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THE OXIDATION AND PYROLYSIS OF ETHYLENE
IN SHOCK WAVES

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THE OXIDATION AND PYROLYSIS OF ETHYLENE

IN SHOCK WAVES

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ABSTRACT

The oxidation of C_2H_4 has been studied in a shock tube by monitoring the infrared emissions from CO and CO_2 and the visible emission from CH^* . The characteristics of this oxidation closely resemble oxidations of C_2H_2 and $C_2H_2 + H_2$. The induction periods and exponential time constants for the early phase of CO formation are the same for all three oxidations over the temperature range of $1500^\circ K$ to $2300^\circ K$ and lead to a common activation energy of 17 ± 1 kcal/mole.

Above $1800^\circ K$, the $C_2H_4 - O_2$ reaction, in its early stages, consists mainly of the pyrolysis of C_2H_4 , and the concurrent oxidation of pyrolysis products, C_2H_2 and H_2 . Later in the reaction, and more prominently so at lower temperatures, the reaction changes in character to a slower direct oxidation of C_2H_4 .

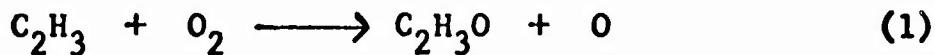
The relative rates of CO and CO_2 production in both $C_2H_4 - O_2$ and $C_2H_2 - O_2$ reactions are reported as a function of temperature.

The pyrolysis of C_2H_4 has also been studied in the shock tube by an infrared technique and its rates determined between $1950^\circ K$ and $2250^\circ K$. The results are in good agreement with previous work and give an activation energy of 52 kcal/mole for the reaction. The oxidation results would indicate that C_2H_4 , above $1800^\circ K$, decomposes mainly by a molecular rather than a radical mechanism.

INTRODUCTION

The shock tube oxidations of ethylene and acetylene have been found previously to be kinetically similar. White,¹ examining very lean mixtures (fuel/oxygen < 0.1), observed that the induction times before detectable heat release from $C_2H_4 + O_2$ and $C_2H_2 + O_2$ reactions are similar over a temperature range of $1100^\circ K$ to $2200^\circ K$ and lead to an essentially common activation energy of ~ 17.3 kcal/mole.

Gay et al,² using C_2H_4/O_2 ratios of 1.5 to 0.1, found the induction times, the time constants of exponential growth, and the total intensity of chemiluminescence from CH^* and of chemi-ionization in the $C_2H_4 - O_2$ reaction to be similar in magnitude to those found earlier in the $C_2H_2 - O_2$ ³ reaction, especially at the higher temperatures of $1800^\circ K$ to $2100^\circ K$. At lower temperatures, towards $1500^\circ K$, both the induction times and time constants were significantly greater than in the case of C_2H_2 , and the complete results fitted an Arrhenius plot of activation energy ~ 24 kcal/mole rather than 17 kcal/mole, found for $C_2H_2 - O_2$.³ They detected quite large concentrations of acetylene during the course of the $C_2H_4 - O_2$ reaction and proposed for this conversion an oxidative radical mechanism. To satisfy the higher activation energy, they suggested the rate determining step:



The pyrolysis of ethylene leads at these temperatures to acetylene and hydrogen. Recently there has been much discussion^{4,5,6} about this reaction, particularly as to a choice between radical and molecular mechanisms.

It is the purpose of this paper to examine the relative importance of the oxidative and pyrolytic decompositions of ethylene in ethylene-oxygen mixtures. To this end, we have studied the rate of production of CO, CO₂ and CH* in the oxidations of acetylene and ethylene and have also checked on the rates previously found^{4,5} for the pyrolysis of ethylene.

EXPERIMENTAL

The 3 in. diameter shock tube used in this work has been described previously.⁷ Two infrared detectors are now simultaneously monitoring separate infrared emissions through diametrically opposite CaF₂ windows. Through improvements in the optics, the sensitivity has been increased by about a factor of four over that previously reported.⁷ Two observation oscilloscopes are used, one set to a higher amplification of signal and a shorter time-base than the other.

Gas mixtures were prepared from gases obtained as in Ref. 7 with the addition of Phillips research grade ethylene (see Ref. 5) which was vacuum distilled before use and Matheson "prepurified" hydrogen.

RESULTS

Oxidation of Ethylene

Two mixtures, 0.5% C₂H₄ + 1% O₂, 0.5% C₂H₄ + 3% O₂, both in argon were examined mainly in reflected shocks, covering a temperature range of 1500° K to 2300° K.

Infrared emissions from CO and CO₂ were recorded simultaneously using the interference filters described in Ref. 7: 4.20 μ for CO₂ and 5.03 μ for CO. The emission from CO and to a lesser extent that from CO₂ were confused by a contribution from C₂H₄ emission, which can be seen as the initial steps in the traces shown in Fig. 1b. Such traces were transferred to plots of log signal versus time by taking the level of the first plateau as the base-line. This procedure gave good linear semilog plots for all but the very extremes of the temperature range.

The infrared signals from CO and CO₂ were calibrated in terms of molecular concentrations as a function of temperature by shocking mixtures of 1% CO₂ in argon and 5% CO + 1% H₂ in argon. Hydrogen was added to this latter mixture to reduce considerably the relaxation time of CO; this allowed a more accurate measurement of emission signal to be made, especially at the lower temperatures. The calibration factors were used to convert the infrared emission traces to concentrations, due corrections being made for the small mutual interference in the signals. As in the oxidation of acetylene,⁷ both [CO] and [CO₂] initially rose exponentially and then while [CO] peaked and fell slowly, [CO₂] increased further. The sum [CO] + [CO₂], once [CO] had peaked, was constant with time.

Three different measurements were made for each record, and all the results are presented in Table I. The exponential time constants, τ_{CO} and τ_{CO_2} , are given for those traces which gave linear semilog plots. Also shown is the induction period, t_i , which was arbitrarily defined as the time between the initial rise of the IR signal (from C₂H₄ interference) on passage of the shock

front and the instant when the combined $\text{CO} + \text{CO}_2$ concentration reached 10% of the final value. Shown also are the ratios $d[\text{CO}_2]/d[\text{CO}]$ in the early phases of the reaction where the semilog plots are very nearly parallel as shown by the near identity of the τ values.

In another series of experiments the emission from CO was compared with the chemiluminescent emission from CH^* , recorded as in Ref. 7.

Fig. 2 shows some of the results. The $[\text{CO}]$ semilog plots, which are linear well beyond 10% oxidation, curve downward later on because of the depletion of the reactants but not exclusively so since the curvature is strongly temperature dependent. At higher temperatures the CH^* signals are strong enough to be observed in the early phases of the reaction and here (Figs. 2a, 2b) the ratio of CH^* and CO slopes is fairly accurately two:

$\tau_{\text{CO}} = 2 \tau_{\text{CH}^*}$. At the lowest temperatures the CH^* signal is observed only after the "break" in the CO signal (Fig. 2c). Even so, log CH^* signal is still quite linear with time, but at these temperatures the exponential time constant bears no simple relationship to that for CO.

To understand better the nature of the $\text{C}_2\text{H}_4 - \text{O}_2$ reaction, CO and CO_2 emissions were recorded from two other mixtures: 0.5% $\text{C}_2\text{H}_2 + 0.8\% \text{ O}_2$, and 0.5% $\text{C}_2\text{H}_2 + 0.5\% \text{ H}_2 + 1\% \text{ O}_2$, both in argon.

C_2H_2 gave interfering signals similar to those from C_2H_4 , and the traces were treated as in the $\text{C}_2\text{H}_4 - \text{O}_2$ case. The initial growths of the signals for

both CO and CO_2 were accurately exponential over almost the complete temperature range of 1400°K to 2400°K . Time constants, induction times to 10% oxidation, and the ratio $d[\text{CO}_2]/d[\text{CO}]$ in the initial region are presented in Table II.

Fig. 3 shows logarithmic plots of the induction periods and time constants for CO production against inverse temperature for the four investigated mixtures. To bring the results from the two $\text{C}_2\text{H}_4 + \text{O}_2$ mixtures onto the same line, it was necessary to multiply t_i and T_{CO} by the square root of oxygen concentrations rather than by the first power as in earlier work.^{2,3}

Fig. 4 shows the effects of temperature on the ratios $d[\text{CO}_2]/d[\text{CO}]$ from the same four ethylene-oxygen and acetylene-oxygen mixtures.

Pyrolysis of Ethylene

Experiments were made to measure the rate of ethylene pyrolysis to acetylene by IR emissions from these compounds. It was found impossible to separate cleanly the two emissions. The best results were obtained by using a long pass filter with a cut-off at 4.76μ and a 2.94μ filter with 0.1μ half-peak width. At equal concentrations of C_2H_4 and C_2H_2 the first filter gave about twice as large a signal from C_2H_4 and the second from C_2H_2 as from the other component. To interpret the resultant traces in terms of the rates of conversion of C_2H_4 into C_2H_2 , it was necessary to assume that the reaction is clearly

$C_2H_4 \rightarrow C_2H_2 + H_2$, that no other species emit observable IR radiation and that at the end of the run only acetylene is present. This restricted the observations to the $1900 \leftrightarrow 2300^{\circ}$ K. because at lower temperatures the pyrolysis was incomplete, and at higher temperatures the signal through the C_2H_4 filter began eventually to rise and that through the C_2H_2 filter to drop, undoubtedly due to the formation of C_4H_8 .

Usable results were obtained between these temperature limits for 0.5% and 1.5% C_2H_4 in argon. An example of the traces obtained with the 4.76μ filter is given in Fig. 1a. Both the ethylene decrease and the acetylene increase with respect to time gave, after the initial 20 - 30 μ sec., good first order plots. The results of several shocks are given in Table III. The no-reaction temperatures calculated from the shock parameters were adjusted to compensate for the endothermicity of the reaction exactly as outlined in Ref. 5. Although looked for, no evidence of an induction period was found.

An Arrhenius plot of the data is shown in Fig. 5, together with the reported results of Gay et al⁵ and Skinner and Sokoloski.⁴ Three-halves order rate constants were calculated, as was suggested by Gay et al, by dividing the first order rate constant by the square root of the total gas density.

The now obtained rate constants show the same temperature dependence as those of Gay et al and those of Skinner and Sokoloski, i.e. 50 - 52 kcal. The absolute

values are within the probable errors from the least-squares line of Gay et al. and are about a factor of 3 higher than the extrapolated data of Skinner and Sokoloski, a trend which can be qualitatively predicted in view of the different methods and conditions used. It should be noted that if first order constants are plotted, not only is the systematic scatter of Gay et al data much larger but the Skinner and Sokoloski data are higher on the plot than the extrapolation of the data from this Laboratory, a rather unlikely result since Skinner and Sokoloski made no temperature correction for the endothermicity of the reaction and their dwell times were long (2 and 10 msec.), thus making the boundary layer effects more significant.

DISCUSSION

The Nature of the C₂H₄ + O₂ Reaction

Under the conditions of most shock wave experiments, i.e. very high temperatures and very low reactant concentrations, the rate of pyrolysis of ethylene is comparable to the rate of reaction in the presence of oxygen. This is illustrated by Table IV in which are shown for several temperatures the times for 10% oxidation (the induction periods as here defined) and the per cent pyrolysis to be expected in these times according to the data of Fig. 5 at a constant total density of 4.5×10^{-3} mol/lit. which is near the mean of the densities in oxidation experiments.

If one bears in mind that oxidation has an

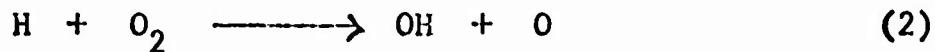
exponentially rising rate whereas that of the pyrolysis decreases with time, it is clear that at higher temperatures ($T > 1800^{\circ}$) the first quarter or even more of CO and CO_2 could be formed by the oxidation of pyrolytically generated acetylene. This is most likely indeed the case because Fig. 3 shows that, except at the lowest temperatures, the induction periods and the time constants are identical for the three mixtures studied.

Further evidence for the unimportance of a direct oxidation of C_2H_4 in the early stages of the reaction is contained in the relationship

$$\tau_{\text{CO}} = \tau_{\text{CO}_2} = 2 \tau_{\text{CH}^*}$$

that is found for the $\text{C}_2\text{H}_4 - \text{O}_2$ reaction above 1800° K and previously⁷ for the $\text{C}_2\text{H}_2 - \text{O}_2$ reaction, the values of τ 's being essentially the same in both. The relationship is strongly suggestive that CH^* formation is due to reactions which are second order in chain intermediates while CO and CO_2 are first order.⁷ For C_2H_4^* to be oxidized to the precursors of CO, CO_2 and CH^* would require the involvement of at least one more reactive intermediate which would have destroyed this relationship of time constants.

The Arrhenius temperature dependence of the data in Fig. 3 is $-17 \text{ kcal}/\text{mole}$ and hence the rate determining step is most likely the reaction



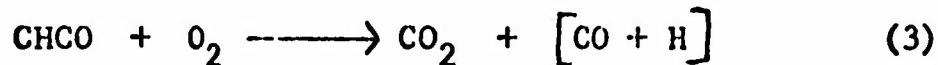
although the fit of the data to the function $\tau[\text{O}_2]^{1/2}$ rather than $\tau[\text{O}_2]$ makes this identification less certain.³

In disagreement with the value of 17 kcal, Gay et al.⁵ reported about 24 kcal for the time constants of CH* chemiluminescence, for chemi-ionization and for H₂O formation. The temperature range covered in their experiments was somewhat lower than in the present work and near the upper end of this range their \bar{T} values are practically identical with those presented here. The discrepancy occurs at lower temperatures where their \bar{T} 's are substantially longer than the values extrapolated with E = 17 kcal/mole from our data. We believe that the fundamental reason is that under these conditions the pyrolysis of ethylene becomes too slow to provide adequate concentrations of C₂H₂ and H₂ for the oxidation chains controlled by reaction (2). The result is longer \bar{T} 's as reported by Gay et al. and as suggested by our Fig. 2. The value of 24 kcal is therefore probably some compromise between the value of 17 kcal fitting their data under conditions where the pyrolytic reaction is fast enough and some value larger than 24 kcal controlling a direct ethylene oxidation mechanism involving such intermediates as postulated by Gay et al.

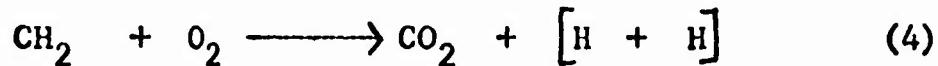
CO₂ Formation

The production of CO₂ in the early stages of the C₂H₂ - O₂ reaction has already been reported⁷ and the ratio of CO₂/CO production at 1800° K was given⁷ as 5%. The present work, reducing this number to 3%, is the more accurate since CO and CO₂ were recorded simultaneously.

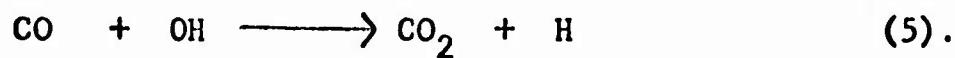
Fig. 4 shows that this ratio for the $C_2H_4 - O_2$ mixtures corresponds to that of the $C_2H_2 - O_2$, and the $C_2H_2 - H_2 - O_2$ reactions only at the highest temperatures, $> 2200^{\circ} K$, where, as Table IV shows, little ethylene is left unpyrolyzed when the oxidation products appear. At lower temperatures less CO_2 is produced in the $C_2H_4 - O_2$ reaction. The easiest explanation for this is that C_2H_4 reacts with a precursor of CO_2 . This precursor must be a minor product of the branching chain and certainly not a main precursor of CO. Thus, following the arguments presented in Ref. 7, the major reaction giving rise to CO_2 in the exponential region of the oxidation probably does not involve C_2H . In addition, since $d [CO_2] / d [CO]$ increases with decreasing temperature, C_2O is an unlikely precursor because its relative yield is expected⁷ to increase at lower temperatures. Hence the reaction leading to CO_2 is probably either:



or



In the later stages of the over-all reaction, $[CO_2]$ follows a similar course in the $C_2H_4 + O_2$ reaction to that reported for the $C_2H_2 + O_2$ reaction. It must then arise by the reaction:

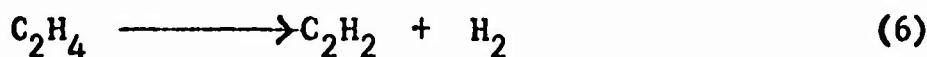


The onset of this reaction is delayed until the nearly complete consumption of C_2H_4 and C_2H_2 allows the OH concentration to rise.⁷

Pyrolysis of C₂H₄

The presently obtained data on the rate of pyrolysis of ethylene provide further support for the evidence^{4,5} that the activation energy of this reaction over a very wide temperature range is near 52 kcal. (Fig. 5). In a previous publication⁵ it was already pointed out that such a low value is very difficult to reconcile with a radical chain mechanism of the pyrolysis but even more so with a molecular mechanism. Benson and Haugen⁶ come, in effect, to the same conclusion as evidenced by their equations for the molecular and radical chain rate constants which have respective activation energies of 85 and 64 kcals/mole.

Previous work from this Laboratory⁵ provided evidence for isotopic exchange which is extremely difficult if not impossible to reconcile with a simple molecular decomposition mechanism:



and hence is in favor of a radical chain at temperatures within the range studied here. The present experiments, however, favor a molecular mechanism because the induction times in the C₂H₄ + O₂ and C₂H₂ + O₂ systems (Fig. 3) are identical at temperatures where the observable oxidation is preceded by extensive pyrolysis of ethylene. Since the exponential time constants (Fig. 3) in both systems are identical, the equality of induction times means equality of the rates of thermal initiation processes that provide the chain carriers until the multiplication process (2) takes over. Since ethylene pyrolyses much faster than

acetylene,⁸ its presence should reduce the length of the induction periods unless no radicals are produced in its pyrolysis or unless these radicals do not start oxidation chains. Neither of these suppositions is very plausible and, therefore, the problem of the mechanism of ethylene pyrolysis remains extremely puzzling.

ACKNOWLEDGMENT

The authors wish to thank the Office of Naval Research for funds which made this research possible.

TABLE 1

CO AND CO₂ FORMATION FROM C₂H₄ - O₂

Mixture	T (°K)	$\rho \times 10^3$ (moles/litre)	τ_{CO} (μsec)	τ_{CO_2} (μsec)	t_i (μsec)	$d[CO_2]/d[CO]$ $\times 10^2$
0.5% C ₂ H ₄ + 1% O ₂ in Ar	1540	5.82	---	---	157	1.9
	1745	5.15	31	26	122	1.7
	1850	4.60	24	24	97	1.6
	1880	3.63	26	27	110	1.8
	1930	4.53	19	18	85	1.7
	2005	4.46	18	19	80	1.5
	2045	4.21	18	18	83	1.3
	2150	3.66	12	---	53	1.5
	2240	3.24	10	---	48	1.5
	2325	3.34	8.5	---	40	1.6
0.5% C ₂ H ₄ + 3% O ₂ in Ar	1505	6.08	29	29	145	2.0
	1515 ^a	3.48	44	48	194	1.8
	1585 ^a	2.74	40	44	193	1.9
	1755	4.90	13	13	74	2.0
	1905	4.00	12	11	60	1.6
	1995	3.80	10	10	51	1.7
	2225	3.14	7.2	7.8	34	1.7

^aIncident Shock.

TABLE II

CO AND CO₂ FORMATION FROM C₂H₂ - O₂ AND C₂H₂ - H₂ - O₂

Mixture	T (°K)	$\rho' \times 10^3$ (moles/litre)	τ_{CO} (μsec)	τ_{CO_2} (μsec)	t_i (μsec)	$d[CO_2]/d[CO]$ $\times 10^2$
0.5% C ₂ H ₂ + O ₂ in Ar	1580	5.90	35	36	170	4.1
	1640	4.95	43	43	196	3.7
	1715	5.15	27	28	140	3.5
	1760	4.95	25	24	132	3.4
	1880	4.35	25	26	118	3.1
	2010	3.80	18	21	84	2.1
	2090	3.50	23	26	90	2.5
	2140	3.60	17	17	70	2.0
	2250	3.45	15	16	59	1.7
	2300	3.20	10	---	51	1.3
0.5% C ₂ H ₂ + H ₂ + O ₂ in Ar	1430	5.85	49	43	230	5.0
0.5% H ₂ + O ₂ in Ar	1580	5.20	30	30	155	3.7
	1650	5.30	28	30	126	3.7
	1800	5.00	22	23	102	2.9
	1910	4.30	16	15	88	2.8
	2010	4.00	17	16	74	2.9
	2120	3.50	11	---	64	2.6
	2270	3.10	10	10	46	1.8
	2400	3.00	7.5	---	30	1.3

TABLE III

FIRST ORDER RATE CONSTANTS FOR C_2H_4 PYROLYSIS

Mixture	T (°K)	$\rho \times 10^{-18}$ (molecules/cc)	$k \times 10^{-3}$ (sec ⁻¹)
1.5% C_2H_4 in Ar	1950	2.38	3.3
	2000	2.27	4.6
	2015	2.32	5.0
	2030	2.28	5.4
	2085	2.16	7.4
	2220	1.94	17
	2260	1.90	20
0.5% C_2H_4 in Ar	1995	2.44	5.4
	2060	2.08	4.8
	2075 ^a	0.83	3.6

^aIncident Shock

TABLE IV

EXTENT OF C_2H_4 PYROLYSIS AT THE TIME OF 10% OXIDATION

AT CONSTANT TOTAL GAS DENSITY OF 4.5×10^{-3} MOLES/LITRE

T (°K)	Time t_i (μ sec) for 10% Oxidation		% C_2H_4 Pyrolysed at Time t_i	
	0.5% C_2H_4 + 1% O_2	0.5% C_2H_4 + 3% O_2	0.5% C_2H_4 + 1% O_2	0.5% C_2H_4 + 3% O_2
2300	40	23	80	60
2200	48	28	69	49
2100	58	34	56	38
2000	71	41	40	26
1900	88	51	28	17
1800	112	65	18	11
1700	150	87	10	5.6
1600	205	118	5.7	3.3
1500	290	167	2.6	1.5

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LEGENDS FOR FIGURES

FIG. 1:

Examples of oscilloscope traces of infrared emission: (a) C_2H_4 pyrolysis at $2075^{\circ} K$, incident shock; (b) $C_2H_4 - O_2$ reaction at $1850^{\circ} K$, reflected shock, upper trace CO , lower trace CO_2 . Both records are $50 \mu\text{sec.}$ per division and shock arrival is at the first rise in signal.

FIG. 2:

Logarithmic increase of signals as function of reaction time, for CO (\bullet) and CH^* (\circ) formed in the $C_2H_4 - O_2$ reaction.
(a) $2020^{\circ} K$, $[O_2] = 1.13 \times 10^{-5}$ moles/litre
(b) $1850^{\circ} K$, $[O_2] = 1.9 \times 10^{-6}$ moles/litre
(c) $1605^{\circ} K$, $[O_2] = 1.61 \times 10^{-5}$ moles/litre.

The arrows of the time axis indicate the time of 10% oxidation.

FIG. 3:

Data for the induction period to 10% combustion, and the time constant for CO formation for the mixtures:

\bullet $0.5\% C_2H_4 + 1\% O_2$,

\blacktriangle $0.5\% + 3\% O_2$,

\circ $0.5\% C_2H_2 + 0.8\% O_2$,

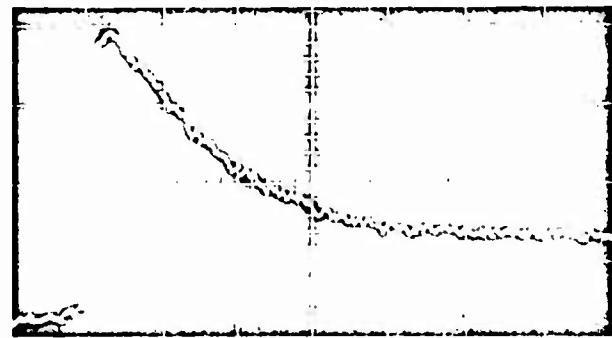
\triangle $0.5\% C_2H_2 + 0.5\% H_2 + 1\% O_2$.

The lines drawn correspond to an activation energy of 17 kcal.

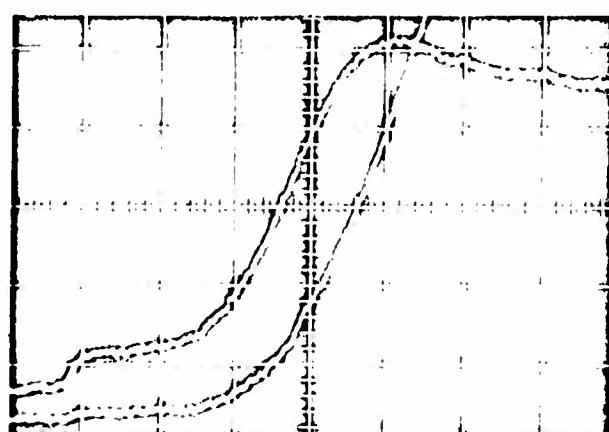
LEGENDS FOR FIGURES -- Page 2

FIG. 4: Ratio of the rates of production of CO_2 and CO in the early stages of oxidation. The symbols have the same significance as in Fig. 3.

FIG. 5: Arrhenius plot of 1.5 - order rate constants for ethylene pyrolysis: \bullet this work,
— least squares of data of Gay et al,⁵
 Δ Skinner and Sokoloski.⁴



a



b

FIG. 1

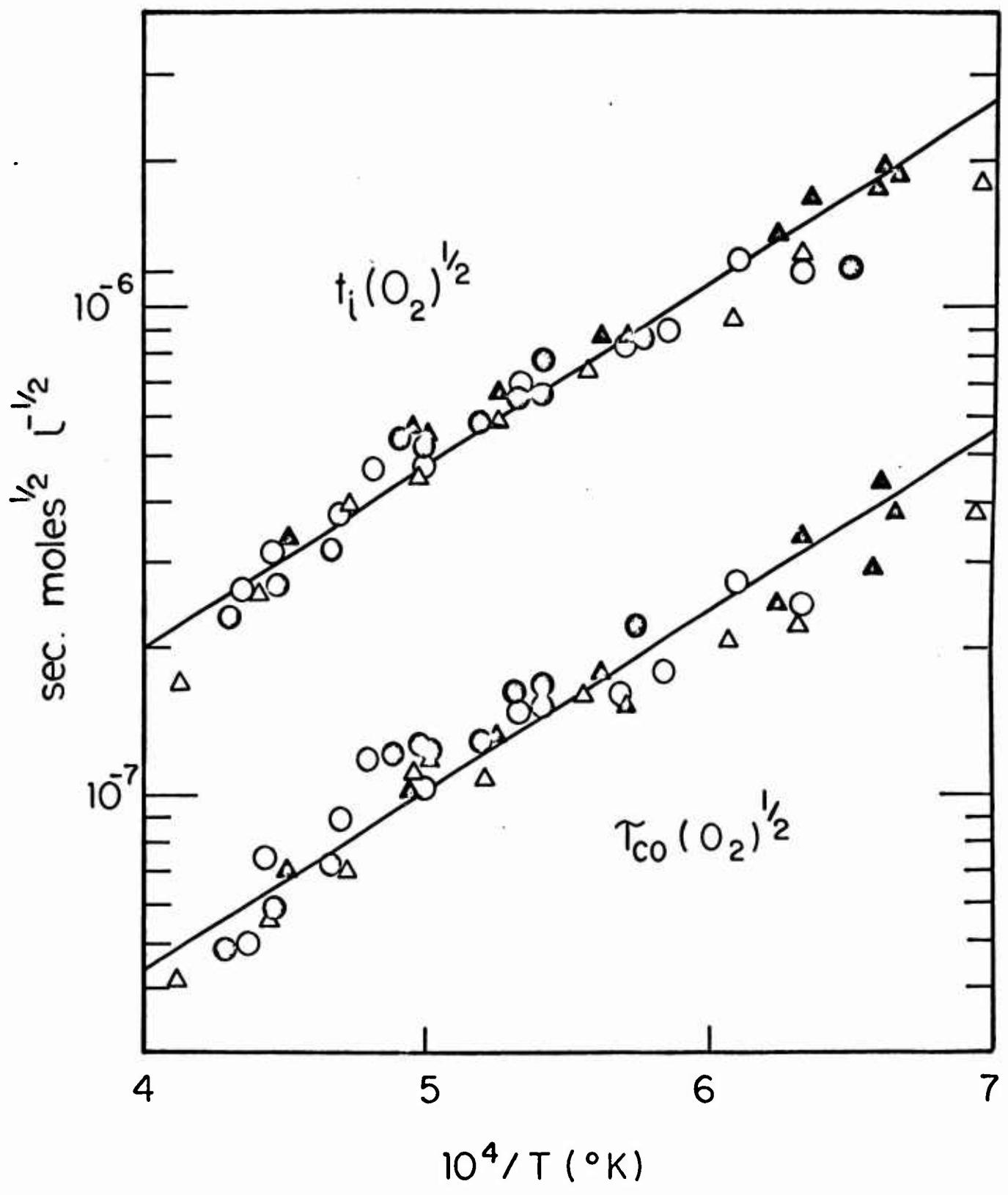
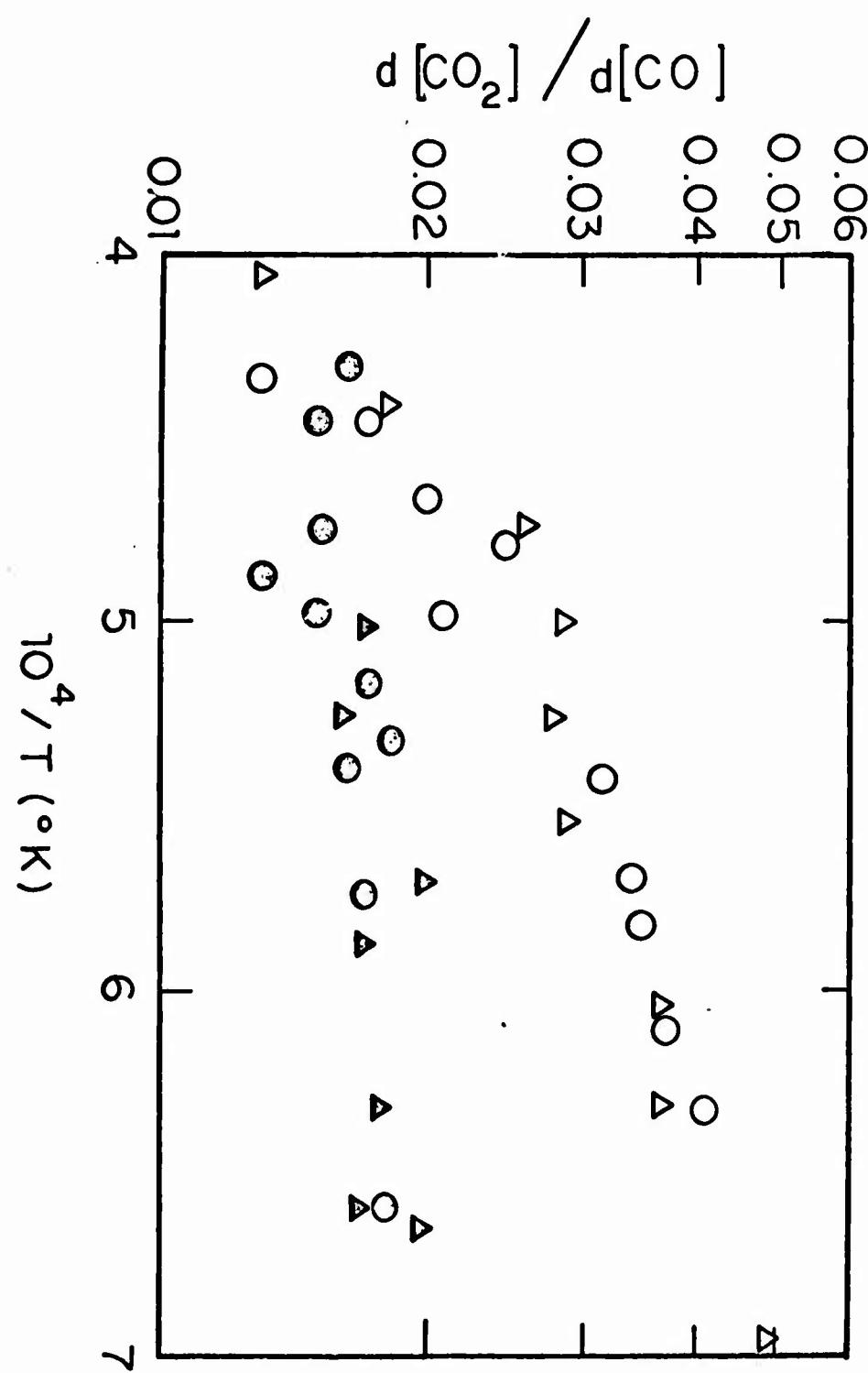


FIG. 3

FIG. 4



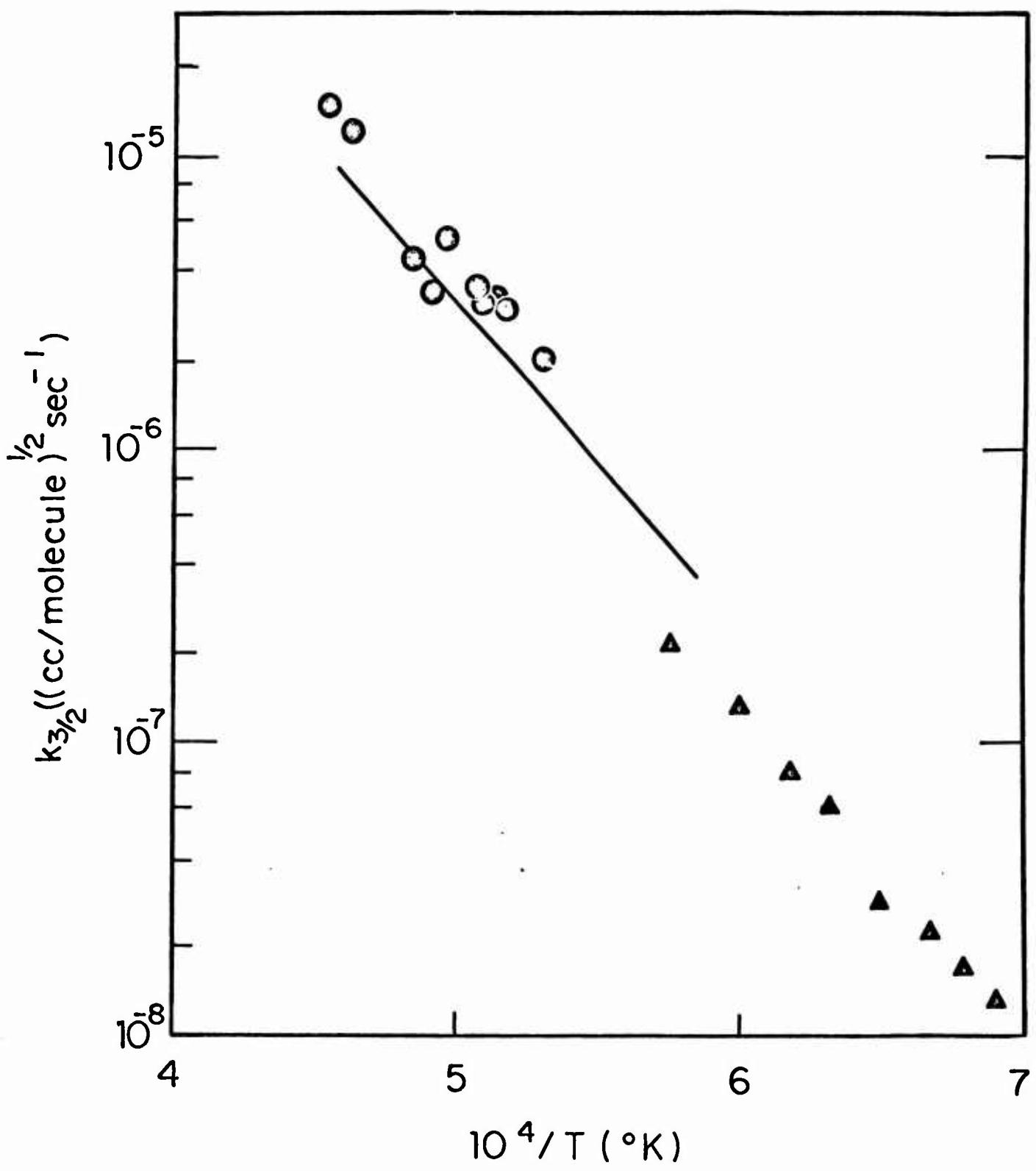


FIG. 5

Unclassified

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

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2b. GROUP		
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13. ABSTRACT The oxidation of C_2H_4 has been studied in a shock tube by monitoring the infrared emissions from CO and CO_2 and the visible emission from CH^* . The characteristics of this oxidation closely resemble oxidations of C_2H_2 and $C_2H_2 + H_2$. The induction periods and exponential time constants for the early phase of CO formation are the same for all three oxidations over the temperature range of $1500^{\circ}K$ to $2300^{\circ}K$ and lead to a common activation energy of 17 ± 1 kcal/mole.

Above $1800^{\circ}K$, the $C_2H_4 - O_2$ reaction, in its early stages, consists mainly of the pyrolysis of C_2H_4 , and the concurrent oxidation of pyrolysis products, C_2H_2 and H_2 . Later in the reaction, and more prominently so at lower temperatures, the reaction changes in character to a slower direct oxidation of C_2H_4 .

The relative rates of CO and CO_2 production in both $C_2H_4 - O_2$ and $C_2H_2 - O_2$ reactions are reported as a function of temperature.

The pyrolysis of C_2H_4 has also been studied in the shock tube by an infrared technique and its rates determined between $1950^{\circ}K$ and $2250^{\circ}K$. The results are in good agreement with previous work and give an activation energy of 52 kcal/mole for the reaction. The oxidation results would indicate that C_2H_4 , above $1800^{\circ}K$, decomposes mainly by

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
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