SELECTIVITY OF NITRATION REACTIONS OF AROMATIC COMPOUNDS ON ZEOLITES H-Y AND H-ZSM-11

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Substrate and positional selectivity in the nitration reactions of benzene and its derivatives (halobenzenes, toluene and o-xylene) by nitric acid and acyl nitrates supported on zeolites H-Y and H-ZSM-11 were studied. The reaction mechanism and effects governing selectivity of the process are discussed.

INTRODUCTION

Recent years have seen an increased tendency for the application of zeolites in fine organic synthesis.^{1,2} In particular, these catalysts have proved to be very efficient in electrophilic aromatic substitution reactions owing to the presence of acidic centres. An important feature of zeolites is their regular (crystalline) structure with channels comparable in size to organic molecules such as benzene. The rigid structure-imposed steric limitations lead to changed reaction selectivity.^{1,2}

Some recent communications have reported a very high *para* selectivity in nitrations of aromatic compounds on zeolie catalysts.³⁻⁶ In this work we studied the substrate and regioselectivity of the nitration of some benzene derivatives by various nitrating agents in the presence of zeolite catalysts of different structural types with the aim of investigating the peculiarities of the mechanism of this reaction.

Such a study seems to be of interest not only for developing new, efficient nitrating systems but also for investigating some general problems in physical organic chemistry, such as the relationship between reactivity and selectivity and medium effects. Further, the results of this study may prove useful in dealing with the problem of the relationship between homogeneous and heterogeneous acid catalysis. It is generally assumed that the mechanisms of acid-catalysed processes are essentially the same under homogeneous and hetero-



geneous conditions^{7,8} but there have been few experimental studies supporting this assumption (see, e.g., Refs 9 and 10).

Nitration is a typical aromatic electrophilic substitution reaction which has been extensively investigated.¹¹⁻¹⁴ For the acid-catalysed reaction with nitric acid as nitrating agent, a mechanism was generally adopted which involves the nitronium cation as an electrophilic species^{13,14} (Scheme 1).

A similar mechanism was suggested for the acidcatalysed nitration of arenes with acyl nitrates, although this reaction may also involve non-dissociated protonated acyl nitrates. $^{15-19}$

RESULTS AND DISCUSSION

We used benzene and its derivatives (1-7) as aromatic substrates, nitric acid and acyl nitrates with various structures (8-11) as nitrating agents and zeolite catalysts H-Y and H-ZSM-11 (Scheme 2).

The reactions were performed at 30 $^{\circ}$ C in hexane, by adding an excess of substrate to a suspension of zeolitesupported nitrating agent. In the absence of catalysts, there was little reaction (cf. Refs 5, 20 and 21). A catalytic effect was produced by the decationized zeolites

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H-Y and H-ZSM-11 and acidic amorphous aluminosilicate (see also Ref. 9), apparently owing to the participation of Brønsted acid centres of the catalyst in the reaction (cf. Refs 7 and 8). The yields of nitro products (calculated from the nitrating agents) in the presence of aluminosilicates were low (usually less than 20%), but this is not caused by any side-reactions, as the GLC data do not show any significant amount of impurites (<2%) which could be formed by these reactions. Mass balances of the reactions under study were 100%. The low yield are possibly explained by blockage of the catalyst channels by the molecules of the reaction products (by their sorption on the surface of the pores); as a consequence, further diffusion into zeolite channels becomes difficult.

Tables 1–3 give the relative reactivities of the substrates obtained by the competing reactions method.¹¹ The relative reactivity sequence of mono-substituted benzene derivatives (halobenzenes < benzene < toluene) for nitration on amorphous aluminosilicate and zeolites H-Y and H-ZSM-11 agrees with that for nitrations under homogeneous conditions and is typical of electrophilic substitution reactions.¹¹

While analysing these data, it should be borne in mind that the reactions on zeolites may have strong diffusion limitations, so that the rate constant ratios will be due not only to electronic effects of substituents in substrates but also the different abilities of the reactant molecules to diffuse to reaction centres according to the equation^{29,30}

$$(k_1/k_2)_{\rm obs} = \sqrt{(k_1/k_2)_{\rm i}(D_1/D_2)}$$
(1)

where $(k_1/k_2)_{obs}$ is the experimentally observed and $(k_1/k_2)_i$ the intrinsic ratio and D_1 and D_2 are diffusion coefficients of the substrates to reaction centres.

In view of the same critical diameter of benzene and its monosubstituted derivatives (1, 2, 4–7), their diffusion coefficients are expected to be similar.^{31,32} Indeed, similar *D* values have been reported for the diffusion of benzene and toluene in zeolites Y and ZSM-5, $^{33-35}$ the latter having nearly the same structure and pore size as ZSM-11.³⁶ For *o*-xylene, having a much lower diffusion coefficient than benzene and toluene in medium-pore zeolites, $^{35-37}$ we observed (Table 1) a decrease in the relative reactivity in nitrations with acetyl and benzoyl nitrates on H-ZSM-11 as compared with homogeneous conditions and amor-

Nitrating agent	Catalyst	$\frac{k_{\rm PhCl}}{k_{\rm PhH}}$	$\frac{k_{\rm PhMe}}{k_{\rm PhH}}$	ko-xylene k _{PhH}
HNO ₃	H ₂ SO ₄	0∙064 ^ь	17°	38°
	H-ZSM-11	0.04	4	0.1
MeCOONO ₂	d	0.033°	23 ^f	
-	H-Y	0.07	6	15
	H-Y–NBu ₃	0.1	9	19
	H-ZSM-11	0.08	5	3
	H-ZSM-11-NBu ₃	0.06	5	0.9
PhCOONO ₂	Amorphous aluminosilicate	0.08	7	21
_	H-Y	0.1	11	23
	H-Y-NBu ₃	0.1	10	26
	H-ZSM-11	0.06	7	5
	H-ZSM-11-NBu ₃	0.07	7	1

Table 1. Relative reactivities of aromatic compounds in nitration reactions^a

^a Data from this work, nitration in hexane at 30 °C (25 °C for HNO₃).

^b From Ref. 22, 71.2% sulphuric acid, 25 °C.

^c From Ref. 23, 68.3% sulphuric adcid, 25 °C.

^d Acetic acid is present in the reaction mixture owing to its formation in the course of reaction.

From Ref. 24, acetic anhydride, 18 °C,

¹From Ref. 25, acetic anhydrie, 30 °C.

	Catalyst	<u>k_{tol.}</u> k _{ben.}	Isomer ratio of nitrotoluenes (%) ^b			
Nitrating agent			para	meta	ortho	<i>para ortho</i> ratio
HNO ₃	H₂SO₄	28°	34.6°	3.4c	62 · 0°	0.6
	H-ZSM-11	4	78	1	21	3.7
MeCOONO ₂	d	23°	37°	5°	58°	0.6
	đ	44.3	37	2	61	0.6
	f		25	35	40	
	H-Y	6	59	2	39	1.5
	H-Y-NBu	9	54	5	41	1.3
	H-ZSM-11	5	66	2	32	2.1
	H-ZSM-11-NBua	5	88	5	7	13
FtCOONO ₂	d	33 · 38	32 ^g	4 ^g	64 ^g	0.5
210001.02	H-ZSM-11-NBu	5	95	2	3	32
t-BuCOONO ₂	H-Y	12	63	2	35	1.8
	H-Y-NBu	14	66	$\overline{2}$	32	2 · 1
PhCOONO ₂	d	30·7 ^g	31 ^g	58	64 ^g	0.5
1 10001102	H ₂ SO ₄	35 · 3 ^h	34 · 5 ^h	3.4 ^h	62 · 1 ^h	0.6
	Amorphous aluminosilicate	7	55	1	44	1.2
	H-Y	11	64	1	35	1.8
	H-Y-NBu	10	63	2	35	1.8
	H-ZSM-11	7	75	1	24	3.1
	H-ZSM-11–NBu ₃	7	98	<1	2	49

Table 2. Nitration of toluene^a

^a Data from this work, nitration in hexane at 30 °C (25 °C for HNO₃).

^bFrom competitive experiments, being independent of the reaction time.

^c From Ref. 26, 30% solution of mixed acids in sulpholane at 25 °C.

^d Corresponding carboxylic acid is present in the reaction mixture owing to its formation in the course of reaction.

^e From Ref. 25, acetic anhydride, 30 °C.

^f Data for the low degree of conversion (2% yield of nitrotoluenes after 2 h). A significant change in selectivities later is observed, probably owing to acetic acid formation during the process.

From Ref. 18, acetonitrile, 25°C.

^h From Ref. 15, acetonitrile, 25 °C.

phous aluminosilicate, and also large-pore H-Y, where the diffusion coefficient of 3 is nearly the same as that of 1 and 2.³³ This obviously indicates that the nitration occurs to great extent in zeolite channels.

This decrease in the relative reactivity of o-xylene nitration by acyl nitrates was even more pronounced when zeolite was treated with tributylamine (NBu₃) (Table 1). The kinetic molecular diameter of the latter $(ca \ 8 \ Å)^{38,39}$ inhibits penetration into ZSM-11 channels, the diameter of which is ca 5.6 Å.¹ Such treatment obviously leads to selective neutralization of acidic centres on the outer surface of the zeolite crystals. For the large-pore Y zeolite (effective pore diameter ca 7.4Å), the diffusion limitations also seem to make NBu₃ react predominantly with surface acidic centres (cf. Refs 38 and 39).

In H-ZSM-11-catalysed nitration by nitric acid, the relative reactivity of o-xylene is lower than in nitrations with acyl nitrates (Table 1), possibly because the more accessible acidic centres on the catalyst surface in the former case are quickly deactivated by water liberated as a result of the reaction (Scheme 1). The carboxylic acids formed in nitrations by acyl nitrates obviously do not lead to such deactivation.

The data given in Tables 1 and 2 indicate that zeolite catalysts produce an essential effect on the regioselectivity of substitution. Nitration of toluene with acetyl nitrate in hexane without any catalyst leads to a low yield of nitrotoluene mixture with a high content of the meta isomer. This possibly indicates the free-radical mechanism of the reaction proceeding in non-polar media in the absence of any catalyst¹⁴ (cf. Ref 20). With conventional nitration systems, the predominant para ortho orientation of substitution is characteristic of reactions proceeding by an electrophilic substitution mechanism.¹⁴ The same orientation persists in the nitration of 2 with nitric acid and acyl nitrates in the presence of aluminosilicate catalysts (Table 2). Remarkably, the *para* ortho ratio of nitrotoluenes increases from amorphous aluminosilicate to wide-pore zeolite Y and further to medium-pore ZSM-11. An even higher *para* ortho ratio was observed when the surface acid centres of H-ZSM-11 were neutralized with NBu₃.

The observed effect of zeolite catalysts on the isomer ratio agrees, within the shape selectivity concept, with the occurrence of the reaction in zeolite pores.^{1,2} Changes in positional selectivity in ZSM-11 channels seem to be determined by the fact that transition states

x	Nitrating agent	Catalyst	<u>k_{PhX}</u> k _{PhH}	Isomer ratio of halonitrobenzenes (%) ^b			
				para	meta	ortho	<i>para ortho</i> ratio
F	MeCOONO ₂	c	0.14 ^d	91 · 3 ^d		8.7 ^d	11
		H-ZSM-11	0.3	93	2	5	19
		H-ZSM-11NBu ₃	0.4	88	5	7	13
Cl	HNO3	H ₂ SO ₄	0.064 °	64°	0 • 94 °	35°	1.8
		H-ZSM-11	0.05	68	27	5	14
	MeCOONO ₂	c	0.033 f	69 · 58	0.98	29.6 ⁸	2.3
	_	h		31	46	23	1.4
		H-Y	0.07	86	2	12	7.2
		H-YNBu ₃	0.1	85	3	12	7.1
		H-ZSM-11	0.08	79	15	6	13
		H-ZSM-11-NBu ₃	0.06	56	40	4	14
	PhCOONO ₂	Amorphous aluminosilicate	0.08	78	2	20	3.9
		H-Y .	0.1	84	3	13	6.5
		H-Y-NBu3	0.15	72	22	6	12
		H-ZSM-11	0.06	90	5	5	18
		H-ZSM-11-NBu ₃	0.07	85	13	2	43
Br	MeCOONO ₂	c	0.03 t	62 · 4 ⁸	1·2 ^g	36.58	1.7
	-	H-ZSM-11	0.07	94	2	4	23
		H-ZSM-11-NBu ₃	0.09	69	28	3	23
I	MeCOONO ₂	c	0·22 ⁸	59·7 ⁸	1 · 8 ^g	38.38	1.6
	-	H-ZSM-11	0.3	89	2	9	10
		H-ZSM-11-NBu3	0.2	86	12	2	43

Table 3. Nitration of halobenzenes PhX^a

^a Data from this work, nitration in hexane, 30 °C (25 °C for HNO₃).

^b From competitive experiments, being independent of the reaction time.

^c Acetic acid is present in the reaction mixture owing to its formation in the course of reaction.

^d From Ref. 27, acetic anhydride at 25 °C.

^e From Ref. 22, 71.2% sulphuric acid at 25 °C.

^fFrom Ref. 18, acetonitrile at 25 °C. ^gFrom Ref. 28, nitromethane at 25 °C.

& Data for the low degree of conversion (3% yield of chloronitronbenzes after 12 h).

formed en route to para- and ortho-substituted products and obviously having different geometries have different energies of interaction with the crystalline environment. The transition state which will be predominantly formed in a constricted channel space is expected to be that where substituent R of the substrate can occupy a position of minimal energy of atom-atom interaction with zeolite channel walls. It would be reasonable to suggest that the contribution of atom-atom repulsion to this interaction will be minimal in para substitution when the substrate's substituent and the electrophilic moiety (E) are located roughly along the channel axis (Scheme 3).

An alternative factor which could give rise to a predominant formation of *p*-nitrotoluene might be the inhibited exit of o- and m-nitrotoluene from zeolite channels as compared with the para isomer having a smaller critical diameter, under conditions of isomer interconversion. Such an effect has been suggested to underlie the higher *para* selectivity of alkylation of alkylbenzenes on zeolites.^{1,2} In our case this is unlikely



in view of the irreversible character of nitration^{11,13} and its mild conditions, under which the nitrotoluenes do not isomerise (cf. Ref 40). Furthermore, it should be noted that on complete destruction of zeolite after nitration no essential changes in the isomer ratio of the products were found. This precludes the possibility of changing the isomer ratio by irreversible adsorption of any isomer on zeolites.

In the reaction of chlorobenzene with acetyl nitrate in hexane without any catalyst, there was insignificant nitration of the substrate, as with toluene, forming a mixture of products with a high meta-isomer content attributable to the free-radical mechanism of the reaction¹⁴ (cf. Ref. 20). With a conventional acid catalyst, the meta-isomer content is insignificant because of the electrophilic mechanism of the substitution reaction. An unexpected isomer ratio was obtained in nitrations of halobenzenes employing zeolite catalysts as acids (Table 3). On the one hand, there is a tendency for an increased para/ortho ratio on passing from solution to zeolite H-Y and further to H-ZSM-11, with the maximum value observed for the latter whose surface was poisoned with NBu₃. This is in agreement with the above data for toluene nitration. Conversely, as opposed to toluene, the meta-isomer content in the nitrohalobenzene mixture is anomalously high, being maximum in the case of H-ZSM-11 treated with NBu₃, where the reaction seems to occur predominantly in the zeolite pores.

It would be reasonable to assume that the mechanisms of zeolite-catalysed nitrations of toluene and halobenzenes are similar and involve an electrophilic attack of the substrate π -system to form a positively charged transition state. This is indicated by the character of the dependence of the reaction rate on the nature of the substituent in the substrate as illustrated in Figure 1 for nitrations with acetyl nitrate on H-ZSM-11 treated with NBu₃. The points proved to be close to the line expressing the previously established⁴¹ correlation of logarithms of the partial rate factors of liquid-phase substitution vs substituent σ^+ -constants ($\rho - 6.5$; HNO₃-H₂SO₄, 25 °C). This indicates localization of significant positive charge on the aromatic ring in the limiting-stage transition state. This transition state can correspond in structure to the Wheland intermediate^{13,14,42} (Scheme 1). Judging from the absence of kinetic isotope effects in the nitration of 1,3,5trideuterobenzene with benzoyl nitrate on H-Y and H-ZSM-11, the stage of proton elimination from the benzenium ion (Scheme 1) is not a limiting one.⁴

The isomer ratios observed in electrophilic substitutions may be explained in terms of the frontier orbital theory.⁴³⁻⁴⁵ This theory explains the predominant *para* orientation in nitrations of toluene and halobenzenes by the higher coefficient values on the *para*- as compared to the *meta*-carbon in HOMOs of these substrates^{44,45} (Figure 2). Under our conditions, the orbital control of reactions is apparently facilitated by the fact that the aromatic substrates ('soft' bases) are nitrated by sufficiently 'soft' electrophiles: the undissociated protonated acyl nitrates or the nitronium cation 'solvated' by the zeolite frame (cf. Ref. 44).

The reason for the higher proportion of the *meta* isomer in nitrations of halobenzenes on H-ZSM-11 may be the changed energies of upper occupied orbitals so that the antisymmetric MO with the greater electron density on the *meta*-carbon as compared to the *para*-carbon becomes the highest in energy. In principle, this



Figure 1. Logarithms of partial rate factor of *para* and *meta* substitution (log f_i) for nitration reactions of compounds 2 and 4–7 with acetyl nitrate on zeolite H-ZSN-11 treated with NBu₃ vs substituent σ^+ constants. In calculating log f_i values, the relative rates of substrate nitration corrected according to equation (1) with the assumption of equality of diffusion coefficients were used

may be induced by the electrostatic field arising in zeolite channels^{46,47} whose strength has been shown to be fairly high.⁴⁸

In order to illustrate the validity of such an assumption, we carried out quantum-chemical MNDO calculations⁴⁸ using the AMPAC program⁴⁹ to simulate external electrostatic field effects by placing point charges around the molecule. The results obtained (Figure 2) show that the external electrostatic field can actually polarize the substituted benzene molecule in such a way that the highest occupied MO will be an orbital of different symmetry. Also, it should be taken into account that the substituted benzene molecules having dipole moments (oppositely directed in toluene and halobenzenes) will be oriented in the field in a definite fashion. According to calculation data on the heat of formation (Figure 2), the most favourable orientation of the chlorobenzene molecule in the model field will arise in the case of antisymmetric HOMO. The toluene molecule will have an opposite orientation in this field, its HOMO being symmetric. Notably, for fluorine as a low-polarisable substituent, the interchange of the two HOMO positions demands a stronger external field. Experimental data (Table 3) show that it is fluorobezene that has the lowest content of the meta



Figure 2. Effect of external electrostatic field on HOMO energies (E) and heats of formation (H) (MNDO calculations) for chlorobenzene, fluorobenzene and toluene

isomer among the halobenzenes nitrated on H-ZSM-11. As Br and I are more bulky substituents than F and Cl (Table 3), the slightly lower proportion of *meta* substitution is probably associated with steric effects due to the reaction inside the zeolite channels.



Figure 3. Data on partial rate factor ratios of *para* and *ortho* nitration of toluene $[\log(f_p|f_o)]$ by nitrating agents (8–11) (R₃COONO₂; R₃ = Me, Et, Ph, *t*-Bu) on NBu₃-treated zeolites H-Y and H-ZSM-11. In calculating the $\log(ft_p|f_o)$ values, we used the relative rates of toluene nitration corrected according to equation (1) with the assumption of equality of diffusion coefficients.

An interesting aspect is the effect of the nature of the nitrating agent on the selectivity of nitration. There is a noteworthy tendency of increasing *p*-nitrotoluene content with increasing the size of substitutent R_3 in the nitrating agent R_3COONO_2 (Me < Et < Ph \approx t-Bu) observed in the presence of zeolite catalysts (Table 2, Figure 3). It should be noted that the value of the *para*to *ortho*-substitution ratio is much more sensitive to the size of R_3 on nitration on H-ZSM-11-NBu₃ than on H-Y-NBu₃. This seems to be a consequence of greater steric requirements for the process in a medium-pore vs large-pore zeolite.

These data suggest that a molecule of the nitrating agent is involved as a whole in the transition state formed at the stage determining the isomer ratio of the products.

The assumption that the attacking electrophiles are the protonated forms of acyl nitrates (structure A or B, Scheme 4) (cf. Ref. 22) is in agreement with the results of MNDO calculations in a molecular approximation⁵⁰ simulating the active centres of the catalyst surface by model molecules. The calculations were performed with full geometry optimization with simulation of the catalytically active centres of the aluminosilicates by structure C (Scheme 4). According to the estimate obtained, the formation of the common electrophile for different nitrating agents, the nitronium cation 'solvated' by the aluminosilicate frame (structure D), is energetically unfavourable (Scheme 4).



CONCLUSION

The data obtained on the selectivity of the nitration of benzene and its derivatives by zeolite-supported nitrating agents indicate the similarity of reaction mechanisms in solution and on the surface of heterogeneous catalysts. Zeolite-supported nitrations may lead to a changed substrate selectivity of the process owing to the different abilities of aromatic molecules to diffuse to reaction sites located inside catalyst's channels ('reagent-shape selectivity'). On the other hand, the zeolite frame can change the regioselectivity of nitration by affecting the energy of transition states leading to different isomers ('restricted transition state shape selectivity') and by polarizing the reactant substrate molecule by the electrostatic field arising in zeolite channels.

EXPERIMENTAL

All the solvents and starting materials were purified by known methods. The characteristics of the organic compounds used agreed with literature data. The following catalysts were used: amorphous aluminosilicate (SiO_2/Al_2O_3) weight ratio = 5.6, Na₂O < 0.05 wt%, specific surface area $S = 360 \text{ m}^2 \text{ g}^{-1}$), zeolite Na-Y made by the Nizhni Novgorod pilot oil industry base $(SiO_2/Al_2O_3 \text{ weight ratio} = 3.5, Na_2O = 7.9 \text{ wt}\%_0, S = 940 \text{ m}^2 \text{ g}^{-1})$, decationized using a standard procedure⁵¹ (SiO_2/Al_2O_3) weight ration = $3 \cdot 5$, $Na_2O = 3.7 \text{ wt\%}, S = 920 \text{ m}^2 \text{ g}^{-1}$, and zeolite H-ZSM-11 made by the Special Design Office Katalizator, Novosibirsk (SiO_2/Al_2O_3) weight ratio = 440. $Na_2O = 0.07 \text{ wt}\%$, $S = 597 \text{ m}^2 \text{ g}^{-1}$). Immediately before use the catalysts were calcined for at 2 h at 500 °C in air.

Hexane solutions of acyl nitrates were prepared immediately before use from the appropriate acyl chlorides and silver nitrate. 20

The nitration reactions were performed according to the following general procedure. To a vigorously stirred suspension of aluminosilicate in hexane at 30 °C (25 °C for nitrations with HNO₃) was added first the nitrating agent (aluminosilicate/nitrating agent weight ratio = 8-10) and then, after stirring for 5 min, the substrate or a tenfold molar excess of equimolar substrate mixture. If necessary, NBu₃ was added to the zeolite before the addition of the acyl nitrate solution (zeolite/amine weight ratio \approx 100). Stirring was continued for 2 h, then the catalyst was filtered off and washed with 25 ml of chloroform. The reaction products were analysed by GLC (flame ionisation detector, 1 m column packed with 15% polydiethylene glycol phthalate on Chromosorb N-AW; special mixtures of products were used for calibration; as nitrobenzene international standard). Occasionally these data were confirmed by ¹H nmr spectra (recorded on a Bruker SF-400 instrument).

In the experiments with zeolite destruction, after standard treatment of the reaction mixture, the catalyst was treated with 0.5 M NaOH solution, then with HF-HClO₄ prepared by mixing equal volumes of 57% perchloric acid and 40% hydrofluorlc acid. Organic compounds were isolated from the resulting solutions by extraction with chloroform and analysed by GLC.

Quantum-chemical calculations were carried out by the MNDO method⁴⁸ using the AMPAC program.⁴⁹ For electrostatic field simulation, point charges were placed within the plane of the aromatic molecule at a distance of 4.5 Å from its symmetry axis at the level of the substituent and benzene ring centre (Figure 2).

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