BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 285—289 (1969)

# Shock Induced Reactions of Methane with Nitrous and Nitric Oxides

L. J. DRUMMOND

*Australian Defence Scientific Service, Weapons Research Establishment, Salisbury, South Australia*

(Received December 5, 1967)

Reflected shock waves, generated in a 5×3 inch shock tube, have been used to ignite mixtures of methane-nitrous oxide and methane-nitric oxide. Monochromators, a pressure transducer and an oscilloscope were used to determine the induction period to ignition ($\tau$) after the reflected wave passed the window. A flash lamp and spectrograph were also used to obtain spectra before and after explosion. For $CH_4$-$N_2O$ mixtures it was found that the plot of $\log(\tau[N_2O]p_5)$ against inverse temperature was linear and the activation energy was about 60 kcal/mol. This indicates that the rate controlling process was the reaction $N_2O(+M) \rightarrow N_2 + O(+M)$. However, the reaction $CH_3 + N_2O \rightarrow CH_2 + N_2 + OH$ may also be important. The results for $CH_4$-NO mixtures could be expressed by $\log(\tau[NO]p_5) = -10.2 + 49000/4.58T$ which suggests to the reaction $CH_2 + NO \rightarrow CH + HNO$ may be rate controlling. Spectrographic plates showed that CN and OH were present during the induction period but only OH was detected after explosion. This indicates that the reactions $CH + NO \rightarrow CN + OH$ and $CN + NO \rightarrow N_2 + CO$ may be a significant mechanism for achieving the reduction of nitric oxide.

The mechanism of methane oxidation with $O_2$ has been thoroughly examined by Miyama and Takeyama[1] who showed that different reactions governed the induction period to explosion of methane-rich and methane-lean mixtures. For the latter type, OH appeared before the rise in pressure due to exothermic reaction. The temperature dependence of these two induction periods indicated that they were associated with the oxidation of $CH_3$ and $CH_2O$ respectively.

Our previous work showed that reaction of ammonia[2] and hydrogen[3] with $N_2O$ was rapid and complete. However, with NO, reactions were incomplete even for temperatures of 2000°K and this was believed due to the formation of HNO and subsequent regeneration of NO.

The study is now extended to include methane, the simplest saturated hydrocarbon, as fuel with the hope of identifying the rate-controlling reaction during the induction period and of assessing the influence of the fuel-oxidant ratio on the mechanisms.

## Experimental

The shock tube and ancillary equipment have been described.[2] The optical path was 14 mm from the end plate in all experiments. The 1 mm wide beam was split so that the upper half entered a Hilger monochromator set to detect absorption at one wavelength, and the lower half passed to a Bausch and Lomb monochromator set to monitor absorption by OH at 3070 Å. The outputs of the photomultiplier tubes were fed to a Tektronix 555 dual beam oscilloscope. A pressure transducer (Kistler 603 A) was installed in the floor of the shock tube with its centre 2.5 mm from the end plate. Its amplified output was placed on one trace of the oscilloscope set in chopped mode. Alternatively, spectrographic plates were obtained with the use of a Hilger medium quartz spectrograph and a small flash lamp (7.5 $\mu$sec duration, 100 J). The signal from the detector station due to arrival of the incident shock, instead of triggering the oscilloscope, was fed to a delay unit and then to the flash lamp. With a series of shocks of comparable strength, progressive increase of the delay allowed absorption spectra to be obtained before, at, and after explosion of reactant mixtures which had been processed at comparable temperatures.

The speed of the incident shock ($U_s$) was measured over 267 mm just before arrival at the end plate. The speed of the reflected shock ($U_r$) was measured over 135 mm after it had travelled 27 mm from the end plate. An IBM 7090 computer program was used to calculate, for a given value of $U_s$, the speed of the reflected shock and the pressure ($p_5$), density and temperature ($T_5$) of the reactant mixture before reaction occurred. For mixtures containing 80% or more of argon it was possible also to calculate these parameters when reactants had passed instantly to equilibrium products behind this shock.

Helium or hydrogen was used as driver gas, and the initial reactant pressure was 44 Torr in all experiments.

Methane (Phillips, 99.98% pure), nitrous oxide (C.I.G., 99.6% pure) and argon (C.I.G., 99.9% pure) were used directly from cylinders. Nitric oxide, prepared from $KNO_2$-KI-$H_2SO_4$, was distilled at low pressure until it was a white solid, melting to a pale

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1) H. Miyama and T. Takeyama, This Bulletin, **38** 37 (1965).

2) L. J. Drummond and S. W. Hiscock, *Aust. J. Chem.*, **30**, 815, 825 (1967).

3) L. J. Drummond, *ibid.*, **30**, 2331 (1967).

green liquid.

Mixtures were made up manometrically to 700 Torr pressure and stirred magnetically for two hours before use.

## Results

**Methane Lean-Nitrous Oxide-Argon Mixtures.** Three mixtures (2/8/90, 4/16/80 and 6/24/70) were used. Induction periods ($\tau_1$) were read as the time intervals between the reflected shock passing the window and attainment of maximum [OH] after reaction occurred. Ignition delays, measured to the commencement of $N_2O$ disappearance, were in agreement with $\tau_1$ values. The delay ($\tau_2$) to the pressure rise at the end plate due to the onset of exothermic reaction behind the reflected shock, was somewhat bigger than the corresponding $\tau_1$ value measured 14 mm from the end plate. Results were obtained for $1495 < T_5 < 1935$°K and $2.5 < p_5 < 4.5$ atm. As $p_5$ was not constant the values of $\tau_1$ and $\tau_2$ were linearly normalised by multiplying by the appropriate $p_5$ value and Fig. 1 shows logarithmic values of $\tau_1 p_5[N_2O]$ and $\tau_2 p_5[N_2O]$ plotted against $1/T$. Least squares treatment yield the equations

$$\log(\tau_1 p_5[N_2O]) = -(13.82 \pm 0.12) + (60540 \pm 900)/4.58T$$

$$\log(\tau_2 p_5[N_2O]) = -(13.34 \pm 0.25) + (57700 \pm 1900)/4.58T$$

If $\tau$ values were not pressure normalised the equations are

$$\log(\tau_1[N_2O]) = -(14.16 \pm 0.16) + (59200 \pm 1200)/4.58T$$

$$\log(\tau_2[N_2O]) = -(13.70 \pm 0.15) + (56500 \pm 1100)/4.58T$$

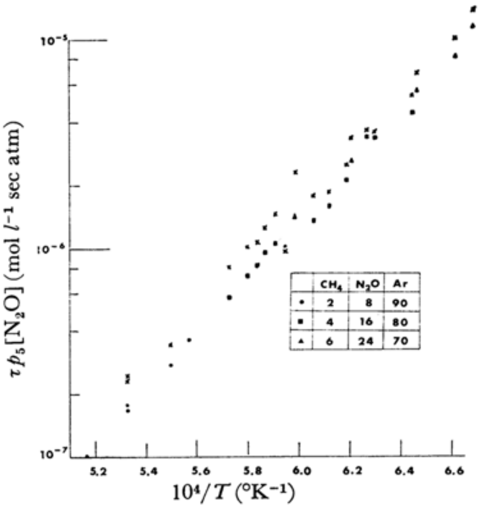

Fig. 1. Plot of $\log(\tau p_5[N_2O])$ against $1/T$ for $CH_4$-$N_2O$-Ar mixtures. Values denoted by X are from pressure records; all others from OH absorption records.

**Methane Rich-Nitrous Oxide-Argon Mixtures.** Three mixtures (3.3/6.7/90, 6.6/13.4/80 and 10/20/70) were studied for the conditions $1500 < T_5 < 1985$°K and $2.8 < p_5 < 4.6$ atm. Results are summarised as

$$\log(\tau_1 p_5[N_2O]) = -(13.91 \pm 0.21) + (62400 \pm 1600)/4.58T$$

$$\log(\tau_2 p_5[N_2O]) = -(13.53 \pm 0.25) + (60200 \pm 1900)/4.58T$$

If $\tau$ values were not pressure normalised the equations are

$$\log(\tau_1[N_2O]) = -(14.22 \pm 0.23) + (60500 \pm 1800)/4.58T$$

$$\log(\tau_2[N_2O]) = -(13.85 \pm 0.18) + (58300 \pm 1400)/4.58T$$

**General Obsevations.** For each mixture there was a certain driver pressure (and hence $T_5$ value) below which reaction was not initiated. The pressure records showed that a drop in pressure occurred about the time that reaction should have taken place. The reactant mixture had been chilled by a rarefaction wave reflected back from the zone of collision between reflected shock and contact surface. Thus the shock tube was too short to obtain measurements of long induction periods (about 600 μsec) at temperatures around 1550°K.

The 4/16/80 mixture was studied at a temperature of about 1730°K using the flash lamp and spectrograph. No absorption bands were found during the induction period. At, and after explosion, strong bands due to OH at 2811 and 3064 Å were present.

Measurement of reflected shock speeds were obtained for all mixtures and those for the 3.3/

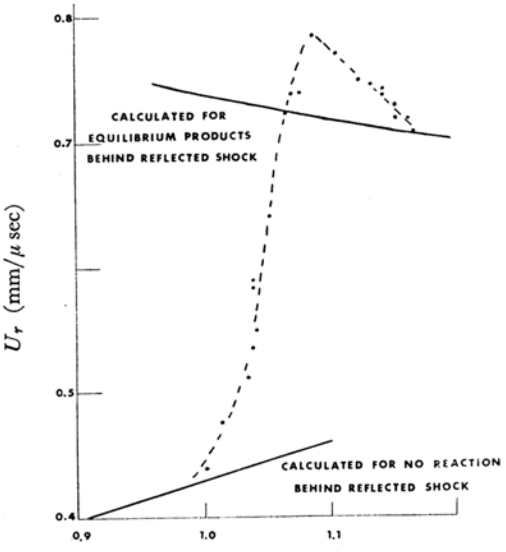

Fig. 2. Shock speed measurements in mixtures of $CH_4$-$N_2O$-Ar (3.3/6.7/90).

6.7/90 mixture are shown in Fig. 2.

The phenomenon of "overshoot" (less marked in other mixtures such as 4/16/80) has been seen in other systems,[2,3] and indicates a region in which an overdriven explosion front travels faster than the anticipated combustion-driven wave.

**Chemical Reactions.** Attempts to identify the rate controlling reaction during the induction period involve choosing a set of reactions such that: the rate determining reaction has an enthalpy change in agreement with the measured activation energy; the number of molecules of fuel ($m$) and oxidant ($n$) involved in this reaction agree with the values required for $\log(\tau[\text{fuel}]^m[\text{oxidant}]^n)$ to have a linear relationship with $1/T$; and the remaining reactions in the set should lead to a number of differential equations satisfying the condition that some of the molecules involved in these reactions are in a stationary state condition. A criticism of this method for discerning the rate determining step concerns the assumption that calculations made for non-stationary state conditions are applicable to the steady state. This matter has been discussed recently by Bradley.[4]

However, if we follow the method of Miyama and Takeyama for $CH_4$-$O_2$ mixtures, there appear to be two feasible mechanisms for $CH_4$-$N_2O$ mixtures:

(a) If the reactions

$$N_2O(+M) \longrightarrow N_2 + O(+M) \qquad (\Delta H = 40\ \text{kcal}) \qquad (1)$$

$$CH_4 + O \longrightarrow CH_3 + OH \qquad (\Delta H = 0\ \text{kcal}) \qquad (2)$$

$$CH_4 + OH \longrightarrow CH_3 + H_2O \qquad (\Delta H = -17\ \text{kcal}) \qquad (3)$$

$$CH_3 + N_2O \longrightarrow CH_2 + N_2 + OH \qquad (\Delta H = 53\ \text{kcal}) \qquad (4)$$

are of importance during the induction period, then, assuming that O and OH are steady state intermediates and that $CH_3$ is the principal chain carrier, it is necessary for $k_1[N_2O][M]\tau$ to be constant. Putting $k_1[M] = k'_1 = A\exp(-E/\boldsymbol{R}T)$, the plot of $\log(\tau[N_2O])$ *vs.* $1/T$ should be a straight line, whose slope is the activation energy of reaction (1). We obtained a value of about 60 kcal/mol and previously[2] had measured 57 kcal/mol in a study of the decomposition of nitrous oxide.

(b) If the reactions (3), (4) and

$$CH_4 + N_2O \longrightarrow CH_3 + N_2 + OH \qquad (\Delta H = 40\ \text{kcal}) \qquad (5)$$

$$CH_3 + OH \longrightarrow CH_2 + H_2O \qquad (\Delta H = -4\ \text{kcal}) \qquad (6)$$

are the important ones, then, assuming that OH is the steady state intermediate and $CH_3$ is the principal chain carrier, it is necessary for $k_4[N_2O]\tau$ to be constant. Thus $\log(\tau[N_2O])$ *vs.* $1/T$ should be a straight line, whose slope is the activation energy of reaction (4).

**Methane - Nitric Oxide - Argon Mixtures.** Three mixtures (2/8/90, 4/16/80 and 5/10/85) were used under the conditions $2085 < T_5 < 2810$°K and $3.8 < p_5 < 5.1$ atm. The third mixture (methane-rich) could only be studied over a narrow temperature range due to the low intensity of the OH absorption signal. At these high temperatures there was not a large increase in pressure when reaction occurred and, for this reason, induction periods were only available from OH absorption records. Maximum values of [OH] did not occur rapidly as in a real explosion, but were achieved over tens of micro-seconds after passing through a point of inflexion. A plot of $\log(\tau p_5[NO])$ *vs.* $1/T$ is shown in Fig. 3. Least squares treatment of all data gave the equations

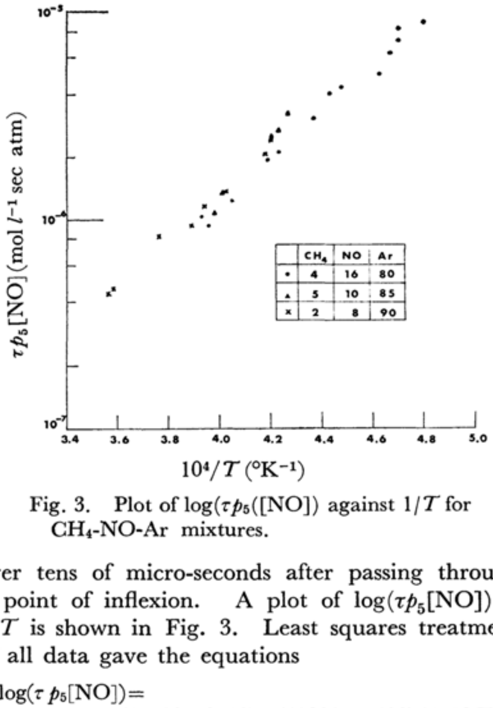

Fig. 3. Plot of $\log(\tau p_5([NO])$ against $1/T$ for $CH_4$-NO-Ar mixtures.

$$\log(\tau p_5[NO]) = -(11.20 \pm 0.13) + (49300 \pm 1400)/4.58T$$

$$\log(\tau [NO]) = -(11.18 \pm 0.16) + (53100 \pm 1800)/4.58T$$

If the methane-rich mixture was ignored

$$\log(\tau p_5[NO]) = -(10.17 \pm 0.11) + (49000 \pm 1200)/4.58T$$

$$\log(\tau [NO]) = -(11.14 \pm 0.17) + (52600 \pm 1800)/4.58T$$

In addition to monitoring OH, monochromator settings of 4320, 3875 and 3360 Å were used. The records indicated that CH and NH were absent but that CN was present during the induction period, disappearing by the time that [OH] had reached about 50% of its maximum value (see Fig. 4). These results were confirmed when the 4/16/80 mixture was studied at a temperature of about 2140°K using the flash lamp and MQ spectrograph. During the induction period the (0,0) and (1,1) bands of the $B^2\Sigma$-$X^2\Sigma$ transition of CN were seen at 3871 and 3883 Å and also,

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[4] J. N. Bradley, *Trans. Faraday Soc.*, **63**, 2945 (1967).

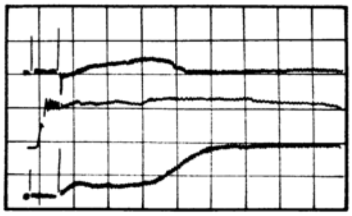

Fig. 4. Oscilloscope record obtained with a mixture of $CH_4$-NO-Ar (4/16/80). Top trace is absorption at 3875Å, centre trace is pressure, bottom trace is absorption at 3070Å ($T_5$ is c. 2260°K, 50 $\mu$sec/division).

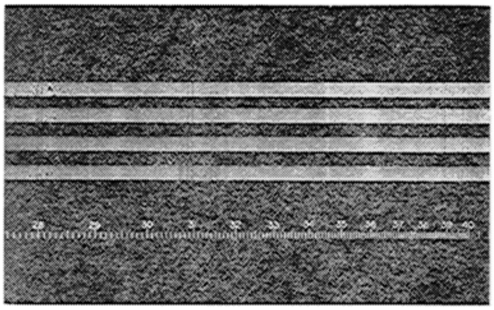

Fig. 5. Spectropgraph obtained with a mixture of $CH_4$-NO-Ar (4/16/80). First exposure, lamp alone; second, lamp fired 250 $\mu$sec after shock passed window; third, delay was 350 $\mu$sec; fourth, delay was 450 $\mu$sec.

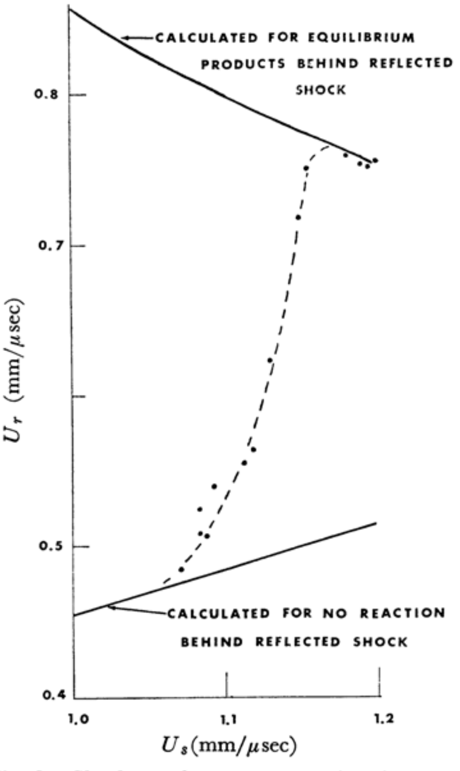

Fig. 6. Shock speed measurements in mixtures of $CH_4$-NO-Ar (4/16/80).

but faintly, the (0,0) band of OH at 3064 Å. After reaction, only intense bands of OH at 2811 and 3064 Å were seen (Fig. 5).

Figure 6 shows that the measured speed of the fully established combustion-driven shock agrees with that computed for conversion to equilibrium products behind the reaction wave. The initiating reaction for this system could be

$$CH_4 + NO \longrightarrow CH_3 + HNO \quad (\Delta H = 52\,\text{kcal}) \quad (7)$$

At these high temperatures HNO would rapidly decompose and thus further oxidations involving NO and producing HNO could be

$$CH_3 + NO \longrightarrow CH_2 + HNO \quad (\Delta H = 65\,\text{kcal}) \quad (8)$$

$$CH_2 + NO \longrightarrow CH + HNO \quad (\Delta H = 49\,\text{kcal}) \quad (9)$$

The presence of CN and OH during the induction period may be explained by the reaction

$$CH + NO \longrightarrow CN + OH \quad (\Delta H = -45\,\text{kcal}) \quad (10)$$

Assuming that $CH_3$ is a steady state intermediate and $CH_2$ is the principal chain carrier it is possible to show that $\log(\tau[NO])$ *vs.* $1/T$ should be a straight line, the slope of which is the activation energy of reaction (9).

Towards the end of the induction period the cyano radical is probably removed by the reaction

$$CN + NO \longrightarrow CO + N_2 \quad (\Delta H = -157\,\text{kcal}) \quad (11)$$

and the heat release of this strongly exothermic reaction causes [OH] to increase, either due to acceleration of reactions (7) through (10) or to reactions such as

$$CH + NO \longrightarrow CO + NH \quad (\Delta H = -101\,\text{kcal}) \quad (12)$$

$$NH + NO \longrightarrow N_2 + OH \quad (\Delta H = -91\,\text{kcal}) \quad (13)$$

## Conclusion

Reactions in $CH_4$-$N_2O$ mixtures have been initiated by reflected shocks at temperatures above 1500°K. The induction period to explosion, determined from the increase in pressure or achievement of maximum [OH], was inversely proportional to $[N_2O]$. The temperature dependence of the ignition lag indicates that the rate controlling reaction was $N_2O(+M) \rightarrow N_2 + O(+M)$. However the possibility exists that the reaction $CH_3 + N_2O \rightarrow CH_2 + N_2 + OH$ is of importance also. A series of comparable shocks and the use of a spectrograph and flash lamp which was fired at progressively increasing delays after the shock had passed the windows, confirmed that OH was present at, and after, explosion. Measurements of the speed of the combustion-driven shock agreed with those computed for equilibrium conditions behind the shock.

Temperatures above 2080°K were used to induce reactions behind reflected shocks in $CH_4$-NO mixtures. Absorption spectroscopy using spectrographic plates showed that CN and OH were present before complete reaction but only OH was detectable afterwards. Absorption records using a monochromator showed that [OH] rose slowly to its maximum value. The induction period to maximum [OH] was inversely proportional to [NO] and the temperature dependence of the ignition delay indicates that the rate controlling reaction prior to complete combustion is $CH_2+NO \rightarrow CH+HNO$. The detection of CN suggests that the reaction $CN+NO \rightarrow CO+N_2$ may be of importance in accounting for the reduction of nitric oxide.

Dr. I. M. Napier is thanked for assistance in obtaining spectrographic exposures using a lamp of his design. Mr. D. Graham assisted with all shock tube experiments.