Mechanochemical Nitration of Organic Compounds

Statement of Need WP-19-2748-F1

SEMS Project Number: WP19-1383

Final Outbrief

Ashvin Vasudevan, Mirko Schoenitz, Edward L. Dreizin
Otto H. York Department of Chemical and Materials Engineering
New Jersey Institute of Technology, Newark, NJ 07102
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14. ABSTRACT
Nitro-products of organic compounds are useful in many applications; they are widely employed as precursors or components of energetic materials. Industrial nitration generates substantial waste and uses aggressive chemicals, making the process unsafe and environmentally objectionable. This work advances the solvent-free process of mechanochemical nitration of aromatic compounds. Feasibility of such nitration with high yield and rate was shown. Nitration is achieved during mechanical milling of the organic precursor, solid powder catalyst, and nitrate, serving as a source of nitronium. However, it remained unclear how important are the choices of the catalyst, organic compound to be nitrated, and nitronium source. Quantifying and understanding such effects will advance the proposed mechanochemical nitration technique and build the foundation for the follow-up work identifying the reaction mechanisms and scaling the process up to pilot-plant level.

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Mechanochemical Nitration, Organic Compounds

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Mechanochemical nitration of aromatic precursors

- Previous SERDP-funded work established possibility of mechanochemical nitration:

$$C_7H_8 + NaNO_3 \xrightarrow{MoO_3} C_7H_7(NO_2) + NaOH$$

Lagoviyer, O.S., Krishtopa, L., Schoenitz, M., Trivedi, N.J., Dreizin, E.L. *Journal of Energetic Materials* pp. 1-11 (2017)

Lagoviyer, O.S., Schoenitz, M., Dreizin, E.L. *Journal of Materials Science* 53, pp. 13690-13700 (2018)

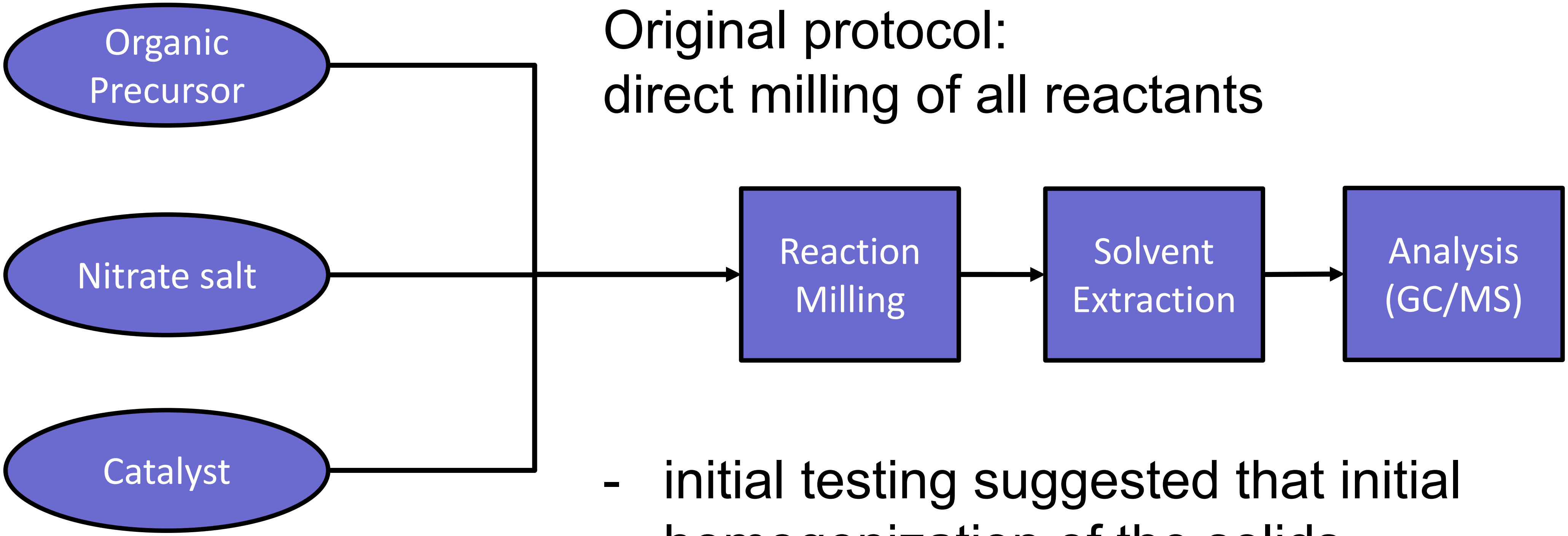
- What processes govern this reaction?

➔ Conduct experiments with systematically varied reactants:
  - **Different catalysts**, nitrating toluene
  - Nitrating **different precursors**
  - **Different nitrates** as nitronium sources

Equipment

- Retsch PM400-MA **planetary mill**
  - 4 × 500 mL milling jars
  - Custom temperature control
- General reactant amounts
  - **aromatic precursor**: 0.5 mL (0.25 mL – 8 mL)
  - **nitrate salt**: 1.67 g (0.4 g – 16 g)
  - **metal oxide catalyst**: 41.63 g
- Exploratory experiments used batch reactor
- Scale up expected to rely on attrition milling enabling semi-batch or continuous synthesis

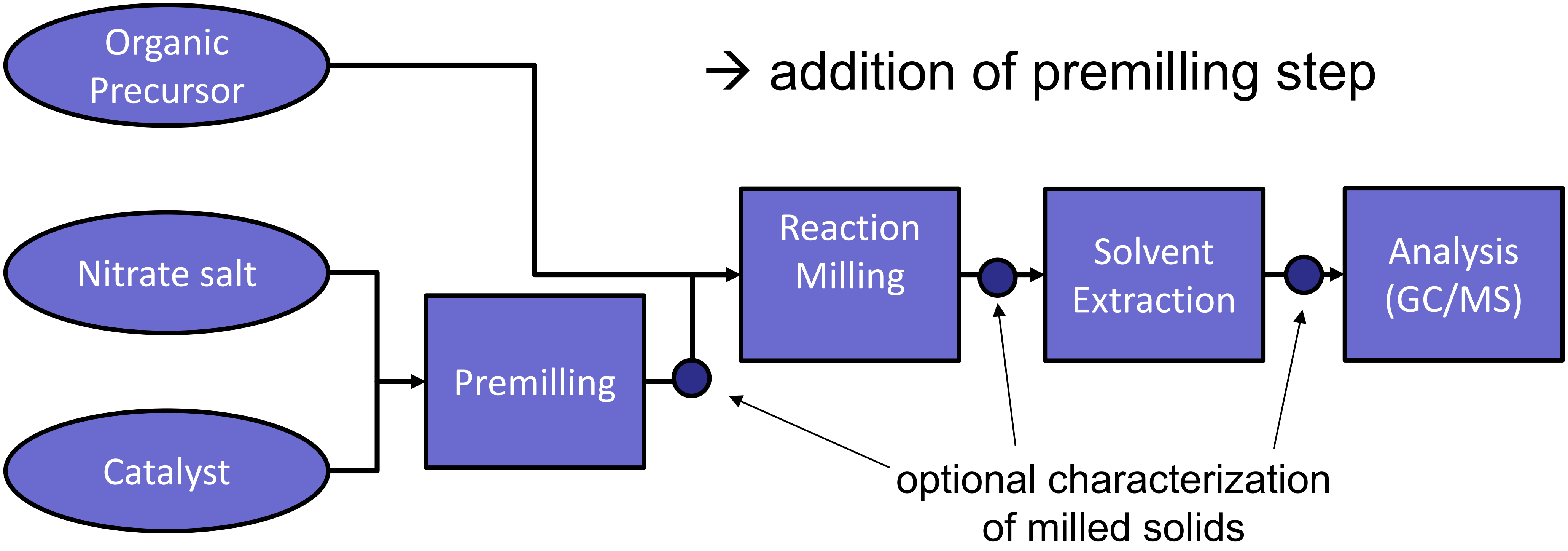
Experimental Protocol



Original protocol:
direct milling of all reactants

- initial testing suggested that initial homogenization of the solids improves outcome

Experimental Protocol



→ addition of premilling step

optional characterization
of milled solids

Part 1. Effect of catalyst on nitration of toluene

- Different inorganic oxide catalysts: Mo, W, V, Mn, Ti, Fe, Al, Bi
  - range of acid strengths (Lewis and Brønsted) of surface sites
- Toluene precursor
- $NaNO_3$ nitrate salt/nitronium source

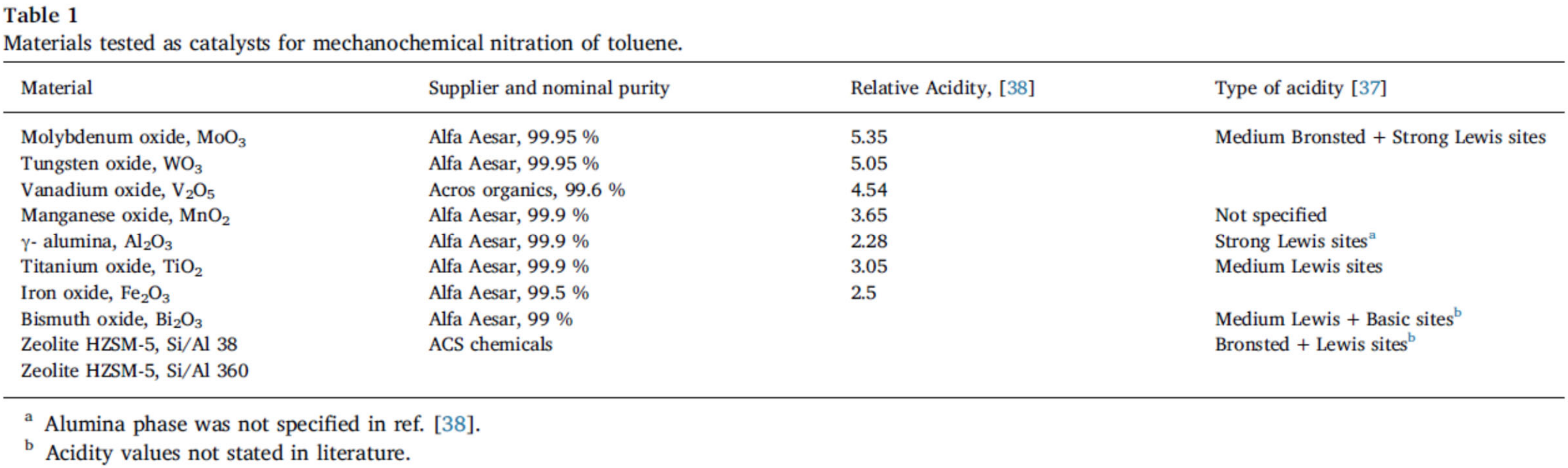


Table 1
Materials tested as catalysts for mechanochemical nitration of toluene.

Material	Supplier and nominal purity	Relative Acidity, [38]	Type of acidity [37]
Molybdenum oxide, MoO_3	Alfa Aesar, 99.95 %	5.35	Medium Bronsted + Strong Lewis sites
Tungsten oxide, WO_3	Alfa Aesar, 99.95 %	5.05	
Vanadium oxide, V_2O_5	Acros organics, 99.6 %	4.54	
Manganese oxide, MnO_2	Alfa Aesar, 99.9 %	3.65	Not specified
γ- alumina, Al_2O_3	Alfa Aesar, 99.9 %	2.28	Strong Lewis sites[a]
Titanium oxide, TiO_2	Alfa Aesar, 99.9 %	3.05	Medium Lewis sites
Iron oxide, Fe_2O_3	Alfa Aesar, 99.5 %	2.5	
Bismuth oxide, Bi_2O_3	Alfa Aesar, 99 %		Medium Lewis + Basic sites[b]
Zeolite HZSM-5, Si/Al 38	ACS chemicals		Bronsted + Lewis sites[b]
Zeolite HZSM-5, Si/Al 360			

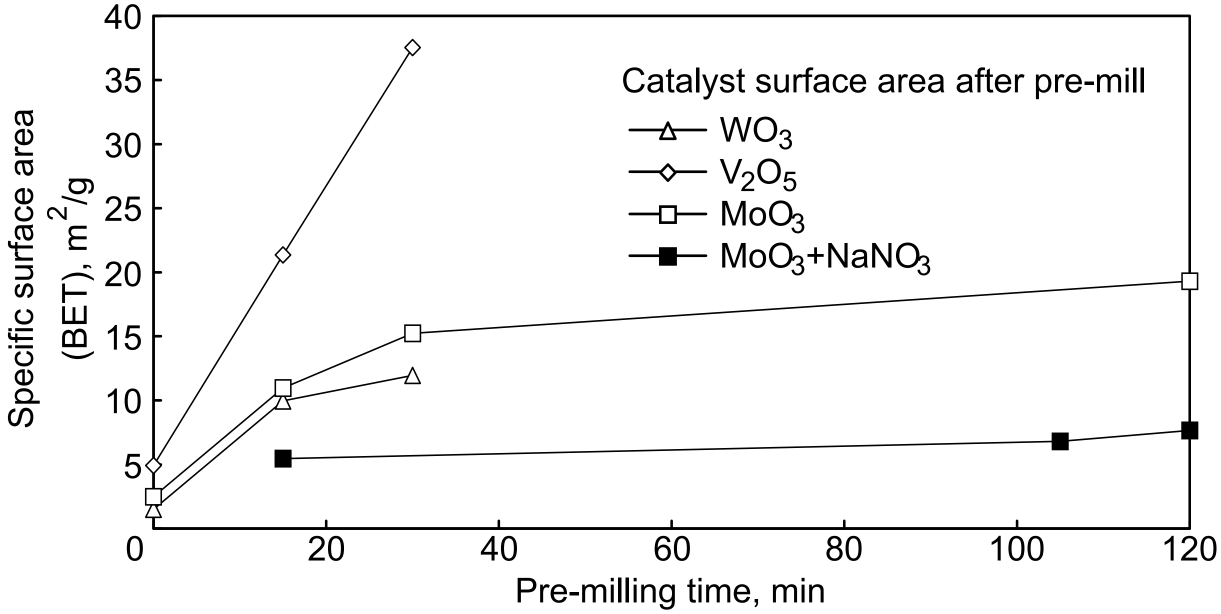
[a] Alumina phase was not specified in ref. [38].
[b] Acidity values not stated in literature.

Evaluation of premilling: Development of catalyst & nitrate

BET specific surface area

- increases with time
- saturated after 2 hours

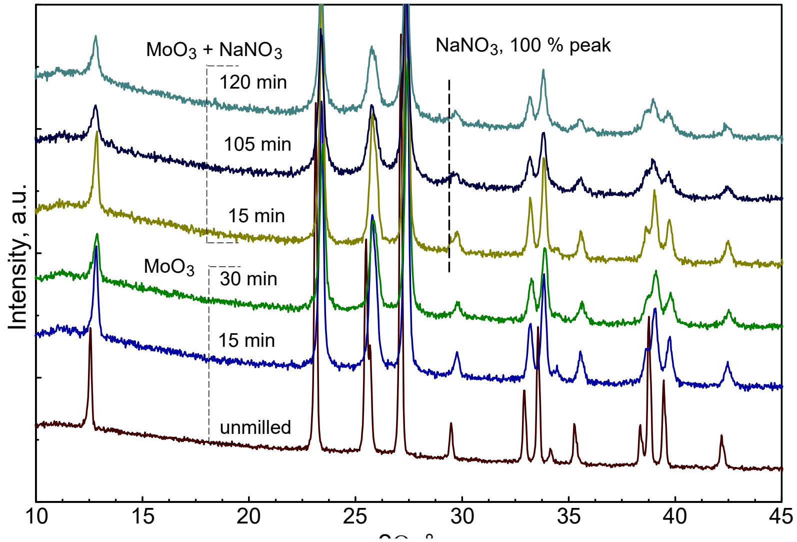
- absolute surface area determined by oxide

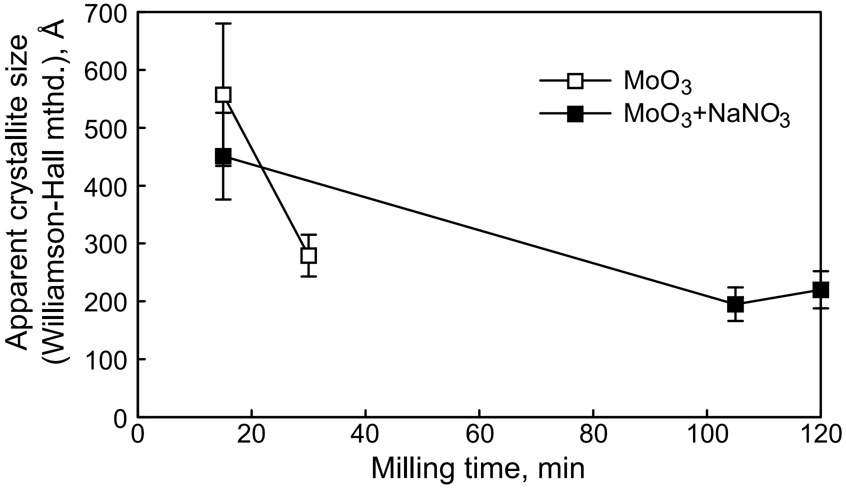


Evaluation of premilling: Development of catalyst & nitrate

XRD: <u>nitrate</u> no longer crystalline enough to be detected after premilling

- <u>Catalyst</u> also shows signs of decreased crystallinity



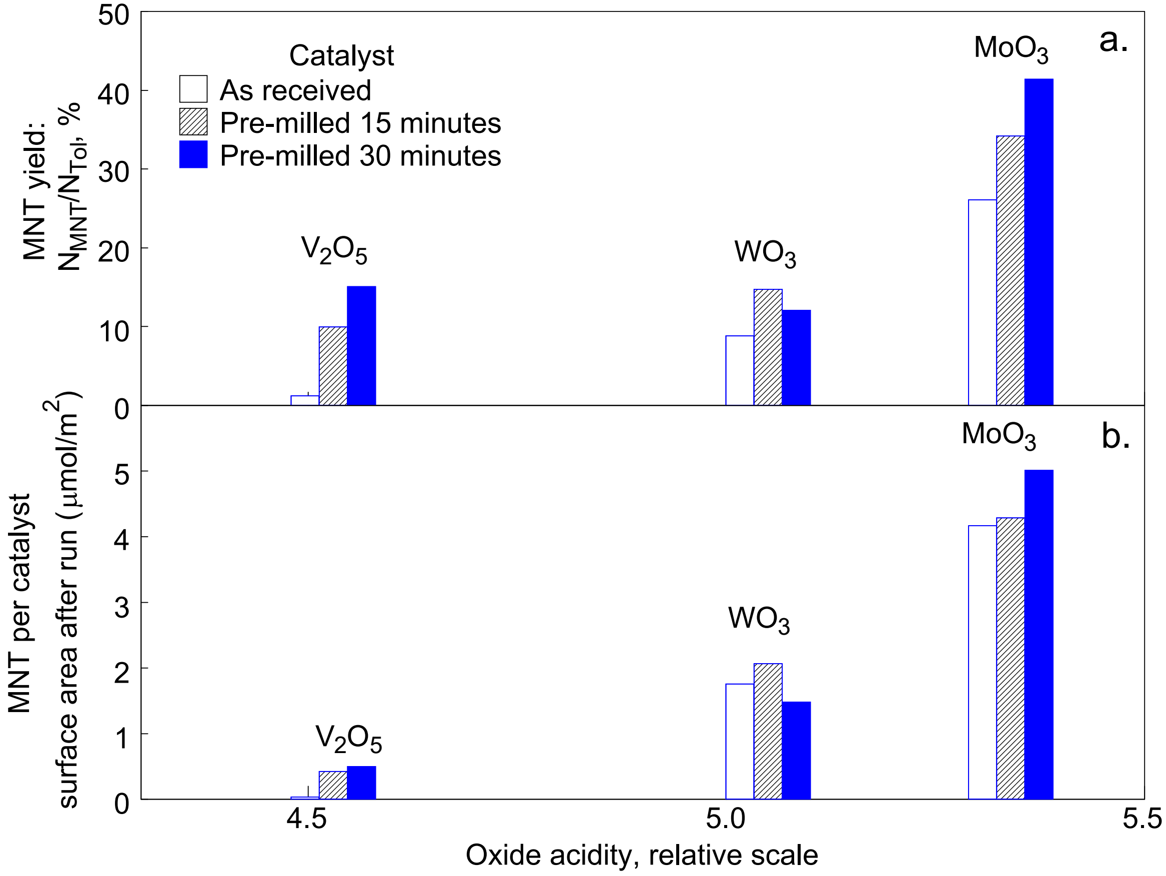


Overall results: Mononitrotoluene yields

- Only Mo, W and V oxides showed quantifiable yields

- Rough correlation with oxide acidity, apparent when normalized by catalyst surface area

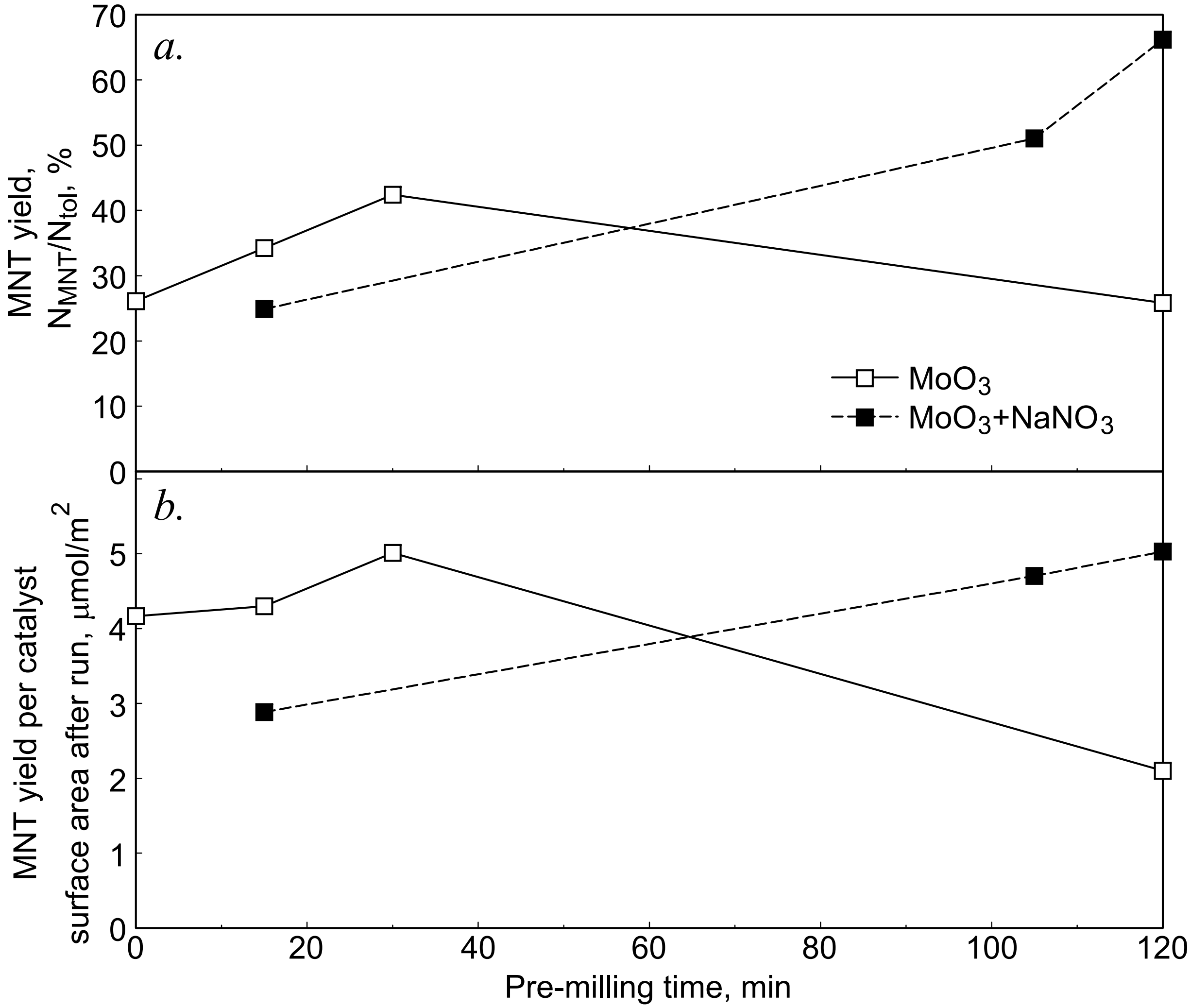
- Premilling catalyst with nitrate affects all catalysts
  - Highest yield with MoO_3



Pre-milling time and distribution of $NaNO_3$

- Effect of **MoO_3 pre-milling time** is **minor**
  - Longer times may be undesired

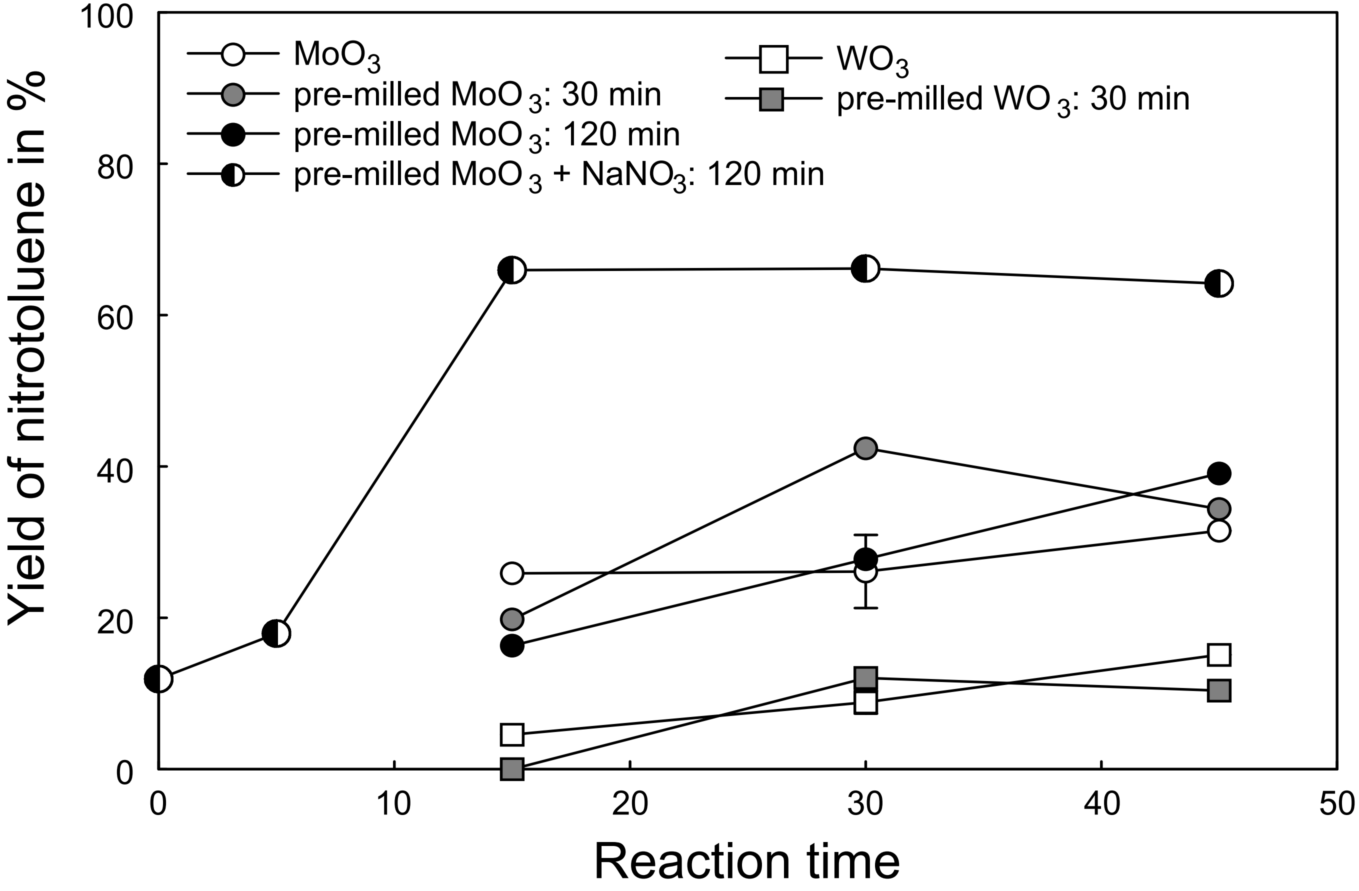
- **Distribution of $NaNO_3$ is important**
  - Longer **pre-milling MoO_3 with $NaNO_3$** leads to a better distribution
  - **Higher yield**



Effect of reaction milling time

- ❑ MoO_3, WO_3: pre-milling the catalyst is not important
  - A weak trend of **yield increasing with the reaction time**

- ❑ MoO_3+$NaNO_3$: yield reaches a **plateau after 15 minutes**
  - **Nearly complete conversion**



Findings guiding further work:

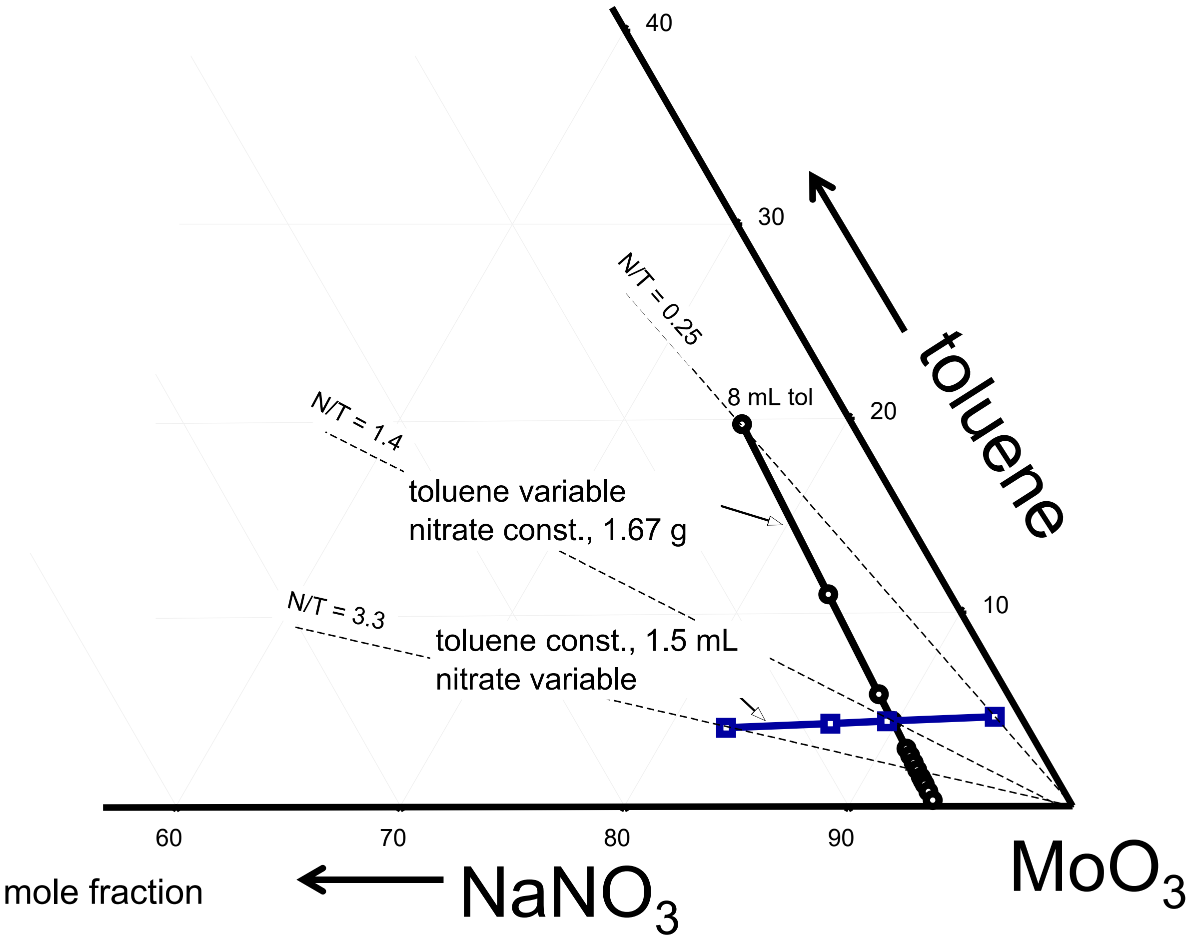
- MoO_3 most suitable catalyst, to be used for further work

- Premilling for 2 h gives most consistently high yields
  - becomes part of standard protocol

Systematic variation of reactant proportions

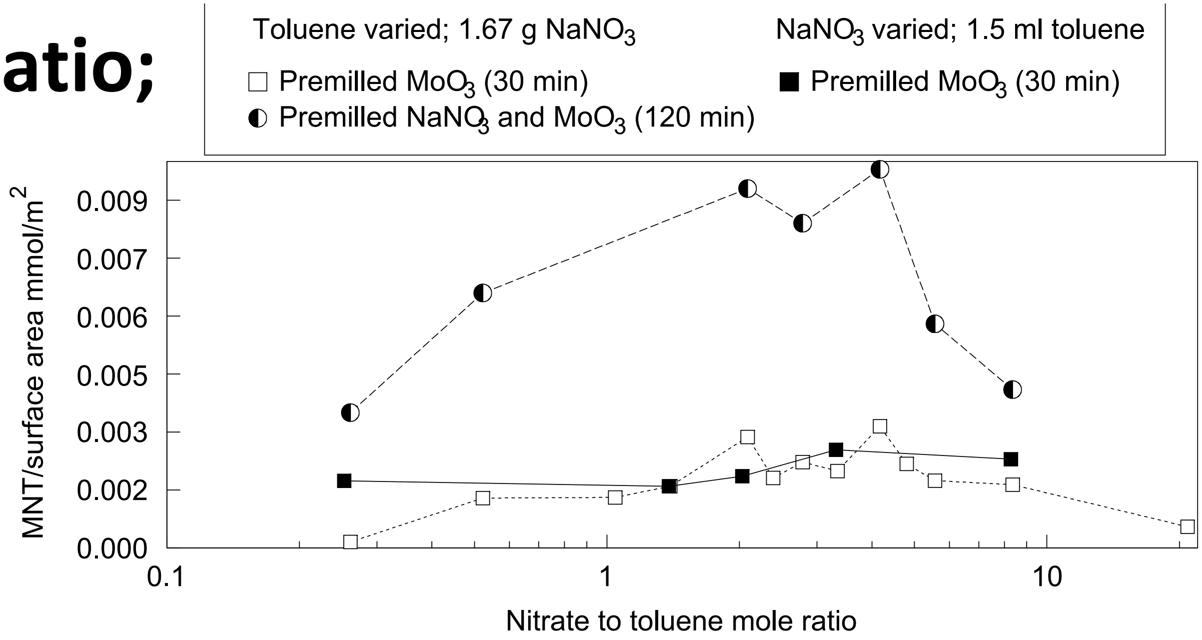
2 experimental series, **varying nitrate/toluene** reactant ratios

- toluene = const.
- nitrate = const.
  - ☐ premilled/not premilled



Effect of $NaNO_3$/toluene ratio; MNT yield

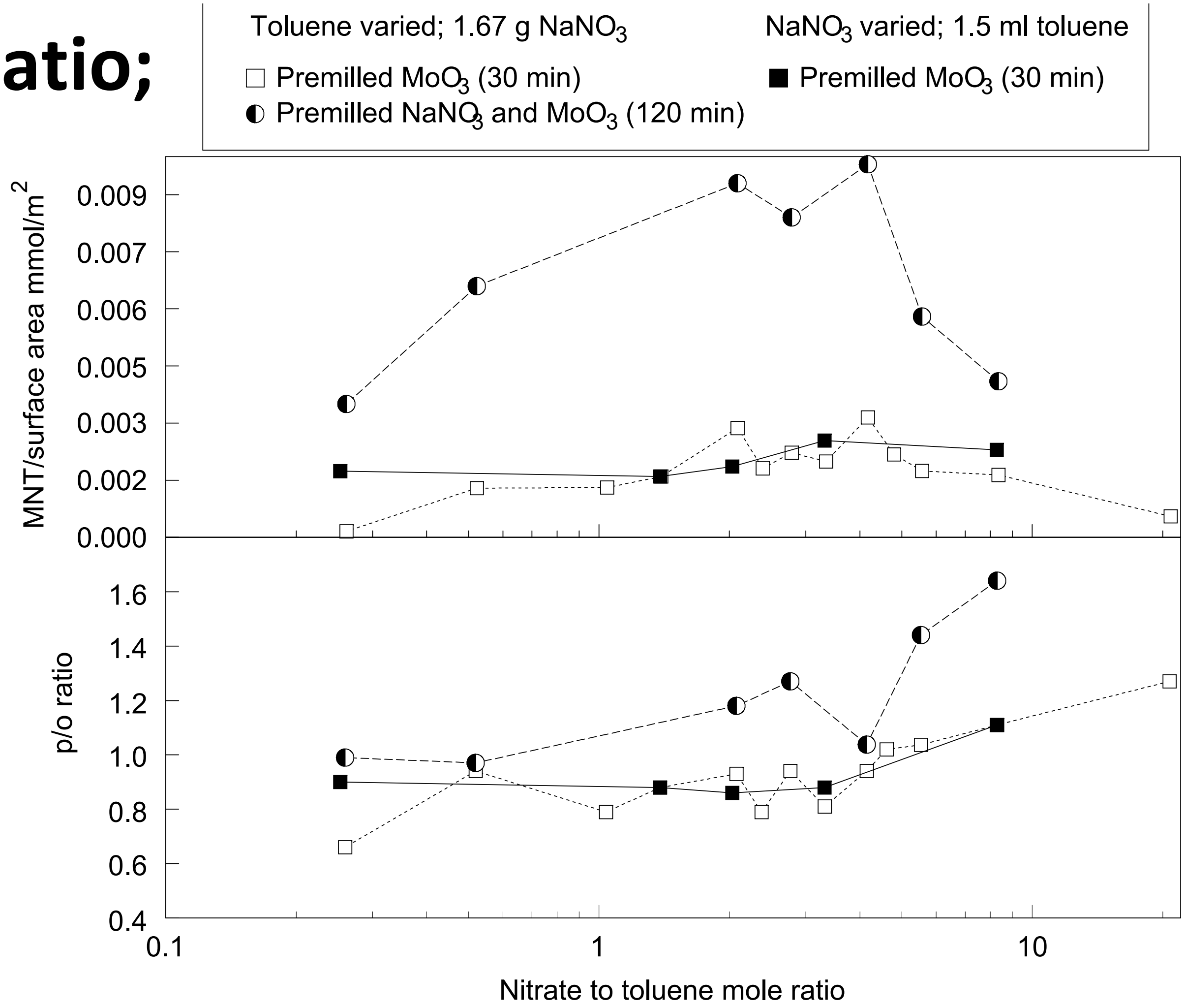
- Varied **toluene**:
  - **A clear peak** in yield for a range of $NaNO_3$/toluene ratios
  - Better seen for pre-milled $NaNO_3$+MoO_3
  - Corresponds to a toluene spread over catalyst in a **very thin layer**
  - Close to **monolayer**
- Varied **$NaNO_3$**
  - No effect
- **Toluene amount** (layer thickness) **matters**



Effect of $NaNO_3$/toluene ratio; MNT isomer ratio

- **Higher p/o ratios** for **greater yield**

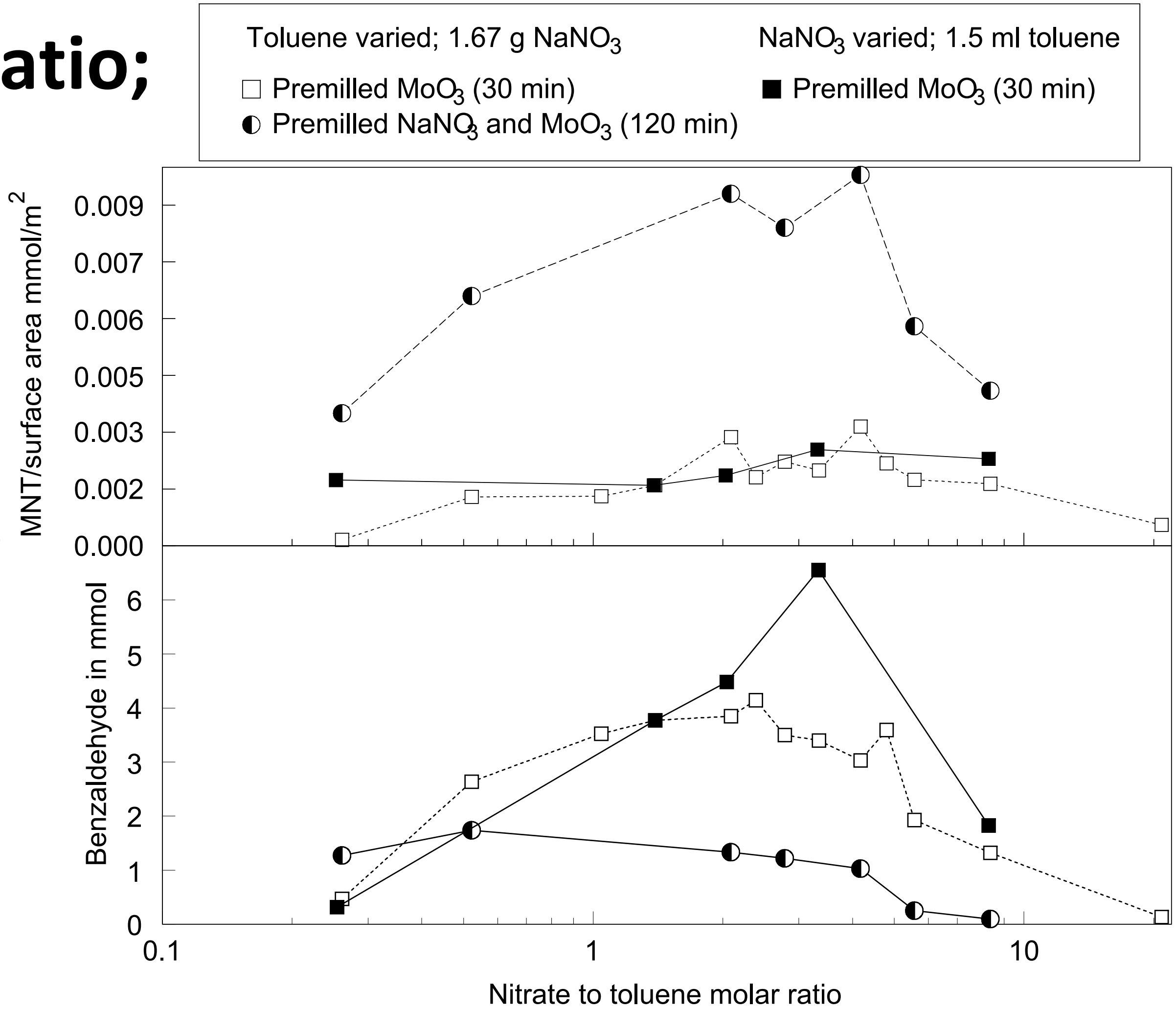
- **Unusually high p/o** ratio for runs **limited by toluene** amount



Effect of $NaNO_3$/toluene ratio;

Oxidized byproducts

- **Benzaldehyde**: main byproduct
- Production **does not** directly **correlate with MNT yield**
- **Lowest** benzaldehyde production **for greatest yield**



Discussion: nitration occurs on surface of catalyst

- Reaction was not detected
  - for catalysts with **low acidity**
  - for **zeolites**: interior of the **pores** where the reaction might be taking place is **poorly accessible**

- For all three **successful catalysts**, MNT **yield scales**
  - with **acidity**
  - With **surface area** of the catalyst

- Pre-milling the catalyst powder has a limited effect on nitration
  - The catalyst is milled again during the reaction

- The effect of **pre-milling** is stronger when **both catalyst (MoO_3) and the solid reactant ($NaNO_3$)** are pre-milled together

Complete toluene conversion to MNT observed

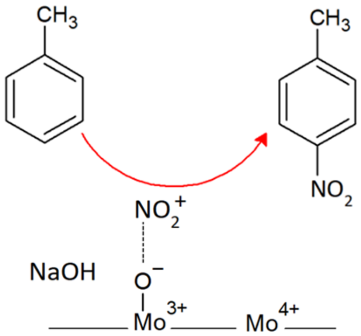
- **High yield** with **short** 15-min **reaction time**
  - 70% conversion measured
  - Close to 20% of toluene could have evaporated
  - Close to 10 % could be unaccounted for

- High yield is only observed when $NaNO_3$ was pre-milled with the catalyst for 120 min.
  - **Homogenizing $NaNO_3$ and the catalyst** was **the rate-limiting process** when the powders were not pre-milled together

- For pre-milled MoO_3 + $NaNO_3$, mechanochemical reaction occurs fast, but some **time is still required**
  - Toluene must be distributed over the catalyst surface
  - New catalyst surface becomes continuously available during milling

Mechanism of mechanochemical nitration

- Toluene is nitrated reacting with **nitronium complexes attached to acid sites**
  - **para MNT** isomer is **preferentially produced**
    - Consistent with the **present high p/o ratios**



- Both **yield** of MNT and **selectivity** are **reduced simultaneously** when the **amounts of toluene are increased**
  - Excess of **toluene** may be **blocking acid sites** from nitronium
  - Formation of nitronium involves interaction of dissolved $NaNO_3$ with Bronsted acid sites
    - **blocked acid sites** may lead to **a less effective production of nitronium** slowing down nitration

Part 1: Summary

- **Mechanochemical nitration** of toluene occurs on **surface** of catalyst
  - High acidity, high surface area lead to high yield

- **Complete conversion** of toluene achieved in **short** 15-min **reaction time**
  - **Pre-milling catalyst and nitrate** prior to reaction accelerates mechanochemical nitration

- Toluene is nitrated reacting with **nitronium complexes attached to acid sites**
  - **High p/o ratio**
  - **Low byproducts**

- Both **yield** of MNT and **selectivity** are **high** for **small amounts of toluene** (close to monolayer on catalyst surface)

Part 2. Nitrating different aromatic precursors

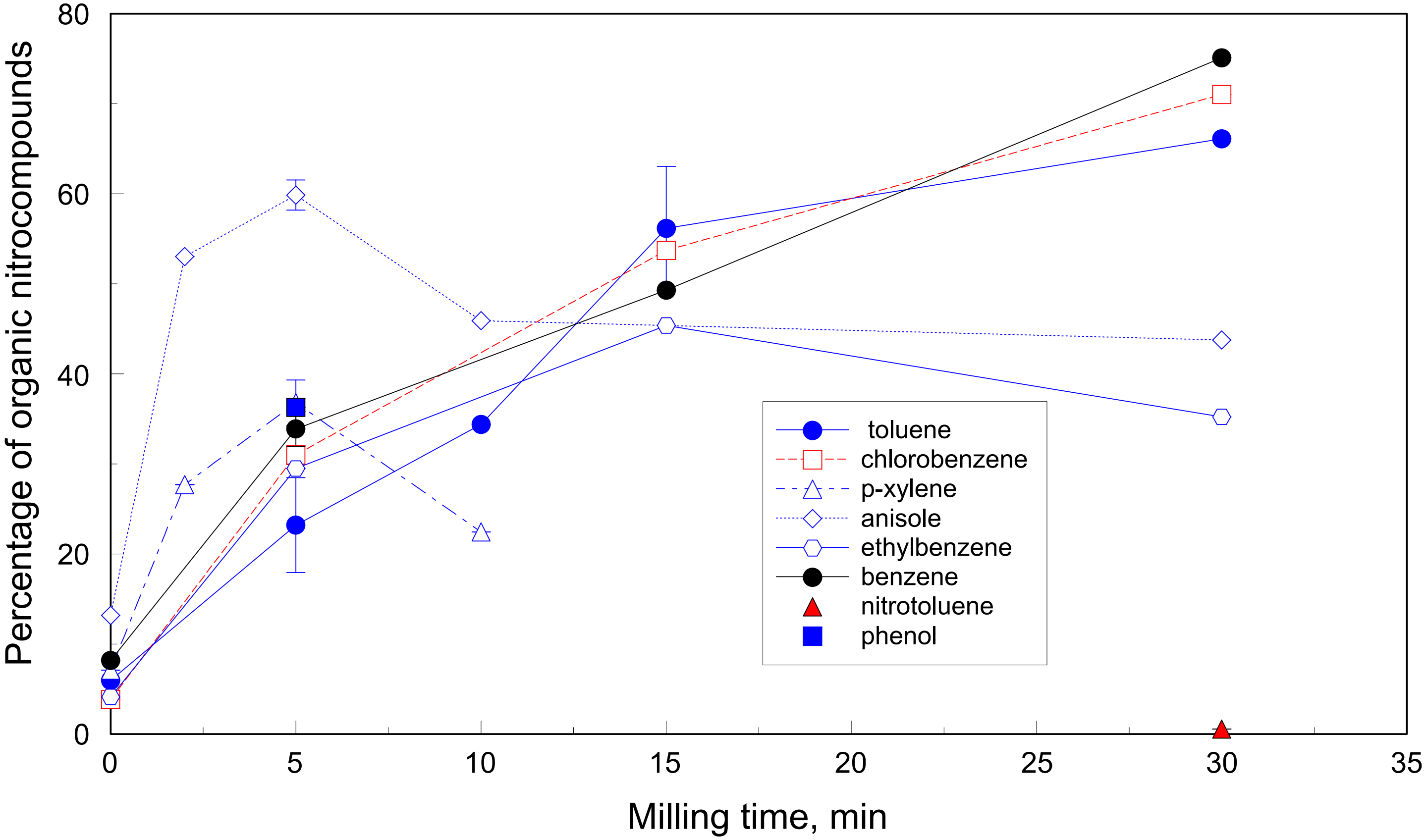
- Various **organic precursors** with wide range of *aromatic activation* and other properties
- MoO_3 as oxide catalyst
- $NaNO_3$ nitrate salt/nitronium source

Precursor	Functional group	Relative rate $\log(k/k_0)$ [1]
4-Nitrotoluene	NO_2	-3.72
Chlorobenzene	Cl	-0.66
Benzene	H	0
Ethyl benzene	C_2H_5	0.9
Toluene	CH_3	1.02
p-Xylene	$(CH_3)_2$	2.04
Phenol	OH	2.22
Anisole	OCH_3	4.68

Observed relative rates in liquid phase nitration using H_2SO_4 and HNO_3 at 25°C
[1] C. Hansch, A. Leo, R.W. Taft, Chemical Reviews, 91 (1991) 165-195

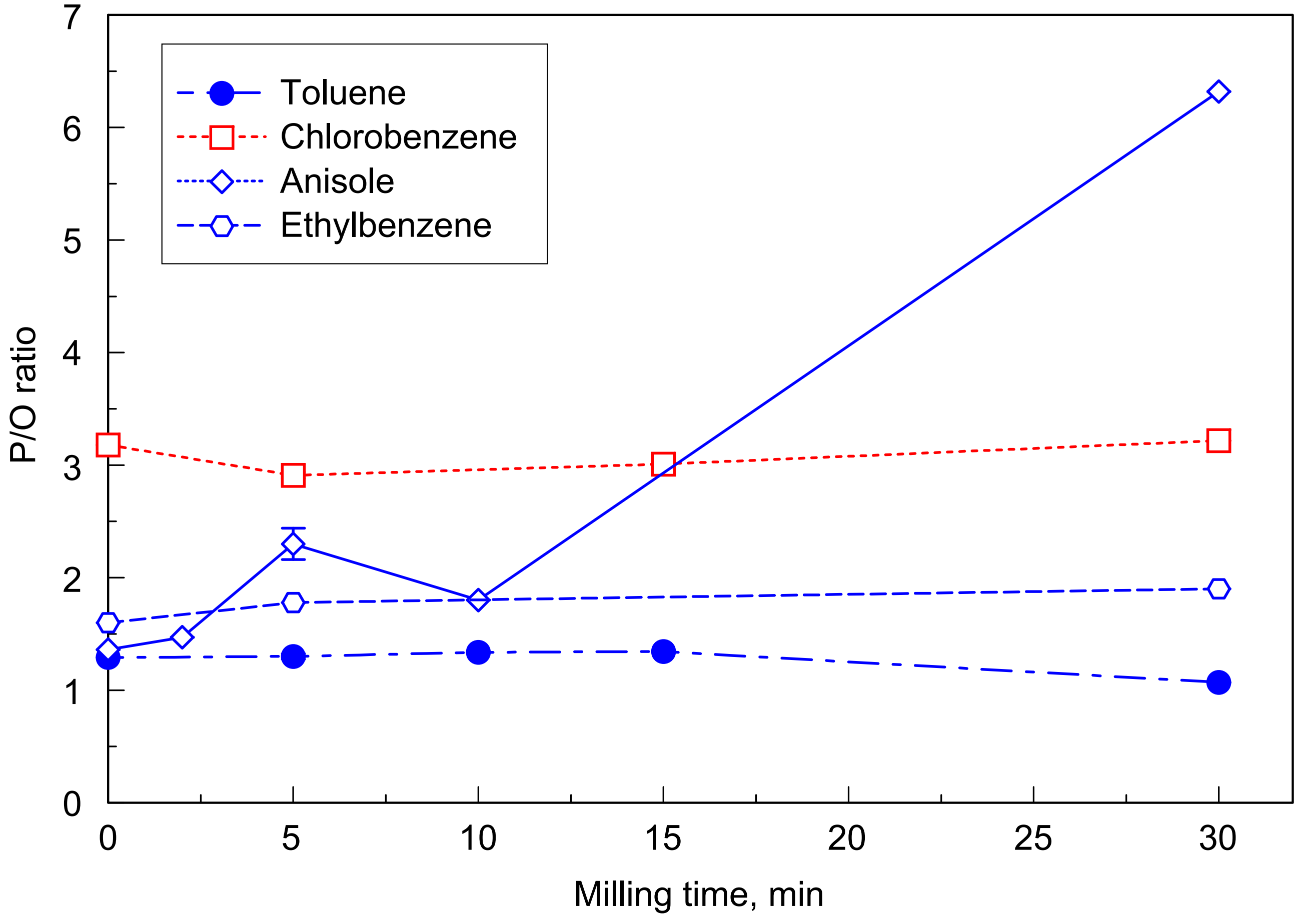
Reaction rate – substituent effects

- **High yield** of nitro products observed for most precursors **in short time**
- **Initial nitration rate** roughly scales with the **activation**
- Nitration **slows down in time** or even reversed for some precursors

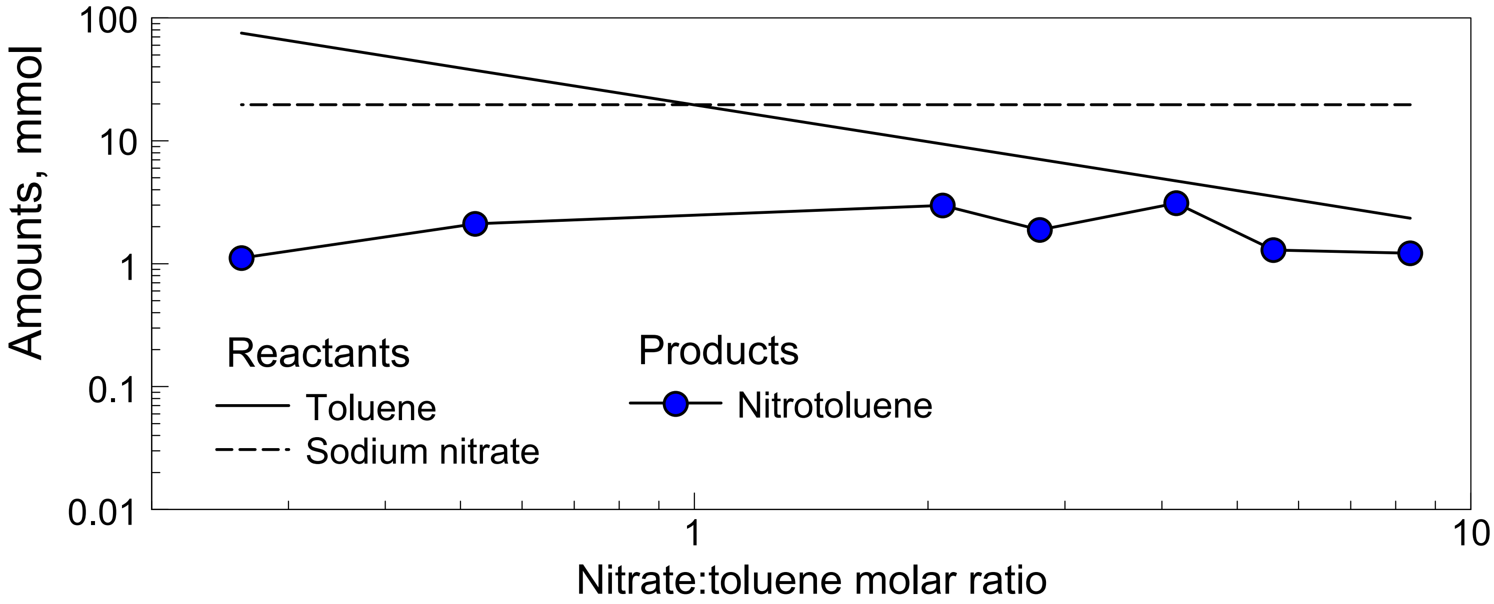


Regioselectivity changes with milling time

- ❑ High p/o ratio at 30 min for anisole is not associated with increased yield
  - may suggest selective decomposition of ortho isomer
- ❑ P/O ratios for other precursors consistent with literature
  - Reactions on surface of catalyst



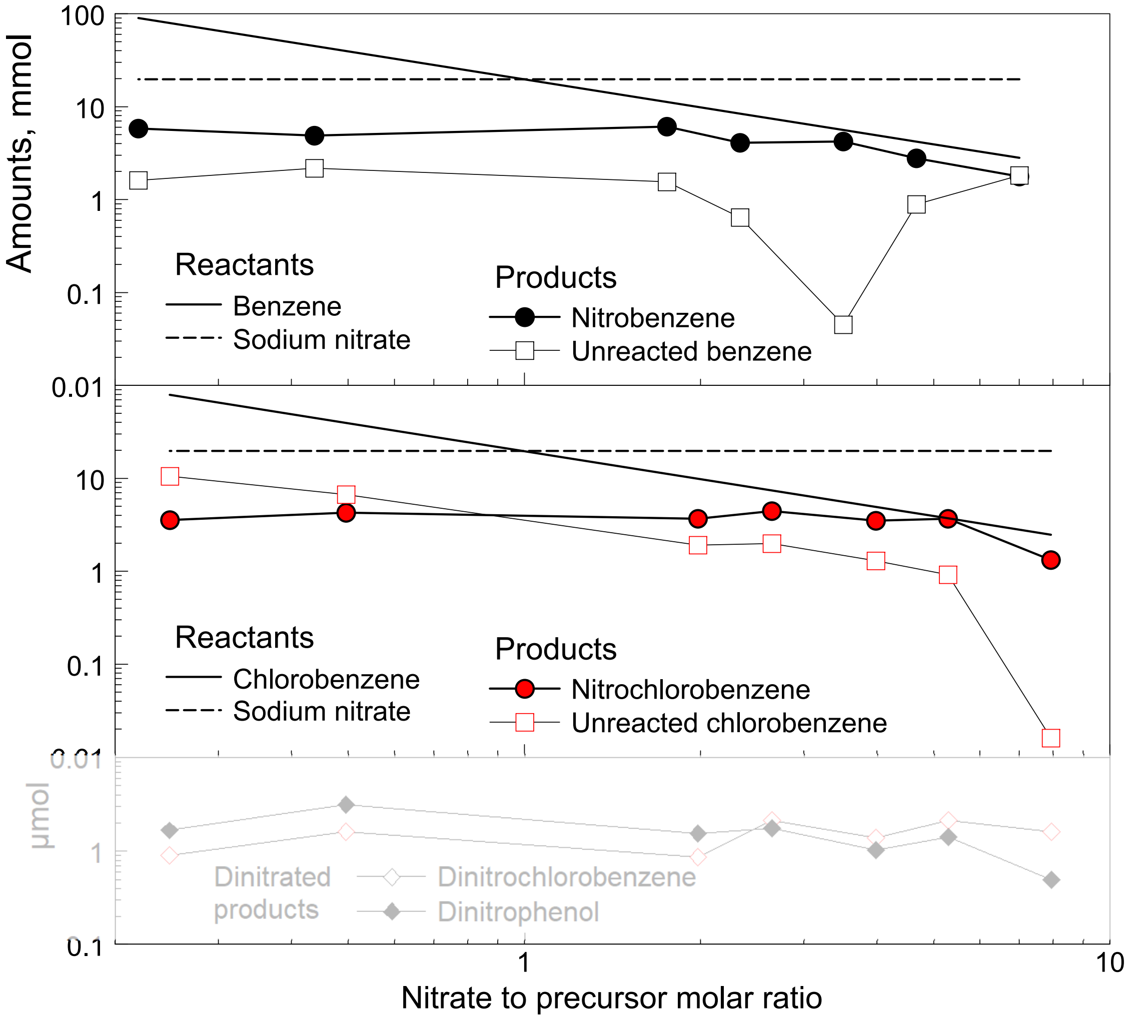
Yield vs. molar reactant ratio: toluene



- **Peak yield** observed near reactant **ratio of 4**
- **Toluene-limited** reactions show **highest yields**
- Excess of nitrate limits nitroproducts, possibly through blockage of active sites

Yield vs. mol. react. ratio: benzene, chlorobenzene

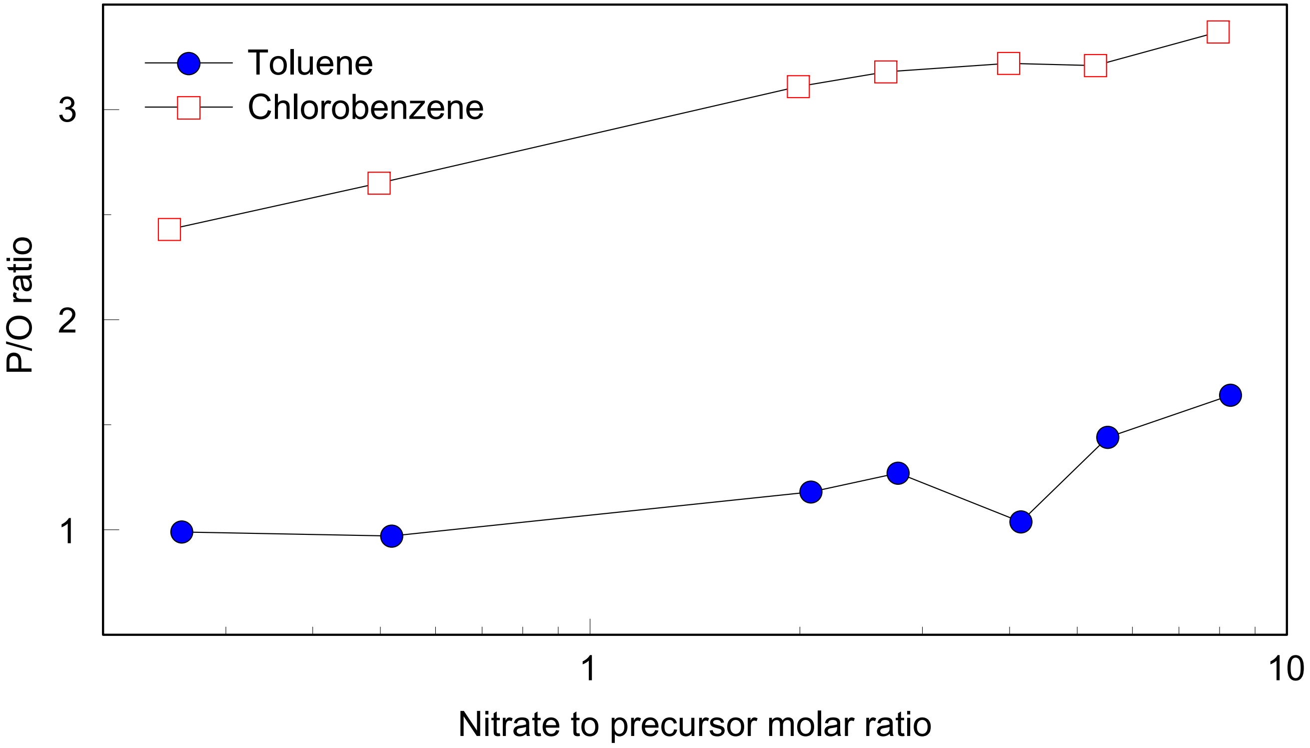
- ☐ Near **complete conversion** observed when reaction is **precursor-limited**
- ☐ Nitration attains **a plateau**, does not approach the limit when the reactants are **nitrate-limited**
- ☐ Small traces of **dinitrated products** formed with chlorobenzene
  - Also observed for other precursors



Regioselectivity

- ☐ Selectivity increases for both toluene and chlorobenzene when the reaction becomes **limited by** the available **precursor**

- ☐ Implication: reaction is favored when it occurs in a **thin layer of precursor on surface of the catalyst**



Which precursor properties *control* mechanochemical nitration?

- Model milling as a **simplified nitration reaction**

$$Precursor\ (P) \rightarrow Nitrated\ product\ (NP)$$

  - **1^{st} order reaction**:
    - $\frac{dC_P}{dt} = -k \cdot C_P \rightarrow\ k = -\ln\left(1 - \frac{C_{NP}}{C_{P,0}}\right) \cdot t^{-1}$
  - Test **correlation of rate constant, *k*, with precursor properties**
  - **Statistical approach,** i properties considered
  - Use **linear models**:
    - $ln(k) = ln(k_0) + \sum_i a_i \cdot \zeta_i$

    ζ_i: precursor properties, a_i: linear coefficients
  - Coefficients a_i determined using least-squares fitting

Properties

Reactant	Active group	Relative rate log k/k_H	Heats of formation		Viscosities		Density	Heat of vapor, reactant	Dipole moment	Steric factors		Proton affinity	Gas basicity	Ioniz. energy
			reactant	product	Kinematic	Dynamic				A-factor	Ligand Repulsive energies			
			kJ/mol	kJ/mol	mm^2/s	cP	g/mL	kJ/mol	Debye	kcal/mol	kcal/mol	kJ/mol	kJ/mol	eV
Nitro-toluene	NO_2	-3.72	-48.2	-66.4	solid	solid	1.1	74.8	1.35	1.10	18	815.2	782.7	9.46
Chloro-benzene	Cl	-0.66	11.5	-48.74	0.92	1.021	1.11	41	1.69	0.53	3.3	753.1	724.6	9.07
Benzene	H	0	49	12.5	0.647	0.567	0.876	33.9	0	0	0	750	725.4	9.24
Ethyl benzene	C_2H_5	0.90	27	-13.22	0.669	0.579	0.866	41	0.59	1.79	34	788	760.3	8.77
Toluene	CH_3	1.02	12	-48.2	0.62	0.538	0.867	37	0.332	1.74	17	784	756.3	8.83
p-Xylene	$(CH_3)_2$	2.04	-24.4	-5.62	0.93	0.800	0.86	42	0	3.48	34	812.1	766.8	8.44
Phenol	OH	2.22	-165	-207	solid	solid	1.07	69.7	1.224	0.60	10	817.3	786.3	8.49
Anisole	OCH_3	4.68	-120	-197	0.99	0.985	0.995	44	1.262	0.75	31	839.6	807.2	8.20

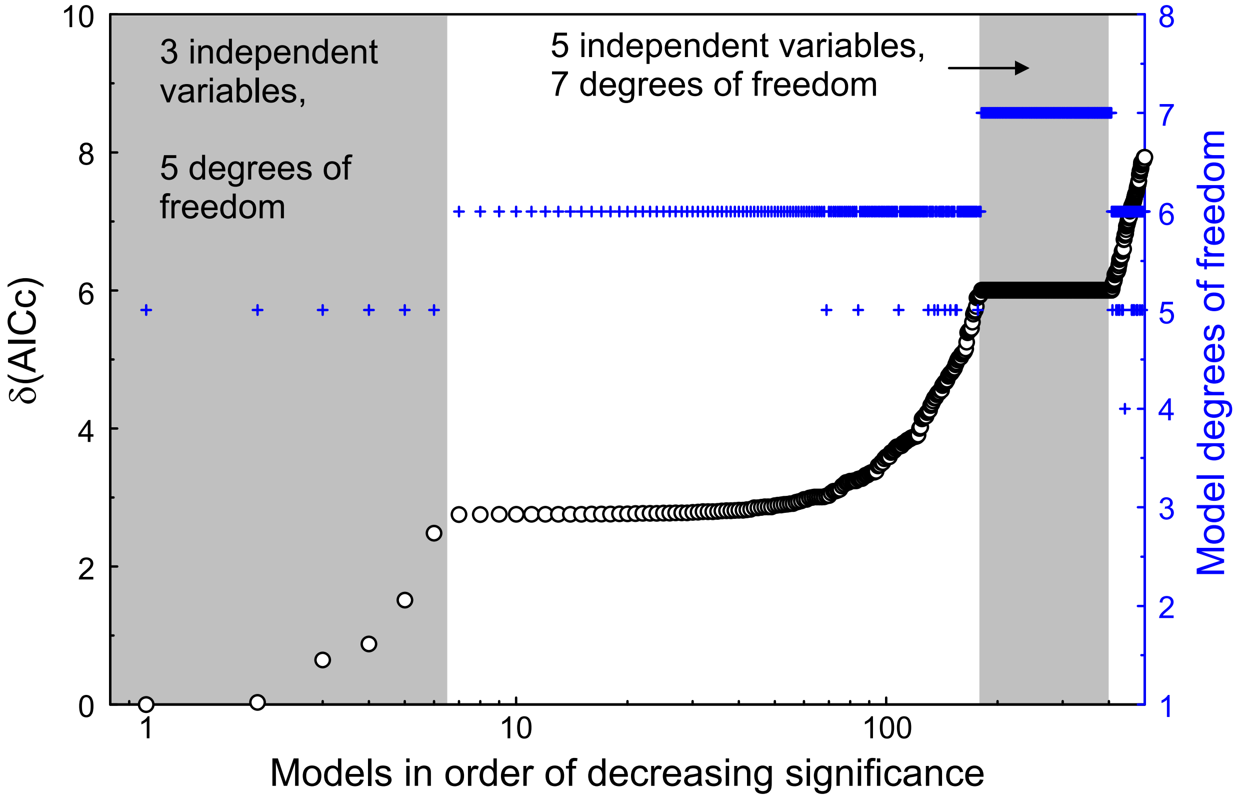
Data Analysis

- **13 solvent properties** considered
- experimental results for **6 different precursors**

→ set of equations is underdetermined

- selection:
  - fit at most 5 = (6-1) coefficients/solvent properties at a time
  - *do not* simultaneously fit coefficients/solvent properties that are *highly correlated*
    - gas basicity & proton affinity
    - kinematic & dynamic viscosity
    - different measures of steric hindrance
- <u>1120</u> parameter combinations remain
  - ranking of statistical significance using logarithmic likelihood of the model fit (highest is best), and the Akaike's information criterion [$\delta(AIC_c)$, lowest is most prudent = "best"]

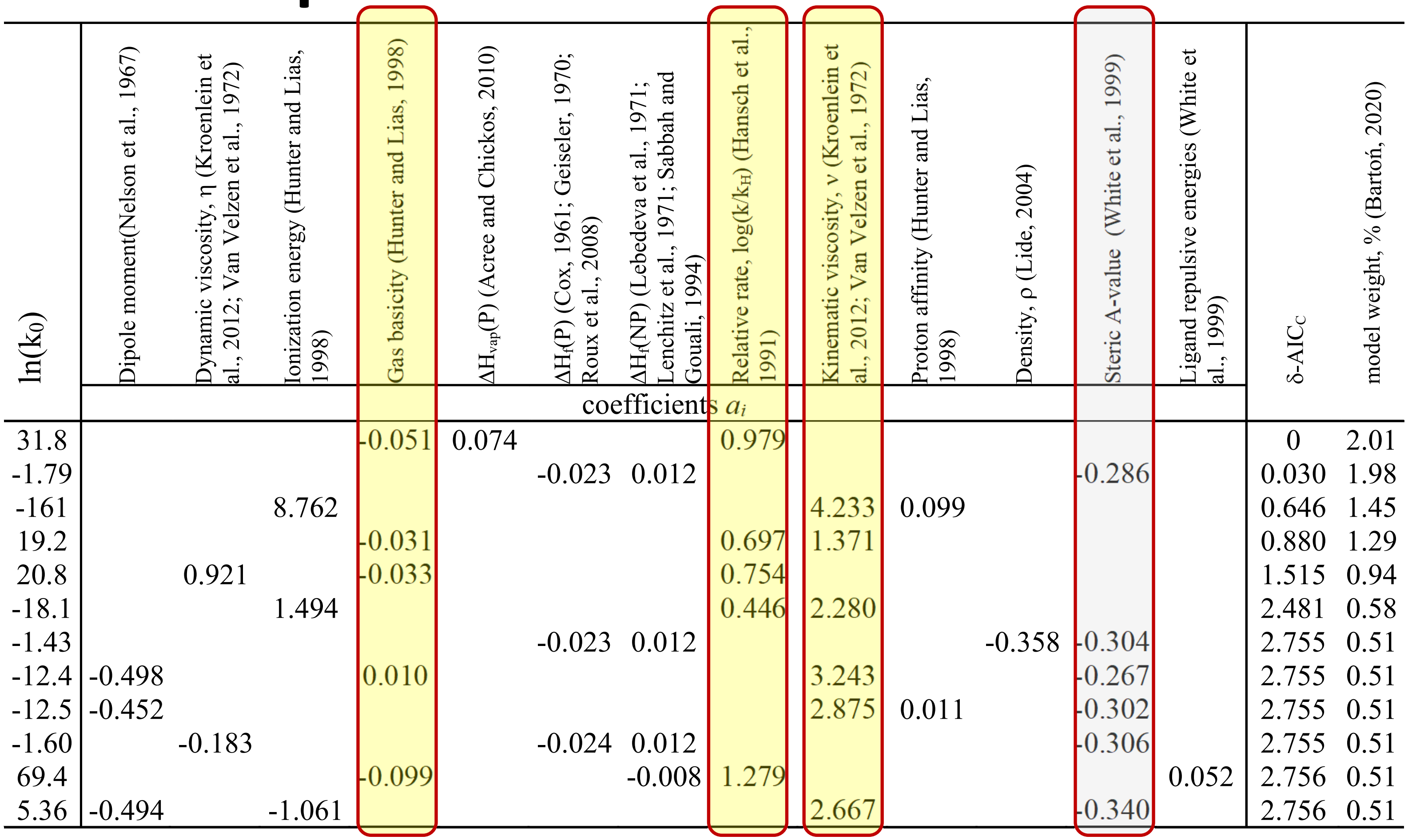
Ranking models



- Major differences in how models fit according to how many properties considered (3, 4, 5)

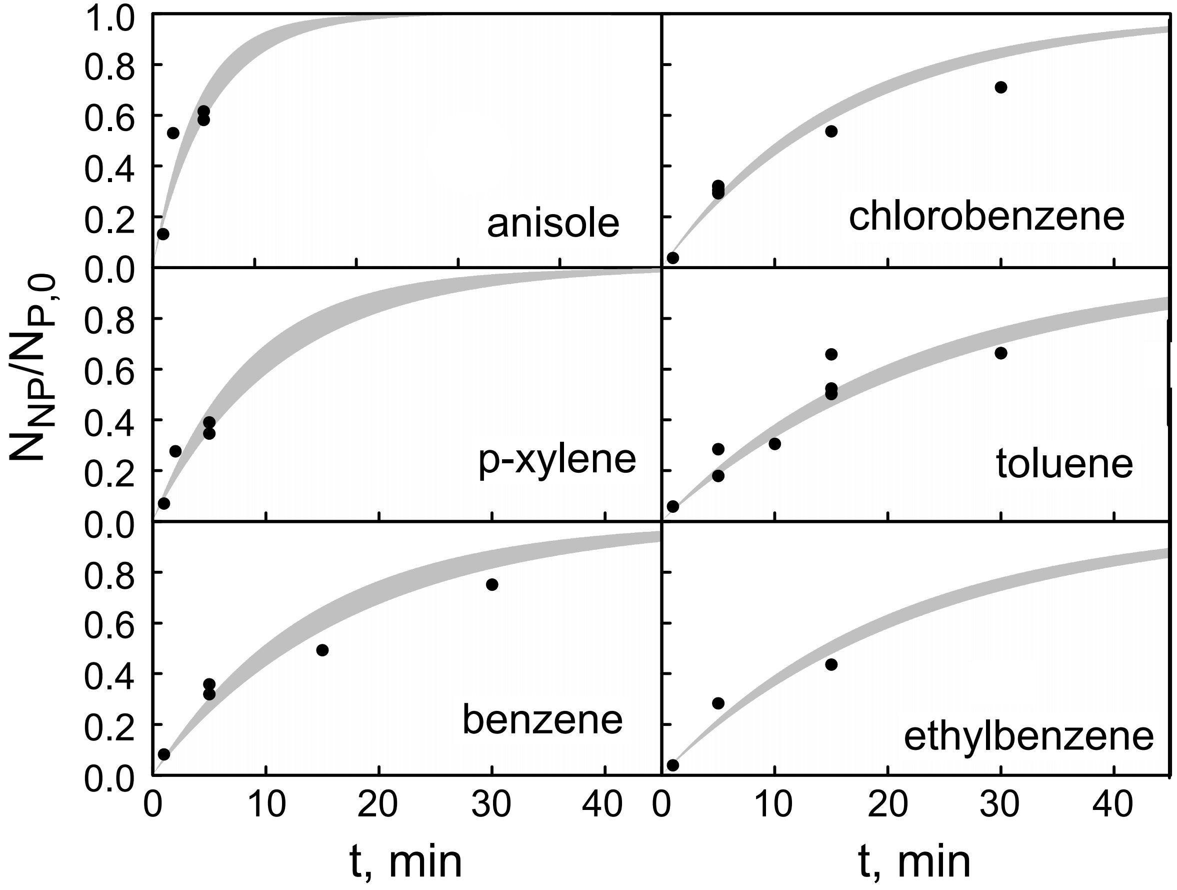
- Practically, **only first handful of models need to be considered**
    - differences between those are minor

Coefficients for top models



$\ln(k_0)$	Dipole moment(Nelson et al., 1967)	Dynamic viscosity, η (Kroenlein et al., 2012; Van Velzen et al., 1972)	Ionization energy (Hunter and Lias, 1998)	Gas basicity (Hunter and Lias, 1998)	$\Delta H_{vap}(P)$ (Acree and Chickos, 2010)	$\Delta H_f(P)$ (Cox, 1961; Geiseler, 1970; Roux et al., 2008)	$\Delta H_f(NP)$ (Lebedeva et al., 1971; Lenchitz et al., 1971; Sabbah and Gouali, 1994)	Relative rate, $\log(k/k_H)$ (Hansch et al., 1991)	Kinematic viscosity, ν (Kroenlein et al., 2012; Van Velzen et al., 1972)	Proton affinity (Hunter and Lias, 1998)	Density, ρ (Lide, 2004)	Steric A-value (White et al., 1999)	Ligand repulsive energies (White et al., 1999)	δ-AIC_C	model weight, % (Bartoń, 2020)
	coefficients a_i														
31.8				-0.051	0.074			0.979						0	2.01
-1.79						-0.023	0.012					-0.286		0.030	1.98
-161			8.762						4.233	0.099				0.646	1.45
19.2				-0.031				0.697	1.371					0.880	1.29
20.8		0.921		-0.033				0.754						1.515	0.94
-18.1			1.494					0.446	2.280					2.481	0.58
-1.43						-0.023	0.012				-0.358	-0.304		2.755	0.51
-12.4	-0.498			0.010					3.243			-0.267		2.755	0.51
-12.5	-0.452								2.875	0.011		-0.302		2.755	0.51
-1.60		-0.183				-0.024	0.012					-0.306		2.755	0.51
69.4				-0.099			-0.008	1.279					0.052	2.756	0.51
5.36	-0.494		-1.061						2.667			-0.340		2.756	0.51

Predictions by the top model vs. experiments



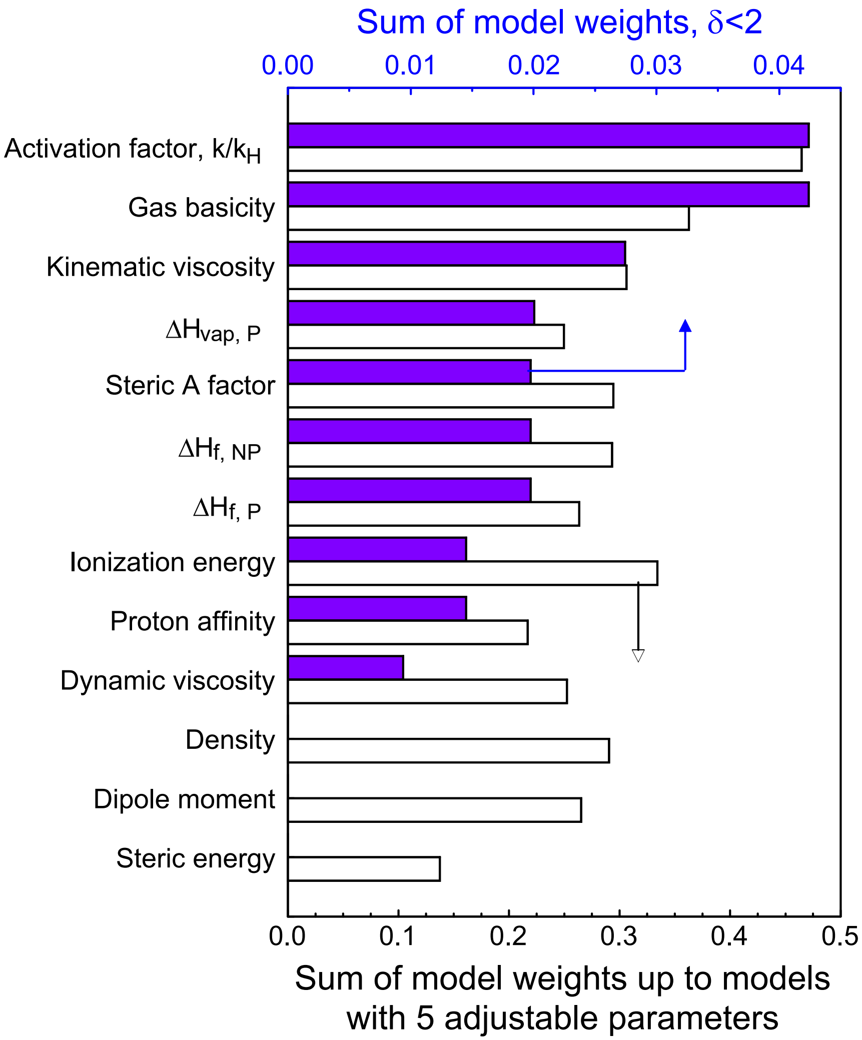
Yields of nitro-products are predicted reasonably well

Influential individual factors

- ❑ "Parameter Importance" calculated as *sum of model weights* of the individual parameters for <u>all models with $\delta_{AICc} \le 2$</u> (5 models)

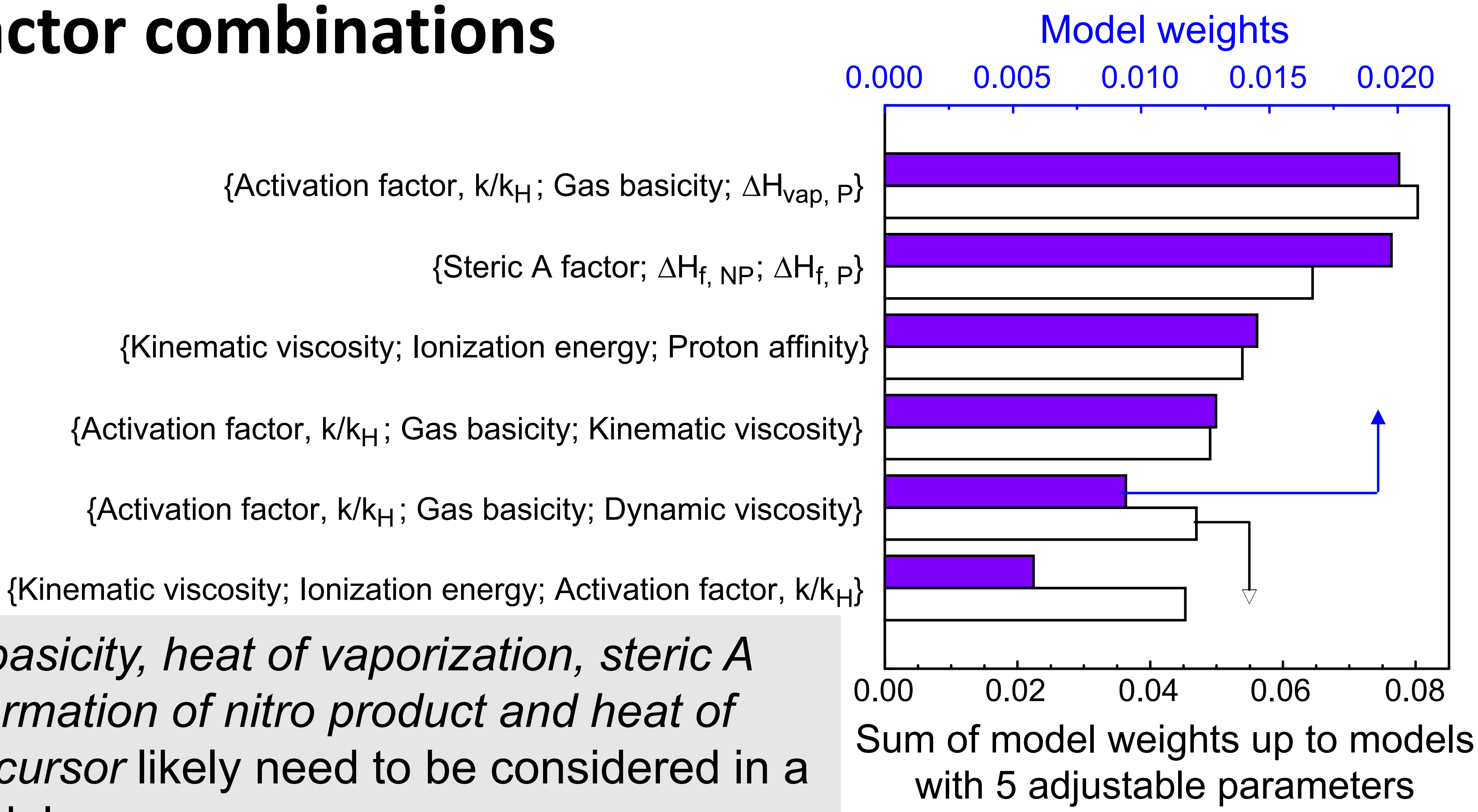
Importance for mechanochemical nitration:

- ❑ **Activation factor** has the strongest effect
- ❑ **Gas basicity, kinematic viscosity** are likely important
- ❑ Effects of density, dipole moment, steric energy on nitration rate are insignificant



Influential factor combinations

- ❑ **Groups** of factors identified in the best ranked models **rank the same as top models**
- ❑ *Activation, gas basicity, heat of vaporization, steric A factor, heat of formation of nitro product and heat of formation of precursor* likely need to be considered in a mechanistic model



Part 2. Summary

- ☐ Near complete **mechanochemical nitration achieved** with a broad **range of aromatic precursors** using MoO_3 as catalyst
  - Small amounts of **dinitrated products** observed in all cases when mononitrated products formed
- ☐ **Selectivity** observed is mostly consistent with earlier work using MoO_3 as catalyst; abnormally high selectivity is observed in certain experiments
- ☐ **Extended milling** may **reduce yield** of nitro products
- ☐ Processing experimental data suggests that mechanochemical nitration rate depends on **properties of aromatic precursor**: **activation**, **gas basicity** and **kinematic viscosity** are most influential
- ☐ Results of data processing indicate **potential avenues for process optimization**, e.g., by varying temperature of mechanochemical nitration

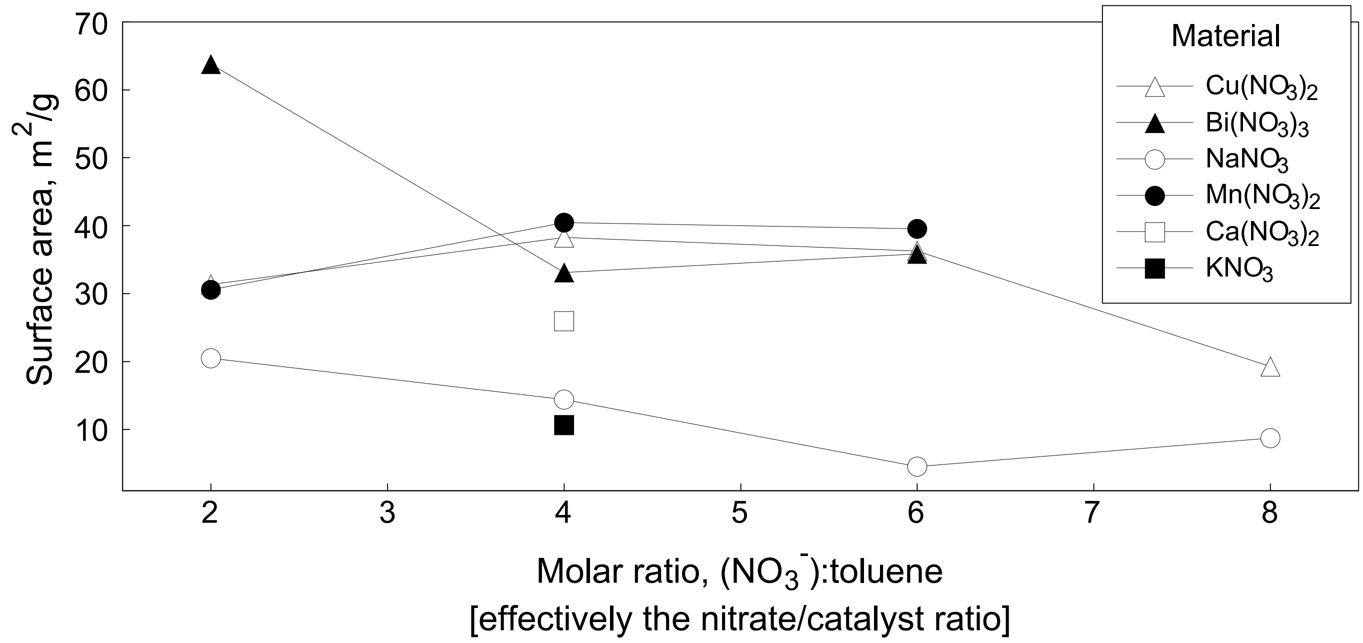
Part 3. Using different nitrate salts as nitronium sources

- Nitrates varied
  - different cation charge
  - different cation electronegativity
  - different hydration states
- Reactant ratio varied
  - expressed as (NO_3)/toluene
  - implies equiv. values of (NO_3)/catalyst
- Toluene precursor, constant amount
- MoO_3 oxide catalyst, constant amount

Nitrate	Mass in g for reactant ratio, (moles of NO_3^-)/(moles of C_7H_8)			
	2	4	6	8
NaNO_3	0.80	1.60	2.40	3.20
KNO_3	0.95	1.91	2.86	3.82
Ca$(NO_3)_2 \cdot 4H_2O$	1.11	2.22	3.33	4.44
Cu$(NO_3)_2 \cdot 2.5H_2O$	1.30	2.60	3.90	5.20
Bi$(NO_3)_3 \cdot 5H_2O$	1.52	3.04	4.58	6.16
Mn$(NO_3)_2 \cdot 6H_2O$	1.18	2.36	3.54	4.72

Effect of nitrate on premilling step

- Gradual changes only
- Anhydrous (Na, K) nitrates show opposite trend compared to hydrated nitrates (Cu, Bi, Mn, Ca)

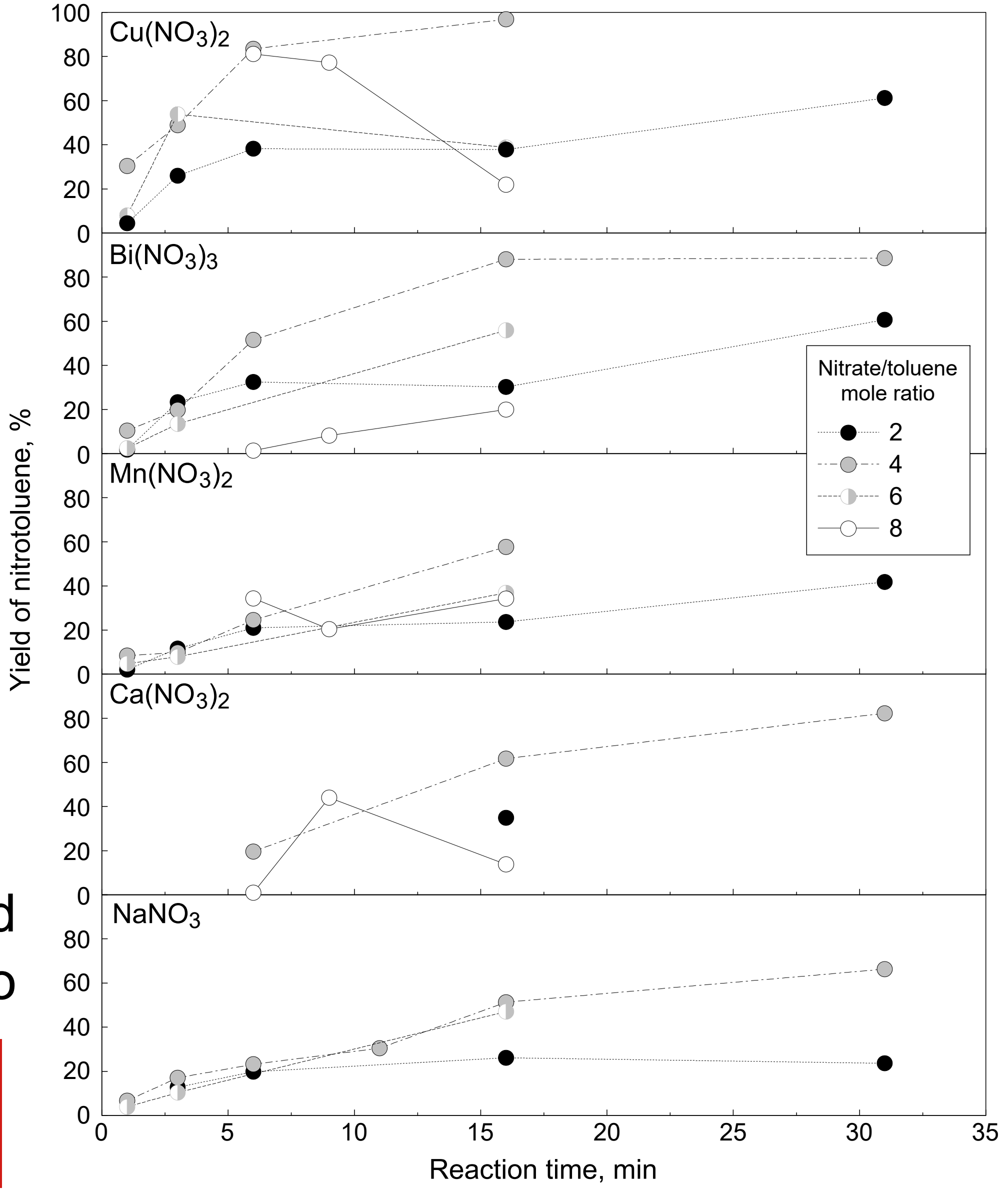


Specific surface areas of MoO_3 catalyst after premilling with different nitrates for 120 min

Effect of nitrate on mechanochemical nitration

Reaction time trends

- Increase for all, as expected
- Rates different for different nitrates
- Reactant ratio shows inconsistent trends

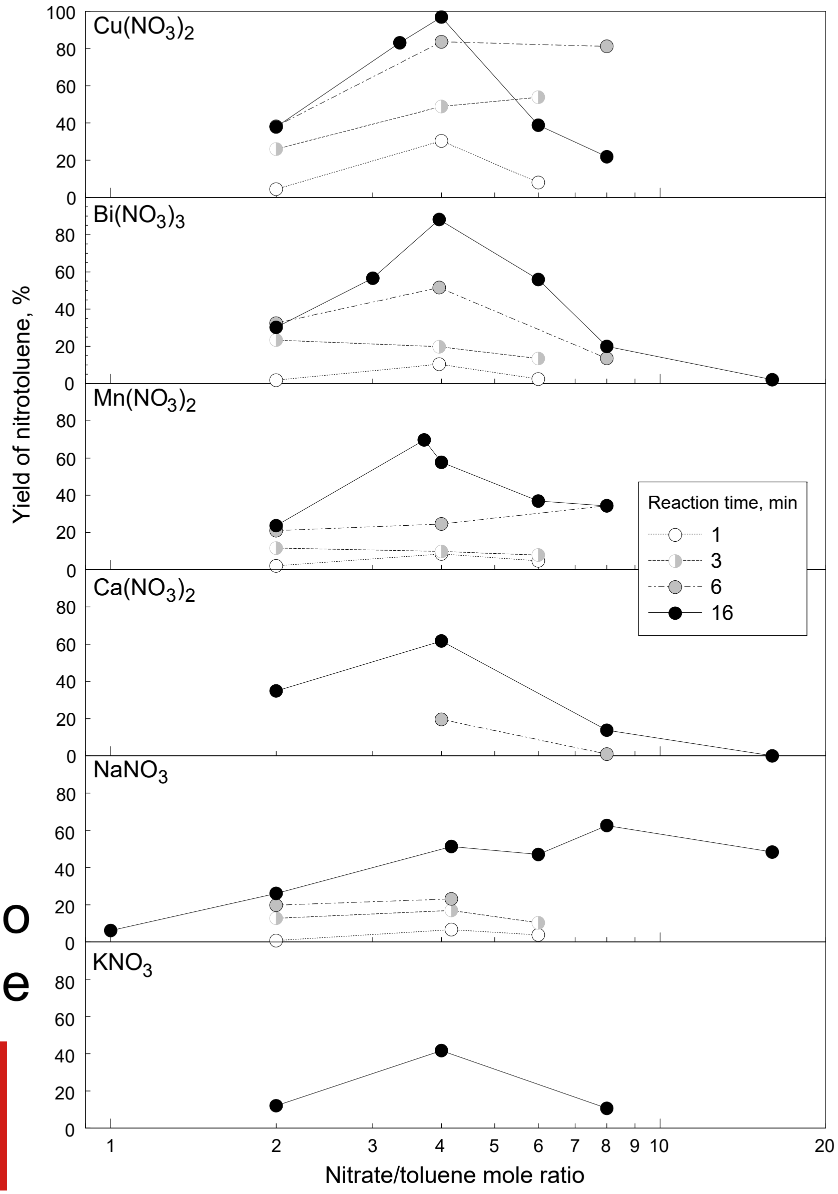


MNT yield vs. time, grouped by nitrate and reactant ratio

Effect of nitrate on mechanochemical nitration

Reactant ratio trends

- Highest yield observed for molar reactant ratio of (NO_3)/toluene = 4
  - ❑ Except for $NaNO_3$



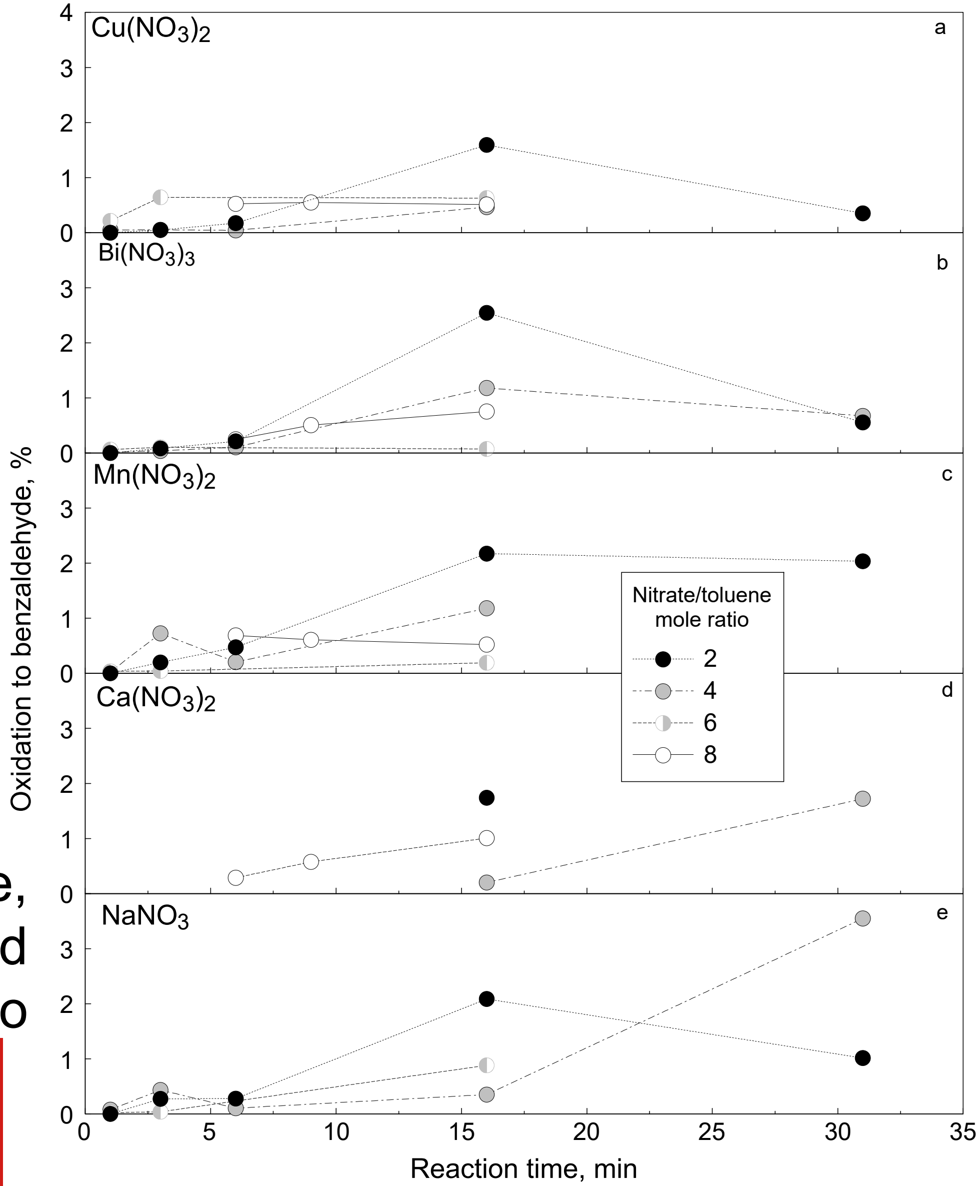
MNT yield vs. reactant ratio grouped by nitrate and time

Oxidation byproduct: benzaldehyde

Reaction time trends

- Amount of oxidation byproducts, spec. benzaldehyde generally increases with increasing reactant ratios

- Nitrates are oxidizers

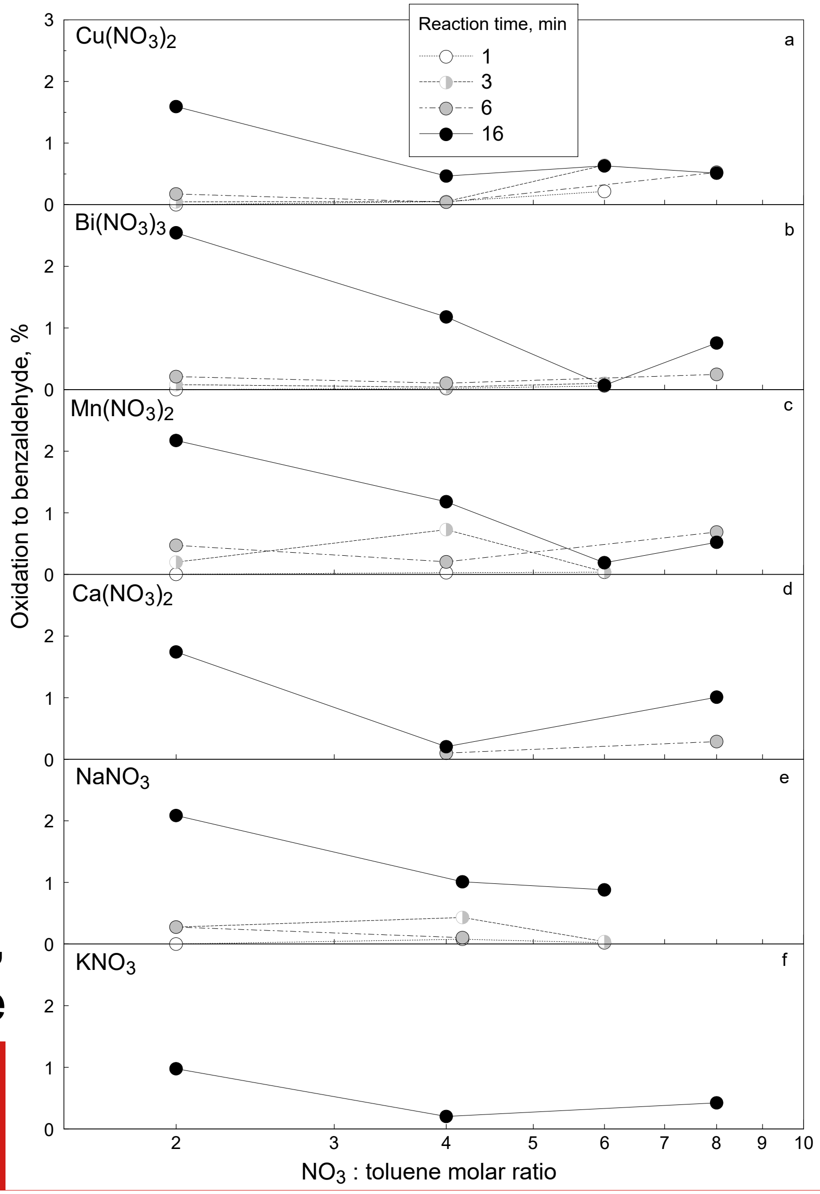


Benzaldehyde vs. time, grouped by nitrate and reactant ratio

Oxidation byproduct: benzaldehyde

Reactant ratio trends

- No comparable highest formation rate observed at reactant ratio of 4
  - Benzaldehyde formation does not correlate with nitration

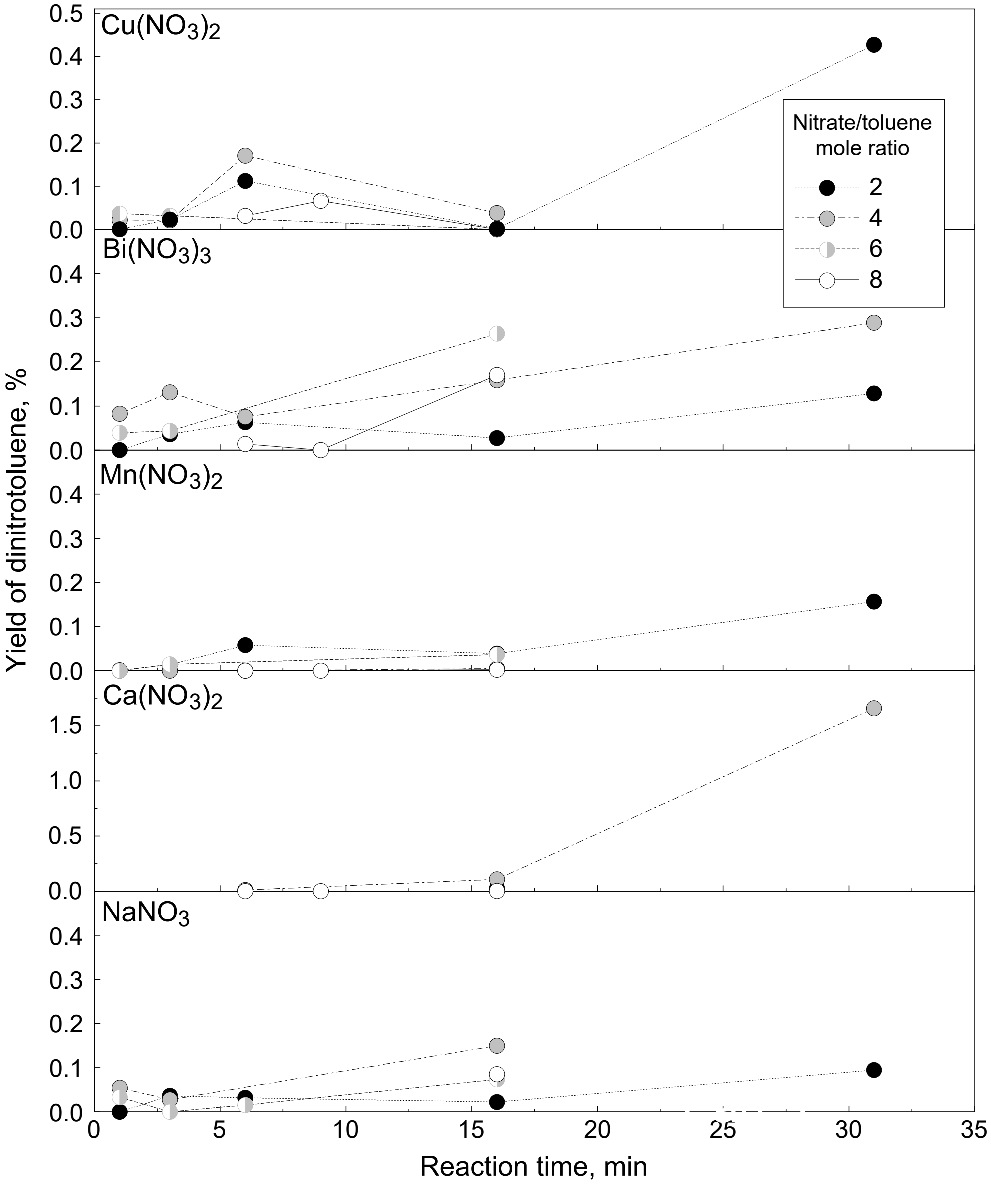


Benzaldehyde vs. reactant ratio, grouped by nitrate and time

Double nitration

Reaction time trends

- Higher nitrate amounts also result in formation of dinitrotoluene (DNT)
- Amounts low, but well detectable



DNT yield vs. time, grouped by nitrate and reactant ratio

New Jersey Institute of Technology

Which nitrate property governs nitration rate?

- Attempts to correlate rates with cation properties showed no trends
  - ☐ electronegativity
  - ☐ charge
  - ☐ hydration state of the nitrate salt

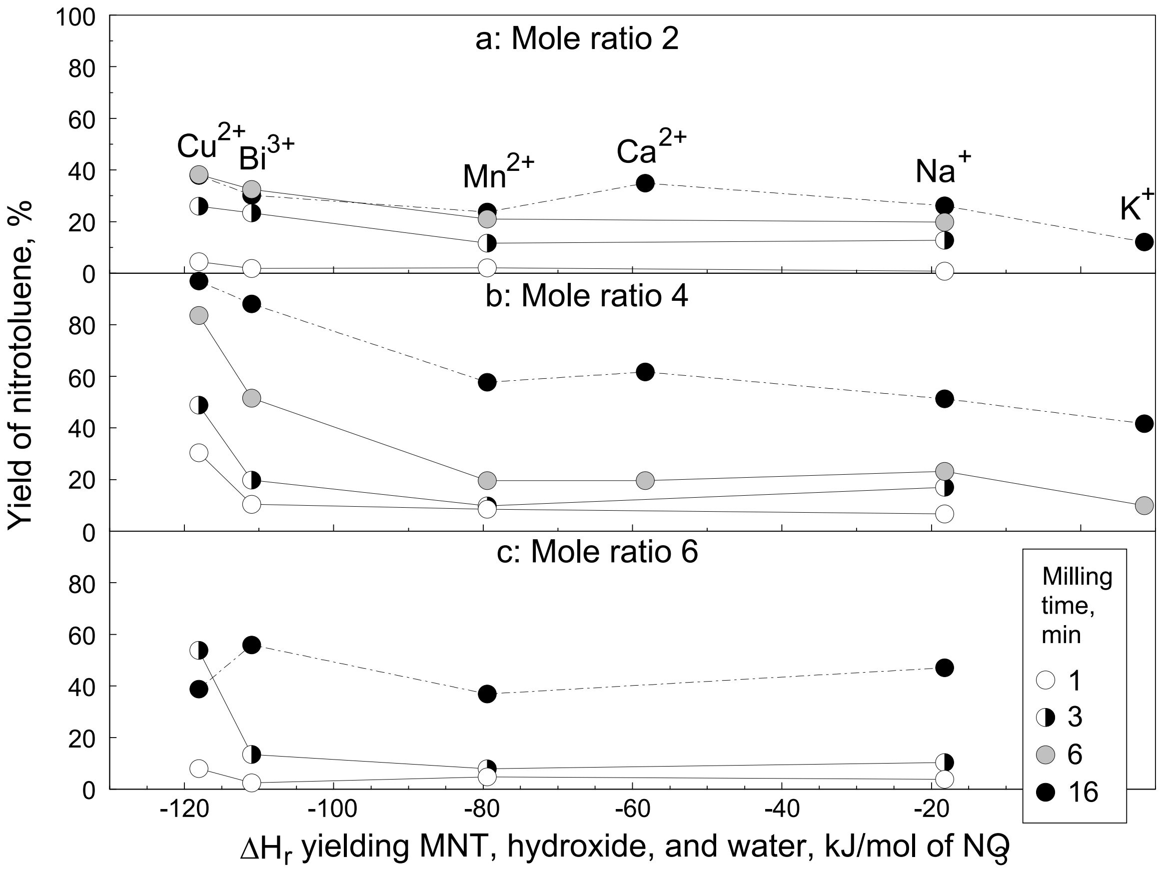
Consider energy of **global reactions**:

- Reactions leading to corresponding **hydroxides** (instead of oxides)

Global reaction	ΔH_r, kJ/mol of NO_3^-
$KNO_3 + C_7H_8 \rightarrow KOH + C_7H_7NO_2$	8.5
$NaNO_3 + C_7H_8 \rightarrow NaOH + C_7H_7NO_2$	-18.23
$Ca(NO_3)_2 \cdot 4H_2O + 2C_7H_8 \rightarrow Ca(OH)_2 + 2C_7H_7NO_2 + 4H_2O$	-58.31
$Bi(NO_3)_3 \cdot 5H_2O + 3C_7H_8 \rightarrow Bi(OH)_3 + 3C_7H_7NO_2 + 5H_2O$	-110.99
$2Cu(NO_3)_2 \cdot 5H_2O + 4C_7H_8 \rightarrow 2Cu(OH)_2 + 4C_7H_7NO_2 + 5H_2O$	-118.06

Yield vs. energy of global nitration reaction

- Correlations observed
- Particularly consistently, for reactant ratio 4



Reaction rate constant vs. energy of global nitration reaction

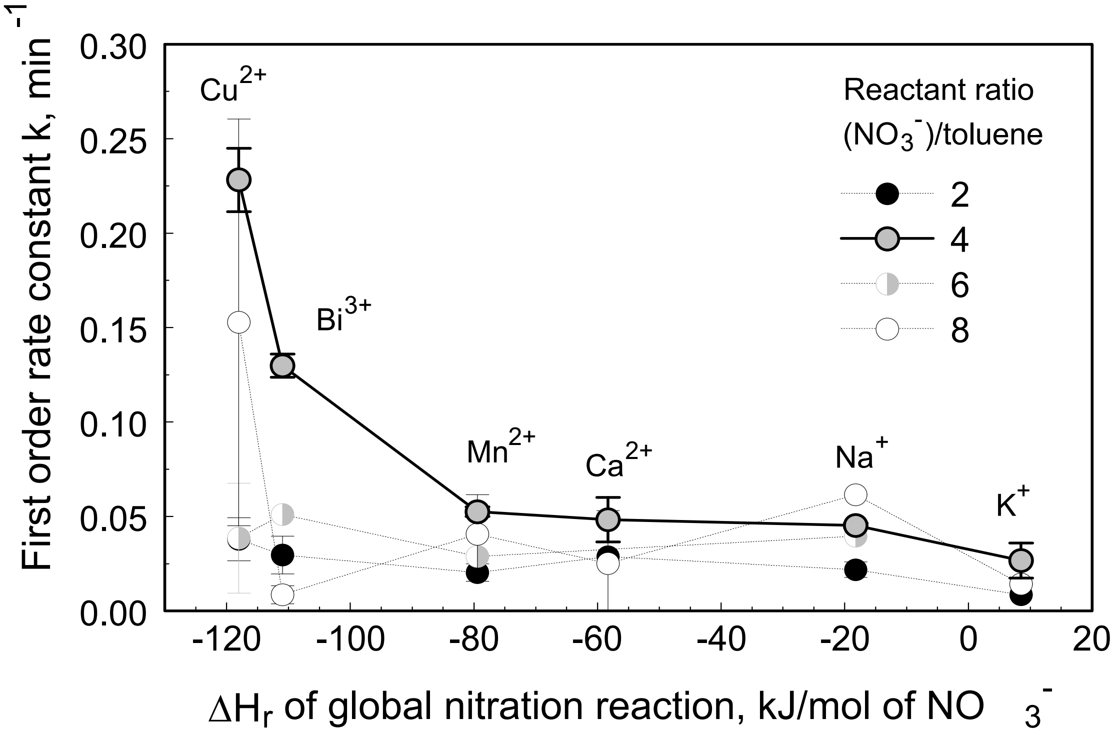
Model milling as simplified nitration reaction

$$Precursor\ (P) \rightarrow Nitrated\ product\ (NP)$$

1st order reaction:

$$\frac{dC_P}{dt} = -k \cdot C_P \rightarrow\ k = -\ln\left(1 - \frac{C_{NP}}{C_{P,0}}\right) \cdot t^{-1}$$

- Correlate rate constant, *k*, with reaction enhalpies



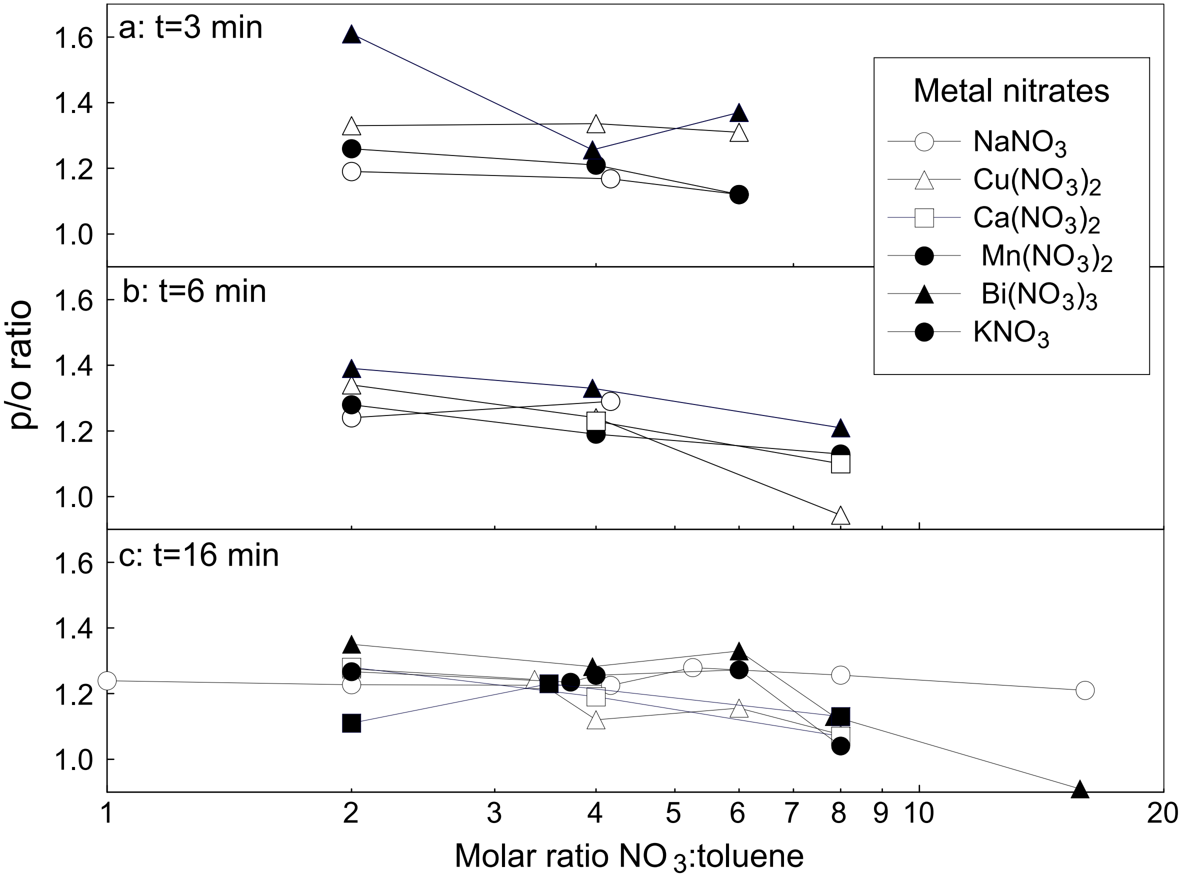
Consistent correlation for reactant ratio 4

Regioselectivity

- *para/ortho* MNT isomer ratios consistently **decrease** with increasing (NO_3)/toluene reactant ratios

- No distinct dependence on type of the nitrate, or milling time

- This is an **opposite trend** from earlier observations where p/o ratio increased w/ increasing reaction ratio

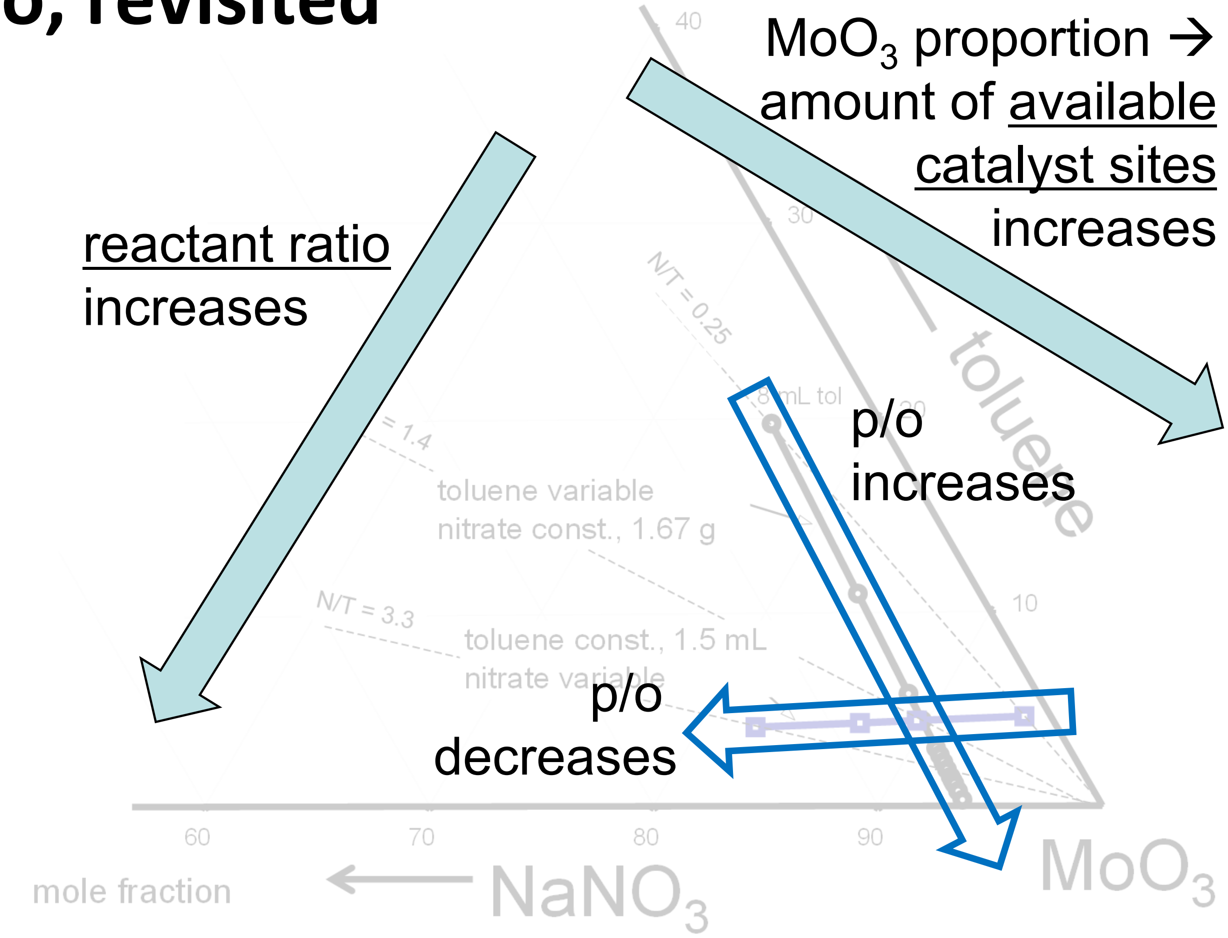


Varying the reactant ratio, revisited

- Experimental series keeping one reactant constant:
  - nitrate variable (precursor const.)
  - precursor variable (nitrate const.)

- This implies changes in the proportion of catalyst in either case

- p/o ratio is determined by available cat. surface



<u>reactant ratio</u> increases

MoO_3 proportion → amount of <u>available catalyst sites</u> increases

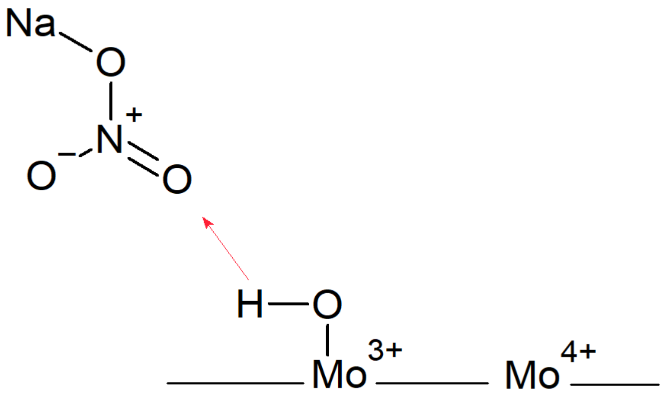
p/o increases

p/o decreases

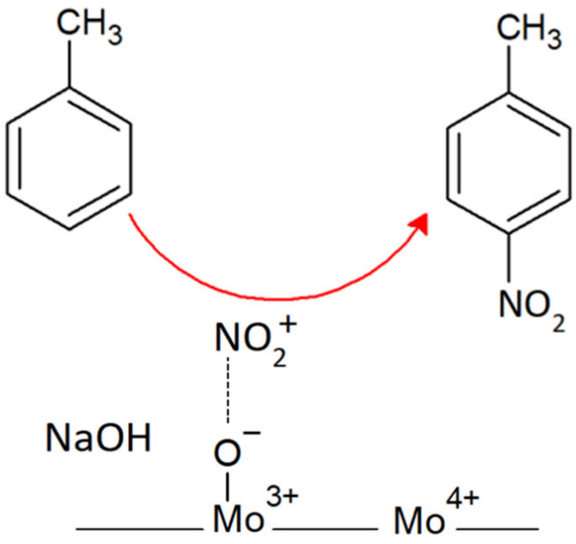
Reaction mechanism

Toluene is nitrated reacting with nitronium complexes

- attached to catalyst surface acid sites
- in the bulk fluid, away from these sites



Step 1: Sodium nitrate forms nitronium complexes on acid sites

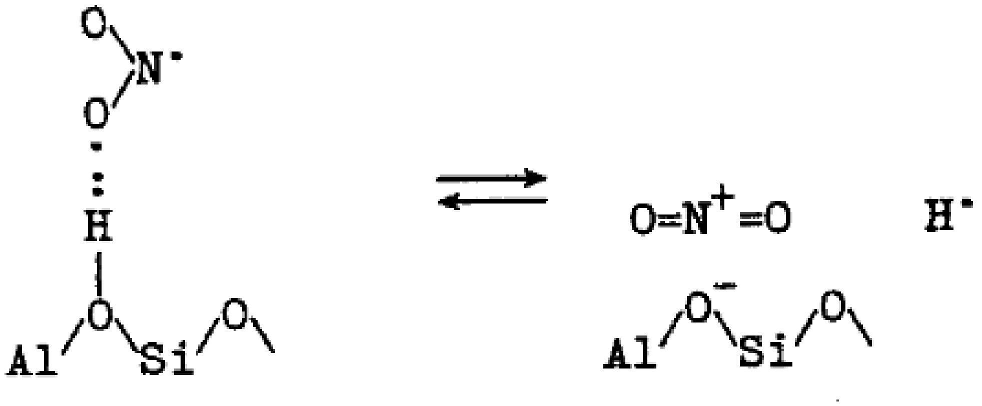


Step 2: aromatic substitution reaction

Reaction mechanism

- NO_2, nitronium, can exist
  - at the catalyst surface, or
  - in the fluid

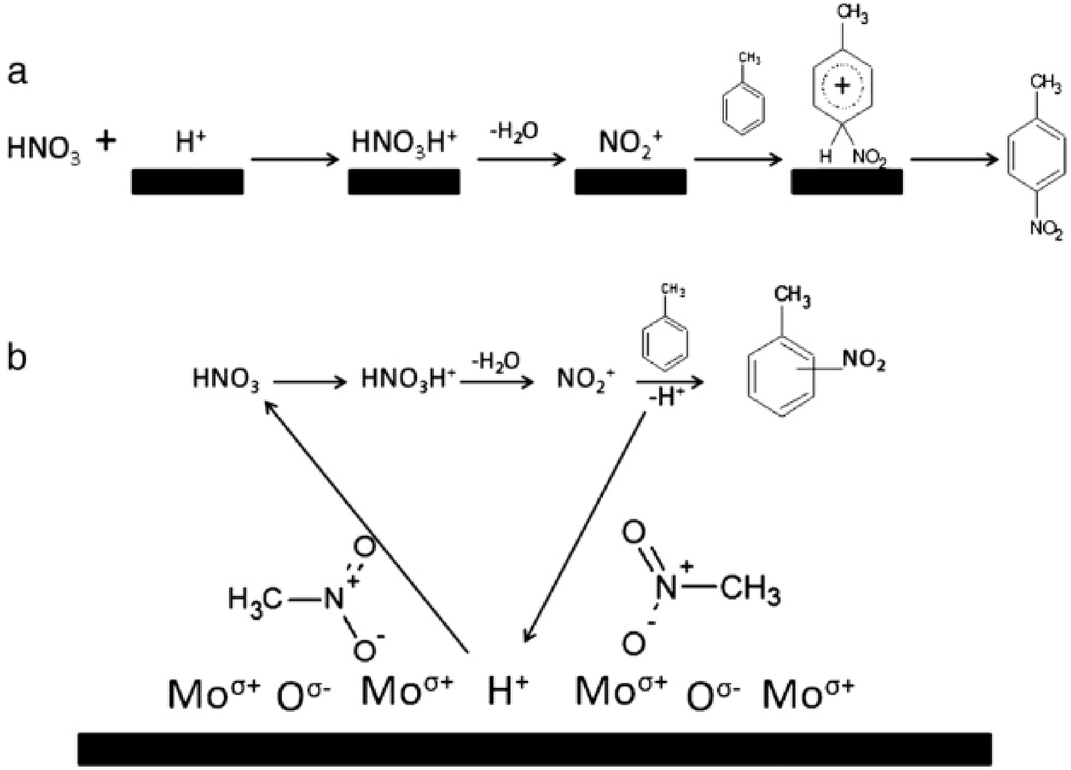
demonstrated in literature for other oxide surfaces



V. MALYSHEVA LUDMILA, A. PAUKSHTIS EUGENE & G. IONE KAZIMIRA (1995) Nitration of Aromatics by Nitrogen Oxides on Zeolite Catalysts: Comparison of Reaction in the Gas Phase and Solutions, Catalysis Reviews, 37:2, 179-226

Reaction mechanism

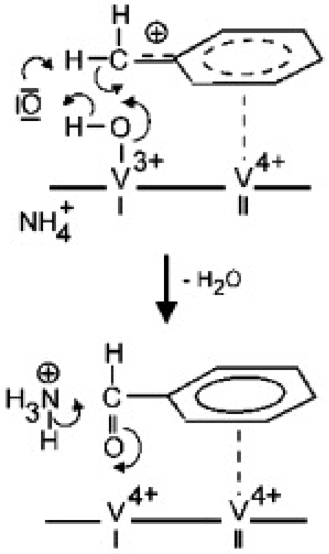
- Reaction at the catalyst surface preferentially produces the para isomer
- Reaction in the bulk fluid does not show this preference
- Increased p/o ratio indicates more reaction occurring at the catalyst surface



Joanna Adamiak, Waldemar Tomaszewski, Wincenty Skupiński, Interaction of nitromethane with MoO_3/SiO_2 and its influence on toluene nitration, Catalysis Communications, Volume 29, 2012, Pages 92-95

Reaction mechanism and oxidized byproducts

- Oxidation of aromatics on catalyst surface described in literature
- May necessitate multiple surface sites
- Consistent with observation that benzaldehyde amount decreases when higher amounts of nitrates block more and more catalyst surface sites (cf. slide 41)



Angelika Brückner (2003) Looking on Heterogeneous Catalytic Systems from Different Perspectives: Multitechnique Approaches as a New Challenge for In Situ Studies, Catalysis Reviews, 45:1, 97-150

Part 3. Summary

- Nitronium source appears to affect nitration only via energy of global reaction
- Optimum reaction rate consistently observed for (NO_3)/precursor molar ratio of 4
- Isomer ratios can be controlled by choice of reactant ratios

Project Summary

- Mechanochemical nitration of organic precursors requires solid catalysts with **high acidity and both, Bronsted and Lewis sites**
  - **MoO_3** was the **preferred catalyst**
- Nearly *complete mechanochemical nitration* was achieved in many experiments
- *Homogenizing catalyst* with nitrate by premilling *accelerates* ensuing *mechanochemical nitration*
- **Mechanochemical nitration** with MoO_3 catalyst was successful for **multiple aromatic compounds**
- The **selectivity was enhanced** and the **yield** of the nitroproduct was **increased** when the **volume of the aromatic precursor was reduced** while the mass of metal oxide catalyst was fixed
  - *The reaction preferably involves nitronium complexes attached on the catalyst surface*
- Reaction depends on the *aromatic activation by the functional group, gas basicity and enthalpy of vaporization of the aromatic precursor*. Additional effect by reaction enthalpies and kinematic viscosity
- The **highest mechanochemical nitration rate observed for $Cu(NO_3)_2$** serving as the source of nitronium.
- The **yield** of MNT as well as the **reaction rate** *correlated* with the **enthalpy of the global nitration reaction** with the corresponding metal hydroxide as a product
- A **second nitration** of the aromatic ring was observed for all the precursors used

Future work

- A path is outlined to further scale-up and optimization of mechanochemical nitration of organic compounds.
- First practical goal: mechanochemical **synthesis of single-nitrated products of aromatic precursors**
  - Use identified relationships between the process parameters, materials, and yield and reaction rate for the nitroproducts
- Challenges:
  - determine conditions necessary to **transfer the reaction parameters** for the **attritor** mill configuration
  - develop methods for **in-situ separation of the reaction products** from the milling tools and catalyst
- Other research:
  - Reusing or recycling the catalyst
  - A detailed mechanism of mechanochemical nitration

Supplement: ARL Effort

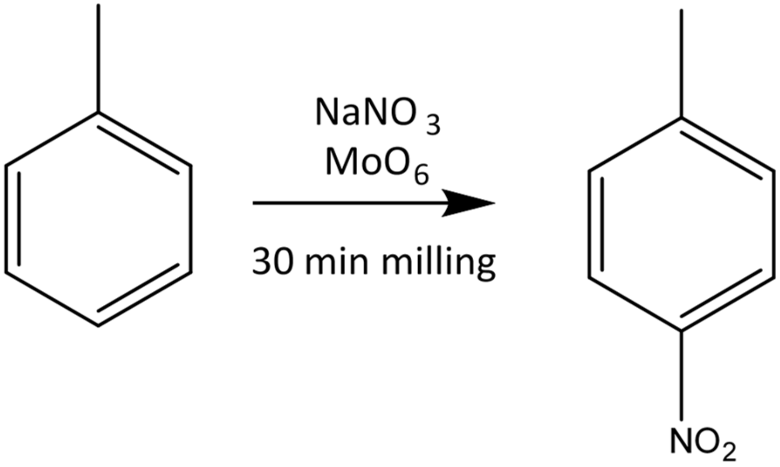
Leah Winhard, PI (WMRD, ARL)

Melissa Garner (ARL Summer student)

ARL's contribution focused on the evaluation of the mechanochemical nitration technique developed by NJIT as viable nitration technique for a range of substrates of interest

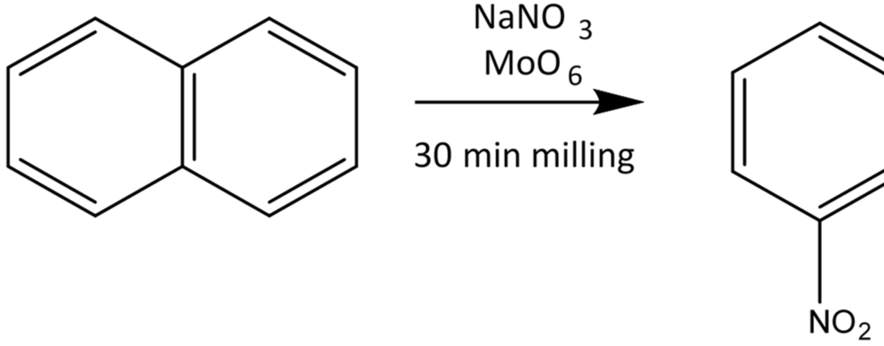
- SOP approved
- Process applied to both commercially available substrates and non-energetic precursors designed and synthesized at ARL

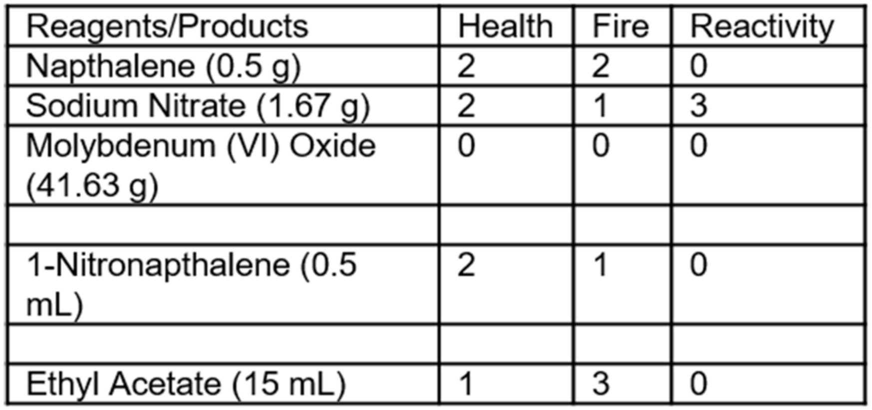
Reaction using toluene as a substrate



Reagents/Products	Health	Fire	Reactivity
Toluene (0.5 mL)	2	3	0
Sodium Nitrate (1.67 g)	2	1	3
Molybdenum (VI) Oxide (41.63 g)	0	0	0
Nitrotoluene (0.5 mL)	2	1	0
Ethyl Acetate (15 mL)	1	3	0

Reaction using naphthalene as a substrate





Reagents/Products	Health	Fire	Reactivity
Napthalene (0.5 g)	2	2	0
Sodium Nitrate (1.67 g)	2	1	3
Molybdenum (VI) Oxide (41.63 g)	0	0	0
1-Nitronapthalene (0.5 mL)	2	1	0
Ethyl Acetate (15 mL)	1	3	0

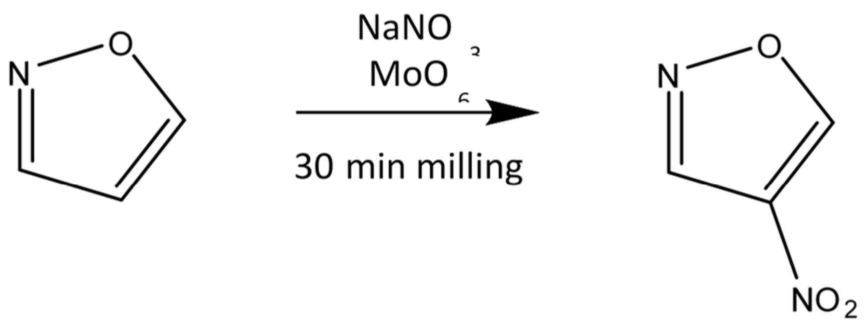
Additional substrates

Milling was also tested with the following list of commercially available substrates:

☐ Isoxazole
☐ 1,2-Benzisoxazole
☐ Maleimide
☐ Pyrazole
☐ Pyrrole

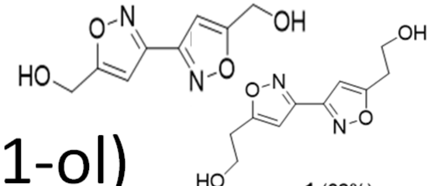
- All reaction mixtures showed some production of nitrated products via IR.
- NMR analysis revealed low yields (<20%) of nitrated products along with unreacted substrate and decomposition products
- For pyrazole substrate, a highly hygroscopic product was formed, and decomposed too rapidly for accurate analysis

Reaction using isoxazole as a substrate



Reagents/Products	Health	Fire	Reactivity
Isoxazole (0.5 g)	0	3	0
Sodium Nitrate (1.67 g)	2	1	3
Molybdenum (VI) Oxide (41.63 g)	0	0	0
Product	?	?	?
Ethyl Acetate (15 mL)	1	3	0

ARL-designed precursors



1 (62%)

- 5,5’-Dihydroxymethyl-3,3’-bis-isoxazole
- 2,2’-([3,3’-biisoxazole]-5,5’-diyl)bis(Ethan-1-ol)
  - Both readily form their respective nitrate ester energetic compounds in high yields (>90%) through traditional wet nitration chemistry.
  - The nitrated compounds are relatively insensitive to impact and friction, concern with milling nitrate esters prompted using very small amounts of precursor (100 mg or less) in the milling process.
- Analysis showed some degree of nitration, yield was low
  - NJIT comment: milling conditions were not optimized, e.g., no premilling catalyst with nitrate was used