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REACTIVITY OF CONCENTRATED AMMONIUM NITRATE SOLUTIONS IN THE PRESENCE OF ORGANIC IMPURITIES

REAKTYWNOŚĆ STĘŻONYCH ROZTWORÓW AZOTANU AMONU W OBECNOŚCI ZANIECZYSZCZEŃ ORGANICZNYCH

Abstract: Assessment of mixtures reactivity under certain conditions is essential for safe and conscious designing and improving manufacturing processes. One commonly used compound, the reactivity of which is very important, is ammonium nitrate and its solutions. The biggest influence on the reactivity of ammonium nitrate has the temperature and presence of other compounds, including impurities, that catalyze reactions leading to degradation. One of such impurities are organic compounds which impact on the ammonium nitrate has not yet been clearly described.

The aim of the research was to investigate the influence of selected organic impurities on the reactivity of aqueous solutions containing up to 50 wt % ammonium nitrate, buffered with 15 wt % diammonium phosphate. The measurements were carried out using differential scanning calorimetry. Solution without organic compounds showed no reactivity up to 240 °C. The addition of 8 wt % ammonium oxalate did not increase the reactivity of ammonium nitrate. It was observed an endothermic decomposition reaction of oxalic acid, beginning at 185 °C. During the measurement of a solution containing 6 wt % phenidone, it was registered an exothermic complex reaction, beginning at 189 °C and showing relatively small thermal effect. Addition of 6 wt % pyrogallol caused a significant increase in reactivity of ammonium nitrate solution. Strongly exothermic reaction beginning at 192 °C was observed. Spectrophotometric measurement showed a clear nitrate concentration loss in the sample after calorimetric measurement. The results show that the nitrate ion selectively oxidizes certain functional groups in organic compounds.

Keywords: ammonium nitrate, organic impurities, reactivity, calorimetry

Introduction

Chemical and technical safety is absolutely essential in industrial production. It extends to the apparatus and appliances design stage, as well as their proper operation,

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by means of complex control systems. The need to ensure an adequate level of safety of people and the environment is regulated by a number of legal acts. The most important of these is the European Parliament and Council Directive 96/82/EC (Seveso II) of 9 December 1996 on the control of major-accident hazards involving dangerous substances, amended by Directive 2003/105/EC of 16 December 2003. Its two main principles are the prevention of major-accident hazards involving dangerous substances, and in case of an accident – reduction of its negative consequences for man and the environment. The Directive covers not only the industrial production but also the storage of dangerous chemical substances [1]. The doctrine of Sustainable Development is also gaining an increasing importance in industrial production. It states that the needs of humanity should be met at the least possible negative impact on the environment. According to this principle, it is necessary to better understand the production processes, for enhancing the safety of people and the environment [2].

The preparation of the majority of the legally required reports and analyses is connected with the necessity of investigations and simulations, allowing for reliable and unambiguous opinion on the safety of the installation. Very often it comes down to the assessment of reactivity of given system and the effects associated with it. Learning them reduces the risk of losing control over the production process and the occurrence of adverse reactions leading to deterioration of the product [3].

One commonly used in the inorganic technology chemical compound susceptible to rapid thermal decomposition is ammonium nitrate and its solutions. It was the cause of many accidents in the industry and in spite of many years of research, the threat has not been completely eliminated [4, 5]. Pure ammonium nitrate is considered to be relatively safe because of its high stability at low temperature. At the stage of its manufacture, storage, transport and use, ammonium nitrate and its solutions often get contaminated by such compounds as inorganic acids, organic oils and others [6]. These pollutants have a significant impact on the reactivity of ammonium nitrate, catalyzing reactions leading to degradation and thermal instability. Therefore, learning about its interactions with other compounds is essential for the safe storage and handling of materials containing ammonium nitrate [7–9].

Trace amounts of chlorine or chlorides may result in an increased explosiveness of ammonium nitrate and reduction of the decomposition temperature by as much as 80 °C. Particularly much attention is paid to the products of stainless steel corrosion. They contain chromium compounds, which destabilizing effect on the ammonium nitrate is comparable with that of chlorides [5, 10]. Organic substances with confirmed negative impact on the safety of ammonium nitrate include: dinitrotoluene, nitro-naphthalene and similar nitro compounds, aliphatic alkylamines and their salts, ethyleneamine dinitrate, aliphatic alcohols and glycerine esters [11–14]. Effect of many organic compounds on the reactivity of ammonium nitrate, however, is not clearly described so far. Furthermore, Oxley et al noted that not only the type of the organic compound, but also the degree of its dispersion, has an influence on the reactivity of the mixture. According to these studies, emulsions are more resistant to thermal decomposition than less dispersed systems. It was demonstrated that this is not due to the presence of water in the system, by repeating the experience for the anhydrous emulsion

and obtaining the same results as for the emulsion with water. Probably, in a highly dispersed system, dissociation of ammonium nitrate is limited, which results in a higher thermal decomposition temperature [15].

For aforementioned reasons, the ability to assess the reactivity of the various systems under certain conditions is essential to safe and conscious designing and improving manufacturing processes. One of the techniques which enable testing the reactivity of the compounds and their mixtures is differential scanning calorimetry [16].

Materials and methods

The dominant component of the test solutions was ammonium nitrate, the nominal content of which was 50 wt %. Diammonium phosphate in an amount of 15 wt % served as a buffering and stabilizing compound. Selected organic substances, such as ammonium oxalate, phenidone and pyrogallol in an amount of 6–8 wt %, were added to the solutions. The nominal content of ammonium nitrate was properly reduced to obtain the same vapor pressure above the solution in each sample.

Reactivity of solutions was evaluated by measuring the thermal effect of the reaction in a differential scanning calorimeter of Calvet type, C80D Setaram. The solutions were placed in a glass tube with a capacity of 2 cm³, and the sample mass was 1 g. As a reference sample, it was used a solution of potassium sulfate at such concentration that the vapor pressure was similar to that in the measuring vessel. The vessel was equipped with a pressure sensor that allows its continuous recording. The concentration of nitrate ions (NO₃⁻) was determined in solutions after the calorimetric measurement. The measurements were made using a spectrophotometer Varian Cary 50 Bio UV/Vis. Nitrate concentration in the solution was calculated from the maximum value of absorbance at a wavelength of 303 nm.

Results and discussion

A solution of the nominal content of ammonium nitrate and diammonium phosphate, without the addition of organic compounds, showed no reactivity during the calorimetric measurement up to 240 °C. It is evidenced by the lack of significant heat effects during the calorimetric measurement and constant pressure value recorded at a constant temperature. Spectrophotometric measurement also confirmed no loss of nitrates in the sample. Overpressure registered in the measuring vessel was used to calculate the saturated vapor pressure above the solution (Fig. 1) which was then expressed in the form of Antoine equation (1):

$$\log p_{\text{H}_2\text{O}} = 9.21041 - \frac{7355.39}{430.514 + T} \quad (1)$$

Pressure of the gaseous products formed during the subsequent calorimetric measurements was determined by subtracting from the total registered overpressure the

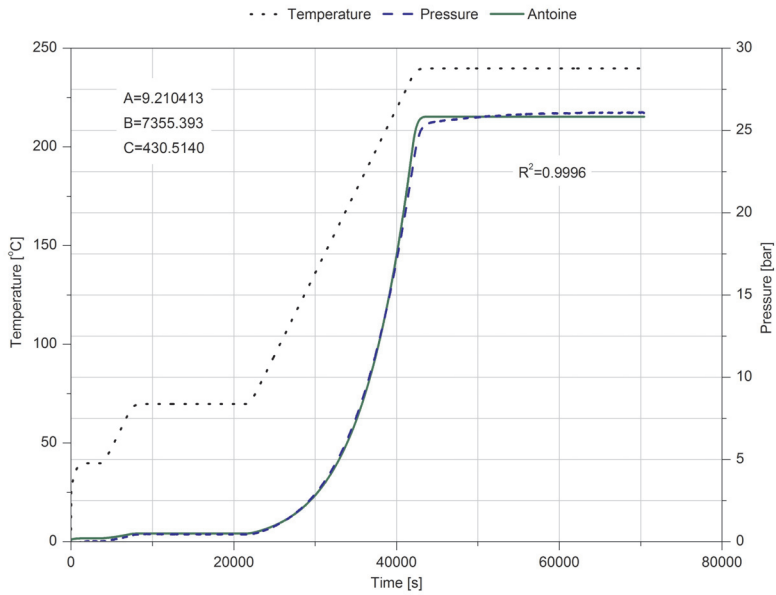


Fig. 1. The pressure of saturated water vapor calculated from calorimetric measurement of solution containing: 50 wt % ammonium nitrate, 15 wt % diammonium phosphate, 35 wt % water, and pressure expressed with Antoine equation

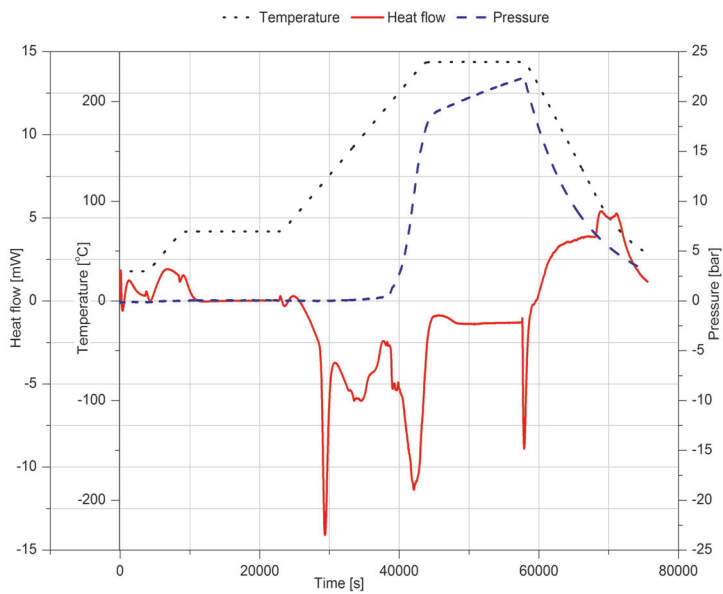


Fig. 2. The result of calorimetric measurement of solution containing: 8 wt % ammonium oxalate, 42 wt % ammonium nitrate, 15 wt % diammonium phosphate, 35 wt % water

air pressure in the measuring vessel and saturated vapor pressure above the solution, calculated according to the Antoine equation (1).

The addition of 8 wt % ammonium oxalate did not increase the reactivity of ammonium nitrate in the solution. During the measurement, it was recorded an endothermic reaction starting at 185 °C, the source of which could be the decomposition of the organic compound (Fig. 2). A spectrophotometric measurement of the nitrates concentration in the sample after the calorimetric measurement shows that the ammonium nitrate did not decompose. The maximum pressure of the gaseous products formed during the measurement was 22.3 bar and probably was generated as a result of decomposition of ammonium oxalate.

During calorimetric measurement of a solution containing 6 wt % phenidone, an exothermic reaction starting at 189°C was registered (Fig. 3). Its thermal effect is however slight, and the course is complex and difficult to interpret. Possibly it is the result of multi-stage transformation and decomposition of the organic compound. Generated pressure of gaseous products is low and reached 9.8 bar. Variability of the inclination angle of pressure increase curve also confirms the complexity of the registered process. The obtained results suggest that the addition of phenidone may slightly increase the reactivity of the ammonium nitrate in the solution.

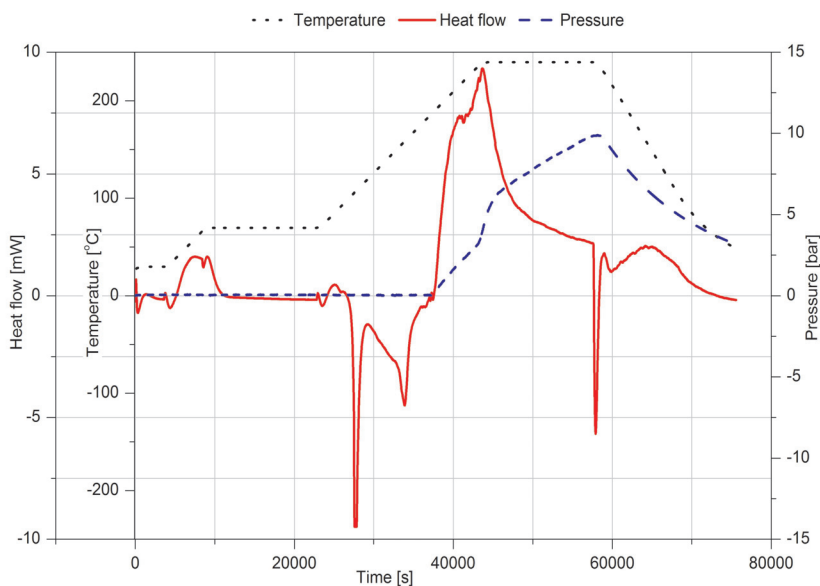


Fig. 3. The result of calorimetric measurement of solution containing: 6 wt % phenidone, 44 wt % ammonium nitrate, 15 wt % diammonium phosphate, 35 wt % water

Addition of 6 wt % pyrogallol significantly increased the reactivity of ammonium nitrate solution. Highly exothermic reaction beginning at 192°C was observed (Fig. 4). Spectrophotometric measurement showed a significant decrease in the concentration of

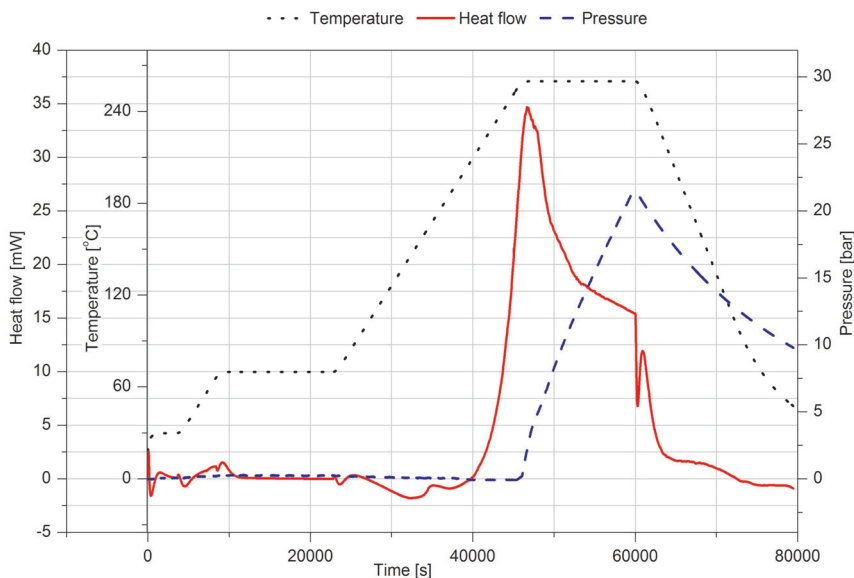


Fig. 4. The result of calorimetric measurement of solution containing: 6 wt % pyrogallol, 44 wt % ammonium nitrate, 15 wt % diammonium phosphate, 35 wt % water

nitrates in the sample after calorimetric measurement. Maximum pressure of formed gaseous products was 21.6 bar. Possibly nitrate ion NO_3^- was reduced to NO_2^- and then to NO , simultaneously oxidizing the hydroxyl groups of pyrogallol. According to the mechanism proposed by Dima et al, formed nitric oxide dimer after reduction to N_2O can decompose to nitrogen gas and other products of disproportionation, generating registered pressure [17].

Based on the results of the analyses summarized in Table 1, it can be seen that only some of the tested organic compounds exhibited the ability to increase the reactivity of ammonium nitrate in buffered solutions. These differences may be related to the type of substituents present in organic compounds. Probably nitrate ion has the ability to selective oxidation of some functional groups in organic compounds, thereby leading to increased reactivity of the ammonium nitrate and its degradation.

Table 1

Results of calorimetric measurements presenting the temperature of the beginning of reaction (T_{ONSET}) and the maximum pressure of the gaseous products (p_{max}) for each of tested organic compounds

Organic additive	Ammonium oxalate	Phenidone	Pyrogallol
Thermal effect	endothermic	exothermic	exothermic
T_{ONSET} [°C]	185	189	192
p_{max} [bar]	22.3	9.8	21.6
Functional groups	2 carboxylic	carbonyl phenyl	3 hydroxyl

Conclusions

Studies conducted using differential scanning calorimetry allowed to assess the influence of selected organic compounds on the reactivity of buffered aqueous solutions of ammonium nitrate. Addition of 8 wt % ammonium oxalate did not affect the reactivity of the test solution. This compound has probably undergone an independent endothermic decomposition at 185 °C. Interaction between 6 wt % phenidone and ammonium nitrate is not straightforward, due to the complexity of the observed changes. At 189 °C it was registered the beginning of an exothermic reaction, accompanied by a small thermal effect. It is conceivable that phenidone slightly increases the reactivity of ammonium nitrate in the solution. Pyrogallol added to the solution in an amount of 6 wt % significantly increased its reactivity. The beginning of strongly exothermic reaction was recorded at 192 °C, while the solution without organic compounds showed no reactivity up to 240 °C. Spectrophotometric measurements showed that in solution with pyrogallol a significant amount of ammonium nitrate reacted. Varied impact of organic compounds on the reactivity of the solution can be associated with the type of substituents present in them. Confirmation of the ability of nitrate ion to the selective oxidation of chosen functional groups requires further investigation.

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REAKTYWNOŚĆ STĘŻONYCH ROZTWORÓW AZOTANU AMONU W OBECNOŚCI ZANIECZYSZCZEŃ ORGANICZNYCH

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Abstrakt: Ocena reaktywności mieszanin w określonych warunkach jest niezbędna, aby móc w sposób bezpieczny i świadomy projektować oraz usprawniać procesy technologiczne. Jednym z powszechnie stosowanych związków, którego reaktywność jest niezwykle ważna, jest azotan amonu i jego roztwory. Największy wpływ na reaktywność azotanu amonu ma temperatura oraz obecność innych związków, w tym zanieczyszczeń, katalizujących reakcje rozkładu. Jednym z takich zanieczyszczeń są związki organiczne, których wpływ na azotan amonu nie został do tej pory jednoznacznie opisany.

Celem pracy było określenie wpływu zanieczyszczeń organicznych na reaktywność wodnych roztworów zawierających do 50 % wag. azotanu(V) amonu, buforowanych wodorofosforanem(V) amonu w ilości 15 % wag. Pomiar wykonano z wykorzystaniem skaningowej kalorymetrii różnicowej. Roztwór pozbawiony zanieczyszczeń organicznych nie wykazał reaktywności do 240 °C. Dodatek 8 % wag. szczawianu amonu nie zwiększył reaktywności azotanu amonu. Zaobserwowano endotermiczną reakcję rozkładu kwasu szczawioowego, rozpoczynającą się w 185 °C. Podczas pomiaru roztworu zawierającego 6 % wag. fenidonu, zarejestrowano w 189 °C egzotermiczną reakcję o złożonym przebiegu, której efekt cieplny jest niewielki. Dodatek 6 % wag. pirogalolu spowodował znaczny wzrost reaktywności roztworu azotanu amonu. Zaobserwowano silnie egzotermiczną reakcję rozpoczynającą się w 192 °C. Pomiar spektrofotometryczny wykazał wyraźny ubytek stężenia azotanów w próbce po pomiarze kalorymetrycznym. Wyniki badań wskazują na to, że jon azotanowy selektywnie utlenia wybrane grupy funkcyjne w związkach organicznych.

Słowa kluczowe: azotan amonu, zanieczyszczenia organiczne, reaktywność, kalorymetria