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**Publisher's version / la version de l'éditeur:**  
*Chemosphere, 79, 2, 2010*

### **Web page / page Web**

<http://dx.doi.org/10.1016/j.chemosphere.2010.01.013>

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## Technical Note

# Microwave-assisted hydrolysis of nitroglycerin (NG) under mild alkaline conditions: New insight into the degradation pathway

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## ARTICLE INFO

## Article history:

Received 7 December 2009

Received in revised form 11 January 2010

Accepted 12 January 2010

Available online 2 February 2010

## Keywords:

Nitroglycerin

Alkaline hydrolysis

Microwave

2-Hydroxypropanedial

Degradation pathway

## ABSTRACT

Nitroglycerin (NG), a nitrate ester, is widely used in the pharmaceutical industry and as an explosive in dynamite and as propellant. Currently NG is considered as a key environmental contaminant due to the discharge of wastewater tainted with the chemical from the military and pharmaceutical industry. The present study describes hydrolytic degradation of NG (200  $\mu\text{M}$ ) at pH 9 using either conventional or microwave-assisted heating at 50 °C. We found that hydrolytic degradation of NG inside the microwave chamber was much higher than its degradation using conventional heating. Products distributions in both heating systems were closely related and included nitrite, nitrate, formic acid, and the novel intermediates 2-hydroxypropanedial ( $\text{O}=\text{CHCH}(\text{OH})\text{HC}=\text{O}$ ) and glycolic acid ( $\text{CH}_2(\text{OH})\text{COOH}$ ). Two other intermediates glycolaldehyde ( $\text{CH}_2(\text{OH})\text{CHO}$ ) and glyoxylic acid ( $\text{CHOCOOH}$ ) were only detected in the microwave treated samples. The molar ratio of nitrite to nitrate in the presence and absence of microwave heating was 2.5 and 2.8, respectively. In both microwave assisted and conventional heating a nitrogen mass balance of 96% and 98% and a carbon mass balance of 58% and 78%, respectively, were obtained. The lower C mass recovery might be attributed to further unknown reactions, e.g., polymerization of the aldehydes  $\text{CH}_2(\text{OH})\text{CHO}$ ,  $\text{CHOCOOH}$  and  $\text{O}=\text{CHCH}(\text{OH})\text{HC}=\text{O}$ . A hydrolytic degradation pathway for NG was proposed involving denitration (loss of 2  $\text{NO}_2^-$ ) from the two primary carbons and the loss of one nitrate from the secondary carbon to produce 2-hydroxypropanedial.

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## 1. Introduction

Nitroglycerin (NG), a nitrate ester of glycerol ( $\text{C}_3\text{H}_5(\text{ONO}_2)_3$ ), was originally discovered by Ascanio Sobrero in 1847 and latter was employed by Alfred Nobel to produce dynamite in the 1860s. Presently NG is recognized for its wide applications in the pharmaceutical and military industry (Urbanski, 1965; Ahlner et al., 1991). Because of its explosive properties NG has been used in the manufacturing of explosives and propellants.

Despite its useful pharmaceutical application, NG is of particular environmental concern because the chemical is xenobiotic that has never occurred naturally and is known to be toxic to various aquatic and terrestrial organisms including algae, vertebrates and invertebrates (Burton et al., 1993). Extensive manufacturing and wide applications of NG have resulted in the wide distribution of the chemical in the environment. Presently NG can be found in waste streams and soils of munitions manufacturing facilities and in areas adjacent to pharmaceutical plants. High concentrations of NG were found in soil at Canadian Forces training areas

(Jenkins et al., 2008) and in wastewaters of US Badger Army ammunition plant (Barabo, WI, 180  $\text{mg L}^{-1}$ ) and Radford Army ammunition plant (Radford, VA, 300–600  $\text{mg L}^{-1}$ ) (Oh et al., 2004). Being toxic (Pesari and Grasso, 1993) NG must thus be removed from contaminated wastewater before it reaches soil and ground water.

In general little information is available on the cleanup of NG in contaminated water. For years, wastes containing explosives have been incinerated releasing atmospheric contaminants into the air and subsequently reaching water and soil (Garg and Castaldini, 1991). Adsorption by activated carbon could also be used for removing explosives contamination from waste waters (Parlette et al., 2005), but this technology leaves the carbon loaded with the explosive and thus become hazardous waste. NG can also be chemically treated in wastewater by digestion in strong caustic solution or denitration with sodium disulfide (Smith et al., 1983). The use of excess amounts of reactants in these methods creates another disposal problem. Few other academic research articles have been reported on the hydrolysis of NG (Boschan et al., 1955; Capellos et al., 1984; Tsaplev, 2004), but little information is available on the eventual fate of the nitrate ester. To provide answers to these questions and to gain new insights into the degradation pathway of NG we studied the hydrolysis of the

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nitrate ester under mild alkaline conditions enhanced with microwave irradiation. Recently microwave technology has received considerable attention as a green technology for various analytical and chemical applications, e.g., to enhance sample preparation and extraction (Walter et al., 1997; Srogi, 2006) and to conduct organic synthesis (Gedye et al., 1991; Clarke et al., 2007). Microwave heating has been successfully used to reduce the time required to extract biopolymers from bacterial cells (Betancourt et al., 2007) and 2,4,6-trinitrotoluene from soil from few hours to few min (Kjellstrom et al., 2008), and to treat soil contaminated with chloramphenicol (Lin et al., 2010). To our knowledge, the use of microwave heating for NG hydrolysis has not been reported before.

The current work thus examines the hydrolysis of NG under mild alkaline conditions using  $\text{Na}_2\text{CO}_3$ , at pH 9 in a microwave focusing on the identification of the NG transformation pathway pinpointing end products and early intermediates of the reaction. Earlier literatures show that NG can be hydrolyzed under high alkaline conditions (pH  $\geq$  12) to produce formate, oxalate, acetate often with a poor mass balance (Boschan et al., 1955; Capellos et al., 1984; Tsaplev, 2004). The use of mild alkaline conditions assisted with microwave irradiation were selected here because, (1) pH 9 is closer to natural environmental conditions found in contaminated soil and water, and (2) rapid hydrolysis by microwave can lead to the formation of intermediates in sufficient amounts that would allow detection thereby helping to gain more insights into the NG decomposition pathway(s).

## 2. Materials and methods

### 2.1. Chemicals

NG, 1,2-dinitrolycerin (1,2-DNG), 1,3-dinitrolycerin (1,3-DNG), 1-mononitrolycerin (1-MNG), 2-mononitrolycerin (2-MNG) standard solutions in acetonitrile ( $1000 \text{ mg L}^{-1}$ ) were purchased from Cerilliant Corporation (Round Rock, TX). Glyceraldehyde, glycolic acid, glyoxylic acid, oxalic acid, glyoxal, dihydroxy acetone, KOH and  $\text{Na}_2\text{CO}_3$  were obtained from Sigma-Aldrich (St. Louis, MO). Sodium nitrite ( $1000 \text{ mg L}^{-1}$ ) and ammonium nitrate ( $1000 \text{ mg L}^{-1}$ ) standards were purchased from Alltech (Deerfield, IL). All solutions were prepared using Milli-Q-UV Plus Ultrapure water system ( $>18 \text{ M}\Omega \text{ cm}$ , Millipore, MA, USA).

### 2.2. Synthesis of 2-hydroxypropanedial

The suspected NG product 2-hydroxy-propanedial was synthesized from dihydroxy acetone in water in the presence of copper acetate at  $60^\circ\text{C}$  for 20 h (Evans and Waring, 1926). The reaction mixture was filtered through a  $0.45 \mu\text{m}$  HV Millipore filter, and derivatized with 2,4-dinitrophenyl hydrazine (DNPH) at room temperature for 1 h. The compound was identified as its 2,4-dinitrophenyl hydrazine derivative using LC/MS analysis and the detection of its deprotonated molecular mass ion  $[\text{M}-\text{H}]^-$  at 267 Da (see below).

### 2.3. Hydrolysis of NG

A MARS Microwave Accelerated Reaction System (Model R-430CSC, CEM Corporation, Matthews, NC, USA) (1.5 kW, 1100 W output, 2.45 GHz) was used for the hydrolysis of NG. Aliquots of NG solutions ( $200 \mu\text{M}$ ) were first added to glass vials (7 mL) followed by the addition of  $\text{Na}_2\text{CO}_3$  or KOH keeping the pH at 9 or 12, respectively. The reaction vials were then placed inside Teflon microwave reaction vessels, one vial in each vessel, and the Teflon tubes were then sealed (screw caps) and placed inside a micro-

wave chamber (power at 225 W). The temperature ( $50 \pm 5^\circ\text{C}$ ) inside the reaction vessel was monitored using an IR sensor. To avoid overheating the reaction was stopped every 2 min by cooling the reaction vessel over ice. In a parallel set of experiments we hydrolyzed NG at either pH 9 or 12 but using a conventional heating block ( $50^\circ\text{C}$ ). A control experiment containing NG in water alone and subjected to microwave heating was conducted. In a separate experiment we followed the behavior of glycerol ( $100 \mu\text{M}$ ) and nitrite ( $100 \mu\text{M}$ ), both are suspected products of NG hydrolysis, in alkaline medium (pH 9) using microwave irradiation under similar conditions to those described above for NG. The pHs of the samples were measured using Orion 3 Star pH meter (Thermo Fisher Scientific, Beverly, MA, USA). All experiments were made in duplicate. NG and its hydrolysis products were analyzed as described below.

### 2.4. Analysis of NG and products

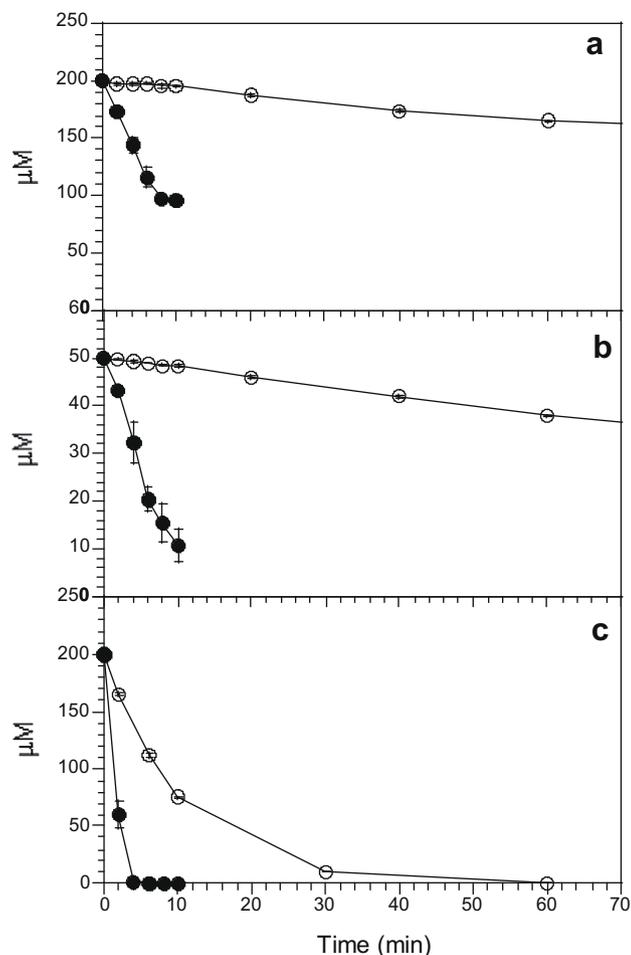
NG and its partially denitrated products 1,3- and 1,2-DNG, and 1- and 2-MNG were analyzed using an HPLC/UV-RI system (Waters Associates, Milford, Mass.) connected to an AnionSep Ice-Ion-310 Fast organic acid column (6.5 mm ID by 150 mm; Transgenomic, Los Angeles, CA, USA) and eluted using 1.73 mM sulfuric acid mobile phase with a flow rate of  $0.6 \text{ mL min}^{-1}$  at  $35^\circ\text{C}$ . The fully denitrated NG products glycolaldehyde, 2-hydroxypropanedial, and 1,3-dihydroxyacetone were first derivatized by DNPH for subsequent analysis using a Bruker MicroTOFQ mass analyzer attached to an HPLC system (Hewlett Packard 1200 Series) equipped with a diode array detector. The samples were injected into a 3.5 micron-pore size Zorbax SB-C18 column (2.1 mm ID by 150 mm; Agilent, Mississauga, Canada) at  $25^\circ\text{C}$ . The solvent system was composed of a  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  gradient (40–80% v/v) at a flow rate of  $0.15 \text{ mL min}^{-1}$ . A negative electrospray ionization mode was employed to generate the deprotonated molecular mass ions  $[\text{M}-\text{H}]^-$  of the derivatized products. The mass range was scanned from 40 to 1000 Da. Formaldehyde, formic acid, glycolic acid, ammonium, nitrate, nitrite were analyzed as described by Balakrishnan et al. (2004). Glycerol was quantified using the HPLC method described for formic acid using an electrochemical detector (Waters Model 2465). Nitric oxide (NO) was determined using Apollo 4000 free radical analyzer (WPI, Sarasota, FL) specific for NO analysis.

## 3. Results and discussion

### 3.1. Alkaline hydrolysis of NG

Fig. 1a shows that more than 50% of NG (initial concentration  $200 \mu\text{M}$ ) degraded using microwave heating ( $50^\circ\text{C}$ ), but less than 5% degraded using conventional heating in 10 min. When the initial concentration of NG was decreased to  $50 \mu\text{M}$  approximately 80% of NG hydrolyzed using microwave treatment (Fig. 1b) but in contrast only 50% of the chemical degraded after 3 h of treatment at pH 9 using conventional heating. If the reaction is carried out at room temperature only 50% removal of NG occurred in 25 d. In addition only 4% of NG was lost in water alone and no NG hydrolysis took place under acidic conditions (pH 2) even when microwave heating ( $50^\circ\text{C}$ ) was used, indicating the necessity of using alkaline conditions to hydrolyze the chemical.

Localized superheating caused by microwave irradiation reportedly is responsible for lowering the time(s) required to complete chemical reactions (e.g., hydrolysis). The presence of large number of ions ( $\text{Na}^+$ ,  $\text{OH}^-$ , and  $\text{CO}_3^{2-}$  in the present system) is also reported to enhance hydrolysis by the superheating effect they cause in the microwave-assisted reaction (Baghurst and Mingos, 1992; Mingos



**Fig. 1.** Hydrolysis of NG at 50 °C using microwave-assisted heating (●) and conventional heating (○): (a) 200 µM of NG at pH 9; (b) 50 µM of NG at pH 9, (c) 200 µM of NG at pH 12.

and Baghurst, 1997). Indeed microwave has been recently used to enhance many chemical reactions including the hydrolysis of amides and proteins (Gedye et al., 1986; Chen et al., 1987), sucrose (Chen et al., 1990), starch (Yu et al., 1996; Corsano et al., 2004), and the time required to carry out the well known Williamson ether synthesis from several hours to as little as one minute (Mingos and Baghurst, 1997).

As Fig. 1 shows hydrolysis of NG at pH 9 inside a microwave chamber was much faster than hydrolysis using conventional heating at 50 °C. We found that disappearance of NG (200 µM) in the microwave chamber was linear with time ( $R = 0.998 \pm 0.002$ ) for the first 6 min (Fig. 1a) with degradation rate reaching  $14.6 \mu\text{M min}^{-1}$ . After that the reaction slowed down and eventually stopped as pH of the reaction dropped down from 9 to 6.5 caused by the formation of acidic products such as formic and glycolic acids. At pH 12 NG (200 µM) completely degraded in 4 min in the microwave chamber but in more than 50 min using conventional heating (Fig. 1c). The effect of microwave irradiation was less pronounced at pH 12 than at pH 9.

### 3.2. Intermediates and products distribution

Using LC/MS we were able to detect several new intermediates (e.g., **Ia**, **Ib** and **II**) identified as derivatives of DNPH (Fig. 2a). Fig. 2b shows the mass spectra of two of these intermediates (**Ia** and **Ib**) each with a negative molecular mass ion  $[M-H]^-$  at  $m/z$  267. Each

of the two detected  $[M-H]^-$  mass ions corresponded to a molecular mass of 88 Da matching an empirical formula of  $C_3H_4O_3$  (**Ia** and **Ib**). The two intermediates **Ia** and **Ib** were identified as a DNPH mono-derivative of the 2-hydroxypropanedial  $[O=CHCH(OH)HC=O]$  and its tautomer hydroxypyruvic aldehyde  $[CH_2(OH)C(O)CHO]$  by comparison with standards prepared as described above. The DNPH derivative of intermediate **II** appeared with a  $[M-H]^-$  at  $m/z$  239 Da corresponding to a molecular mass of 60 Da, matching an empirical formula of  $C_2H_4O_2$ . The intermediate was identified as hydroxyl-acetaldehyde (glycolaldehyde),  $[HOCH_2CHO]$ , and confirmed by comparison with an authentic standard. Products **Ia**, **Ib** and **II** are new NG products that have never been reported before.

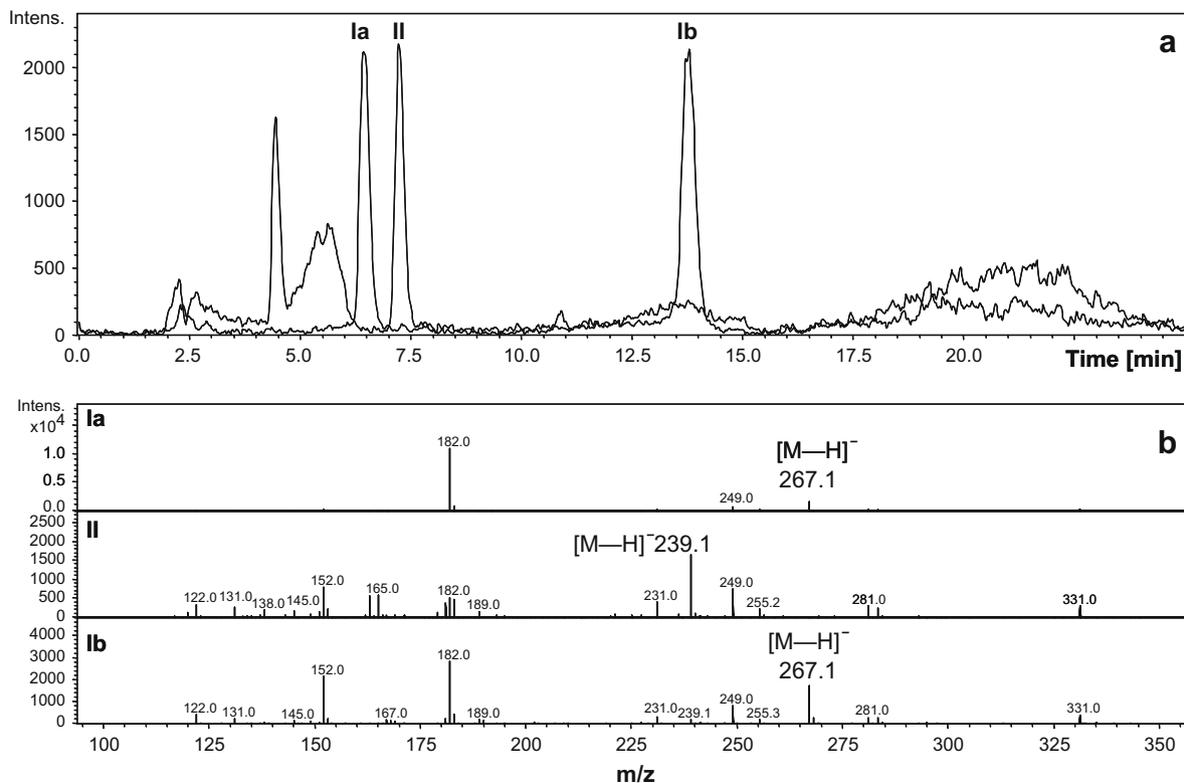
Table 1 summarizes products distribution of the hydrolysis of NG in aqueous alkaline solutions at pH 9 in the presence and absence of microwave heating. Products include nitrite, nitrate, 2-hydroxypropanedial, glycolaldehyde, glycolic acid, formic acid, and traces of glyoxylic acid.

We found the molar ratio of nitrogen containing products ( $NO_2^-$  and  $NO_3^-$ ) formed to NG degraded inside a microwave chamber or a block heater to be equal to 2.88 and 2.94 (representing a total N recovery of 96% and 98%, respectively). In the absence or presence of microwave heating we found that hydrolysis of NG at pH 12 also produced  $NO_2^-$  and  $NO_3^-$  with molar yields equaled to 2.3–2.5 (data not shown).

When nitrite was microwave heated at pH 9 the anion stayed intact indicating that the anion did not reduce to ammonia as observed during treatment of NG with Fe(0) where the three  $-NO_2$  groups in the nitrate ester reduced to ammonia (Oh et al., 2004). The same nitrite control did not give nitrate during microwave-assisted hydrolysis, indicating that nitrite and nitrate originated from NG independently during NG hydrolysis. On the other hand we did not observe any nitric oxide as a hydrolytic degradation product of NG. Nitric oxide has been described as an important degradation product inside mammalian cells and was identified of being responsible in the signaling mechanism in mammalian cells (Di Carlo, 1975; Ignarro et al., 1981; Ignarro, 2002; Kozlov et al., 2003).

Finally, neither of the partially denitrated NG products 1,2-DNG, 1,3-DNG, 1-MNG, nor 2-MNG, was detected. This is in line with the observation made earlier by Capellos et al. (1984) in the absence of the partially denitrated DNGs and MNGs from NG hydrolysis (pH 12). Likewise we did not observe the fully denitrated NG product glycerol which is known to be the final product of NG reaction with Fe(0) (Oh et al., 2004) and frequently found during biodegradation of the nitrate ester (Wendt et al., 1978; Servent et al., 1991; Meng et al., 1995; Marshall and White, 2001). When glycerol was allowed to react under the same conditions (pH 9) the chemical stayed intact indicating that glycerol is not a product of NG hydrolysis. At pH 12 NG hydrolyzed to products (glycolic, glyoxylic, and formic acids) were closely related to those observed at pH 9 under both conventional and microwave assisted condition. Also oxalic acid and trace amounts of glyoxal were detected under these conditions. Interestingly the key initial product 2-hydroxy-propanedial was not detected at pH 12. Once again no glycerol was detected in either case.

In both conventional and microwave-assisted heating a nitrogen mass balance of 98% and 96% and a carbon mass balance of 78% and 58%, respectively were obtained at pH 9. The C and N mass balances at pH 12 were 49% and 89%, respectively using microwave-assisted heating. The lower C mass recovery might be attributed to further unknown reactions, e.g., polymerization of the aldehydes  $CH_2(OH)CHO$ ,  $CHOCOOH$  and  $O=CHCH(OH)HC=O$  (Table 1). In general hydrolytic cleavage of NG has been reported to be very complex in nature and is attributed to the potential occurrence of complex secondary reactions (Lowry et al., 1920; Urbanski, 1965).



**Fig. 2.** LC-MS extracted ion chromatograms at  $m/z$  267 and  $m/z$  239 (a), and mass spectra of compounds (b) detected during microwave enhanced alkaline hydrolysis (pH 9) of NG.

**Table 1**  
Products distribution and carbon and nitrogen mass balance (%) of NG hydrolysis (see Fig. 1a) at pH 9 and 50 °C using microwave (10 min) and conventional (60 min) heating.

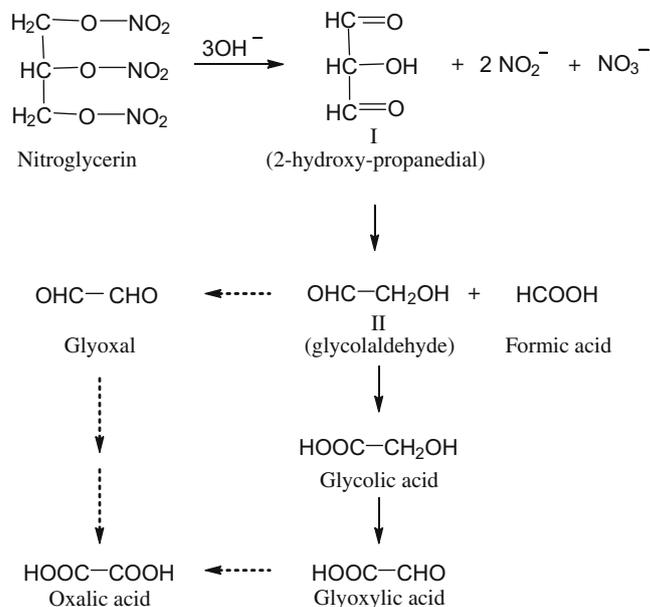
Products	Microwave		Conventional	
	Carbon (%)	Nitrogen (%)	Carbon (%)	Nitrogen (%)
2-Hydroxypropanedial <sup>a</sup>	10 ± 0.92	NA	17 ± 0.45	NA
Glycolaldehyde	2 ± 0.18	NA	0	NA
Glycolate	29 ± 0.24	NA	39 ± 0.58	NA
Formate	17 ± 0.33	NA	22 ± 0.13	NA
Nitrite	NA	68 ± 0.52	NA	72 ± 0.43
Nitrate	NA	28 ± 0.45	NA	26 ± 0.38
Total	58	96	78	98

NA: not applicable.

<sup>a</sup> Total of 2-hydroxypropanedial and its tautomer hydroxypyruvic aldehyde.

### 3.3. Hydrolysis pathways of NG

The formation of  $\text{NO}_2^-$  and 2-hydroxypropanedial,  $\text{O}=\text{CHCH}(\text{OH})\text{C}=\text{O}$ , confirms the occurrence of  $\beta$ -hydrogen elimination from the two primary Cs in NG. Such reaction often called carbonyl elimination,  $E_{\text{CO}2}$  (Baker and Hegg, 1955), is enhanced by the availability of acidic hydrogen on the two primary Cs in NG. Whereas the formation of  $\text{NO}_3^-$  was possibly caused by a  $\beta$ -hydrogen elimination and/or by substitution of  $\text{OH}^-$  at the secondary C in NG as commonly seen in secondary alkyl nitrates (Baker and Easty, 1952; Boschan et al., 1955). In the present study the ratio of nitrite to nitrate calculated from Table 1 in the presence and absence of microwave heating was 2.5 and 2.8, respectively. Capellos et al. (1984) and Wheals and Ellison (1989) found that the nitrite/nitrate ratio ranged between 2 and 3. These findings suggested that  $\beta$ -hydrogen elimination reaction is the main route to nitrite forma-



**Fig. 3.** Constructed hydrolytic degradation pathway of nitroglycerin using microwave-assisted heating (225 W, 50 °C) at pH 9 (plain arrow) and pH 12 (dashed arrow).

tion in the NG hydrolysis in which the two primary Cs gave the two nitrite anion while the remaining secondary one gave the nitrate anion.

The formation of hydroxy acetic acid (glycolic acid) and formic acid is an indication of the occurrence of C–C bond cleavage in the C backbone of NG. As we mentioned above neither the dinitrated

(1,3- and 1,2-DNG) nor the mono-nitrated (1- and 2-MNG) derivatives of NG were detected. Taking all experimental evidences gathered thus far we constructed a hydrolytic degradation pathway for NG as shown in Fig. 3. The pathway excludes the sequential denitration of NG to eventually produce glycerol. In support of this conclusion we were unable to detect any glycerol during NG hydrolysis in the present study. In contrast reductive sequential denitration of NG to glycerol has been frequently reported for the treatment of NG with Fe(0) and during anaerobic biodegradation with subsequent formation of 1,3-DNG, 1,2-DNG, 1-MNG, and 2-MNG.

In conclusion the trinitrate ester of glycerin, NG, can be easily denitrated under mild alkaline conditions (pH 9) using microwave heating at 50 °C. The environmental significance of the reaction lies in the transformation of the xenobiotic and hazardous chemical to simple and more ubiquitous ones such as nitrite, nitrate, HCOOH, glycolic acid and  $O=CHCH(OH)HC=O$ . Indeed  $O=CHCH(OH)HC=O$  is a natural product occurring in certain musts and wine (Guillou et al., 1997).

### Acknowledgments

We would like to thank Mr. Stephane Deschamps, and Mme Louise Paquet for technical assistance. Financial support of DRDC DND, Valcartier Canada is highly appreciated.

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