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HIGH-TEMPERATURE CHEMICAL KINETIC STUDY OF THE H₂-CO-CO₂-NO REACTION SYSTEM

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HIGH-TEMPERATURE CHEMICAL KINETIC STUDY OF THE H₂-CO-CO₂-NO REACTION SYSTEM

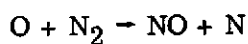
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SUMMARY

An experimental study of the kinetics of the H₂-CO-CO₂-NO reaction system was made behind incident shock waves at temperatures of 2460 and 2950 K. The overall rate of the reaction was measured by monitoring radiation from the CO + O → CO₂ + hν reaction. Correlation of these data with a detailed reaction mechanism showed that the high-temperature rate of the reaction N + OH → NO + H can be described by the low-temperature (320 K) rate coefficient. Catalytic dissociation of molecular hydrogen was also an important reaction under the test conditions.

INTRODUCTION

Interest in predicting nitric oxide emissions from combustion devices such as gas turbines, flame burners, and jet-stirred combustors has resulted in the formulation of various analytical reaction schemes for nitric oxide formation (refs. 1 to 3). Most of these schemes are based on a mechanism in which nitric oxide is formed primarily through the nitrogen-oxygen reactions,

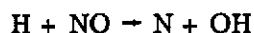


with the reaction between the nitrogen atom and the hydroxyl radical,



being of some importance in fuel-rich mixtures. The accuracy of these reaction schemes depends on the accuracy of the rate coefficients for these reactions. The rate coefficients for the nitrogen-oxygen reactions are known very well (refs. 4 and 5). However, high-temperature rate coefficient data are not available for the reaction between nitrogen atoms and hydroxyl radicals, and the rate coefficient currently used is based on measurements obtained at 320 K (ref. 6).

The purpose of this study was to examine the validity of using the low-temperature rate coefficient for the reaction between the nitrogen atom and the hydroxyl radical at temperatures typical of combustion reactions. Because it was not experimentally feasible to generate sufficient levels of nitrogen atoms at temperatures below 3000 K, a direct study of this reaction could not be made. Instead, the reverse reaction,



was studied, and the forward rate coefficient was obtained by assuming that the forward and reverse rate coefficients are related through the equilibrium constant.

The experimental study was made by shock heating a mixture of hydrogen, carbon dioxide, carbon monoxide, and nitric oxide diluted in argon and monitoring the radiation from the $\text{CO} + \text{O} \rightarrow \text{CO}_2 + h\nu$ reaction. The intensity of this radiation is proportional to the product of the carbon monoxide and oxygen atom concentrations (ref. 7), and therefore it provides a means for monitoring changes in the product $[\text{O}][\text{CO}]$. Kinetic information on the reaction $\text{H} + \text{NO} \rightarrow \text{N} + \text{OH}$ was obtained by comparing the measured $[\text{O}][\text{CO}]$ profiles with computations based on a detailed chemical mechanism for the H_2 -CO-CO₂-NO reaction system.

SYMBOLS

k	rate coefficient, $\text{cm}^3/\text{mol}\text{-sec}$ for bimolecular reactions, $\text{cm}^6/\text{mol}^2\text{-sec}$ for termolecular reactions
$[\text{O}], [\text{CO}]$	concentrations of oxygen atom and carbon monoxide, respectively, mol/cm^3
p	pressure, mm Hg or atm (1 mm Hg = 133.3 Pa; 1 atm = 101.3 kPa)
T	absolute temperature, K
t_l	laboratory time, μsec
Subscripts:	
1	initial value prior to shock heating
2	average value immediately behind shock

EXPERIMENTAL APPARATUS AND PROCEDURE

All experimental data were obtained behind incident shock waves in a stainless-steel shock tube with internal diameter of 8.9 cm. The tube had a 214-cm-long driver section and a 580-cm-long driven section. Plastic diaphragms clamped between the driver and driven sections were ruptured by increasing the pressure in the driver section. Helium was used as the driver gas. The velocity of the shock wave was measured with a raster system (ref. 8) upon which timing marks were superimposed at 10- μ sec intervals. Test gas mixtures were prepared by the method of partial pressures from ultrapure research-grade commercial gases without further purification.

Radiation from the shocked gas was monitored through a calcium fluoride window. A quartz lens was used to image the light from the center of the tube onto the entrance slit of a 0.5-m Czerny-Turner type of monochromator with a 1200 lines/mm grating blazed at 3000 \AA (1 \AA = 0.0001 μ m). The monochromator was set to pass radiation at 3660 \AA with a 32- \AA half-width. The light from the exit slit of the monochromator was detected by a 9558Q photomultiplier, and the resulting signal was fed to an oscilloscope. The sweep of the oscilloscope was triggered by a signal from a platinum resistance gage located 39.2 cm from the observation point. The sweep speeds and the delay generator of the oscilloscope were periodically calibrated with a crystal oscillator. The time constant of the recording system was 1.5 μ sec for all the experimental tests. The transit time of the incident shock past the window was less than 2 μ sec.

A quantitative relationship between the intensity of the emission from the reaction $\text{O} + \text{CO} \rightarrow \text{CO}_2 + h\nu$ and the concentration product $[\text{O}][\text{CO}]$ was obtained by calibrating the optical system with the radiation produced by shock heating various $\text{H}_2\text{-O}_2\text{-CO-CO}_2\text{-Ar}$ gas mixtures. Additional details of the calibration procedure are given in reference 9.

Experiments were carried out with the gas mixtures listed in table I. The results from experiments with mixture 1 were used to verify the assumed reaction scheme for the $\text{H}_2\text{-CO-CO}_2\text{-Ar}$ system. An oscilloscope tracing of the emission from a test with mixture 1 is shown in figure 1. Similar emission profiles were obtained from tests at 2460 and 2950 K with mixture 2 which contains 1 percent NO. Data on $[\text{O}][\text{CO}]$ as a function of laboratory time t_l were read from oscillograms, such as figure 1, with an optical comparator. The $[\text{O}][\text{CO}]$ profiles determined in this way are shown in figures 2 and 3 with the calculated results that are discussed in the following section. Each figure represents the average of two identical runs. The vertical bars represent the uncertainty in the $[\text{O}][\text{CO}]$ product calculated from the oscillogram traces. This uncertainty was determined from results of the calibration experiments and from the ratio of observed signal to noise from each test. The temperature T_2 and pressure p_2 are the average values immediately behind the shock, assuming no reaction; p_1 is the initial gas pressure in the test section prior to shock heating.

DISCUSSION OF RESULTS

In order to evaluate the experimental results in terms of a kinetic scheme, the experimental $[O][CO]$ profiles were compared with the results obtained from an analytical study of the reaction mechanism and rate coefficients given in table II. The rate coefficients listed in table II were taken from references 4 to 6 and 10 to 26. The $[O][CO]$ product profile was determined from $[O]$ and $[CO]$ profiles calculated by means of a non-equilibrium computer program (ref. 26). This program numerically integrated the reaction rate equations subject to the constraints imposed by the conservation equations for a shock wave and the effect of boundary-layer formation behind the shock wave.

In the analytical study, the rate coefficients for all reactions listed in table II were varied individually by factors of up to 10, and the effect on the calculated $[O][CO]$ profiles was noted. The results of this parametric study were as follows. Reactions (1), (2), and (10) had the most significant effect on the calculated $[O][CO]$ profiles for the H_2 -CO-CO₂-Ar reaction system (mixture 1). The H_2 -CO-CO₂-Ar reaction scheme and rate coefficients listed in table II (reactions (1) to (11)) reproduced reasonably well the measured $[O][CO]$ profiles for mixture 1. (See fig. 2.)

For the H_2 -CO-CO₂-NO-Ar reaction system (mixture 2), reactions (1), (2), (10), and (12) to (16) had the most significant effect on the calculated $[O][CO]$ profiles. The parametric study also revealed that reactions (17) to (25) could be omitted from the H_2 -CO-CO₂-NO-Ar reaction scheme without measurably affecting the calculated $[O][CO]$ profiles. These reactions made no appreciable contribution to the overall rate of the reaction under the test conditions.

Since the rate coefficients selected for reactions (1), (2), and (10) resulted in very good agreement between the calculated and measured $[O][CO]$ profiles for mixture 1, any differences between the calculated and measured $[O][CO]$ profiles for mixture 2 were assumed to be the result of reactions (12) to (16). There were, however, no measurable differences between the calculated and measured results for mixture 2. The rate coefficients selected for reactions (12) to (16) reproduced the measured profiles very well. (See fig. 3.)

The effect of reactions (15) and (16) and reaction (14) on the $[O][CO]$ product is shown in figure 4. The catalytic dissociation of molecular hydrogen, reactions (15) and (16), plays an important role during the initial stages of the reaction, whereas reaction (14) becomes important during the later stages. As shown in figure 4, reaction (14) must be included in the reaction mechanism to obtain agreement with the experimental results. Adjusting the rate coefficient for reaction (14) up to 30 percent also gave good agreement. It was not possible to adjust the rate coefficients for reactions (15) and (16), while omitting reaction (14), and still obtain reasonable agreement between the calculated

and measured $[O][CO]$ profiles. The rate coefficients for reactions (12) and (13) are known very well; therefore, no adjustment to these values seemed justified.

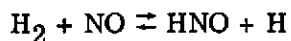
CONCLUDING REMARKS

By an experimental and analytical study of the kinetics of the H_2 -CO-CO₂-NO-Ar reaction system, it was determined that the low-temperature rate coefficient for the reaction between the nitrogen atom and the hydroxyl radical,



is also adequate to describe the rate of this reaction at high temperatures. Therefore, the use of the low-temperature rate coefficient for this reaction in high-temperature nitric oxide formation schemes is justified.

It was also determined that nitric oxide plays a significant role in the catalytic dissociation of molecular hydrogen through the reaction sequence



Langley Research Center,
National Aeronautics and Space Administration,
Hampton, Va., February 28, 1975.

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TABLE I.- COMPOSITION OF EXPERIMENTAL GAS MIXTURES

Chemical species	Percent by mole in --	
	Mixture 1	Mixture 2
H ₂	4	4
CO	2	2
CO ₂	1	1
NO	0	1
Ar	93	92

TABLE II.- H₂-CO-CO₂-NO-Ar REACTION MECHANISM

Reaction	Rate coefficient, k (a)	Refs.
(1) H ₂ + Ar → 2H + Ar	$9.35 \times 10^{13} \exp(-44740/T)$	10
(2) CO ₂ + Ar → CO + O + Ar	Obtained from $k_{-2} = 6 \times 10^{13}$	11
(3) OH + H ₂ → H ₂ O + H	$5.2 \times 10^{13} \exp(-3271/T)$	12
(4) H + O ₂ → OH + O	$1.22 \times 10^{17} T^{-0.907} \exp(-8369/T)$	13
(5) O + H ₂ → OH + H	$2.07 \times 10^{14} \exp(-6920/T)$	13
(6) OH + CO → CO ₂ + H	$4.0 \times 10^{12} \exp(-4026/T)$	12
(7) CO + O ₂ → CO ₂ + O	$1.6 \times 10^{13} \exp(-20634/T)$	14
(8) OH + OH → H ₂ O + O	$5.5 \times 10^{13} \exp(-3523/T)$	12
(9) O ₂ + Ar → 2O + Ar	$1.4 \times 10^{21} T^{-1.8} \exp(-59400/T)$	15
(10) H + OH + Ar → H ₂ O + Ar	$8.4 \times 10^{21} T^{-2.0}$	16
(11) H ₂ + O ₂ → OH + OH	$1.7 \times 10^{13} \exp(-24232/T)$	17
(12) O + NO → N + O ₂	$3.2 \times 10^9 T \exp(-19677/T)$	4
(13) N + NO → O + N ₂	$3.1 \times 10^{13} \exp(-168/T)$	5
(14) H + NO → N + OH	Obtained from $k_{-14} = 4 \times 10^{13}$	6
(15) H ₂ + NO → HNO + H	$1.4 \times 10^{13} \exp(-27630/T)$	18, 19
(16) HNO + Ar → H + NO + Ar	$1.0 \times 10^{19} T^{-1.0} \exp(-23150/T)$	18, 19
(17) HNO + NO → N ₂ O + OH	$2.0 \times 10^{12} \exp(-13085/T)$	19
(18) H + N ₂ O → N ₂ + OH	$4.0 \times 10^{13} \exp(-6039/T)$	20
(19) N ₂ O + Ar → N ₂ + O + Ar	$1.2 \times 10^{13} \exp(-22194/T)$	21
(20) OH + HNO → NO + H ₂ O	9.0×10^{13}	18
(21) N ₂ O + CO → N ₂ + CO ₂	$2.1 \times 10^{11} \exp(-8706/T)$	22
(22) NO + CO ₂ → NO ₂ + CO	Obtained from $k_{-22} = 1.2 \times 10^{13} \exp(-15903/T)$	23
(23) NO + N ₂ O → NO ₂ + N ₂	$2.0 \times 10^{14} \exp(-25163/T)$	24
(24) NO + NO → N ₂ O + O	$2.4 \times 10^{10} \exp(-14595/T)$	25
(25) NO ₂ + Ar → NO + O + Ar	$1.1 \times 10^{16} \exp(-32713/T)$	26

^aThe units for k are cm³/mol-sec for bimolecular reactions and cm⁶/mol²-sec for termolecular reactions. Subscripts to k correspond to reaction number; negative subscripts denote reverse reactions.

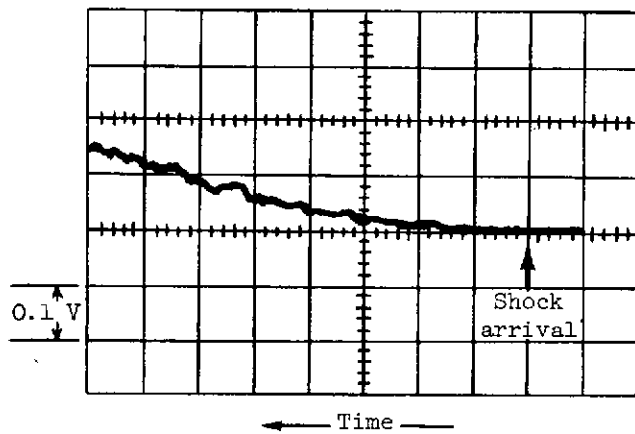
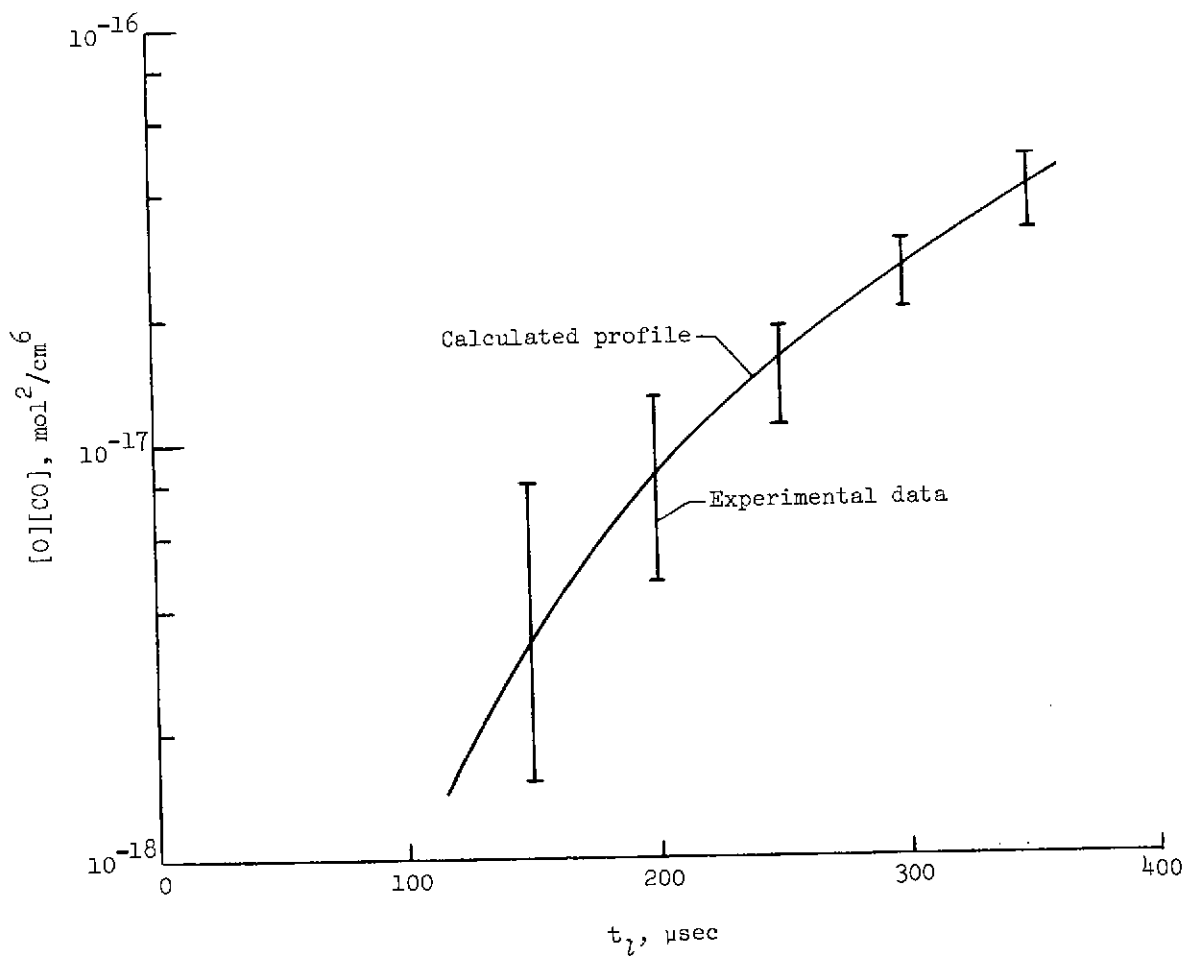
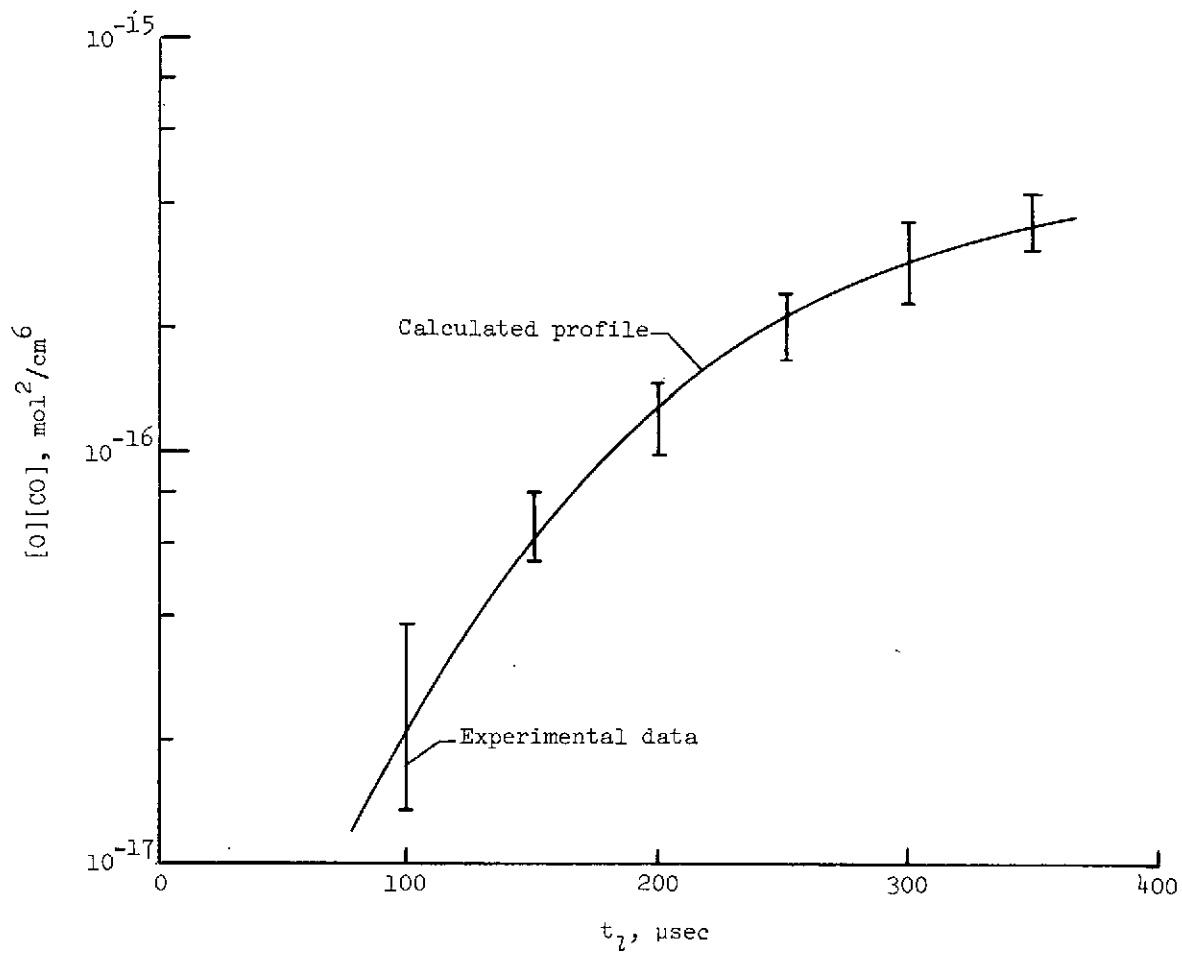


Figure 1.- Oscillogram tracing of the emission profile for the $\text{H}_2\text{-CO-CO}_2\text{-Ar}$ gas mixture. $T_2 = 2910 \text{ K}$; $p_2 = 0.98 \text{ atm}$; $50 \mu\text{sec/cm}$ sweep.



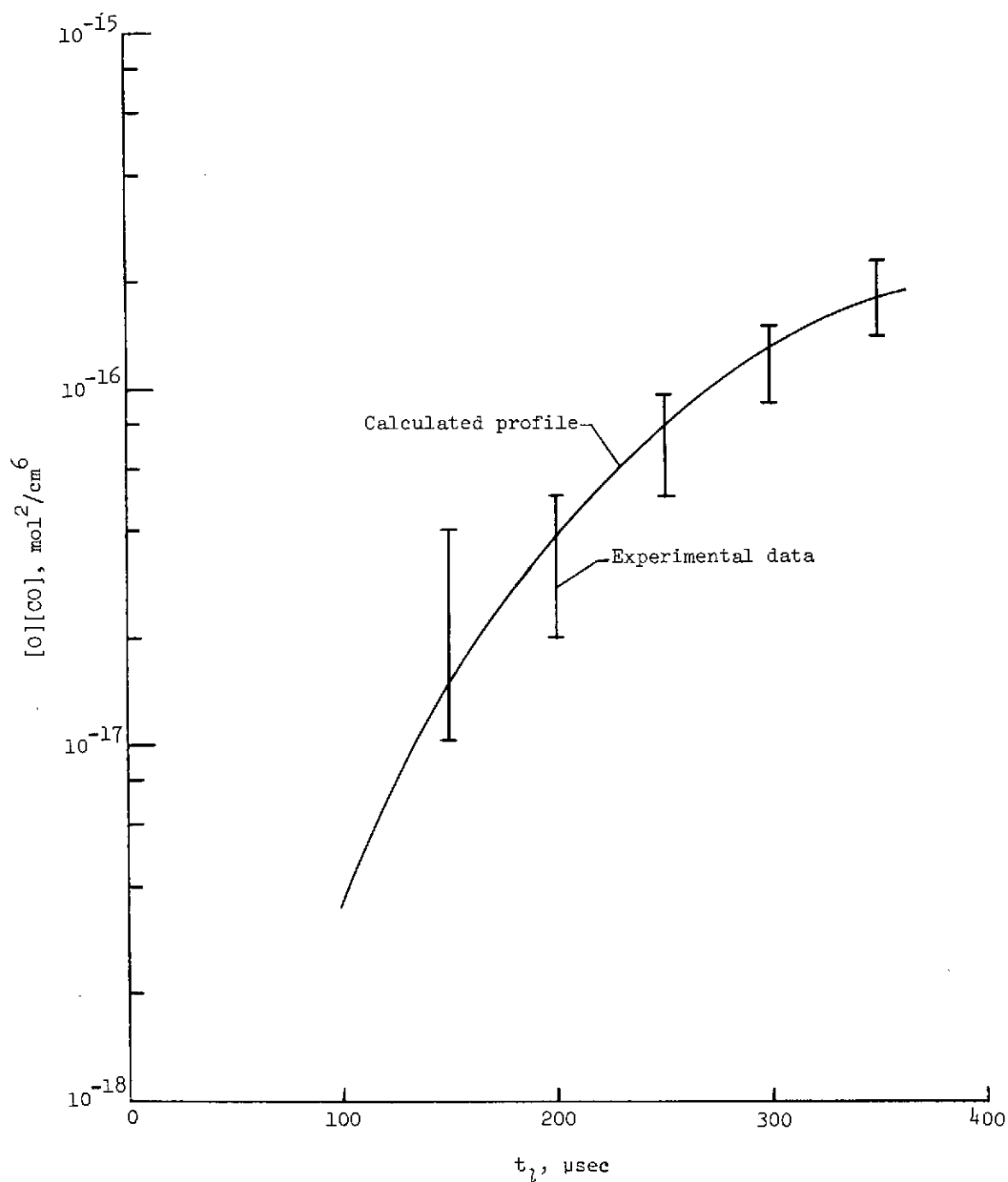
(a) $p_1 = 20 \text{ mm Hg}$; $T_2 = 2690 \pm 60 \text{ K}$; $p_2 = 0.90 \pm 0.05 \text{ atm}$.

Figure 2.- Calculated and experimental $[O][CO]$ profiles for $\text{H}_2\text{-CO-CO}_2\text{-Ar}$ gas mixture.



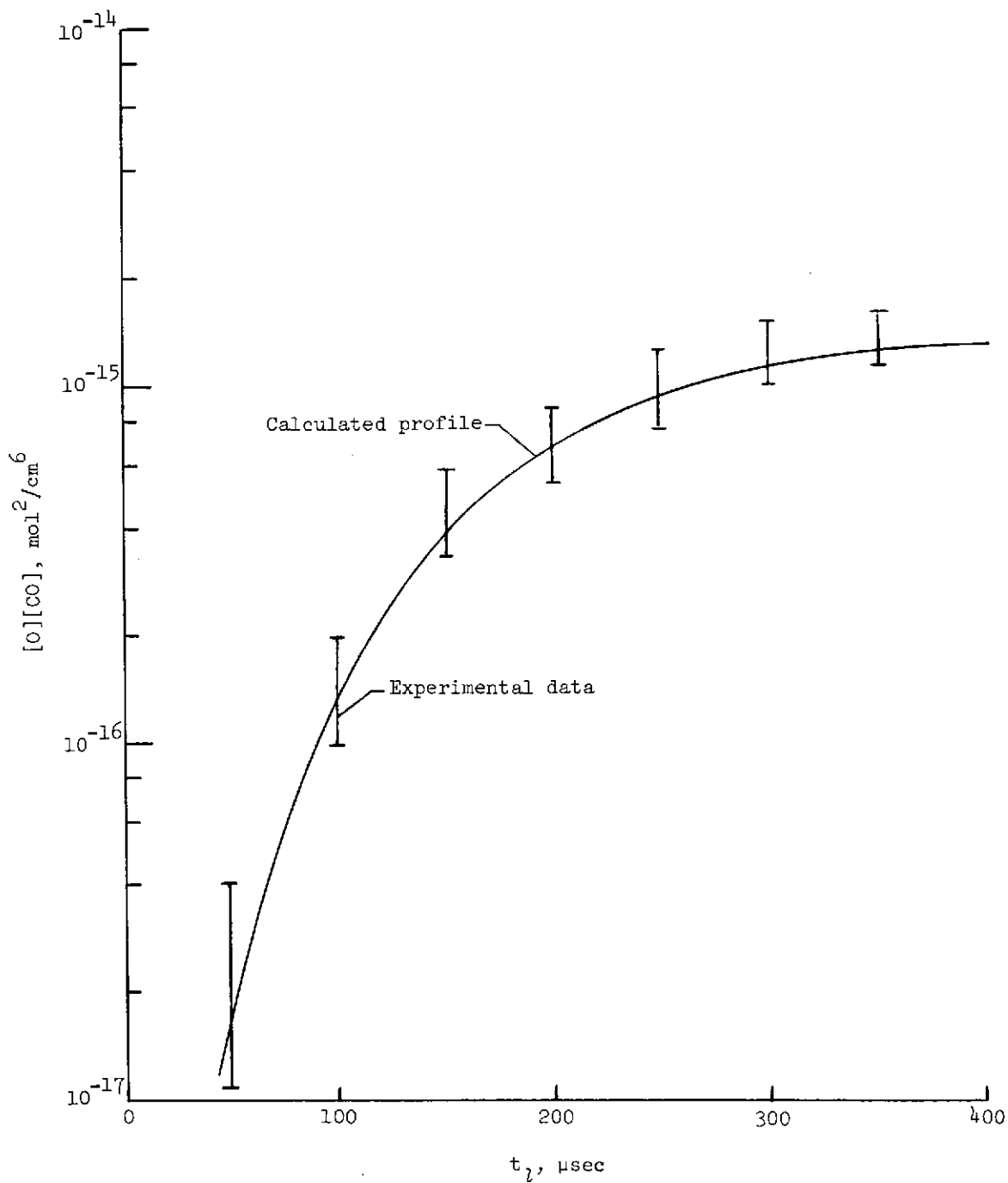
(b) $p_1 = 20$ mm Hg; $T_2 = 2920 \pm 20$ K; $p_2 = 0.99 \pm 0.01$ atm.

Figure 2.- Concluded.



(a) $p_1 = 40$ mm Hg; $T_2 = 2960 \pm 20$ K; $p_2 = 1.64 \pm 0.03$ atm.

Figure 3.- Calculated and experimental $[O][CO]$ profiles for H_2 -CO-CO₂-NO-Ar gas mixture.



(b) $p_1 = 20 \text{ mm Hg}$; $T_2 = 2950 \pm 30 \text{ K}$; $p_2 = 1.01 \pm 0.03 \text{ atm}$.

Figure 3.- Concluded.

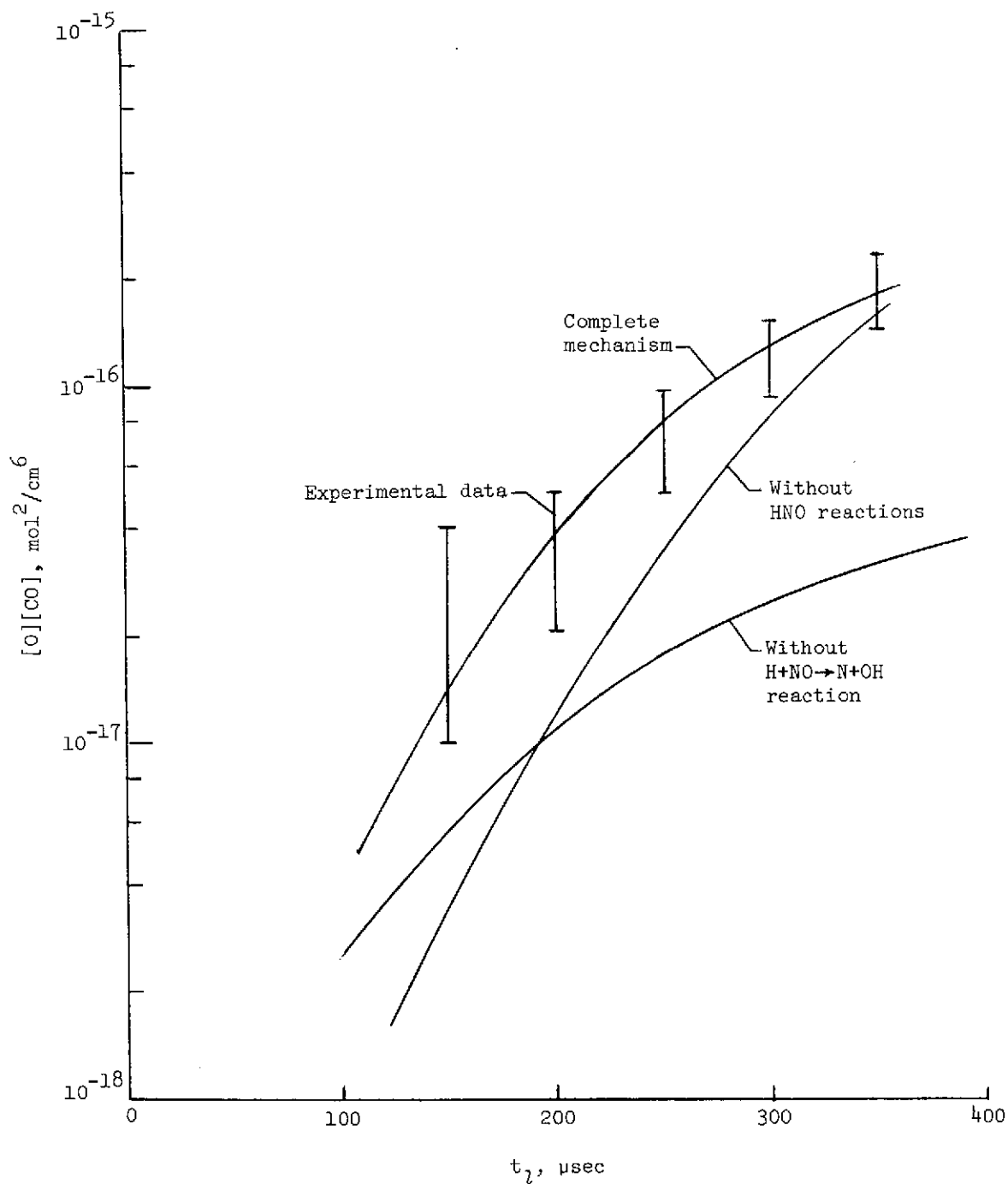


Figure 4.- Calculated $[O][CO]$ profiles for complete mechanism (reactions (1) to (16)), without $H + NO \rightarrow N + OH$ reaction (reaction (14)), and without HNO reactions (reactions (15) and (16)). $p_1 = 40$ mm Hg; $T_2 = 2460$ K; $p_2 = 1.64$ atm.