



Hexachloroethane Evaporation: The Case on the Loss of Blue Flame in Pyrotechnic Mixture

Romero-Valdés Juan Jesús, Cortés-Camargo Stefani, Jiménez-Rosales Angélica, Acuña-Avila Pedro Estanislao*

Zinacantepec Technological University, Nanotechnology Department, Zinacantepec, Mexico, Mexico.

Email: pedro.avila@utzin.edu.mx

Pyrotechnic is one of the most dangerous and polluting human activity, however in Latin American countries is a tradition related to religion rituals concerned with agricultural cycles, and of course with many other kinds of festivities. Governments do campaigns of safety and good practices among pyrotechnicians and restrict areas of production under military surveillance. Pyrotechnicians usually learn about the use of chemical compounds through oral tradition with recommendations of companies that sell the chemicals compounds, only a few of them have higher educational skills to search strategies to use safer and eco-friendly mixtures. In each region pyrotechnicians promote among them the mixtures that they consider the best, in our case, some mexican pyrotechnicians use hexachloroethane to obtain an intense blue flame; however, they observed that after two-three months of the production of fireworks the blue flame diminishes. The aim of this research is to demonstrate the theoretical explanation of the evaporation. For this purpose, we used infrared spectroscopy, uv-vis spectroscopy, scanning electron microscopy coupled with chemical analysis of hexachloroethane in presence of barium nitrate, a strong oxidizing agent, in methanol medium. We observed a simultaneous change on both compounds, basically barium nitrate dissolves and recrystallizes depending on the temperature (20-40°C) meanwhile hexachloroethane evaporates.

Keywords: Hexachloroethane, blue flame, pyrotechnics, barium nitrate.

1. Introduction

Hexachloroethane (C_2Cl_6) has been used as a component in pyrotechnic mixtures to obtain white smoke [1,2,3]. Mexican pyrotechnicians use it to obtain intense blue light that it is more difficult to obtain compared to red, green or yellow flames; to achieve a long-lasting, deep and intense blue flame is a real challenge [4] considering that a lot of knowledge is just transmitted orally and when chemical compounds are not always available.

HC is a chlorine donor, as well as other chlorinated compounds such as hexachlorobenzene,

that can be obtained through the pyrolysis of chlorinated compounds with metal oxides such as Cr_2O_3 [5]. HC has interesting properties owing to its crystalline structure, allotropic changes, and vapor pressure in the solid state. Pyrotechnic formulations usually contain Magnesium (Mg) and barium nitrate $\text{Ba}(\text{NO}_3)_2$ because of their fuel-oxidant properties which are well known by pyrotechnicians [6]. Other compounds are used as resins to stabilize the flames or to avoid humidity inside the bullets containing the mixtures. When HC is used in these mixtures, a blue light is obtained; however, if the mixture is kept at room temperature for more than two months the expected blue light turns green-white (Figure 1).

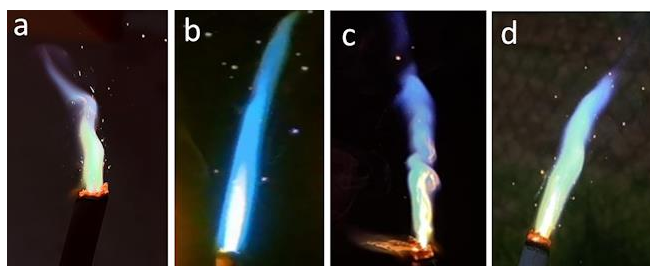


Figure 1. Ignition of pyrotechnic mixtures. a) Pyrotechnic mixture without C_2Cl_6 , b) Pyrotechnic mixture with C_2Cl_6 , c) Mixture with C_2Cl_6 after one month of preparation, d) Mixtures with C_2Cl_6 after two months of preparation

In our case, we observed that the specific problem detected by pyrotechnicians is not reported in the literature. In this work, we wanted to explore the interactions of HC and barium nitrate (BN) in methanol at 20,30 and 40°C to evaluate changes through UV-vis spectrometry, FTIR, SEM, EDS and DRX of both compounds to observe changes to confirm the evaporation of HC. This aimed to evaluate the changes in HC in the presence of barium nitrate, a strong oxidizing agent, to identify the loss of the intense blue light. Furthermore, we wanted to demonstrate that evaporation occurs to warn pyrotechnicians that other compounds must be necessary to avoid health issues and ecological damage [7].

2. Methods and methodology

HC and BN were purchased in local market specialized in pyrotechnic compounds. FTIR of both compounds were acquired from 4000 to 400 cm^{-1} with 16 scans in a Perkin Elmer UATR Two. DRX were performed on Empyrean Malvern-Panalytical with PIXel 1D-Medipix3 detector operated at 45 kV, 40 mA, Bragg-Brentano configuration and $\text{CuK}\alpha 1$ radiation ($\lambda = 1.5406 \text{ \AA}$). Signals were compared with ICDD cards for barium nitrate (01-076-1376, 00-024-0053) and hexachloroethane (00-011-0841). Scanning electron microscopy (SEM) was acquired from dried drops over double carbon tape into electronic microscope (JSM-IT100 InTouchScope, JEOL) at a high vacuum and was observed at an acceleration voltage of 20 kV with secondary electron detector. Energy dispersive spectrometry (EDS) analysis was performed with QUANTAX-EDS X-FLASH 6L 30 (BRUKER) detector, and elements were quantified with ESPRIT software. To evaluate changes, UV-Visible (UV-Vis) spectroscopy was performed (DR6000 spectrophotometer, HACH, USA) in a 1 cm path length quartz cuvette and scanning over 200-800 nm wavelength range. The quartz cuvette was cleaned constantly with methanol to avoid cross-interference between readings of the samples.

3. Results and discussion

UV-VIS OBSERVATIONS AT DIFFERENT TEMPERATURES

HC and BN were mixed in methanol at 2.3×10^{-2} M by separate and together to observe if changes can be monitored by UV-Vis transmission spectroscopy. HC had an absorption band at 215 nm, meanwhile BN showed a large absorption at 225 nm and a small absorption at 279 nm. We used methanol due to HC is hydrophobic, meanwhile BN is hydrophilic and not mixable in organic solvents. HC is dissolved in methanol and BN was apparently indissoluble in methanol, but the changes on UV-Vis give us idea that some proportion of BN was soluble in methanol and could give us information if some interaction occurs among HC and BN faster than in their solid state.

In the insert of Figure 2, a spectrum of the mixture and the HC absorption peak is observed. In the Figure 2, the increase of the absorption at 279 nm is observed over the time at 20°C, 30°C and 40°C. The peak of absorption increases to 283 nm, showed by asterisk. Furthermore, visually the BN changed their aspect, and a white powder were obtained when solution was filtered and dried. This indicated a change of BN in methanol that depends on the temperature. We did not see a change on HC because their peak of absorption overlaps with that of nitrate.

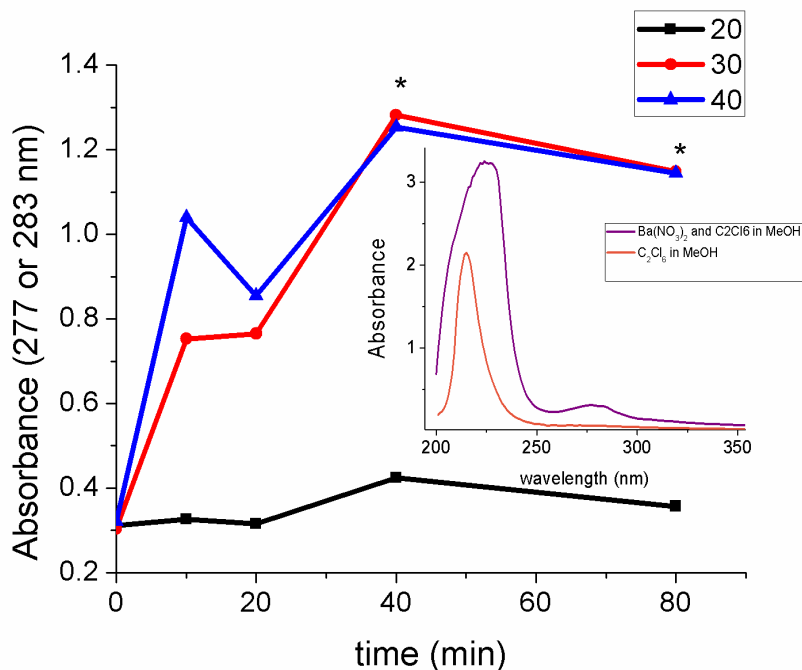


Figure 2. Absorbance of BN and HC in methanol at 277 or 288* nm at increased time. Insert of the spectrum at 0 minute is observed.

We wanted to know if the change is dependent of the quantity of compounds in methanol, then we use 1.15×10^{-2} M of nitrate and 2.3×10^{-2} of barium nitrate at 30°C and 40°C for 10 minutes and we observed that that the absorbance is also dependent on the initial concentration of

barium nitrate (Figure 3). Absorbance at 277-283 nm was evidence of a clearly change on BN in methanol that depends on temperature.

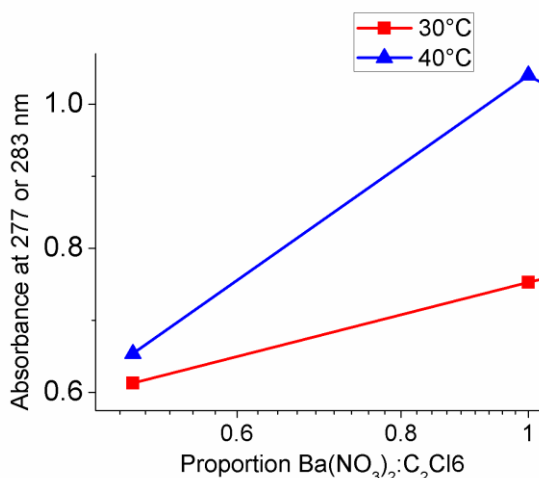


Figure 3. Absorbance at 10 minutes of BN and HC in methanol at 277 or 288* nm at increased time

INFRARED, SCANNING ELECTRON MICROSCOPY, AND X-RAY DIFFRACTION

We obtained infrared spectra (Figure 4) of the mixture BN and HC, and the white powder obtained after the filtration of the mixtures after 10 min at 40°C. HC had three representative absorption bands at 1093, 767 and 674 cm^{-1} that matches visually with databases from SpectraBase® (ID:e2ekxN2VLD). BN had four prominent peaks at 1416, 1334, 818 and 729 cm^{-1} that matches well with that of SpectraBase® (ID:AGicLYj4zxA). From this information we can be sure that the compounds used in this work are not fake or altered. The fresh mixtures of both compounds showed the seven bands expected for both components. The white powder obtained after filtration and dried of the methanol which contains the mixture after 10 min at 40°C showed the same spectra as BN without trace of HC. With these spectra is possible to assume that there is simultaneous change on both compounds: BN dissolves into methanol meanwhile HC are evaporating, and both processes are dependent of the temperature.

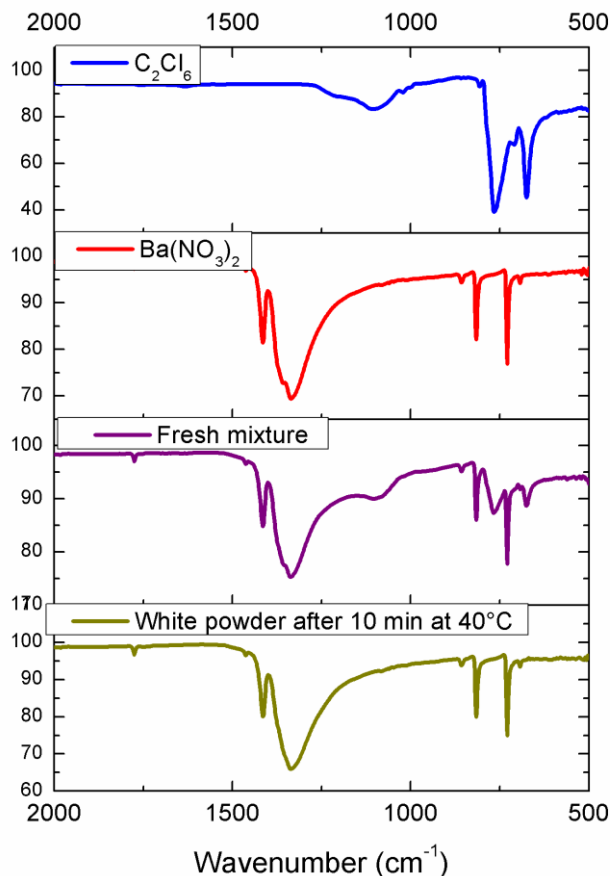


Figure 4. Infrared spectra of C₂Cl₆, Ba(NO₃)₂, a fresh mixture of both, and the white powder obtained after 10 min at 40°C in methanol filtered and dried

However, DRX and SEM give us more evidence about the simultaneous change observed. DRX and SEM (Figure 5) were obtained of the fresh mixture and the white powder after filtration and dried of the mixture in methanol during 10 min at 40°C. On fresh mixture, we observed both particles, and each one had specific morphology. That of BN were rounded particles of approximately 30 nm, their EDX spectrum showed the presence of Ba, N and O in atomic proportion of 13.8, 23.8 and 62.3 % respectively which is very close to expected. HC morphology was like crushed ellipsoid with shinier areas, their EDX spectrum showed a soft presence of Cl and most of the signals detected were not related to Cl or C, as if the HC was not present. However, DRX were capable to detect both compounds in a fresh mixture, they overlapped at 31° and the peak obtained was sharp. Signals of HC agreed with ICDD number (00-011-0841) confirmed their presence and crystallinity with greater signals corresponding to the planes (120),(040) and (041). Signals of BN agreed with ICDD number (01-076-1376) confirmed their presence and crystallinity with greater signals corresponding to the planes (111),(200),(210),(211),(220),(311) and (222). The white powder obtained after filtration and dried of the mixture in methanol at 40°C for 10 minutes were analyzed too, SEM

showed little elongated ellipses of about 5 to 7 μm in length and 2 μm width with EDX spectra similar to that obtained of BN and with absence of Cl, DRX of this white powder agreed with BN but in a different crystalline texture (ICCD 00-024-0053). These results show evidence that part of BN is dissolved and recrystallized in methanol at 40°C with increasing crystalline texture on plane (222) and at the same conditions, HC was evaporated with no signals detected neither by SEM-EDX nor DRX

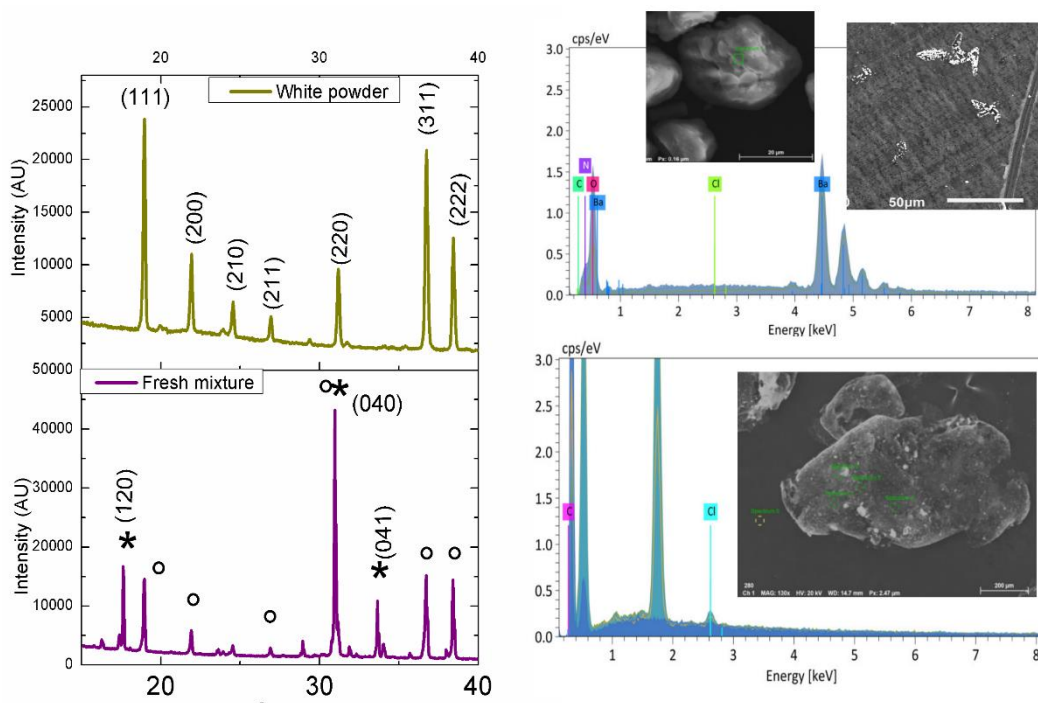


Figure 5. DRX, SEM and EDS of particles of fresh mixture and the white powder obtained after filtration and dried after 10 min at 40°C.

4. Conclusion

This work has the purpose to demonstrate experimentally the loss of C_2Cl_6 by evaporation that can explain the loss of blue flame registered in pyrotechnic mixtures after two months of preparation. We used a mixture of $\text{Ba}(\text{NO}_3)_2$ and C_2Cl_6 in methanol to increase the rate of interaction among these compounds. We observed that part of $\text{Ba}(\text{NO}_3)_2$ was dissolved and recrystallized, simultaneously at the evaporation of C_2Cl_6 at 40°C. We think that there is enough evidence to support our statement, that chemical interaction among these compounds are negligible as theoretically expected.

Acknowledgements

The authors wish to thank to SNII for the economic support and to the Zinacantepec Technological University for the equipment support.

Funding Statement

The authors did not receive financing for the development of this research.

Data Availability:

The data that support the findings of this study are available from the corresponding author

Conflict of interest:

The authors declare that there is no conflict of interest.

References

1. Hartley, F., Murray, S., Williams, M., & Jones, D. (1982). Smoke generators. I. The Ignition of Pyrotechnic White Smoke compositions containing hexachloroethane and silumin by means of an electrically heated coil. *Propellants, explosives, pyrotechnics* 7, 12-17.
2. Jarvis, A. (1970). The combustion reactions of a pyrotechnic white smoke composition. *Combustion and flame* 14, 313-320.
3. Karlsson, N., Cassel, G., Fängmark, I., & Bergman, F. (1986). A comparative study of the acute inhalation toxicity of smoke from TiO₂-hexachloroethane and Zn-hexachloroethane pyrotechnic mixtures. *Archives of Toxicology* 59, 160-166.
4. Contini, A.E. (2010). Blue Flame Pyrotechnic Compositions: A Concise Review. *Journal of Pyrotechnics*, Issue 29, 3-11.
5. Stevenson, C., & Rudman, R. (1994). High-Temperature Synthesis of Anhydrous CrCl₃ and Thermally Controlled Formation of C₆Cl₆ and C₂Cl₆. *Journal of chemical education* 71, 704-707.
6. Ouyang, D.-h. (2013). Effect of Different Binders on the Combustion Characteristics of Ba(NO₃)₂/Mg-containing Pyrotechnic Mixtures. *Central European Journal of Energetic Materials* 10, 209-215.
7. CDC. (s.f.). ATSDR. Obtained from atsdr.cdc.gov/es/toxfaqs/es_tfacts97.html#