

Synthesis of 2,2-dinitroethene-1,1-diamine from 2-methylpyrimidine-4,6-diol and treatment of the dinitromethane produced

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Abstract:

2,2-Dinitroethene-1,1-diamine (FOX-7) was prepared from 2-methylpyrimidine-4,6-diol. Dinitromethane remaining in the spent acid was disposed of by thermal decomposition or reduction with iron. Dinitromethane content in reaction mixtures was monitored by FTIR, UV-Vis spectroscopy and thin layer chromatography (TLC). Possible reuse of dinitromethane is discussed. The thermal decomposition of the spent acid was studied using accelerating rate calorimetry (ARC).

Keywords: dinitromethane; 2,2-dinitroethene-1,1-diamine, infrared spectroscopy

1 Introduction

2,2-Dinitroethene-1,1-diamine (FOX-7) is an insensitive explosive suitable for different applications in energetic materials [1-8]. Recently, it has also been used as the starting material for other energetic compounds [9-22], including FOX-7 salts [23] and complex compounds [24].

Scalable procedures for 2,2-dinitroethene-1,1-diamine are based on nitration and subsequent hydrolysis of heterocyclic precursors derived from 2-methylimidazole-4,6-dione [9,25-27] or 2-methylpyrimidine-4,6-diol [28].

Recently, we described a scalable preparation of FOX-7 using the intermediate 2-hydroxy-2-methylimidazolidine-4,6-dione, which eliminates the formation of both dinitromethane and nitrate esters in the reaction medium [27]. The main disadvantage of the process is the need for at least three steps using commercially available materials, leading to an overall yield of less than 50%. From the viewpoint of process economy, the procedure starting from 2-methylpyrimidine-4,6-diol (**1**) is more effective. Scaling up and various studies of this method have been frequently described in the literature [29-39].

In this way, starting material **1** is nitrated to produce 2-(dinitromethylidene)-5,5-dinitroimidazopyrimidin-4,6(1*H*,5*H*)-dione (**2**), which is then hydrolysed in an acid medium to FOX-7 (Figure 1). The tetranitro intermediate **2** can be isolated by filtration or, more simply, by pouring the reaction mixture into dilute sulphuric acid, the hydrolysis can be carried out in diluted sulphuric acid. The hydrolysis of **2** produces FOX-7, dinitromethane (**3**) and carbon dioxide.

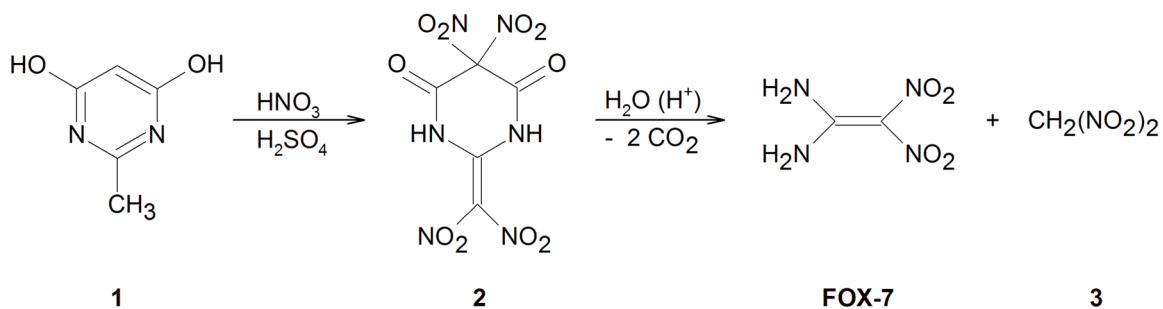


Figure 1: Synthesis of 2,2-dinitroethene-1,1-diamine from 2-methylpyrimidine-4,6-diol.

The main disadvantage of the method starting from **1** is the formation of dinitromethane (**3**), which is an unstable compound that decomposes immediately or over time depending on its purity or the temperature [40-42]. Also, several runaway reactions connected with dinitromethane during 2,2-dinitroethene-1,1-diamine preparation have been reported [29,33,37]. Because **3** is present in the spent acid after FOX-7 formation, it is necessary to find ways of eliminating it prior to further treatment of the spent acid. Thus, this work has focused on identification, determination, disposal or reuse of dinitromethane formed in the 2-methylpyrimidine-4,6-diol process.

2 Experimental

2.1 General procedures

The infrared spectra were collected using a Nicolet iS50 FT-IR spectrometer (Thermo, USA) with an ATR single reflection diamond accessory GladiATR (PIKE, USA). Measurement parameters were: spectral region 4000–400 cm^{-1} , resolution 4 cm^{-1} and number of scans 64. Spectral manipulation was done using Omnic 9.2 software. Detection of dinitromethane by FTIR in the spent acid after preparation of FOX-7 was carried out using the following procedure: 20 ml of spent acid was stirred with 5 ml of isopropyl acetate for five minutes. The organic layer was washed with 2 ml of water and then placed on the diamond crystal with the accessory for liquid sample measurements.

The Raman spectra were measured using a Nicolet iS50 Raman spectrometer with the following parameter: Excitation laser 1064 nm, power of laser 10-50mW, spectral region 4000–100 cm^{-1} , resolution 4 cm^{-1} and number of scans 96.

UV spectra were recorded using a Helios gamma spectrometer (Thermo, USA). Cuvettes made of quartz glass having a 1 cm optical length were used. Measurement of the dinitromethane concentration in the spent acid was made using the following procedure: Approx. 200-250 mg of mixture (with an accuracy of 0.1 mg) was weighed and put into a 100 ml flask. 50 ml of water, 10 ml of 0.2 M potassium hydroxide were added and finally water was added to 100 ml. 5 ml of the solution was pipetted into a 25 ml flask and water was added. These solutions were added to the cuvette to perform the measurement using distilled water as a blank. Absorbance at 363 nm was used for determination of the dinitromethane concentration.

Thin layer chromatography (TLC) was performed on Silufol plates with silica gel as a stationary phase with fluorescent indicator UV₃₆₆ (Sklárny Kavalier). The mobile phase was hexane acetone (3:1). Reaction mixtures were applied to chromatoplates without solvent or as ethyl acetate extracts. Dinitromethane and FOX-7 have $R_f \sim 0.4$ and 0.05 respectively.

Differential thermal analysis was carried out with a DTA 550 Ex thermal analyser produced by OZM Research (Czech Republic). The samples were tested in open glass microtest tubes in contact with air. The heating rate was 5 $^{\circ}\text{C min}^{-1}$.

The thermal decomposition of the spent acid was studied using accelerating rate calorimetry. The calorimeter ARC-es, manufactured by THT (UK) was used. The experiments were carried out in heat-wait-search mode, with starting temperature 50°C. Temperature steps of 3°C and lengths of 30 minutes were used until the exothermic decomposition was detected. A temperature rate of 0.02°C/min was used as a limit to detect an exotherm. Hastelloy bombs HC-LBQ (14.2 g, 0.42 J/g°C) with a diameter of 25.4 mm and a volume of 9.8 ml were used for the experiments. 3.03 g of spent acid containing 1.3% of dinitromethane was used here.

2.2 Syntheses

2.2.1 2,2-Dinitroethene-1,1-diamine (FOX-7) [28,29]

2-Methylpyrimidine-4,6-diol **1** (180 g, 1.43 mol) was dissolved in 96% sulphuric acid (620 g, 11.1 mol) and 98% nitric acid (438 g, 6.81 mol) was added dropwise over 60 min at a temperature of 15-20°C followed by stirring for an additional 3 hours. Then the reaction mixture was poured into ice-water (8 l) and stirred for 16 hrs. at room temperature. The precipitated solid was filtered off, washed with 100 ml of cold water, placed in 1400 ml of warm water (50-60°C) and stirred for one hour. The product was filtered and washed with water to give 187 g (88%) of FOX 7. DTA (50 mg), decomposition: start 224°C, maximum 244°C. Elemental analysis (%) calc. for C₂H₄N₄O₄: C 16.22, H 2.72, N 37.84; found: C 16.22, H 2.72, N 37.59. FTIR (cm⁻¹): 3402s, 3321m, 3295s, 1618s, 1604s, 1498s, 1469s, 1386m, 1325m, 1189s, 1159s, 1138s, 1066sh, 1018s, 858w, 789w, 749m, 620m, 578m, 531m, 445s. Raman (cm⁻¹): 3418w, 3327m, 3221w, 1602m, 1514m, 1481m, 1344s, 1219s, 1166s, 1066m, 1024m, 861s, 792w, 759w, 742w, 681w, 624m, 480m, 458m, 396w, 330w, 246w, 163, 114.

2.2.2 Decomposition of dinitromethane in spent acid

Spent acid from FOX-7 synthesis (100 ml) was stirred and heated for 3 hours at 80°C. The content of dinitromethane was monitored by TLC and FTIR as described in section 2.1. With FTIR, peaks at 1578 cm⁻¹ and 1567 cm⁻¹ respectively indicate the presence of dinitromethane and its intermediate decomposition product. Dinitromethane content at various reaction temperatures can be determined by UV as described in section 2.1.

2.2.3 Reduction of dinitromethane in spent acid with iron

Iron chips (6.3 g, 113 mmol) were gradually added to stirred spent acid (92 g) from the procedure described in section 2.2.1 (11.6 mmol of dinitromethane) with gentle cooling in order to keep the temperature below 30°C. The mixture was heated at 65°C for 2.5 hrs. The dinitromethane presence was monitored by TLC and FTIR as described in 2.1. After three hours, no dinitromethane was detected, the reaction mixture was alkalisied with potassium hydroxide and then distilled into a flask containing dilute hydrochloric acid (27 mmol). The distillate was evaporated to dryness using a vacuum rotary evaporator to give 1.0 g of a white solid (71%, calculated for expected ammonium chloride and methylamine hydrochloride). FTIR spectra of the product were compared with ammonium chloride and methylammonium hydrochloride standards.

2.2.4 Potassium dinitromethanide

Spent acid (67 g) from FOX-7 synthesis described in section 2.2.1 (9.0 mmol of dinitromethane) was extracted with isopropyl acetate (3 x 20 ml). The combined extracts were washed with a 10% sodium chloride solution (2 x 10 ml) to obtain pH 7. Potassium hydroxide (0.5 g, 8.9 mmol) was gradually added at room temperature to the isopropyl extract and the mixture was stirred for an additional 15 min. The resulting solid was filtered and washed with 2 x 5 ml of methanol. The yield was 0.95 g (73.2 %). DTA (15 mg), decomposition: start 190°C, maximum

206°C (explosion). Elemental analysis (%) calc. for CHKN_2O_4 : C 8.33, H 0.70; N 19.44; found: C 8.58, H 0.68, N 18.85. FTIR (cm^{-1}): 3147m, 1486m, 1460s, 1438s, 1365s, 1290vs, 1174vs, 1078vs, 1002s, 944m, 785s, 743s, 685s, 473w, 425m. Raman (cm^{-1}): 3144m, 1500w, 1488w, 1461w, 1408w, 1354m, 1326m, 1093m, 1009s, 749w, 733w, 671w, 473m, 428w, 280m, 195m, 121m.

2.2.5 Sodium dinitromethanide

Spent acid (207 g) from FOX-7 synthesis described in section 2.2.1 (26.21 mmol of dinitromethane), was extracted with isopropyl acetate (3 x 50 ml). The combined extracts were washed with a 10% sodium chloride solution (2 x 10 ml) to obtain pH 7. Sodium hydroxide (1.0 g, 25 mmol) in methanol (11 ml) was added to the extract. After several seconds, a yellow solid precipitated. The yield was 1.91 g (57.4%). DTA (15 mg), decomposition: start 161°C, maximum 207°C. Elemental analysis (%) calc. for CHN_2NaO_4 : C 9.38, H 0.79; N 21.88; found: C 9.60, H 0.76; N 20.92. FTIR (cm^{-1}): 3139m, 1513w, 1493w, 1451m, 1412s, 1332s, 1181s, 1091s, 1012s, 835m, 780s, 751s, 719s, 658m, 586m, 436m. Raman (cm^{-1}): 3144m, 1501w, 1361m, 1303m, 1158w, 1073m, 1015s, 782s, 483w, 290w, 179m, 161m.

3 Results and discussion

Using the procedure starting with 2-methylpyrimidine-4,6-diol, FOX-7 was prepared with a yield of 88%. The spent acid in the process without isolation of tetranitrate intermediate **2** is ~ 20% sulphuric acid, with rest being nitric acid (~ 1.5%), dinitromethane (~ 1.5%) and traces of dissolved FOX-7. Dinitromethane presence in the spent acid may be monitored by thin layer chromatography, FTIR or UV spectroscopy. Using TLC, silica gel plates with fluorescent indicator UV₃₆₆ are most suitable. UV-Vis spectroscopy is a suitable method for quantifying the dinitromethane content. After alkalisation, it is possible to measure the concentration of **3** by UV, the appropriate wavelength being 363 nm.

On standing at room temperature, dinitromethane in spent acid slowly decomposes, but the reaction rate is slow. The decrease in dinitromethane content is approximately 20% after ten days. If the spent acid is stirred, the dinitromethane decomposition rate is very dependent on temperature. At room temperature, dinitromethane is decomposed within four days; at 33°C, the decomposition takes less than two days (Figure 2). Heating to over 70°C shortens the decomposition time to several hours. The products of dinitromethane decomposition at 80°C have recently been proved by DTA-FTIR to be nitrous oxide and carbon dioxide [43] with nitrocyanoxide as the anticipated intermediate [44-45].

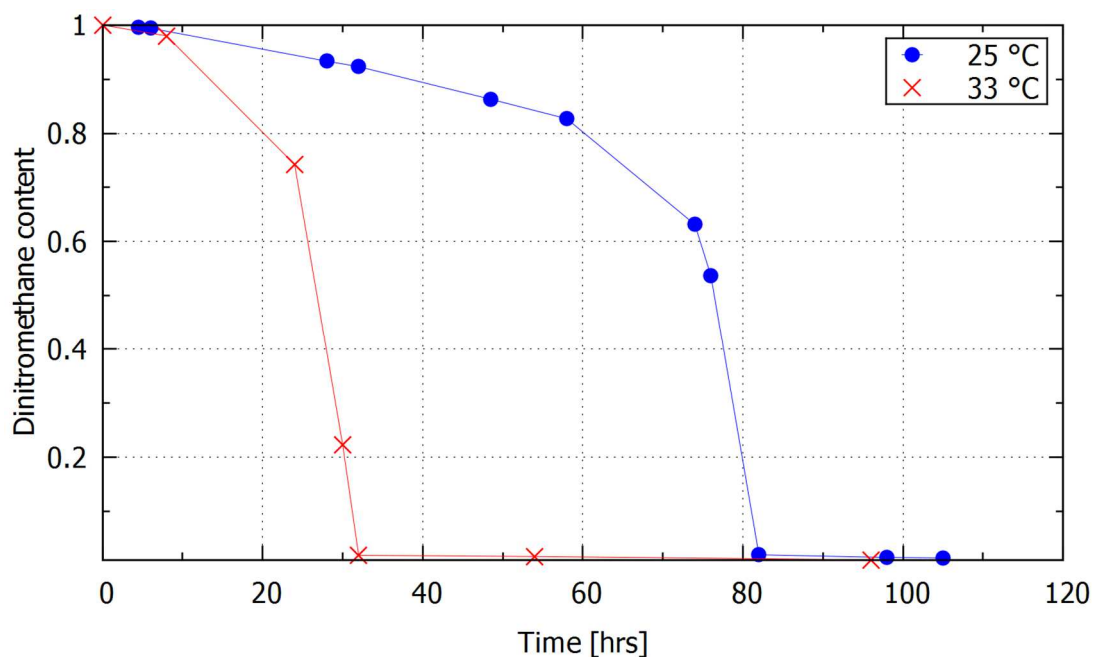


Figure 2: Decomposition of dinitromethane in spent acid at 25°C and 33°C.

By FTIR, dinitromethane was analysed with a diamond ATR crystal after extraction with ethyl acetate or isopropyl acetate. A medium intensity band appears at 1578 cm^{-1} . Bands with weak intensity at 800 cm^{-1} , 696 cm^{-1} and 579 cm^{-1} are also present in the spectrum (Figure 3). The same spectra are found in the isopropyl acetate extract of potassium dinitromethanide after acidification, thus demonstrating that the bands correspond to dinitromethane.

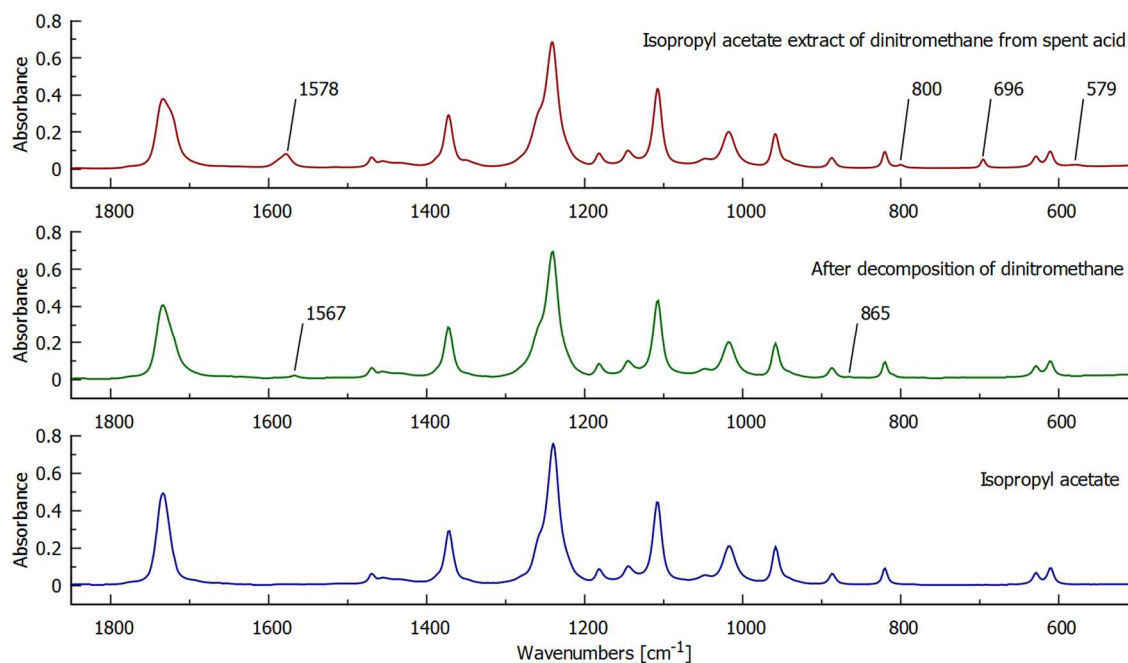


Figure 3: Identification by FTIR of dinitromethane and the product after its decomposition in isopropyl acetate extract.

During decomposition of dinitromethane in spent acid, UV absorption of dinitromethane with maximum at 363 nm disappeared; however a new maximum at 315 nm appeared and new bands at 1567 cm^{-1} and 865 cm^{-1} in FTIR spectrum appear as shown in Figure 2. As a result of aforementioned, the presence of an intermediate was indicated.

The thermal decomposition of the spent acid was also studied using accelerating rate calorimetry. The temperature (black) and pressure (red) profile of DNM decomposition measured with ARC can be seen in Figure 4. The exotherm starts at $65.7\text{ }^{\circ}\text{C}$. Raw ΔT equals $10.9\text{ }^{\circ}\text{C}$. The Φ -factor¹ for this experimental setup is 2.97, which means that the Φ -corrected ΔT_{ad} value is $32.4\text{ }^{\circ}\text{C}$. Heat of the decomposition was 32.6 J/g .

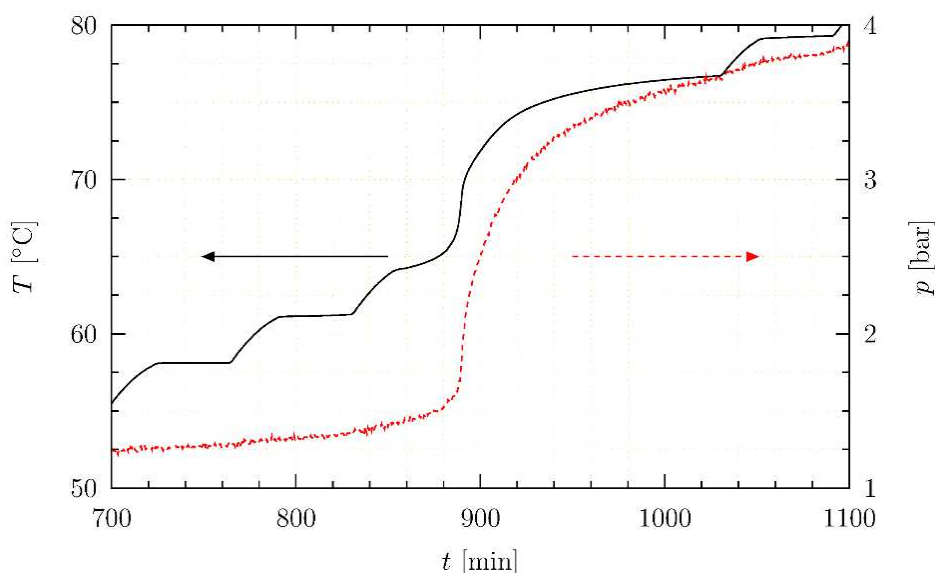


Figure 4: The thermogram of thermal decomposition of DNM, measured with ARC.

One of the key parameters, which can be easily calculated from ARC data, is time to maximum rate (TMR_{ad}). It can be used to estimate how long the sample lasts at a given temperature. This TMR-temperature dependence is plotted in Figure 5. The blue points were directly measured with ARC, black points include the Φ -correction and the red line is the extrapolation to lower temperatures.

¹ Since the adiabatic conditions in the calorimeter are not ideal, the obtained parameters must be corrected by Φ -factor, which is the measure of the adiabaticity. The Φ -factor is given by the relationship between thermal masses of the sample and its surroundings: $\Phi = 1 + \frac{m_B c_B}{m_S c_S}$

where m are masses, c are specific heats, indices S are for the sample and indices B are for the surroundings (bomb). In the case of ideal adiabaticity, the Φ -factor would be equal to 1, but the bomb serves as a cooler, absorbing a part of the released heat, increasing the Φ -factor.

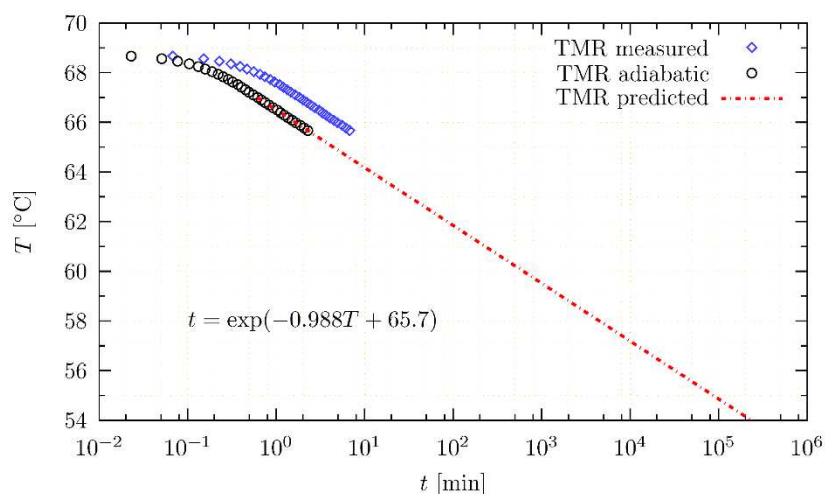


Figure 5: The time to maximum rate (TMR_{ad}) prediction for DNM from ARC data.

As a second option, we used reduction as a potentially industrially exploitable method for elimination of dinitromethane. Recently, we have described reduction of dinitromethane using zinc, the products being established as ammonia and methylamine, proved by NMR as ammonium chloride and methylammonium chloride [46-47]. In the present work, we reduced dinitromethane with iron. In this case, the dinitromethane reduction products were also ammonia and methylamine, as indicated by its chlorides using FTIR spectroscopy after comparison with ammonium chloride and methylamine hydrochloride standards (Figure 6). The spectrum of methylamine hydrochloride in the reduction product is largely overlapped by ammonium chloride bands, but after software subtraction, the presence of methylamine hydrochloride as reduction product is clearly evident.

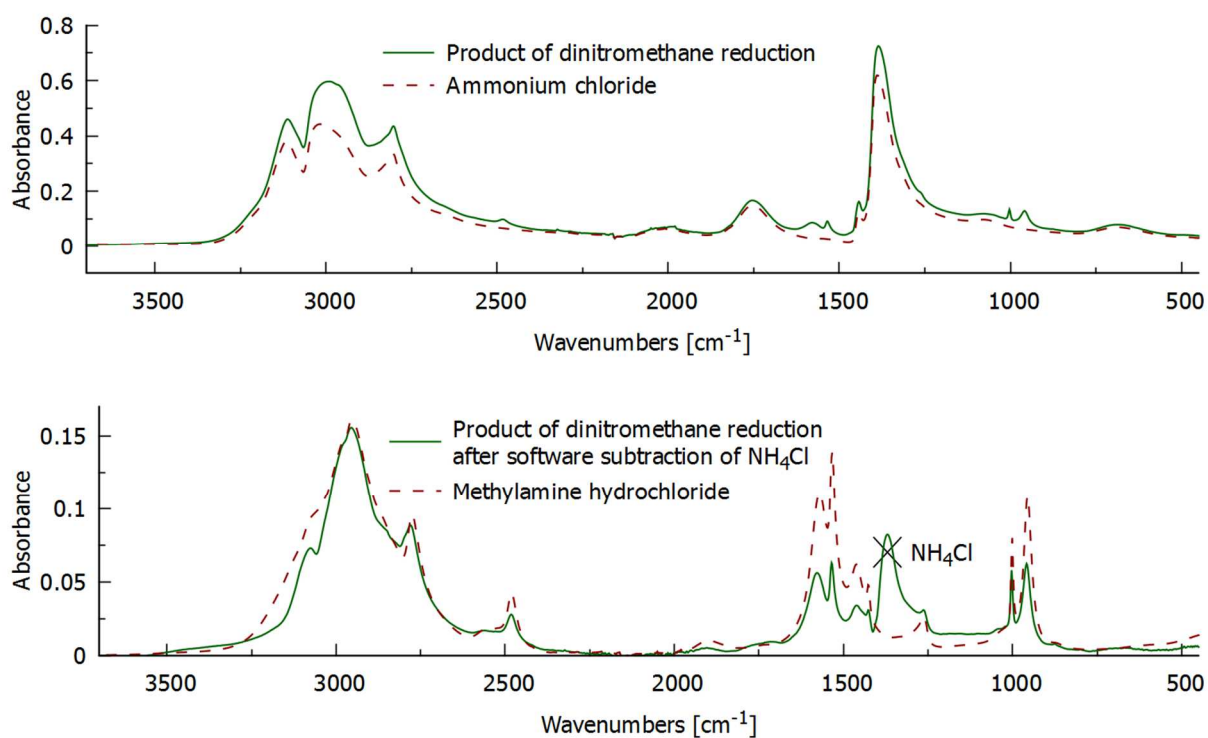


Figure 6: FTIR spectra of dinitromethane reduction products (ammonia and methylamine), proved as ammonium chloride and methylamine hydrochloride and comparison with standards.

Another possibility that can be considered for dinitromethane is its use itself or as a starting material for various syntheses. One product class - dinitromethane salts with organic bases - suffers from chemical and thermal stability. As an exception, the guanidine salt could be mentioned [48-51]. Low viscosity dinitromethane salt ionic liquids [52] have been reported. For use as a starting material, dinitromethane extract in ethyl acetate or potassium dinitromethane are possible. Both may be used for chemical synthesis of different types of compounds, such as energetic plasticisers containing gem-dinitro group [53-54] or even synthesis of FOX-7 from the potassium salt of dinitromethane may be possibility [55-57].

4 Conclusions

Dinitromethane from FOX-7 synthesis may be removed from the reaction mixture by thermal decomposition or by using chemical reduction. Thermal decomposition produces carbon dioxide and nitrous oxide, reduction with iron produces ammonia and methylamine in the form of its salts with sulphuric acid. Also, dinitromethane may be extracted from the reaction mixture and converted to its salts, e.g. potassium dinitromethanide or generally used as a source of dinitromethane for chemical syntheses. FTIR, TLC and UV are suitable methods for identification and determination of dinitromethane in spent acid.

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