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Shock Tube Measurement of Nitric Oxide and Atomic Oxygen by Chemiluminescent Radiation

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A method is developed for the shock tube measurement of nitric oxide and atomic oxygen from the chemiluminescent radiation which is proportional to the product of their concentrations. The method is dependent on the assumptions that the nitric oxide formation is governed by the Zeldovich mechanism, and is not close to chemical equilibrium, and offers the advantage of determining both [NO] and [O] from a single measurement. Time-resolved profiles of these species in mixtures with hydrogen or methane as fuel show good agreement with chemical kinetics calculations, although some difficulty was experienced with background radiation. The background radiation, which could not be eliminated, limits the minimum measurable mole fraction product to $X_{NO}X_O = 6.397 \exp(-82037/R_0T)$ for mixtures diluted with argon. Determination of [CO], which required an additional measurement, was also made in the methane mixtures. However, the measured trends do not agree with those calculated, although correct levels are obtained.

Nomenclature

h = Planck's constant
I = absolute intensity of radiation
I_λ = spectral intensity of radiation
K_c = equilibrium constant (concentration)
k = chemical kinetic or chemiluminescent rate constant
M = third molecule
R_0 = universal gas constant
T = absolute temperature
t = time
λ = wavelength
ν = frequency of radiation

Subscripts

1 = radiation at 6116 Å ($\Delta\lambda = 60$ Å)
2 = radiation at 3958 Å ($\Delta\lambda = 98$ Å)
$1b,2b,3b$ = backward direction for reaction I, II, or III
$1f,2f,3f$ = forward direction for reaction I, II, or III
a = due to background radiation
c = due to CO-O radiation
e = equilibrium value
n = due to NO-O radiation
t = due to NO_2 thermal radiation

Introduction

TWO basic methods have been used almost exclusively for the measurement of nitric oxide in the shock tube—ultraviolet absorption and infrared emission. Both methods are characterized by sophisticated systems such as hollow cathode lamps, cryogenically cooled photovoltaic and photoconductive detectors, and their associated amplifier circuits. In addition, these techniques are usually complicated by interference from the surrounding atmosphere or the test gas itself.

A much simpler method has been developed by Lavoie et al.,[1,2] for measurement of NO in a CFR internal combustion engine. This technique has been used recently in a shock tube by Dabora et al.[3] The basis of Lavoie's method is the measurement of the chemiluminescent radiation emitted in the two reactions:

$$NO + O \rightleftharpoons NO_2 + h\nu \tag{1}$$

$$CO + O \rightleftharpoons CO_2 + h\nu \tag{2}$$

Clyne and Thrush[4] have shown that the intensity of radiation from these two reactions is proportional to the concentration of the reactants. Thus,

$$I_{1n} = k_1 [NO][O] \tag{3}$$

$$I_{2c} = k_2 [CO][O] \tag{4}$$

Here, the intensity of radiation is defined as the total energy emitted per unit volume per unit time in a solid angle of 4π sr.

The measurement of I_{1n} and I_{2c} as a function of time determines the two concentration products, [NO][O] and [CO][O], when k_1 and k_2 are known. Lavoie was able to show that in his experiments, [CO] was always in chemical equilibrium and thus could be calculated easily. In this case, time-resolved [NO] and [O] profiles could be obtained from the radiation measurements, I_{1n} and I_{2c}, through Eqs. (3) and (4).

The advantage of Lavoie's method over ultraviolet absorption and infrared emission techniques is that radiation measurements are taken in the visible region of the spectrum; hence, a simple photomultiplier tube arrangement may be used. Lavoie performed his measurements in 100 Å bands at 3800 Å and 6100 Å, which are near the peaks of the CO-O and NO-O chemiluminescent continua, respectively.

In the aforementioned study by Dabora et al., equilibrium of [CO] could not be assumed; therefore, [CO] was determined from chemical kinetics calculations. Baulch et al.[5] indicate that considerable uncertainty exists in the rates for CO kinetics at combustion temperatures (2000-3000 K). In fact, adjustment of the rate constants for two of the major reactions in the CO system was required by Dabora et al. in

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order to obtain reasonable agreement between measured and calculated values of the [NO] [O] and [CO] [O] concentration products.

Thus, it appears that for applications where the assumption of equilibration of [CO] cannot be assumed, such as in some shock tube experiments, some revisions in the method are required. The objective of the present investigation is to remove the dependence of the chemiluminescent method on the calculation of [CO]. In this way, the accuracy of [NO] measurement may be improved.

Method of [NO] Measurement

The method which is developed here will be restricted to those cases where the NO formation process is governed by the so-called extended Zeldovich mechanism

$$N_2 + O \rightleftharpoons NO + N \qquad (I)$$

$$O_2 + N \rightleftharpoons NO + O \qquad (II)$$

$$OH + N \rightleftharpoons NO + H \qquad (III)$$

The time rate of change of [NO] may be obtained by applying the law of mass action to the preceding system. Thus,

$$\frac{d[NO]}{dt} = k_{1f}[O][N_2] + k_{2f}[O_2][N] + k_{3f}[N][OH] - k_{1b}[NO][N] - k_{2b}[NO][O] - k_{3b}[NO][H] \qquad (5)$$

In order to obtain a solution for [NO], it is necessary to eliminate [N]. For combustion processes which do not involve fuel nitrogen, the only source of N atoms is the Zeldovich mechanism. Thus, a similar expression is obtained for atomic nitrogen, namely,

$$\frac{d[N]}{dt} = k_{1f}[O][N_2] - k_{2f}[O_2][N] - k_{3f}[N][OH] - k_{1b}[NO][N] + k_{2b}[NO][O] + k_{3b}[NO][H] \qquad (6)$$

The amount of [N] produced in reactions (I-III) is several orders of magnitude less than [NO], and [N] rapidly reaches a slowly shifting equilibrium so that, except for very early times, the assumption of steady [N] applies. The numerical calculations of Laurendeau and Sawyer[6] have confirmed this assumption, which is widely used.[7] Applying the steady-state assumption, and adding Eqs. (5) and (6), several terms cancel out, yielding

$$\frac{d[NO]}{dt} = 2k_{1f}[O][N_2] - 2k_{1b}[NO][N] \qquad (7)$$

The last term may be neglected when

$$\frac{[NO][N]}{[O][N_2]} \ll \frac{k_{1f}}{k_{1b}} = K_{c1} \qquad (8)$$

Fortunately, reaction I is the slowest in the Zeldovich mechanism, and the assumption can be justified in many instances. In this case, Eq. (7) reduces to

$$\frac{d[NO]}{dt} = 2k_{1f}[O][N_2] \qquad (9)$$

Now the quantity I_{1n} can be measured as a function of time; thus, using Eq. (3), we have

$$[NO]\frac{d[NO]}{dt} = \frac{2k_{1f}}{k_1}[N_2]I_{1n}(t) \qquad (10)$$

Also, the depletion of N_2 due to the formation of NO and N is quite small, so that $[N_2]$ may be considered constant and equal to its equilibrium value. In this case, the right-side of Eq. (10) is a known function of time and may be integrated to obtain

$$[NO] = \left\{\frac{4k_{1f}}{k_1}[N_2]_e \int_0^t I_{1n}(t)\,dt\right\}^{1/2} \qquad (11)$$

The oxygen atom concentration follows directly from Eq. (3),

$$[O] = I_{1n}/k_1[NO] \qquad (12)$$

Thus, under the assumptions of steady [N] and nonequilibrium of the Zeldovich mechanism, time-resolved [NO] and [O] profiles may be uniquely determined from the single radiation measurement, I_{1n}.

This technique has certain advantages over Lavoie's method. First, a second radiation measurement to determine [O] is not required in order to extract [NO] from the measured [NO] [O] product. Second, the value of [CO] is not needed at all in order to determine [NO]. Hence, the method can be applied to cases where [CO] is not even present.

However, in the general case where both NO-O and CO-O radiation are present, two measurements must be taken in order to determine I_{1n}. These two measurements should be taken near the peaks of the respective chemiluminescent continua in order to maximize sensitivity. Another complicating factor which must be accounted for is the presence of thermal radiation from NO_2 above 4000 Å. Thus, the two radiation measurements will consist of the following components:

$$I_1 = I_{1n} + I_{1c} + I_{1t} \qquad (13)$$

$$I_2 = I_{2c} + I_{2n} \qquad (14)$$

where I_1 is measured near the peak of the NO-O continuum and I_2 is measured near the peak of the CO-O continuum. Introducing continua shape factors, I_{2n}/I_{1n} and I_{1c}/I_{2c}, and normalizing I_{1t} results in

$$I_1 = (1 + I_{1t}/I_{1n})I_{1n} + (I_{1c}/I_{2c})I_{2c} \qquad (15)$$

$$I_2 = (I_{2n}/I_{1n})I_{1n} + I_{2c} \qquad (16)$$

These two algebraic equations may be solved for I_{1n} and I_{2c} when the three quantitites I_{1t}/I_{1n}, I_{1c}/I_{2c}, and I_{2n}/I_{1n} are known. Once I_{1n} and I_{2c} are determined, then [CO] can also be measured after determining [NO] and [O] from Eqs. (11) and (12). This follows directly from Eq. (4), i.e.,

$$[CO] = I_{2c}/k_2[O] \qquad (17)$$

In this study, I_{1t}/I_{1n} was determined from the semiempirical theory of Levitt[8,9] together with the assumption that the reaction

$$NO + O \rightleftharpoons NO_2 \qquad (18)$$

is in shifting equilibrium. Kinetic calculations have confirmed the validity of this assumption.

There is only a minimal amount of high-temperature data available for the spectral shapes of the NO-O and CO-O continua. These data are insufficient to establish the temperature variation of the other two required quantities, I_{2n}/I_{1n} and I_{1c}/I_{2c}. For this reason, they were experimentally determined in this investigation.

Experimental Apparatus

The experiments were conducted behind reflected shock waves in a 5.08 cm^2 aluminum and stainless steel vertical shock tube. The driven section is 2.74 m long and originally contained 8 windows, which were replaced first with aluminum blanks and later with stainless steel blanks. An aluminum reflecting block was installed in the upper end of the tube which was sealed with a steel flange. The aluminum block was also eventually replaced with stainless steel. The test section was originally located 1.96 m from the diaphragm section, but was moved up to a point 2.61 m away in order to increase the test time to about 500 μs. The pressure in the test section was monitored with a Kistler model 613F pressure transducer, placed 7 mm from the end wall. A second transducer was mounted at a distance of 61 cm ahead of the first to time the incident shock wave. The measured Mach number was used to calculate the temperature behind the reflected wave. Aluminum diaphragms were used for all runs.

A McPherson model 216.5 polychromator was used to monitor light emission from the test section through a 5.04-cm-diam quartz window. Two RCA 1P28 photomultiplier tubes were mounted behind slits in the exit plane of the polychromator to record the intensities of radiation, I_2 and I_1 at 3958 Å and 6116 Å in effectively full-intensity bandwidths of 98 Å and 60 Å, respectively. Each photomultiplier tube was calibrated with an Epply Laboratories tungsten ribbon lamp which had been calibrated against an NBS lamp by the manufacturer. Additional details concerning the construction, operation, and calibration of the shock tube and optical system may be found in Ref. 10.

All gases used in the experiments were obtained from the Matheson Gas Products Company. Mixtures were prepared manometrically and allowed to stand overnight before use.

Background Radiation

Initial experiments revealed the presence of a background radiation that could not be eliminated. Some of these results have been reported previously by Dabora et al.[3] Measurable radiation was detected at both 3958 Å and 6116 Å in runs made with pure argon, which was used as a diluent in all gas mixtures. The radiation observed at 3958 Å was considerably less than the levels of the CO-O radiation expected with mixtures containing carbon compounds and, therefore, presented no difficulty. However, the background at 6116 Å was found to be of the same order of magnitude as the expected NO-O levels. Several attempts were made to identify the source of the background by such means as mass spectrometer analysis and filtering of test gases, thorough cleaning of the tube and diaphragms, installation of a cold trap on vacuum pumps, and sealing of leaks around the reflecting block. These all had little effect on the background.

Additional experiments were then performed to investigate the nature of the background. Several runs were made with pure argon with initial pressures varying from 0.6-0.03 atm at temperatures ranging from 2500-3800 K. The data taken at 100 μs after the passage of the reflected wave are shown in Fig. 1, where the intensity of radiation measured at 6116 Å, normalized by the square of the argon concentration behind the reflected shock, is plotted against reciprocal temperature. The temperature was determined from the incident shock Mach number using the Gordon and McBride[11] computer program. It can be seen that the data correlate quite well with a single least-squares straight line, although there is some scatter. These data indicate a rapid increase in the radiation with temperature, with an activation energy of about 69 k cal/mole. Additional data were taken at an initial pressure of 0.25 atm with the aluminum blanks and reflecting block replaced with stainless steel. These are shown as the solid symbols in Fig. 1, and indicate a decrease in the radiation by a factor of about 5 and a reduction in activitation energy of about 10%.

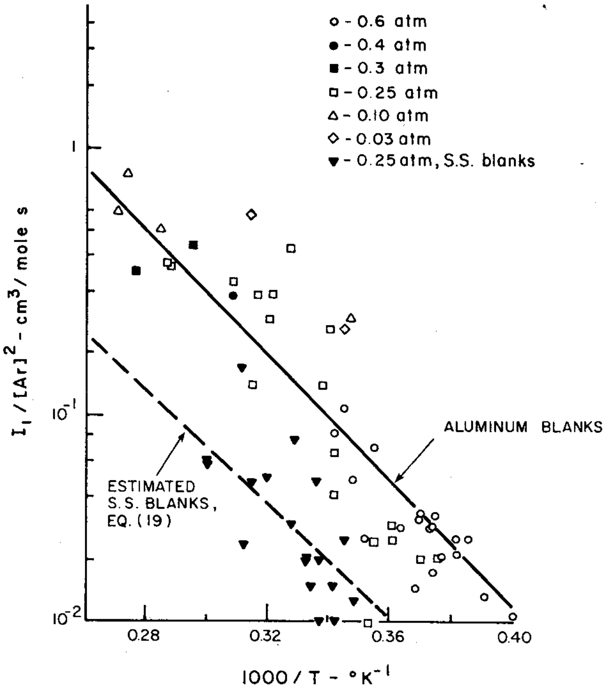

Fig. 1 Intensity of radiation at 6116 Å from argon at $t = 100$ μs.

The data taken at 6116 Å for other times showed that the radiation also increases with time, but more slowly at the higher temperatures. Measurements taken at 3958 Å also showed an increase in intensity with both time and temperature, but here the time rate of change increased with temperature, suggesting that two different phenomena may be involved at the two wavelengths.

The reason for the decrease in background radiation with stainless steel walls could not be pinpointed. Photographic spectra taken in multiple open shutter exposures with both aluminum and stainless steel blanks showed no essential differences. The only spectral lines observed near 6116 Å were from the argon spectrum and these occurred sporadically in the higher temperature runs near 4000 K. These lines were reasoned to be prominent in the open shutter spectra because of contact surface-wave interactions which appear in the test section at times beyond the ordinarily usable test time. Thus, it is felt that the argon spectrum was not responsible for the background radiation during the actual test time. Two strong aluminum emission lines (3944 and 3962 Å) were found in the lower bandwidth centered at 3958 Å, and may be related to the small background observed there.

A spectral survey taken with the photomultiplier tube from 6000-6200 Å in two sets of intervals (15.2 and 30.4 Å) at a temperature of 2840±50 K revealed a relatively flat continuum with an intensity approximately 10^{-4} times less than blackbody radiation in this region. Thus there are no "windows" near the peak of the NO-O chemiluminescent continuum which are free of background radiation. These results also confirm the conclusion reached earlier—that the background radiation near 6116 Å is not from the argon emission spectrum.

The observations that the background is a continuum whose intensity varies with the square of the argon concentration suggest that the background may be the result of Bremsstrahlung radiation. At the relatively low temperatures reached in the present experiments, ionization is quite small and, therefore, if Bremsstrahlung radiation does exist, it is much more likely to result from the interactions of free electrons with neutral argon atoms rather than with ions.

Cross sections for neutral Bremsstrahlung radiation have not been measured at low temperatures. The data taken by

Taylor and Caledonia[12] in a 9000-12,000 K temperature range indicates that, while neutral Bremsstrahlung radiation from argon varies strongly with temperature, this is due mainly to the large variation in the degree of ionization. The variation in the effective cross sections is relatively weak, being on the order of the square root of the temperature. Thus, extrapolation of their data should give results which are correct to within an order of magnitude. When this is done, radiative absorption cross sections on the order of 4×10^{-39} cm^5 are obtained near 6000 Å. These values appear to be more reasonable than those calculated by Geltman[13] which are about 10^{-40} cm^5 at 2840 K. Using the extrapolated data, the electron mole fraction which is required to produce the intensity of radiation measured from argon near 6116 Å at a temperature of 2840 K, is 10^{-5}. While this figure is relatively large compared to the degree of ionization at this temperature (less than 10^{-8}), it is not totally unreasonable and implies that some source other than ionization is responsible for the radiation. Aluminum particles from the diaphragms are suspected to be a possible source.

Since the background radiation at 6116 Å could not be eliminated, there is a limitation on the level of NO-O chemiluminescent radiation which can be measured accurately. Taking the radiation intensity at a time of 100 μs as representative, and correcting the data taken with aluminum blanks (the solid line in Fig. 1) for the effect of stainless steel walls, the following expression is obtained:

$$I_{la}/[\mathrm{Ar}]^2 = 8.501 \times 10^2 \exp(-62{,}223/R_0T)\,\mathrm{cm}^3/\mathrm{mole\ s} \quad (19)$$

This equation is shown as the dashed line in Fig. 1. The NO-O radiation must be significantly above this value for accurate measurement.

Measurement of [NO] and [O]

Time-resolved [NO] and [O] profiles were measured behind reflected shocks with mixtures consisting of $1H_2 + 10O_2 + 9N_2 + 80Ar$ and $0.66CH_4 + 9.74O_2 + 9.60N_2 + 80Ar$. These were selected so that the measurements could be made both with and without interference from CO-O radiation. Also, the composition of each mixture was selected such that the magnitude of the chemiluminescent radiation would be well above the background, in accordance with Eq. (19).

The rate constant for the NO-O radiation, k_l, was determined from radiation measurements taken with a mixture of $3NO_2 + 97Ar$ in a temperature range 2300-2700 K. Kinetic calculations were performed for this mixture using the kinetic scheme of Weinberger,[14] rate constants from Baulch,[5] and the NASA computer program developed by Bittker and Scullin,[15] assuming a constant volume process behind the reflected shock. These results indicated that in the time period of interest, the NO_2 dissociates to NO and O in a quasiequilibrium state in which the conversion of NO to N_2O proceeds slowly. The measured [NO] [O] profiles showed that the quasiequilibrium state lasted progressively shorter times as the temperature increased, but was at least 100 μs in all cases.

In order to account for background radiation, the argon data were plotted in Arrhenius form and fit with least-squares straight lines for discrete times of 50-400 μs in 50 μs intervals. These corrections were applied to the measurements taken with the NO_2-Ar mixture and were less than 10%. Additional corrections on the order of 6-12% were made for NO_2 thermal radiation using the Levitt[8,9] theory and required an iterative process since k_l was unknown at this stage of the calculations. The [NO] [O] product and the temperature in the quasiequilibrium state were calculated using the equilibrium program of Gordon and McBride[11] by omitting the products N, N_2, and N_2O to simulate quasiequilibrium. Selected kinetic calculations gave nearly the same results.

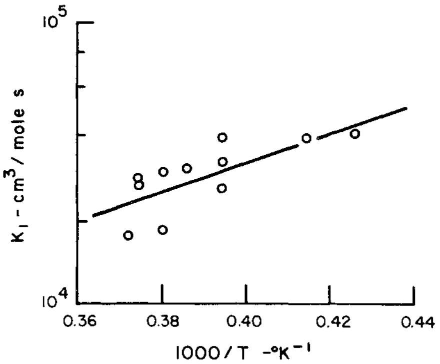

Fig. 2 Measured values of the NO-O chemiluminescent rate constant vs temperture.

The values of k_l obtained from the NO-O radiation measured at a time of 100 μs converged within 2% in three iterations. These are shown plotted in Arrhenius form in Fig. 2. The straight line is a least-squares fit which results in

$$k_l = 5.136 \times 10^2 \exp(19814/R_0T) \text{ for } 2300 \leq T \leq 2700\,\mathrm{K} \quad (20)$$

Equation (20) gives values of k_l which are 2-3 times higher than those estimated by Dabora et al.[3] from limited experimental data.

Equations (19) and (20) can now be used to establish the minimum [NO] [O] concentration product which can be measured with the present method. If it is assumed that the NO-O radiation should be at least a factor of four greater than the background as reasonable, and also that the mixtures are diluted largely with argon, the following expression is derived for the minimum measurable mole fraction product

$$X_{\mathrm{NO}} X_{\mathrm{O}} = 6.397 \exp(-82037/R_0T) \quad (21)$$

This expression gives values which are approximately 17 times lower than those quoted in Ref. 3. This discrepancy can be attributed to the effect of the stainless steel walls, and also to an overly restrictive criterion used in that reference.

Several runs were made with the H_2-O_2-N_2-Ar mixture over an equilibrium temperature range of 2500-2900 K behind the reflected shock at an initial pressure of 0.25 atm. The radiation measurements taken at 6116 Å were corrected for background using the least-squares fits to the argon data and the Levitt theory for NO_2 thermal radiation as before. The background corrections were on the order of 20%, although 40% was reached at a few isolated points. The NO_2 corrections were less than 10%. Using Eq. (20) for k_l, Eq. (11) was integrated to 400 μs using 50 μs intervals and a simple trapezoidal rule. The recommended expression from Baulch[5] was used for k_{lf}, using the average temperature in the 50-400 μs time period. This was generally within 20-30 K of the equilibrium temperature and was determined from the kinetic calculations to be described later. The value of $[N_2]_e$ was obtained with the Gordon and McBride computer program.

The resulting [NO] and [O] profiles were compared to chemical kinetics solutions obtained with the Bittker and Scullin[15] computer program. The kinetic scheme used is given in Table 1. The reactions and rates for the H_2-O_2-N_2 system were taken from Bowman[16] and are based on the earlier work of Schott.[17] Again, rates for the Zeldovich mechanism are from Baulch. Initial values of all variables were taken as the frozen conditions immediately behind the reflected shock, as determined with the Gordon-McBride program.

In general, the shapes of the measured [NO] and [O] profiles showed good agreement with the calculated values, especially for [O] which reaches equilibrium quickly. The measured [NO] [O] profile was consistently low by about a factor of 2, resulting in the [O] and [NO] profiles being low by

Table 1 Reaction mechanism for H_2-O_2-N_2-Ar mixture

Reaction	Rate constant[a]
	Zeldovich mechanism[5]
$0+N_2=NO+N$	$7.6\times10^{13}\exp(-75506/R_0T)$
$N+O_2=NO+O$	$6.4\times10^{9}T^{1.0}\exp(-6239/R_0T)$
$N+OH=NO+H$	4.0×10^{13}
	H_2-O_2-N_2 system[16]
$H_2+O_2=OH+OH$	$2.5\times10^{12}\exp(-39046/R_0T)$
$H+O_2=OH+O$	$2.2\times10^{14}\exp(-16790/R_0T)$
$O+H_2=OH+H$	$1.7\times10^{13}\exp(-9458/R_0T)$
$H+H_2O=H_2+OH$	$8.4\times10^{13}\exp(-20069/R_0T)$
$O+H_2O=OH+OH$	$5.8\times10^{13}\exp(-18022/R_0T)$
$H+H+Ar=H_2+Ar$	$1.0\times10^{18}T^{-1.0}$
$H+H+N_2=H_2+N_2$	$1.5\times10^{18}T^{-1.0}$
$O+O+Ar=O_2+Ar$	$3.0\times10^{17}T^{-1.0}$
$O+O+N_2=O_2+N_2$	$4.0\times10^{17}T^{-1.0}$
$M+H+OH=H_2O+M$	$2.0\times10^{19}T^{-1.0}$
$M+H+O_2=HO_2+M$	$1.6\times10^{15}\exp(1001/R_0T)$

[a] Units: cm, K, mole, s.

about a factor of $\sqrt{2}$. The results for two runs in about the middle of the temperature range are shown in Fig. 3. Calculated equilibrium values are also indicated.

The reason for the discrepancy between the experimental and calculated results was postulated to be due to the presence of oscillatory pressure variations of small amplitude (less than 5% of the pressure level) and to a decrease in pressure of about 20% within the usable test time. Such pressure records are believed to be due to detonationlike phenomena and have been observed in similar mixtures[18] and methane mixtures.[19]

The effects of the pressure variations could not be taken into consideration in establishing the initial conditions for the kinetic calculations.

In order to examine the accuracy of the experimental method when CO-O radiation is present, several runs were made with the CH_4-O_2-N_2-Ar mixture. The continuum shape factor I_{2n}/I_{In} was determined from measurements taken at 3958 Å together with those at 6116 Å taken with the NO_2-Ar and H_2-O_2-N_2-Ar mixtures used previously. Additional runs were made with a mixture consisting of 2 H_2 + 8.8 O_2 + 9.2 N_2 + 80 Ar. The measured values of the ratio of the spectral intensities $I_{\lambda 2n}/I_{\lambda In}$ are shown in Fig. 4. These values represent averages over appropriate time intervals and the straight line is a least-squares fit. Shown in the same figure is the deduced I_{2n}/I_{In} which is related to $I_{\lambda 2n}/I_{\lambda In}$ by the factor of 98/60 representing the ratio of the spectral intervals used. The experimental data result in

$$\log_{10}(I_{\lambda 2n}/I_{\lambda In}) = 0.982\times10^{-3}T - 3.673 \qquad (22)$$

Similar experiments were carried out with a 3 CO + 2.75 O_2 + 94.25 Ar mixture to determine $I_{\lambda Ic}/I_{\lambda 2c}$. Values obtained at times of 100 and 200 μs are shown in Fig. 5 along with the deduced ratio of I_{Ic}/I_{2c} which can be approximated by

$$I_{\lambda Ic}/I_{\lambda 2c} = 0.666 - 0.118\times10^{-3}T \qquad (23)$$

Again, the straight lines are least-squares fits used for data reduction. The data presented in Figs. 4 and 5 show that the spectral shape of each chemiluminescent continuum, particularly the NO-O continuum, changes with temperature.

The fact that $I_{\lambda 2n}/I_{\lambda In}$ changes much faster with temperature than $I_{\lambda Ic}/I_{\lambda 2c}$ is consistent with the characteristic shapes of the continua. Both continua are considerably steeper on the blue side of the peak than on the red side. Thus, a small shift in the location of the peak would have a larger

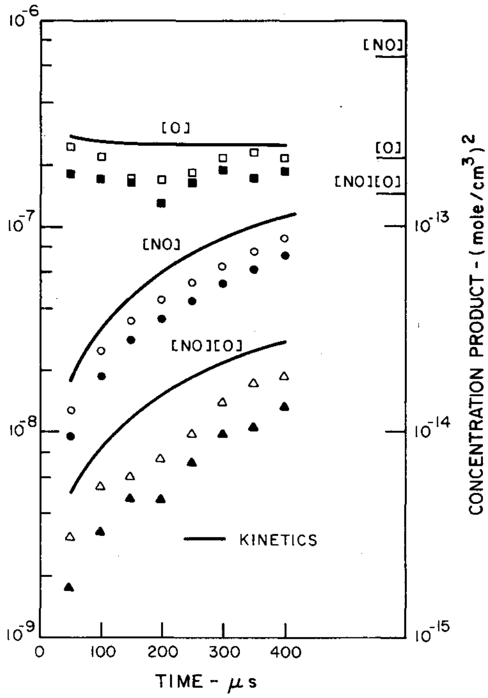

Fig. 3 Comparison of measured [NO] and [O] profiles with kinetic calculation for 1 H_2 + 10 O_2 + 9N_2 + 80 AR mixture (T_e = 2695 K, P_e = 20.57 atm, open symbols: run 866, filled symbols: run 867).

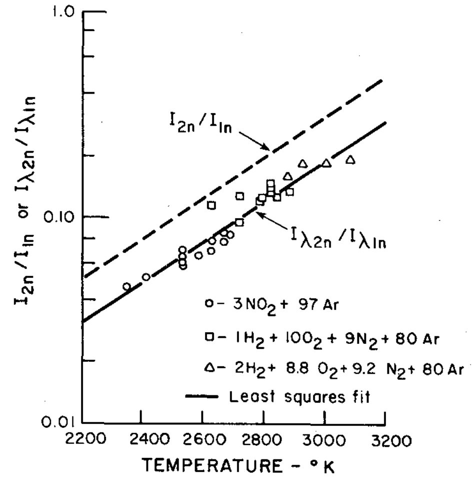

Fig. 4 Continuum shape factors, I_{2n}/I_{In} and $I_{\lambda 2n}/I_{\lambda In}$ vs temperature.

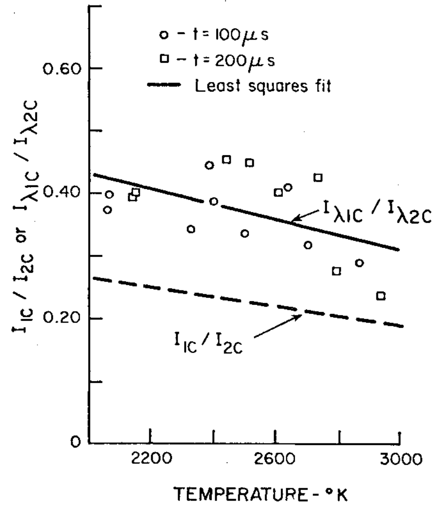

Fig. 5 Continuum shape factors, I_{Ic}/I_{2c} and $I_{\lambda Ic}/I_{\lambda 2c}$ vs temperature.

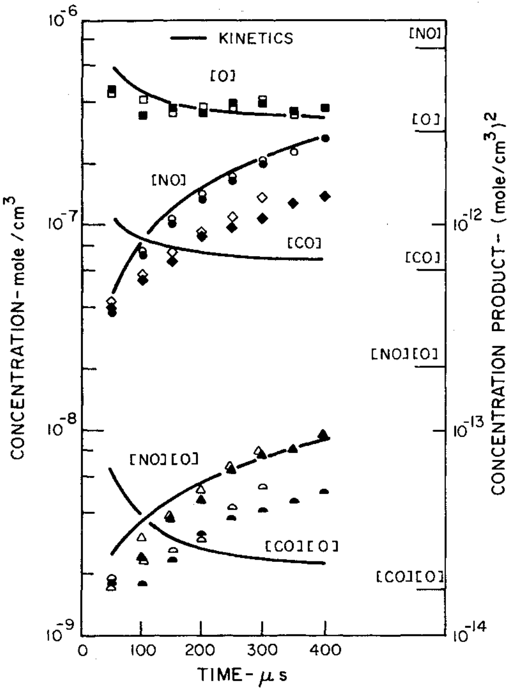

Fig. 6 Comparison of measured [NO], [O], and [CO] profiles with kinetic calculations for $0.66CH_4 + 9.74O_2 + 9.60N_2 + 80Ar$ mixture ($T_e = 2785$ K, $P_e = 21.04$ atm, open symbols: run 837, filled symbols: run 838).

effect on $I_{\lambda 2n}/I_{\lambda 1n}$, which is essentially a blue side-to-peak ratio, than on $I_{\lambda 1c}/I_{\lambda 2c}$, which is a red side-to-peak ratio.

The rate constant for the CO-O radiation was estimated by combining the data of Myers and Bartle[20] and Hartunian[21] to obtain

$$k_2 = 2.187 \times 10^4 \exp(-2500/R_0 T) \qquad (24)$$

In order to arrive at this equation, it was necessary to assume that the shape of the CO-O continuum did not change with temperature between 2600 and 3000 K. While the data in Fig. 5 indicate this is not strictly true, the error is not large and in any case would only effect the [CO] measurement.

Several shock tube runs were made with the methane mixture over a temperature range of 2600-2950 K. The initial pressure was 0.25 atm. The [NO] [O] and [CO] [O] concentration products were obtained from the radiation measurements at 6116 Å and 3958 Å using Eqs. (3), (4), (15), (16), (20), and (24) with the data in Figs. 4 and 5. Background corrections were less than 10% for I_l and 2% for I_2. Equation (11) was integrated as before with a trapezoidal rule at 50 μs intervals to obtain [NO], after which [O] and [CO] followed from Eqs. (12) and (17).

Theoretical calculations were made using the methane oxidation scheme of Jachimowski[22] which appears in Table 2, and the rates for the Zeldovich mechanism from Table 1. Initial conditions were taken as the frozen conditions behind the reflected shock as before. Excellent agreement between the theoretical and experimental [NO] and [O] profiles was obtained for this mixture. It is to be noted that no pressure decrease was observed behind the reflected shock for these runs. On the other hand, the measured [CO] [O] and [CO] profiles show complete disagreement with the theoretical trend as the measured values increase with time while the theoretical values decrease with time. However, the general levels are about the same. The results from two typical runs are shown in Fig. 6.

The difference between measured and calculated [CO] [O] and [CO] profiles cannot be readily explained. Unfortunately, Jachimowski does not present [CO] profiles, so it is not known how accurate the complete scheme is relative to this one specie; therefore, the question cannot be resolved.

Table 2 Methane oxidation mechanism[22]

Reaction	Forward rate constant[a]
$CH_4 + Ar = CH_3 + H + Ar$	$2.0 \times 10^{17} \exp(-44500/T)$
$H + CH_4 = CH_3 + H_2$	$1.26 \times 10^{14} \exp(-5989/T)$
$O + CH_4 = CH_3 + OH$	$2.0 \times 10^{13} \exp(-4640/T)$
$OH + CH_4 = CH_3 + H_2O$	$3.0 \times 10^{13} \exp(-3020/T)$
$CH_3 + O_2 = CH_2O + OH$	1.0×10^{11}
$CH_3 + O = CH_2O + H$	$1.3 \times 10^{14} \exp(-1006/T)$
$CH_2O + OH = HCO + H_2O$	2.3×10^{13}
$HCO + OH = CO + H_2O$	1.0×10^{13}
$CH_2O + Ar = CO + H_2 + Ar$	$2.10 \times 10^{16} \exp(-17614/T)$
$HCO + Ar = H + CO + Ar$	$2.00 \times 10^{12} T^{0.5} \exp(-14400/T)$
$OH + CO = CO_2 + H$	$4.0 \times 10^{12} \exp(-4026/T)$
$CO + O_2 = CO_2 + O$	$1.6 \times 10^{13} \exp(-20634/T)$
$CO + O + Ar = CO_2 + Ar$	4.0×10^{13}
$O + H_2 = OH + H$	$2.1 \times 10^{14} \exp(-6920/T)$
$H + O_2 = OH + O$	$1.2 \times 10^{17} T^{-0.907} \exp(-8369/T)$
$OH + H_2 = H_2O + H$	$5.2 \times 10^{13} \exp(-3271/T)$
$OH + OH = H_2O + O$	$5.5 \times 10^{13} \exp(-3522/T)$
$H + H + Ar = H_2 + Ar$	$6.4 \times 10^{17} T^{-1.0}$
$H + OH + Ar = H_2O + Ar$	$8.4 \times 10^{21} T^{-2.0}$
$H_2 + O_2 = 2OH$	$1.7 \times 10^{13} \exp(24230/T)$
$O_2 + Ar = O + O + Ar$	$2.6 \times 10^{18} T^{-1.0} \exp(-59386/T)$

Units: cm, K, mole, s.

Conclusions

A simple method for measuring time-resolved [NO] and [O] from a single radiation measurement of the NO-O chemiluminescence was developed. For mixtures containing carbon compounds, the method requires a second radiation measurement corresponding to the CO-O chemiluminescence and offers the added capability of [CO] measurement. The method was used with mixtures of H_2-O_2-N_2-Ar and CH_4-O_2-N_2-Ar and was found to give excellent results for [NO] and [O] in the latter case. With the hydrogen mixture, measured values of [NO] and [O] were about 40% higher than the calculated values. This discrepancy may not be due to a deficiency in the experimental method but rather to the presence of a detonationlike phenomenon which was not modeled in the calculations.

The greatest difficulty with the method is caused by background radiation. While there is some evidence that aluminum fragments from the diaphragm may be responsible, the exact cause of this radiation still needs to be determined with certainty. However, for those situations where there is enough freedom in the choice of mixtures to overcome the background, the present method should prove useful in some applications. As a guide, the measurable threshold of the product [NO] [O] was determined.

For mixtures requiring a double radiation measurement, it was necessary to determine the interference in the two wavelength regimes, or the so-called shape factor. For both the NO-O and CO-O radiation, the shape factors in the temperature range of interest were determined experimentally and shown to have strong temperature dependence in the former, but a weak dependence in the latter.

Finally, the method seems to be inadequate for the measurement of [CO], if the current kinetic scheme responsible for the CO formation is assumed to be acceptable. Further investigation is needed to establish the extent of the applicability of the method as far as CO is concerned.

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