# Modelling Nitromethane Combustion

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#### Modellierung der Nitromethan-Verbrennung

In der Verbrennungsforschung gilt Nitromethan als ein wichtiger Treibststoff der wegen seiner Nitrogruppe eine hohe Leistung anbietet. Darüberhinaus kann er als Modellsubstanz dienen, um Verbrennungsphänomene von Festtreibstoffen zu verstehen. Gegenstand der Untersuchungen sind die Abbrandgeschwindigkeit und das Spektrum im UV/VIS-Spektralbereich wegen der starken Emission von Radikalen, wie sie auch in den Flammen vieler energetischer Materialien vorkommen. Die Ergebnisse werden auf der Basis detaillierter chemischer Kinetik und eines linearen Verbrennungsmodells mit einem reduzierten Mechanismus diskutiert.

## Summary

In combustion research, nitromethane is an important nitro-compounded liquid propellant offering high performance. Additionally it can be used as a model substance for understanding mechanisms of combustion of solid propellants. The objectives of investigations were the burning behaviour and the flame spectrum in the UV/VIS spectral range because of the appearance of strong radical emissions also present in flames of other energetic materials. The evaluation is based on a detailed chemical kinetics and a linear combustion model including a reduced mechanism.

## 1. Introduction

Nitromethane is an important solvent or liquid propellant offering high performance<sup>(1)</sup>. In addition, it can be considered as a model substance to be investigated for a better understanding of the mechanisms of the combustion of solid propellants which contain nitro-compounds and hydrocarbons. In prior studies burning rates were measured depending on  $pressure^{(2,3)}$ . To get an insight into the combustion process profiles of the emission of radicals using a simple pool fire arrangements were performed and the results analysed with respect to the distribution of temperatures and species<sup>(4)</sup>. The reaction mechanism in the flame seemed to be similar to that of the flame of methane, nitrous oxide and  $oxygen^{(6,7)}$  or to the flames of nitramines<sup>(5,22,23)</sup>. The initial step of the decomposition of nitromethane was assumed to be the bond scission of C-N forming CH<sub>3</sub> and NO<sub>2</sub>. The main emitters of these flames are the diatomic molecules NO, OH, NH and CN which are similarly also observed in nitramine flames. These radicals are all included in the reaction mechanisms of the flame of CH<sub>4</sub>/NO<sub>2</sub>/O<sub>2</sub> which are discussed in more detail in the literature<sup>(6-9)</sup>. NO, OH, NH and CN are intermediates in the reaction schemes whereas CN is involved in strongly exothermal reactions<sup>(4)</sup>. The temperatures of the flame, determined on the radiative emission of OH and NH diatomic molecules, lie close to the adiabatic value. However, the CN molecule the radiative lifetime of

## Modélisation de la combustion de nitrométhane

Dans la recherche en matière de combustion, le nitrométhane est considéré comme un propergol liquide important, qui offre des performances élevées en raison de ses groupes nitro. Par ailleurs, il peut être utilisé comme substance de modélisation pour comprendre les phénomènes de combustion de propergols solides. L'objet de la présente étude est la vitesse de combustion et le spectre dans le domaine spectral UV/VIS en raison de la forte émission de radicaux, qui sont également présents dans les flammes de nombreux matériaux énergétiques. Les résultats sont analysés sur la base d'une cinétique chimique détaillée et d'un modèle de combustion linéaire incluant un mécanisme réduit.

which (see comparison in Refs. 4,6) is lowest, is not observed in a thermal equilibrium.

It is the objective of the present study to measure burning rates of strand-like nitromethane samples at low pressures and compare the results with calculations using the computer code of Zarko *et al.*<sup>(10)</sup>. The kinetic parameters of the gas phase reactions require a reduced mechanism which was derived from a detailed mechanism starting with the fission of the C—N bond.

## 2. Experimental

For the measurement of the burning rates pure nitromethane was filled into plastic tubes of a diameter of 5 mm. The filled plastic 'strands' were burnt in an optical bomb, a high pressure autoclave equipped with quartz windows allowing the application of non-intrusive combustion measurement techniques like pyrometry, spectroscopy and cinematography. The experimental setup is described in detail in other publications<sup>(11,12)</sup>. The burning rates are derived from video records. The method of evaluation uses simple image processing to obtain burning rates from video data<sup>(13)</sup>.

Emission spectra in the UV and VIS spectral range have been detected using a Tracor Northern grating spectrometer and a Jarrel Ash monochromator (focal length 275 mm, entrance slit 50 µm). To get rotationally resolved spectra, a grating with 2400 lines/mm has been chosen (wavelength resolution 20 cm<sup>-1</sup>). The detector is equipped with a 1024 element diode array. The minimum time resolution of the system is 10 ms. If no rotational resolution was needed, a grating with 300 lines/mm has been used. Spectra in the NIR and IR (1 to 14 µm) have been recorded<sup>(14)</sup> applying a rotating filter wheel spectrometer developed at the ICT<sup>(15)</sup>. The flame has been focused on an aperture (diameter 2 mm) which has been focused onto the entrance slit of the spectrometer. This setup allows a spatial resolution of  $20 \times 0.05 \text{ mm}^2$ .



**Figure 1.** Burning rates of nitromethane depending on pressure. The rates above 4 MPa are taken from the literature<sup>(2,3)</sup>.

#### 3. Burning of Nitromethane

The burning of the nitromethane strands was investigated in the optical bomb described above at pressures up to 4 MPa where no experimental data were available. It is difficult to ignite a stable and sustained combustion in an inert atmosphere. Therefore most experiments were performed under air. The burning rates depending on pressure are plotted in Figure 1, where also the burning rates obtained from the literature<sup>(2,3)</sup> are marked. There exists obviously a low pressure limit of the burning rate at about 0.02 cm/s.

The flames of nitromethane in pool fires or strands emit in the UV/VIS-spectral range bands of diatomic radicals. In contrast to the results of atmospheric pool fires, the strong OH radical emission is dominating accompanied only by weak intensities of CN above a broad band continuum emission. A profile of spectra obtained of the strand burning is found in Figure 2. A rotationally resolved OH band in the UV-spectrum of nitromethane burning in air at 1 MPa is shown in Figure 3. The least squares fit of the band (see Ref. 16) gives a temperature of about 2600 K which is slightly above the adiabatic flame temperature of 2450 K to  $2750 \text{ K}^{(17)}$ , depending on the available air ratio.

In the IR spectral range investigations were performed by application of a rotating filter wheel spectrometer developed at the  $ICT^{(15)}$  (Figure 4). The spectrometers consist of fast rotating wheels containing interference filter segments which continuously vary the transparency in the wavelength regions from 1200 nm to 2500 nm (InSb-detector) and 2450 nm to 14000 nm (InSb/HgCdTe-sandwich-detector). The spectrometer was developed at the ICT. In addition, a FTIR spectrometer of Midac adapted for emission measurements was used. The intensity calibration was carried out by recording reference spectra of a black body radiator. The evaluation uses the BAM-code<sup>(14)</sup> of the ICT which is based of a single line group model and tabulated data of H<sub>2</sub>O and CO<sub>2</sub> to analyse bands of reaction products in the flame<sup>(18,19)</sup>. A series of emission spectra of the nitromethane strand combustion is plotted in Figure 2. NO emission at 5.1 µm was found accompanying the main combustion products water and carbon dioxide (Figure 4). It is obviously a transient product revealing a slow decay downstream of the flame. A least squares fit by the BAM-code gives temperatures of 2050 K.

## 4. The Mechanism of Nitromethane Combustion

Nitromethane which is a liquid at room temperature, evaporates at 374 K under normal pressure and decomposes on heating above 520 K. This decomposition was studied on heating in a heatable infrared cell<sup>(11,12)</sup>. The results were analysed combining an evaporation model of droplets with a decomposition reaction assuming a first order reaction<sup>(12)</sup>. The kinetic parameters applying the combined model to the curves obtained by these experiments are listed in Table 1. The kinetic parameters of the thermal decomposition are



Figure 2. Subsequently recorded UV-VIS spectra of nitromethane at a pressure of 1 MPa.



**Figure 3.** The least squares fit of the OH band of nitromethane at a pressure of 1 MPa. It gives a temperature of 2600 K.

assigned to the fission of the C—N bond in  $CH_3$ -NO<sub>2</sub> which initiates the reaction and should also control the overall rate of a first group of subsequent reactions.

The following reaction mechanism of the nitromethane flame seems to be similar to that of the flame of methanenitrous oxide and-oxygen<sup>(6,8)</sup> or to the flames of nitramines<sup>(14)</sup>. The prime components of the nitromethane decomposition are in the gaseous phase CH<sub>3</sub> and NO<sub>2</sub>, in cases when air is entrained also N<sub>2</sub> and O<sub>2</sub> have to be taken into account. The main emitters of these flames in the UV-VIS spectral range are the diatomic molecules NO, OH, NH and CN. These radicals are all involved in the reaction mechanisms of the flame of a mixture composed of CH<sub>4</sub>/NO<sub>2</sub>/O<sub>2</sub>. These mechanisms are discussed in the literature<sup>(6-9)</sup> in more detail. NO, NH and CN appear as intermediates in the reaction schemes whereas CN participates in strongly exothermal reactions. Therefore, the CN molecule the radiative lifetime of which (see comparison in Ref. 6) is lowest, is not observed in thermal equilibrium as indicated in Ref. 4.

The measured kinetic parameters of the decomposition of nitromethane in Ref. 12 ( $K_1$  in Table 1) provide the initiating step of the formation of CH<sub>3</sub> and NO<sub>2</sub>. Integrating this step

Table 1. Parameters of Reduced Mechanism

	Log A (pre-exponential)	Activation energy (cal/mol)	Enthalpy (cal/g)
1st step $K_1$	14.0	55000	1150
(noni Kei. 12) 2nd step $K_2$	7.7	42000	400

into the elementary reaction mechanisms of Miller and Bowman<sup>(9)</sup> complete reaction schemes are available for nitromethane flames or nitromethane/air flames. The mechanism of Miller and Bowman which hold for the mechanisms of the flame of  $CH_4/NO_2/O_2$  are not repeated here explicitly. The CHEMKIN II code allowed the calculation of detailed profiles of species and temperatures on adiabatic conditions. A plot of important flame radicals OH, CN, NH and NO is shown in Figure 5.

An application of the kinetic processes in the flame into models of heterogeneous combustion requires the reduction of the numerous reaction steps in elementary reaction schemes to some representative steps of simplified mechanisms. In principle, the reduction of the mechanism should account for the dominating features, conversion, time and temperature scales of the original one.

The reduction used here assumes a reaction of two consecutive steps of 1st order:  $A \Rightarrow B \Rightarrow P$ , the differential equation of which can be solved analytically. The 1st reaction step is assigned to the experimental values of the fission of the C—N bond ( $K_1$  in Table 1). The parameters of the 2nd step are set to values resulting in 95% conversion at the same times as 95% conversion is calculated by CHEMKIN II when starting from the same initial temperatures. The reaction constant  $K_2$  agrees well with the Arrhenius relation above 1500 K giving the kinetic parameters  $K_2$  listed in Table 1.

The result is a strongly simplified mechanism including two consecutive steps of 1st order. The parameters are listed



Figure 4. IR spectrum of the nitromethane flame.



Figure 5. Radicals of nitromethane decomposition calculated by the CHEMKIN II code on adiabatic conditions.

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in Table 1. The related reaction enthalpies are estimates from assigned groups of reactions and the occurrence of the second step at a temperature of about 1800 K.

# 5. Calculation of Burning Rates

To compare the measured burning rates with calculations the method of Zarko and Rychkov<sup>(10,20,21)</sup> was applied. Zarko and Rychkov developed a 1-dimensional computer code CTEM (Combustion Transients of Energetic Materials) which simulates the transient burning of heterogeneous energetic materials. The computer code takes also into account time-dependent phenomena of condensed propellants subjected to time-variable heat flux and under varying pressure conditions. It allows to study the combustion response under modulated irradiation, varied pressure and under heat flux and pressure variation to investigate the stability of ignition and combustion. CTEM can include a solid and a liquid phase allowing the solid propellant to melt and evaporate at the surface. Depending on the optical properties of the propellant the radiant flux is absorbed in the depth of radiation penetration. In the condensed phase the heat flow equation is solved numerically. Also chemical conversions can occur both in the condensed and gas phases. In the gaseous phase, in addition to the heat flow, the diffusion of three species is assumed which can undergo a two-step consecutive reaction.

The kinetic parameters in Table 1 were inserted into twostep consecutive reaction scheme including also all available chemical and physical constants of nitromethane like specific heat capacity, heat of evaporation, thermal conductivity, density etc. The ignition was arranged by heat flux which decreased in intensity after 10 ms and an initial heater (5 ms– 15 ms) for the gaseous phase. The later is needed as the reactions of the second step occur only above 1800 K and excluding the second step in the beginning no stable combustion could be obtained. This correlates well to the observation



Figure 6. NO concentration profile of nitromethane decomposition calculated by the CHEMKIN II code on adiabatic conditions.

that nitromethane is difficult to ignite when compared with solid propellants of similar overall composition. The series of pictures in Figure 8 shows the flame behaviour on the described ignition conditions. Each picture gives the temperature and concentration profiles for the indicated time after the start. The pictures on the left side show the evaporation of nitromethane by external heat flux and after 5 ms the heating of the gas by the additional heater. After 10 ms the external heat flux is reduced so that the gas flow velocity is reduced. Therefore the gas is heated to much higher temperatures by the gas heater and the reaction starts. This is shown in the picture on the top of the right side. 15 ms after the start the gas heater stops and the temperature is reduced to the flame temperature.

The calculations at low pressures deliver a burning rate (Fig. 7) which agrees well with the measured rates at the low pressure limit of about 0.02 cm/s to 0.03 cm/s. The profile of the intermediate of the consecutive reaction shows a similar profile (Figure 8 right side) as the NO component obtained in adiabatic CHEMKIN II calculation (Figure 6). So it is suggested to assign the rate determining step of the second reaction step to the conversion of NO which is known to be relatively stable at flame conditions at higher temperatures. Some results which show the profile of the species of the reduced mechanism are plotted in Figure 8.

## 6. Conclusions

The integration of the kinetics of the C—N bond scission of nitromethane allows to establish an elementary reaction scheme. The reduction to a strongly simplified mechanism gives the reactions for a transient combustion calculation according to Zarko *et al.* The theoretical results obtained on the profiles of temperatures, species and burning rates agree roughly with the experimental data of strand burner measurements.



Figure 7. Transient burning rates after ignition which shows the tendency of the reaching values of about 0.02 cm/s to 0.03 cm/s.



Figure 8. Flame behaviour of the nitromethane flame on ignition.

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