

OXIDATION OF UNSYMMETRICAL DIMETHYLHYDRAZINE IN ENVIRONMENT, PRODUCTS AND MECHANISTIC INVESTIGATIONS: A REVIEW

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Abstract

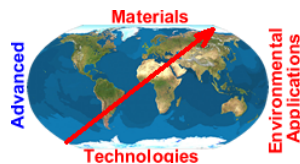
The oxidation of unsymmetrical dimethylhydrazine(UDMH) with different oxidizing agents in atmosphere, water and soil has been reviewed. Emphasis is put on comparison of the oxidative products and the oxidation mechanism in different systems rather than on individual results. The number of the detected oxidative products are more than 30, and major identified products are N-nitrosodimethylamine, Formaldehyde dimethylhydrazones, Dimethylamine, Tetramethyl-tetrazene, Formaldehyde, which are proved to have serious environment and human health impact. The main detailed pathway in ozone and oxygen reaction is primary abstracting hydrogen for N-H bond with formation N-amine radical or diazene, followed by add oxygen to form N-oxides radicals; Moreover, the N-oxides radicals undergo disproportion forming NDMA and the diazene leads to dimerization to tetramethyltetrazene, cleavage to dimethylamine; while the hydroxide radical tends to abstract hydrogen from C-H bond leads to formaldehyde and formaldehyde dimethylhydrazone. In order to clarify understanding the mechanism, the evaluation of transformation products quantitative analysis, as well as the advancement in theoretical and computational methods is the key role for the further study.

Keywords: unsymmetrical dimethylhydrazine, oxidative products, mechanism

1. Introduction

Unsymmetrical Dimethylhydrazine(UDMH) has been the main high energy fuels for rocket launching in China, Russian and Kazakhstan for decades. Taking into account the possibility of emergency spills of the fuels in its transportation, storage and filling, and also in falls of the spent stages of

launched rocket, the environment would be polluted by these substance, either evaporating or penetrating soil. UDMH is known as a primary eco-toxicant with the maximum allowable concentration (MAC) is in air, 0.001 mg/L [1], in water, 0.01mg/L [2], in soil, 0.1mg/kg [3]; therefore, attention has been put on high temperature dissociation [4, 5],



treatment to improve degradation efficiently [6, 7] and develop and evaluate specific catalyst [8, 9] for control the by-products. However, the dangers of UDMH are its high reactivity under natural conditions and a huge list of oxidative products, considerable amounts of which are equally or even more toxic than the UDMH (Figure 1). An example is N-nitrosodimethylamine (NDMA), which has received a great deal of attention as a human carcinogen. Risk assessments from the US EPA identify a theoretical cancer risk level for drinking water was 0.7ng/L [10, 11]. Moreover, it should be noted that UDMH is identified as a precursor of NDMA during chlorination incorporating ozone treatment of impaired source waters. Others like tetramethyltetrazene, hydrogen cyanide, formaldehyde, hydrazines and hydrazones, are also predicted to exhibit high probabilities for potential carcinogenicity, mutagenicity, teratogenicity [12-16].

Therefore, these transformation products not only have potential environment impacts but also pose direct threat to human beings. In order to better understand the UDMH transformation, the chemical structure transformation products and the mechanism of oxidative action of these toxic transformations should be explored.

This review article aims to assist the interested readers both involved in UDMH treatment and the environment fate of UDMH. This article is segregated into three parts (atmosphere, water, soil), which focus on the main transformation products and pathways in different oxygen systems. The detailed mechanism of UDMH different pathways in reaction with the oxides (O_2 , O_3 , OH) was also discussed. Finally, the

obstacles and the opportunities for further work are suggested.

2. Oxidation in atmosphere

The high amount of oxygen plays an important role in atmospheric oxidation chemical. Further, it was thought that almost all oxidation reactions could also be initiated by a very small number of chemical species: OH radicals, NO_3 radicals, O_3 , O_2 and halogen atoms such as Cl or Br . Hence, the UDMH atmospheric oxidation chemistry undergo a major transformation is complexity [17]. This manuscript introduces several reports about UDMH reaction with oxygen(O_2), ozone(O_3), oxygen atom(O).

2.1. Oxygen molecule

With strong reducing properties, UDMH would be oxidized by oxygen to give various products (Table 1), D.A. Stones [18] studied UDMH vapor oxidation by oxygen. The experiment sample (43uL UDMH, 150 Torr of oxygen and 575 torr of helium at 25°C) reacted 71 hours. The main oxidative products FDMH, with traces of DMA, FMH, and TMA was detected by the GC-MS. Moreover, even though with the oxygen concentration increased (43uL UDMH, 725Torr of O_2), there was no any methane detected, nevertheless, NDMA was present. The kinetic results show that the UDMH followed approximately pseudo first order with a rate constant of $8.3 \times 10^{-3} \text{ hr}^{-1}$ and decay with a half-life of about 84 hours. They also demonstrate that the temperature effects may be major importance in UDMH oxidation besides humidity [18].

The main product was FDMH. As long as the

oxygen is excessive, the NDMA will be present. Moreover, the oxygen in atmosphere is enough relative to UDMH, so the NDMA is unable to avoid. The kinetic results also predict that UDMH and its oxidative product NDMA are persist and difficult to remove in atmosphere.

2.2 Ozone

2.2.1 Analysis of Oxidation Products

Since the UDMH do not photolyze in the solar actinic region, its possible reaction pathways in the atmosphere is reaction with ozone, which is generated

in photochemical air pollution as well as being present in the unpolluted troposphere. Hence, James N. *et.al.* [19] and Ernesto C. Tuazon, *et.al.* [20] investigated the reaction of unsymmetrical dimethylhydrazine with ozone. The products during the oxidation were detected by FT-IR. Jame N's experiment was done with the initial concentration of 1.7ppm and 2ppm in the dark or sunlight. The main products is NDMA, which content almost reached 50%. In addition to the products (i.e. HONO, O₃, HCHO, NO, NO₂, HCOOH), CO and traces of CH₃NO₂ were also found at the end of the irradiation.

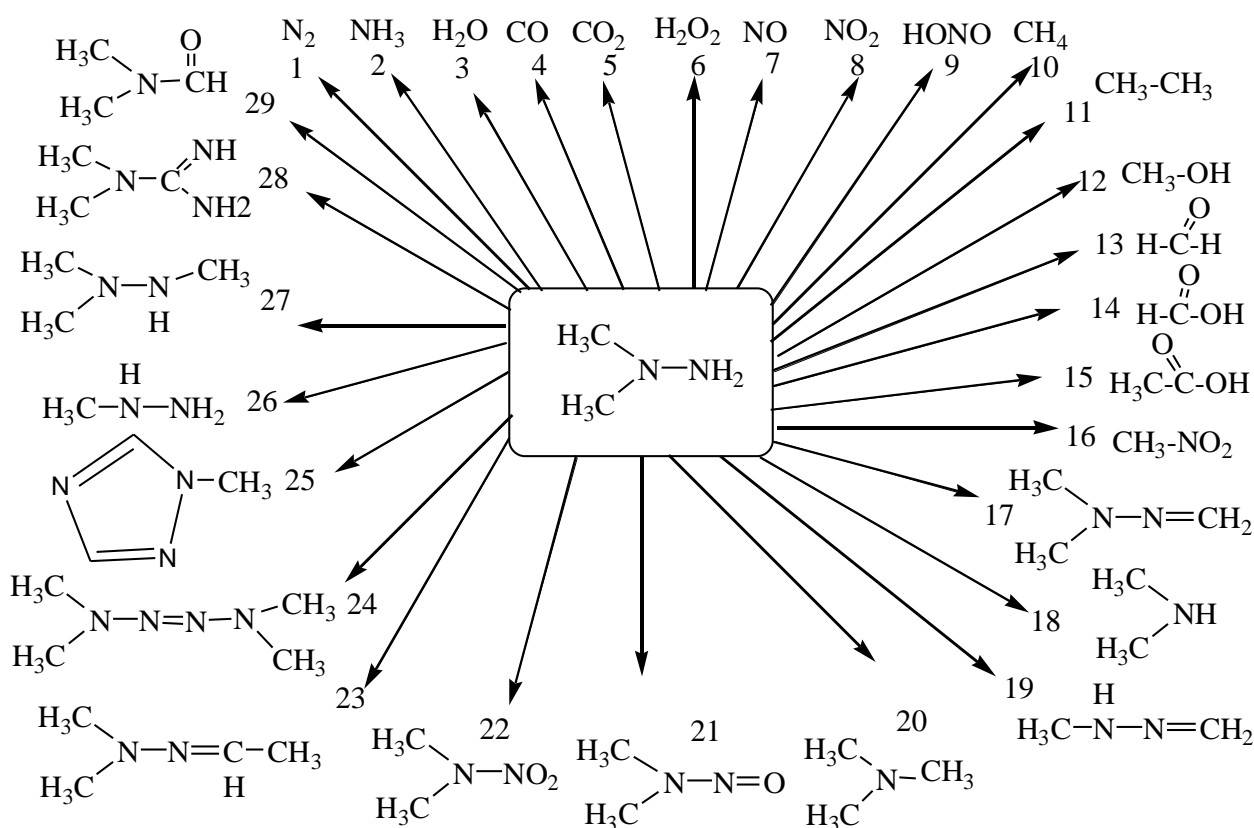


Figure 1. Oxidative products of 1,1-Dimethylhydrazine

Table 1. Structures of the reaction products of 1,1-Dimethylhydrazine

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No	Compound name	CAS no	In atmosphere		In aqueous		
			O ₂ ^[9]	O ₃ ^[10,11]	O ₂	O ₃	OH
1	Nitrogen	7727-37-9			+		
2	Ammonia	7664-41-7			+		
3	Water	7732-18-5			+		
4	Carbon monoxide	630-08-0		+			
5	Carbon dioxide	124-38-9			+		
6	Hydrogen peroxide	7722-84-1	+		+		
7	Nitric oxide	10102-43-9		+			
8	Nitrogen dioxide	7722-77-6		+			
9	Nitrous acid	14797-65-0		+			
10	Methane	74-82-8			+		
11	Ethane	74-84-0			+		
12	Methanol (MeOH)	67-56-1	+		+	+	
13	Formaldehyde	50-00-0		+	+		
14	Formic acid	64-18-6					+
15	Acetate	71-50-1		+			+
16	Nitromethane	75-52-5		+		+	+
17	Formaldehyde dimethylhydrazone (FDMH)	2035-89-4	+		+	+	
18	Dimethylamine (DMA)	124-40-3	+		+		
19	Formaldehyde monomethylhydrazone (FMH)	36214-48-9	+			+	
20	Trimethylamine (TMA)	75-50-3	+				
21	N-nitrosodimethylamine (NDMA)	62-75-9	+	+	+	+	
22	Dimethylnitramine	4164-28-7		+			
23	Acetaldehyde dimethylhydrazone (ADMH)	7422-90-4			+		
24	1,1,4,4-tetramethyl-1,2-tetrazene (TMT)	6130-87-6			+	+	
25	1-methyl-1,2,4-triazole (MT)	6086-21-1			+		
26	Methylhydrazine (MH)	60-34-4			+		
27	Trimethylhydrazine (TMH)	1741-01-1			+		
28	N,N-dimethylguanidine (DMG)	6145-42-2			+		
29	Dimethylformamide (DMF)	4472-41-7					

Note: '+' have been detected



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Table 2. Experimental conditions at selected times of UDMH with Ozone (reprinted with permission from Ref [20])

Conditions				Concentration, ppm								
Expt No.	T (av) °C	Rel humidity	Elapsed time, min	UDMH	O ₃	(CH ₃) ₂ NNO	H ₂ O ₂	HCHO	NH ₃	HONO	Nitrate(gas)	(CH ₃) ₂ NNO ₂
1	21	10	-7	1.71	a	a	a	a	0.116		0.02	a
			0	2.0 ^c	INJECTED							
			2	0.386	a	0.81	0.14	0.19	0.106	0.023		a
			61	0.170	a	0.78	0.08	0.08	0.079	0.062	0.92	a
			69	START OF SUNLIGHT IRRADIATION (1401 PDT, May 9, 1980)								
			79	a	a	0.41	0.07	0.34	0.077	0.19	0.86	0.15
			128	a	0.51	a	a	0.50	a	a	0.68	0.48
2	21	10	-9	1.93	a	a	a	a	0.116	a	0.106	a
			0	2.0 ^c	INJECTED							
			3	0.479	a	0.82	0.13	0.17	0.099	a		a
			73	0.293	a	0.77	0.045	0.051	0.069	0.052	0.83	a
			84	2.0 ^c	INJECTED							
			88	a	1.47	1.09	0.13	0.21	a	0.066	1.42	a
			120	a	1.09	1.11	0.15	0.22	a	0.058	1.22	a

a Below FT-IR detection sensitivity; blank means no measurement

In order to assess more precisely the effects of UDMH emissions in the atmosphere, Ernesto C. Tuazon *et.al.* [20-22] carried out the reaction of UDMH with O_3 at varying reactant ratios, both in the presence and absence of radical traps. Several experiments involving the reaction of O_3 with UDMH was taken in a large outdoor environmental chamber at concentrations in the ppm range (2.86-3.77ppm) in air. When the O_3 /UDMH stoichiometry was $\sim 1.5:1$, NDMA was formed in 60% yields within 2-3min. Other products observed (Table 2) were consistent with James N. When the O_3 /UDMH stoichiometry was $\leq 1:1$. No CO was formed in the dark reaction, however, in excess O_3 at prolonged reaction times and during sunlight irradiation, significantly high yields of CO were formed, and the yield of NDMA was increased. It implies that NDMA is unable to remove by the excess O_3 . It is worth noticeable that with OH radical traps,

NDMA yield more than that without OH radical traps. Upon irradiation, the $(CH_3)_2NNO$ would be partial converted to dimethylnitramine $((CH_3)_2NNO_2)$.

Therefore, the amount of NDMA produced in the reaction with ozone is much higher than that in the reaction with oxygen. The concentration of HCHO has been changing, so HCHO may be the intermediate during the ozonation process. With excess O_3 , the yield of NDMA would not decrease and high yields of CO were formed. The content of NDMA can be decreased only in the presence of OH radical or upon irradiation.

2.2.2 Mechanism

The literature values for room temperature rate constants of reactions of UDMH with ozone shows in Table 3. The rate of UDMH ozonation is faster than that of reaction with O_2 .

Table 3. The rate of UDMH reaction with O_3

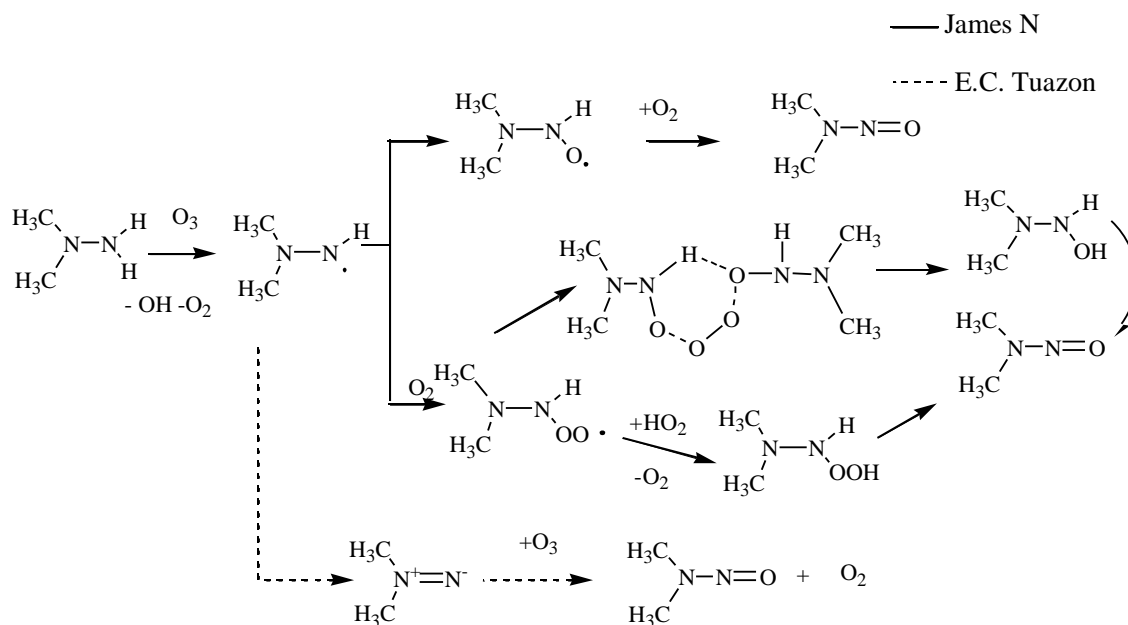
	UDMH Molec cm^{-3}	O_3 Molec cm^{-3}	Rate constants ($cm^3 \text{ molecule}^{-1} \text{ sec}^{-1}$)	Ref
Second order	$\sim 4.0 \times 10^{15}$	$\sim 2.5 \times 10^{16}$	$\geq 1.4 \times 10^{-15}$	[20]
Pseudo-first-order	$5.18-19.5 \times 10^{13}$	$6.14-23.9 \times 10^{14}$	$5.5 \pm 1.3 \times 10^{-14}$	[21]

The reaction mechanism was suggested which mainly accounts for the observed formation of $(CH_3)_2NNO$, CH_2O . James N proposed that the initial reaction with ozone is assumed to be hydrogen abstraction with the OH formed contributing to additional UDMH consumption (Scheme 1).

Subsequently, instead of formation of a diazene by means of β -hydrogen abstraction, the N-amino radical could either react with O_3 or add O_2 formed N-oxide radical. The formation of NDMA could be though N-oxide radical either self-reaction or reaction with O_2 , HO_2 .

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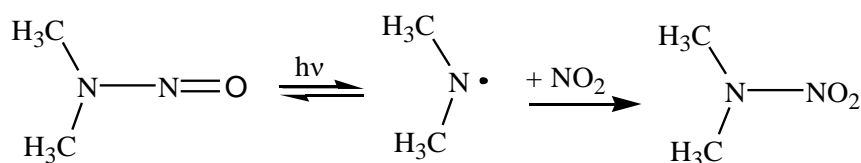
Scheme 1 Mechanism of NDMA formation during UDMH ozonation in atmosphere (reprinted with permission of Ref [19, 20])

However, Ernesto C. Tuazon [22] proposed another pathway about the NDMA formation. They suggested that O_3 or OH would abstract the β -hydrogen to form diazene as the intermediate observed in experiment. And the diazene would react with O_3 to form NDMA. It was suggested by means of

abstraction hydrogen from C-H bond followed by final product HCHO and MMH.

It has been agreed, the NDMA would cleavage undergo rapid photolysis producing the nitramine.

The detail pathway was shown in Scheme 2.



Scheme 2. NDMA cleavage under photolysis (reproduced with permission of Ref [22])

2.3 Oxygen atom

Unburned liquid rocket propellants are often ejected into the atmosphere at an altitude where ground-state atomic oxygen ($O(3P)$) is a predominant species. Some experimental and theoretical studies have been performed to study the

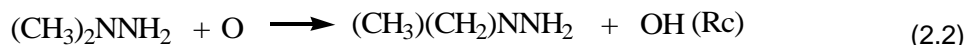
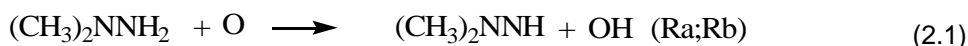
reaction of UDMH with the oxygen (O) atom. In 1992, Lang studied the reaction and measured the rate constant $((2.3 \pm 0.34) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ at 296 K [23]. Later, Vaghjian [24] reported the dynamic properties of the title reaction in a temperature range of 232–644 K and obtained the corresponding

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Arrhenius expression: $k = (1.94 \pm 0.34) \times 10^{-11} \exp[(25 \pm 25)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The rate constants decrease slightly with increasing temperature because of the low negative activation energy. Nevertheless, the detailed mechanism were

not discussed. Jinmiao Wen [25] used a dual-level direct dynamics method to investigate the mechanism and dynamics of multi-channel H-abstraction over a wide temperature range (200–2000 K). Three distinct pathways were discussed as follows:



The calculation results showed the barrier heights ($\Delta E(0\text{K})$) (in $\text{kcal} \cdot \text{mol}^{-1}$) were about 0.23(Ra), 2.21(Rb), 6.67(Rc). The paper also resulted that the channels related with H-abstraction from $-\text{NH}_2$ position dominate the reaction below 1200 K, whereas the reaction channel Rc (H-abstraction from $-\text{CH}_3$ group) become the major channel.

3 Oxidation in water

Many utilities are considering chloramination incorporating ozone treatment of impaired source waters, such as those impacted by upstream wastewater discharges, to expand water supplies [26]. As early as 1960s, it has been reported UDMH was the precursor of NDMA. And it undergoes oxidative produce a wide range of products (see table 1), parts of which are toxic, i.e. NDMA, TMT, FDMH, HCHO. The chemistry transformation of UDMH attracts much attention in water in recent years.

3.1 Oxygen

3.1.1 Analysis of oxidation products

Already in 1980, Milap. A.M. Arthur and Harry. H. Sisler [27] investigated the oxidation of 1,1-dimethylhydrazine with elemental oxygen to

determine if NDMA is produced and identify the other oxidation products. 0.2 M solution of UDMH reacted with $91 \pm 0.5 \text{ mmol}$ of O_2 in solutions of diethyl ether or cyclohexane between 20 and 30°C. They demonstrated that the principal products of this oxidation reaction under these conditions is FDMH, H_2O , N_2 , CH_4 , NH_3 , TMT, FMH, and NDMA were also identified products. Wang Xuan-Jun *et al.* [28] study the autoxidation of pure 1,1-dimethylhydrazine by air which was carried out at normal temperature. The oxidation products were characterized by gas chromatography-mass spectrometry. The results show that the main oxidation products were DMA, UDMH, FDMH, NDMA, ADMH, TMT. S. Banerjee *et al.* reported that aeration of dilute UDMH solutions ($1 \times 10^{-4} \text{ M}$) in the presence of CuSO_4 led to HCHO (30%), TMT, FDMH. The formation of NDMA depends upon the initial UDMH concentrations. NDMA formation increases with increasing UDMH content, reaches a maximum at 60–80% UDMH (by volume) and then decreases. Z.R. Ismagilov [29] carried out a series of experiments using the $\text{Cu}_x\text{Mg}_1-x\text{Cr}_2\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ catalyst, for catalytic combustion in the fluidized bed reactors in the temperature range 200–300°C. In

addition to deep oxidation products CO_2 , H_2O and N_2 at temperatures above 300°C , the main compounds CH_4 , DMA, FDMH, FMH were identified by GC-MS. It is remarkable that Methane and FDMH are present in the reaction products in a wide temperature range. H_2O_2 was confirmed as the product of UDMH by V. I. Bruskov [30]. It is supposed the influence the hydrogen peroxide formation were heat and light.

In order to the simultaneous determination of the UDMH and its decomposition products, ion-pair chromatography (IPC) is alternative [31]. IPC is a more selective method that allows one to separate both charged and uncharged compounds. Under the selected chromatographic conditions (40mM ammonia acetate buffer (pH 5.5), 20% v/v of acetonitrile), it is possible to separate up to seven compounds (NDMA, MT, ADMH, MH, DMA, TMH, DMG, UDMH) in 22min within limits of detection at the $\mu\text{g/L}$ level. They also demonstrated the products of an initial UDMH concentration of 500 mg/L that had undergone spontaneous oxidation by atmospheric oxygen after 6 months. Among the studied products, the highest concentrations were found for DMA ($34 \pm 5 \text{ mg/L}$), NDMA ($3.0 \pm 0.4 \text{ mg/L}$) and low concentrations of MH ($0.88 \pm 0.11 \text{ mg/L}$) were also present. The concentrations of hydrazine and TMT in the studied sample were lower than the detection limit.

The use of GC/MS allowed us to identify 14 products of the UDMH oxidation. However, it is still difficult for us to quantitative analysis the fourteen oxidation products. Ion pair chromatography could not only assure the simultaneous determination of

the UDMH and its oxidation products, but also provide quantitative data of the oxidation products. The main products are FDMH, DMA and TMT and DMA is the most stable compounds in water.

3.1.2 Mechanism

Urry *et al.* [32] have reported that the reaction of dimethylhydrazine with molecular oxygen in the gas phase is zero order with respect to oxygen. So Milap presumed the reaction was first order with respect to dimethylhydrazine. The values of k at 20, 25, and 30°C , respectively, as obtained for the reaction in cyclohexane are 1.8×10^{-6} , 2.2×10^{-6} , and $6.4 \times 10^{-6} \text{ s}^{-1}$. Corresponding values for the reactions in diethyl ether are 1.4×10^{-6} , 3.8×10^{-6} and $7.0 \times 10^{-6} \text{ s}^{-1}$. They indicate the activation energy values close to 100 kJ/mol in each solvent. Kinetic studies of UDMH oxidation in water was obtained by Sujit Banerjee *et al.* [33]. The kinetic procedure was that stirred solutions of aerated buffer containing CuSO_4 were temperature equilibrated at $30.0 \sim 0.1^\circ\text{C}$ for 10 minutes [33]. The oxidation kinetics of UDMH were zero-order with respect to oxygen and first-order with respect to substrate at constant Cu^{2+} concentration and pH. The first-order rate is about $20\text{-}100 \times 10^4 \text{ min}^{-1}$ which is vary with different $[\text{Cu}]$ and pH. The developed method of ion chromatographic determination [31] was used to study the kinetics of product accumulation during the UDMH transformation in distilled water upon exposure to atmospheric oxygen.

As follows from the observed results (Table 4), they supposed that MH and TMH are formed from

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UDMH and then subsequently undergo transformation. MT and DHMA may occur due to their formation not straight from UDMH, but rather through intermediate products.

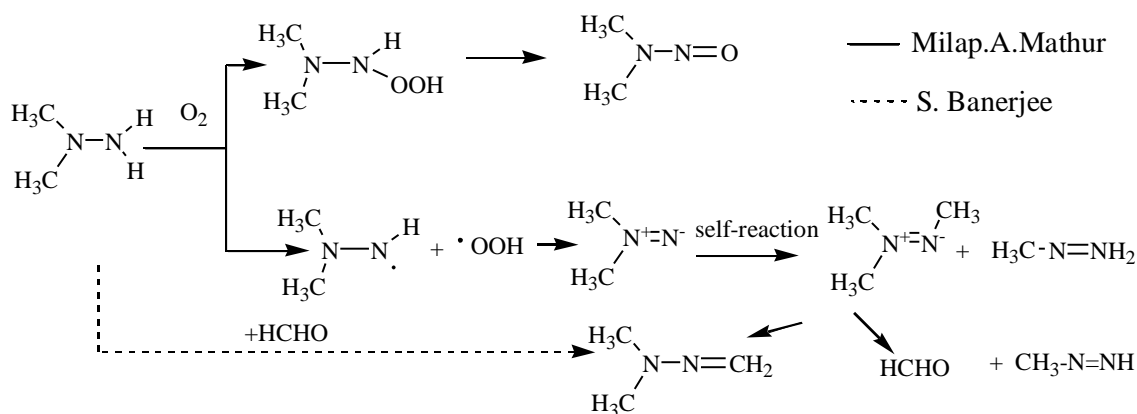
Mechanisms for the formation of the main products (FDMH, NDMA, HCHO) are suggested and will be summarized here[34]. One way of the reaction of UDMH with oxygen may add oxygen to UDMH, initially formed a peroxide complex, such as dimethylhydrazine hydroperoxide $(\text{CH}_3)_2\text{N}-\text{N}(\text{H})\text{OOH}$,

which can lead to the end-products NDMA. The other pathway may be initiated by abstract hydrogen from N-H bond.

As shown in Scheme 3, there are two different possible pathways about FDMH formation. One way is through the intermediate dimethyl diazene $[(\text{CH}_3)_2\text{N}^+=\text{N}^-]$ isomerization. Another possible pathway may be through the reaction of UDMH reacted with HCHO.

Table 4. Kinetics of accumulation of reaction products during the oxidation of UDMH by atmospheric oxygen in distilled water solution(mg/L, initial UDMH concentration is 500mg/L) (reprinted with permission of Ref [31])

Compound	Decompositions time, days				
	6	10	20	40	70
DMA	2.3±0.2	3.1±0.3	5.5±0.5	12±2	32±5
MH	0.11±0.03	0.14±0.03	0.22±0.02	0.21±0.02	0.28±0.02
TMH	0.14±0.03	0.22±0.04	0.19±0.03	0.38±0.08	0.18±0.04
MT	-	-	-	3.8±0.4	22±3
DHMA	-	-	0.55±0.13	28±3	70±10



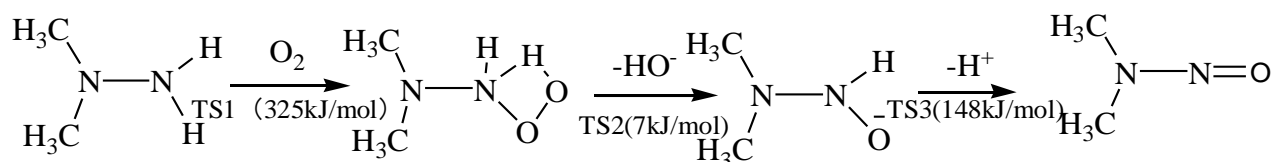
Scheme 3. Mechanism of NDMA formation during UDMH oxygen oxidation in water

(reproduced with permission of Ref [27,33])

The oxidation of UDMH with O_2 to form NDMA was discussed by Zhang *et al.* [35] with DFT calculations performed at the B3LYP/6-311G (d,p) level. The pathways and the active energies values calculated are shown in Scheme 4. That is different from the three-step process proposed for Yong Dong Liu's [36] calculation results demonstrate that it undergoes a four-step pathway (Scheme5). First, an oxygen molecule inserts into the N-H bond of UDMH, then two isomerization reactions occur, finally the other hydrogen of N-H moiety transfers to the newly

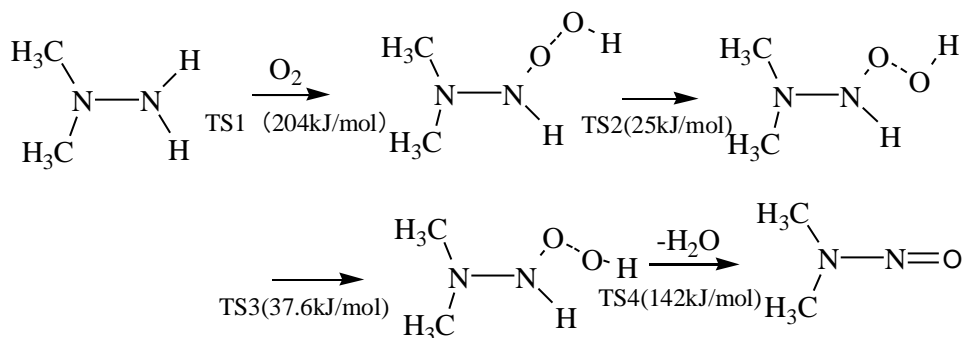
formed hydroxyl moiety with a water molecule and NDMA simultaneously generated. It can be found from Scheme 5 that the first step for the oxygen molecule adding to the UDMH is the rate-limiting step.

In summary, the experimental results and the calculation results are in agreement with that the oxidation of UDMH by molecular oxygen is thermodynamically unfavorable and kinetically implausible in water.



Scheme 4. Oxidation mechanism of UDMH reaction with oxygen by Zhang *et al.*

(reproduced with permission of Ref [35])



Scheme 5. Oxidation mechanism of UDMH reaction with oxygen by Yong Dong Liu *et al.*

(reproduced with permission from Ref [36])

3.2. Ozone

3.2.1 Analysis of oxidation products

One of SIERKA's [37] research centered on the treatment of aqueous solutions of hydrazine(H), monomethylhydrazine (MMH), and unsymmetrical

dimethylhydrazine (UDMH) by ozone. Compounds (UDMH, FMH, FMDH, NDMA, DMF, TMT) in ozonated UDMH solution with initial concentration 0.01mol/L were detected by GC/MS. H.S. Judeikis and D.E. Damschen [38] used the GC, GC-FIR, MS

detected the ozonation products of UDMH. Several compounds were found as intermediates that were CH_3OH , TMT, NDMA, FDMH. The end-products were CH_3OH , TMT, NDMA, CH_3NO_2 . NDMA and HCHO were also identified as the reaction products of UDMH ozonation by Sungeun Lim [39]. In recent years, research groups most focus on identification the precursors for NDMA formation on ozonation [40, 41]. They [39, 42-45] agreed with that not only UDMH ozonation produced NDMA at a high concentration, but also amounts of its oxidative products, like FDM, FDMH, TMT, ADMH could contribute to the NDMA formation, the formation yields of FDM, FDMH, and ADMH with 140mg/L were 89%, 85%, and 84%, respectively, and these values were comparable to that of UDMH (80%)[45].

The main product in UDMH ozonation is NDMA at high concentration, which could reach 80%. The content is much higher than that produced in UDMH reaction with oxygen. Furthermore, transformation products from the ozonation of UDMH, such as FDMH, FDH, ADMH, TMT also led to the formation of NDMA.

3.2.2 Mechanism

Various studies pay close attention to the formation mechanism of NDMA. During the UDMH ozonation process, the potential $\cdot\text{OH}$ oxidation would be produced through (3.1-3.2) [28]



Molecular ozone is the main oxidant responsible, while the $\cdot\text{OH}$ may play a minor role in NDMA formation [29]. Some authors are interested in the effects of the $\cdot\text{OH}$ during NDMA formation. They agree that hydroxyl radical scavenging during ozonation leads to increased NDMA formation. It was suggested that TMT or intermediates in the conversion of UDMH to NDMA reacted with hydroxyl radical and the products other than NDMA were formed. Kosaka *et al* [45]. speculated that UDMH reacts strongly with ozone with formation NDMA because the structure “-N=C-” was changed to “-N=O”. Sungeun Lim [39] investigates the reaction kinetics, pathways, and mechanisms of NDMA formation during ozonation of UDMH and their results shows the apparent second-order rate constants for the reaction of ozone with UDMH, as a function of pH (3-10). the k_{O_3} of the reaction of ozone was $6.4 \times 10^3 \text{ M}^{-1}\text{S}^{-1}$ at PH 3 and increased with increasing pH to 7 and maintained at $\sim 2 \times 10^6 \text{ M}^{-1} \text{S}^{-1}$ within the PH range of 7-10. The reaction mechanism of UDMH with ozone was proposed on the basis of the obtained kinetic, stoichiometric, and products information (Scheme 6). The reaction was initiated by an ozone adduct at the nitrogen next to N,N-dimethylamine followed the further reactions of N-oxide intermediate. Moreover, the N-oxide radicals intermediates undergo disproportionation forming NDMA, as a final product.

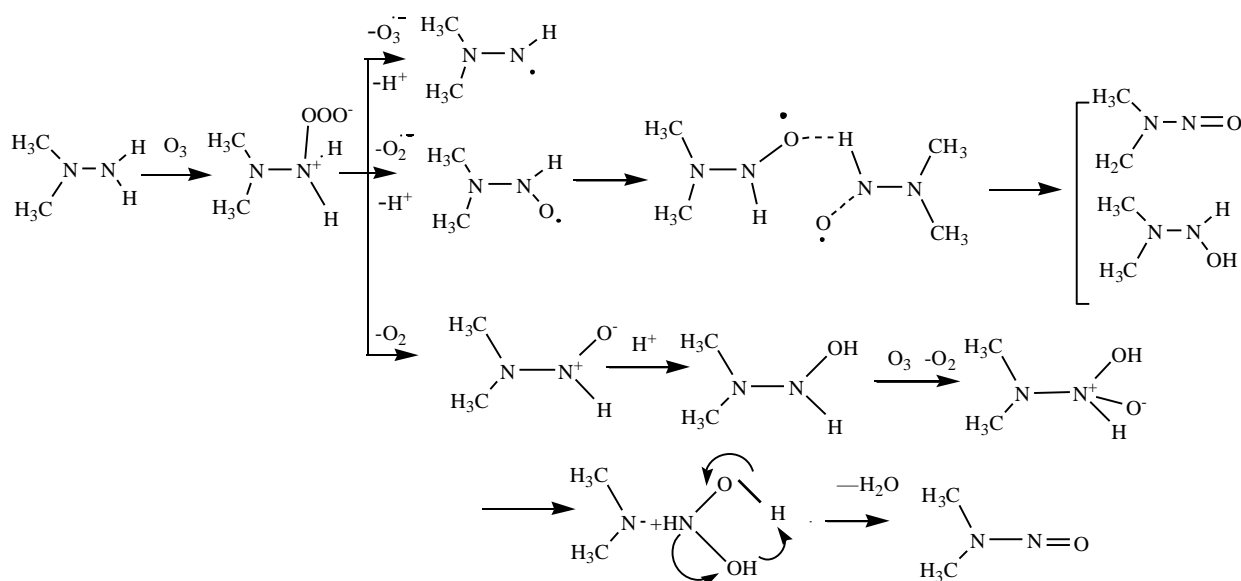
Computational calculations with GAUSSIAN-09 for NDMA formation mechanism of NDMA in ozonation of UDMH provided insights into the mechanistic pathways. The composite Gaussian-4

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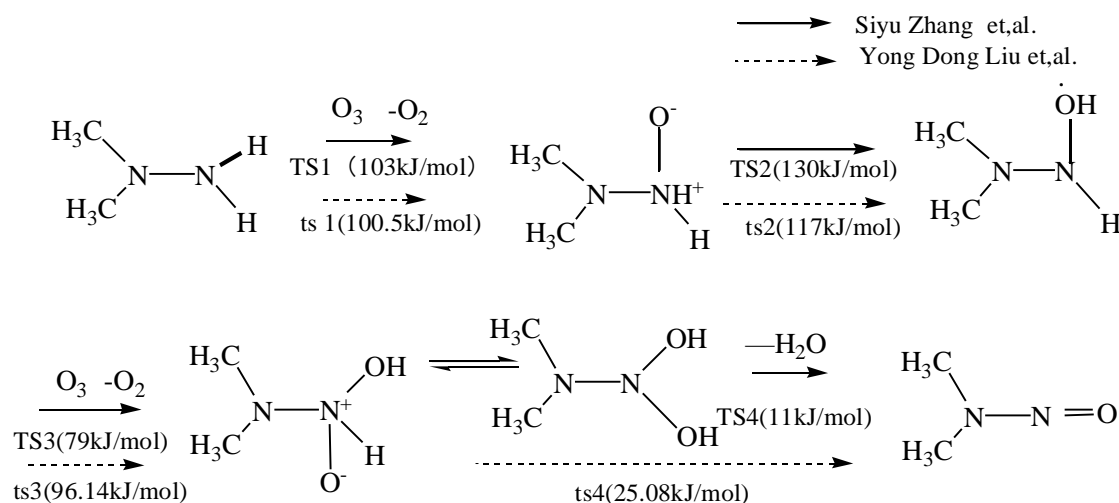
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(G4) method was used by Yong Dong Liu *et al.* and DFT calculations were performed at the B3LYP/6-311G(d,p) level. The overall NDMA formation pathway upon ozonation of UDMH are outlined in Scheme 7. Their results are almost in consistent with that the -N-OH bond formation from -NH-O-bond remains to be the rate-determining step

for the overall reaction with barriers energies $\sim 120\text{kJ/mol}$. Based on the experiments results, this is in good agreement with Sungeun Lim's proposed mechanism [39]. However, the calculations results show the active energy is high, which is not in accordance with the experiments results.



Scheme 6. Mechanism of NDMA formation during UDMH ozonation in water (reproduced with permission from Ref [39])



Scheme 7. Oxidation of UDMH in ozonation (Values in brackets are energy barriers) (reproduced with permission from Ref [35,36])

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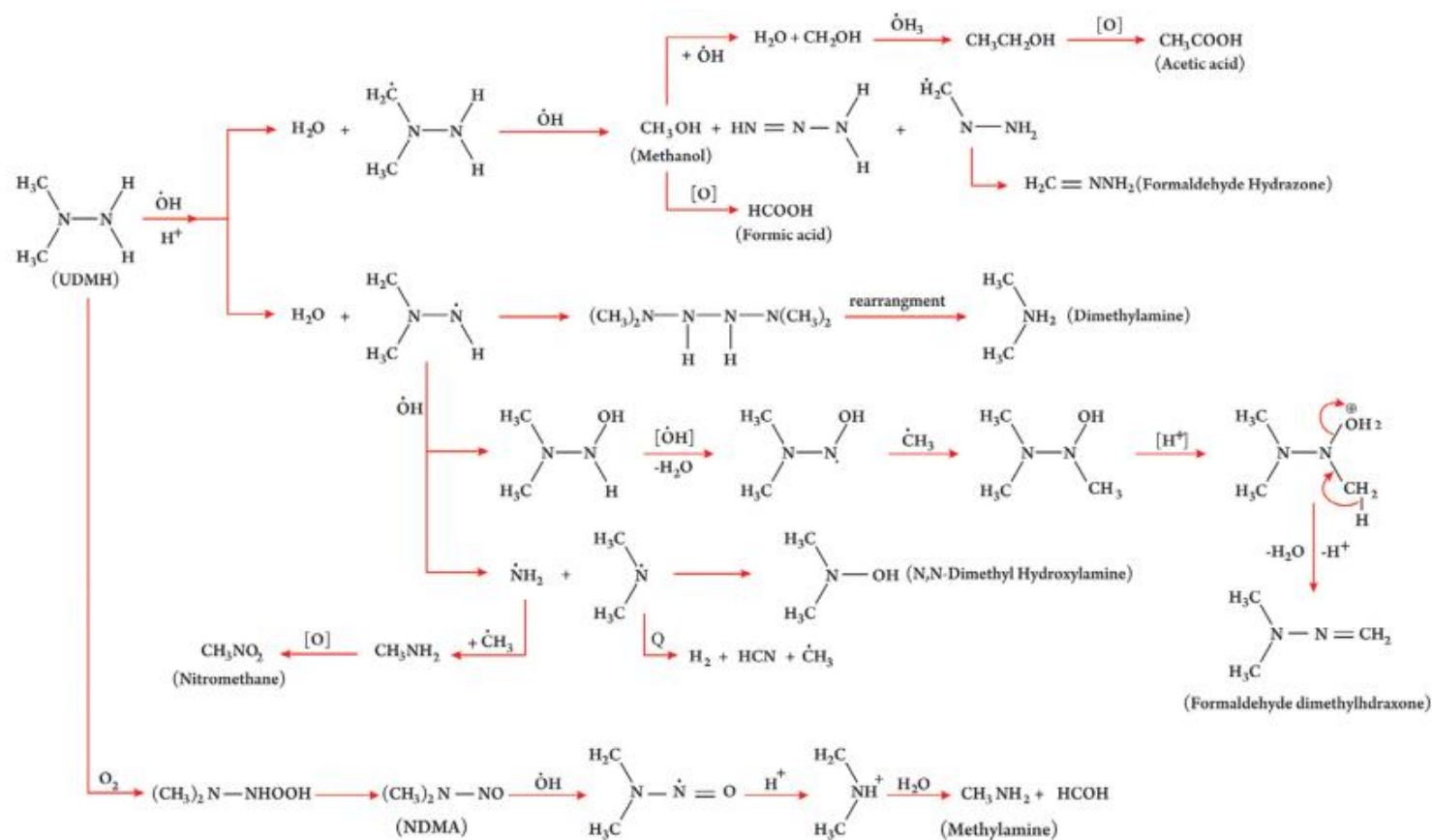


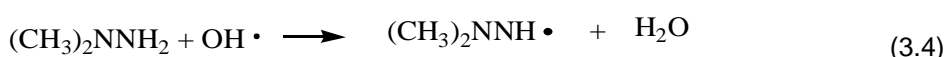
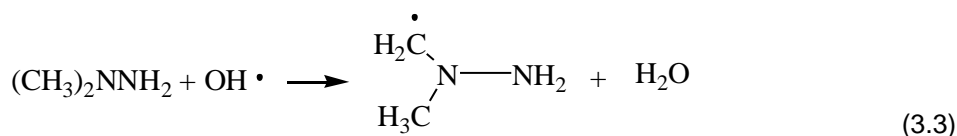
Figure 2. Possible pathways of UDMH oxidation initiated by hydroxyl radicals (reprinted with permission from Ref [46])

3.3 Hydroxide radical

Mahmood Torabi Angaji [46, 47] studied decontamination of UDMH waste water (2-15mg/L) by hydrodynamic cavitation-induced advanced Fenton process or a combination of hydrodynamic cavitation and acoustic cavitation. UDMH was oxidized by hydroxyl radical (a strong oxidizing agent) which was produced by the cavitation. Quantitative analysis of the products was conducted with GC-MS.

It has been observed that CH_3NO_2 , HCOOH and CH_3COOH were the only carbon-containing end-products without toxic by-products (especially NDMA).

They also proposed the UDMH oxidation mechanism by hydroxyl radical. The attack of hydroxyl radicals to the UDMH molecules can be done through its methyl group or amino group according to the following reactions:



As shown in Figure 1, these two reactions can be continued in many ways, the studies just paid attention to the formation of oxidation end-products of UDMH.

There was some greater reported that the oxidation of alkyl-hydrazines proceeds to a substantial extent via radical mechanisms, with the formation of a number of intermediates bearing unpaired electrons [48, 49]. So N.V. Ul'yanovskii [50] proposed the initial stage of the oxidative transformation of UDMH for the reaction of 1,1-dimethylhydrazine with hydrogen peroxide shown in Figure 3. Radical species of eight types formation was explained (including resonance structures), which can play key roles in the UDMH

transformation to give a very wide range of products, amounts of them could be hardly detected by gas chromatography. Therefore, the detail mechanism is difficult to explain by experiment, it could be expected to result from advances in theoretical and computational methods.

The detail mechanism is difficult for researches to study by experiments. In order to further understand the microscopic mechanism of the degradation process, Zhang Guangyou *et al.* [51] used computational methods of quantum chemistry on the theoretical level to study the detail UDMH oxidation-dimethyldizene. The two-reactions mechanism of $(\text{CH}_3)_2\text{NNH}_2$ and OH to form $\text{CH}_3\text{N}=\text{NCH}_3$ were proposed.

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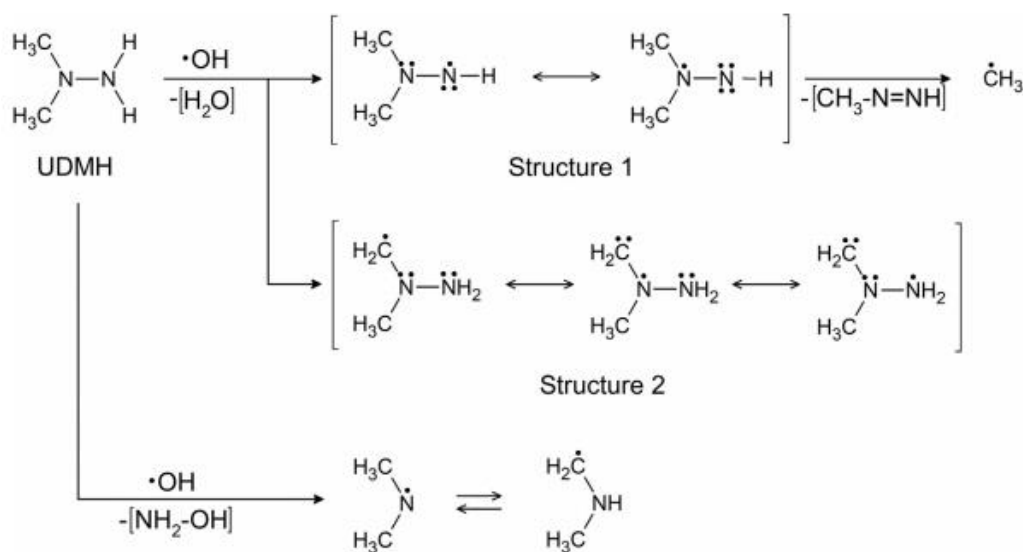
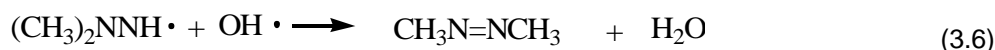
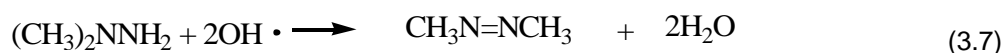


Figure 3. Scheme of formation of reactive radical in the oxidation of UDMH with hydroxyl radical
(reprinted with permission from Ref[50])

Reaction channel 1: two H atoms get away step by step:



Reaction channel 2: two H atoms simultaneously get away



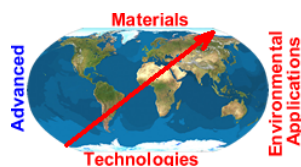
The calculation results showed the energy barrier of channel1 is 2896.4kJ/mol and channel 2 is 2893.77 kJ/mol. The reaction channel is the rate-limiting step during the all UDMH oxidation process.

4 Oxidation in soil

4.1 Analysis of transformation products

In order to assess the environment impacts of UDMH in soil, various analytical techniques such as high performance liquid chromatography (HPLC), HPLC-MS, HPLC-MS/MS, GC-MS, GC-MS/MS, 1H and 13C NMR, and UV spectroscopy were used for

identification and quantitative determination of trace amounts of 1,1-dimethylhydrazine and products of its oxidation. The main obstacle for the analysis the soil sample is sample preparation. It appeared that solid phase micro-extraction (SPME) would be an appropriate technology for rapid assessment to achieve high sensitivity, speed, low labor consumption. With the use of HS-SPME, the number of confirmed transformations products could reach more than 30. Except for the oxidative products of UDMH oxidized by O₃, O₂, OH, the other 20 transformations were recovered and identified (Table 5).



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Table 5. The list of compound detected and identified

No	Compound name	CAS no.	GC- MS/MS	SPME/ GC-MS [52]	HS GC-MS [13]	HPLC [53]	SPME/ GC-MS [54]
1	Methyl formate	107-31-3		+			
2	2-Butanone	78-93-3		+			
3	Acetonitrile	75-05-8		+			+
4	Pyrazine	290-37-9		+			
5	Dimethylamino acetonitrile	926-64-7		+	+		+
6	1-Methyl-1H-pyrazole	930-36-9		+	+		+
7	1,3-Dimethyl-1H-pyrazole	694-48-4		+			+
8	1,4-Dimethyl-1H-pyrazole	1072-68-0		+			+
9	Dimethyl cyanamide	1467-79-4		+			+
10	1,5-Dimethyl-1H-pyrazole	694-31-5		+			+
11	N,N-Dimethylacetamide	127-19-5		+			
12	1,3-Dimethyl-1H-1,2,4-triazole	16778-76-0		+	+		+
13	1-Formyl-2,2-dimethylhydrazine	3298-49-5	+	+	+	+	+
14	1-Methyl-1H-imidazole	616-47-7		+			
15	Formamide	75-12-7		+			
16	Benzyl alcohol	100-51-6		+			
17	1H-Imidazole	288-32-4		+			
18	1H-1,2,4-Triazole	288-88-00		+			
19	Hydrogen cyanide	74-90-8			+		
20	Furaldehyde dimethylhydrazone	14064-21-2	+				

Note: "+" have been detected, AFDMH: 1-Formyl-2,2-dimethylhydrazine, DMHFur: Furaldehyde dimethylhydrazone

Quantitative determination of UDMH and sample preparation is challenging due to transformation products using HS SPME as sampling significant effects of soil type, composition and

moisture content on recovery of analytes. In order to assess the UDMH and its transformation products oxidation on time, it is necessary to develop quantitative analysis. Several researches have reported quantitative determination of MT, TMT, FADMH, NDMA, etc. (Table 6). The sensitivity and selectivity of analysis of such complex matrixes as extracts from soils with the high contents of organic substance can be increased. The rapid simultaneous determination of the main transformation products of UDMH was achieved by Dmitry S. Kosyakov and N.V. Ul'yanovskii [55].

Lars Carlsen *et al* [13] focused on the potential environmental and human health impact by UDMH

and its transformation products. They used Quantitative Structure Activity/Toxicity ((Q)SAR/ (Q)STR) modelling, including both ADME models and models for acute toxicity predict the biological activity of the compounds. They resulted that the hydrazines and hydrazones may contribute to the overall environmental toxicity. Apart from hydrogen cyanide be acutely toxic, the several compounds among these with N-N bond were predicted to exhibit high probabilities for potential carcinogenicity, mutagenicity, teratogenicity and/or embryotoxicity. According to their predicted human health impact, the compounds toxic ranked NDMA = TMT > TMH > ADMH > UDMH > AFDMH > FDMH. [13, 56-58].

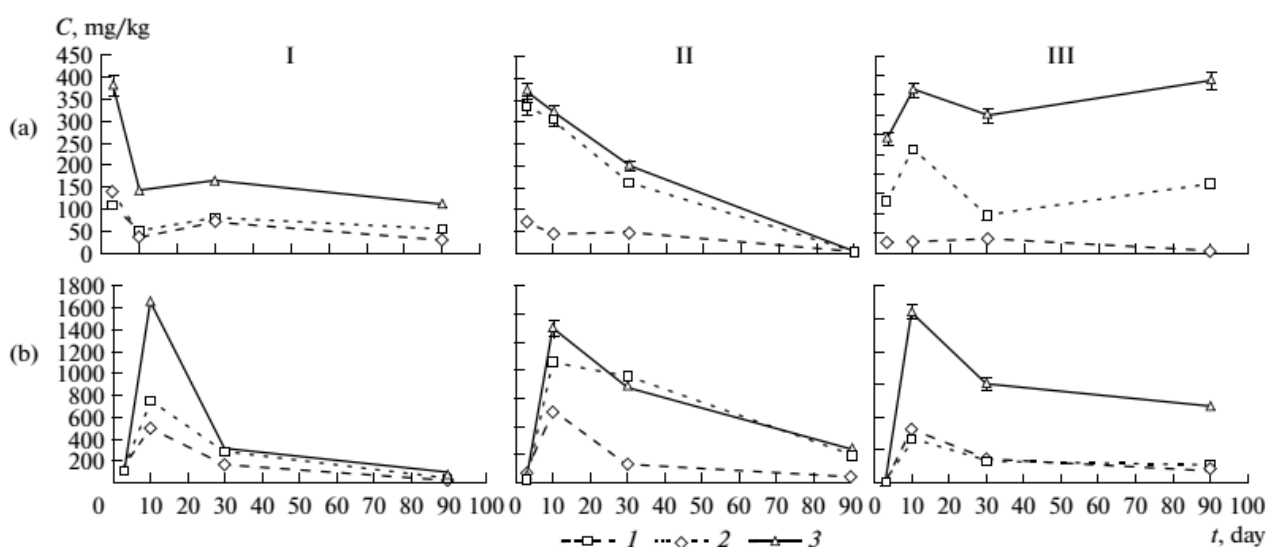
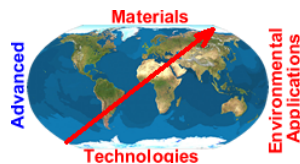


Figure 4. The kinetic curves describing the changes in the concentrations of AFDMH(I), MT (II), and DMA (III) in the air dry (a) and wet (b) soils: 1—desert sandy; 2—desert sandyloamy graybrown, 3—loamy soddypodzolic (reprinted with permission from Ref[3])

As shown in Table 1 and 5, Transformation products of UDMH in soil is much more than in atmosphere and in water. The reason may be the

existence various microorganism, however the UDMH is hardly oxidized by microorganism because of its toxic [59, 60]. So this is mainly because of the



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soil complex oxidative environment with high contents of organic compounds. Apart from hydrogen cyanide, the hydrazines with N-N bond (NDMA, TMT, TMH), and the hydrazones (ADMH, DMHFA, FDMH) were predicted human health impact, and further attention should be given to these toxic products.

4.2 Mechanism

The kinetic regularities of UDMH and the transformations leached out from dry and wet soils were investigated 3,10,30,90 days after UDMH at a dose of 240g/kg entering the soil (Figure 4) [3]. The study revealed that, in the course of the transformation of the UDMH entering the soils during fuel spills, AFDMH, MT, DMA, and DMG are formed in detectable amounts and preserved for a long time. Their results also show the DMG is a secondary product forming not from UDMH but from the primary products of its oxidation. So, the control of the environment pollution by the UDMH transformation needs to be further study.

5 Conclusion and outlook

This article reviews the UDMH oxidation in the atmosphere, water and soil including the analysis of various products and mechanism during the UDMH reaction with oxygen, ozone and hydroxide radical. The following general conclusions can be drawn based from the available literature:

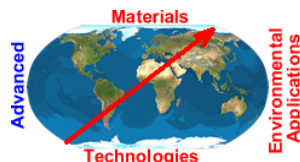
(1) With the development of analysis method, the number of the various oxidation products is more than 30 in environment, among these several

compounds with N-N bond is predicted harmful impact environment and human, such as NDMA, TMT, DMA, FDMH include HCN.

(2) The attack of ozone and oxygen to the UDMH molecules is proposed though its amino group forming N-oxides radicals intermediate and diazene. Further, the N-oxides radical undergo disproportion forming NDMA; and the diazene leads to dimerization to tetramethyltetrazone, cleavage to dimethylamine. Whereas hydroxyl radicals tends to attack its methyl group formed FDMH and HCHO, avoiding NDMA formation.

(3) The changes of the transformations content imply that FDMH, TMT, HCHO, FDM may be the intermediate products and NDMA, DMA would be the end-products. NDMA not only could form directly from UDMH, but also from the primary oxidation products, such as TMT, FDMH.

Only few studies reported the detailed formation mechanism of the main toxic products. Quantitative data about the relative importance of the different routes of toxic transformations formation would help in the mechanistic studies of the oxidation reactions. Lots of work should be done also in the quantification of these intermediates. Nevertheless, amounts of these intermediates were radicals, which can be hardly detected by modern analytical technique in experiment. It is expected to result from advances in theoretical and computational methods, the key-action is prediction the all possible reaction pathways at the level of elementary steps in order to the identification of the minimum energy pathways.



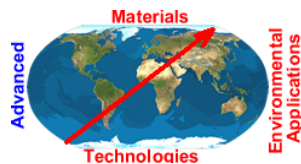
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Indeed, the DFT approach can effectively be used to estimate the interaction energies of atomic or molecular species. The better understanding of the detail oxidative mechanism could predict the UDMH fate in environment and offer opportunities to control and remove the toxic oxidative products in source.

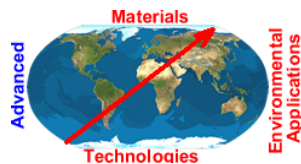
Table 6. Summary of the current analytical methods for quantitative determination of UDMH transformation products in soil

Analytical	Sample preparation	Target compounds	LOD	LLOQ	Recovery %	Ref
GC-MS	Soxhlet extration	MT	0.005mg/kg	0.020-100mg/ kg	95	[61]
GC-MS	Extraction with dichloromethane	MT	0.02mg/kg	0.05-50mg/kg	89	[62]
		AFDMH	0.02mg/kg	0.05-50mg/kg	97	
HPLC-MS /MS	Supercritical fluid Extraction with acid, alkaline distillation	MT	1.9ng/mL	6-12000ng/mL	94	[55]
		TMT	0.7 ng/mL	2-10000 ng/mL	94	
		DMF	1.8 ng/mL	6-25000 ng/mL	103	
		NDMA	11 ng/mL	40-10000 ng/mL	97	
		DMG	0.04 ng/mL	0.1-1000 ng/mL	98	
		UDMH	12.8 ng/mL	40-20000 ng/mL	95	
GC/ MS-MS	Extraction with acetonitrile from a saturated solution of sodium	MH	17.6 ng/mL	60-20000 ng/mL	103	[63]
		FDMH	0.3ug/L	1.0- ug/L	91±10	
		ADMH	0.5 ug/L	1.7- ug/L	120±10	
		TMT	0.5 ug/L	1.7- ug/L	114±8	
		NDMA	0.3 ug/L	1.0- ug/L	101±16	
		DMF	0.9 ug/L	3.0- ug/L	87±15	
		MT	0.4 ug/L	1.3- ug/L	6±14	
		AFDMH	2.2 ug/L	7.3- ug/L	72±7	
		DMHFur	2.3 ug/L	7.6- ug/L	162±16	



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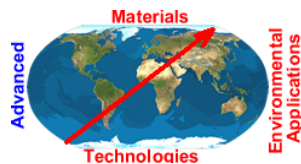
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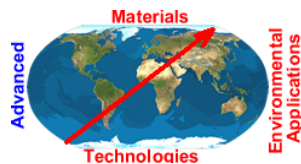
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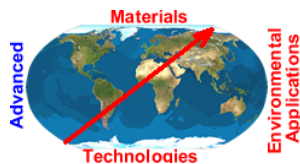
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