-.03 to -0.05	-.04 to -0.05	0 to -0.02	0
VI	-.10 to -0.02	-.12 to -0.01	-.63 to 0.07	-.84 to -0.01
VII	-.89 to -0.62	-.42 to -0.15	-.89 to -0.04	-.35 to -0.02
VIII	.04 to 0.07	.19 to 0.24	.03 to 0.32	.05 to 0.33
IX	-.87 to -0.68	-.43 to -0.22	-.28 to -0.13	-.08 to -0.12
X	.88 to 0.70	.43 to 0.23	.28 to 0.14	.08 to 0.12
-X	0	-.01 to 0	0	0
XI	.70 to -0.39	.33 to 0.12	.89 to 0.03	.85 to 0.04
XII	-.02 to -.01	-.06 to -0.03	-.01 to 0	-.01 to 0

TABLE II. - EXPERIMENTAL RESULTS

Temperature, K	Pressure, atm	Growth constant, $\lambda, \text{sec}^{-1}$	Temperature range, K	Pressure range, atm	Time range, $\mu\text{sec}$	
Mixture 1						
1596	1.1589	$26.62 \times 10^3$	1576 - 1616	1.15 - 1.16	220 - 340	b
1934	1.2472	20.94	1514 - 1554	1.24 - 1.25	220 - 340	a
1524	1.1084	17.12	1490 - 1557	1.10 - 1.12	190 - 420	c
1506	1.1988	16.45	1480 - 1531	1.19 - 1.21	340 - 540	a
1493	1.3505	18.28	1483 - 1503	1.34 - 1.36	650 - 825	b
1481	1.3864	18.42	1460 - 1501	1.38 - 1.39	340 - 500	a
1469	1.3871	16.93	1463 - 1474	1.38 - 1.39	1100 - 1300	b
1463	1.4840	17.99	1457 - 1469	1.48 - 1.49	1000 - 1180	b
Mixture 2						
1598	1.0958	$31.99 \times 10^3$	1592 - 1603	1.09 - 1.10	150 - 240	
1573	1.1485	29.53	1567 - 1578	1.14 - 1.15	180 - 270	
1571	1.1337	30.50	1563 - 1578	1.13 - 1.14	150 - 260	
1526	1.1658	26.32	1519 - 1533	1.16 - 1.17	190 - 310	
1495	1.2598	23.99	1490 - 1498	1.25 - 1.26	230 - 305	
1442	1.3257	21.93	1435 - 1448	1.32 - 1.34	260 - 420	
1410	1.4137	23.38	1405 - 1414	1.41 - 1.42	380 - 510	
Mixture 3						
2053	0.2193	$11.000 \times 10^3$	2038 - 2068	0.204 - 0.216	100 - 300	
2027	.1472	8.550	2013 - 2041	.145 - 0.149	100 - 450	
2022	.2331	11.250	2010 - 2034	.230 - 0.236	75 - 300	
1832	.2187	12.250	1823 - 1841	.217 - 0.220	150 - 400	
1774	.1571	7.425	1757 - 1780	.155 - 0.159	200 - 700	
1728	.1781	7.533	1719 - 1738	.177 - 0.179	350 - 675	
1669	.2078	8.200	1658 - 1680	.206 - 0.209	300 - 675	
1618	.1714	8.220	1609 - 1624	.170 - 0.172	525 - 850	
1611	.1989	7.967	1602 - 1620	.197 - 0.200	275 - 700	
1611	.1706	5.580	1600 - 1622	.169 - 0.172	550 - 1000	
1557	.1401	4.860	1547 - 1567	.138 - 0.142	550 - 1150	
1351	.2524	3.125	1343 - 1358	.250 - 0.254	1300 - 2300	
1342	.1414	3.224	1338 - 1346	.140 - 0.142	1700 - 2750	
1297	.1285	2.305	1293 - 1301	.127 - 0.129	2300 - 3900	
1296	.1342	2.515	1291 - 1301	.133 - 0.135	2100 - 3900	
1266	.1470	2.320	1263 - 1268	.146 - 0.148	2900 - 3950	
1258	.1445	2.940	1253 - 1262	.143 - 0.146	1600 - 2750	
1211	.1458	1.870	1208 - 1214	.145 - 0.147	3400 - 5200	

Table II. - Concluded

Temperature, K	Pressure, atm	Growth constant, $\lambda, \text{sec}^{-1}$	Temperature range, K	Pressure range, atm	Time range, $\mu\text{sec}$
Mixture 4					
2007	0.1804	$9.202 \times 10^3$	1989 - 2024	0.178 - 0.183	80 - 400
1812	.2260	9.146	1794 - 1830	.223 - 0.229	100 - 500
1695	.2750	10.909	1684 - 1706	.273 - 0.277	120 - 420
1679	.2147	10.563	1668 - 1690	.212 - 0.217	120 - 460
1659	.2255	8.824	1648 - 1670	.223 - 0.228	160 - 520
1604	.2444	9.464	1595 - 1612	.242 - 0.247	120 - 480
1572	.1917	6.985	1563 - 1580	.189 - 0.194	200 - 650
1512	.2148	7.100	1506 - 1517	.213 - 0.216	325 - 725
1444	.1992	5.950	1438 - 1449	.197 - 0.201	400 - 950
1443	.1782	3.960	1435 - 1450	.176 - 0.181	275 - 1000
1399	.1525	3.520	1391 - 1406	.150 - 0.155	500 - 1650
1337	.1691	3.565	1333 - 1342	.168 - 0.170	1000 - 1850
1335	.1405	2.985	1329 - 1340	.139 - 0.142	900 - 2100
1297	.1628	3.130	1294 - 1301	.162 - 0.164	1150 - 2050
1288	.2073	4.250	1283 - 1292	.205 - 0.209	700 - 1650
1270	.1240	2.342	1267 - 1273	.123 - 0.125	2300 - 3500
1225	.1582	3.109	1222 - 1228	.157 - 0.159	1850 - 2900

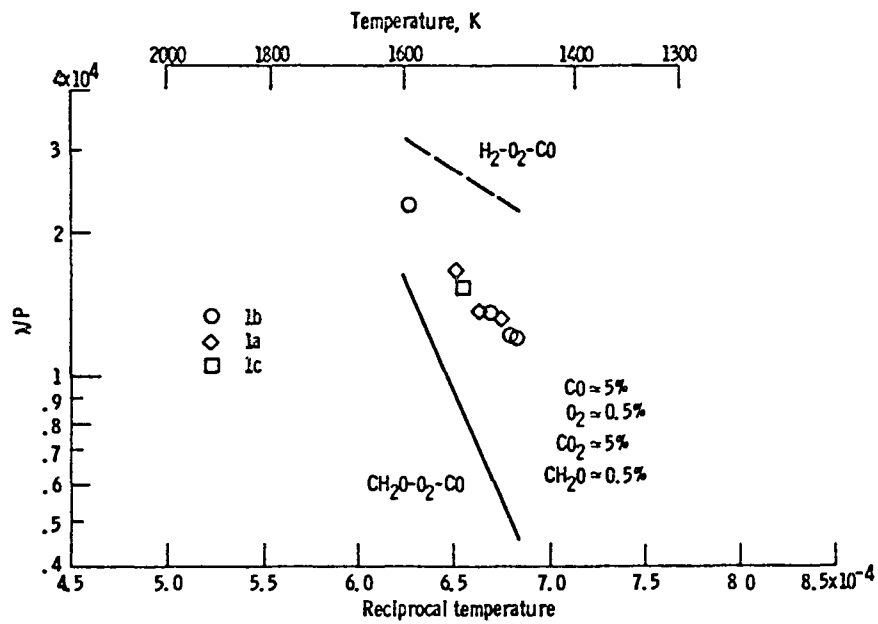


Figure 1 - Experimental and computed growth constants as a function of temperature. Mixture 1.

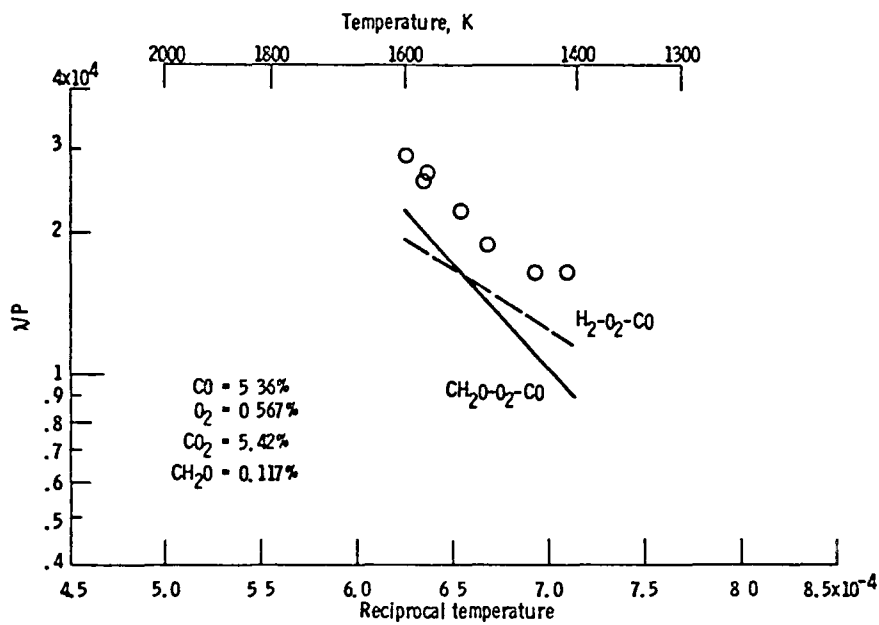


Figure 2 - Experimental and computed growth constants as a function of temperature. Mixture 2.

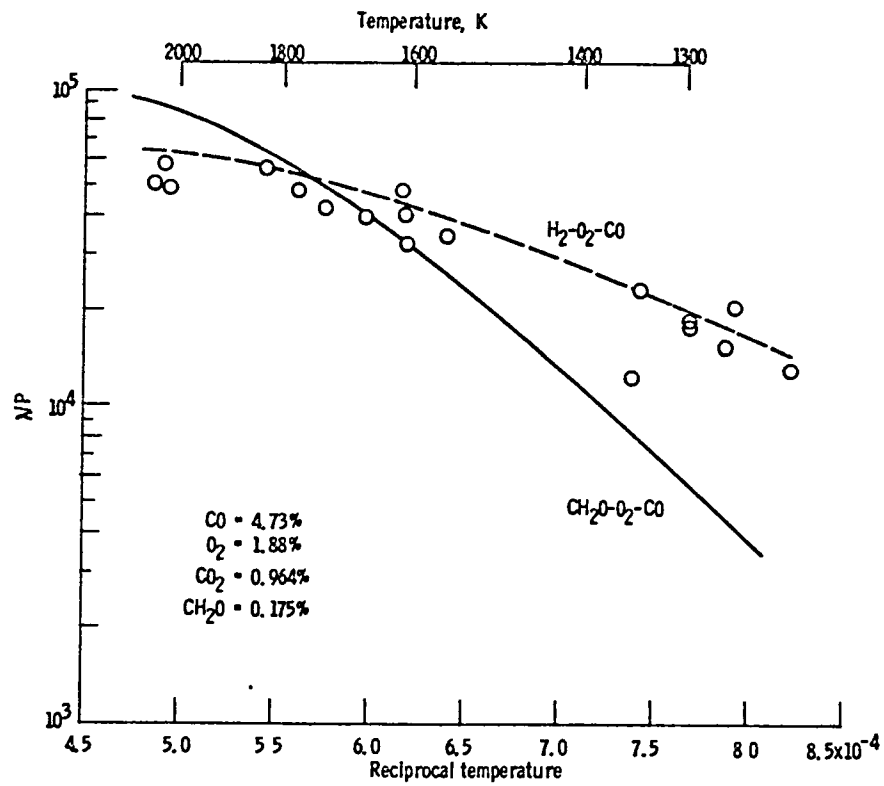


Figure 3. - Experimental and computed growth constants as a function of temperature, Mixture 3.

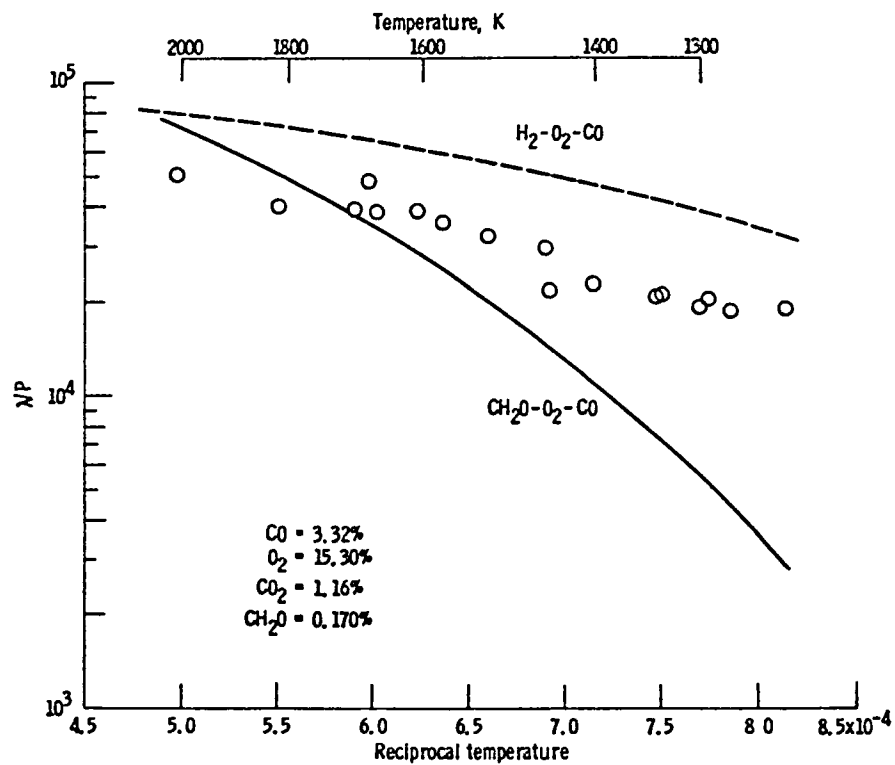


Figure 4. - Experimental and computer growth constants as a function of temperature, Mixture 4.





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15 Supplementary Notes Theodore A. Brabbs, Lewis Research Center; Richard S. Brokaw, Baldwin-Wallace College, Berea, Ohio.			
16 Abstract Exponential free-radical growth constants have been measured for formaldehyde-carbon monoxide-oxygen systems 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 2000 K. The data have been analyzed using a formaldehyde oxidation mechanism involving 12 elementary reaction steps. The computed growth constants are roughly in accord with experimental values, but are much more temperature dependent. The data have also been analyzed assuming formaldehyde is rapidly decomposed to carbon monoxide and hydrogen. Growth constants computed for the resulting carbon monoxide-hydrogen-oxygen mixtures have a temperature dependence similar to experiments; however, for most mixtures, the computed growth constants were larger than experimental values.			
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