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NASA TECHNICAL MEMORANDUM

NASA TM X-71534

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(NASA-TM-X-71534) SHOCK TUBE MEASUREMENTS
OF SPECIFIC REACTION RATES IN BRANCHED
CHAIN CH4-CO-O2 SYSTEM (NASA) 21 p HC
$4.25
CSCL 07D
G3/06
N74-19774
Unclas
34369

SHOCK TUBE MEASUREMENTS OF SPECIFIC REACTION RATES IN THE BRANCHED CHAIN CH_4-CO-O_2 SYSTEM

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TECHNICAL PAPER proposed for presentation at
Fifteenth International Symposium on Combustion
Tokyo, Japan, August 25-31, 1974

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ABSTRACT

Rate constants of two elementary bimolecular reactions involved in the oxidation of methane have been determined by monitoring the exponential growth of CO flame band emission behind incident shocks in three suitably chosen gas mixtures. Results are as follows: $O + CH_4 \rightarrow CH_3 + OH$, $k_7 = 1.9 \times 10^{14} \exp(-5900/T)$ $cm^3\ mole^{-1}\ sec^{-1}$ (1300 - 2000K) and $CH_3 + O_2 \rightarrow CH_3O + O$, $k_{10} = 2.4 \times 10^{13} \exp(-14500/T)$ (1200 - 1800K) assuming $CH_3O + M \rightarrow CH_2O + H + M$. (If it is assumed that $CH_3O + CO \rightarrow CO_2 + CH_3$, then $k_{10} = 5.9 \times 10^{13} \exp(-14500/T)$.) The data do not support a mechanism which invokes the four center process $CH_3 + O_2 \rightarrow CH_2O + OH$ for the reaction of methyl with oxygen.

INTRODUCTION

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

$$CO + O_2 \rightarrow CO_2 + O.$$

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

$$H + O_2 \xrightarrow{k_2} OH + O \qquad (II)$$

$$OH + CO \xrightarrow{k_5} CO_2 + H \qquad (V)$$

$$O + CH_4 \xrightarrow{k_7} CH_3 + OH. \qquad (VII)$$

Chains may be terminated by the reactions

$$H + O_2 + M \xrightarrow{k_4} HO_2 + M \qquad (IV)$$

$$O + CO + M \xrightarrow{k_6} CO_2 + M. \qquad (VI)$$

The reactions

$$H + CH_4 \xrightarrow{k_8} H_2 + CH_3 \qquad (VIII)$$

$$OH + CH_4 \xrightarrow{k_9} H_2O + CH_3 \qquad (IX)$$

may also serve as chain terminations under circumstances where methyl radicals are unreactive. (There reactions have been numbered to be compatible with notation used in a previous study of the H_2 - CO - O_2 system.[1])

Theory shows[2,3] that in such chain-branched systems the atom and radical concentrations increase as expλt (except very early in the reaction). The growth constant λ depends on the rate constants of the elementary chemical reactions and the concentrations of stable reactants--in this case CO, O_2, and CH_4.

This paper reports experimental growth constants measured behind incident shocks for a range of pressures, temperatures and gas compositions. It is found that reactions (II) - (IX) do not suffice to explain the experimental results; rather, it is necessary to consider reaction of the methyl radical with oxygen. The data are consistent with reactions (II) - (IX) and with methyl reacting according to

$$CH_3 + O_2 \xrightarrow{k_{10}} CH_3O + O \tag{X}$$

followed by either

$$CH_3O + M \xrightarrow{k_{11}} CH_2O + H + M \tag{XI}$$

or

$$CH_3O + CO \xrightarrow{k_{12}} CH_3 + CO_2. \tag{XII}$$

The data are <u>not</u> consistent with the four center reaction

$$CH_3 + O_2 \xrightarrow{k'_{10}} CH_2O + OH \tag{X'}$$

which has often been proposed[4] for the reaction of methyl radicals in combustion processes.

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,[5] and since very 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.[6]

Gas mixtures contained small amounts of CH_4 with varying amounts of CO, O_2, and in one mixture CO_2, diluted with argon. (Carbon dioxide was added to ensure vibrational relaxation of carbon monoxide in the mixture with a large CO concentration.) Methane, oxygen, and argon were high-purity tank gases and were used without further purification. Carbon monoxide and carbon dioxide were purified as previously described.[1]

It has been shown[6,7] 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[8] which integrates the equations of chemical change for a shocked gas accounting for the effects of boundary layer buildup; the procedure has been described in reference 7 for laminar boundary layers. In this work the boundary layer was turbulent; the maximum separation distance between shock and contact surface was calculated according to reference 9.

Exponential growth constants were obtained from plots of the logarithm of observed light intensity versus gas time.[10] The relation between gas and laboratory times was obtained from the computer calculations.

THEORETICAL CONSIDERATIONS

The analytic solution of the differential equations describing the ignition kinetics in chain-branched systems involving hydrogen, oxygen and carbon monoxide has been discussed in detail in previous publications.[2, 3, 11] 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 are assured to be small in comparison to the concentrations of reactants 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. That these assumptions were in fact satisfied was confirmed by numerical computations.[8]

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 $\exp \lambda t$ (except very early in the reaction). The growth constant λ is the positive root of a polynomial of a degree dependent on the number of chain carriers. Thus with

H, OH, O, CH_3, and CH_3O as chain carriers a quintic equation is obtained. Actually there is little information in the literature as to rates of reaction of the methoxy radical. We carried out numerical calculations assuming reasonable but rapid rates for reactions (XI) and (XII). (The rate constant for reaction (XI) was assumed to be $k_{11} = 5 \times 10^{13} \exp(-10,500/T)$, based on a reasonable preexponential factor with an activation energy set equal to the endothermicity of the reaction. The rate constant for reaction (XII) was assumed equal to the known rate for the analogous reaction (V)) The numerical calculations showed that the relation between CH_3O and CH_3 concentrations is in reasonable agreement with the steady state approximation,

$$k_{10}[O_2][CH_3] = (k_{11}[M] + k_{12}[CO])[CH_3O]. \qquad (1)$$

Equation (1) was substituted into the differential equations describing the chemical kinetic to eliminate the methoxy radical concentration. This reduced the polynomial in λ to the quartic equation

$$\begin{vmatrix} -(\nu_2+\nu_4+\nu_8+\lambda) & \nu_5 & 0 & \alpha\nu_{10} \\ \nu_2 & -(\nu_5+\nu_9+\lambda) & \nu_7 & \nu'_{10} \\ \nu_2 & 0 & -(\nu_6+\nu_7+\lambda) & \nu_{10} \\ \nu_8 & \nu_9 & \nu_7 & -(\alpha\nu_{10}+\nu'_{10}+\lambda) \end{vmatrix} = 0 \qquad (2)$$

Where $\nu_2 \equiv k_2[O_2]$, $\nu_4 \equiv k_4[O_2][M]$, $\nu_5 \equiv k_5[CO]$,

$\nu_6 \equiv k_6[CO][M]$, $\nu_7 \equiv k_7[CH_4]$, $\nu_8 \equiv k_8[CH_4]$, $\nu_9 \equiv k_9[CH_4]$, $\nu_{10} \equiv k_{10}[O_2]$, $\nu_{10}' \equiv k_{10}'[O_2]$, and $\alpha \equiv k_{11}[M] / (k_{11}[M] + k_{12}[CO])$. If the methoxy radical reacts only via reaction (XI) $\alpha = 1$; if it reacts only via reaction (XII), $\alpha = 0$.

Equation (2) was used in the data analysis to obtain rate constants for the individual reactions k_7, k_{10}', and k_{10}. For example, it can be solved for ν_7 and hence k_7 to obtain an expression involving the rates of the other reactions in the scheme and the experimental growth constant.

RESULTS AND DISCUSSION

The compositions of the three gas mixtures which were investigated are given in Table I. (Table I also has calculated sensitivities which show the importance of each reaction in determining the growth constant.) Initially two mixtures, A and B, were studied. In mixture A the concentrations of methane and oxygen are small, so that the growth constant should depend principally on the rates of reactions (II) and (VII). On the other hand in mixture B the methane and carbon monoxide concentrations are small so that the growth constant should depend principally on the rates of reactions (V) and (VII). This is confirmed by the growth constant sensitivities shown in Table I.

Initially it was assumed that the methyl radical did not react with either carbon monoxide or oxygen. In this event the expression for the growth constant reduces to a cubic, the determinant of the first three rows and columns of equation (2) equated to zero. The cubic was solved for k_7 and values of k_7 were calculated from experimental growth constants for mixtures A and B, with rate constants for the other reactions shown in Table II. The rate constants for reactions (II) and (V), which are important, were determined in our apparatus. Rate constants for reactions (IV), (VI), (VIII) and (IX) have less effect on growth constants; they are in the nature of corrections. Reactions (IV) and (VI) are completely negligible except at the lower temperatures. The rate for reaction (IV) was deduced from unpublished shock tube experiments at Lewis Research Center by M. R. Lauver. This value, obtained near 1100K, is consistent with the data obtained in this paper inasmuch as the rate constants of reference 1 were used in obtaining k_4. (Third body efficiencies were taken from reference 14.)

Rate constants computed for reaction (VII) are shown in figure 1. Values computed from mixture A are in rough agreement with an extrapolation of the low temperature data of Wong and Potter.[15] However, rate constants derived from mixture B are substantially larger, particularly at the higher temperatures. Mixture B contained a large amount of oxygen; thus it appears that the methyl radical is in fact reacting with oxygen and continuing the chain. Consequently we expanded our analysis to account for reaction of the methyl radical according to reactions (X′) and (X); the methoxy radical produced in reaction (X) may either be decomposed in reaction (XI) ($\alpha = 1$) or or react with carbon monoxide in reaction (XII) ($\alpha = 0$).

In order to investigate these possible reaction paths mixture C was prepared, similar to mixture B except for a tenfold increase in methane concentration. Equation (2) was solved for k_{10}' and k_{10} and the resulting expressions were used to compute these rate constants from the experimental growth constants using other rate constants cited in table II along with a rate for reaction (VII) from reference 15.

Rate constants derived from mixture B and C assuming methyl and oxygen react via the four center reaction (X') are shown in figure 2(a). Rate constants from the two mixtures differ by almost an order of magnitude. Further if the Arrhenius equation is applied to the less scattered data from mixture C, the preexponential factor is about 2×10^{17}--about three orders of magnitude in excess of collision frequency! Thus we conclude the reaction of methyl with oxygen via reaction (X') cannot describe our results.

Rate constants derived assuming methyl and oxygen react via reaction (X) to form methoxy and atomic oxygen are shown in figure 2(b) and (c). The data scatter much less than in figure 2(a). Furthermore the preexponential Arrhenius factor is reasonable; 2.4×10^{13} if CH_3O decomposes via reaction (XI) $(\alpha = 1)$, or 5.9×10^{13} if it reacts with carbon monoxide via reaction (XII) $(\alpha = 0)$. Finally, the activation temperature E/R, about 14500K, is very close to a minimum value of 14600K based on the endothermicity of reaction (X)[16]. Thus it seems probable that methyl and oxygen react via the simple abstraction process (X), although it is not possible to reach a conclusion from figure 2(b) and (c) as to the fate of methoxy.

In an attempt to resolve this point, rate constants for reaction (X) (the lines of figure 2(b) and (c)) derived from mixture C were used to calculate rates for reaction (V) from mixture B which were then compared with values previously obtained from a study of the H_2-CO-O_2 system.[1] Agreement was slightly better for values calculated assuming decomposition of methoxy, reaction (XI), especially as to the trend with temperature. Furthermore, there is evidence that at room temperature the reaction between carbon monoxide and methoxy is slow,[17] with a rate 10^{-3} to 10^{-4} of reaction (V) between carbon monoxide and hydroxyl.[18] Thus we favor reaction (XI) over reaction (XII) and have assumed this path in our final data analysis, although reaction (XII) can also adequately account for our data.

Table III presents experimental temperatures and pressures (corrected for boundary layer effects) with growth constants for mixtures A, B, and C. Also shown are rate constants for reactions (VII) and (X) based on the final data analysis. These values were obtained as follows: Equation (2) was solved to obtain expressions for k_7 and k_{10}, with $k_{10}' = 0$ and $\alpha = 1$. A trial value of k_{10} from figure 2(b) was used with other rate constants from Table II to compute values of k_7 from growth constants from mixtures A and B. The resulting rate constants were fitted to an Arrhenius equation and used with growth constants from mixture C to compute values of k_{10}. These values of k_{10} were in turn fitted to an Arrhenius equation and used to recompute values of k_7. The process was repeated until values of k_7 and k_{10} no longer changed. (One recomputation of k_7 and k_{10} sufficed.)

In contrast to the results shown in figure 1, values of k_7 from mixtures A and B were similar, and are shown in figure 3. A least squares fit to the data for both mixtures gives

$$k_7 = 1.9 \times 10^{14} \exp(-5900/T)\ \mathrm{cm^3\,mole^{-1}\,sec^{-1}} \qquad (3)$$

in the temperature range 1300 - 2000K, in reasonable agreement with the low temperature data of reference 15. The standard deviation in the activation temperature is 570K and the standard deviation in $\ln k_7$ is 0.24, or about 28%.

A least squares fit to the rate constants for reaction (X) from mixture C is also shown in figure 3. The rate constant is

$$k_{10} = 2.4 \times 10^{13} \exp(-14500/T)\ \mathrm{cm^3\,mole^{-1}\,sec^{-1}} \qquad (4)$$

in the temperature range 1200 - 1800K. The standard deviation in the activation temperature is 870K and the standard deviation in $\ln k_{10}$ is 0.15, or about 16%. Equation (4) was derived assuming destruction of methoxy via reaction (XI); if methoxy is consumed by reaction (XII) the preexponential factor in equation (4) should be increased to 5.9×10^{13}.

Finally the sensitivities of the growth constants to the various rate constants were computed numerically from equation (2) and tabulated in Table I. In general, growth constants depend most strongly on the rates of reactions (II), (V), (VII) and (X) which have been determined in the shock tube used here. However, there is appreciable sensitivity to the rates of reactions (VIII) and (IX), taken from reference 13. If in the future high temperature studies indicate appreciably different rates for reactions (VIII) and (IX) a reanalysis of the data obtained in this paper would be in order to obtain improved values of k_7 and k_{10}. We very much doubt that any changes in k_8 and k_9 could alter our conclusion as to the course of the reaction between the methyl radical and oxygen.

CONCLUDING REMARKS

An important result of this paper is the conclusion that in the high temperature oxidation of methane the methyl radical reacts with oxygen to form methoxy and atomic oxygen, rather than formaldehyde and hydroxyl as has frequently been assumed heretofore.

In addition, high temperature reaction rates have been obtained for the reactions $O + CH_4 \rightarrow CH_3 + OH$ and $CH_3 + O_2 \rightarrow CH_3O + O$, in the range 1200 - 2000K.

Acknowledgement

We are indebted to Dr. Sidney W. Benson for pointing out that reaction (X) is an energetically permissible path for the reaction of methyl with oxygen.

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TABLE I.

MIXTURE COMPOSITIONS AND GROWTH CONSTANT SENSITIVITIES

	Mixture		
	A	B	C
Composition, %			
CH_4	0.0194	0.0193	0.205
CO	18.72	1.032	1.056
O_2	1.033	19.41	19.54
CO_2	5.68	-	-
Ar	74.5	79.5	79.2
Sensitivities (1500K)			
$\partial\ln\lambda/\partial\ln\nu_2$	0.74	0.06	0.07
$\partial\ln\lambda/\partial\ln\nu_4$	-.07	-.03	-.02
$\partial\ln\lambda/\partial\ln\nu_5$	.12	.47	.30
$\partial\ln\lambda/\partial\ln\nu_6$	-.12	.00	.00
$\partial\ln\lambda/\partial\ln\nu_7$	.56	.41	.15
$\partial\ln\lambda/\partial\ln\nu_8$	-.19	.00	-.03
$\partial\ln\lambda/\partial\ln\nu_9$	-.05	-.15	-.20
$\partial\ln\lambda/\partial\ln\nu_{10}$	.02	.24	.74

TABLE II.

RATE CONSTANTS USED IN DATA ANALYSIS

	Reaction	Rate Constant (mole, cm, sec, K units)	Reference
(II)	$H + O_2 \rightarrow OH + O$	$1.38 \times 10^{14} \exp(-8250/T)$	7
(IV)	$H + O_2 + M \rightarrow HO_2 + M$	10^{15} (M=Ar)	See Text
(V)	$OH + CO \rightarrow CO_2 + H$	$4.2 \times 10^{11} \exp(-500/T)$	1
(VI)	$O + CO + M \rightarrow CO_2 + M$	$3 \times 10^{14} \exp(-1510/T)$	12
(VII)	$H + CH_4 \rightarrow H_2 + CH_3$	$1.24 \times 10^{14} \exp(-6000/T)$	13
(IX)	$OH + CH_4 \rightarrow H_2O + CH_3$	$2.5 \times 10^{13} \exp(-2520/T)$	13

TABLE III. - EXPERIMENTAL RESULTS

T(K)	P(atm)	λ (sec^{-1})	k (cm^3 mole^{-1} sec^{-1})
Mixture A			k_7
1200	1.26	3.01×10^3	2.14×10^{12}
1302	1.39	4.92	2.08
1372	.99	6.89	3.41
1498	1.11	9.84	3.54
1519	1.12	10.56	3.69
1546	1.15	11.46	3.84
1672	.94	14.08	5.93
1719	.97	15.45	6.17
1817	.87	17.99	8.91
1990	.78	23.03	15.63
Mixture B			k_7
1221	1.84	5.71×10^3	1.15×10^{12}
1255	1.69	7.09	1.63
1281	1.62	8.25	2.13
1347	1.49	8.93	2.36
1353	1.62	8.59	1.85
1404	1.45	9.80	2.60
1434	1.37	9.29	2.41
1444	1.00	7.57	2.91
1460	1.26	12.51	5.49
1515	1.06	10.42	4.57
1515	1.06	9.97	4.09
1536	1.21	11.02	3.59
1578	1.11	10.01	3.14
1624	1.15	11.40	3.53
1670	1.04	12.18	4.76
1762	.95	12.51	5.19
Mixture C			k_{10}
1278	2.00	8.11×10^3	$.37 \times 10^9$
1407	1.48	9.80	.68
1431	1.75	12.58	.77
1464	1.42	12.31	.99
1499	1.32	15.25	1.46
1499	1.59	17.92	1.43
1546	1.41	24.24	2.11
1587	1.50	22.36	2.61
1601	1.14	20.20	2.73
1654	1.33	31.12	4.16
1677	1.20	29.90	4.58

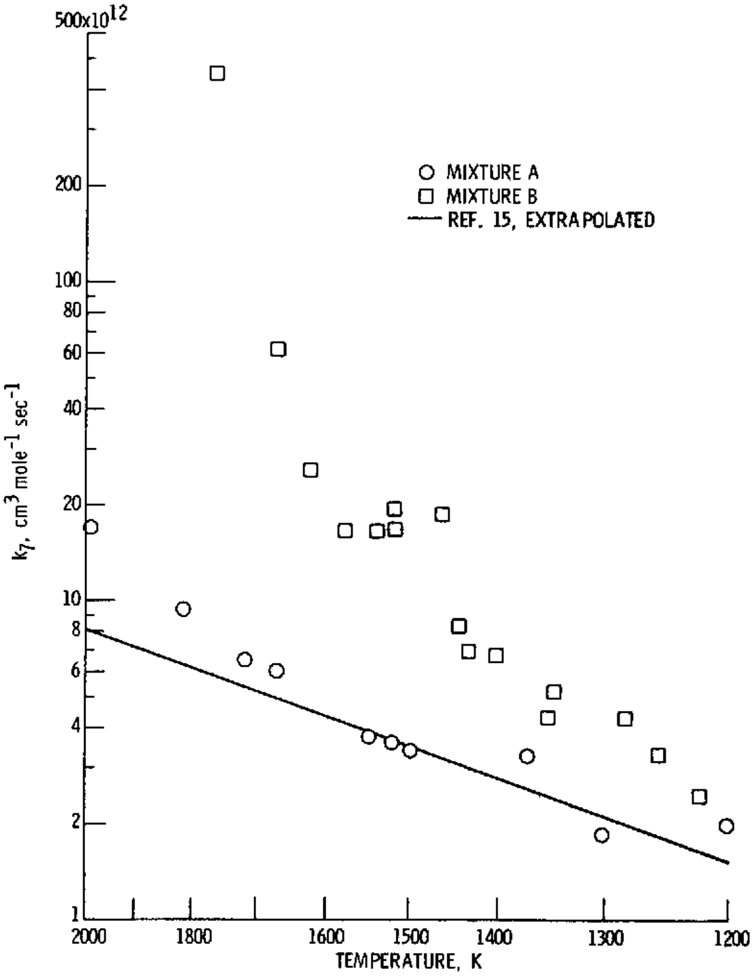
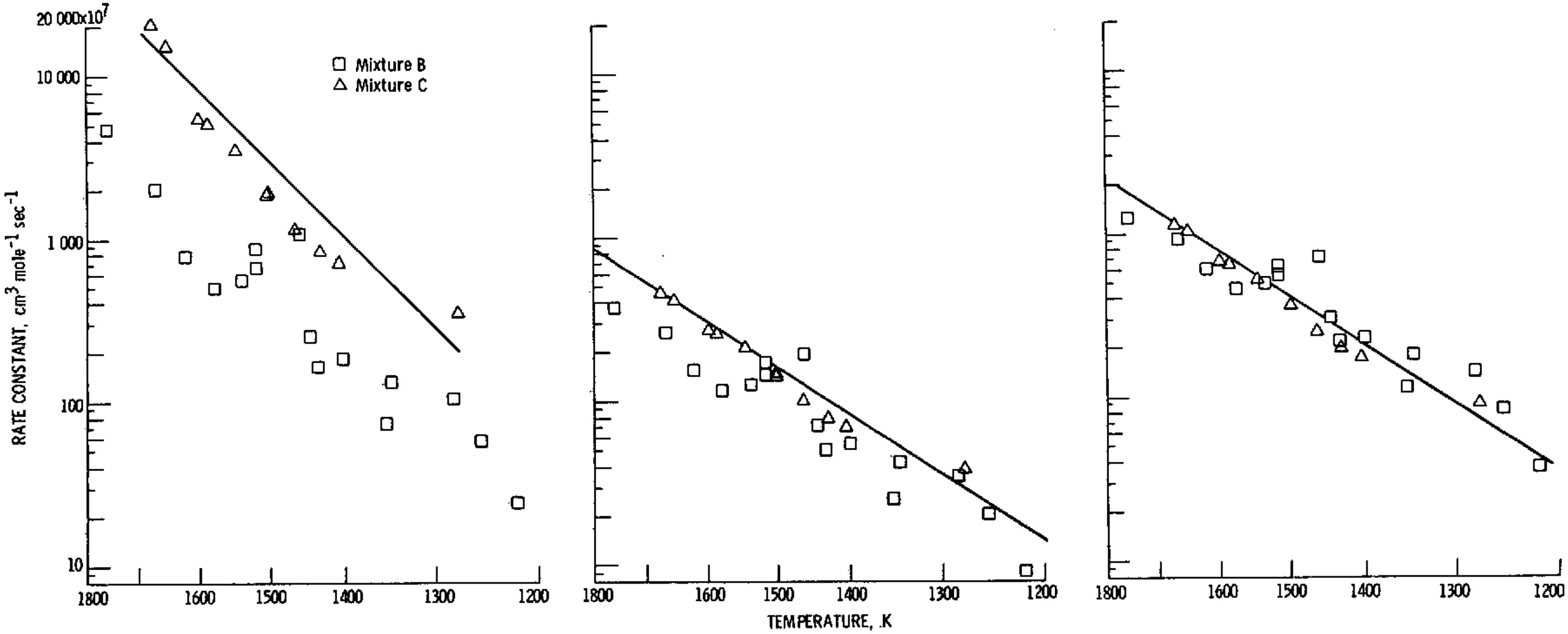


Figure 1. - Rate constants for reaction (VII) assuming methyl unreactive with CO and O_2.



(a) $CH_3 + O_2 \rightarrow CH_2O + OH$.

(b) $CH_3 + O_2 \rightarrow CH_3O + O$; $CH_3O + M \rightarrow CH_2O + H + M$.

(c) $CH_3 + O_2 \rightarrow CH_3O + O$; $CH_3O + CO \rightarrow CO_2 + CH_3$.

Figure 2. - Rate constants for reaction of CH_3 with O_2.

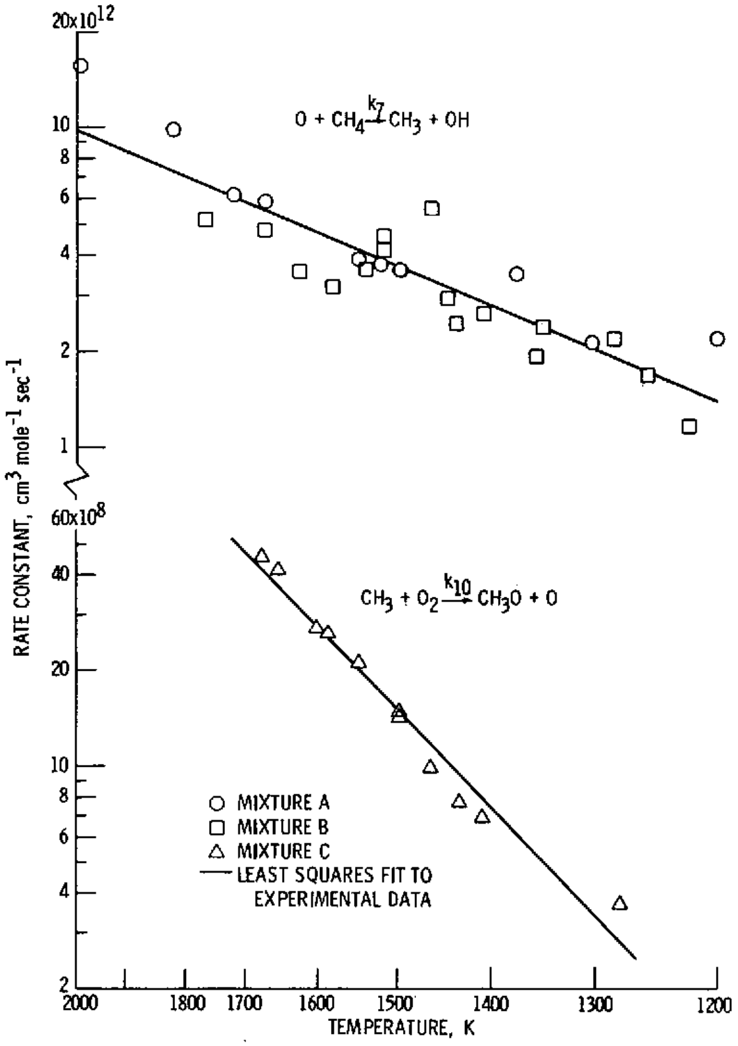


Figure 3. - Final rate constants for reactions (VII) and (X).