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EFFECT OF CARBON DIOXIDE AND WATER VAPOR ON THE INDUCTION PERIOD OF THE HYDROGEN-OXYGEN REACTION

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SUMMARY

The effect of carbon dioxide and water vapor on the induction-period kinetics of the hydrogen-oxygen reaction was studied in a shock tube at temperatures between 1000° and 1500° K. The results show that carbon dioxide does not produce any noticeable effect, whereas water vapor appears to accelerate the hydrogen-oxygen reaction. The analysis of experimental data indicates that the accelerating influence of water vapor is due to two processes. One process is dominant at the higher temperatures, the chain-branching reaction $O + H_2O \rightarrow 2OH$, and the other, an unidentified process, is dominant at the lower temperatures.

INTRODUCTION

When gaseous mixtures of hydrogen, oxygen, and argon are suddenly heated, for example, by means of a shock wave, ignition is preceded by a short induction period. During the induction period, chain branching occurs which results in an exponential growth of free radical concentrations at essentially constant temperature and pressure. The mechanism of the hydrogen-oxygen reaction has been studied quite extensively and it has been fairly well established that the dominant reactions during the induction period are:

$$\text{Initiation} \rightarrow H, O, \text{ or } OH \qquad \text{(I)}$$

$$OH + H_2 \rightarrow H_2O + H \qquad \text{(II)}$$

$$H + O_2 \rightarrow OH + O \qquad \text{(III)}$$

$$O + H_2 \rightarrow OH + H \qquad \text{(IV)}$$

During the initiation period, which is a very small portion of the total induction period, a small concentration of free radicals is produced according to reaction (I). These free radicals permit the chain-propagating reaction (II) and the chain-branching reactions (III) and (IV) to proceed. At pressures of 1 atm and greater and temperatures below about 1200° K, the inhibiting termolecular reaction

$$H + O_2 + M \rightarrow HO_2 + M \qquad \text{(V)}$$

also becomes important (where M is any third body). Discussions of this set of reactions, with references to additional experimental work, can be found in references 1, 2, and 3.

The length of the induction period, or the induction time, has been shown to be governed by the rates of the individual reactions occurring in this period (refs. 3 and 4). Thus measurement of induction times permit an indirect study of chain-branching and chain-propagating processes occurring during the induction period. The end of the induction period, of course, must be defined somewhat arbitrarily. In experiments where the hydroxyl-radical concentration has been monitored, the induction period has been defined as the time between shock heating and the first observable trace of hydroxyl-radical concentration (ref. 1). The onset of light emission from electronically excited OH has also been used to define the end of the induction period (ref. 5).

The purpose of this investigation was to determine the effect of carbon dioxide and water vapor on the induction-period kinetics of the hydrogen-oxygen reaction. Carbon dioxide and water vapor are contaminants found in the stream of combustion-heated wind tunnels. An understanding of how these contaminants effect the ignition delay time is an important factor in the testing and operation of supersonic combustion systems in such tunnels, especially under the conditions where the ignition delay can occupy a sizable fraction of the length of the combustion chamber (for example, where $T \leqq 1500^\circ$ K and $p \geqq 1$ atm).

The induction-time measurements undertaken in this investigation were carried out with the use of a shock tube. The length of the induction period, or the induction time, was defined as the time interval between shock heating and the onset of light emitted at 3065 Å by the electronically excited hydroxyl radical.

SYMBOLS

$k_1, k_2 \ldots, k_9$	rate constants, cm^3/mole-sec for bimolecular reactions and $cm^6/mole^2$-sec for termolecular reactions
$[O_2]$	initial oxygen concentration, $moles/cm^3$
p	pressure, atmospheres (1 atm = 101.325 kN/m^2)

p_i	initial pressure, atmospheres
p_r	reaction pressure, atmospheres
R	gas constant, calories/°K-mole (joules/°K-mole)
T	absolute temperature, degrees Kelvin
t_i	induction time, seconds

EXPERIMENT

The shock tube was constructed of stainless-steel tubing having an inside diameter of 9.0 cm with a 214-cm-long driver section and a 580-cm-long test section. Mylar diaphragms clamped between the driver and test sections were ruptured by increasing the pressure in the driver section beyond their yield strength. Helium-nitrogen gas mixtures served as the driver gas. Six platinum-deposited resistance gages were used in conjunction with a raster oscilloscope for shock-velocity measurements.

Ignition of the shocked-gas mixture was detected photoelectrically by observing the radiation emitted by the (O,O) band of OH at 3065 Å. Observations were made through a quartz window with a 2-mm by 25-mm collimating slit. A quartz lens was used to image the light from the slit onto an f/4 quartz-prism monochromator. The monochromator had a bandpass of approximately 100 Å centered at 3065 Å. The radiation at the exit slit of the monochromator was detected by a 9558Q photomultiplier and the resulting signal was fed to an oscilloscope. Typical oscilloscope settings used were 2.0 volts per division for the vertical deflection and 20 microseconds per division for the sweep rate. The sweep of the oscilloscope was triggered by a signal from a platinum resistance gage located 30.5 cm from the observation point. The sweep speeds and the delay generator of the oscilloscope were periodically calibrated with a crystal oscillator. The response time of the recording system was less than 2 microseconds for all the experimental conditions. The oscilloscope trace was recorded on film.

Gas mixtures were prepared from commercial hydrogen (99.9 percent), dry oxygen (99.6 percent), carbon dioxide (99.7 percent), and argon (99.995 percent) without further purification. The test gas mixtures of H_2-O_2-Ar and H_2-O_2-CO_2-Ar were prepared by partial pressure and were accurate within 1/2 percent. Gas mixtures containing water vapor were prepared by bubbling H_2-O_2-Ar mixtures through degassed, distilled water. The resulting mixture was passed into the test section. The amount of water introduced into the tube was varied by adjusting the rate of flow of gas through the bubbler. Analysis of the gas mixture was done by withdrawing a 1/2-liter (500-cm^3) sample of gas from the test section and condensing the water vapor with a liquid nitrogen—ethyl alcohol cold trap. After the uncondensed gases were pumped off, the water was allowed to evaporate and its pressure measured. Water content in samples withdrawn within 5 minutes of each other agreed within 3 percent. The time interval between sampling the gas and shock heating it, on the average, never exceeded 2 minutes.

The data obtained in each run consisted of the recorded initial conditions, the shock velocity contained in the photograph from the raster oscilloscope, and the emission record contained in the oscilloscope photograph of the photoelectric signal. Calculations based on the conservation equations were used to calculate the temperature, pressure, density, and concentrations in moles/cm^3 just behind the incident shock from the initial condition and the measured shock velocity. Frozen chemistry and complete rotational and vibrational equilibrium were assumed just behind the shock. The temperature and pressure during the induction period were assumed to be the same as those calculated just behind the shock. Induction times obtained from the emission records were multiplied by the density ratio across the shock to convert from laboratory time to gas time.

The composition of the experimental mixtures studied and the summary of the experimental conditions are given in table I. A tracing of a typical record of the oscilloscope display of OH emission is shown in figure 1.

TABLE I.- COMPOSITION OF EXPERIMENTAL MIXTURES AND SUMMARY OF EXPERIMENTAL CONDITIONS

Mixture	Composition, mole percent	Number of runs	p_i, atm	T, °K	p_r, atm
A	4.0% H_2 – 2.0% O_2 – 94.0% Ar	34	0.050 to 0.100	1000 to 1520	0.95 to 1.21
B	4.0% H_2 – 2.0% O_2 – 2.0% CO_2 – 92.0% Ar	16	.050 to .100	1000 to 1480	.95 to 1.17
C	4.0% H_2 – 2.0% O_2 – 4.0% CO_2 – 90.0% Ar	18	.050 to .100	1020 to 1540	.96 to 1.21
D	4.0% H_2 – 2.0% O_2 – 2.0% H_2O – 92.0% Ar	18	.050 to .100	1030 to 1470	.95 to 1.25
E	4.0% H_2 – 2.0% O_2 – 4.0% H_2O – 90.0% Ar	24	.050 to .100	1010 to 1480	.97 to 1.22

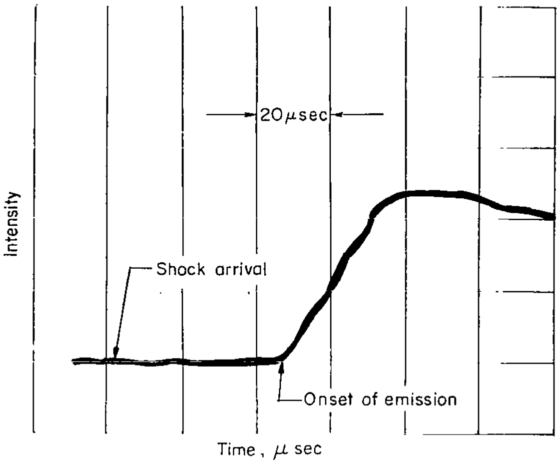

Figure 1.- Oscilloscope record for a 4%H_2-2%O_2-94%Ar mixture. T = 1230° K before reaction.

RESULTS AND DISCUSSION

The experimentally determined induction times for mixtures B, C, D, and E are compared with the measured induction times for reference mixture A in figures 2, 3, 4, and 5, respectively. The data have been correlated by plotting the product of the induction time t_i, in seconds, and the initial oxygen concentration, in moles per cm^3, against the reciprocal of the absolute temperature. Figures 2 and 3 show that the presence of carbon dioxide apparently does not affect the induction period of the hydrogen-oxygen reaction. Figures 4 and 5 show that in the presence of water vapor the hydrogen-oxygen reaction is accelerated for mixture E whereas no detectable effect is observed for mixture D. The influence of water vapor on the induction period of the hydrogen-oxygen reaction was also studied in a shock tube by Snyder and coworkers (ref. 6) over a temperature range from about 900° to 1000° K at 2 atm. (Stoichiometric hydrogen-air mixtures containing 10, 15, and 20 mole percent of water vapor were studied.) They found that water vapor inhibits the hydrogen-oxygen reaction below about 950° K although above this temperature the reaction appears to be accelerated in the presence of water vapor.

In order to correlate the experimental results with kinetic data, induction times have been calculated by numerically integrating a set of rate equations that describe the rate of growth of free radicals during the induction period. The set of rate equations was integrated on a computer using a modified Runge-Kutta scheme with a variable step size. All calculations were made for a total gas pressure of 1 atm. The chemical reactions

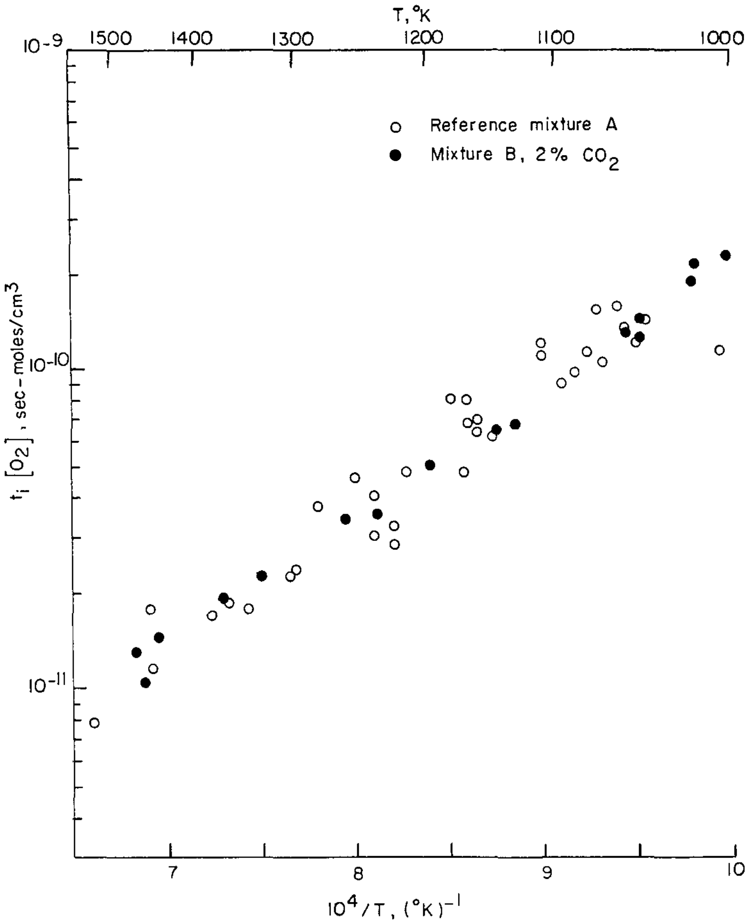

Figure 2.- Induction-time data for mixtures A and B as a function of temperature.

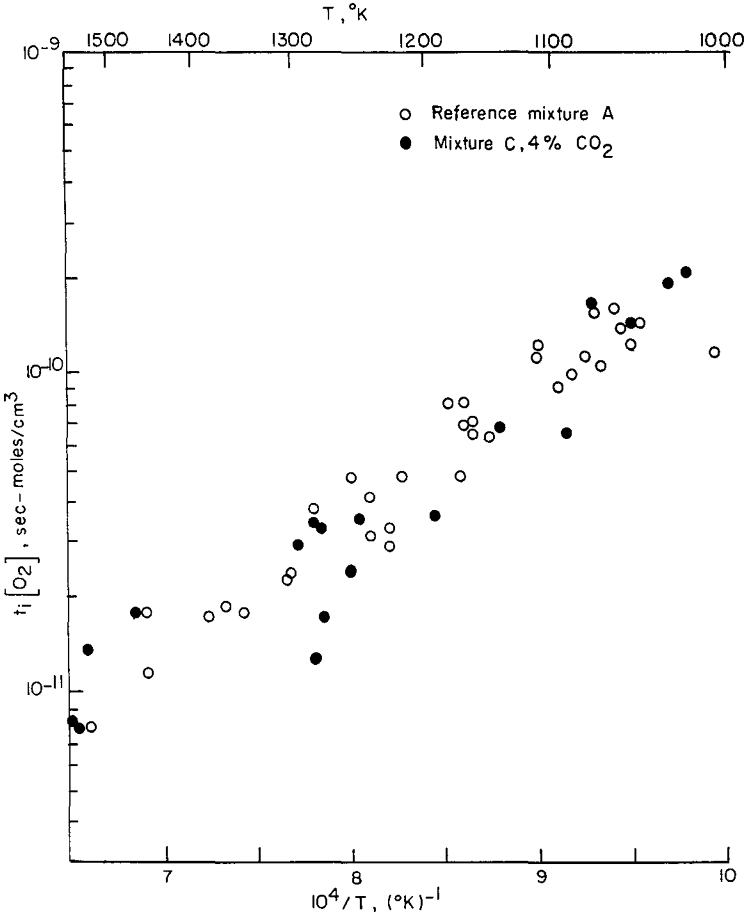

Figure 3.- Induction-time data for mixtures A and C as a function of temperature.

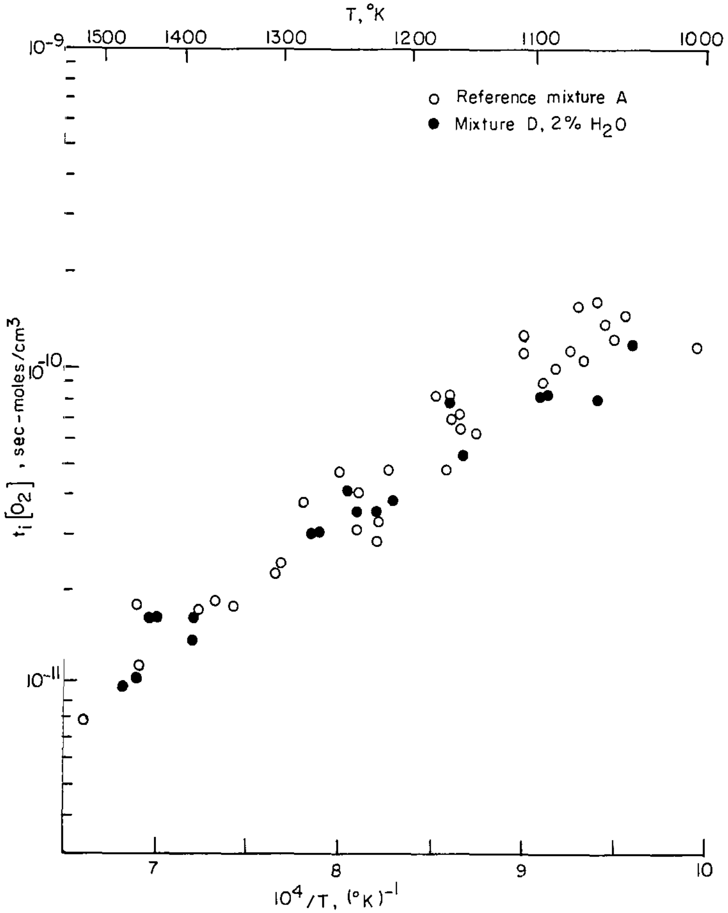

Figure 4.- Induction-time data for mixtures A and D as a function of temperature.

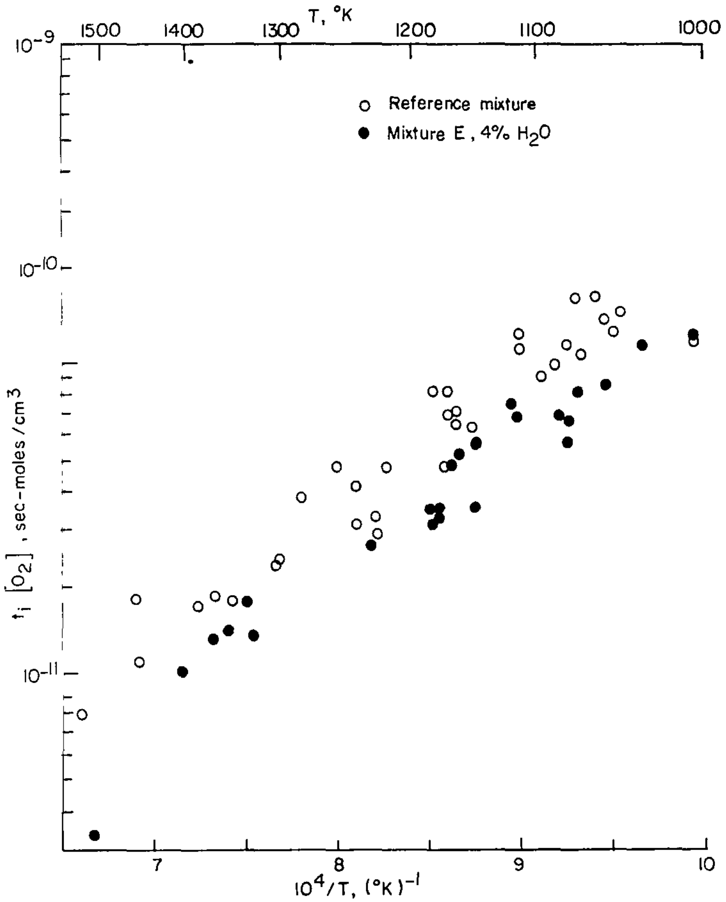

Figure 5.- Induction-time data for mixtures A and E as a function of temperature.

that are believed to describe the results best included reactions (I) to (V) together with the following reactions:

$$H + CO_2 \rightarrow OH + CO \qquad \text{(VI)}$$

$$O + H_2O \rightarrow 2OH \qquad \text{(VII)}$$

$$H + H_2O \rightarrow OH + H_2 \qquad \text{(VIII)}$$

Reaction (I), the initiation reaction, can also be written as

$$H_2 + O_2 \rightarrow 2OH \qquad \text{(I)}$$

The effect of H_2, O_2, CO_2, H_2O, and Ar as third bodies was taken into account in reaction (V).

For calculation purposes the induction time was taken as the time required to reach a hydroxyl concentration of 10^{-9} moles/cm^3. This value is that used by Schott and Kinsey (ref. 1). As noted previously, induction time in this study was defined as the time interval between shock heating and the onset of emission. These two definitions should be consistent, at least within experimental error, since the concentration of ground-state OH radicals and the emission from excited OH radicals both increase markedly as the reaction becomes rapid at the end of the induction period.

Calculations were made for reference mixture A. The rate constants used in the calculations were obtained from references 2, 3, and 7 to 11 and are given in table II.

TABLE II.- RATE CONSTANTS

Reaction	Rate constant (*)	Reference
$H_2 + O_2 \rightarrow 2OH$	$k_1 = 2.5 \times 10^{12} \exp(-39\,000/RT)$	3
$OH + H_2 \rightarrow H_2O + H$	$k_2 = 2.3 \times 10^{13} \exp(-5\,200/RT)$	7
$H + O_2 \rightarrow OH + O$	$k_3 = 2.14 \times 10^{14} \exp(-16\,600/RT)$	8
$O + H_2 \rightarrow OH + H$	$k_4 = 1.2 \times 10^{13} \exp(-9\,200/RT)$	9
$H + O_2 + M \rightarrow HO_2 + M$	$k_5(M = Ar) = 8.6 \times 10^{14} \exp(1\,280/RT)$	2
	$k_5(M = H_2) = 5\, k_5(M = Ar)$	10
	$k_5(M = O_2) = 1.75\, k_5(M = Ar)$	10
	$k_5(M = H_2O) = 30\, k_5(M = Ar)$	2
	$k_5(M = CO_2) = 7\, k_5(M = Ar)$	10
$H + CO_2 \rightarrow OH + CO$	$k_6 = 5.3 \times 10^{13} \exp(-23\,600/RT)$	Obtained from $k_{-6} = 3.1 \times 10^{11} \exp(600/RT)$, ref. 7
$O + H_2O \rightarrow 2OH$	$k_7 = 3.8 \times 10^{14} \exp(-19\,500/RT)$	11
$H + H_2O \rightarrow OH + H_2$	$k_8 = 2.5 \times 10^{14} \exp(-22\,260/RT)$	Obtained from k_2

*Rate constant is expressed in cm^3/mole-sec for bimolecular reactions and in cm^6/mole^2-sec for termolecular reactions.

The calculated curve and the experimental data for reference mixture A are shown in figure 6. In general, the calculated values of induction times agree well with the experimental data.

Induction-time calculations for mixture C show, in agreement with experiment, that carbon dioxide should have no detectable effect on the kinetics of the induction period. The calculated curve and experimental data for mixture C are shown in figure 7.

The calculated curves for mixtures A and E together with the experimental data for mixture E are shown in figure 8. The solid curve for mixture E shows that according to our reaction model, the presence of water vapor should inhibit the hydrogen-oxygen reaction over most of the temperature range considered. The inhibition is due to the participation of H_2O in reaction (V) (where $M = H_2O$). A slight accelerating effect, due to the chain-branching reaction (VII), is predicted at the higher temperatures. However, the experimental data (mixture E) pointedly show that water vapor produces an accelerating effect over the entire temperature range. To determine the influence of k_7 on the calculated induction times, calculations were made with k_7 increased by a factor of 10. The result is shown by the dash-line curve in figure 8. Fair agreement is shown between experiment and the calculated curve at the higher temperatures, but not at the lower temperatures.

In the presence of water vapor, the calculated induction-time curve is sensitive to the choice for k_5 and k_7. It would seem that calculation and experiment could be brought into better agreement with slight modification of the rate constants k_5 and k_7. Decreasing $k_5(Ar)$ by a factor of 1.5 and increasing k_7 by a factor of 5 gives good agreement between experiment and calculation over most of the temperature range. The calculations and the experimental data are shown in figure 9. Also shown in figure 9 are the calculated and experimental induction times for mixture A where the modified k_5 was used in the calculations. Good agreement is obtained between the calculated and experimental induction times for mixture A even with the adjusted k_5.

It was not possible to obtain a good fit to the experimental data for mixture E at the lower temperatures without assuming unreasonably small values for k_5 and unreasonably large values for k_7. This seems to suggest that the acceleration process at the lower temperatures is different from the accelerating process at the higher temperatures; that is, the accelerating influence of H_2O appears to be due to two processes. One process is dominant at the higher temperatures, the chain-branching reaction $O + H_2O \rightarrow 2OH$, and the other is dominant at the lower temperatures, possibly a process involving the HO_2 radical. Levy (ref. 12) suggested that perhaps the reaction

$$HO_2 + H_2O \rightarrow H_2O_2 + OH \qquad \text{(IX)}$$

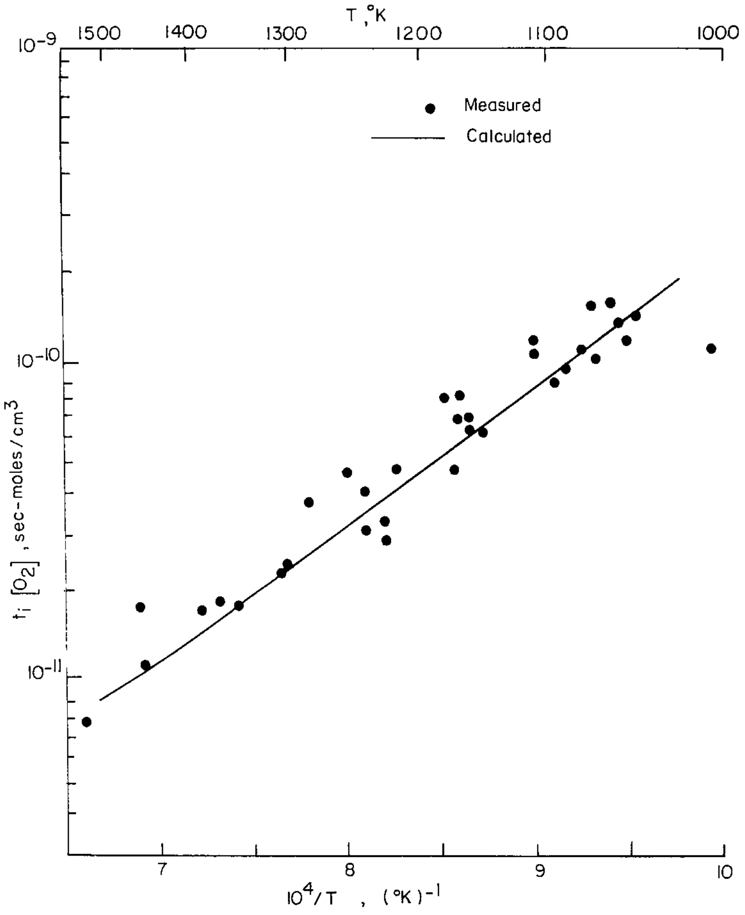

Figure 6.- Comparison of calculated and experimental induction times for reference mixture A (4%H_2-2%O_2-94%Ar).

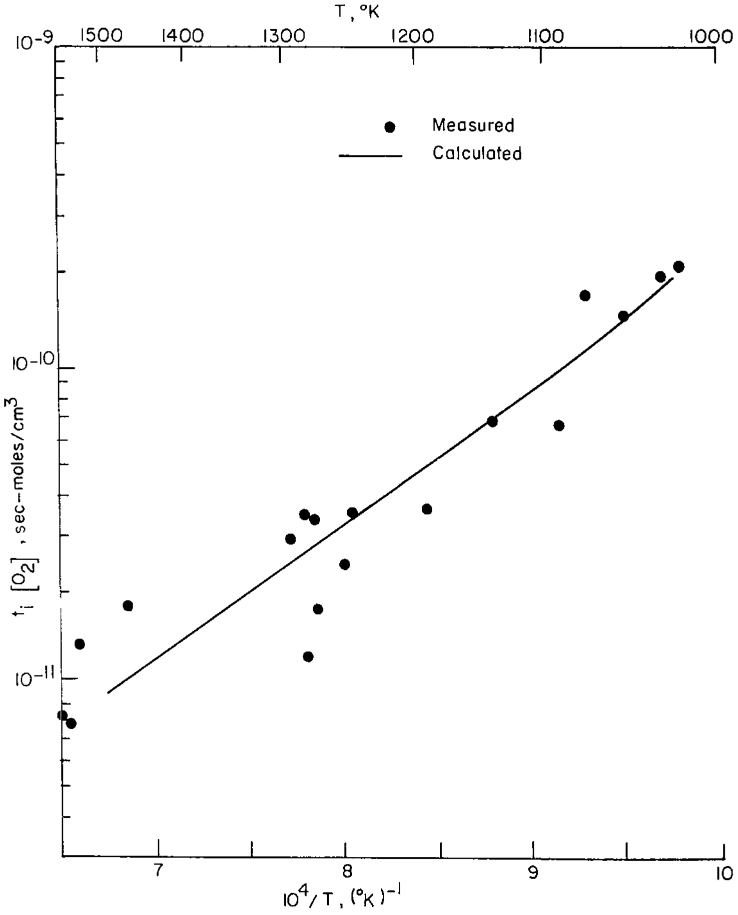

Figure 7.- Comparison of calculated and experimental induction times for mixture C (4% CO_2).

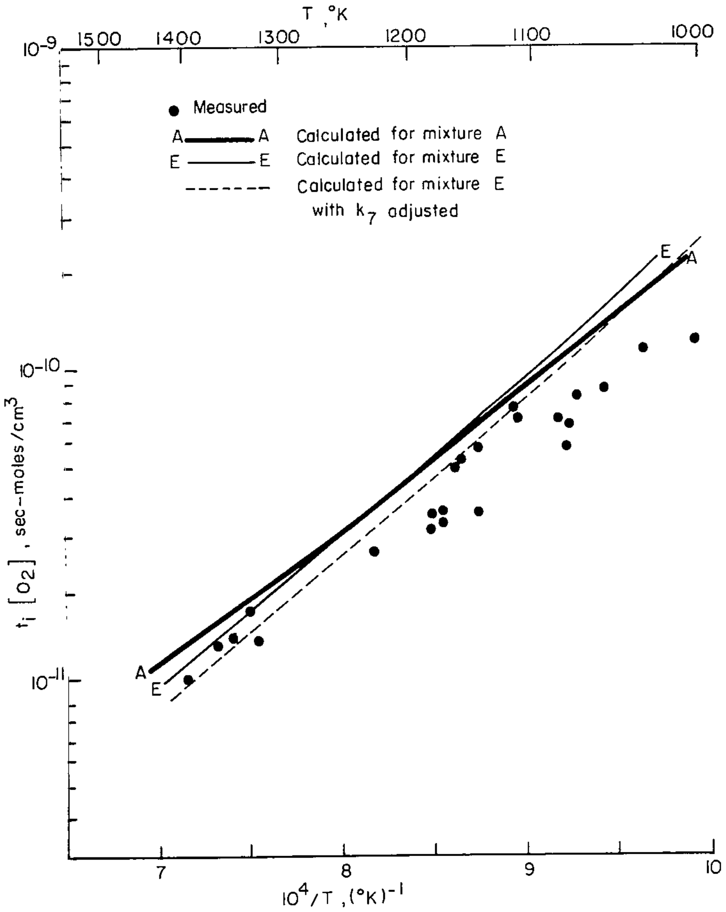

Figure 8.- Comparison of calculated and experimental induction times for mixture E (4% H_2O).

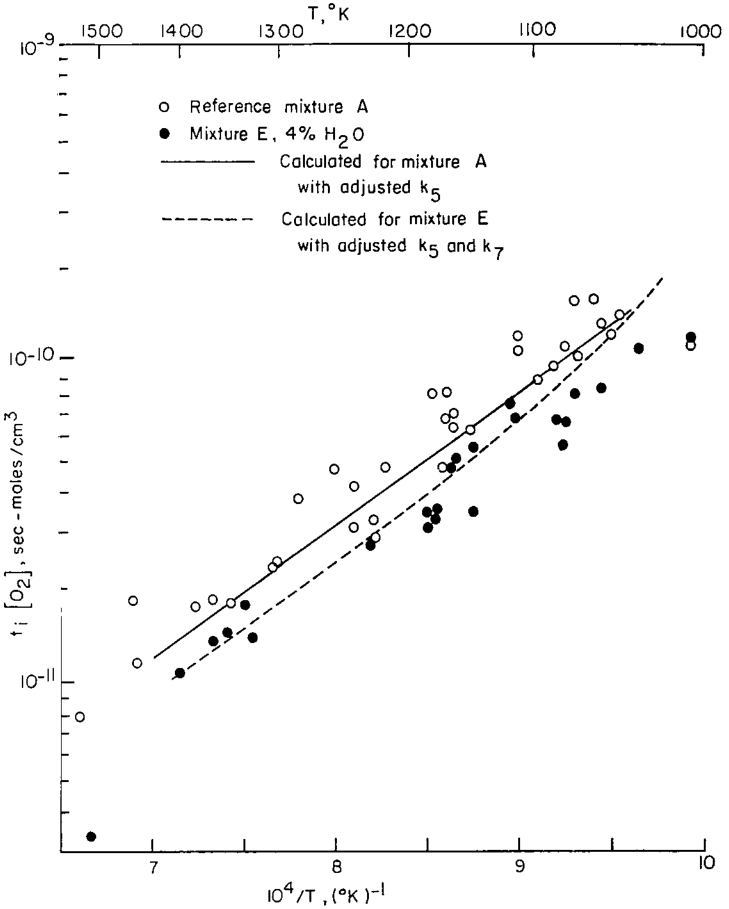

Figure 9.- Comparison of calculated and experimental induction times for mixtures A and E. Adjusted rate constants k_5 and k_7 were used in the calculations.

may be important when water vapor is present in sufficient concentration. Reaction (IX) could account for the accelerating effect observed at the lower temperatures if a value of 10^{10} cm^3/mole-sec is assumed for k_9 at 1100° K together with the modified rate constants for k_5 and k_7. However, if a preexponential factor of 10^{11} and an activation energy of 30 kcal (126 kJ) equal to the heat of reaction at 1100° K are assumed, then k_9 would only be of the order of 10^8 cm^3/mole-sec at 1100° K, a factor of 10^2 lower than needed.

CONCLUDING REMARKS

Carbon dioxide appears to have no noticeable effect on the kinetics of the hydrogen-oxygen reaction during the induction period for the conditions studied and would probably not be an important factor in combustion-heated wind tunnels.

Water vapor, when present in sufficient quantities, appears to accelerate the hydrogen-oxygen reaction resulting in shorter delay times. Acceleration at the higher temperatures is probably due to the chain-branching reaction $O + H_2O \rightarrow 2OH$. The accelerating effect at the lower temperatures could not be explained in terms of a satisfactory kinetic scheme. Since the amount of water encountered in combustion-heated wind tunnels relative to the amount of hydrogen and oxygen is usually not as large as that used in this study, the presence of water vapor will probably have no effect on ignition delay times, at least for the conditions studied.

Langley Research Center,
National Aeronautics and Space Administration,
Langley Station, Hampton, Va., March 18, 1968,
129-01-01-02-23.

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