

# Decomposition of energetic chemicals contaminated with iron or stainless steel

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Available online 29 September 2005

## Abstract

Contamination of chemicals or reaction mixtures with iron or stainless steel is likely to take place during chemical processing. If energetic and thermally unstable chemicals are involved in a manufacturing process, contamination with iron or stainless steel can impact the decomposition characteristics of these chemicals and, subsequently, the safety of the processes, and should be investigated.

The goal of this project was to undertake a systematic approach to study the impact of iron or stainless steel contamination on the decomposition characteristics of different chemical classes.

Differential scanning calorimetry (DSC) was used to study the decomposition reaction by testing each chemical pure, and in mixtures with iron and stainless steel. The following classes of energetic chemicals were investigated: nitrobenzenes, tetrazoles, hydrazines, hydroxylamines and oximes, sulfonic acid derivatives and monomers. The following non-energetic groups were investigated for contributing effects: halogens, hydroxyls, amines, amides, nitriles, sulfonic acid esters, carbonyl halides and salts of hydrochloric acid.

Based on the results obtained, conclusions were drawn regarding the sensitivity of the decomposition reaction to contamination with iron and stainless steel for the chemical classes listed above. It was demonstrated that the most sensitive classes are hydrazines and hydroxylamines/oximes. Contamination of these chemicals with iron or stainless steel not only destabilizes them, leading to decomposition at significantly lower temperatures, but also sometimes causes increased severity of the decomposition. The sensitivity of nitrobenzenes to contamination with iron or stainless steel depended upon the presence of other contributing groups: the presence of such groups as acid chlorides or chlorine/fluorine significantly increased the effect of contamination on decomposition characteristics of nitrobenzenes. The decomposition of sulfonic acid derivatives and tetrazoles was not impacted by presence of iron or stainless steel.

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**Keywords:** Decomposition; Contamination; Stainless steel; Iron; Energetic chemicals; Differential scanning calorimetry

## 1. Introduction

Contamination of energetic and thermally unstable chemicals with iron or stainless steel can happen easily during chemical handling and processing operations. Understanding the impact of contamination with iron or stainless steel on thermal stability of energetic chemicals is vital for determining safe chemical handling and processing conditions.

Some chemicals such as hydroxylamine, hydrogen peroxide, epoxides and acid chlorides are generally known and documented to be sensitive to iron contamination [1]. However, the effects of metal contamination on the thermal sta-

bility of many chemical processes are often unknown until an in-depth study is precipitated by an incident.

The goal of this project was to identify energetic functional groups and contributing substituents that are destabilized by contamination with iron or stainless steel, leading to decomposition at lower temperatures or faster decomposition rates. The conclusions drawn in this project are intended to be used to screen chemical processes, based on the chemical structures, to determine the need for additional investigation of the consequences of iron or stainless steel contamination.

## 2. Experimental

Standard DSC experiments were conducted using a TA Instruments Model 2920 calorimeter. A total sample of

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approximately 1 mg was sealed under nitrogen in a glass capillary, placed in a silver cradle and heated in scanning mode at 10 °C/min from 25 to 420 °C [2]. The instrument was calibrated using a dedicated 1 mg indium standard in a glass capillary at 10 °C/min. The TA2920 DSC computer automatically updated the cell constant, onset slope and temperature correction factors. 316 Stainless steel fines were made using a hand file on a coupon of 316SS. Iron powder was obtained from Aldrich (26,795-3, particle size 10 µm, 99.9%).

### 3. Results and discussion

DSC experiments were performed on 17 chemicals that represent seven classes of energetic materials and contain various non-energetic substituting groups that can potentially interact with iron or stainless steel. Experiments were performed on pure chemicals, as well as the chemicals mixed with small amounts of iron or stainless steel (typically 10 wt%). The following characteristics of decomposition were recorded:

- decomposition onset temperature ( $T_o$ , °C);
- temperature at the maximum heat flow rate (peak of the exotherm) ( $T_{mhr}$ , °C);
- maximum heat flow rate during decomposition (peak height) ( $R$ , W/g).

The first two characteristics are indicative of the sensitivity to decomposition, and the last one of the severity of decomposition.

The following characteristics of decomposition of chemicals and mixtures were calculated to compare decomposition of pure versus contaminated chemicals:

- difference in decomposition onset temperatures between the contaminated and the pure chemicals, ( $dT_o = T_o \text{ cont} - T_o \text{ pure}$ , °C), difference of less than 10 °C magnitude was considered insignificant;
- difference in temperatures at the exotherm peak between the contaminated and the pure chemicals ( $dT_{mhr} = T_{mhr} \text{ cont} - T_{mhr} \text{ pure}$ , °C), difference of less than 10 °C magnitude was considered insignificant;
- ratio of the maximum heat flow rate of the contaminated and the pure chemical ( $R_c/R_p$ ).

The overlay DSC curves of pure and contaminated chemicals for three selected chemicals that demonstrated a significant sensitivity to contamination with iron and stainless steel are presented in Figs. 1–3.

Results of DSC tests of all 17 compounds pure and contaminated with either iron or stainless steel were analyzed, and the differences in the decomposition onset and peak temperatures and ratios of maximum heat flows of pure versus contaminated chemicals were calculated and are presented in Figs. 4–6.

From the analysis of the data presented in Figs. 4–6 we can see that decomposition of certain classes of unstable

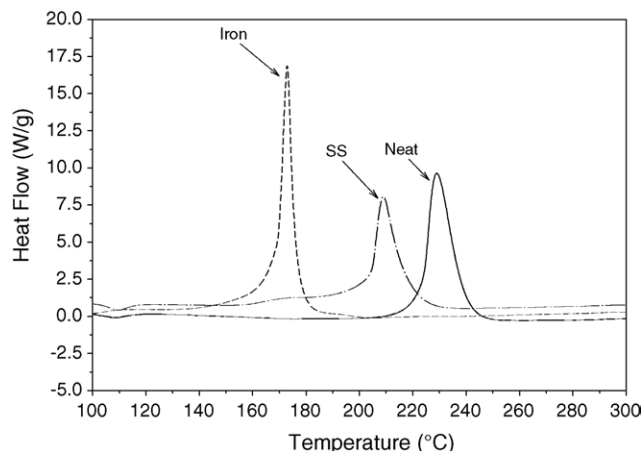


Fig. 1. Overlay of DSC curves of pure and contaminated with iron and stainless steel energetic chemical containing  $\text{NHNH}_2 \cdot \text{HCl}$  functional group.

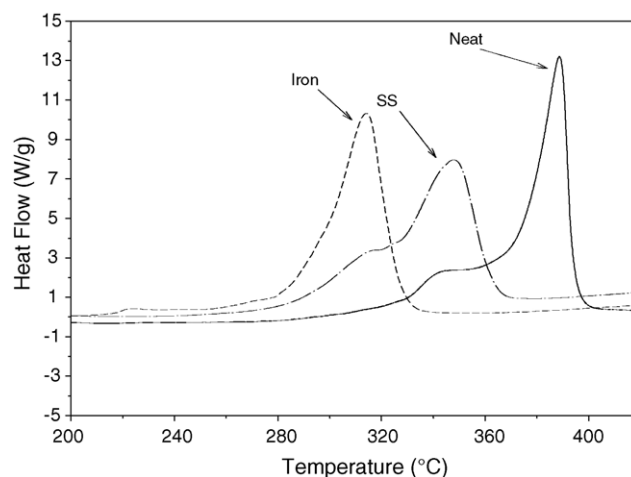


Fig. 2. Overlay of DSC curves of pure and contaminated with iron and stainless steel energetic chemical containing  $\text{NO}_2$ ,  $\text{COCl}$  functional groups.

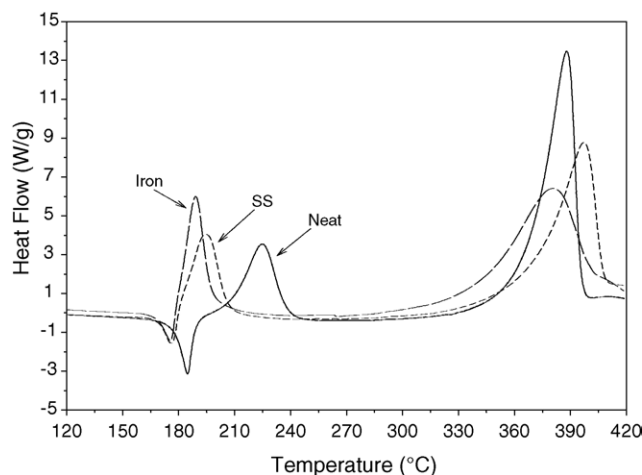


Fig. 3. Overlay of DSC curves of pure and contaminated with iron and stainless steel energetic chemical containing  $\text{NO}_2$ ,  $\text{NOH}$ ,  $\text{NH}$  functional groups.

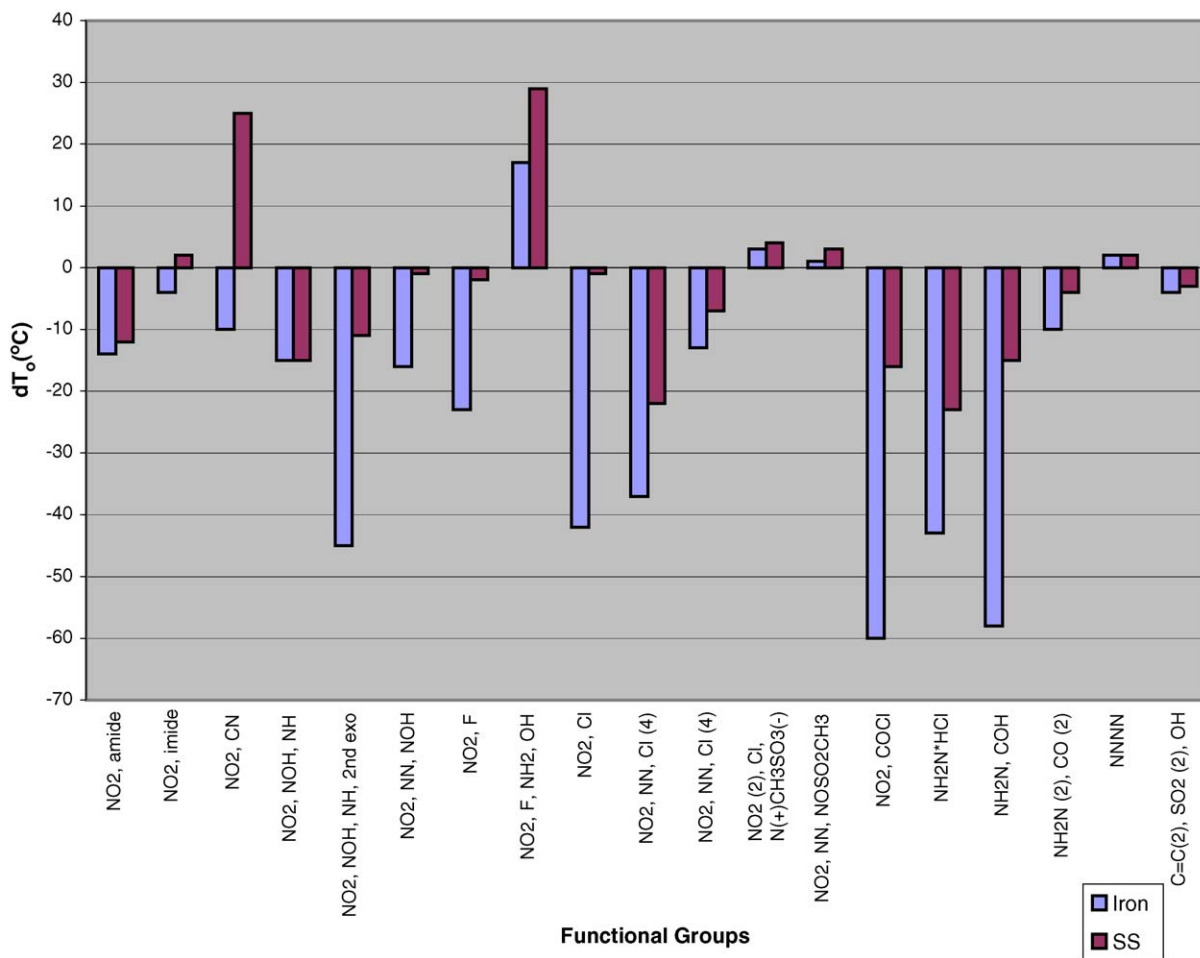


Fig. 4. Change in DSC onset temperature between pure and contaminated with iron or stainless steel chemicals. Negative value indicates a decreased onset temperature or increased sensitivity to decomposition when contaminated.

energetic chemicals, e.g., tetrazole (NNNN) does not change significantly when contaminated with either iron or stainless steel. Other energetic chemical classes, such as hydroxylamine (NOH, Fig. 3) or hydrazine (NH<sub>2</sub>N, Fig. 1) derivatives, show a significant decrease in the decomposition temperatures and sometimes an increase in the decomposition maximum heat flow rate when contaminated. The analysis of the behavior of the nitrobenzene derivatives leads us to a conclusion that, by itself, the nitro group is not sensitive to contamination; however, if the molecule contains other non-energetic substituents that are reactive with iron or stainless steel, the whole molecule becomes less stable when contaminated and the decomposition of the nitro group happens at significantly lower temperature (Fig. 2). The results of the tests and calculations of the change in decomposition temperature and maximum heat flow rate for all 17 chemicals are summarized in Table 1 for all energetic chemical classes and the non-energetic substituting groups.

The following observations can be made from the data summarized in Table 1.

- Overall, iron had a greater impact on the thermal stability of these chemicals than did stainless steel.
- Hydrazine and hydroxylamine/oxime derivatives showed the greatest sensitivity to iron and stainless steel.
- Nitrobenzene derivatives did not demonstrate a significant destabilization by iron unless acid chloride or halogen groups were present. Presence of fluorine in the molecule had a smaller effect than chlorine. Presence of such groups as amino, hydroxy, amide, imide, cyano, or sulfonic acid derivatives did not have any significant impact on the stability of contaminated nitrobenzenes.
- Sulfonic acid derivatives, which are moderately energetic groups themselves, showed no sensitivity to contamination by iron or stainless steel.
- Decomposition characteristics of tetrazole did not change when contaminated with iron or stainless steel; however, the impact of such contributing groups as chloro or acid chloride on stability of tetrazoles was not investigated in this work and needs to be addressed in the future.
- The only monomer tested showed some sensitivity to iron but not to stainless steel.

Table 1  
Sensitivity to contamination by stainless steel and iron of various energetic chemicals

	Energetic group	Contributing substituent	Iron $dT_o/dT_{mhr}/R_c/R_p$	Conclusion <sup>a</sup>	SS $dT_o/dT_{mhr}/R_c/R_p$	Conclusion <sup>a</sup>
1	NO <sub>2</sub>	Amide	-14/-19/0.5	Slightly sensitive	-12/-7/0.4	Slightly sensitive
2	NO <sub>2</sub>	Imide	-4/-6/0.7	Not sensitive	2/3/0.7	Not sensitive
3	NO <sub>2</sub>	CN	-10/-18/0.6	Slightly sensitive	25/5/0.8	Not sensitive
4	NO <sub>2</sub> , NOH	NH	-15/-36/1.5	Very sensitive	-15/-30/1.1	Sensitive
5	NO <sub>2</sub> , NN, NOH		-16/-30/1.4	Very sensitive	-1/-8/0.9	Not sensitive
6	NO <sub>2</sub>	F	-23/-15/0.7	Sensitive	-2/0/1	Not sensitive
7	NO <sub>2</sub>	F, NH <sub>2</sub> , OH	17/11/1.2	Slightly sensitive	29/9/1.5	Slightly sensitive
8	NO <sub>2</sub>	Cl	-42/-27/1.8	Very sensitive		
9	NO <sub>2</sub> , NN	Cl (4 gr.)	-37/-29/1.7	Very sensitive	-22/-28/0.4	Sensitive
	NO <sub>2</sub> , NN	Cl (4 gr.)	-13/-24/2.1	Very sensitive	-7/-15/0.8	Slightly sensitive
10	NO <sub>2</sub> , NN	N(+) <chem>SO3CH3(-)</chem>	3/-10/1.4	Slightly sensitive	4/-7/0.9	Not sensitive
11	NO <sub>2</sub> , NN	<chem>NOSO2CH3</chem>	1/-2/0.8	Not sensitive	3/0/1	Not sensitive
12	NO <sub>2</sub>	COCl	-60/-75/0.8	Very sensitive	-16/-41/0.6	Very sensitive
13	<chem>NHNH2*HCl</chem>		-43/-56/1.7	Very sensitive	-23/20/0.8	Sensitive
14	<chem>NH2NH</chem>	COH	-58/-13/1.3	Very sensitive	-15/-9/1.8	Sensitive
15	<chem>NH2N</chem> (2 gr.)	CO (2 gr.)	-10/-20/3.2	Very sensitive	-4/-9/1.8	Sensitive
16	NNNN		2/2/1.0	Not sensitive	2/2/1.2	Not sensitive
17	<chem>C=C</chem> (2 gr.), SO <sub>2</sub> (2 gr.)	OH	-4/-21/0.6	Sensitive	-3/-5/0.7	Not sensitive

<sup>a</sup> The following criteria was used for classifying sensitivity to contamination:

- slightly sensitive  $10^\circ\text{C} < |dT_o|$  or  $|dT_{mhr}| \leq 20^\circ\text{C}$  or  $1.2 < R_c/R_n \leq 1.5$ ;
- sensitive  $20^\circ\text{C} < |dT_o|$  or  $|dT_{mhr}| \leq 40^\circ\text{C}$  or  $1.5 < R_c/R_n \leq 2.0$ ;
- very sensitive  $|dT_o|$  or  $|dT_{mhr}| > 40^\circ\text{C}$  or  $R_c/R_n > 2.0$ ;
- In the case when both decomposition characteristics change significantly (temperature decreases and heat flow rate increases) because of contamination, the chemical is considered very sensitive.

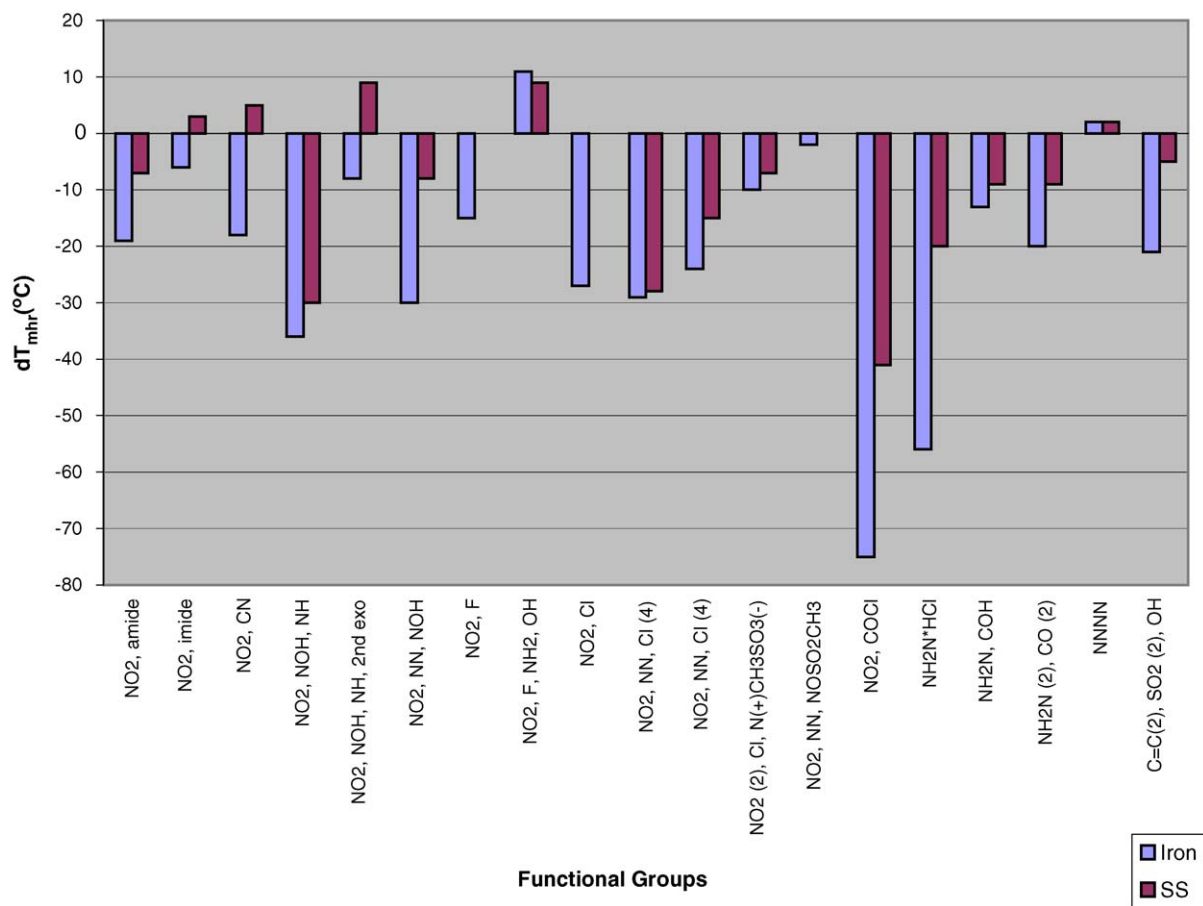


Fig. 5. Change in DSC temperature at the exotherm peak between pure and contaminated with iron or stainless steel chemicals. Negative value indicates a decreased peak temperature or increased sensitivity to decomposition when contaminated.

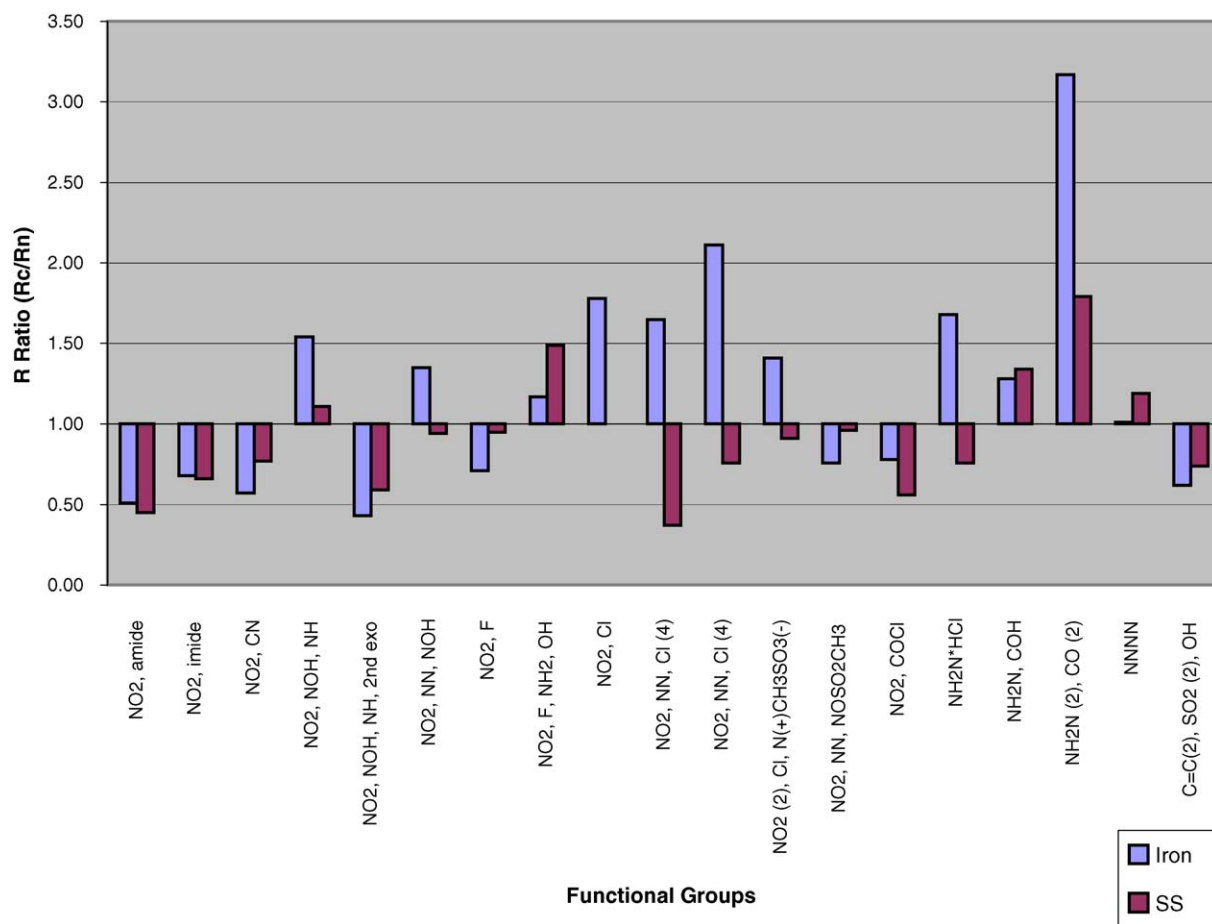


Fig. 6. Ratio of the DSC maximum heat flow rate of pure and contaminated with iron or stainless steel chemicals. A value higher than 1 indicates an increased heat flow rate or severity of decomposition when contaminated.

#### 4. Conclusions

Based on the comparison of DSC decomposition characteristics of pure and contaminated with iron or stainless steel energetic chemicals, it was demonstrated that hydrazine and hydroxylamine/oxime derivatives exhibit the most significant destabilization when contaminated, resulting in significantly lower decomposition temperatures and increased severity of decomposition. Nitrobenzenes were not sensitive to the contamination themselves; however, if acid chloride or chlorine substituents were present in the molecule, a significant destabilization of the nitro group occurred. Decomposition of such chemical classes as tetrazoles and sulfonic acid derivatives did not change when contaminated, but the impact of other

substituents on the decomposition of these classes was not evaluated. Identity of non-energetic/low energy substituents can significantly impact the sensitivity to contamination and severity of decomposition of an energetic group. Caution needs to be exercised in generalizing across an entire chemical class and when extrapolating from simple mixture experiments to more complex reaction mixtures.

#### References

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