

Effect of metal nitrate on mechanochemical nitration of toluene

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Supplement

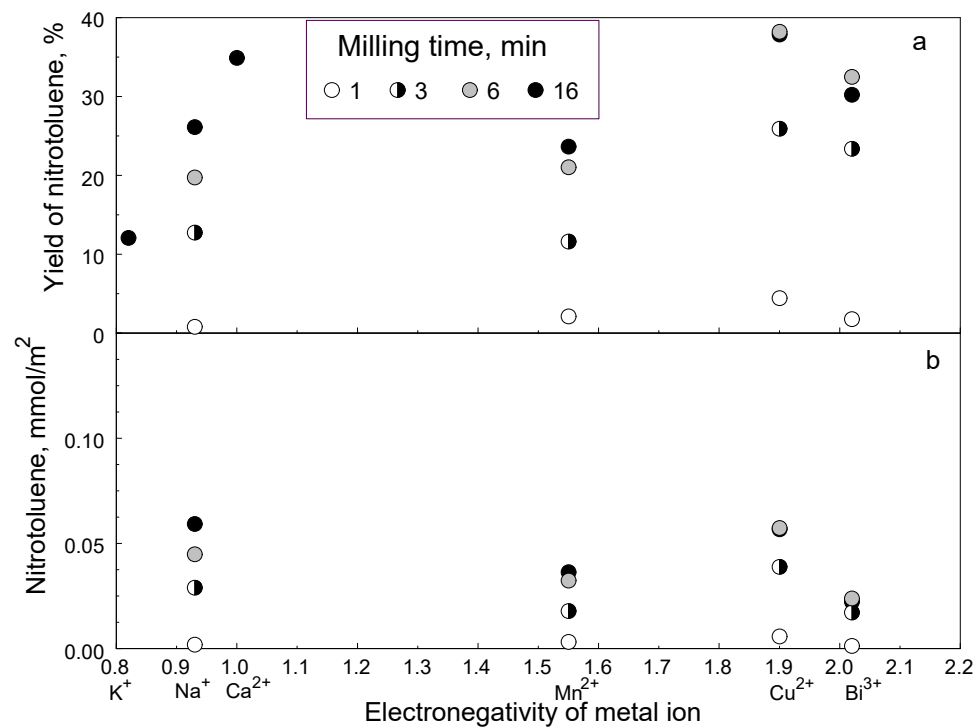


Figure S1. Effect of electronegativity on production of MNT for reactant ratio 2: a) Yield of MNT for various reaction times; b) MNT generated per surface area for various reaction times.

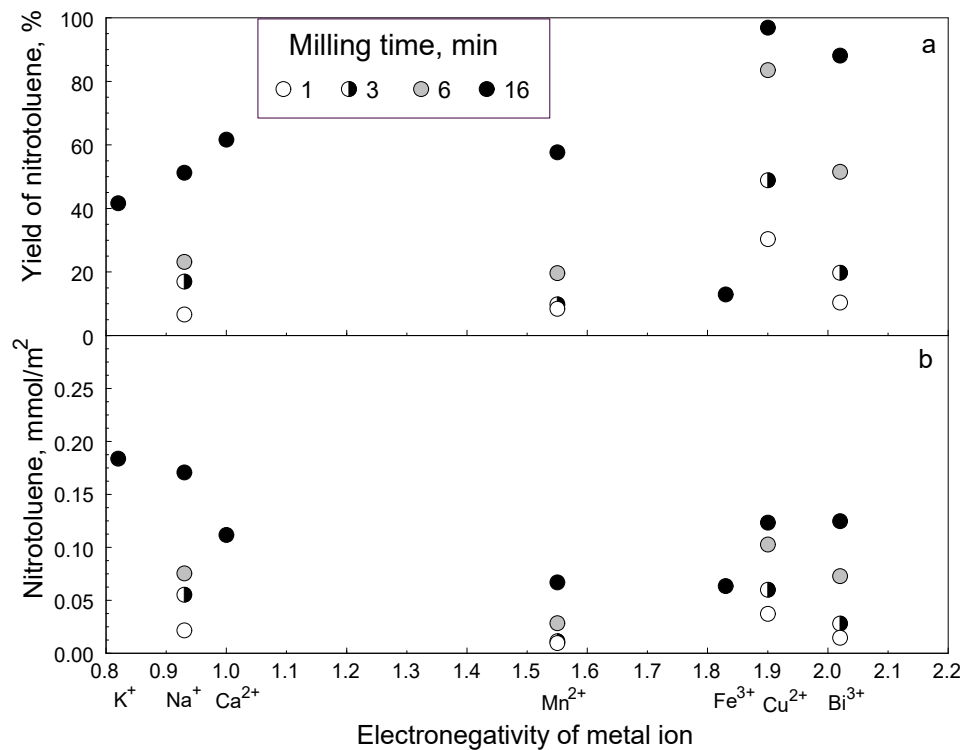


Figure S2. Effect of electronegativity on production of MNT for reactant ratio 4: a) Yield of MNT for various reaction times; b) MNT generated per surface area for various reaction times.

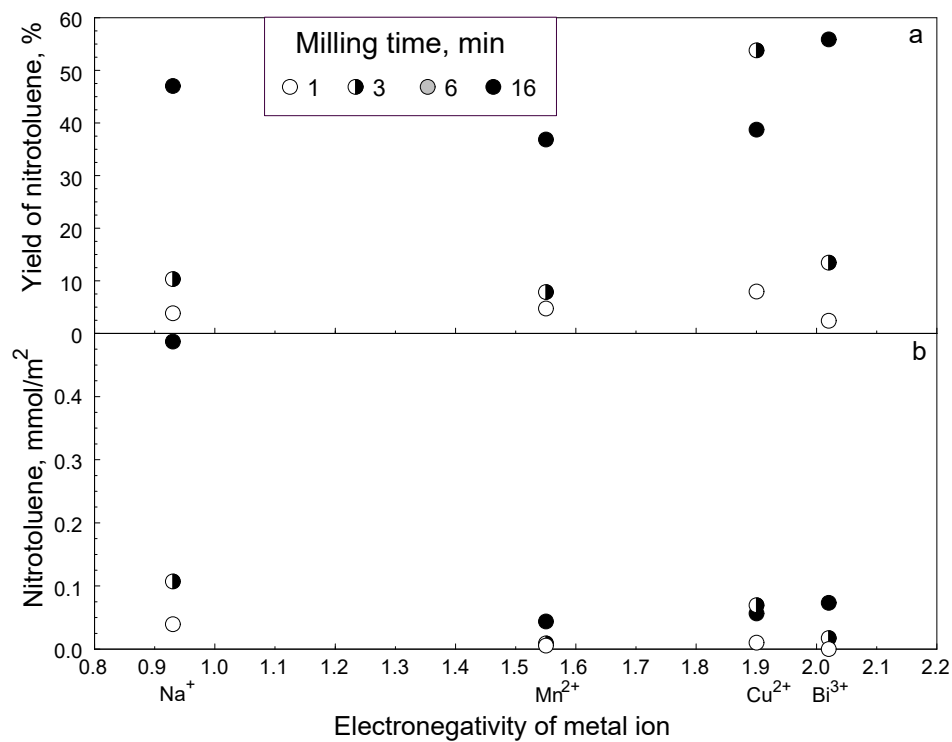


Figure S3. Effect of electronegativity on production of MNT for reactant ratio 6: a) Yield of MNT for various reaction times; b) MNT generated per surface area for various reaction times.

Table S1. Summary of results for mechanochemical nitration of toluene with copper, bismuth, sodium, manganese, calcium and potassium nitrates

Premilled powder: molybdenum oxide (41.63 g) and copper nitrate										
Reaction mixture: molybdenum oxide (41.63 g), copper nitrate and toluene (0.5 ml)										
Nitrate, g	Molar ratio (NO ₃ : toluene)	Milling time, min		Conversion, in % of toluene						MNT p/o ratio
		Nominal	Effective	MNT	Toluene recovered	Benzaldehyde	DNT	Di-nitro-phenol	Toluene loss	
1.3	2	0	1	4.45	20.96	0.01	0.0005	0.59	73.99	1.15
1.3	2	2	3	25.92	20.14	0.47	0.02	0.61	52.84	1.33
1.3	2	5	6	38.23	17.33	0.18	0.01	0.53	43.72	1.34
1.3	2	15	16	37.86	17.73	1.59	0.002	0.02	42.79	1.28
1.3	2	30	31	61.27	0.33	0.35	0.04	0.59	37.42	1.33
2.2	3.38	15	16	83.07	1.63	0.08	1.62	0.01	13.6	1.3
2.6	4	0	1	30.36	29.7	0.05	0.02	0	39.87	1.5
2.6	4	2	3	48.9	26.78	0.05	0.02	0	24.25	1.34
2.6	4	5	6	83.55	10.22	0.04	0.17	0.03	5.99	1.24
2.6	4	15	16	93.48	1.34	0.75	0.01	0.04	4.35	1.16
2.6	4	15	16	100.3	0.93	0.67	0.01	0.07	-2.04	1.08
3.9	6	0	1	8.01	32.45	0.07	0.04	0.7	58.73	1.32
3.9	6	2	3	53.82	32.79	0.64	0.03	1.13	11.59	1.31
3.9	6	15	16	38.76	11.12	0.57	0	0	49.55	1.16
5.2	8	5	6	81.2	0.3	0.52	0.03	0.03	17.92	0.94
5.2	8	8	9	77.32	13.93	0.55	0.001	0.07	8.2	0.95
5.2	8	15	16	21.88	49.15	0.5	0	0	28.47	1.08
Premilled powder: molybdenum oxide (41.63 g) and bismuth nitrate										
Reaction mixture: molybdenum oxide (41.63 g), bismuth nitrate and toluene (0.5 ml)										
1.52	2	0	1	17.93	21.63	0.04	0	0.55	59.85	1.12
1.52	2	2	3	23.38	26.37	0.08	0.04	0.63	49.50	1.61
1.52	2	5	6	32.48	23.31	0.2	0.06	0.6	43.35	1.47
1.52	2	15	16	30.23	16.93	2.54	0.03	0.49	49.78	1.35
1.52	2	30	31	60.66	0.65	0.15	0.13	0.49	37.91	1.39
2.3	3	15	16	56.57	12.37	0.58	0.21	0.23	30.04	1.32
3.04	4	0	1	10.42	37.46	0.02	0.08	0	52.02	1.48
3.04	4	2	3	19.8	32.67	0.04	0.13	0	47.36	1.26

3.04	4	5	6	51.53	24.4	0.1	0.10	0.08	23.79	1.32
3.04	4	15	16	88.12	7.41	0	0.16	0.38	3.93	1.28
3.04	4	30	31	88.6	1.34	0.74	0.29	0.06	8.97	1.21
4.58	6	0	1	0.24	27.08	0.06	0.04	0.59	71.99	1.33
4.58	6	2	3	13.46	43.6	0.1	0.04	0.95	41.85	1.37
4.58	6	15	16	31.25	9.62	0.07	0.26	0	58.8	1.33
6.16	8	5	6	1.36	15.89	0.25	0.01	0.08	82.41	1.21
6.16	8	8	9	8.14	11.03	0.51	0	0.05	80.27	1.07
6.16	8	15	16	19.92	29.15	0.87	0.17	1.32	48.57	1.13
6.16	8	15	16	19.62	36.52	0.75	0	0.17	42.94	1.16
12.32	16	15	16	2.06	40.78	0.62	0	0	56.54	0.91
Premilled powder: molybdenum oxide (41.63 g) and sodium nitrate										
Reaction mixture: molybdenum oxide (41.63 g), nitrate and toluene (0.5 ml)										
0.4	1	15	16	6.18	20.26	3.4	0	0	70.16	1.24
0.8	2	0	1	0.82	25.38	0.01	0	0.07	73.72	0.88
0.8	2	2	3	12.76	25.3	0.28	0.04	0.04	61.58	1.19
0.8	2	5	6	19.76	21.1	0.28	0.03	0.05	58.78	1.25
0.8	2	15	16	26.14	24.01	2.09	0.02	0.03	47.71	1.23
0.8	2	30	31	23.66	2.49	1.01	0.1	0.23	72.51	1.24
1.67	4.17	0	1	6.65	29.13	0.08	0.05	0.05	64.04	1.28
1.67	4.17	2	3	16.99	30.7	0.04	0.03	0.03	52.21	1.17
1.67	4.17	5	6	23.2	36.6	0.15	0		40.05	1.31
1.67	4.17	15	16	50.2	10.64	0.55	0.15		38.46	1.24
1.67	4.17	15	16	52.39	12.63	0.16	0.08		34.74	1.22
1.67	4.17	30	31	66.3	14.74	3.55	0		15.41	1.08
2.4	6	0	1	3.86	30.99	0.02	0	0.06	65.07	1.22
2.4	6	2	3	10.36	32.46	0.04	0	0.07	57.07	1.12
2.4	6	15	16	47.03	9.6	0.88	0.07	0.03	42.39	1.26
3.2	8	5	6	15.89	14.01	0.03	0.02	0.01	70.04	1.23
3.2	8	15	16	62.6	14.21	0.75	0.09	0.03	22.32	1.28
6.4	16	15	16	48.38	0.99	0.58	0.02	0.01	50.02	1.21
Premilled powder: molybdenum oxide (41.63 g) and manganese nitrate										
Reaction mixture: molybdenum oxide (41.63 g), manganese nitrate and toluene (0.5 ml)										
1.18	2	0	1	2.12	22.87	0.02	0.001	1.65	73.34	1.08

1.18	2	2	3	11.62	30.04	0.19	0.01	1.66	56.48	1.26
1.18	2	5	6	21.03	23.33	0.47	0.06	1.41	53.7	1.28
1.18	2	15	16	23.67	24.07	2.17	0.04	0.12	49.93	1.27
1.18	2	30	31	41.88	3.8	2.03	0.16	1.15	50.98	1.27
2.2	3.78	15	16	69.68	4.88	1.04	0.19	1.18	23.03	1.25
2.2	3.78	15	16	68.64	7.21	0.55	0.10	1.22	22.28	1.22
2.36	4	0	1	8.46	31.56	0.03	0.11	0.2	59.64	1.36
2.36	4	2	3	9.82	30.43	0.82	0.1	0.17	58.66	1.21
2.36	4	5	6	24.56	26.25	2.03	0	0.6	46.66	1.19
2.36	4	15	16	57.71	16.99	1.18	0.01	0.23	23.88	1.26
3.54	6	0	1	4.77	32.5	0.04	0	1.68	62.01	1.26
3.54	6	2	3	7.87	40.55	0.04	0.01	1.77	50.76	1.25
3.54	6	15	16	36.87	15.23	0.19	0.04	0.23	47.44	1.27
4.72	8	5	6	34.36	25.2	0.68	0	0.47	39.29	1.13
4.72	8	8	9	20.38	30.52	0.6	0	0.19	48.31	1.12
4.72	8	15	16	34.31	33.74	0.68	0.04	0.04	31.19	1.04
Premilled powder: molybdenum oxide (41.63 g) and calcium nitrate										
Reaction mixture: molybdenum oxide (41.63 g), calcium nitrate and toluene (0.5 ml)										
1.11	2	15	16	34.92	15.56	1.74	0.03	0.24	47.51	1.28
2.22	4	5	6	19.66	23.78	0.1	0.01	0.13	56.32	1.35
2.22	4	15	16	61.72	12.01	0.2	0.11	0.37	25.53	1.19
2.22	4	30	31	82.28	12.01	0.2	0.11	3.4	2.0	1.24
4.44	8	5	6	0.98	18.22	0.29	0	0	80.51	1.11
4.44	8	8	9	44.01	10.69	0.63	0.03	0.01	44.63	1.22
4.44	8	15	16	13.85	31.2	1.01	0.09	0.2	53.65	1.07
Premilled powder: molybdenum oxide (41.63 g) and potassium nitrate										
Reaction mixture: molybdenum oxide (41.63 g), potassium nitrate and toluene (0.5 ml)										
0.95	2	15	16	12.09	17.31	0.97	0.36	0.21	69.06	1.11
1.91	4	5	6	9.91	16.65	0.33	0.13	0	72.98	1.22
1.91	4	15	16	41.69	11.66	0.51	0.12	0.14	45.88	1.23
3.92	8	15	16	10.69	21.07	0.42	0.01	0.09	67.73	1.13