Advanced Oxidation of RDX and HMX Wastes using Fenton Reagent

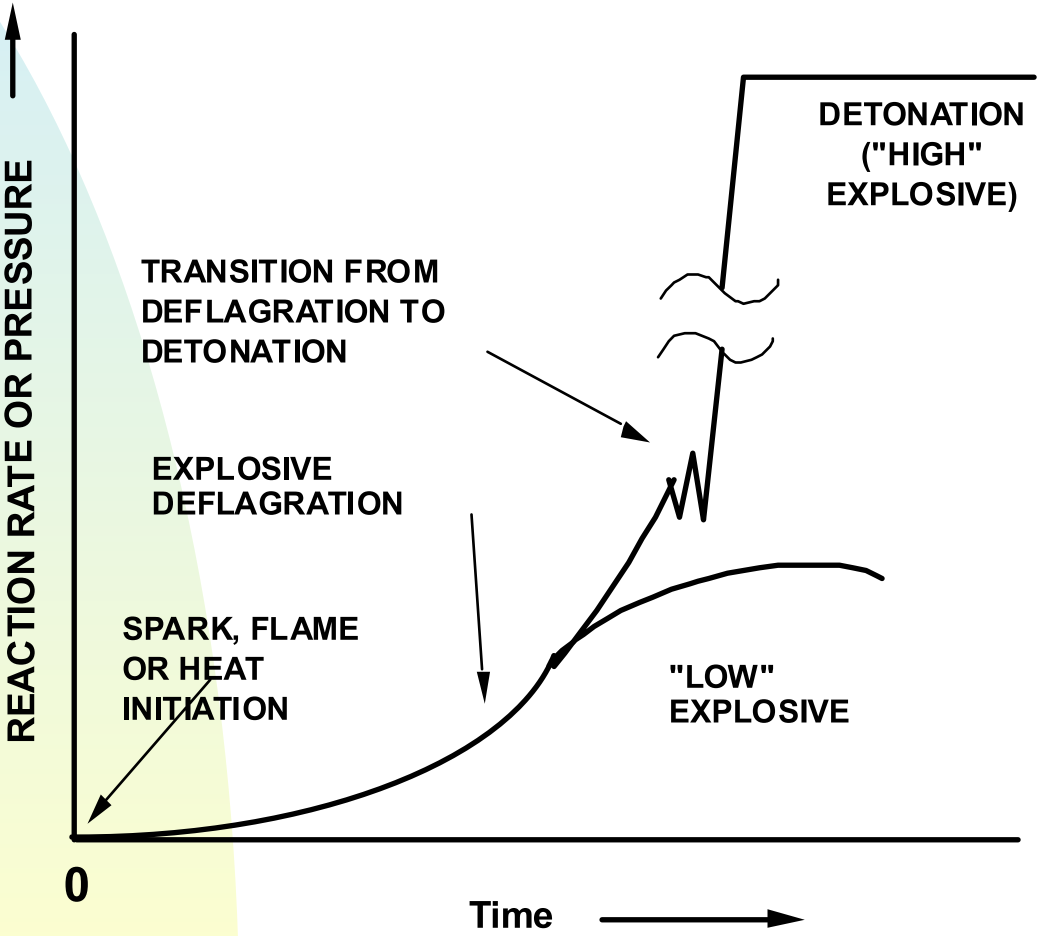
Kyung-Duk Zoh and Michael K. Stenstrom*

*Dept. of Civil and Environmental Engineering
University of California, Los Angeles

High Explosives

- Defined by their rate of reaction (high versus "low" or "normal" explosives)
- Some typical HE - RDX, HMX, TNT, PETN, Ammonium-Nitrate
- Low Explosives - gunpowder, nitroglycerin

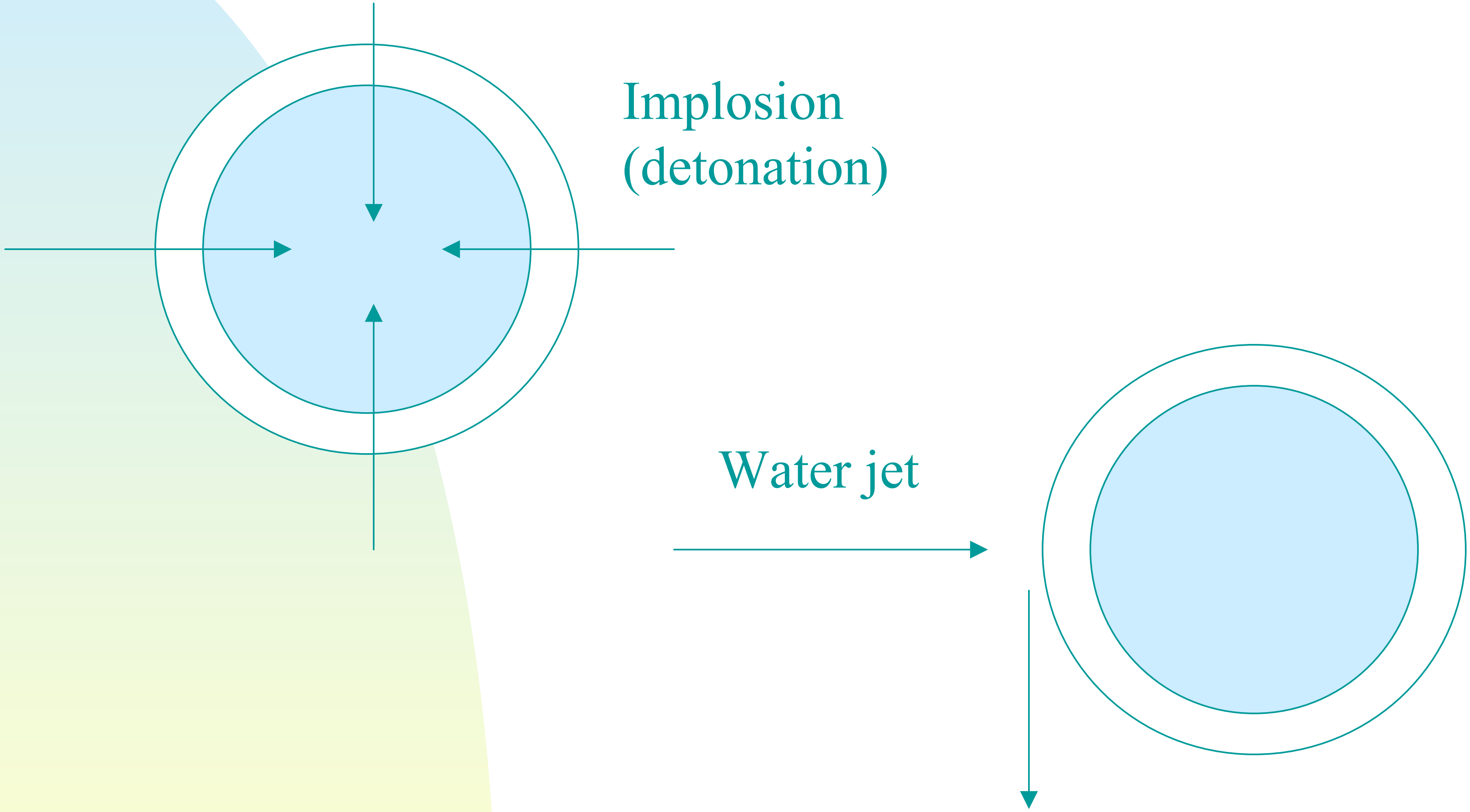
Pressure Curve



Usage

- Commercial blasting - coal mining, tunneling, road building
- Military usage - bombs, artillery shells, various warheads
- Nuclear weapons - creates the implosion
- Some explosives had other uses, e.g., RDX used as rat poison

DOE Application – Plutonium Pits



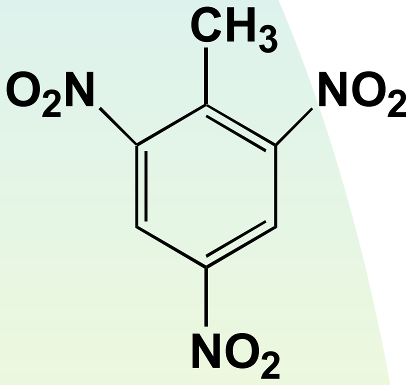
Implosion
(detonation)

Water jet

HE sludge and water with HE

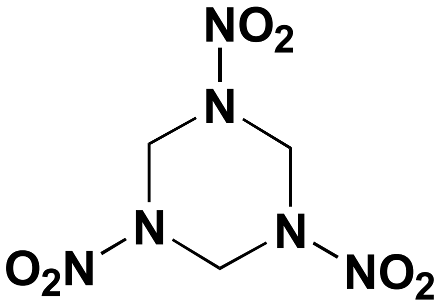
Explosive Wastes

TNT



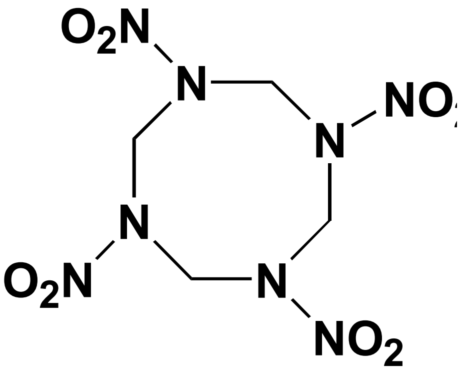
(2,4,6-Trinitrotoluene)

RDX



(Hexahydro-1,3,5-trinitro-1,3,5-triazine; *R*oyal *D*emolition e*X*plosive)

HMX



(Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; *H*igh *M*elting e*X*plosive)

Health Hazards

- RDX
  - a hazardous waste (EPA)
  - Health Advisory by EPA
    - 2 µg/L for lifetime exposure for adults in drinking water
  - A possible human carcinogen (Class C)
- HMX
  - a hazardous waste (EPA)
  - Health Advisory (1989) - Class D Carcinogen

Explosives Contamination

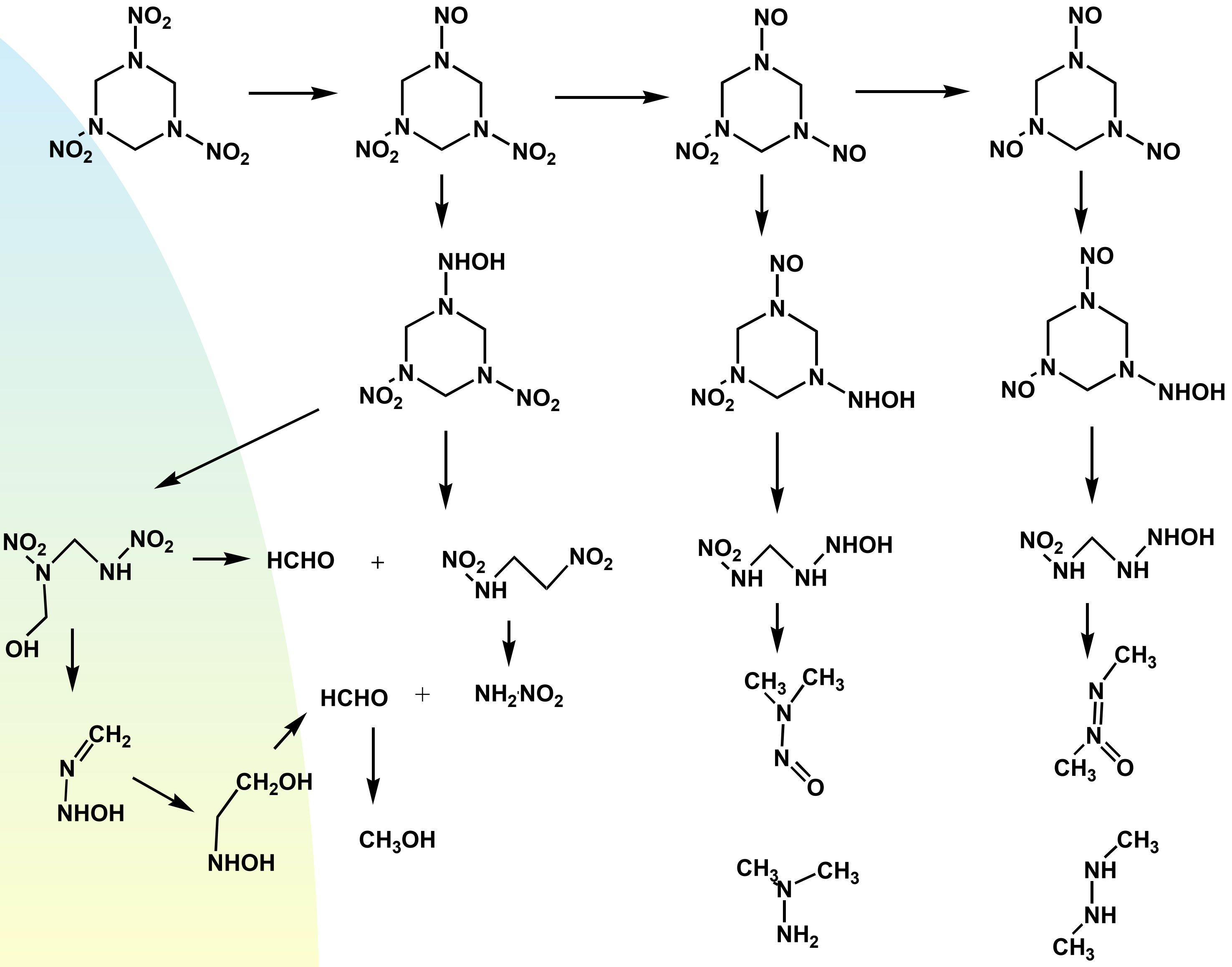
- Munitions production over the past years led to widespread and persistent contamination at government facilities.
- The current emphasis on demilitarization.
- Past methods for disposal include dumping at lagoon, at landfill areas, open burning.
- RDX and HMX pose risks to human health, and can be toxic to aquatic and terrestrial organisms.
- Thousands acres of highly toxic soils and groundwaters need to be cleaned up.

Existing Technology for Treatment

- Physical
  - Incineration
  - Excavation
  - Adsorption
- Biological
  - Aerobic
  - Anaerobic
  - Composting
- Chemical
  - Hydrolysis + Biological treatment (zoh *et al*., 1999)
  - Advanced oxidation

Anaerobic Biotransformation of RDX

(McCormick *et al*., 1981)



Advanced Oxidation Processes (AOPs)

- AOP processes (O_3, UV, O_3/H_2O_2, Fenton reagents, TiO_2) were commonly used for remediating wastes and wastewaters contaminated with recalcitrant organic compounds.
- Fenton reaction is one of the oldest, most powerful oxidation treatments available.
- The chemical kinetics of Fenton oxidation of RDX and HMX and identification and quantification of intermediate products were investigated

Fenton Oxidation Mechanism

$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + HO\cdot$

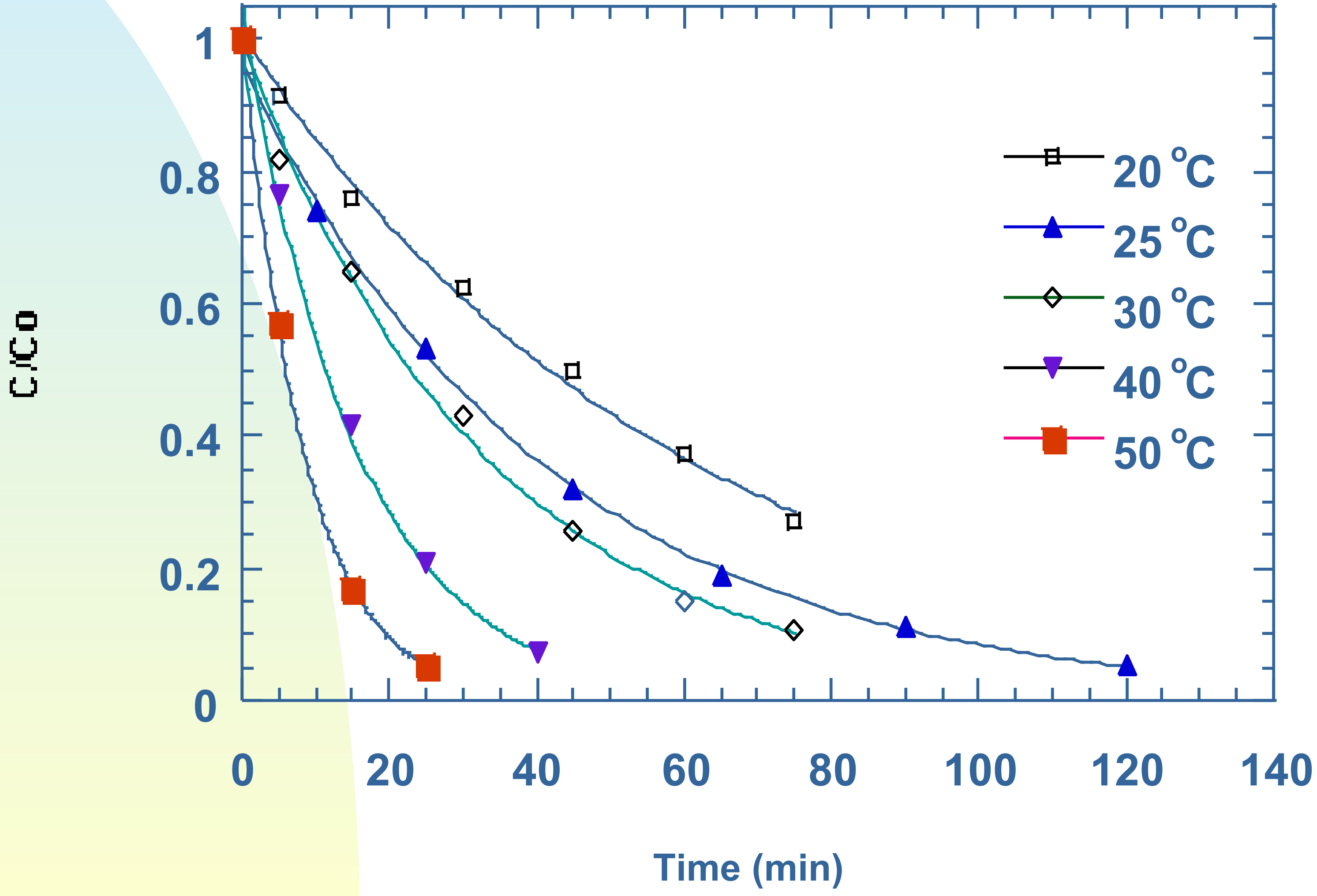
$HO\cdot + R \rightarrow \text{oxidized products}$

Experimental for Kinetics

- Performed in a water bath between 20 and 50 °C
- Conducted in a flask in the dark conditions
- $[Fe^{2+}]$ is the form of $FeSO_4 \cdot 7H_2O$, and calculated amount of 30% H_2O_2.
- Initial RDX and HMX was 10 mg/L (0.045 mmol/L) and 4.5 mg/L (0.015 mmol/L).
- pH was fixed to 3 using 1N H_2SO_4.
- Samples were collected, and were immediately filtered into cooled (0 °C) HPLC vials, and were analyzed using HPLC (236 nm)

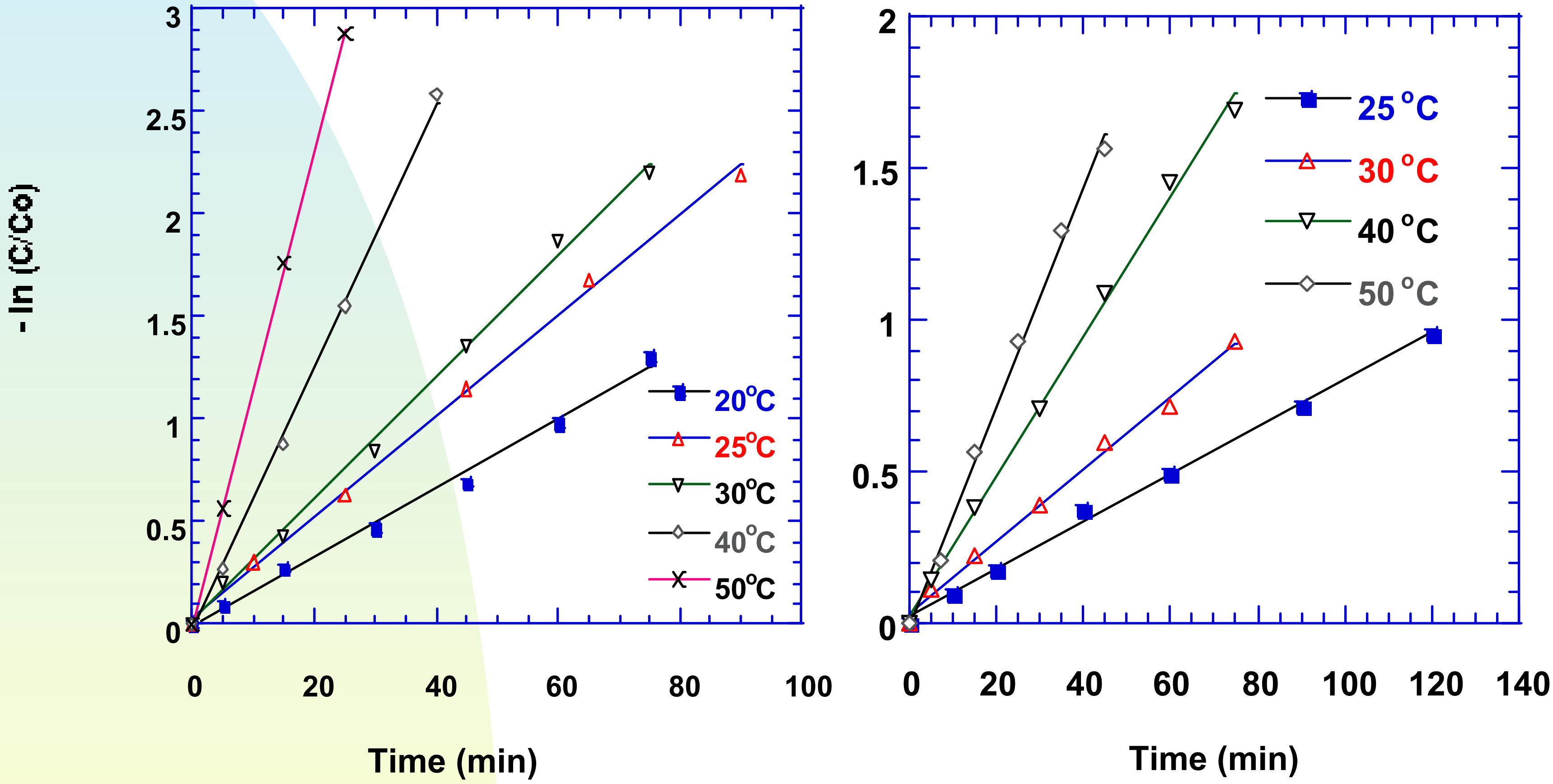
Fenton Oxidation of RDX at Different Temperature

([RDX] =0.045 mmol/L, $[H_2O_2]$ = 210 mmol/L, $[Fe^{2+}]$=2.16 mmol/L, pH=3



Fenton Oxidation of RDX and HMX at Different Temperature

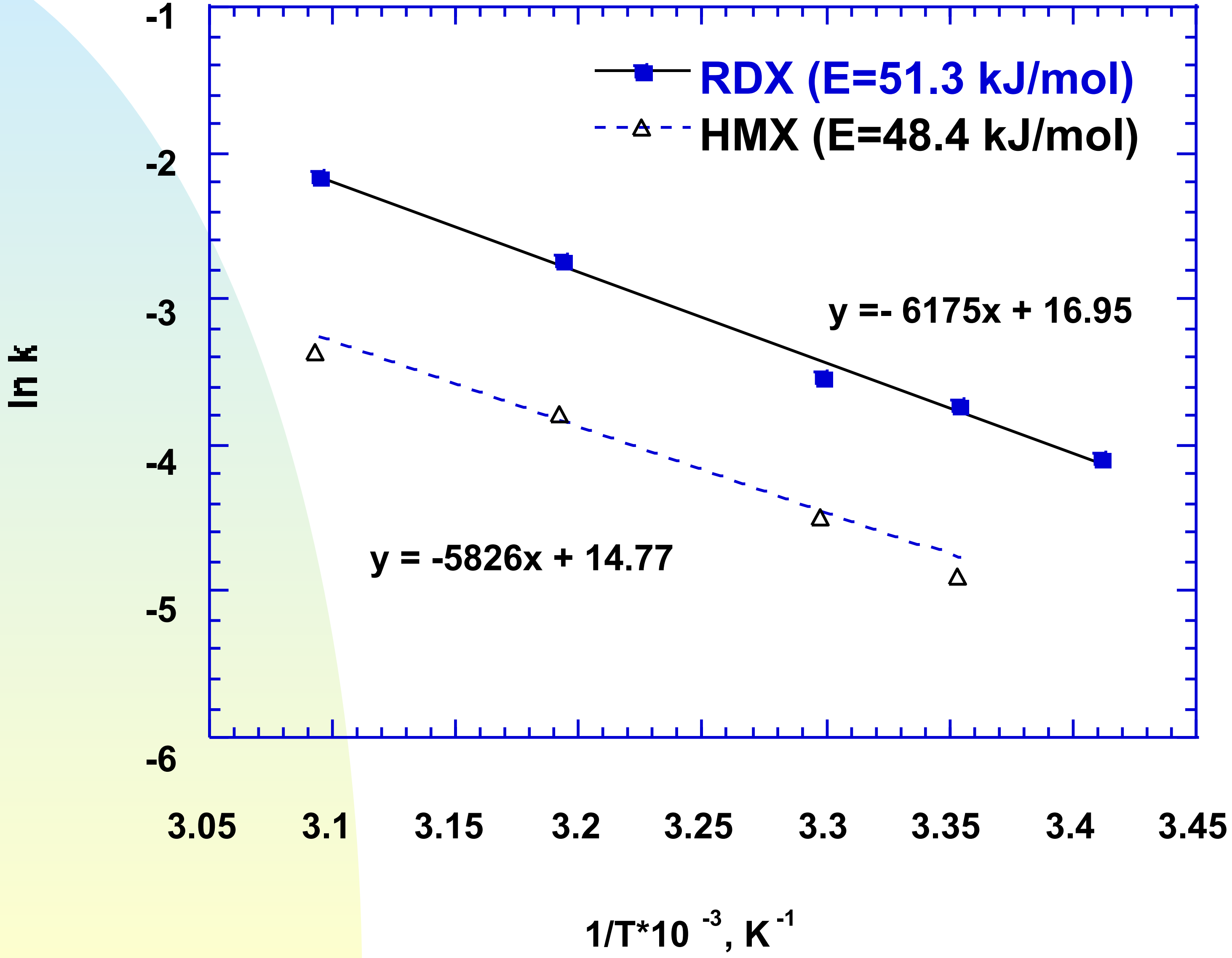
([RDX] = 0.045, [H_2O_2] = 210, [Fe^{2+}] = 2.16 mmol/L, pH=3; [HMX] = 0.015, [H_2O_2] = 69.2, [Fe^{2+}] = 0.72 mmol/L, pH=3).



$$\frac{dC_{HE}}{dt} = -k_{HE}\, C_{HE}\, C_{OH\bullet}$$

$$\ln \frac{C_{HE}}{C_{HE,t=0}} = -k_{HE}{}'\, t$$

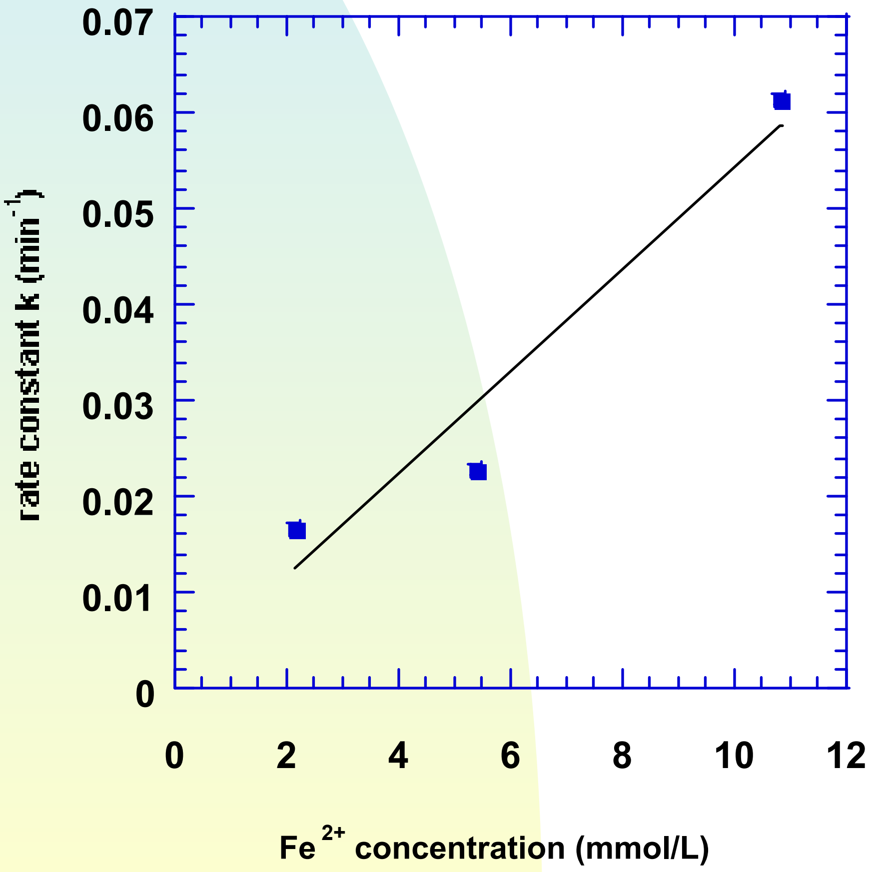
Temperature dependency of rate constants on Fenton oxidation of RDX and HMX



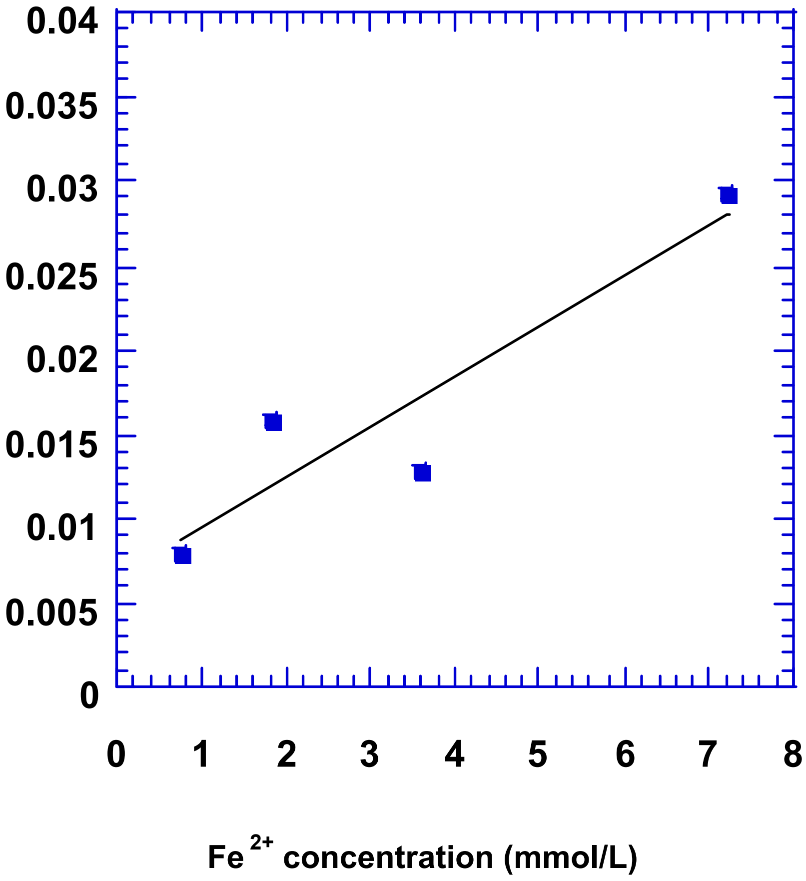
The impact of increasing Fenton reagents concentration on rate constant of RDX and HMX oxidation

(RDX = 0.045 mmol/L, HMX = 0.015 mmol/L, Fe^{2+}: H_2O_2 = 1:95, pH=3)

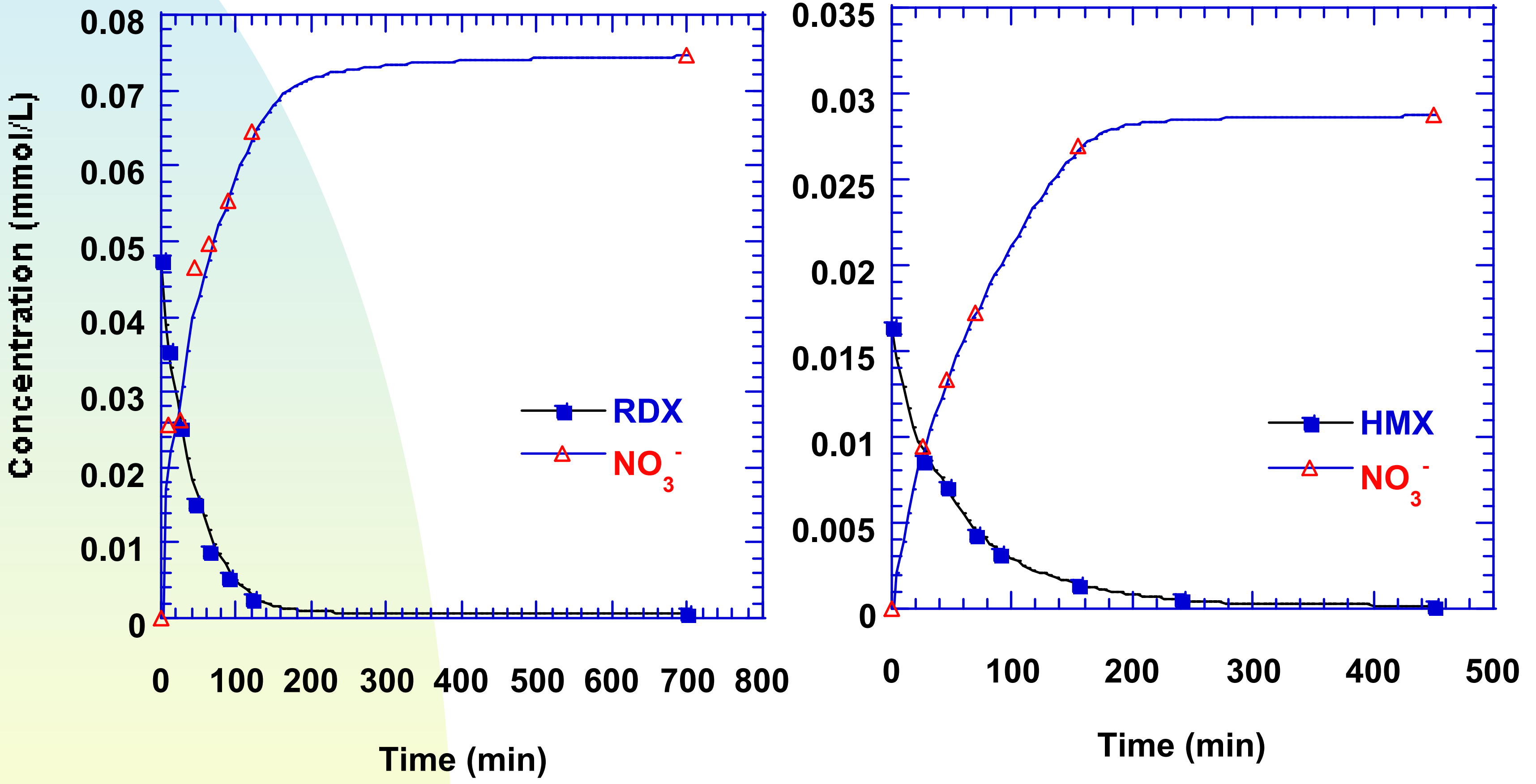
RDX



HMX



Nitrogen Balance:
The Kinetics of RDX and HMX degradation and Nitrate (NO_3^-) Formation



Gas Analysis Results

5-mg/L of RDX and HMX were put into a gas tight glass reactor.
The system was sealed and purged with Helium gas.
The syringes were attached to measure gas volume after the reaction.
The gas samples were analyzed with GC with TCD.
Using ideal gas law, measured gas volume, concentration of produced gas were calculated.

	RDX	*HMX*
N_2 (%)	**0.41%**	**0.34%**
The remains (O_2, Argon, H_2O)	**71.0%**	**67.9%**
Total mole produced	**0.053 mol N_2**	**0.033 mol N_2**
Normalized Yield	**2.36 M N_2/ M RDX**	**1.94 M N_2/ M HMX**

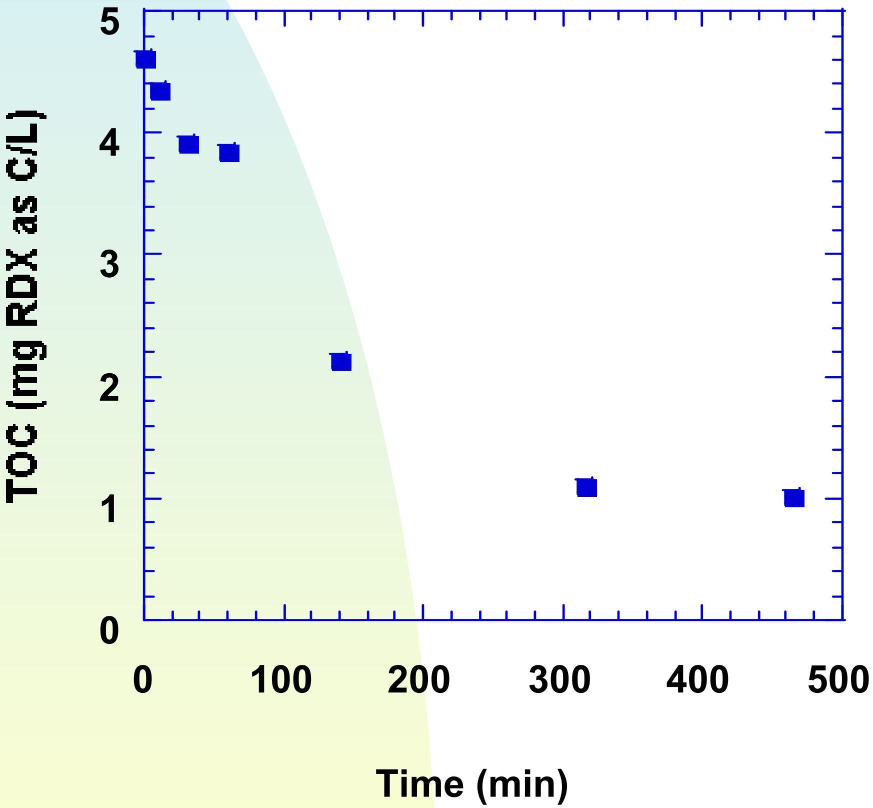
Normalized molar yields for Fenton Oxidation products

Byproducts	RDX	HMX
NO_3^-	1.50	1.75
N_2	2.36	1.94
Total N	6.22/6	5.63/8

*M product formed / M RDX (or HMX) oxidized.

Mineralization of RDX Oxidation

1. TOC Measurement during reaction of RDX with Fenton reagent (RDX = 0.045 mmol/L, Fe^{2+} = 2.16 mmol/L, H_2O_2 = 210 mmol/L)
2. ^{14}C study (100-mL solution were spiked 10 mg of RDX and 5 µCi of [U-^{14}C] RDX).



	CPM
Initial Solution	306259
#1	85390
#2	29058
#3	179
Sum	114627
Final Solution	113716
Recovery	**75 %**
^{14}C %	**37 %**

Other Studies of Advanced Oxidation on Explosives

- Using UV, UV/H_2O_2, O_3, O_3/H_2O_2, and UV/O_3, RDX degradation was investigated. There was no mineralization, 50% of nitrogen was transformed to NO_3^- (Bose *et al*., 1998)
- TNT destruction using Fenton reagent yielded oxalate, CO_2, and NO_3^- (Li *et al*., 1997). Fenton oxidation of TNT (70-mg/L) solution resulted in complete destruction within 8 h, and 40% mineralization within 24 h.

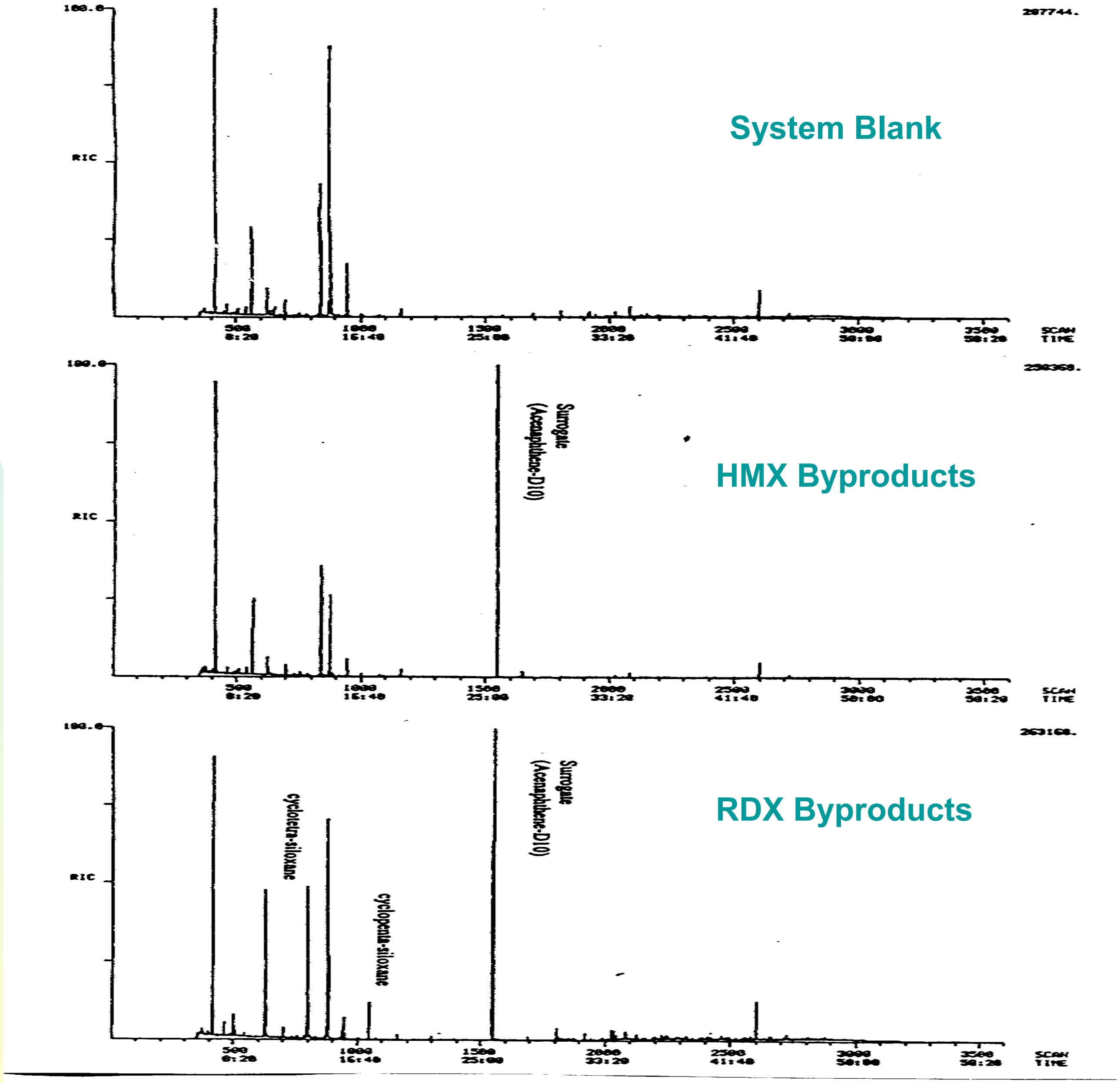
Carbon Byproducts - Formaldehyde (HCHO) Formation

- Formaldehyde analysis using 2,4-dinitrophenylhydrazine (DNPH) solution.
- From HPLC analysis, the derivative (dinitrophenylhydrazone) was detected at the initial phase of the reaction, and then the peak decreased and finally disappeared.
- Formaldehyde can be the intermediate during oxidation of RDX, and can be further oxidized to final products such as CO_2.

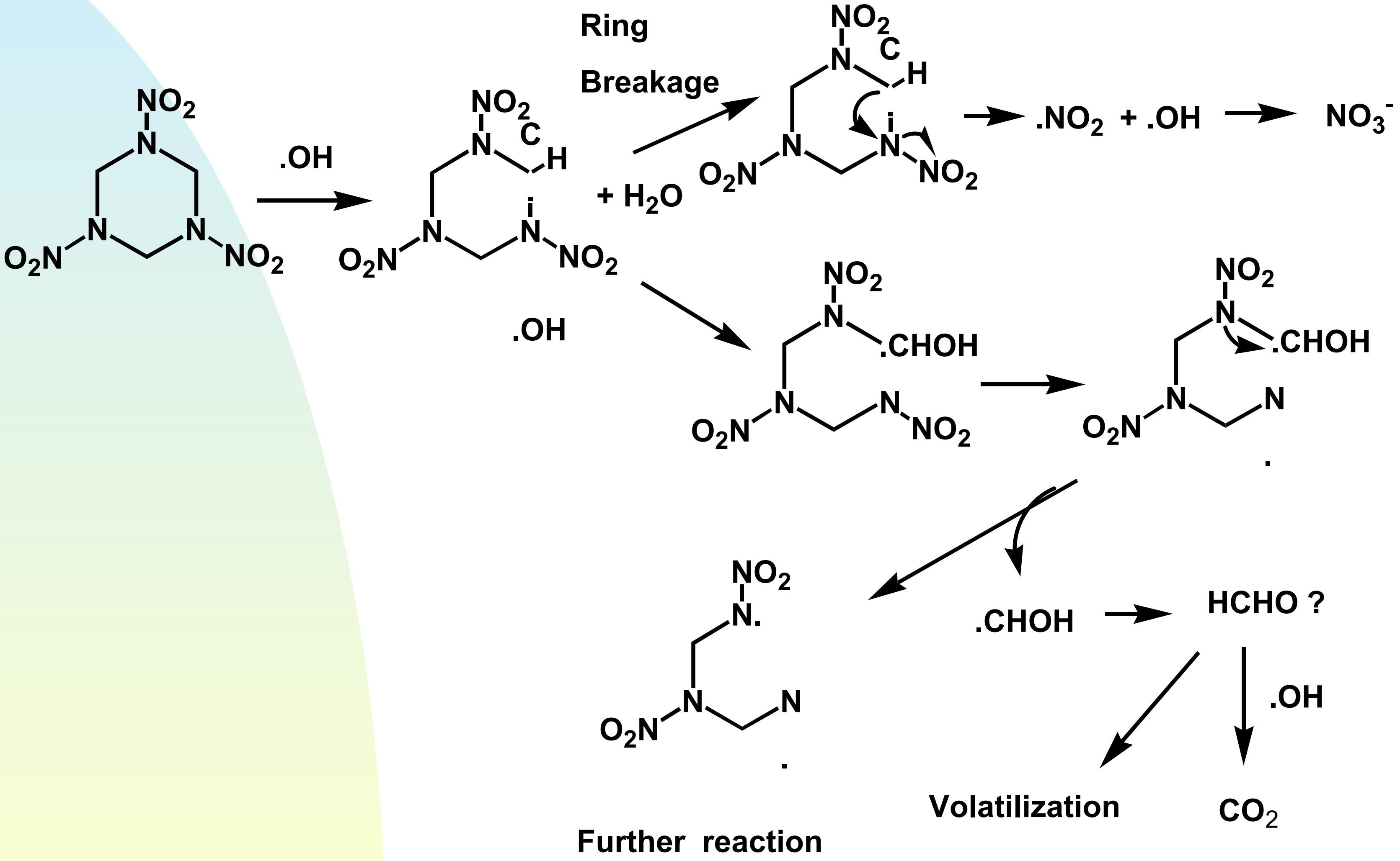
Organic Carbon Byproducts - GC/MS Analysis

- The reaction end products of RDX and HMX were analyzed using LLE followed by GC/MS.
- Any non-polar intermediates and extractable by CH_2Cl_2 can be detected.
- A comprehensive set of blank samples were also extracted LLE and analyzed with GC/MS

GC-MS chromatogram



Proposed Mechanism of RDX Fenton Oxidation



Ring

Breakage

Further reaction

Volatilization

Conclusions

- RDX and HMX Fenton oxidation are rapid between 20 and 50 °C.
- Experimental data could be fit to a pseudo first-order rate equation.
- Reaction rate coefficient was strongly dependent on temperature, H_2O_2 and Fe^{2+} concentrations.
- The activation energy using Arrhenius equation was 51.3 (RDX) and 48.6 (HMX) $kJ \cdot mol^{-1}$.
- The byproducts (NO_3^- and N_2) and mineralization of the oxidation of RDX and HMX were discussed.
- No further non-polar unknown end-products could be detected by GC/MS.