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> ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Control over *m*-Nitrotoluene Concentration in Products of Heterogeneous Mononitration of Toluene

A. V. Artemov, I. V. Tselinskii, S. A. Kukushkin, E. V. Filatova, and V. V. Ashikhin

St. Petersburg State Institute of Technology (Technical University), St. Petersburg, Russia

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Abstract—Heterogeneous mononitration of toluene with sulfuric–nitric acid mixtures, occurring in the charged interfacial monolayer with high *para* selectivity, was studied. Ways to suppress the *meta* substitution in the toluene mononitration stage by controlling the nitrating mixture composition, process parameters, and catalytic additives were found.

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The isomeric distribution of dinitrotoluenes (DNT) in the second stage of toluene nitration (2,4-/2,6-DNT ratio and concentration of *ortho* isomers) is significant in production of toluylene diisocyanate (TDI), whose world-wide annual output is about 1 million tons [1]. The DNT isomer ratio in the second nitration stage is controlled by largely the yield ratio of mononitrotoluene isomers in the first stage.

The problem of control over the nitrotoluene (NT) isomer ratio can be subdivided into two main tasks: (1) to change the o-/p-NT ratio and (2) to decrease the concentration of *m*-nitrotoluene (*m*-NT), which is an undesirable by-product in production of di- and trinitrotoluene [2].

Table 1 summarizes the published data [2-4] on the *m*-NT content of NT isomer mixtures obtained in titration of toluene with nitric acid and sulfuric–nitric acid mixtures at various temperatures. As can be seen, the *m*-NT content changes moderately (by no more than a factor of 2) over a wide temperature range from -30 to +60°C. Nevertheless, the *m*-NT content increased with temperature in all the cases.

It is known that the activation energy of toluene nitration at the *meta* position is higher than that at the *para* position by 1.1 kcal mol⁻¹ [5] (1.62 [3]). Therefore, an increase in temperature accelerates nitration at the *meta* position to a greater extent. Evidently, as temperature increases, the competition of these reactions results that the *m*-NT content grows, which is consistent with the available experimental data.

Another factor having a considerable effect on the yield of *m*-NT is the nitrating power of the acid mixture. For example, Orlova [2] reported that, in toluene nitration with sulfuric–nitric acid mixtures containing 10 wt % HNO₃ at 55°C, an increase in the H₂SO₄ concentration in the acid mixture from 28 to 47 mol %, which corresponds to rise in the nitrating acid efficiency factor from 68 to 82%, lowers the yield

Table 1. Influence of the temperature and acid mixture composition on the m-NT content of the NT isomer mixture [2-4]

Т,	<i>m</i> -NT percentage in isomer mixture*									
°C	1	2	3	4	5	6	7	8		
-30	3.5	_	_	_	3.0	_	_	_		
0	3.9	2.5	4.5	3.3	5.7	_	_	_		
20	_	4.3	4.5	3.9	_	_	_	_		
25	_	_	_	_	_		2.2	_		
30	4.4	_	_	_	4.4	3.9		1.9		
35	_	_	_	_	_	_	1.1	_		
40	_	_	4.2	_	_	_		_		
50	_	_	4.3	_	_	4.5	8.6	1.6		
60	5.1	_	_	_	4.9	4.9	_			

* (1) 55-61% HNO₃, (2) 94% HNO₃, (3) 23.8% HNO₃ + 58.7% H₂SO₄, (4) 13.7% HNO₃ + 64.4% H₂SO₄, (5) 5.5% HNO₃ + 71.4% H₂SO₄ + 1.75% HNO₂, (6) 0.5% HNO₃ + 71.7% H₂SO₄; (7) HNO₃ in the system CF₃COOH-H₂O (95.0% CF₃COOH); and (8) HNO₃ : H₂SO₄ : (CH₃CO)₂O = 1:1:30.



Fig. 1. Yield of *m*-NT vs. the nitrating acid efficiency factor Φ in heterogeneous nitration of toluene with sulfuric–nitric acid mixtures (10 wt % HNO₃) at constant temperature [3].

of the *meta* isomer by a factor of 2.4 (Fig. 1). Because toluene nitration with the indicated acid mixtures is accompanied by the formation of di- and trinitrotoluenes, data presented in Fig. 1 were obtained by recalculation of the amounts of *o*-dinitrotoluenes (3,4-, 2,3-, and 2,5-DNT) and asymmetrical isomers of TNT, contained in trotyl, to the *m*-NT content of the mononitration product. Similar results were obtained in heterogeneous nitration of toluene diluted with *n*-heptane, thus confirming the generality of this trend (Table 2) [3].

Thus, in nitration of toluene with acid mixtures commonly used in industrial processes, the yield of m-NT, and, therefore, of the so-called *ortho* isomers of DNT, formed in the second nitration step, can be reduced by carrying out nitration at low temperatures and, probably, by using more concentrated nitrating mixtures [2, 3]. Unfortunately, the technically feasible temperature variation range is rather narrow, and the composition range of the industrial acid mixtures

Table 2. Influence of the sulfuric acid content on the *m*-NT percentage in the isomer mixture [3] (35 mol % HNO₃, 30°C, mineral to organic phase volume ratio 100:1, 5% toluene in heptane)

···· NT 0/	H ₂ SO ₄				
<i>m</i> -1 N 1, %	mol %	wt %			
4.04 2.70 1.49 [*]	32.0 46.0 62.0	71.7 82.0 89.88			

^{*} *m*-NT content was estimated taking into account the 2,5-, 3,4-, and 2,3-DNT concentrations in the second stage [2].

used in the mononitration step is limited for a number of reasons as well.

The yield of the *meta* isomer can be influenced by various additives. Addition of sodium nitrite allows reduction of the yield of the *meta* isomer [2]. However, it should be pointed out that addition of NaNO₂ in amounts above 6% produces remarkable amounts of side products:

Yield of *m*-NT in toluene nitration in the presence of NaNO₂ [2] (Φ 73%, HNO₃ content of the acid mixture 10 wt %)

NaNO ₂ , wt %	0	1.5	3.0	4.5	5.9	8.6	11.0
<i>m</i> -NT, wt %	5.4	4.3	4.1	3.5	2.8	2.7	2.6

Hanson et al. [6] reported the effects of the solvent and external electric field on the isomer ratio in the continuous mononitration of toluene. Since the temperature was constant, and the amount of m-NT remained unchanged throughout the experiment, primarily the *ortho/para* isomer ratio was considered, which ranged from 1.20 to 1.97. In the cited paper, an empirical model was suggested, which allows prediction of the *ortho/para* isomer ratio from the electrical and physical properties of the solvent and field-induced dipole moment.

A low (1.6%) *m*-NT yield can be achieved in toluene nitration in the system $HNO_3 : H_2SO_4 : (CH_3CO)_2O = 1 : 1 : 30$ at 50°C [7]. A zero yield of *m*-NT has been reported for toluene nitration with a mixture of 32% HNO_3 and 68% (CH₃CO)₂O at 10°C [3]. However, in these cases, an abnormal *ortho/para* isomer ration was obtained (88 and 12%, respectively), which is unsuitable in the common TDI production process.

The mass-exchange effect on the regioselectivity of nitration of toluene and other aromatic hydrocarbons is an important aspect of the problem of two-phase heterogeneous nitration. This aspect was discussed in [8, 9] in terms of the mechanism of nitration in the interfacial adsorption monolayer, which is suggested to be operative along with the ordinary nitration mechanism (in the bulk of the acid phase). Modak and Juvekar [8] examined the nitration of mononitrobenzene and suggested that the approach they used is applicable primarily to nitration of polar molecules, such as mononitro derivatives of aromatic hydrocarbons.

The key point of the interfacial nitration mechanism is that nitroaromatic molecules adsorbed at the interfacial monolayer react with the nitronium cations from the acid phase. Evidently, the electric field formed at the interface as a result of the adsorption of polar molecules affects the nitration regioselectivi-



Fig. 2. Orientation of toluene and mononitrotoluene molecules at the interface.

ty in this region. The total nitration selectivity with respect to a given isomer is a weighted average of the bulk and interfacial selectivities. When passing across the interface, nitrotoluene molecules are oriented in the interfacial layer so that the hydrophobic methyl groups are directed toward the organic phase as a result of repulsive action of the hydrophilic mineral layer (Fig. 2) [8].

The contribution of the interfacial mechanism is controlled by the interface area, i.e., by the stirring rate. It should be expected that the above statements are valid for a relatively slow nitration of nitrobenzene and other mono- and dinitro derivatives of aromatic hydrocarbons, i.e., for the cases when diffusion of the substrate to the bulk of the acid phase is not a rate-determining stage under common process conditions, in contrast to the nitration of the starting hydrocarbons.

Since the starting aromatic hydrocarbons are lowpolar, one may expect that the adsorption of NO_2^+ at the interface is insignificant if the organic phase contains no nitration products. At the same time, if the organic phase contains nitro derivatives, the negative charge of the interfacial layer facilitates adsorption of the NO_2^+ cation, thus favoring interfacial nitration.

Based on the common knowledge, it can be suggested that the contribution of the interfacial mechanism to the nitration of aromatic hydrocarbons, such as toluene and benzene, can be raised in three cases: (1) when the reaction rate in the interfacial layer is higher or well-comparable with the rate of substrate diffusion across the interface to the interfacial layer, as it occurs in nitration of aromatic hydrocarbons with acid mixtures with high sulfuric acid content (above 35 mol %); (2) when the reaction proceeds in an intermediate mode between the diffusion and kinetic control, which occurs in nitration of aromatic hydrocarbons with sulfuric–nitric acid mixtures of low nitrating efficiency at high stirring rate (>3000 rpm); and (3) in continuous nitration of aromatic hydrocarbons, i.e., at a sufficiently high concentration of a nitro derivative in the organic phase.

Previously [8-10], it has been demonstrated that the selectivity of the interfacial nitration differs from that in the bulk of the acid phase, and the *ortho/para* isomer ratio can be altered by changing the contribution of any of the two principal nitration mechanisms.

EXPERIMENTAL

Toluene nitration was carried out in a 30-ml glass reactor equipped with a temperature-control jacket, four-blade turbine stirrer, vertical baffle walls, and thermocouple for measuring the temperature of the reaction mass. The baffle walls were arranged at right angles relative to each other to avoid formation of a whirlpool and projected by 5 cm over the reaction mass to improve the aeration of the acid mixture. In the experiments, the stirring rate was varied from 200 to 5000 rpm.

The gas content of the acid mixture was determined from the increase in the reaction mass volume under given conditions with or without stirring. The mixture was poured into the reactor up to the lower overflow level. The temperature was raised to a desired value by circulating water in the jacket, and the reaction mass was allowed to stand for 10 min without stirring. The volume of the acid mixture remaining in the reactor, V_1 , corresponded to the loss for thermal expansion. Similarly we determined the mixture volume V_2 after stirring for 5 min. The gas content

 Γ (vol %) of the mixture under given conditions was estimated as

$$\Gamma = \frac{V_1 - V_2}{V_1} \times 100.$$

The results are listed in Table 3 for various temperatures and stirring rates.

In the experiments, we used nitric and sulfuric acids of pure grade and chromatographically pure toluene. The composition of the acid mixtures was determined titrimetrically to within 0.02%. The acid mixtures were prepared by successive mixing of the concentrated acids with double-distilled water at 0°C. The compositions of the acid mixtures are specified in the tables.

The isomeric composition of the products and residual toluene content were determined by gas chromatography on a KhROMOS 1000.1 instrument with a flame ionization detector (SUPELCO column, 30 m × 0.32 mm; stationary phase 5% polydiphenyl + 95% polydimethylsiloxane; carrier gas helium, flow rate 30 ml min⁻¹). The relative error of determination of NT isomers and DNT was $\pm 5\%$.

In toluene nitration, a calculated amount of toluene was introduced with a syringe into the reactor with an acid mixture at a fixed temperature with stirring. After a fixed time, stirring was switched off, and the reaction mass was poured into a fivefold volume of cold water (10–15°C). The nitration products were extracted twice with chloroform taken in an amount of 6 ml per gram of toluene used for nitration. The combined extracts were washed with the equal volume of water. Finally, the products were analyzed for mono- and dinitro derivatives.

The main focus of this study was to characterize parameters controlling the reaction zones in which particular NT isomers are preferentially formed and to elucidate factors that could decrease the formation rate and yield of *meta*-nitrotoluene.

Our results show that, in toluene nitration with sulfuric-nitric acid mixtures with low molar concentration of sulfuric acid (acid mixtures were prepared from 50% H_2SO_4) and high content of HNO_3 and water, an increase in the temperature remarkably changes the *o*- and *m*-NT contents, but only slightly, the *p*-NT content (Fig. 3, Table 4).

As a hypothesis we suggested that the *para* selectivity of nitration is higher in the charged interfacial monolayer in which the nitrating agent reacts with the spatially oriented substrate molecules, and



Fig. 3. Yield of *m*-NT vs. the temperature *T* in heterogeneous nitration of toluene with sulfuric–nitric acid mixtures. HNO_3 : toluene molar ratio 1.5. Acid mixture composition, mol %: (1) HNO_3 42.54, (2, 3) H_2SO_4 10.2, and (4) H_2SO_4 7.60. N, rpm: (1, 2, 4) 300 and (3) 800.

ortho- and *meta-*nitrotoluenes are predominantly formed in the bulk of the acid phase.

Indeed, the observed decrease in the *m*-NT yield with increasing nitration efficiency factor of the acid mixture, accompanied by a decrease in the o-/p-NT ratio (Fig. 1) [2, 3], also suggests that an increase in the H₂SO₄ molar concentration promotes the interfacial nitration, whose rate grows with the H₂SO₄ concentration much more strongly than does the rate of the reaction in the bulk of the acid phase [8]. It follows from the aforesaid that, in the interfacial monolayer, the nitronium cation attacks essentially the *para* position, thus reducing the relative content of o- and *m*-isomers in the product.

To check this hypothesis for consistency, we carried out a series of experiments on toluene nitration under conditions similar to those indicated above with sulfuric–nitric acid mixtures containing various contents of sulfuric acid (14.07, 35.70, and 52.62 mol %). We

Table 3. Gas content Γ (vol %) of sulfuric–nitric acid mixture at various temperatures

Stirring rate N,	Γ, vol %, at indicated $T \pm 1$ °C					
rpm	25	50	75			
5000	65.2	70.8	76.1			
3000	39.5	46.5	48.8			
2000	29.7	34.4	36.1			
1500	12.9	14.9	15.6			
1000	4.9	5.6	5.9			
700	-	<1	<1			

		N/ mm	Toluono 0/	NT iso	ion, %		
Φ	1, C	7v, 1pm	Toluene, %	o-NT	<i>m</i> -NT	<i>p</i> -NT	orino/para-in i
Φ =	38.2; 10.20) mol % H_2S	D ₄ , 30.41 HNC	0 ₃ , 59.37 H ₂ O	(25.1% H ₂ SO ₄	, 48.08 HNO ₃ ,	26.82 H ₂ O)
1 2 3 4 5 6 7 8 9 10	10 25 50 75 95 10 25 50 75 95	800 300	68.60 56.04 41.66 26.22 14.23 93.89 69.11 39.60 35.90 14.89	59.17 58.38 57.73 56.11 55.24 60.46 58.83 57.32 54.84 53.32	3.68 4.50 5.08 6.40 7.85 1.45 3.40 4.86 8.21 10.67	37.15 37.12 37.19 37.49 36.90 38.09 37.78 37.82 36.95 36.01	$ \begin{array}{r} 1.59 \\ 1.57 \\ 1.55 \\ 1.50 \\ 1.49 \\ 1.59 \\ 1.56 \\ 1.52 \\ 1.48 \\ 1.48 \\ \end{array} $
Φ =	30.9; 7.60	mol % H ₂ SO	4, 45.32 HNO3	, 47.07 H ₂ O (16.76% H ₂ SO ₄	, 64.19 HNO ₃ ,	19.05 H ₂ O)
11 12 13 14 15	10 25 50 75 95	800	42.82 21.98 20.69 15.01 8.73	59.77 56.87 57.01 55.91 55.83	$\begin{array}{c} 0.73 \\ 4.07 \\ 4.10 \\ 5.55 \\ 5.64 \end{array}$	39.50 39.06 38.90 38.54 38.51	1.51 1.46 1.47 1.45 1.45
			42.54 mol	% HNO ₃ , 57.	45 H ₂ O		
16 17 18 19 20	10 25 50 75 95	300	93.61 84.77 64.30 54.47 45.72	59.27 58.64 55.42 52.01 49.75	2.95 3.72 7.17 11.39 15.07	37.78 37.64 37.41 36.60 35.18	$ 1.57 \\ 1.55 \\ 1.48 \\ 1.42 \\ 1.41 $

Table 4. Temperature effect on the isomeric composition^{*} of nitrotoluenes in toluene nitration with sulfuric–nitric acid mixtures of low nitrating efficiency (reaction time 60 min, HNO_3 /toluene molar ratio 1.5)

* By isomeric composition is meant the percentage of mononitrotoluene isomers in the three-component mixture.

Table 5. Influence of the stirring rate on the NT isomer ratio in toluene nitration with sulfuric–nitric acid mixture with $\Phi = 48$ at various temperatures [reaction time 60 min, HNO₃/toluene = 1.5; HNO₃ 15.98%, H₂SO₄ 41.72, and H₂O 42.29 (HNO₃ 8.39, H₂SO₄ 14.07, and H₂O 77.54 mol %)]

Dun no	T °C	N rom	Toluono 0/	NT isc	ortho/nava NT		
Kull IIO.	<i>I</i> , C	<i>I</i> v, 1pm	Toluelle, %	o-NT	<i>m</i> -NT	<i>p</i> -NT	ormo/para-in i
21 [*]	25	} 400 {	68.31	58.73	35.77	5.50	1.64
22 [*]	50		55.75	59.03	34.46	6.51	1.71
23	75		2.99	55.29	37.98	6.73	1.46
24	95		0	55.85	29.4	5.12	1.90
25 [*]	10		99.4	0	0	0	0
26*	25	2000	61.45	57.94	37.83	4.24	1.53
27*	50		59.40	58.12	38.08	3.80	1.53
28	75		32.63	60.22	37.27	2.52	1.62
29	95		1.47	58.51	37.93	3.57	1.54
30*	25	} 3000 {	99.21	0	0	0	0
31*	50		96.8	65.15	32.09	2.76	2.03
32	75		85.26	61.78	35.46	2.77	2.34
33	95		4.12	58.85	38.05	3.10	1.74
34	10	5000	92.69	62.50	35.10	2.40	1.78
35	25		38.75	68.40	29.16	2.44	2.35
36	50		17.57	61.82	35.48	2.70	1.74
37	95		3.90	54.97	42.16	2.87	1.30

^{*} In run nos. 21, 22, 25–27, 30, and 31, the reaction time was 100 min.

Run	τ, min	N,	Г,	Toluene,	NT ison	neric compos	ition, %		DNT,
no.	min	rpm	vol %	%	o-NT	<i>m</i> -NT	p-NT	ortho/para-N I	%
Φ = 75.1; 74.55% H ₂ SO ₄ , 1.11 HNO ₃ , 24.34 H ₂ O (35.70 mol % H ₂ SO ₄ , 0.83 HNO ₃ , 63.47 H ₂ O)								H ₂ O)	
38	[] f	200	0	66.59	57.39	5.40	37.21	1.54	3.10
39		600	<0	17.02	59.72	4.14	36.13	165	1.57
40		800	5	2.11	58.96	3.74	37.30	1.58	7.36
	15	5000							
41		2000	34.4	2.35	57.84	4.01	38.16	1.52	0.84
42		3000	46.5	12.69	59.15	4.04	36.81	1.61	0.75
43	} [5000	70.8	12.31	60.11	3.60	36.29	1.66	0
Φ	= 85.8;	85.42% H	$H_2SO_4, 0.6$	53 HNO ₃ ,	13.95 H ₂ O	(52.62 mol %	6 H ₂ SO ₄ , 0	.61 HNO ₃ , 46.77	H ₂ O)
44		200	0	58.82	65.40	3.01	33.92	1.93	35.6
45		600	<1	23.28	58.91	3.20	37.90	1.55	65.6
46		800	5	22.33	54.96	4.07	40.97	1.34	53.3
47	7	1500	14.9	11.45	58.64	4.073	37.28	1.30	67.3
48		2000	34.4	7.31	58.64	4.07	27.28	1.13	54.8
49		3000	46.5	0.99	48.45	5.77	45.78	1.06	65.4
50	þ t	5000	70.8	0.00	47.67	5.39	46.94	1.02	58.5
	1	1	1	1	1	1		1	1

Table 6. Influence of the reaction time and stirring rate on the NT isomer ratio in toluene nitration with sulfuric-nitric acid mixture with Φ 75.1 and 85.8 (HNO₃/toluene molar ratio 1.04, $T = 50^{\circ}$ C)

believed that it is sulfuric acid that controls the acidity of the nitrating mixture, and, therefore, the reaction rate, depending on the stirring rate, gas content, and temperature (Tables 5, 6).

Our results show that the effects of the stirring rate, gas content, and temperature on the m-NT yield are more clearly pronounced in toluene nitration with



Fig. 4. *m*-NT content of toluene nitration products vs. the stirring rate N at 50°C. H_2SO_4 concentration in the mixed acid, mol %) (1) 52.62, (2) 35.70, and (3) 14.07.

an acid mixture of low nitration activity (14.07 mol % H_2SO_4 , Φ 48). At low stirring rate (400 rpm), the *m*-NT yield is higher than ordinary, 3–4%, and tends to increase with temperature (Table 5, run nos. 1–4). With increasing stirring rate, the temperature dependence of the *m*-NT yield becomes more complex (Table 5, run nos. 25–29, 34–37). At a constant temperature, the *m*-NT yield steadily decreased in most of the experiments from 6.5 to 2.5–2.7 at 3000 rpm with increasing stirring rate and gas content of the reaction mass. This additionally confirmed our concept that an increase in the contribution of the interfacial nitration mechanism can reduce the *o*- and *m*-NT content of the isomer mixture (Fig. 4).

In toluene nitration with an acid mixture with an initial sulfuric acid content of 35.70 mol % at a 4% molar excess of nitric acid, the *m*-NT yield also tends to decrease from 5.4 to 3.6% with increasing stirring rate. Note that this tendency is considerably less pronounced than that in nitration with the low-activity acid mixture containing 14.07 mol % H_2SO_4 (Fig. 4; Table 6, run nos. 38–43).

However, in toluene nitration with a high-activity acid mixture (initial sulfuric acid concentration 52.62 mol %, 4% molar excess of nitric acid), the *m*-NT yield increases with the stirring rate. In this case, the *m*-NT yield significantly increases at a stirring rate exceeding 2000 rpm, when the reaction mass is saturated with air bubbles. The increase in the contribution of the interfacial nitration is also evidenced by the decrease in the *ortho/para* ratio approximately by half as the stirring rate is raised from 400 to 5000 rpm (Table 6, run nos. 44-50).

The observed increase in the *m*-NT yield with the H_2SO_4 concentration can be attributed to specific solvation of the toluene molecules with sulfuric acid. The solubility of toluene in sulfuric acid is more than doubled as the H_2SO_4 content is raised from 35.70 to 52.62 mol % [2]. This suggests that association occurs via formation of hydrogen bonds with the π -electron system of toluene, the hydrogen bonding being the strongest in the areas with the maximal electron density, i.e., at the *ortho* and *para* positions of the aromatic ring. In such associates, the hydrogen bonds partially block the *ortho* and *para* positions, while the meta position of the ring remains accessible to the attack by the nitronium ion [11].

This suggestion is confirmed by low *m*-NT content of the products of toluene mononitration with nitration agents of low acidity, e.g., with mixtures of nitric acid with acetic anhydride, trifluoroacetic acid, or nitronium salts [2, 11].

The hydrogen bonding in toluene– H_2SO_4 associates is accompanied by at significant loss of entropy, which is particularly pronounced for the reaction in the bulk of the mineral phase. At the same time, the entropy loss caused by the formation of hydrogen bonds should be less significant in the case of the interfacial nitration, when the toluene molecules are spatially oriented. Therefore, the effect of specific solvation of toluene is more pronounced at the highest stirring rates, when the contribution of the interfacial nitration dominates.

Our experiments show that, in toluene nitration with low-activity acid mixtures with a sulfuric acid content of 7.60-14.07 mol %, at low stirring rate (below 1000 rpm), i.e., when the effect of specific solvation of toluene is insignificant, an increase in the H₂SO₄ concentration at a fixed temperature results in a decrease in the *m*-NT yield (Fig. 3; Table 4, run nos. 1–10 and others).

To study the possibility of controlling the *m*-NT yield by changing the diffusion and kinetic contributions to the total nitration rate, we carried out experiments on toluene nitration with acid mixtures containing various concentrations of sulfuric acid and various molar excesses (25, 50, and 75%) of nitric acid, as influenced by the temperature. Selected results are presented in Figs. 5 and 6.

At the minimal (4%) molar excess of nitric acid, the dependence of the *m*-NT yield on the sulfuric



Fig. 5. *m*-NT yield vs. the H_2SO_4 concentration in the acid mixture. HNO₃/toluene molar ratio 1.04, N = 800 rpm. *T*, °C: (*1*) 10, (2) 50, (3) 75, and (4) 95.



Fig. 6. *m*-NT yield vs. the H_2SO_4 concentration in the acid mixture. N = 800 rpm, $T = 50^{\circ}$ C. HNO₃/toluene molar ratio: (1) 1.25, (2) 1.5, and (3) 1.75.

acid content is rather complex with a distinct minimum at an H_2SO_4 content of 28–35 mol % (Fig. 5). In this case, the temperature effect is not the least important of the factors.

At a high molar excess of nitric acid (see Fig. 6, $HNO_3/toluene 1.25$, 1.50, and 1.75) and at fixed temperature (50°C), the *m*-NT yield tends to decrease the H_2SO_4 content is raised to 27–30%. With a further increase in the H_2SO_4 content, the *m*-NT yield remains unchanged or only slightly increases. Evidently, the reaction zone shifts toward the bulk of the acid phase by virtue of the increase in the toluene solubility with the HNO_3 content os the sulfuric–nitric acid mixtures. As the H_2SO_4 content increases, and, therefore, the nitration rate grows, the rate of sub-

Run Γ, <i>N</i> ,		Ν,	Salt concen-	Toluene,	NT isom	eric compo	sition, %	outho/nava NT	2 4 /2 6 DNT	DNT,
no.	vol %	rpm	tration, M	%	o-NT	m-NT p-NT		2,4-/2,0-DINI	%	
	KNO ₃ additive									
51 52	<1	800 {	1.58 0.79	1.16 0.38	57.71 56.86	3.68 3.97	38.61 39.18	1.49 1.45	2.07 2.49 2.20	12.12 17.51
55 54	J	l	0.40	2.11	53.37	3.38	33.77	1.58	2.43	7.36
NaNO ₃ additive										
55	70	5000	1.58	0	34.0	5.89	58.1	0.585	2.46	59.70
56	30	2000	1.58	0	48.96	5.23	45.81	1.07	2.44	43.25
56		ſ	1.58	0	35.14	7.78	57.09	0.62	2.48	75.95
57	2 -1	800 3	0.79	0	42.55	6.05	51.39	0.83	2.07	56.56
58	<1	800	0.40	0	49.24	5.00	45.75	1.08	2.43	43.83
59	J	l	0	2.11	53.37	3.38	33.77	1.59	2.43	7.36
					LiNO	3 additive				
60	70	5000	1.58	0	39.10	5.76	55.15	0.71	2.40	66.51
61	30	2000	1.58	0	40.14	7.10	52.76	0.76	2.74	67.84
62)	ſ	1.58	0	40.96	6.38	52.66	0.78	2.23	58.41
63	.1	000	0.79	0	44.67	5.88	49.46	0.90	2.31	51.19
64	r <1	800 1	0.40	0	52.34	4.37	43.29	1.21	1.88	28.15
65	J	l	0	2.11	53.37	3.38	33.77	1.58	2.43	7.36

Table 7. Influence of alkali metal nitrates on the NT isomer ratio $[\Phi = 75.1; \text{HNO}_3/\text{toluene molar ratio } 1.04, T = 50^{\circ}\text{C},$ nitration time 15 min; H₂SO₄ 74.55, HNO₃ 1.11, and H₂O 24.34% (H₂SO₄ 35.70, HNO₃ 0.83, and H₂O 63.47 mol %)]

strate diffusion from the organic phase to the acid phase becomes insufficient for the acid phase to be saturated with toluene, and the reaction zone shifts toward the interface, where, as demonstrated above,



Fig. 7. *m*-NT yield vs. the inorganic salt concentration c_s in the acid mixture of the composition (mol %): H₂SO₄ 35.70, HNO₃ 0.83, and H₂O 63.47. HNO₃/toluene molar ratio 1.04, 50°C, N = 800 rpm. (1) NaNO₃, (2) LiNO₃, and (3) KNO₃.

the nitration proceeds with a higher *para* selectivity. At the same time, raising the H_2SO_4 content to above 30 mol % provides a slight increase in the *m*-NT yield as a result of an enhanced specific solvation of toluene.

To study the effect of inorganic salt additives on the formation of *m*-NT and on the *ortho/para* ratio, we performed a series of experiments on toluene nitration with an acid mixture containing 35.70 mol % H_2SO_4 and 4% molar excess of HNO_3 in the presence of Li, K, and Na nitrates. All the salts were calcined and added to the mixed acid just prior to use.

The salt concentrations were chosen taking into account the data from [4, 7]. Some of the results obtained are listed in Table 7 and presented in Figs. 7 and 8.

Our results show that the salt additives promote the formation of the *meta* and *para* isomers, and the *ortho/para* ratio decreases (Table 7). In the presence of the inorganic nitrates, the *m*-NT yield is more than twice that in the experiments without salt additives (Table 7, run nos. 51-65; Fig. 7). It is known [11] that the dipole moment of the nitrotoluene mol-

ecules and, therefore, of the π complexes with the nitronium ion, increases in the order *o*-NT < *m*-NT < *p*-NT. Therefore, addition of the electrolytes should primarily affect the *meta* and *para* selectivity, which is confirmed by the experimental data (Fig. 8; Table 7, run nos. 56–59, 62–65, and others).

The effect of the salt additives on the regioselectivity of toluene nitration decreases in the order Na^+ > $Li^+ > K^+$. The maximal increase in the *m*-NT yield and the maximal decrease in the ortho/para ratio were observed as the concentration of sodium nitrate in the acid mixture increased, but not with increasing concentration of lithium nitrate, as would be expected, i.e., this trend is inconsistent with the order in which the cation charge density grows (Fig. 7). Evidently, the lithium cation is considerably more strongly solvated in the acid mixture than the sodium cation. As a result, the effective radius of the lithium solvate is higher, and, therefore, it is more weakly adsorbed at the interface and increases the charge of the electric double layer to a lesser extent, compared to the sodium solvate. Thus, the increase in the contribution of the interfacial nitration is more clearly pronounced in the presence of the sodium cation.

Upon addition of LiNO₃, which has a higher affinity for water and exists as a crystal hydrate under ambient conditions, the *m*-NT yield increases against the reference experiment, and the dependence of the *m*-NT yield on the stirring rate passes through a maximum (Fig. 8). As the stirring rate is raised above 2000 rpm, i.e., when the gas content of the reaction mass starts to be an important factor, the *m*-NT yield decreases, probably due to a rise in the contribution of the interfacial nitration, as demonstrated by an increase in the *p*-NT yield and a decrease in the *ortho/ para* ratio (Table 7, run nos. 62–65 and others).

Presumably, these salts bound water to form stable hydrates, thus making higher the nitration activity of the acid mixture and shifting the reaction zone toward the interface, i.e., promoting the interfacial nitration and raising the para selectivity.

CONCLUSIONS

(1) *Para*-selective two-phase toluene nitration with sulfuric–nitric acid mixtures proceeds in the charged interfacial monolayer, in which the nitrating agent reacts with the spatially oriented toluene molecules, while the formation of *ortho-* and *meta*-nitrotoluenes occurs essentially in the bulk of the acid phase.

(2) To reduce the *meta*-substitution rate in toluene nitration, it is necessary to diminish the mass-transfer



Fig. 8. *m*-NT yield vs. the stirring rate N (rpm) in heterogeneous nitration of toluene with the acid mixture of composition (mol %): H₂SO₄ 35.70, HNO₃ 0.83, and H₂O 63.47 in the presence of alkali metal nitrate additives (1.58 M): (*I*) LiNO₃, (*2*) NaNO₃, and (*3*) KNO₃. HNO₃/toluene molar ratio 1.04, 50°C.

effect on the total reaction rate and to raise the contribution of the interfacial reactions. This can be done lowering the reaction temperature, raising the sulfuric acid concentration in the acid mixture, and raising the stirring rate to 3000–5000 rpm, when a gas-filled emulsion is formed the reaction mass is saturated with air bubbles).

(3) Addition of alkali metal nitrates affects the rates of both the interfacial and bulk nitration. The former effect is caused by an increase in the positive charge in the electric double layer at the interface, and the latter effect, by a decrease in the steady-state toluene concentration in the bulk of the acid phase (salting-out effect).

(4) Introduction of alkali metal nitrates raises the yields of *meta-* and *para-*nitrotoluenes by promoting the nitration at the *para* and *meta* positions of the aromatic ring, since the corresponding reaction intermediates have a higher dipole moment, compared to *ortho*-nitrotoluene.

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