NIR-SPECTROSCOPIC IN-SITU MEASUREMENTS ON THE DECOMPOSITION OF BURNING LIQUIDS AND GELS WITH H₂O₂-NITROMETHANE

Viñas Quero-Lopez, Volker Weiser, Francisco Hidalgo, Yvonne Plitzko

Fraunhofer-Institut Chemische Technologie (ICT) Joseph-von-Fraunhoferstr. 7 76327 Pfinztal (Berghausen), Germany

Abstract

A spectroscopic method was introduced to investigate the decomposition of hydrogen peroxide in nitromethane closely below the burning surface of gelled and liquid model propellants using a fast NIR-spectrometer. The method response on a wavelength shift of absorption bands related to the H_2O_2 concentration.

Introduction

The decomposition reactions inside the condensed phase of a burning propellant have an important influence on the burning behaviour. Usually the reaction zone under the propellant surface is very thin, but the opacity of the material prevents spectroscopic investigations, which would be fast and selective enough to look inside the material structure.

Liquid and gelled mixtures of hydrogen peroxide with nitromethane are transparent in a wide spectral range. During the combustion process bubbles appear some millimetres below the surface. They indicate an intense reactivity in the condensed phase probably induced by heat radiation from the above flame. It was assumed that the bubbles are caused by the decomposition of hydrogen peroxide to water and oxygen. In this case the concentration of hydrogen peroxide should reduce in relation to nitromethane. To investigate this effect, spectroscopic transmission measurements were performed using a fast NIR spectrometer.

Experimental

Hydrogen peroxide of 85% purity was mixed with nitromethane in equal mass ratios. Aerosil 200 was used as a gellant. To avoid stability investigations, the samples were prepared just before the experiment. The mixture was filled in test tubes of glass (\emptyset 5 mm, length 70 mm). The glass showed full transmittance in the applied NIR spectral range. The filled test tube was fixed close to the entrance of the spectral detector aperture (\emptyset 100 µm) in the middle of the height of the test tube. A blackbody radiator was used as background emission source. The small pin aperture combined with the small distance to the test tube of about 10 mm allows a good local resolution in the sample. The mixture was ignited with a pit flame. The mixtures burned with a constant rate of 0.4 mm s⁻¹ (liquid) and 1.5 mm s⁻¹ (gelled).

The near infrared spectra were recorded using a HGS 1700. The system is based on a Zeiss MCS 511 grating spectrometer equipped with a 256 element InGaAs diode array as detector (spectral range 0.9 to1.7 μ m). The spectral resolution was about 15 nm at a scan rate of 100 spectra per second [1], [2].

Results

Single NIR-spectra

Fig. 1 shows example spectra of pure nitromethane, hydrogen peroxide (85%) and an equal-in-mass mixture of both components. It shows that the pure spectra differ significantly, and the spectrum of the mixture is more or less an average of the spectra of both components. No significant difference could be observed between the spectra of the liquid sample and the gelled one (compare Fig. 1). Transmittance spectra of different H_2O_2 /nitromethan mixtures with mass ratios between 40:60 and 80:20 presented in Fig. 2 indicate an interesting shift of the wavelength position of the absorption minima at about 1000, 1160 and 1230 nm in direction to higher wavelength related to the H_2O_2 concentration. Fig. 3 presents an example of the transmission ratios at 1231.5 and 1237.7 nm

reclaimed from averaged spectra at different mass ratios at room temperture. This signalize that this ratio was suitable for a rough but simple concentration analysis of the applied mixtures.

Combustion experiments

Fig. 4 provides a typical series of spectra shortly before the burning zone passes the measurement volume. The position of the liquid/gas interface is marked with an arrow. It is obvious that the opacity of the sample decreases strongly close to the burning surface, which is probably a temperature effect of the heating. A qualitative analysis of the absorption band minima like it is done in Fig. 5 shows indeed a significant decrease of the hydrogen peroxide concentration some millimeters below the liquid surface as it was expected from the above mentioned hydrogen peroxide decomposition. The decomposition zone of the liquid mixtures was three times larger as in the gelled samples. Unfortunately the quantitative calibration as made in Fig. 3 cannot be applied because of the unknown temperature rise in this region.

References

- [1] Eckl, W.; Weiser, V.; Weindel; M.; Determination of the Temperature in an Isopropanol Diffusion and a Premixed Propane-Air Flame; Application Note - HGS-1700 der Fa. WMM Sensorik Gmbh & Co.KG
- [2] Weiser, V.; Eckl, W.; Eisenreich, N.; Langer, G.; Weindel, M.; Analyzing Molecular IR-Emission Spectra of Deflagrating Methane Air Mixtures at Different Pressures; 17th International Colloquium on the Dynamics of Explosions and Reactive Systems (ICDERS); July 25-30,1999; Heidelberg, Germany; Presentation 90; <u>http://reaflow.iwr.uniheidelberg.de/~icders99/program.htm</u>



Fig. 1 Transmittance spectra of nitromethane, hydrogen peroxide and a 50:50 mixture of both components



Fig. 2 Transmittance spectra of different liquid mixtures of nitromethane and hydrogen peroxide



Fig. 3 Ratio of transmittance values at 1231.5 and 1237 µm at different mixture ratios



Fig. 4 Evolution of transmittance spectra in the condensed propellant phase



Fig. 5 Qualitative distribution of hydrogen peroxid content in the liquid phase of a burning nitromethane and hydrogen peroxide mixture