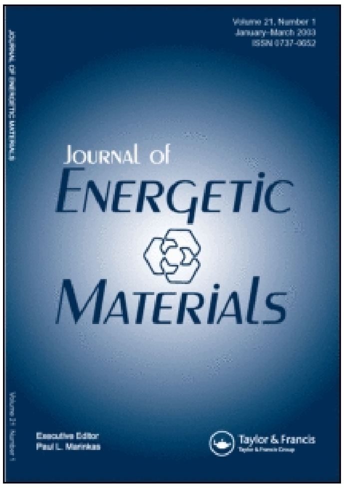

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Gaseous Products of Dinitromethane Decomposition Determined by DTA/FTIR

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Gaseous products of the thermal decomposition of dinitromethane and potassium dinitromethanide were investigated by simultaneous DTA/FTIR analyses. Both isothermal and non-isothermal DTA regimes were applied. Nitrous oxide and carbon dioxide were detected by FTIR.

Keywords: decomposition, dinitromethane, DTA, FTIR, potassium dinitromethanide

Introduction

Both thermal and chemical stabilities of dinitromethane (DNM) are significantly lower than stabilities of other polynitromethanes. Pure dinitromethane can be prepared in small quantities [1] and stored at low temperatures for prolonged periods, but at room temperatures it decomposes in approximately

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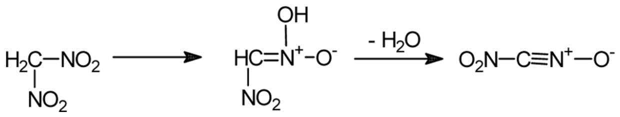
1 day [2]. The use of organic solvents extracts of dinitromethane or potassium dinitromethanide is less dangerous than pure dinitromethane.

In the field of synthesis of energetic materials, dinitromethane is a by-product of 2,2-dinitroethene-1,1-diamine (FOX-7) production [3,4]. In this procedure, dinitromethane remains dissolved in waste acids after isolation of FOX-7 and presents a tedious by-product due to its explosive and toxic properties. Salts of dinitromethane are suggested as an intermediate product and starting material for synthesis of explosives and propellants containing *gem*-dinitro groups [5]. Potassium dinitromethanide is also a starting material for synthesis of new energetic plasticizers derived from 2,2-dinitropropane-1,3-diol [6].

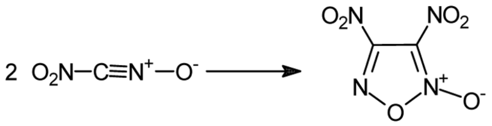
In contrast with the gas-phase decomposition of nitro compounds [7], the decomposition in the liquid state has not been studied well enough. The most typical reaction of nitroalkane salts in acid solutions is the Nef reaction [8,9], yielding an aldehyde or ketone together with nitrous oxide.

This work deals with the thermal decomposition of dinitromethane in diluted acid, organic solvents and with the decomposition of potassium dinitromethanide.

Khrapovsky et al. [10] suggested theoretical mechanism of dinitromethane decomposition in liquid phase. Nitroformonitril oxide is a potential intermediate of dinitromethane decomposition.



Nitroformonitril oxide is also considered as an intermediate in synthesis of 4,5-dinitrofuroxane from dinitromethane in concentrated sulphuric acid or oleum [11].



Torsell and Ryhage [12] described thermal decomposition of aliphatic nitrocompounds: potassium trinitromethanide, potassium 1,1-dinitroethanide, nitronitroso alkanes, and halogen nitroalkanes in organic solvents. Nitrous oxide and carbon dioxide together with little amounts of nitric oxide, nitrogen dioxide, and potassium salts (KNO_2 , KNO_3 , KOAc) were found as the decomposition products of potassium trinitromethanide (in dimethoxyethane) and potassium 1,1-dinitroethanide (in dimethylformamide).

Rahman and Clapp [13] reported that thermal decomposition of potassium 1,1-dinitroethanide and potassium 1,1-dinitropropanide in dimethylformamide at 80°C gave acetic and propionic acid, respectively and potassium nitrite.

Duden [14] described thermal decomposition of potassium dinitromethanide at 205°C yielding potassium carbonate, water, carbon dioxide, nitric oxide, and nitrogen.

Experimental

Caution: All polynitro compounds are considered toxic and potentially explosive and should be handled with appropriate precautions. Free dinitromethane is unstable even at room temperature; potassium dinitromethanide may be sensitive to electric spark, friction, and impact.

Syntheses of Dinitromethane and Potassium Dinitromethanide

1. From barbituric acid [15,16]. Barbituric acid (Aldrich, 99%) was nitrated to form 5,5-dinitrobarbituric acid, which was subsequently hydrolyzed with potassium hydroxide. Resulting potassium dinitromethanide was isolated in the yield of 67.5%, m.p. 221–222°C. The salt was directly used for DTA/FTIR study or for preparation of dinitromethane solutions in diluted sulphuric acid and dinitromethane solutions in organic solvents.
2. From 2-methylpyrimidine-4,6-diol [3,4]. 2-Methylpyrimidine-4,6-diol (Aldrich, 97%) was nitrated with mixed acid. After nitration, the reaction mixture was poured into water. The resulting 2,2-dinitroethene-1,1-diamine

was filtered off and the reaction mixture containing dinitromethane was submitted to DTA/FTIR analysis.

DTA/FTIR Analysis

Differential thermal analysis measurements were determined on a DTA 551-Ex apparatus (OZM Research, CZ), constructed especially for the analyses of explosive substances [17]. Massive construction of the apparatus makes possible to measure the thermal decomposition of primary and secondary explosives, propellants, and pyrotechnics. Analyses were carried out in glass microtubes, with the heating rate of 5°C min^{-1} or as isothermal measurement at desired temperature.

Infrared spectra were determined on a Nicolet Protégé 460 spectrometer. The inlet of FTIR with GC interface (Nicolet Corporation) was connected into the DTA test tube (see Fig. 1). To avoid breakage of test tubes and/or the KBr windows inside the GC interface, the charge of the liquid sample was 150 mg. A peristaltic pump was connected to GC interface outlet, so that the waste gases were sucked with a constant rate 90 mL min^{-1}. Volume of the FTIR/GC sampling space is about 4.5 mL. The transfer line as well as the cell was heated to 120°C. The optical length of the sampling cell is 20 m.

After the sample had been put into the test tube and connected with the GC interface, the system was flushed with gaseous nitrogen and then both DTA and FTIR analysis were launched. The heating rate was 5°C min^{-1} or 0°C min^{-1} in the case of isothermal measurement was applied, spectral resolution was 2 cm^{-1} and spectra were scanned each 3.7s. Before each measurement the inner space of the machine and the experimental space were flushed with nitrogen.

Evaluation of DTA Records and Spectra

The time was obtained from the time-concentration record, when the concentration of gases

1. started to increase;
2. approached the maximum.

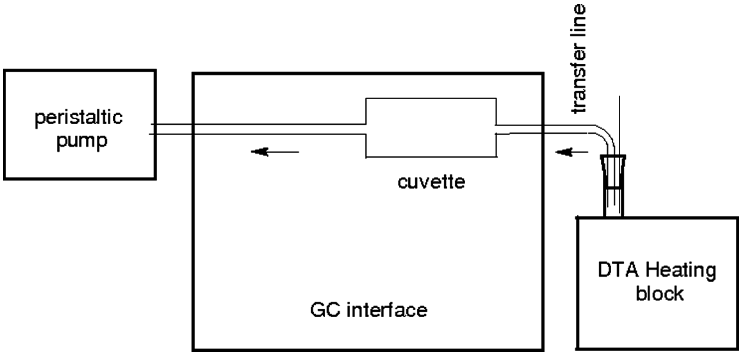


Figure 1. A block diagram of the FTIR/DTA experiments arrangement.

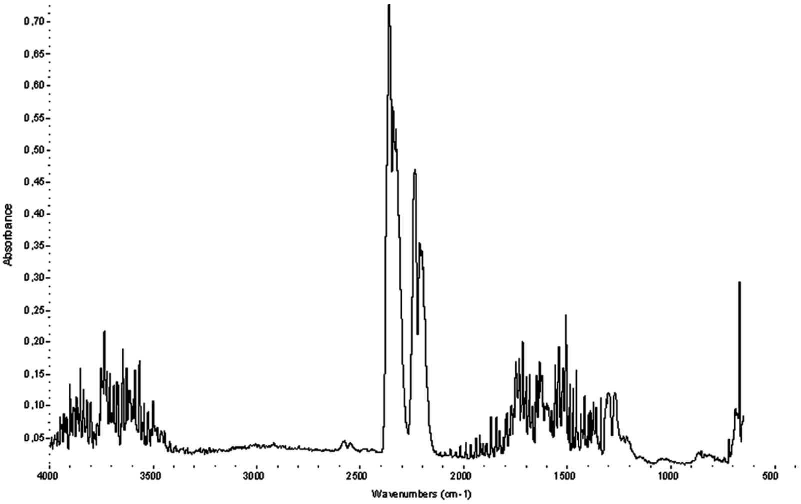


Figure 2. FTIR spectra of decomposition products of water solution of DNM (7.5%) in H_2 SO_4 (20.0%). Clear are absorption strips for CO_2 (2360, 2340 cm^{-1}) and N_2O (2240, 2220 cm^{-1}). Noticeable are strips for NO_2 (1630, 1600 cm^{-1}); however, they are in combination with water strips. *Note.* No additional operations with spectra were performed.

Table 1
FTIR results of thermal decomposition of dinitromethane (DNM) and potassium dinitromethanide

DTA conditions	Sample composition	FTIR results
Isothermal 80°C	Water solution of dinitromethane[a]1.5% DNM 20.0% H_2SO_4, max. 0.7% HNO_3	N_2O, CO_2 (H_2O) start: 14 min max 20 min
Isothermal 80°C	Water solution of dinitromethane[b] 1.5% DNM, 20.0% H_2SO_4	[c]
Isothermal 80°C	Water solution of dinitromethane[b] 1.5% DNM, 20.0% H_2SO_4, 0.7% HNO_3	[c]
Non-isothermal up to 100°C, 5°C/min	Water solution of dinitromethane[a] 1.5% DNM, 20.0% H_2SO_4, max. 0.7% HNO_3	N_2O, CO_2 (H_2O) start: 14 min (80°C) max 15 min (85°C)
Non-isothermal up to 100°C, 5°C/min	Water solution of dinitromethane[b] 1.5% DNM, 20.0% H_2SO_4, 0,7% HNO_3	N_2O, CO_2 (H_2O) start: 16 min (85°C) max 19 min (96°C)
Isothermal 90°C	Water solution of dinitromethane[b] 1.5% DNM, 20.0% H_2SO_4, 0,7% HNO_3	[c]
Non-isothermal up to 100°C, 5°C/min	Water solution of dinitromethane[b] 7.5% DNM, 20.0% H_2SO_4	N_2O, CO_2, NO_2 traces, (H_2O) start: 8 min (62°C) max 14 min (88°C)

(*Continued*)

Table 1
Continued

DTA conditions	Sample composition	FTIR results
Isothermal 90°C	Water solution of dinitromethane(b) 7.5% DNM, 20.0% H_2SO_4	N_2O, CO_2 (H_2O) start 17 min, max 22 min
Non-isothermal up to 250°C, 5°C/min	Potassium dinitromethanide(d)	N_2O, CO_2, H_2O start 30 min (197°C) max 33 min (213°C)
Non-isothermal up to 100°C, 5°C/min	Solution of dinitromethane in ethyl acetate(e) 4% DNM	(*f*)
Isothermal 90°C	Solution of dinitromethane in ethyl acetate(e) 4% DNM	N_2O, CO_2 (H_2O) start 1 min maximum: 10 min
25–100°C	Solution of dinitromethane in diethyl ether (acidic solution) 4% DNM	N_2O, CO_2 (H_2O) start 1 min (40°C) max 6 min (50°C)
25–100°C	Solution of dinitromethane in diethyl ether (neutral, dried over $CaCl_2$) 4% DNM	N_2O, CO_2, H_2O start: 7 min (40°C) max 11 min (50°C)

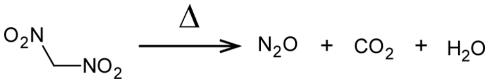
(a) The reaction mixture from 2,2-dmitroethene-1,1-diamine synthesis [3,4] (theoretical composition).
(b) Prepared from $KCH(NO_2)_2$, corresponding content of K_2SO_4.
(c) No gases were detected by FTTR during two hours of heating.
(d) 10 mg of the sample. **Caution!** Explosion took place.
(e) Prepared by neutralization of $KHC(NO_2)_2$ and extraction into solvent, dried over $CaCl_2$.
(f) The strips of ethyl acetate are distinctive only.

From the DTA records the appropriate temperatures were recognized. In the case of isothermal measurement only the time was evaluated. Note that the concentration was determined according to $2240\,\text{cm}^{-1}$ (N_2O) strip. A sample of FTIR spectra is presented in Fig. 2.

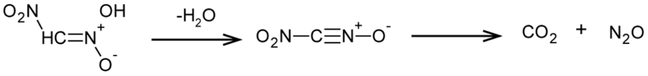
Results and Discussion

The FTIR results of dinitromethane and potassium dinitromethane decompositions are summarized in Table 1. In the case of dinitromethane solutions, water is shown in parentheses (because it is not possible to detect it by the method used because water comes both from water solutions of diluted acids and from dinitromethane decomposition). But in principle, water is supposed to be among the decomposition product.

According to the results stated in Table 1, we suggest the following equation of thermal decomposition of dinitromethane.



This is in accordance with the theory about formation of nitroformonitril oxide [18] followed by its decomposition to carbon dioxide and nitrous oxide.



Conclusions

It was found by FTIR that dinitromethane in diluted sulphuric acid, ethyl acetate, and diethyl ether decomposes to nitrous oxide and carbon dioxide. Further, it was found that potassium salt of dinitromethane decomposes into the same gaseous products. These products are relatively nontoxic and nonexplosive. Thanks to the safe and environmentally friendly disposal of this dinitromethane thermal decomposition, the method may be used in a solving of the ecological problems of some methods of the FOX-7 production.

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