AD-A064 434 PURDUE UNIV LAFAYETTE IND PROJECT SQUID HEADQUARTERS F/G 7/3

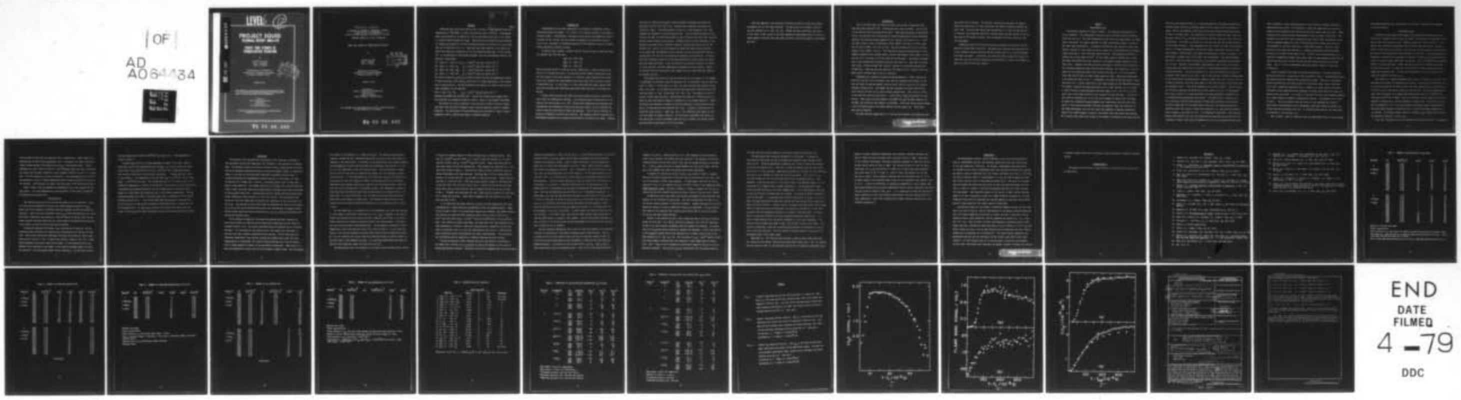
SHOCK TUBE STUDIES OF FORMALDEHYDE OXIDATION. (U)

JAN 79 A M DEAN, R L JOHNSON, D C STEINER N00014-75-C-1143

UNCLASSIFIED SQUID-UMO-4-PU NL

1 OF 1

AD A064434



END

DATE FILMED

4-79

DDC

PROJECT SQUID

TECHNICAL REPORT UMO-4-PU

SHOCK TUBE STUDIES OF FORMALDEHYDE OXIDATION

BY

ANTHONY M. DEAN
RON L. JOHNSON
DON C. STEINER

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MISSOURI-COLUMBIA
COLUMBIA, MISSOURI 65211

A053 695
A041 340

JANUARY 1979

Project SQUID is a cooperative program of basic research relating to Jet Propulsion. It is sponsored by the Office of Naval Research and is assisted by Purdue University through Contract N00014-75-C-1143, NR-098-038.

Published by
School of Mechanical Engineering
Chaffee Hall
Purdue University
West Lafayette, Indiana 47907

PROJECT SQUID

A COOPERATIVE PROGRAM OF FUNDAMENTAL RESEARCH
AS RELATED TO JET PROPULSION
OFFICE OF NAVAL RESEARCH, DEPARTMENT OF THE NAVY

CONTRACT N00014-75-C-1143, NR-098-038

SHOCK TUBE STUDIES OF FORMALDEHYDE OXIDATION

by

Anthony M. Dean
Ron L. Johnson
Don C. Steiner

Department of Chemistry
University of Missouri-Columbia
Columbia, Missouri 65211

January, 1979

Published by
School of Mechanical Engineering
Chaffee Hall
Purdue University
West Lafayette, Indiana 47907

ABSTRACT

Reflected shock waves were used to heat a variety of formaldehyde mixtures to temperatures of 1600-3000K at total concentrations near $5 \times 10^{18}/cm^3$. Formaldehyde decay was monitored by IR emission at 3.50 μm using both O_2 and N_2O as the oxidant in mixtures highly diluted with argon. Other mixtures with added CO were monitored for oxygen atom production via the flame-band emission at 450 nm and for CO_2 production via IR emission at 4.27 μm. These data were then compared to the results obtained from numerical integration of the rate equations based upon a likely mechanism. It was possible to achieve good agreement with the formaldehyde reaction rate constants listed below:

(1) $CH_2O + M = HCO + H + M$, $k_1 = 5.5 \times 10^{-8} \exp(-339\ \text{kJ/RT})\ cm^3\ s^{-1}$

(2) $CH_2O + H = HCO + H_2$, $k_2 = 5.5 \times 10^{-10} \exp(-43.9\ \text{kJ/RT})\ cm^3\ s^{-1}$

(3) $CH_2O + OH = HCO + H_2O$, $k_3 = 1.25 \times 10^{-11} \exp(-0.7\ \text{kJ/RT})\ cm^3\ s^{-1}$

(4) $CH_2O + O = HCO + OH$, $k_4 = 3.0 \times 10^{-11} \exp(-12.9\ \text{kJ/RT})\ cm^3\ s^{-1}$

The values listed for k_3 and k_4 are taken directly from the low temperature studies of these reactions; the k_1 and k_2 values also fit recent experiments in this laboratory on CH_2O pyrolysis. The N_2O experiments also served as a check on the rate constant assignment for the reaction:

(19) $H + N_2O = N_2 + OH$, $k_{19} = 1.5 \times 10^{-9} \exp(-92\ \text{kJ/RT})\ cm^3\ s^{-1}$.

Reasonable agreement was achieved here. Sensitivity studies would suggest these rate constants are probably accurate to within a factor of two between 1700-2500K.

The values of k_1 and k_3 obtained in this work are at least an order of magnitude lower than the values frequently used in current modeling studies of methane oxidation. The implications of these differences are discussed in light of recent suggestions that C_2 species participate in methane oxidation.

INTRODUCTION

Formaldehyde has long been recognized as an important intermediate in many hydrocarbon oxidation systems. As a result, it is usually included in the various oxidation models. Unfortunately, remarkably little direct high temperature data is available on this system; the rate constant assignments are therefore uncertain. This in turn introduces a considerable ambiguity into mechanistic analysis of even simple hydrocarbon oxidation systems.

To amplify these comments, consider that the recent review of Jensen and Jones [1] suggests that the reactions

$$CH_2O + OH \rightarrow HCO + H_2O$$

$$CH_2O + H \rightarrow HCO + H_2$$

$$CH_2O + O \rightarrow HCO + OH$$

have uncertainty factors of 100, 30, and 30, respectively. (Here the uncertainty factor UF is defined such that k x UF and k/UF provide probable approximate upper and lower bounds to the rate constant k.) Similarly, shock tube and flame studies report rate constants for formaldehyde dissociation that differ by several orders of magnitude [2,3]. In this light, it is not surprising that some combustion modelers have advocated that additional experiments need to be done on the CH_2O system [4].

To date, there have been only three shock tube studies which have focused directly upon the formaldehyde reactions. The pioneering study of both pyrolysis and oxidation was done by Gay, et al. [5]. Several chain mechanisms with hydrogen atom intermediates were proposed to explain the pyrolysis results, but all predicted activation energies significantly higher than observed. Thus it was not possible to assign any elementary reaction rate constants. The oxidation studies suggested that formaldehyde decomposition is greatly accelerated by the addition of oxygen. Schecker and Jost [2] studied the pyrolysis reaction between 1400-2200K and varied the CH_2O mole fraction from 0.02% to 1%. The data were reasonably consistent with the earlier study. They were analyzed in terms of a chain mechanism, and a rate constant was reported for the dissociation step. The one troubling aspect of this analysis was that the activation energy for the 1% mixtures was lower than one would expect from the steady state analysis. Recently, studies in this laboratory of the pyrolysis reactions used an extensive numerical integration study as part of the analysis [6]. Here it was not necessary to invoke the steady state assumption. It was shown that the mechanism used by Schecker and Jost was consistent with the observations, but that the rate constant assignments must be modified. The decay data were influenced primarily by the CH_2O dissociation reaction and by the hydrogen atom attack upon CH_2O. It was not possible to completely separate the effects of these reactions, and thus unambiguous assignments were not possible. However, it was evident that the dissociation rate constant was much lower than that reported by Schecker and Jost.

The present CH_2O oxidation study was initiated for two reasons: (1) To attempt to complement the pyrolysis study by separating the contributions from the reactions $CH_2O + M \rightarrow HCO + H + M$ and $CH_2O + H \rightarrow HCO + H_2$, thus allowing rate constant assignments to be made. (2) To obtain more direct high temperature information about the reactions $CH_2O + O \rightarrow HCO + OH$ and $CH_2O + OH \rightarrow HCO + H_2O$. The approach utilized is similar to that used previously; concentration-time behavior is monitored and compared to that calculated by numerical integration of the assumed mechanism. Several techniques were employed to attempt to minimize ambiguity in rate constant assignments: (1) Concentration-time profiles over large extents of reaction were obtained for three species -- CH_2O, CO_2, and O. (2) Conditions were chosen to minimize the number of unknown variables. (3) Additional experiments with N_2O as oxidant were used to confirm assignments made with O_2 as oxidant; the radical concentrations differ significantly in the two systems.

With this approach it was possible to analyze the data to yield rate constant assignments for all four CH_2O reactions. The N_2O system also allowed a check on the rate constant for $H + N_2O \rightarrow OH + N_2$. Perhaps the most significant conclusion of this work is that several of the high temperature formaldehyde reaction rate constants appear to be much lower than those currently utilized in modeling calculations [4,7-10].

EXPERIMENTAL

The 7.6 cm shock tube, gas handling system, and optical configuration have been described previously [11]. Infrared emissions were collimated by two slits 1.5 mm wide and 5 mm high placed 50 mm apart. After passing through an appropriate filter, the emissions were focused upon a liquid-nitrogen-cooled indium antimonide detector; the detector-preamp combination had a nominal rise time of 1 μs. To follow CH_2O, either a 3.50 μm interference filter (FWHM = 0.12 μm) or a filter wheel set at 3.50 μm (FWHM = 0.15 μm) was used. CO_2 was monitored with a 4.27 μm interference filter (FWHM = 0.18 μm). The flame-band emissions were monitored by a RCA 1P28A/V1 photomultiplier mounted behind a 450 nm interference filter (FWHM = 6.5 nm) and two slits 1 mm wide by 2 mm high which were 38 mm apart. The measured response time of the photomultiplier/preamp system was less than 2 μs. Data were collected with either a Biomation Model 805 transient recorder or the system previously described [12]. Biomation data was typically collected at 0.5 μs intervals while the other device collected data at 10.0 μs intervals.

Formaldehye was prepared by heating paraformaldehyde to ∿ 100°C, passing the distillate through a dry ice-acetone trap, and then condensing the monomer at 77K. Care was taken to keep the monomer pressure below 1 kPa (7.5 torr) at all times to minimize polymerization. The monomer was then subjected to several bulb-to-bulb distillations from dry ice to liquid nitrogen temperatures. Then, while at -78°C, it was distilled into the mixing bulb. A fresh batch of CH_2O was prepared for each mixture. Other gases used were AIRCO Ar (99.9995%) and N_2O (99.995%), Matheson CO (99.99%), and Scientific Gas Products O_2 (99.999%). The CO was slowly passed through a coil of copper tubing at 77K before addition to the vacuum line. Other gases were used as supplied.

The shock tube was pumped down to ∿ 3 mPa and the observed leak-outgassing rate was usually near 4 mPa/min. The tube was isolated from the pumps for approximately one minute prior to shock initiation; the nominal background pressure was near 7 mPa. Since the test section was pressurized to 2.7 kPa with the mixtures of interest, the background impurities from the shock tube were present in the low ppm range in the shocked mixtures. Mylar diaphragms and helium driver gas were used throughout.

Temperature behind the reflected shocks were computed in the usual way from measured incident shock velocities. Reflected shock pressures were measured with a fast response pressure transducer and were always found to be in good agreement with those calculated. Furthermore, the reflected shock pressure was always constant over the time interval that data were collected; as a result, no attempt was made to correct for non-ideal effects.

RESULTS

Formaldehyde Decay

The mixtures studied are listed in Table 1. All data were collected at 0.2-0.5 μs intervals. The interference filter was used for Mixture A while the filter wheel was used in B. The light transmitted by the filter was approximately six times that of the wheel; the signals observed in A were significantly greater in spite of the lower CH_2O concentration. In Mixture B the emission was observed to decay completely, whereas in A the signal was seen to decay to a small, approximately constant signal which was 5 - 10% of the peak signal observed. The background emission is probably due to H_2O and/or OH [13]. No such signal would be expected for B; here the lower sensitivity would have resulted in a background signal comparable to the noise level. Attempts were made to correct the signal in Mixture A by subtracting the estimated background signal from the total observed. For simplicity, it was assumed that the background signal rose linearly from zero at $t = 0$ to the constant level seen shortly after the total signal ceased to decay. Results utilizing such a correction are shown in Fig. 1. Fortunately, the shape of the CH_2O signal is such that much of it is quite insensitive to the shape assumed for the background emission. For example, assuming the background signal to be a step function at $t = 0$ yields a signal virtually indistinguishable from that shown in Fig. 1 for $10 \leq t \leq 50$ μs; even at 60 μs this other version of the correction is only 10% lower. In spite of this relative insensitivity, it was felt that attempts to characterize the signal in terms of an exponential decay parameter were unwarranted; not only could small errors in the correction markedly influence the apparent decay rate since this is the slope measurement, but also the signal only appeared to approach exponential decay in the region between 1.0 and 0.1 volts where there are obvious S/N problems. As a result, three points were chosen in an attempt to characterize the decay profile.

The first, the induction time, t_i, is only applicable for the lower temperature experiments where there was an obvious plateau in the signal prior to the onset of decay. Here t_i was defined as the time at which the corrected signal had decayed 5% from its plateau value. For convenience in the data reduction, these times are measured relative to t_0, the time at which the reflected shock was first visible to the detector. This point is typically 5 μs earlier than the time of shock passage of the window mid-point. (The consequences of this finite slit width are discussed later.) At higher temperatures, the plateau became a peak and no induction times were recorded. Operationally, the signal was considered to exhibit a plateau if it maintained a constant level for at least five microseconds. The second parameter used was t', the time (again relative to t_0) at which the corrected signal decayed to 3.0 volts. Typically this parameter characterizes a point early in the decay profile where any uncertainties in the level of the background emission should have a negligible effect. The final parameter is t", the time relative to t_0 when the corrected signal decayed to 0.3 volts. Use of this parameter allowed for measurement of the time interval corresponding to a decade of decay, but at the price of some additional uncertainty since the total signal at this point was only two to three times the background level. These three parameters are listed in Table 1. An error analysis of these parameters considered three likely sources of error: (1) Measurement errors due to noise in a single experiment (including additional uncertainties in t" introduced by the background corrections). (2) Uncertainty in location of t_0: This value was calculated from measured incident shock velocities to avoid bias; extensive comparisons of calculated values versus the first measurable baseline deviations when step function signals were expected (i.e., CO_2 calibration experiments) suggest t_0 was known to ±2 μs. (3) Temperature uncertainty: Using the procedures described earlier [11], each experiment was characterized in terms of both a constant incident shock velocity temperature as well as one obtained assuming the small variations in time intervals between various velocity stations indicated an accelerating shock front. The difference in these two temperatures was used as a measure of the temperature uncertainty and typically ranged from zero to 50K. These differences for a given mixture were averaged to give an overall uncertainty. The average values were then used in conjunction with "local slope" measurements of the various parameter-temperature plots to estimate the errors likely to be caused in the parameter by the small variations in temperature expected. The three likely sources of error were then combined in a standard propagation-of-error treatment to obtain an estimate of the overall error. Plots of the various parameters as a function of temperature yielded curves where there was good agreement between the observed deviations from a fitted line and the error bars calculated as described above. Thus it is felt the parameters chosen are reliable indices of CH_2O decay in Mixture A.

Similar parameters were used to characterize Mixture B. The only differences here were choices of 1.0 volt and 0.1 volt to define t' and t". As mentioned earlier, the smaller observed intensity here required this change. There was no background emission problem here, and semilog plots of the emission signal versus time often were linear, suggesting exponential decay. However, the lower region of the plots invariably had an appreciable noise component, and there could have easily been curvature within the scatter. As a result, it was felt that the time parameter approach was a better method to attempt to characterize the data. The parameters are listed in Table 1. The error analysis here was similar to that employed for Mixture A. Again plots of the parameters versus temperature indicated a degree of scatter consistent with the calculated error bars. It should be noted that all the times here, as in Mixture A, are relative to t_0.

Note in Table 1 that the induction times are appreciably larger in the O_2 system even though the decay rate, once reaction is initiated, appears to be comparable in the two systems.

Flame-band Signal

Information about oxygen atom production was obtained by observing emissions at 450 nm in systems to which CO has been added. The procedure is completely analogous to that used previously [14]. Mixtures studied are listed in Table 2. As in earlier work, additional experiments were performed which were similar to those in Table 2 except that CO was omitted. Here the time resolved emissions were recorded and used as the background for the experiments of interest. It was observed that no background corrections were necessary for Mixture C (containing O_2) whereas Mixtures D and E (containing N_2O) needed small corrections. The calibration factors reported earlier [14] were used here. Checks made during the course of these experiments verified those values. In this way it was possible in effect to monitor absolute oxygen atom concentrations. All data were collected at 0.2-0.5 μs intervals, and times were measured relative to t_o.

The results of a typical experiment with Mixture C is shown in Fig. 2(a). Four parameters were chosen to characterize the signal. The first is the induction time t_i which was defined as the time at which the signal reached 0.02 V, the lowest signal which could be reproducibly extracted from the data. For the CO concentration used, this corresponds to an oxygen atom concentration equal to $4.4\times10^{14}/cm^3$ at 1705K and $2.5\times10^{14}/cm^3$ at 2455K. After the induction time the signal rose rapidly, achieved a maximum value, and then decayed at a slower rate. The initial rise may well be exponential, but it does not continue sufficiently long to measure an unequivocal growth constant; instead the time t' at which the signal reached 0.2 V is recorded. The maximum voltage reached is recorded as V_m, and the time at which the maximum is reached is listed as t_m.

Fig. 2(b) illustrates the results observed with Mixtures D and E. As expected from the earlier work [14], no induction time is evident here. These signals are characterized in terms of two parameters: here t' designates the time at which the signal reached one-half its maximum value and V_m is the maximum signal. (These parameters are also listed in Table 2.) The flame-band signal here does not exhibit the obvious decline seen in Mixture C, and it was more difficult to assign a t_m value here. For this reason no t_m values are reported. The corresponding plots of all of the parameters in Table 2 versus temperature exhibit scatter consistent with the error analysis. (This analysis included a 10% uncertainty in the calibration factor.)

Note in Table 2 that the temperature dependence of V_m is much greater for the N_2O systems. This same phenomenon was observed earlier in the study of oxidation of hydrogen by O_2 and N_2O [14].

CO_2 Production

The infrared emissions at 4.27 μm were collected at 10.0 μs intervals. Here all time data were measured relative to the window midpoint passage time (t_{mp}). Notice that this procedure is different from that employed for the flame-band and CH_2O data. Here it was more convenient to use t_{mp} so that calculated profiles could be directly compared to those observed. Both the nature of the CO_2 signal and the slower sampling rate here meant that the finite width of the observation window had little effect; no explicit corrections need be applied.

The emission observed from Mixture C was corrected for CO emission and the resulting signal converted to an absolute CO_2 concentration as in the earlier work [14]. (More recent calibration experiments indicated the calibration factor used earlier was in error by ∿ 5%.) A typical CO_2 profile is shown in Fig. 3(a). Here three parameters were used to describe the signal: (1) The induction time t_i was defined as the intercept of the tangent to the region of maximum growth rate with the time axis. (2) The maximum growth rate was labelled S. (3) The time at which the CO_2 concentration reached $4.5\times10^{16}/cm^3$ was listed as t". The parameters are listed in Table 3.

A typical CO_2 profile for an N_2O experiment is shown in Fig. 3(b). Here an additional correction for N_2O emission must be made. As a result it was felt that points with a CO_2 concentration less than $\sim 5\times10^{15}/cm^3$ were potentially suspect. Thus the early time behavior here was not considered. Instead two later points on the profile, t', corresponding to the time when $[CO_2] = 5\times10^{15}/cm^3$, and t", when $[CO_2] = 1.5\times10^{15}/cm^3$ were used. The minimum exhibited for t" in both D and E at intermediate temperatures is similar to the behavior seen earlier in the H_2 studies [14]. The maximum CO_2 production was seen at the lower temperatures in Mixtures D and E, whereas in C the largest CO_2 production came at the highest temperatures. The CO_2 production was generally lower in the N_2O system; this is reflected in the different defining relations for t". As with the other reaction parameters discussed above, an error analysis of the CO_2 data indicates the observed scatter is consistent with the assigned errors. In some cases, the error bars become very large; after the "knee" in the CO_2 profiles small calibration errors translate into large time errors.

DISCUSSION

As outlined in the Introduction, the purpose of this study was to attempt to more accurately assign high temperature rate constants to the reactions of formaldehyde. The approach used was to collect a variety of data on CH_2O systems and couple this with information obtained from earlier studies on simpler systems to reduce the number of variables to the point where meaningful assignments could be made. A plausible mechanism for formaldehyde oxidation where O_2 is the oxidant is listed as Reactions (1) through (15) in Table 4. Fortunately quite a bit is known about many of these reactions. For example, Reactions (9) through (15), with the rate constants listed, have been shown to be quantitatively consistent with recent experiments on the $H_2/O_2/CO$ system [14]. Likewise CH_2O pyrolysis studies [6] have yielded appreciable information about Reactions (1), (2), (5), and (6). The calculations done during this work have shown that the results are insensitive to the values used for k_7 and k_8. Thus the goal of this study could be interpreted as trying to find values of k_3 and k_4 that would satisfactorily explain the reported data in CH_2O/O_2 systems with the added constraint that the choices for k_1, k_2, k_5, and k_6 be consistent with the earlier pyrolysis work.

In the process of comparing calculated and observed profiles, adequate provision must be made for both the finite observation window width and the finite instrument response time. The results described below were obtained by the following procedure: (1) The system of rate equations was first numerically integrated in the usual way [14] to obtain concentration-time profiles. (2) For both CH_2O and flame-band comparisons, these profiles ($[CH_2O]$ and $[CO][O]$ versus time) were then integrated over a trapezoidal slit function whose dimensions were fixed by application of simple geometrical optics to the collimation system used. These results, in turn, were modified to account for the finite detector response time. Here the detector was treated as the capacitor in a simple RC circuit. The equation describing the capacitor voltage was then integrated numerically to yield a result which could be compared to the observations. In practice it was observed that the detector response could be adequately treated simply by adding the approximate time constant (1 μs for IR, 2 μs for flame-band) to the slit routine output. The modification to account for the finite window width was substantially greater than the subsequent response time correction. In the flame-band case, the calibration factor was included in the calculations so the final output was simply a voltage-time profile to be directly compared to that observed; there was no need for any normalization here. Given the fact that the CO concentration is reasonably constant, this comparison in effect relates calculated and observed oxygen atom concentrations on an absolute basis. For CH_2O, there is no such calibration. Here the observed and calculated results are normalized at the plateau (or peak) value. This method of comparison of slit-corrected output to the data dictated the choice of t_0 as the reference time in Tables 1 and 2.

For CO_2 comparisons, slit effects are of no consequence since the first meaningful data comes at sufficiently long times that use of t_{mp} is adequate. Here the calculated and observed profiles could be directly compared; again there is no normalization required since absolute calibration factors have been measured. The comparisons were normally made at three temperatures. The experimental parameters of these temperatures, with associated error bars, are listed in Table 5. In most cases the values of the various parameters have been taken directly from the appropriate Table, but in a few instances the values listed were adjusted slightly to better conform to the other data in that temperature range. (In cases where adjustments were made, the amount of the change was always less than the error bar.)

The observations were first compared to calculated values resulting from a choice of CH_2O rate constants typical of those presently used in modeling studies. Set I has $k_1 = 8.3 \times 10^{-8} \exp(-301 \text{ kJ/RT})$, $k_2 = 3.3 \times 10^{-11} \exp(-13.8 \text{ kJ/RT})$, $k_3 = 8.3 \times 10^{-9} \exp(-54.3 \text{ kJ/RT})$, and $k_4 = 8.3 \times 10^{-11} \exp(-19.2 \text{ kJ/RT})$. These values were used in the recent study of Olson and Gardiner [4]. Rate constants for Reactions (5) - (15) were those listed in Table 4. Note this Set (Table 5) yields calculated values in marked disagreement with those observed. Both CH_2O decay in A and oxygen atom production in C is much too fast. V_m at 2455K is also much too high. Likewise the CO_2 profiles in C don't fit well. Since the recent pyrolysis study [6] indicated that k_1 was much lower than the value used in Set I, a series of calculations were done using the k_1 and k_2 values from Ref. [6] in conjunction with the k_3 and k_4 values of Set I. Although some improvement was seen, these results suggested the rates were still larger than observed. These results suggested that the k_3 and/or k_4 values were too high in Set I.

It is likely that the lower limits of k_3 and k_4 at high temperatures are those represented by a simple Arrhenius extrapolation of the low temperature data. These values (listed in Table 4) have both been reported very recently, and another calculation (Set II) was done with these values and the k_1 and k_2 values of Ref. 6 [$k_1 = 6 \times 10^{-7} \exp(-364 \text{ kJ/RT})$ and $k_2 = 4.2 \times 10^{-11} \exp(-16.0 \text{ kJ/RT})$] which fit the pyrolysis data. Here there was further improvement, but there were still some problems at the high temperatures in Mixture C where this combination still appeared to be too fast (note in particular that $t'-t_i$ for the flame-band was only 4 μs vs. 7 observed and that the maximum rate of CO_2 production was higher than observed). This conclusion was verified by explicit comparison of complete concentration-time profiles.

The earlier pyrolysis study indicated that one could achieve a satisfactory fit there with a variety of k_1, k_2 choices as long as the product of the values remained approximately constant. Additional calculations suggested that the rate constant combination designated in Table 5 as Set III (k_1 = 5.5×10^{-8} exp(-339 kJ/RT), k_2=5.5×10^{-10} exp(-43.9 kJ/RT), k_3 and k_4 same as Set II) gave a reasonable fit to both the CH_2O oxidation and pyrolysis studies. Note in Table 5 that most of the calculated parameters now lie within the experimental error bars. Again, explicit profile comparisons confirm the adequacy of the fit. Fig. 1 illustrates this fit for Mixture A and Figs. 2(a) and 3(a) demonstrate the fit for Mixture C. Of the three parameter values that don't fall within the error bars, there appear to be reasonable explanations for the deviations. The most serious deviation is seen for Mixture A at 1670 where the calculated t" is too early. A possible explanation for this discrepancy was discussed earlier; t" measurements may be unduly influenced by the background emissions here. Note the low temperature data on Mixture C are in reasonable agreement. It would appear that the only way one could slow down the calculation to fit the reported t" value at 1670 would be either to use k_3 and/or k_4 values lower than used here or use a k_1, k_2 combination which would not be consistent with the pyrolysis results. Given the definitive nature of the low temperature studies, it is unlikely that such an adjustment in k_3 or k_4 is justified. It would appear then that the fault here lies with the data. In a similar light, the slightly higher maximum rates calculated at 1705 and 1940K appear to present no real problem. Here the calculated parameters are just slightly out of the error bars and the measurements are difficult since data were only collected at 10 μs intervals.

The rate constant combinations used in Set III would thus appear to be remarkably successful at explaining a large body of disparate data on CH_2O systems. (The k_1, k_2 values of Set III also quantitatively describe the pyrolysis results of Ref. 6.) A particularly satisfying aspect of the assignments is that very few rate constants needed adjustment. In essence the only variables were k_1 and k_2. Note k_3 and k_4 were taken directly from low temperature data. There is still some uncertainty with respect to k_5 and k_6. Recently Reilly, et al. [24] suggested a room temperature value of k_6 a factor of two larger than that used here. The pyrolysis studies [6] indicated simply that the ratio used in that work was needed to achieve a reasonable fit. If the k_6 value used here is indeed somewhat low, this would simply indicate k_5 is also somewhat low; other conclusions would remain unaffected.

A sequence of calculations using various k_1, k_2 values on Mixture C suggests that one can swing from one end of the error bars to the other with less than a factor of two changes in these rate constants. It would appear then that the values specified in Set III are probably accurate to within a factor of two within the 1700-2500K temperature range. Similarly, studies on Mixture A suggest that the k_3, k_4 values used here are probably accurate to within a factor of two over this interval.

An additional check upon these rate constant assignments could be obtained from analysis of the oxidation of CH_2O by N_2O. Here the concentration-time behavior of the various reactive species is radically different. Another advantage of using this system for analysis is that no additional unknowns are generated. The N_2O dissociation kinetics are reasonably well characterized [20,25] and its use as an oxidant for H_2 has also been studied [14,26].

Earlier it was pointed out that a small change was made in the CO_2 calibration factor for this work. As a result, the earlier hydrogen work [14] was reexamined to see if any rate constant assignments made then needed to be changed. An examination of the $H_2/O_2/CO$ system indicated no changes were mandated. A better description of the $H_2/N_2O/CO$ system could now be obtained with a slightly larger value of the rate constant for $H + N_2O = N_2 + OH$. This new value is $k_{19} = 1.5 \times 10^{-9} \exp(-92\ kJ/RT)$; this value compares favorably with that reported at lower temperatures by Albers, et al. [27]. There is still evidence of non-Arrhenius behavior, but not as much as previously reported. This value of k_{19} was incorporated into the present analysis.

The other N_2O rate constants (Table 4) were taken from the earlier work [14].

The N_2O studies were conducted analogously to the O_2 work. In Mixture B, CH_2O decay was monitored, and CO_2 and oxygen atom production were followed in Mixtures D and E. Selected experimental parameters are listed in Table 6 and compared to various calculated results. Here Set I of the calculations used the same values used in Set I of the O_2 system. Again some mismatches are evident, but the differences tend not to be as dramatic as those seen with the O_2 system. Use of Set III (the set which worked well for the O_2 system) again yields encouraging results. Good agreement is seen with Mixture B. In Mixtures D and E, two problems appear: (1) The calculated V_m is somewhat high at higher temperatures. (2) CO_2 production seems a little slow (particularly at the lower temperatures). It is interesting to note that in each case Mixture E presents more of a problem. The causes of these discrepancies are not understood. It is possible that they are experimental in origin. On the one hand, the CH_2O concentrations were very low here and there may well be an adsorption and/or desorption problem -- changes induced by these events would have a much greater effect in these low concentration mixtures. An alternative explanation is that there are more difficult background corrections to be made in the N_2O system. Of course, there is always the possibility of some unexpected mechanistic complexities. In spite of some problems here, the overall agreement is still quite reasonable. The explicit profile comparisons shown in Figs. 2(b) and 3(b) reinforce this point. Particularly noteworthy is that the fit achieved was obtained with absolutely no variation in any rate constants. This fact seems to reinforce the basic accuracy of the assignments made in the oxygen system.

Reactions (1) - (15) with the rate constants listed in Table 4 were then used in a series of calculations simulating the experiments of Gay, et al. [5]. As expected from the results of Ref. 6, the calculated results for the pyrolysis experiments suggested a stronger temperature dependence than reported; reasonable agreement was seen at 1950K, but the calculated results were much slower at 1550K. Conversely, in the oxidation experiments, there was reasonable agreement at 1550K with the calculated results being too fast at 1980K. One interesting point is that the calculated CH_2O, CO, H_2, and H_2O profiles at 1550K are in surprisingly good agreement with those shown in Fig. 2 in Ref. 5. Even at 1710K, the reported time for 20% reaction of CH_2O of 120 μs compares favorably with the calculated value of 112 μs. By 1980K, however, the calculated time is only 32 μs as opposed to the reported value of 70 μs. In spite of differences in temperature dependencies it would appear that the present mechanism/rate constant combination predicts results reasonably consistent with the oxidation studies of Gay, et al. It is significant to note that the experimental conditions of that work differed significantly from that reported here (i.e., lower temperatures, lower total concentrations, higher reactant concentrations, and different diagnostics).

CONCLUSIONS

The formaldehyde oxidation results presented in this work are interpreted in terms of formaldehyde reaction rate constants appreciably lower than usually seen in the high temperature literature. For example, formaldehyde dissociation here is reported to be an order of magnitude slower than reported by Schecker and Jost [2] and several orders of magnitude lower than Peeters and Mahnen [3] suggest. Similarly, the rate of hydroxyl attack on formaldehyde is at least an order of magnitude lower than values currently used in some modeling studies [4,9]. The values for hydrogen atom and oxygen atom attack are much closer to those now used; the oxygen rate constant is lower by a factor of two while the hydrogen atom value is higher by about this same amount. One interesting aspect of the results is that O and OH reactions appear to be best interpreted in terms of a simple Arrhenius extrapolation of lower temperature data while the hydrogen atom reaction appears to have some non-Arrhenius character when compared to the recent results of Klemm [28].

One possible reason for the dramatic differences between this work and the literature could well be due to a lack of understanding of the methane oxidation mechanism. Until the recent suggestions [9,29] that C_2 species may play a significant role in methane oxidation, most mechanistic studies suggested the sequence $CH_4 \rightarrow CH_3 \rightarrow CH_2O \rightarrow HCO \rightarrow CO \rightarrow CO_2$. Given the lack of direct high temperature information about formaldehyde reactions, explanations based upon decay of CH_4 or formation of CO or CO_2 could easily assign too large a rate to CH_2O reactions <u>if</u> an alternative path were actually present but not accounted for in the analysis. The recent studies suggesting such analternate path may well be consistent with the present study which could simply indicate (in this context) that all of the CH_4 doesn't follow the CH_2O sequence. In this light, the present work highlights the dangers inherent in mechanistic analysis in complex systems where there are simply too many variables for adequate characterization.

ACKNOWLEDGEMENT

The authors wish to thank Dr. Bruce Klemm for furnishing us his results prior to publication.

REFERENCES

1. Jensen, D.E., and Jones, G.A., Combust. Flame, 32, 1 (1978).
2. Schecker, H.G., and Jost, W., Ber. Bunsenges. Physik. Chem., 73, 521 (1969).
3. Peeters, J., and Mahnen, G., Fourteenth Symposium (International) on Combustion, p. 133, Combustion Institute, 1973.
4. Olson, D.B., and Gardiner, W.C., Jr., Combust. Flame, 32, 151 (1978).
5. Gay, I.D., Glass, G.P., Kistiakowsky, G.B., and Niki, H., J. Chem. Phys., 43, 4017 (1965).
6. Dean, A.M., Craig, B.L., Johnson, R.L., Schultz, M.C., and Wang, E.E., Seventeenth Symposium (International) on Combustion, Combustion Institute (in press).
7. Bowman, C.T., Fifteenth Symposium (International) on Combustion, p. 869, Combustion Institute, 1975.
8. Tsuboi, T., Japan J. Appl. Phys., 15, 159 (1976).
9. Westbrook, C.K., Creighton, J., Lund, C., and Dryer, F.L., J. Phys. Chem., 81, 2542 (1977).
10. Jachimowski, C.J., Combust. Flame, 29, 55 (1977).
11. Baber, S.C., and Dean, A.M., Int. J. Chem. Kinet., 7, 381 (1975) and references therein.
12. Megargle, R., and Dean, A.M., Chem. Instrumentation, 5, 109 (1973).
13. Gaydon, A.G., The Spectroscopy of Flames, Second Edition, p. 229, Wiley, 1974.
14. Dean, A.M., Steiner, D.C., and Wang, E.E., Combust. Flame, 32, 73 (1978).
15. Atkinson, R. , and Pitts, J.N., J. Chem. Phys., 68, 3581 (1978).
16. Klemm, B., private communication.
17. Schott, G.L., Combust. Flame, 21, 357 (1973).
18. Schott, G.L., Getzinger, R.W., and Seitz, W.A., Int. J. Chem. Kinet., 6, 921 (197
19. Baulch, D.L., Drysdale, D.D., Horne, D.G., and Lloyd, A.C., Evaluated Kinetic Data for High Temperature Reactions, Vol. 1, p. 109, Butterworth, London, 1972.
20. Dean, A.M., and Steiner, D.C., J. Chem. Phys., 66, 598 (1977).
21. Ref. 19, p. 77.

22. Gardiner, W.C., Jr., Mallard, W.G., McFarland, M., Morinaga, K., Owen, J.H. Rawlins, W.T., Takeyama, T., and Walker, B.F., Ref. 3, p. 61.

23. Dean, A.M., and Kistiakowsky, G.B., J. Chem. Phys., 53, 830 (1970).

24. Reilly, J.P., Clark, J.H., Moore, C.B., and Pimentel, G.C., J. Chem. Phys., 69, 4381 (1978).

25. Monat, J.P., Hanson, R.K., and Kruger, C.H., Combust. Sci. and Tech., 16, 21 (1977).

26. Henrici, H., and Bauer, S.H., J. Chem. Phys., 50, 1333 (1969).

27. Albers, E.A., Hoyermann, K., Schacke, H., Schmatjko, K.J., Wagner, H. Gg., and Wolfrum, J., Ref. 7, p. 765.

28. Klemm, R.B., Rate Parameters for Reactions of CH_2O with H and O Over a Temperature Range 250-470K. (Paper presented at the Fall, 1977 Meeting of the Eastern States Section of the Combustion Institute.)

29. Olson, D.B., and Gardiner, W.C., Jr., J. Phys. Chem., 81, 2514 (1977).

TABLE 1. SUMMARY OF OBSERVATIONS ON CH_2O DECAY

Mixture[a]	T/K	$M/10^{18}cm^{-3}$[b]	$t_i/\mu s$[c]	$t'/\mu s$[d]	$t''/\mu s$[e]
	2455	4.62	-	11	17
A	2400	4.63	-	10	17
	2370	4.55	-	13	20
0.50% CH_2O	2235	4.49	-	13	22
	2185	4.37	-	16	26
0.88% O_2	2120	4.36	-	21	33
	2005	4.31	23	30	50
	1980	4.14	22	31	53
	1970	4.24	22	32	55
	1935	4.09	28	36	64
	1850	4.14	37	45	84
	1815	4.06	46	50	102
	1780	4.09	47	50	110
	1750	4.06	60	72	136
	1670	4.09	78	-	175
B	2275	4.73	-	11	19
	2225	4.70	-	10	20
1.01% CH_2O	2165	4.74	-	12	19
	2130	4.65	-	13	21
1.07% N_2O	2120	4.61	-	13	25
	2040	4.48	-	17	32
	1990	4.40	-	23	45
	1965	4.36	-	20	42
	1940	4.42	-	18	40
	1900	4.39	19	25	65
	1895	4.38	18	24	55
	1785	4.26	22	32	82
	1755	4.27	26	36	96
	1740	4.22	30	34	124
	1685	4.09	40	40	148

[a] Balance of mixture was argon.

[b] Total concentration

[c] Time relative to t_o (see text) for signal to decay 5% from an early constant signal.

[d] For Mixture A, time relative to t_o when the CH_2O emission drops to 3.0 volts. For B, time when the emission drops to 1.0 volts.

[e] For A, time when emission drops to 0.3 V; for B, time when emission drops to 0.1 V.

TABLE 2. SUMMARY OF FLAME-BAND OBSERVATIONS

Mixture[a]	T/K	$M/10^{18}cm^{-3}$[b]	$t_i/\mu s$[c]	$t'/\mu s$[d]	$t_m/\mu s$[e]	V_m/volts[f]
C	2455	5.14	6	13	63	1.63
	2380	5.15	5	13	70	1.55
0.50%CH_2O	2290	5.08	8	19	78	1.33
	2265	5.07	6	17	78	1.40
0.92%O_2	2160	4.93	12	23	85	1.15
	2025	4.93	15	37	96	1.08
9.15%CO	1950	4.74	27	46	124	1.03
	1940	4.64	32	54	140	0.90
	1940	4.58	33	55	135	0.95
	1845	4.55	61	87	172	0.78
	1810	4.56	74	102	200	0.80
	1800	4.51	70	103	180	0.77
	1735	4.42	71	104	190	0.75
	1705	4.29	82	126	205	0.67
	1660	4.28	148	190	285	0.60
	1605	4.32	219	275	385	0.60
D	3010	5.59		5		2.51
	2890	5.49		7		2.10
0.049%CH_2O	2825	5.42		7		2.15
	2805	5.45		5		2.08
1.02%N_2O	2680	5.33		7		1.64
	2540	5.25		10		1.33
8.21%CO	2440	5.15		12		1.17
	2315	5.08		17		0.87
	2215	4.99		21		0.63
	2180	4.90		25		0.65
	2125	4.87		24		0.49
	2060	4.77		37		0.37
	2010	4.74		52		0.30
	1950	4.66		52		0.22
	1905	4.78		63		0.17

(continued)

TABLE 2. SUMMARY OF FLAME-BAND OBSERVATIONS (continued)

Mixture[a]	T/K	$M/10^{18}\,cm^{-3}$ [b]	$t_i/\mu s$ [c]	$t'/\mu s$ [d]	$t_m/\mu s$ [e]	V_m/volts [f]
E	3045	5.54		5		2.64
	2955	5.49		6		2.55
0.026% CH_2O	2895	5.47		7		2.43
	2850	5.41		6		2.26
1.02% N_2O	2705	5.36		8		1.92
	2650	5.28		9		1.77
8.10%CO	2575	5.25		11		1.68
	2470	5.15		15		1.33
	2385	5.06		15		1.17
	2145	4.88		30		0.72
	2085	4.82		39		0.48
	1940	4.66		74		0.30

[a] Balance was argon.

[b] *Total concentration*

[c] Time relative to t_o (see text) when signal = 0.02 V.

[d] For C, time when signal = 0.20 volts. For D and E, time when signal is one-half maximum value.

[e] Time relative to t_o when maximum signal achieved.

[f] Maximum signal.

TABLE 3. SUMMARY OF CO_2 OBSERVATIONS

Mixture[a]	T/K	$M/10^{18}cm^{-3}$[b]	t_i[c]	$S/10^{20}cm^{-3}s^{-1}$[d]	$t'/\mu s$[e]	$t''/\mu s$[f]
C	2455	5.14	6	19.5		32
	2380	5.15	8	19.8		35
0.50%CH_2O	2290	5.08	11	16.0		44
	2265	5.07	8	15.7		41
0.92%O_2	2160	4.93	15	12.6		58
	2140	5.01	14	12.7		56
9.15%CO	2025	4.93	21	9.26		79
	1950	4.74	32	8.68		97
	1940	4.64	34	6.79		120
	1940	4.58	37	6.66		120
	1845	4.55	60	4.61		200
	1810	4.56	75	4.67		202
	1800	4.51	76	4.49		208
	1735	4.42	74	4.32		209
	1705	4.29	92	4.19		238
	1660	4.28	146	2.83		370
	1605	4.32	218	2.32		560
D	3010	5.59			5	325
	2890	5.49			8	235
0.049%CH_2O	2825	5.42			5	160
	2805	5.45			5	112
1.02%N_2O	2680	5.33			5	65
	2540	5.25			7	25
8.21%CO	2440	5.15			8	23
	2315	5.08			9	25
	2215	4.99			13	33
	2180	4.90			13	32
	2125	4.87			14	37
	2060	4.77			22	54
	2010	4.74			25	63
	1950	4.66			36	82
	1905	4.78			45	106

(continued)

TABLE 3. SUMMARY OF CO_2 OBSERVATIONS (continued)

Mixture[a]	T/K	$M/10^{18}cm^{-3}$[b]	t_1[c]	$S/10^{20}cm^{-3}s^{-1}$[d]	$t'/\mu s$[e]	$t''/\mu s$[f]
E	3045	5.54			13	557
	2955	5.49			10	475
0.026%CH_2O	2895	5.47			10	425
	2850	5.41			9	380
1.02%N_2O	2705	5.36			8	278
	2650	5.28			10	278
8.10%CO	2575	5.25			9	200
	2470	5.15			10	60
	2385	5.06			11	47
	2260	4.99			15	46
	2145	4.88			20	52
	2085	4.82			27	72
	1940	4.66			42	105

[a]Balance was argon.

[b]Total concentration.

[c]Time relative to t_{mp} (see text) when tangent to $[CO_2]$-time plot intercepts t-axis.

[d]Slope of initial region (after induction period) of plot of $[CO_2]$ vs. time.

[e]Time relative to t_{mp} when $[CO_2] = 5x10^{15}/cm^3$.

[f]For Mixture C, time relative to t_{mp} when $[CO_2] = 4.5x10^{16}/cm^3$; for D and E, time when $[CO_2] = 1.5x10^{16}/cm^3$.

TABLE 4. MECHANISM AND RATE CONSTANTS

Reaction	Rate Constant[a] $\log_{10} A$	n	E_A	Reference
1. $CH_2O + M = HCO + H + M$	-7.26	0	339	this work
2. $CH_2O + H = HCO + H_2$	-9.26	0	44	this work
3. $CH_2O + OH = HCO + H_2O$	-10.90	0	0.7	15
4. $CH_2O + O = HCO + OH$	-10.52	0	12.9	16
5. $HCO + M = H + CO + M$	-9.59	0	61.4	2
6. $HCO + H = H_2 + CO$	-9.48	0	0	7
7. $HCO + OH = H_2O + CO$	-9.77	0	0	7
8. $HCO + O = OH + CO$	-9.77	0	0	7
9. $H + O_2 = OH + O$	-6.69	-.91	69.5	17
10. $O + H_2 = OH + H$	-9.44	0	57.5	18
11. $O + H_2O = OH + OH$	-9.96	0	76.8	19
12. $O + CO + M = CO_2 + M$	-33.80	0	0	20
13. $OH + H_2 = H_2O + H$	-10.44	0	21.5	21
14. $OH + CO = CO_2 + H$	-11.18	0	33.4	22
15. $CO + O_2 = CO_2 + O$	-11.24	0	209	23
16. $N_2O + M = N_2 + O + M$	-9.57	0	216	14
17. $N_2O + O = NO + NO$	-10.11	0	117	20
18. $N_2O + O = N_2 + O_2$	-10.11	0	117	20
19. $N_2O + H = OH + N_2$	-8.82	0	92	this work

[a]Expressed in the form $k = AT^n \exp(-E_A/RT)$ in cm^3, molecule, sec, and kJ units.

TABLE 5. COMPARISON OF CALCULATIONS AND OBSERVATIONS (O_2 SYSTEMS)

Mixture[a]	Parameter[b]	T/K	Observed	Set I [c]	Set II[d]	Set III[e]
A	t_i	1670	78±11	32	66	68
		1935	28± 6	-	23	24
	t'	1935	36± 5	-	34	36
		2455	11± 2	10	11	11
	t"	1670	175±21	74	137	140
		1935	64±12	-	65	66
		2455	17± 2	13	18	19
C	t_i(F.B.)	1705	97±24	46	78	86
		1940	32± 5	-	28	34
		2455	6± 2	5	6	8
	t'(F.B.)	1705	135±20	79	117	125
		1940	54± 6	-	49	56
		2455	13± 2	8	10	14
	t_m(F.B.)	1705	228±28	180	212	222
		1940	135±21	-	112	122
		2455	63±20	48	48	51
	V_m(F.B.)	1705	0.67±.09	0.61	0.59	0.61
		1940	0.94±.10	-	0.89	0.90
		2455	1.63±.17	2.25	1.85	1.65
	$t_i(CO_2)$	1705	100±13	53	83	94
		1940	35± 5	-	33	40
		2455	6± 3	4	5	8
	$S(CO_2)$	1705	3.7±0.6	3.8	4.2	4.4
		1940	7.4±0.9	-	8.5	8.8
		2455	20.6±3.5	22.6	25.8	22.7
	$t''(CO_2)$	1705	270±32	209	229	239
		1940	115±15	-	102	107
		2455	32± 4	47	33	35

[a]See Tables 1 and 2 for composition.

[b]See Tables 1, 2 and 3 for definitions.

[c]"Literature values"; see text for details.

[d]"Original Pyrolysis Fit"; see text for details.

[e]"Modified Pyrolysis Fit"; see text for details.

TABLE 6. COMPARISON OF CALCULATIONS AND OBSERVATIONS (N_2O SYSTEMS)

Mixture[a]	Parameter[b]	T/K	Observed	Set I[c]	Set III[d]
B	t_i	1740	30± 7	25	25
		1900	19± 3	-	17
	t'	1740	36± 5	29	31
		1900	24± 3	-	23
		2275	11± 2	10	11
	t"	1740	115±21	93	109
		1900	60±11	-	54
		2275	19± 3	13	19
D	t'(F.B.)	1950	56± 8	47	47
		2540	10± 2	-	12
		2890	7± 2	9	9
	V_m(F.B.)	1950	0.22±.04	0.26	0.23
		2540	1.37±.17	-	1.47
		2890	2.24±.25	2.53	2.57
	t'(CO_2)	1950	36± 7	45	41
		2540	7± 3	-	10
		2890	6± 3	5	6
	t"(CO_2)	1950	82±13	109	84
		2540	25±12	-	29
		2890	215±55	197	221
E	t'(F.B.)	1940	74±13	60	61
		2470	14± 3	-	15
		2955	6± 3	9	9
	V_m(F.B.)	1940	0.30±.05	0.33	0.30
		2470	1.33±.14	-	1.51
		2955	2.55±.29	3.03	3.06
	t'(CO_2)	1940	42± 4	60	54
		2470	10± 3	-	16
		2955	10± 5	9	11
	t"(CO_2)	1940	105±10	159	125
		2450	80±29	-	124
		2955	475±63	625	641

[a] See Tables 1 and 2 for composition.

[b] Defined in Tables 1, 2, and 3.

[c] "Literature values"; see text.

[d] "Modified Pyrolysis Fit"; see text.

<u>LEGENDS</u>

Fig. 1. A typical CH_2O decay plot of the log (corrected I.R. signal) vs. time. Here t_0 is the time at which the reflected shock front first enters the detector's field of view. The open circles designate every fourth data point obtained with Mixture A at 1935K; the closed circles are the calculated results using Set III. (See text.)

Fig. 2. Typical flame-band emission profiles. Here t_0 is the time at which the reflected shock front first enters the detector's field of view. The open circles designate every twentieth data point observed; the closed circles represent calculated profiles using Set III. (See text.)

(a) Mixture C, T = 1940K, M = $4.64 \times 10^{18}/cm^3$.

(b) Mixture D, T = 1950K, M = $4.66 \times 10^{18}/cm^3$.

Fig. 3. Typical CO_2 production profiles. Here t_{mp} is the time the reflected shock front passes the center of the observation window. The open circles designate experimental data; closed circles represent calculated profiles using Set III. (See text.)

(a) Mixture C, T = 1940K, M = $4.64 \times 10^{18}/cm^3$.

(b) Mixture D, T = 1950K, M = $4.66 \times 10^{18}/cm^3$.

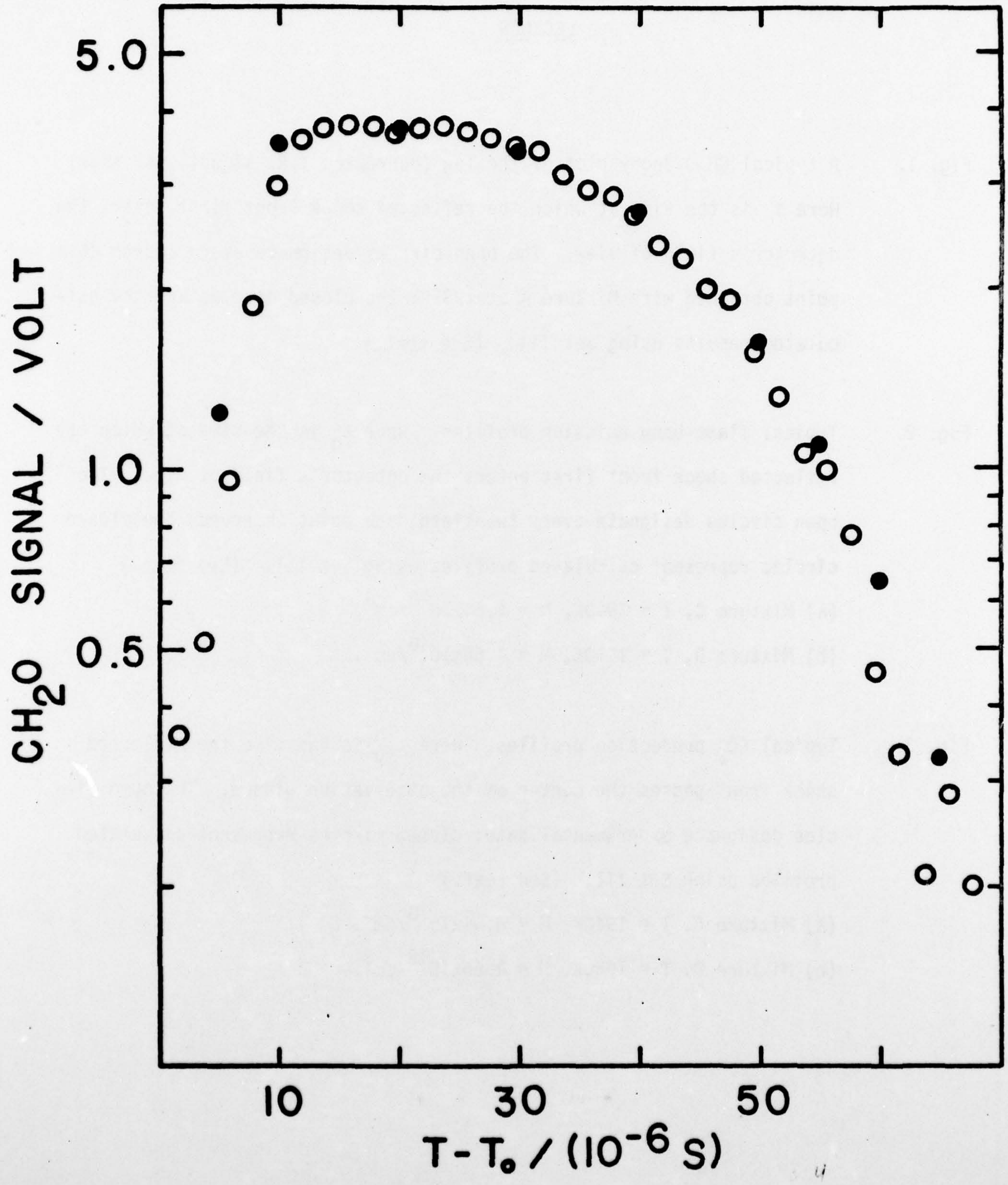


FIG. 1

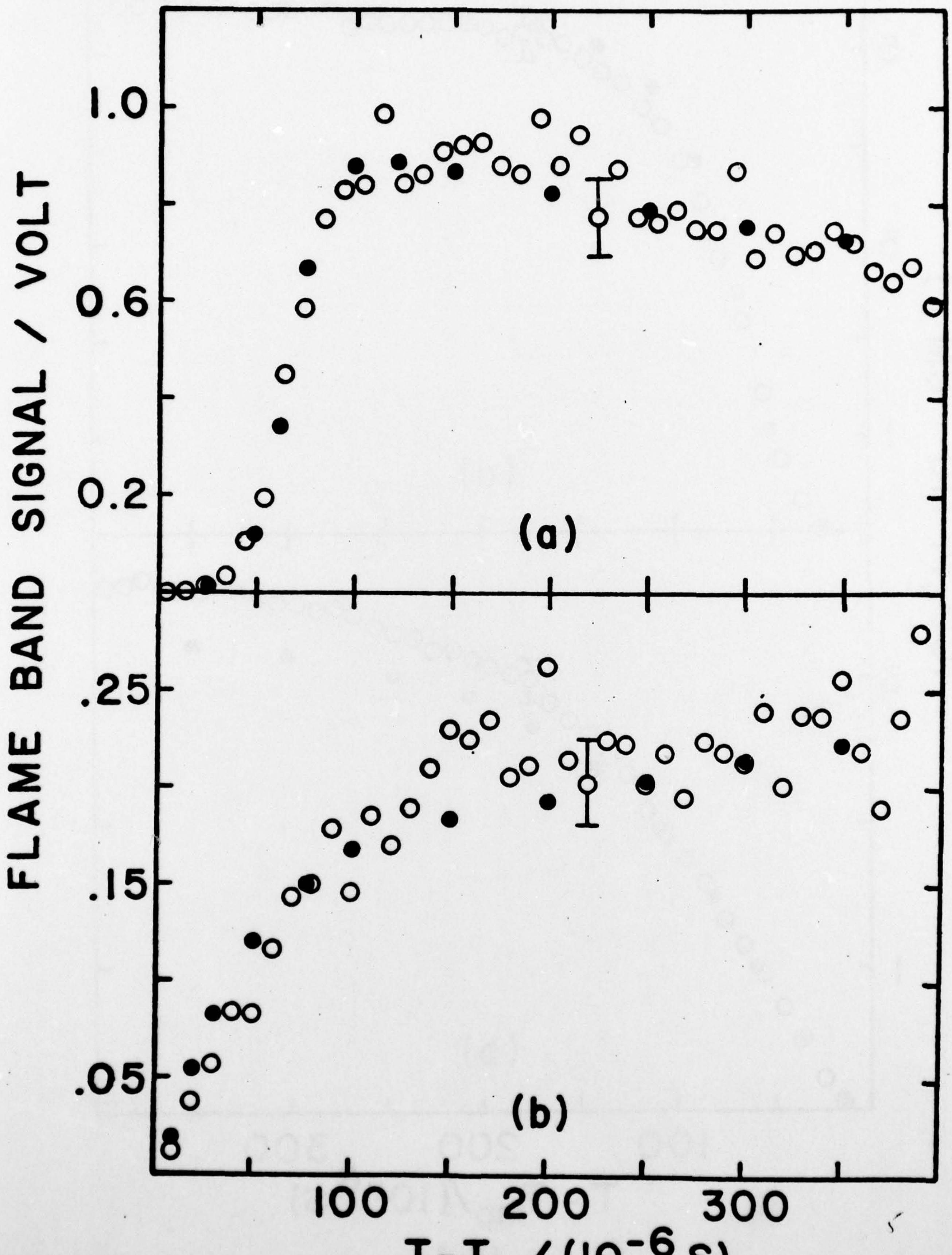


FIG. 2

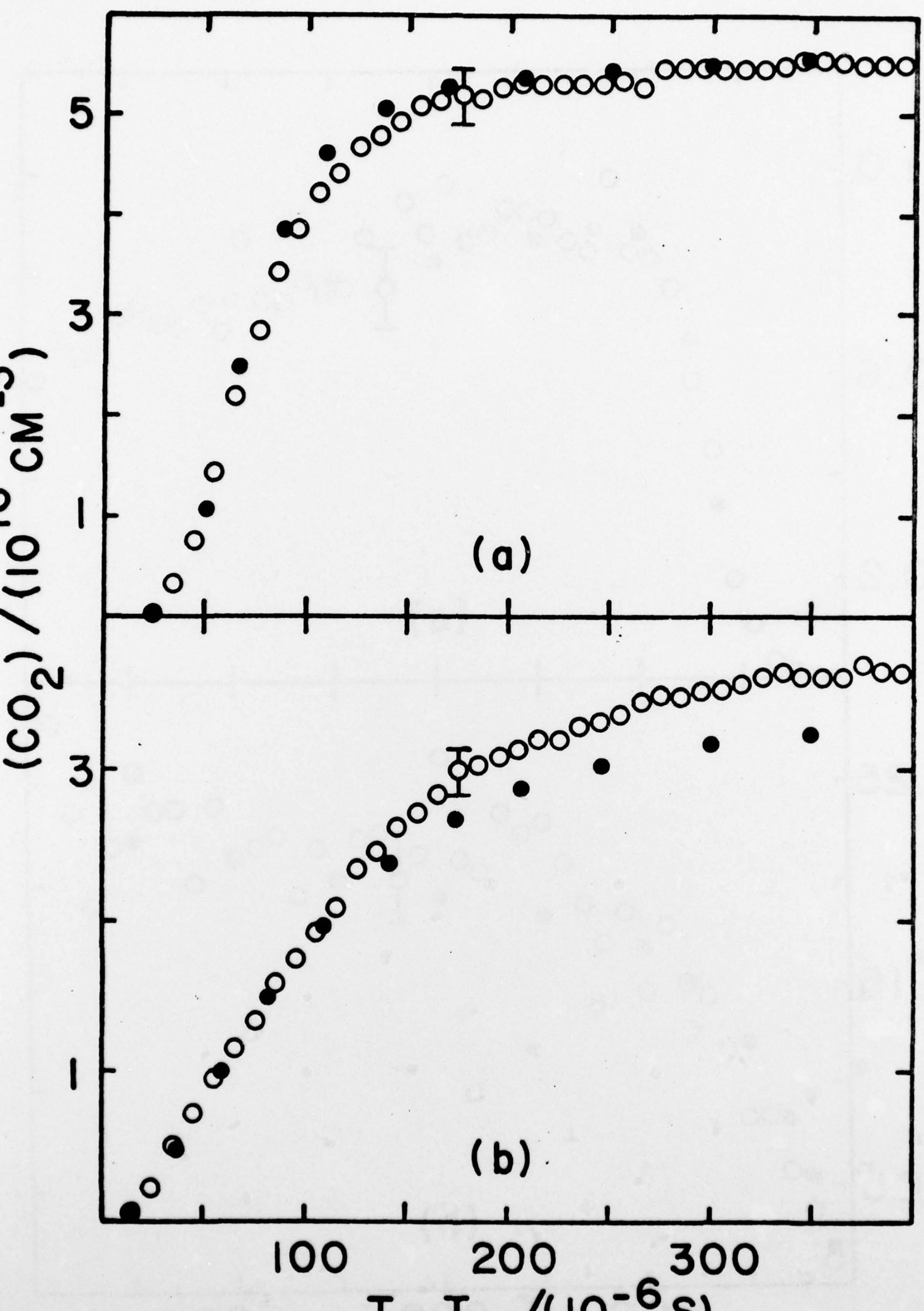


FIG. 3

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER
UMO-4-PU

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
6 SHOCK TUBE STUDIES OF FORMALDEHYDE OXIDATION.

5. TYPE OF REPORT & PERIOD COVERED

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
10 Anthony M. Dean, Ron L. Johnson, Don C. Steiner

8. CONTRACT OR GRANT NUMBER(s)
15 N00014-75-C-1143

9. PERFORMING ORGANIZATION NAME AND ADDRESS
University of Missouri-Columbia
Department of Chemistry
Columbia, MO 65211

403 882

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
NR-098-038

11. CONTROLLING OFFICE NAME AND ADDRESS
Project SQUID Headquarters
Chaffee Hall, Purdue University
West Lafayette, Indiana 47907

12. REPORT DATE
11 Jan[redacted]79

13. ~~NUMBER OF PAGES~~

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)
Office of Naval Research, Power Program, Code 473
Department of the Navy
800 No. Quincy Street
Arlington, VA 22217

15. SECURITY CLASS. (of this report)

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

This document has been approved for public release and sale; its distribution is unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

Same

14 SQUID-UMO-4-PU

18. SUPPLEMENTARY NOTES

9 Technical rept.,

12 39 p.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Formaldehyde Oxidation
Shock Tube
Reaction rate

5x10 to the 18th power/cc.

micrometers

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Reflected shock waves were used to heat a variety of formaldehyde mixtures to temperatures of 1600-3000K at total concentrations near $5 \times 10^{18}/cm^3$. Formaldehyde decay was monitored by IR emission at 3.50 μm using both O_2 and N_2O as oxidant in mixtures highly diluted with argon. Other mixtures with added CO were monitored for oxygen atom production via the flame-band emission at 450 nm and for CO_2 production via IR emission at 4.27 μm. These data were then compared to the results obtained from numerical integration of the rate equations based upon a likely mechanism. It was possible to achieve good agreement with

DD FORM 1473 1 JAN 73 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

403 677

the formaldehyde reaction rate constants listed below:

(1) $CH_2O + M = HCO + H + M$, $k_1 = 5.5 \times 10^{-8} \exp(-339 \text{ kJ/RT}) \text{ cm}^3 \text{ s}^{-1}$

(2) $CH_2O + H = HCO + H_2$, $k_2 = 5.5 \times 10^{-10} \exp(-43.9 \text{ kJ/RT}) \text{ cm}^3 \text{ s}^{-1}$

(3) $CH_2O + OH = HCO + H_2O$, $k_3 = 1.25 \times 10^{-11} \exp(-0.7 \text{ kJ/RT}) \text{ cm}^3 \text{ s}^{-1}$

(4) $CH_2O + O = HCO + OH$, $k_4 = 3.0 \times 10^{-11} \exp(-12.9 \text{ kJ/RT}) \text{ cm}^3 \text{ s}^{-1}$

The values listed for k_3 and k_4 are taken directly from the low temperature studies of these reactions; the k_1 and k_2 values also fit recent experiments in this laboratory on CH_2O pyrolysis. The N_2O experiments also served as a check on the rate constant assignment for the reaction:

(19) $H + N_2O = N_2 + OH$, $k_{19} = 1.5 \times 10^{-9} \exp(-92 \text{ kJ/RT}) \text{ cm}^3 \text{ s}^{-1}$.

Reasonable agreement was achieved here. Sensitivity studies would suggest these rate constants are probably accurate to within a factor of two between 1700-2500K.

The values of k_1 and k_3 obtained in this work are at least an order of magnitude lower than the values frequently used in current modeling studies of methane oxidation. The implications of these differences are discussed in light of recent suggestions that C_2 species participate in methane oxidation.