Catalysis Letters 69 (2000) 113–116

Reaction of N-phenylhydroxylamine in the presence of clay catalysts

Dana Grošková, Magdaléna Štolcová and Milan Hronec

Department of Organic Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovak Republic
E-mail: dgroskova@hotmail.com; stolcova@chtf.stuba.sk

Received 21 March 2000; accepted 7 July 2000

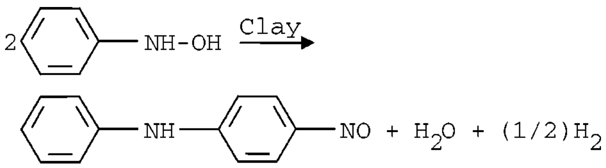
The condensation reaction of N-phenylhydroxylamine in the presence of clay catalysts was studied. The main products of this reaction are azoxybenzene, aniline and nitrosobenzene. In contrast with the previously published results, p-nitrosodiphenylamine is not formed during the condensation reaction.

Keywords: N-phenylhydroxylamine, montmorillonite, clay catalysts, rearrangement, nitrosobenzene, azoxybenzene

1. Introduction

N-phenylhydroxylamine (N-PHA) is an unstable substance, which easily undergoes redox disproportionation reactions or rearrangement in dependence on pH of the medium and the catalyst used. Reactions of N-PHA in neutral and basic media lead to the formation of aniline, nitrosobenzene, nitrobenzene and azoxybenzene [1–6] and in the presence of inorganic acids to p-aminophenol [7,8].

Recently Naicker et al. [9] have described an unexpected formation of p-nitrosodiphenylamine from N-phenylhydroxylamine in the presence of montmorillonite K10 clay as catalyst:



The authors propose that the mechanism of this reaction involves protonation of the –NHOH group by the Brønsted acid sites, followed by the attack of a second molecule of N-PHA resulting in the formation of a dimeric intermediate which simultaneously loses hydrogen. The formed p-nitrosodiphenylamine is in the presence of some cation-exchanged clays the only reaction product obtained with almost 100% yield.

Hydrogenation of p-nitrosodiphenylamine leads to p-aminodiphenylamine, which is industrially a very important material for the synthesis of rubber antioxidants and antiozonants.

The present paper describes the study of N-phenylhydroxylamine condensation under various reaction conditions in the presence of similar clay catalysts as Naicker et al. described [9].

2. Experimental

2.1. Reagents and catalysts

N-phenylhydroxylamine was prepared by the reduction of nitrobenzene at 65 °C with zinc dust in the presence of an aqueous solution of ammonium chloride [10]. The raw N-phenylhydroxylamine was crystallized from benzene and its purity checked by HPLC and NMR analyses.

Montmorillonite K10 (surface area 240 $m^2\,g^{-1}$) and KSF clays (surface area 35 $m^2\,g^{-1}$) were used as recieved (Aldrich). Bentonite (surface area 85 $m^2\,g^{-1}$, Slovak Republic) was activated 1 h with 1 N HCl at 80 °C. Their cation-exchanged forms were prepared by the procedure given in [9]: sodium exchanged clay (1 g) was mixed with 25 ml of 1 M Mn(II) nitrate solution and stirred at room temperature for 3 days. The solution was filtered, washed repeatedly with distilled water and dried overnight in an oven at 100–110 °C.

Zeolite H-mordenite with module 14.5 (Zeolon 100 H, Norton) was activated 5 h at 450 °C.

2.2. Reaction procedure

The experiments were carried out exactly according to the reaction procedure described in [9]: to 0.2 g of N-phenylhydroxylamine in 2 ml of distilled water (or methanol, ether, dichloromethane, aniline), 0.2 g of clay material was added and the reaction mixture was stirred at ambient temperature for 15–30 min. After reaction, the reaction mixture was treated by two different methods:

Method A: the reaction mixture was extracted (3 × 20 ml) with tetrachloromethane. The solvent was removed under reduced pressure and the residue dissolved in methanol and analyzed by HPLC.

Method B: the reaction mixture was dissolved in methanol and analyzed by HPLC.

For solid state reaction (in the absence of a solvent) 0.2 g of the substrate was mixed with 0.2 g of the catalyst. The reaction mixture was treated as described above.

2.3. Analysis

The analyses of reaction mixtures were carried out on a Shimadzu LC-10AD high performance liquid chromatograph equipped with a photodiode-array detector SPD-M10Avp. Compounds were separated on a reverse phase column (Separon CGX RPS 150 × 3.6 ID mm, partical size 7 μm) with a guard column (30 × 3.6 ID mm) filled with the same phase. The composition of the mobile phase was methanol : 25 mM aqueous solution of potassium *tert*-citrate = 45 : 55 (vol) with elution gradient up to the content of methanol 83%. The flow rate of the mobile phase was 0.6 ml min^{-1}. The individual compounds were detected at the following wavelengths: aniline at 230 nm, nitrobenzene at 260 nm, nitrosobenzene and diphenylamine at 280 nm, azoxybenzene and azobenzene at 317 nm. For quantitative analysis an internal standard was used.

The purity of N-phenylhydroxylamine and the presence of compounds in the reaction mixture were confirmed by NMR technique (Varian VXR-300). Samples were dissolved in CD_3OD at a concentration of 5 mg ml^{-1} and measured at ambient temperature.

3. Results and discussion

In the preliminary study, the rearrangement of N-phenylhydroxylamine catalyzed by montmorillonite K10 in the presence and in the absence of distilled water was studied [9]. To our surprise, neither the production of p-nitrosodiphenylamine nor Bamberger rearrangement products were observed. Instead of p-nitrosodiphenylamine, aniline (AN), nitrosobenzene (NOB) and azoxybenzene (AOB) were determined as the main products of this reaction. p-aminophenol, the product of the Bamberger reaction, was absent in the reacion mixture.

In table 1 the results of the N-phenylhydroxylamine reaction catalyzed by monmorillonite K10 are given.

In the absence of a solvent the main reaction products are aniline and azoxybenzene at total conversion of N-phenylhydroxylamine. No formation of nitrosobenzene was confirmed. The product distribution is practically independent of the method of reaction mixture treatment.

Table 1
The product distribution in the reaction catalyzed by montmorillonite K10.[a]

Solvent	N-PHA conv. (%)	Selectivity (%)		
		Aniline	NOB	AOB
–[b]	100	32.1	0	39.7
–[c]	100	27.9	0	35.6
Water[b]	100	27.2	0	42.4
Water[c]	19.1	34.0	30.9	24.1

[a] Conditions: 0.2 g N-PHA, 0.2 g montmorillonite K10, 2 ml of water, $T = 25\,^\circ$C, reaction time 15–30 min.

[b] Method A.

[c] Method B.

On the other hand, when distilled water was used as a solvent, the treatment of the reaction mixture has a significant influence on the product distribution. Thus, in the sample extracted into CCl_4 no nitrosobenzene was detected (at total conversion of N-phenylhydroxylamine), but when the reaction mixture was not extracted before analysis, nitrosobenzene was detected. In this case the conversion of N-phenylhydroxylamine was only 19.1% and the selectivity to nitrosobenzene 30.9%.

The obtained results indicate that also during sample treatment the transformation of N-PHA to various products proceeds. From these reasons the reaction mixtures were analyzed without extraction into tetrachloromethane.

The failure of p-nitrosodiphenylamine synthesis from N-phenylhydroxylamine under the given conditions prompted us to investigate the effect of other clay catalysts and various solvents on N-phenylhydroxylamine rearrangement. The results summarized in table 2 show that the reaction mixtures always contain only aniline, nitrosobenzene and azoxybenzene as the reaction products. However, the distribution of obtained products and the conversion of N-phenylhydroxylamine depend on the catalyst and the solvent used. No relationship between the polarity of the solvent and the formation of the reaction products was found. The highest amount of nitrosobenzene is formed in water and methanol as solvents, but in aniline as a solvent this compound is practically not formed.

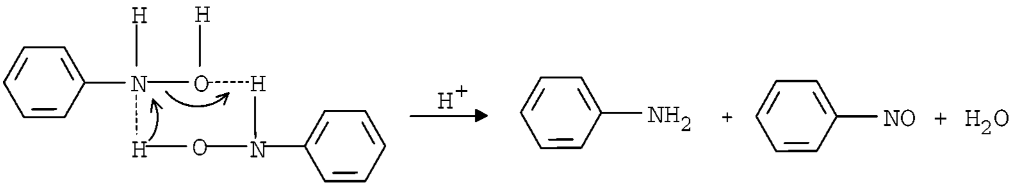
p-nitrosodiphenylamine is not the reaction product either with other clay materials or H-mordenite as the catalysts (table 3).

The present study of N-PHA reaction catalyzed by solid catalysts confirms that the disproportionation of N-PHA to aniline and nitrosobenzene is the preferred reaction (scheme 1) [11,12]. However, under the reaction conditions the reactivity of the obtained products leads to azoxybenzene as a consecutive product. In dependence on the pH of the medium the formation of azoxybenzene probably proceeds by two simultaneous ways (scheme 2) [13–15]. While in an acidic medium the condensation of N-PHA with protonated nitrosobenzene becomes important (mech-

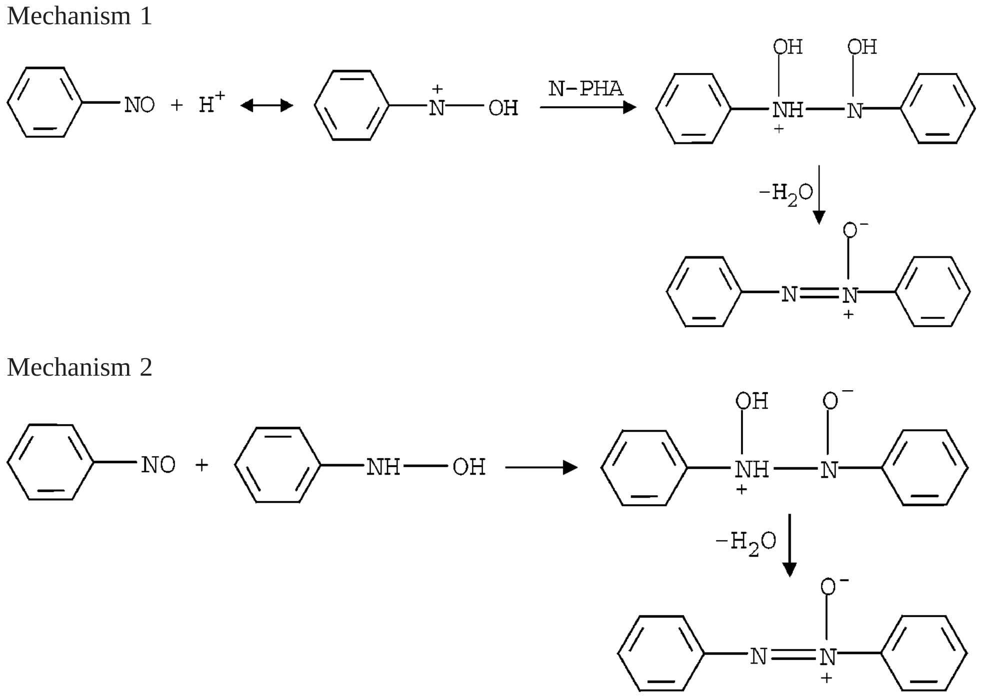
Table 2
The effect of the solvent on the product distribution.[a]

Solvent	N-PHA conv. (%)	Selectivity (%)		
		Aniline	NOB	AOB
Toluene	100	34.3	9.0	41.8
Dichloromethane	56.3	9.8	7.6	17.8
Diethyl ether	69.4	19.9	4.8	76.2
Methanol	43.9	24.4	12.1	49.4
Water	19.1	34.0	30.9	24.1
Aniline	100	–	0	60.7

[a] Conditions: 0.2 g N-PHA, 0.2 g montmorillonite K10, 2 ml of solvent, $T = 25\,^\circ$C, reaction time 30 min, method B for analysis.



Scheme 1.


Mechanism 1

Mechanism 2

Scheme 2.

Table 3
The reaction of N-phenylhydroxylamine in the presence of solid catalysts.[a]

Catalyst	Solvent	N-PHA conv. (%)	Selectivity (%)		
			Aniline	NOB	AOB
Mont. KSF	–	72.1	27.7	3.2	69.6
Mont. KSF	Water	51.4	47.1	8.3	54.9
Bentonite	–	57.8	14.4	17.8	27.3
Bentonite	Water	51.9	14.5	18.3	69.2
Bentonite-Mn^{2+}	–	45.1	6.9	16.0	82.7
Bentonite-Mn^{2+}	Water	38.8	0	42.3	59.3
H-mordenite	–	65.3	0	5.4	3.5
H-mordenite	Water	95.8	0	6.7	56.8

[a] Conditions: 0.2 g N-PHA, 0.2 g of catalyst, 2 ml of water, $T = 25\,^{\circ}$C, reaction time 15–30 min, method B for analysis.

anism 1), in a neutral medium the reaction of free N-PHA with free nitrosobenzene is predominant (mechanism 2). The rate of N-PHA condensation with nitrosobenzene is proportional to the concentration of both reactants and varies depending on the pH of the medium [15].

In some experiments, the sum of determined products (HPLC method) is much lower than 100%. This is probably caused by consecutive reactions of primarily formed reaction products. It is known [16] that azoxy compounds and amines easy undergo polymerization reactions.

4. Conclusions

The presented study of N-phenylhydroxylamine reaction in the presence of clay type catalysts has confirmed that N-phenylhydroxylamine is an extremely reactive compound which is easily disproportionated by a redox reaction to aniline, nitrosobenzene and azoxybenzene. Under the same reaction conditions and in the presence of similar clay catalysts as were described by Naicker et al. [9], *p*-nitrosodiphenylamine is not the product of the studied reaction.

References

[1] Y. Ogata and T. Morimoto, J. Org. Chem. 53 (1965) 3118.
[2] E.L. Pitara, B. N'Zemba, J. Barbier, F. Barbot and Miginiac, J. Mol. Catal. A 106 (1996) 235.
[3] A. Nose and T. Kudo, Chem. Pharm. Bull. 29 (1981) 1159.
[4] C.J. Casewit, D.E. Coons, L. Wright, W.K. Miller and M.R. DuBois, Organometallics 5 (1986) 951.
[5] V.M. Belousov, G.I. Korenyako and O.M. Negomedzyanova, Kinet. Katal. 17 (1979) 74.
[6] T. Sone, Y. Tokuda, T. Sakai, S. Shinkai and O. Manabe, J. Chem. Soc. Perkin Trans. II (1981) 298.
[7] E. Bamberger, Berichte 27 (1894) 1347.

[8] K. Shudo, T. Ohta and T. Okamoto, J. Am. Chem. Soc. 103 (1981) 645.
[9] K.P. Naicker, K. Pitchumani and R.S. Varma, Catal. Lett. 54 (1998) 165.
[10] A.H. Blatt, *Organic Synthesis*, Vol. I (Wiley, 1961) p. 445.
[11] I.A. Makaryan, V.I. Sauchenko and K.A. Brikenshtein, Izv. Akad. Nauk SSSR Ser. Khim. 4 (1983) 760.
[12] R.C. White, T. Selvam, H. Ihmesl and W.J. Adam, Photochem. Photobiol. A 122 (1999) 7.
[13] M.G. Pizzolatti and R.A. Yunes, J. Chem. Soc. Perkin Trans. II 5 (1990) 759.
[14] A. Darchen, C. Moinet and D. Goulian, Bull. Soc. Chim. Fr. (1976) 812.
[15] Y. Ogata, M. Tsuchida and Y. Takagi, J. Am. Chem. Soc. 79 (1957) 3397.
[16] S. Hashimoto, Proc. Faculty Eng. Keiogijuku Univ. 1 (1948) 32.