Zeolite catalysis of aromatic nitrations with dinitrogen pentoxide

Robert P. Claridge,[a] N. Llewellyn Lancaster,[b] Ross W. Millar,[a] Roy B. Moodie *[b] and John P. B. Sandall[b]

[a] *Defence Evaluation and Research Agency, Fort Halsted, Sevenoaks, Kent, UK TN14 7BP*
[b] *Department of Chemistry, University of Exeter, Exeter, UK EX4 4QD*

Received (in Cambridge, UK) 25th June 1999, Accepted 19th July 1999

The reactions of 2-nitrotoluene, 1-chloro-2-nitrobenzene, and 1-chloro-4-nitrobenzene with dinitrogen pentoxide in dichloromethane at 0 °C are strongly catalysed by some zeolites notably H-Faujasite-720, catalysis by which is investigated in detail. Yields of the nitrated aromatics are near-quantitative. In the first two substrates nitration occurs more regioselectively at the 4-position compared to the uncatalysed reaction. The reaction of 1-chloro-2-nitrobenzene shows a kinetic form which is close to first-order with a rate-constant independent of the concentration of N_2O_5 and proportional to the mass of zeolite. Initial addition of the major product, 1-chloro-2,4-dinitrobenzene, causes rate-inhibition. Mechanisms are discussed.

Introduction

The use of zeolites in nitrations of reactive aromatic compounds with acyl[1,2] or alkyl[3] nitrates is an area of active study, and considerable enhancements of regioselectivity have been reported.[1] We were interested in extending these studies to deactivated aromatic compounds and in the use of dinitrogen pentoxide[4] as the nitrating agent, which has not previously been used with zeolites. Initially we chose 2-nitrotoluene as our aromatic substrate. This gives on nitration a mixture of 2,4- and 2,6-dinitrotoluene in an approximately 2:1 ratio in the uncatalysed reaction. A procedure using "Claycop" (montmorillonite clay impregnated with copper nitrate) with acetic anhydride and nitric acid in tetrachloromethane has been described for the nitration of this material,[5] but we have shown that the solid support does not enhance the rate or the selectivity.[6] We now report that certain zeolites, with N_2O_5, can enhance both rate and selectivity in this and related reactions.

Results

The kinetics of nitration of 2-nitrotoluene catalysed by various zeolites

Preliminary tests showed that drying the zeolites was beneficial. A standard procedure of furnace drying of the zeolite under vacuum, with subsequent transfer to a dry glove-box for all further operations, was adopted. To avoid as far as possible concomitant decomposition of the N_2O_5, runs were carried out at the reduced temperature of 0 °C. This was achieved by circulating cooling fluid from an external cold bath through the jacket of the magnetically-stirred reaction vessel in the glove box. Comparison amongst several runs with different zeolites using these procedures is made in Table 1.

The first entry is for the reaction in the absence of zeolite under otherwise standard conditions. Six percent of dinitrotoluenes were formed in 3 h in the expected 2:1 ratio. The H-ZSM 5 zeolite, which has been much used in related reactions,[2,3] did not significantly enhance the rate or the selectivity. H-Mordenite showed promise, but H-Faujasite 720 was better, giving a near quantitative yield 3 minutes after mixing, with a selectivity of 4.3:1 compared to 2:1 for the uncatalysed reaction. The two acid (H) faujasites investigated (720 and 780) differed in their aluminium content, the SiO_2/Al_2O_3 ratios being 30 and 80 respectively. The former gave the better selectivity. The Na form of the zeolite was ineffective. A full description of the structures of these and other zeolites can be found elsewhere.[7]

Rather than investigate a wider range of zeolites, it seemed preferable at this stage to gain more insight into the nature of the reaction involved with H-Faujasite 720. Because the reaction of 2-nitrotoluene was too rapid under our conditions for convenient kinetic study, a more deactivated substrate, 1-chloro-2-nitrobenzene, was chosen for further investigation.

The kinetics of nitration of 1-chloro-2-nitrobenzene catalysed by H-Faujasite 720

In the absence of zeolite there was no observable reaction between this substrate and N_2O_5 in dichloromethane at 0 °C in 2 hours. To provide a background datum therefore the nitration was conducted in a nitric–sulfuric acid mixture and yielded quantitatively a mixture of 1-chloro-2,4- and -2,6-dinitrobenzene in 10.6:1 molar ratio. In the zeolite-catalysed

Table 1 Comparisons of furnace-dried zeolites for nitration of 2-nitrotoluene at 0 °C

Zeolite	$[N_2O_5]$	Time	R[a]	Conversion[b]	Yield[c]
None	0.28	3 h	1.9	6	95
H-ZSM-5	0.17	1.5 h	2.0	7	96
H-Mordenite	0.17	15 min	3.3	85	93
H-Faujasite 780	0.18	3 min	3.6	88	95
H-Faujasite 720	0.17	3 min	4.3	92	94
Na-Faujasite	0.17	1 h	3.0	16	95

[a] R = Yield of 2,4-dinitrotoluene/yield of 2,6-dinitrotoluene. [b] Combined yields of dinitrotoluenes as a percentage of the initial 2-nitrotoluene. [c] The sum of the yields of 2-nitrotoluene and the dinitrotoluenes as a percentage of the initial 2-nitrotoluene.

Table 2 First-order rate constants k and specific constants k_z ($k_z = k/z$) in the reaction of 1-chloro-2- and -4-nitrobenzene (initial concentration 0.10–0.12 mol dm^{-3}) with N_2O_5 at 0 °C in dichloromethane (6–7 cm^3) in the presence of a mass z of H-Faujasite 720

$[N_2O_5]^a$/ mol dm^{-3}	[2,4-DNCB]^b/ mol dm^{-3}	$[HNO_3]^b$/ mol dm^{-3}	z/mg	$k/10^{-3}$ s^{-1} ± 5%	$k_z/10^{-3}$ s^{-1} g^{-1}
1-Chloro-2-nitrobenzene					
0.434	0	0	151	2.67	17.6
0.353	0	0	149	2.17	14.6
0.230	0	0	144	2.83	19.6
0.160	0	0	144	2.17^c	15.1
0.157	0	0	144	3.00^c	20.8
0.230	0	0	10	0.217	21.7
0.260	0	0	50	0.933	18.7
0.260	0	0	59	1.02	17.3
0.230	0	0	387	(11.7)^d	(30)^d
0.214	0	0.11	152	2.17	14.3
0.230	0	0.23	43	0.517	12.0
0.260	0.025	0	50	0.267	5.34
0.267	0.088	0	143	1.03^e	7.2
0.220	0.10	0	160	0.830	5.2
0.230	0.10	0	41	0.250	6.1
0.220	0.22	0	60	0.283	4.7
1-Chloro-4-nitrobenzene					
0.230	0	0	358	0.167	0.466
0.230	0	0	148	0.072	0.486

[a] Initial concentration of N_2O_5. [b] Initial concentration of a product. [c] These reactions did not go to completion; see text. [d] This reaction was too fast for accurate determination of the rate constant by the method used; k ± 30%. [e] The zeolite in this run had already been used; see text.

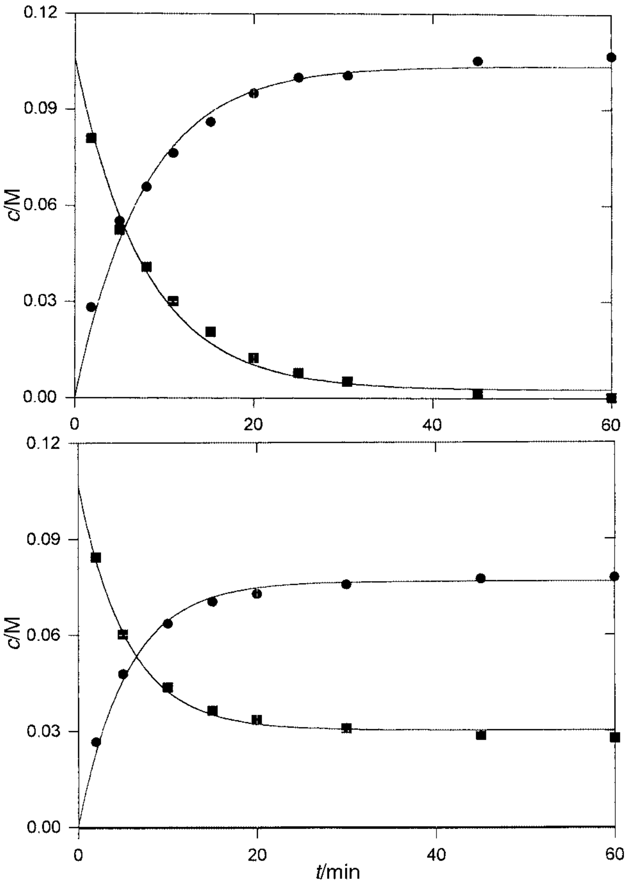

Fig. 1 Graphs of concentration c against time t in the nitration of 1-chloro-2-nitrobenzene by N_2O_5 in the presence of H-Faujasite 720. Circles: 1-chloro-2-nitrobenzene. Squares: 1-chloro-2,4-dinitrobenzene plus 1-chloro-2,6-dinitrobenzene, of which >95% is the former. Curves are computer fitted first-order curves. Upper graph, $[N_2O_5] = 0.353$ mol dm^{-3}, $z = 149$ mg. Lower graph, $[N_2O_5] = 0.157$ mol dm^{-3}, $z = 144$ mg. Conditions as in Table 2.

reactions described below the conversion to 1-chloro-2,4-dinitrobenzene was nearly quantitative; the selectivity was greater than 20 : 1. Clearly the zeolite-catalysed reaction is more selective than that in mixed acid. Examples of concentration–time profiles for the reaction of 1-chloro-2-nitrobenzene with dinitrogen pentoxide in dichloromethane catalysed by H-faujasite 720 are given in Fig. 1. Several points of interest follow from these and similar profiles: a) the zeolite is strongly catalytic (no reaction occurred in its absence). b) The disappearance of aromatic reactant, and the appearance of the dinitrochlorobenzene product, fitted simultaneously, conform quite closely to a first-order rate law as exemplified in Fig. 1 where the curves through the experimental points are computer best-fits to such a rate law. The close to first-order nature of the reaction was unexpected because the reaction is heterogeneous, likely to have a mechanism that is far from simple, and one of the reagents is not present in a large excess over the other. The near-adherence to such a kinetic form means that the rates of reactions under a variety of conditions can be compared satisfactorily by means of their fitted first-order rate constants. These are in Table 2. c) The reaction is quantitative provided that the initial ratio of concentrations of N_2O_5 and 1-chloro-2-nitrobenzene is greater than 2 : 1. Reactions with less than a 2-fold equivalence of N_2O_5 (one such is illustrated in Fig. 1) became very slow before all the reactant had all been consumed. d) The first order rate-constants are approximately independent of the initial concentration of N_2O_5, and proportional to the mass of zeolite used. This is illustrated by the specific constants k_z obtained by dividing the first order rate constants by the mass of zeolite. Values of k_z vary little for a range of concentrations of N_2O_5 and masses of zeolite (first 9 runs listed in Table 2.) e) The last 7 runs listed under 1-chloro-2-nitrobenzene in Table 2 were conducted in order to discover if either or both of the products of the reaction were inhibitory. It is clear from the values of k_z that initial addition of nitric acid has only a marginal inhibitory effect. This result is important because it means that the rigorous drying procedures used here for zeolite, solvent dichloromethane and N_2O_5 could be circumvented, with little loss in rate, if one were to sacrifice a sufficient excess of N_2O_5 to react with the water present. Initial addition of 1-chloro-2,4-dinitrobenzene had a more pronounced but still modest inhibitory effect, concentrations up to 0.22 mol dm^{-3} causing a *ca.* 3 fold decrease in the value of k_z. A run in which substrate

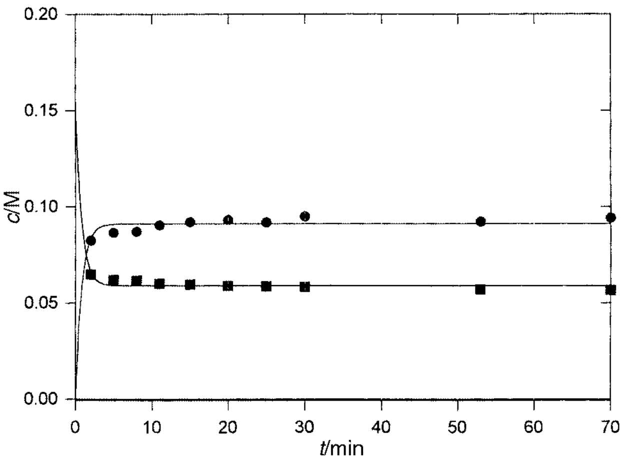

Fig. 2 Graph of concentration *c* against time *t* in the nitration of 2-nitrotoluene by N_2O_5 (initial concentrations both 0.155 mol dm^{-3}) in the presence of H-Faujasite 720 (100 mg). Circles: 2-nitrotoluene. Squares: 2,4-dinitrotoluene plus 2,6-dinitrotoluene, formed in a constant ratio of 4.3 : 1.

was converted completely into product by allowing 10 half-lives for reaction, followed by recharging the reaction mixture with N_2O_5 and aromatic substrate, proceeded at the rate expected when this inhibition is taken into account. This shows that the zeolite can be re-used without significant loss of catalytic activity (see run with footnote *e* in Table 2).

In an attempt to discover if the inhibition by aromatic product was connected with slow diffusion, or desorption, of the product from the pores of the zeolite, the reaction of 1-chloro-4-nitrobenzene, which gives the same product, 2,4-dichloro-1-nitrobenzene, was investigated.

The kinetics of nitration of 1-chloro-4-nitrobenzene catalysed by H-Faujasite 720

This reaction was found to yield 1-chloro-2,4-dinitrobenzene quantitatively but much more slowly. The reaction again conformed quite closely to a first-order rate law, though these slow reactions were followed for only 2 half-lives. Two runs with different masses of zeolite gave the same value k_z within experimental error, and this was approximately 40 times smaller than the corresponding quantity for 1-chloro-2-nitrobenzene.

The stoichiometry of the nitration of 2-nitrotoluene catalysed by H-Faujasite 720

The apparent failure of the reactions of 1-chloro-2-nitrobenzene to go to completion when there was less than a two-fold excess of N_2O_5 over aromatic substrate led us to re-examine the much faster reaction of 2-nitrotoluene, but now under equimolar conditions. Reactions with different masses of zeolite gave closely similar results, typified in Fig. 2.

Approximately 60% of the aromatic substrate reacted within 2 minutes, and a further 4% reacted in the next 68 minutes. Clearly there is an initial fast reaction, but then a much slower reaction sets in. This slower reaction is not that of nitric acid; separate studies showed that there was no reaction at all between 2-nitrotoluene and nitric acid with or without the zeolite under the same conditions.

Discussion

The rates of reaction of 2-nitrotoluene, 1-chloro-2-nitrobenzene, and 1-chloro-4-nitrobenzene in dichloromethane with N_2O_5 are very markedly enhanced by H-Faujasite 720. The mechanism of this zeolite-catalysed reaction is likely to be complex, and not all the results reported above are readily interpreted; much more work will be necessary before a clear picture emerges. However several useful indications arise from the results. The reaction is heterogeneous, yet the results are independent of stirring rate which indicates that this is not an important parameter. The close to first-order nature of the reaction, the proportionality of the first-order rate constant to the mass of zeolite used, and the independence of the same quantity of the concentration of N_2O_5, all point to a mechanism of the type outlined in Scheme 1. In this scheme A represents the aromatic reactant and P the aromatic product(s).

$$ZH + N_2O_5 \xrightleftharpoons{\text{fast}} ZN + HNO_3$$

$$ZN + A \xrightarrow{\text{slow}} ZH + P$$

Scheme 1

The potential sites on the zeolite for reaction are called ZH and these are converted to an active nitrating form ZN by reaction with N_2O_5. With the first step a fast pre-equilibrium with the equilibrium position lying well to the right, and the second step slow and rate-determining, a constant number of active sites ZN would remain throughout the reaction because each site when freed by reaction with A would be immediately reactivated to ZN by N_2O_5. This would lead to the disappearance of aromatic substrate and the appearance of aromatic product following a first-order rate law, with a rate constant independent of the concentration of N_2O_5 but proportional to the mass of zeolite used, as observed.

The mechanism in Scheme 1 whilst providing a satisfactory outline for explaining the main features of the mechanism, leaves unexplained the slight rate retardation by initial addition of nitric acid, and the more significant retardation by the initial addition of the aromatic product. The fact that 2- and 4-nitro-1-chlorobenzene give the same aromatic product but react at different rates rules out rate determining desorption of the aromatic product. It may be that there are rapid adsorption–desorption equilibria of the products which decrease the number of available active sites. Further progress in understanding these phenomena must await a separate investigation of these equilibria.

A more difficult feature to explain is the apparent failure of the reaction to go to completion when initially the N_2O_5 is present in less than a *ca.* 2-fold excess over the aromatic substrate. Our results (see Fig. 2) show that this is not a genuine 2 : 1 stoichiometry. The reaction with initially equimolar reagents does not come to a complete halt when 50% of the aromatic has been consumed, but slows down dramatically when about 60% has reacted. The slow reaction which follows is not with nitric acid. (Separate studies show that there is no reaction between the aromatic and nitric acid under the conditions.) This observation makes it unlikely that the result is entirely due to hydrolysis of some of the N_2O_5 to nitric acid by adventitious water. Another explanation, that there is catalysed decomposition of the N_2O_5 on the zeolite occurring on the same time scale as the reaction, can be ruled out because there was no loss of reactivity when the slurry containing zeolite and N_2O_5 was kept for 40 minutes rather than the usual 10 minutes before addition of the aromatic substrate. We have also shown that the zeolite can be re-used immediately in the same solution without loss of reactivity, so deactivation of the zeolite does not occur.

It is possible that when the concentration of N_2O_5 drops, the activation of the zeolite (first step in the scheme) is no longer sufficiently rapid or extensive to maintain a constant number of activated sites ZN.

This work does not cast light on the nature of the activated site nor on the nature of the nitration step. It is significant however that the relative reactivity of 2- and 4-nitro-1-chlorobenzenes is similar to that in normal nitronium ion nitration, which gives an indication that in the reaction the activated site may provide an incipient nitronium ion for reaction. There is no reason to suppose the reaction is radical in character.

Experimental

Materials

Dichloromethane was dried by distillation in silanised vessels from calcium hydride. Dinitrogen pentoxide[8] and anhydrous nitric acid[9] were prepared as described. 1-Chloro-2-nitrobenzene, 1-chloro-4-nitrobenzene, 1-chloro-2,4-dinitrobenzene, 3,5-dichloro-1-nitrobenzene, 2-nitrotoluene, 2,4-dinitrotoluene, and 2,6-dinitrotoluene were used without further purification.

Zeolites H-ZSM-5, H-Faujasite 720, and H-Faujasite 780 had SiO_2/Al_2O_3 ratios of 1000, 30, and 80 respectively and were obtained from Zeolyst International. H-Mordenite and Na-Faujasite had SiO_2/Al_2O_3 ratios of 2.5 and 9 respectively and were obtained from LaPorte Inorganics.

Drying zeolites

In all cases zeolites were dried before use by the following procedure: the zeolite (*ca.* 0.5 g) was put into a glass boat inside a tube attached to vacuum (<0.01 mmHg). This assembly was heated steadily to 350 °C using a tube furnace. This temperature was maintained (± 10 °C) for one hour, then the zeolite was allowed to cool steadily, still under vacuum. When the zeolite had reached room temperature, the system was sealed under vacuum and the tube containing the zeolite was transferred to the dry glove box, ready to use.

GC conditions and response factors

The Pye Unicam PU4500 chromatograph was fitted with a PU4700 autojector. The column was 7 foot long, packed with Dexsil 400 (10%). Each sample was analysed 4 times. The nitrogen flow rate was 40 $cm^3\ min^{-1}$; injection port was at 230 °C, column was at 200 °C; detector was at 250 °C. The internal standard used throughout was 3,5-dichloronitrobenzene. Compounds (retention times/minutes, response factors) were as follows: 3,5-dichloro-1-nitrobenzene (3.8, 1), 2-nitrotoluene (2.2, 1.163), 2,4-dinitrotoluene (9.2, 1.014), 2,6-dinitrotoluene (6.2, 1.065), 1-chloro-2-nitrobenzene (3.1, 0.978), 1-chloro-4-nitrobenzene (3.0, 0.902), 1-chloro-2,4-dinitrobenzene (9.8, 0.859), 1-chloro-2,6-dinitrobenzene (10.1, 0.824).

The nitration of 2-nitrotoluene

In a dry glove box, dried zeolite (0.05 g) and a magnetic follower were put into the jacketed reaction vessel, through the jacket of which was pumped cooling fluid from an external thermostat. Dinitrogen pentoxide (0.1 g, 1 mmol) in dichloromethane (5 cm^3) was added and stirred. After 10 minutes, a solution of 2-nitrotoluene (0.11 g, 0.802 mmol) and 3,5-dichloro-1-nitrobenzene (0.04 g, 0.208 mmol, GC reference standard) in dichloromethane (1 cm^3) was added.

Samples (*ca.* 0.5 cm^3) were taken by pipette, put into a sample tube and then removed from the glove box before quenching into saturated sodium hydrogen carbonate solution (20 cm^3) with dichloromethane (2 cm^3). The organic layer was separated and then analysed by GC. The total time from taking a sample to quenching was typically 60 seconds.

The nitrations of 2- and 4-nitro-1-chlorobenzenes in the presence of zeolite

The procedure was similar except that in most cases samples (*ca.* 0.5 cm^3) were taken by syringe and quenched immediately by injection into saturated sodium hydrogen carbonate solution (20 cm^3) with dichloromethane (2 cm^3) through a subaseal into containers in the glove box. The organic layers were subsequently separated and analysed by GC. The products from the nitration of 1-chloro-2-nitrobenzene were 1-chloro-2,4- and -2,6-dinitrobenzene and these were analysed together being insufficiently separated on GC. Separate NMR investigation revealed that in all cases the 2,4- to 2,6-ratio exceeded 20 : 1. It was not more precisely determined.

Where either nitric acid or 1-chloro-2,4-dinitrobenzene were added, these were introduced 10 minutes after addition of dinitrogen pentoxide. Stirring was maintained for a further 10 minutes before addition of the substrate.

The nitration of 1-chloro-2-nitrobenzene by mixed acid

Sulfuric acid (100 cm^3, specific gravity 1.84) was poured into a round bottom flask (250 cm^3) and stirred. Nitric acid (10 cm^3, 70%) was added carefully and a calcium chloride guard tube was fitted. To this mixture at room temperature was added 1-chloro-2-nitrobenzene (0.115 g, 0.727 mmol) in acetonitrile (5 cm^3). After 3 hours the mixture was quenched in ice–water (*ca.* 500 cm^3). The products were extracted with dichloromethane (4 × 10 cm^3) and combined before being treated with sodium hydrogen carbonate solution (30 cm^3, saturated solution) and separated; then with water (20 cm^3) and separated. Dichloromethane was removed from the organic layer and the residue dissolved in deuterated chloroform and analysed by ^1H NMR (300 MHz).

Acknowledgements

We thank the Defence Evaluation and Research Agency for support, and Zeolyst International, Inc for the gift of samples of zeolites.

References

1 K. Smith, A. Musson and G. A. DeBoos, *Chem. Commun.*, 1996, 469.
2 S. M. Nagy, K. A. Yarovoy and V. G. Shubin, *J. Phys. Org. Chem.*, 1994, **7**, 385.
3 T. J. Kwok, K. Jayasuriya, R. Damavarapu and B. W. Brodman, *J. Org. Chem.* 1994, **59**, 4939.
4 J. W. Fischer, in *Nitro Compounds, Recent Advances in Synthesis and Chemistry*, H. Feuer and A. T. Nielson, Eds., VCH, New York, 1990.
5 B. Gigante, A. O. Prazeres, M. J. Marcelo-Curto, A. Cornelis and P. Lazlo, *J. Org. Chem.*, 1995, **60**, 3445.
6 N. L. Lancaster, R. B. Moodie and J. P. B. Sandall, *J. Chem. Soc., Perkin Trans. 2*, 1997, 847.
7 J. V. Smith, *Chem. Rev.*, 1988, **88**, 149.
8 R. J. Lewis and R. B. Moodie, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1315.
9 K. A. Hylands and R. B. Moodie, *J. Chem. Soc., Perkin Trans. 2*, 1996, 2073.

Paper 9/05118J