Amination of benzene and toluene with hydroxylamine in the presence of transition metal redox catalysts

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Abstract

The amination of benzene and toluene to aniline and toluidines with hydroxylamine sulfate has been investigated in water–acetic acid and water–acetic acid–sulfuric acid media in the presence of transition metal compounds as catalysts. The process yields are strongly dependent on the temperature, added sulfuric acid and the composition of catalyst. For the amination of benzene, the soluble catalysts, $NaVO_3$ and Fe(III) salts produce high yields of aniline without addition of H_2SO_4, whereas Na_2MoO_4 and $FeSO_4$ exhibit substantial activity only in 5 M H_2SO_4. Amination is accompanied by a disproportionation of hydroxylamine catalyzed by the redox active transition metal ions. The favorable effect of H_2SO_4 on the amination is due mostly to the greater stability of hydroxylamine in the strongly acidic medium. Mixed oxides containing V(V) and Mo(VI) are active amination catalysts when suspended in 5 M solution of H_2SO_4 in acetic acid. Introduction of metallic Pd into these oxide catalysts improves performance increasing the yield and selectivity of amination with respect to the aromatic substrate. Toluene exhibited a close to benzene reactivity in amination giving approximately equal yields of *o*-, *m*-, *p*-toluidines. Mechanistic considerations based on literature data and results of ab initio quantum mechanics calculations suggest that the aminating species is the protonated amino radical $\cdot NH_3^+$, which in the rate-determining step reacts with benzene and toluene to yield the corresponding aminocyclohexadienyl and aminomethylcyclohexadienyl radical intermediates. These are then oxidatively aromatized to give, respectively, aniline and a non-regiospecific mixture of toluidines. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Benzene amination; Hydroxylamine; Acid media catalysis

1. Introduction

The conventional route to aromatic amines is through nitration of the aromatic substrate followed by hydrogenation of the nitro group. A direct amination of benzene with ammonia has been realized in the gas phase and over Ni/NiO cataloreactants [1,2], or in the presence of Group VIII metal catalysts [3]. Both processes are characterized by only very low yields, even at extreme conditions of temperature and pressure. More productive direct syntheses of aromatic amines can be realized in liquid media with aminating reagents of general formula R_2NX, where

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R is H or alkyl and X is a halogen, OH or OSO_3H group, in the presence of electron-rich species [4,5]. For instance N-chloroalkylamines $ClNR_2$ act as very effective aminating reagents in the presence of Fe(II), Ti(III), Cu(I), Cr(II) salts. The reactions are carried out under mild conditions and characterized by a high rate and selectivity (e.g., Ref. [6]). Recent research progress on a direct synthesis of hydroxylamine by the oxidation of ammonia with hydrogen peroxide in the presence of Ti-silicalite [7] stimulated our interest in its potential use for the amination of benzene. The amination of aromatics with hydroxylamine NH_2OH is known and usually, stringent conditions are required to give only modest results. Several catalytic systems have been examined utilizing hydroxylamine: BF_3 in anhydrous HF [8]; $FeSO_4$, $VOSO_4$, V_2O_5 or $(NH_4)_2MoO_4$ in concentrated H_2SO_4 [9–14] or in a mixture of H_2SO_4 and acetic acid [15]. No information is available on other catalysts and of mechanistic details for the amination of aromatic substrates with hydroxylamine. Significantly, all the aminations were done in relatively strong acid media.

The present study was focused on finding systems for the catalytic amination of benzene and toluene, with hydroxylamine sulfate in reaction media of minimal acidity, and possibly, even without the use of sulfuric acid. A synthesis of the aromatic amines in such media would facilitate the separation and recovery of these products as the free bases. The performance of a number of catalysts and the effect of various reaction conditions were investigated. Some of the new catalyst compositions exhibited better performance than previously known systems.

2. Experimental

2.1. Preparation of catalysts

Various transition metal compounds were tested as homogeneous catalysts for benzene and toluene amination. Analytical grade $NaVO_3 \cdot 2H_2O$, $Na_2MoO_4 \cdot 2H_2O$, $FeSO_4 \cdot 7H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ and $Fe(C_6H_5COO)_3$ salts were used. Solutions of $Na_4PW_{11}O_{39}Fe(H_2O)$ were prepared as described in Ref. [16]. The supported oxide samples, 18%

V_2O_5/SiO_2 and 15% MoO_3/SiO_2, were prepared by impregnation of SiO_2 ($S = 200$ m^2/g) with an aqueous solution of NH_4VO_3 and $(NH_4)_2MoO_4$ followed by calcination for 3 h at 500°C. The catalysts, 1%Pd/18% V_2O_5/SiO_2 and 1%Pd/15%$MoO_3/$SiO_2 were prepared from the above oxide samples by impregnation with a solution of H_2PdCl_4 and then calcination at 500°C (3 h) followed by reduction in a flow of $H_2/N_2 = 1/1$ at 300°C, for 1 h. The supported oxide samples, 6.5%V_2O_5/TiO_2 ($S = 272$ m^2/g) and 0.7%$V_2O_5/$ 10% WO_3/TiO_2 (16 m^2/g) were a gift of Dr. G.B. Barannik, (Boreskov Institute of Catalysis). The series (1) catalyst solutions (refer to Fig. 1) were prepared by adding 99.5% CH_3COOH to aqueous solutions of the cited transition metal compounds, to a ratio of $H_2O:CH_3COOH = 1:9$ (v/v). In the case of $Na_4PW_{11}O_{39}Fe(H_2O)$, the ratio of $H_2O:CH_3COOH$ was varied from 1:9 to 7:3. The series (2) catalyst solutions (Fig. 1) were prepared in
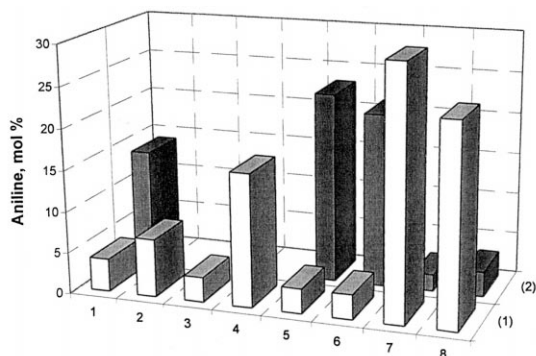
1. $FeSO_4$ $5 \cdot 10^{-3}$ mol
2. $Fe(NO_3)_3$ $5 \cdot 10^{-4}$ mol
3. $Fe(C_6H_5COO)_3$ $5 \cdot 10^{-4}$ mol
4. $Na_4PW_{11}O_{39}Fe(H_2O)$ $2 \cdot 10^{-4}$ mol
5. Na_2MoO_4 $2 \cdot 10^{-4}$ mol
6. Na_2MoO_4 $2 \cdot 10^{-4}$ mol, $Pd(CH_3COO)_2$ $4 \cdot 10^{-5}$ mol
7. $NaVO_3$ $2 \cdot 10^{-4}$ mol
8. $NaVO_3$ $2 \cdot 10^{-4}$ mol, $Pd(CH_3COO)_2$ $4 \cdot 10^{-5}$ mol

Fig. 1. The (mol%) yield of aniline referred to starting C_6H_6 in the presence of the listed (1 to 8) homogeneous catalysts at specified concentrations. Conditions: T 90°C, reaction time 5 h, 10 mmol C_6H_6, 10 mmol $(NH_2OH)_2 \cdot H_2SO_4$, 15 ml of the solvent: $H_2O:CH_3COOH = 1:9$ (v/v) (1) or $H_2O:CH_3COOH:$ $H_2SO_4 = 1:6:3$ (v/v) (2).

the same way, using, instead of 99.5% CH_3COOH, a mixture of this acid and 95% H_2SO_4 at a v/v ratio of 2:1. The resulting solutions contained $H_2O:CH_3COOH:H_2SO_4 = 1:6:3$ (v/v) or about 5 M H_2SO_4.

2.2. Reaction chemistry

Reaction of benzene with hydroxylamine sulfate was carried out in a thermostatted glass flask fixed to a vibrating table. A catalyst solution (or suspension), together with a weighed portion of $(NH_2OH)_2 \cdot H_2SO_4$ was poured into the reactor. As specified, the reactor was flushed either with O_2 or an inert gas. After the introduction of benzene or toluene, the reactor was sealed and heated from 75°C to 90°C, while being subjected to intensive agitation.

After a certain time, the reaction product mixture was cooled, and neutralized by a 30% solution of NaOH. Aromatic compounds were extracted with ether and analyzed by GLC (0.4% 1-nitroanilinoanthraquinone on carbon black column) with an FID detector in a temperature-programmed regime. The regioisomers of toluidine were analyzed by ^{1}H NMR and GC-MS.

Decomposition of hydroxylamine studies were carried out at atmospheric pressure with the reactor connected to a calibrated gas burette through a reflux condenser. The composition of the collected gas was determined by GC (NaA zeolite column); nitrogen containing compounds in solution were analyzed by ^{14}N NMR. The amount of hydroxylamine remaining was estimated by its reaction with cyclohexanone to give cyclohexanone oxime, which was determined by GLC using a TENAX column.

2.3. Ab initio quantum mechanics calculations

The calculations were done using the Jaguar package [17], utilizing density functional theory under the generalized gradient approximation. A B3LYP functional coupled with 6-31G** basis sets was used. The total electronic energies of the various species, evaluated at their fully optimized geometries both in the idealized gas phase and in water, were used to estimate the overall energy changes (ΔE) for specific transformations.

3. Results and discussion

The reaction chemistry of benzene and, to a lesser extent, toluene, with hydroxylamine sulfate, was studied in the presence of a variety of redox catalysts in (1) acetic acid, water and (2) acetic acid, water and H_2SO_4 solvent media. With benzene, after suitable work-up, aniline was the only identified product, although there were, in some cases, unknown tarry residues. Toluene afforded mixtures of toluidines with no apparent regioselectivity. In all cases, the amination of the aromatics was accompanied by some decomposition of the hydroxylamine with an evident evolution of nitrous oxide [18].

Following is a report of our initial scoping studies utilizing various soluble and supported solid, transition metal redox oxide catalysts for the amination of benzene in moderately acidic media.

4. Amination of benzene

4.1. Homogeneous systems

The benzene and $(NH_2OH)_2 \cdot H_2SO_4$ reaction was examined with a series of soluble, transition metal redox catalysts, in the two above noted aqueous acid solvent media. Results are collected in Fig. 1. The yield of aniline (expressed as 10^2 mol of $C_6H_5NH_2$ per mole of starting benzene) is plotted in the bar graph for various added catalysts. The front facing series (1) on the ordinate in Fig. 1 is for a 1:9 v/v $H_2O:CH_3COOH$ solvent system; the background (series (2)) scale in the figure is for the same system to which has been added H_2SO_4 to a ratio $H_2O:CH_3COOH:H_2SO_4 = 1:6:3$ (v/v).

In the H_2O:acetic acid medium, the iron salts (1–4 in Fig. 1) catalyze the synthesis of aniline, and of these, the Fe(III) heteropolytungstate $Na_4PW_{11}O_{39}Fe(H_2O)$ (4) exhibited by far, the highest activity. The analogous heteropolytungstates of Co(II), Mn(II) and Cu(II) gave only traces of aniline, while the corresponding $Na_7PW_{11}O_{39}$ salt was totally inactive. Sodium vanadate proved to be the best catalyst in this series. At 90°C, 5 h in 1:9 v/v $H_2O:CH_3COOH$, about 10 mol of aniline were pro-

duced per mole of $NaVO_3$. The addition of Pd(II) (as $Pd(CH_3COO)_2$) which is subjected to reduction at the reaction conditions, did not have a favorable effect. A reduction of the palladium acetate to palladium black was visually evident at the reaction conditions.

Data collected in the upper two curves of Fig. 2 show how the concentration of the sodium vanadate and Fe(III) heteropolytungstate catalysts influence the yield of aniline. Also, there is an indication of the amination reaction kinetics for the Fe(III) heteropolytungstate salt and $FeSO_4$ systems. While the yield of aniline can be improved by having a higher concentration of catalyst and longer reaction times, there is a limiting effect because of accompanying unproductive redox reactions of the catalyst components (e.g. Fe(III)) with hydroxylamine (vide infra).

In the context of our original objective of finding a minimally acidic reaction system, we investigated the use of more aqueous acetic acid solvents. As seen in Fig. 3, the best performance with the $Na_4PW_{11}O_{39}Fe(H_2O)$ catalyst was seen at a water content of about 15 vol.%, but interestingly, the yield of aniline was at about one half of the maximum in a solvent of only 30 vol.% CH_3COOH in water.

The incorporation of sulfuric acid into the H_2O:acetic acid reaction medium had a profound effect on the amination chemistry (Fig. 1, series 2).
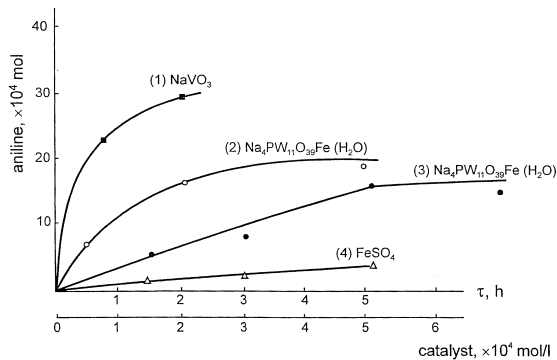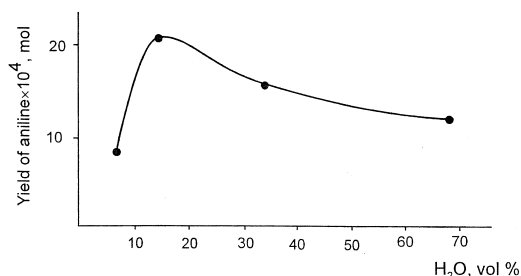

Fig. 3. The (mol%) yield of aniline referred to starting C_6H_6 vs. content of water (vol.%) in acetic acid solution. Conditions: *T* 90°C, reaction time 5 h, 0.2 mmol $Na_4PW_{11}O_{39}Fe(H_2O)$, 10 mmol C_6H_6, 10 mmol $(NH_2OH)_2 \cdot H_2SO_4$.

In the 1:6:3 v/v $H_2O:CH_3COOH:H_2SO_4$ system, the Fe(II) and Mo(VI) catalysts became more effective, while the activity of $NaVO_3$, the most active catalyst in the aqueous acetic acid solvent, was now almost totally quenched. This is ascribed to a lower redox activity of the vanadium species due to the formation of a $VOSO_4$ complex [19]. The addition of other strong Bronsted acids, CF_3COOH and $H_3PW_{12}O_{40}$ to the H_2O:acetic acid reaction medium did not show a promotional effect. Thus, the yield of aniline was invariant to the addition of 0.03 M $H_3PW_{12}O_{40}$ to the $FeSO_4$/1:9 $H_2O:CH_3COOH$ system, and here, amination was completely suppressed in the presence of 1 M CF_3COOH.

4.2. Solid oxide and Pd-containing oxide catalysts

Solid catalysts consisting of V_2O_5, MoO_3 and Pd supported on SiO_2 or TiO_2 were next examined for the amination of benzene with NH_2OH in the same aqueous acetic and acetic, sulfuric acid systems. Surprisingly, these supported catalysts were only active in the presence of sulfuric acid. Yields of aniline based on starting benzene for reactions conducted in the presence of various solid catalysts in 2:1 v/v $CH_3COOH:H_2SO_4$ at 90°C for 5 h are given in Fig. 4. The most active catalysts were 6.5% V_2O_5/TiO_2 and 1% Pd/15% MoO_3/SiO_2. Analysis of the vanadium system after completion of the reaction revealed that 54% of the initial V and 62% of the initial Ti were now in solution. Nevertheless, the solid V(V) oxide is clearly the active catalyst

Fig. 2. The (mol%) yield of aniline referred to starting C_6H_6 vs. (a) the concentration of catalyst: curves (1) and (2); and (b) reaction time (τ): curves (3) and (4). Conditions: *T* 90°C, 10 mmol C_6H_6, 10 mmol $(NH_2OH)_2 \cdot H_2SO_4$, 15 ml of the solvent $H_2O:CH_3COOH = 1:9$ (v/v), reaction time 5 h for (1) and (2). Catalysts: $NaVO_3$ (1), $Na_4PW_{11}O_{39}Fe(H_2O)$ (2), 0.2 mmol $Na_4PW_{11}O_{39}Fe(H_2O)$ (3), 5 mmol $FeSO_4$ (4).
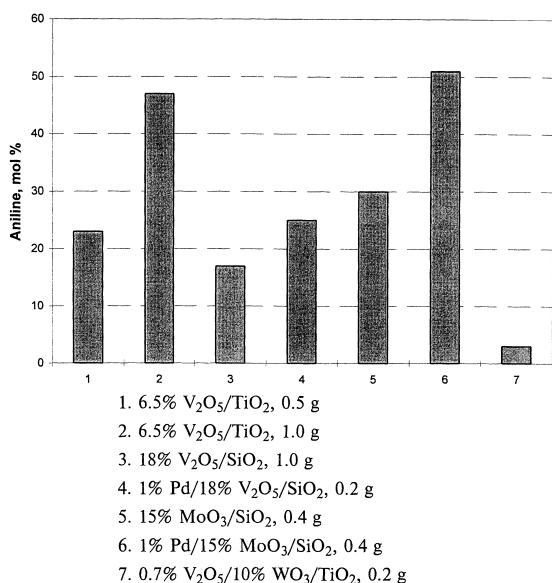
Fig. 4. The % molar yield of aniline referred to starting C_6H_6 in the presence of the various listed oxides and Pd containing oxide catalysts. Conditions: T 90°C, reaction time 5 h, 10 mmol C_6H_6, 10 mmol $(NH_2OH)_2 \cdot H_2SO_4$, 15 ml of $CH_3COOH:H_2SO_4 = 2:1$ (v/v).

1. 6.5% V_2O_5/TiO_2, 0.5 g
2. 6.5% V_2O_5/TiO_2, 1.0 g
3. 18% V_2O_5/SiO_2, 1.0 g
4. 1% Pd/18% V_2O_5/SiO_2, 0.2 g
5. 15% MoO_3/SiO_2, 0.4 g
6. 1% Pd/15% MoO_3/SiO_2, 0.4 g
7. 0.7% $V_2O_5/10\%$ WO_3/TiO_2, 0.2 g

component, since V(V) salts in solution in the presence of 5 M H_2SO_4 show very little activity for benzene amination (vide supra Fig. 1, catalyst 7, series (2)). The Na_2MoO_4 soluble salt and the 15% MoO_3/SiO_2 (Fig. 4) catalyst had about the same activity per gram-atom of molybdenum. In the latter case, 65% of the molybdenum was found in solution after the process, which suggests that the solid and dissolved species are almost equally effective.

The introduction of Pd into the oxide samples resulted in a significant promotion of these catalysts.

Most effective was the above cited 1% Pd/15% MoO_3/SiO_2 system. No palladium ions were present in solution. A control reaction employing palladium alone on an inert oxide (Pd/SiO_2) did not yield any aniline. The solid Pd–Mo-oxide species are probably the most active component in the system.

4.3. Optimal catalyst systems and process selectivity

The most effective catalyst/reaction systems for the amination of benzene identified in the above scoping study were further examined with respect to the overall process selectivities. Results for four reaction systems taken to ca. 50% conversion of benzene are collected in Table 1. For the $NaVO_3$ and $Na_2MoO_4/Pd(CH_3COO)_2$ soluble systems, the selectivity for aniline formation with respect to consumed benzene (S_B) was only about 50%; the remainder of the benzene was transformed to intractable polymeric species. Use of the silica supported Pd/MoO_3 catalyst systems leads to a much more efficient utilization of benzene (Table 1, runs 3 and 4).

In the utilization of hydroxylamine, the soluble systems (Nos. 1 and 2 in Table 1) are quite inefficient: the selectivity with respect to hydroxylamine consumed, S_{HA}, is only ∼ 20%. There is clearly a considerable accompanying disproportionation of the amine to N_2O and NH_4^+. The evolved nitrous oxide was identified by G.C. and quantified volumetrically; the ammonium ion was detected and determined by ^{14}N NMR (pentet with a maximum $\delta = -353$ ppm vs. NO_3^- [20]). The supported solid catalyst systems (Nos. 3 and 4 in Table 1) were far more efficient in

Table 1

Yields of aniline and N_2O, and selectivity of aniline formation with respect to benzene ($S_B = 100 \cdot C_6H_5NH_2/C_6H_6$ consumed) and hydroxylamine ($S_{HA} = 100 \cdot C_6H_5NH_2/NH_2OH$ consumed). Conditions: 10 mmol C_6H_6, 10 mmol $(NH_2OH)_2 \cdot H_2SO_4$, 15 ml of solvent, 90°C, reaction time 5 h, in air (No. 1–3), in N_2 (No. 4).

No.	Catalyst	Solvent, $H_2O:CH_3COOH:$ H_2SO_4 (v/v)	Aniline, (mmol)	N_2O, (mmol)	S_B (%)	S_{HA} (%)
1	$NaVO_3$, 0.2 mmol	1:9:0	2.7	2.9	45	19
2	Na_2MoO_4, 0.2 mmol + $Pd(CH_3COO)_2$, 0.04 mmol	1:6:3	2.1	1.0	49	21
3	1% Pd/15% MoO_3/SiO_2, 0.4 g	0:2:1	5.1	0.7	70	64
4	1% Pd/15% MoO_3/SiO_2, 0.4 g	0:2:1	5.6	0.7	72	67

terms of hydroxylamine consumption and concomitantly less by-product N_2O; here, S_{HA} was about 65%. [14]NMR spectra of the reaction product solutions gave signals for aniline (-325 ppm vs. NO_3^-), NH_4^+ (-353 ppm) and unreacted hydroxylamine (-291 ppm). No other nitrogen compounds were detected.

Some limited studies were done to better understand the causes and conditions for this accompanying disproportionation of hydroxylamine [18]:

$$4HONH_{3^+} \rightarrow N_2O + 2NH_{4^+} + 2H^+ + 3H_2O \qquad (1)$$
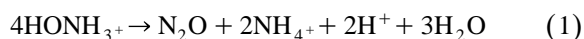
The decomposition of hydroxylamine sulfate at the catalytic amination conditions, but in the absence of aromatic substrate was followed by measuring the amount of N_2O evolved over time. Results are summarized in Fig. 5. A detailed analysis of this data is not warranted, but there are some useful general observations. As expected, hydroxylamine decomposes more rapidly in the 90% acetic acid medium than in the clearly more acidic H_2SO_4 containing system (Nos. 1–4 vs. 7,8) where it will be more extensively protonated. At these conditions, the supported V_2O_5 and MoO_3, Pd systems (Nos. 7 and 8 in Fig. 5) least affect the disproportionation of hydroxylamine and are, in terms of this reagent, the most efficient catalysts for the amination of benzene to aniline.
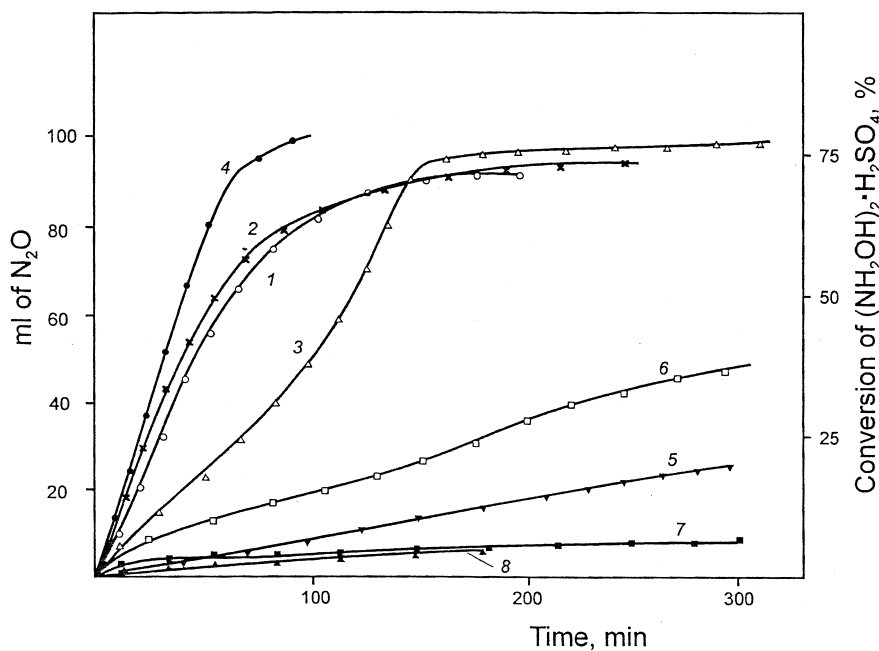

Fig. 5. Volume of N_2O evolved and conversion of $(NH_2OH)_2 \cdot H_2SO_4$ in the course of hydroxylamine dismutation in the presence of the listed (1–8) catalytic systems (both vertical scales apply to all curves). Conditions are the same as given in captions for Figs. 1 and 4. Table for Fig. 5.
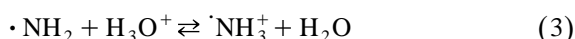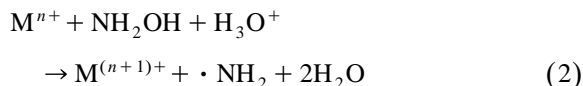
No.	Catalyst	Solvent system
1	$NaVO_3$	1:9 v/v H_2O:CH_3COOH
2	$NaVO_3$, $Pd(CH_3COO)_2$	1:9 v/v H_2O:CH_3COOH
3	Na_2MoO_4	1:9 v/v H_2O:CH_3COOH
4	Na_2MoO_4, $Pd(CH_3COO)_2$	1:9 v/v H_2O:CH_3COOH
5	Na_2MoO_4, $Pd(CH_3COO)_2$	1:6:3 v/v H_2O:CH_3COOH:H_2SO_4
6	$Na_4PW_{11}O_{39}Fe(H_2O)$	1:9 v/v H_2O:CH_3COOH
7	$V_2O_5/Ti/O_2$	2:1 v/v CH_3COOH:H_2SO_4
8	1% Pd/15% MoO_3/SiO_2	2:1 v/v CH_3COOH:H_2SO_4

5. Amination of toluene

We were aware of only one report on the amination of toluene with hydroxylamine sulfate [15], and it was, therefore, of interest to examine for this purpose catalytic systems which had shown activity for the amination of benzene. Amination reactions carried out at the same conditions: 90°C, 5 h in 1:9 v/v $H_2O:CH_3COOH$ and in 5 M H_2SO_4 in 1:6:3 v/v $H_2O:CH_3COOH:H_2SO_4$, resulted in a mixture of toluidines. Details are given in Table 2. The soluble Fe heteropolytungstate catalyst and the supported Pd, V_2O_5/SiO_2 system had about the same level of activity as for the amination of benzene (compare with data in Figs. 1 and 4), while the supported vanadium catalyst was somewhat less active. For all the examined reactions, there was no evident regioselectivity.

6. Amination reaction pathways

The amination of benzene and toluene with hydroxylamine takes place in a range of acidic media in the presence of a variety of redox transition metal reactants and catalysts. The essential first step here is the generation of amino, $\cdot NH_2$ or protonated amino, $\cdot NH_3^+$ radicals by a reduction of hydroxylamine:

$$M^{n+} + NH_2OH + H_3O^+$$

$$\rightarrow M^{(n+1)+} + \cdot NH_2 + 2H_2O \qquad (2)$$

$$\cdot NH_2 + H_3O^+ \rightleftarrows \cdot NH_3^+ + H_2O \qquad (3)$$

There is a considerable literature precedent [21–23] for reaction (2) with chemically or electrochemi-cally generated Ti(III), V(III), Cu(I), etc. The pK_a of $\cdot NH_3^+$ has been variously reported [23] as 3.75 and 6.7, which strongly indicates that in our relatively acidic reaction systems, $\cdot NH_3^+$, rather than the neutral amino radical, should predominate.

In the subsequent step, the $\cdot NH_2$ or $\cdot NH_3^+$ radical species react with the aromatic substrates to yield, respectively, in the case of benzene, an aminocyclohexadienyl or protonated aminocyclo-hexadienyl intermediate. This is then oxidized by the transition metal systems to the aromatic amine product:
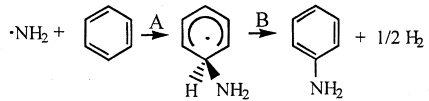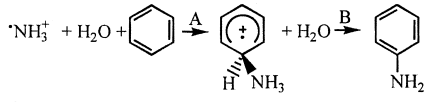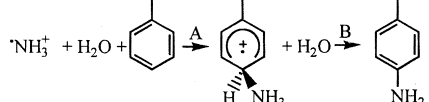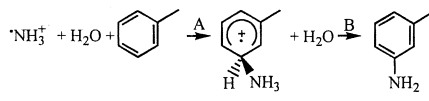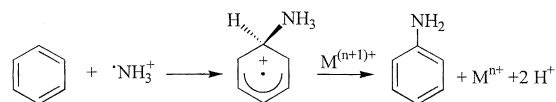

$$(4)$$
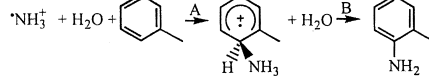
Particularly illustrative of this chemistry is the VO^+/NH_2OH system in acid solution, which, in the presence of electrochemically generated Cu^+, efficiently yields aniline; in this case, VO^+ is the metal oxidant [21]. The putative aminating agent is $\cdot NH_2$, but in view of the acidity of this medium, and the reported non-reactivity of $\cdot NH_2$, as prepared by reaction of the $\cdot OH$ radical with aqueous ammonia [24] with benzene, it is much more likely that the aminating agent here — and also in our transition metal/NH_2OH/H_3O^+ systems, is in fact $\cdot NH_3^+$.

In order to gain further insight into the possible benzene and toluene amination pathways with $\cdot NH_2$ and $\cdot NH_3^+$, we have performed relatively high level ab initio quantum mechanics calculations which have

Table 2
Yield of toluidines (mol%, referred to starting toluene) in reaction of toluene with hydroxylamine. Conditions: 15 ml of solvent, 10 mmol of $(NH_2OH)_2 \cdot H_2SO_4$, 10 mmol of toluene, T 90°C, reaction time 5 h.

No.	Catalyst	Solvent, $H_2O:CH_3COOH:$ H_2SO_4 (v/v)	Yield of toluidines (%)		
			ortho-	meta-	para-
1	$Na_4PW_{11}O_{39}Fe(H_2O)$, (0.2 mmol)	1:9:0	5	8	7
2	6.5% V_2O_5/TiO_2 (1 g)	0:2:1	7	10	8
3	1% Pd/5% V_2O_5/SiO_2 (1 g)	0:2:1	8	10	8

Reaction	Step A		Step B	
	gas phase	water	gas phase	water
$\cdot NH_2$ + benzene $\xrightarrow{A}$ (Wehland intermediate, H, NH₂) $\xrightarrow{B}$ aniline (NH₂) + 1/2 H_2	-4.12	-2.19	-38.59	-37.46
$\cdot NH_3^+$ + H_2O + benzene $\xrightarrow{A}$ (intermediate, H, NH₃) + H_2O $\xrightarrow{B}$ aniline (NH₂) + 1/2 H_2 + H_3O^+	-47.21	1.46	23.61	-40.56
$\cdot NH_3^+$ + H_2O + toluene $\xrightarrow{A}$ (intermediate, H, NH₃) + H_2O $\xrightarrow{B}$ (NH₂, para) + 1/2 H_2 + H_3O^+	-53.85	3.40	30.69	-38.86
$\cdot NH_3^+$ + H_2O + toluene $\xrightarrow{A}$ (intermediate, H, NH₃) + H_2O $\xrightarrow{B}$ (NH₂, meta) + 1/2 H_2 + H_3O^+	-49.94	3.23	26.20	-40.50
$\cdot NH_3^+$ + H_2O + toluene $\xrightarrow{A}$ (intermediate, H, NH₃) + H_2O $\xrightarrow{B}$ (NH₂, ortho) + 1/2 H_2 + H_3O^+	-49.85	3.35	26.28	-39.75

Scheme 1. Calculated reaction energies, ΔE (kcal/mol).

provided a very instructive set of reaction energies. Results are presented in Scheme 1. Here, the first step (A) is the amination by $\cdot NH_2$ or $\cdot NH_3^+$ to give the Wehland intermediate (as in Eq. (4)), which is then (step B) converted to the aromatic amine and H_2 or H_2 and H_3O^+. The transition metal redox system, which in this model, may simply be regarded as an oxidant for the by-product hydrogen, was not considered in these calculations. For all the reaction systems in water, the second step is highly exothermic which strongly suggests that it is the initial amination step that is rate-determining. Reaction energies for attack of benzene by $\cdot NH_2$ and $\cdot NH_3^+$ in a water medium (-2.19 and 1.46 kcal/mol, respectively) do not differ greatly, and considering also the gas phase data, the magnitude of ΔE for the reaction of $\cdot NH_3^+$ with benzene is clearly very sensitive to the solvation model. On the basis of these reaction energy calculations alone, it is, thus, not possible to a priori discern the relative reactivity of the two aminating species. However, the fact that the amination of benzene and toluene only takes place in acidic media where the protonation of $\cdot NH_2$ is

clearly favored (calculated ΔE for reaction 3 in water = -14.51 kcal/mol), strongly suggests the involvement of $\cdot NH_3^+$.

For the amination of toluene with $\cdot NH_3^+$, the reaction energies for forming the three possible isomeric methylcyclohexadienyl radical cations are very similar. This suggests that there should be no significant regioselectivity, which is consistent with our experimental findings for this reaction.

7. Conclusions

The catalytic amination of benzene with NH_2OH can take place with reasonable yields, but requires acidic, although not highly acidic, reaction media. The soluble catalyst, $Na_4PW_{11}O_{39}Fe(H_2O)$, shows its best performance in 85% CH_3COOH, and loses only half of its activity in 30% aqueous acetic acid. Most active is the heterogeneous (slurry phase) $Pd/MoO_3/SiO_2$ catalyst in $H_2SO_4:CH_3COOH =$ 1:2 (v/v), which produces aniline with a high utilization of benzene, and about 60% selectivity to-

wards hydroxylamine. Toluene is aminated to yield a non-regiospecific mixture of toluidines. It is postulated on the basis of literature data and ab initio quantum mechanics calculations that the reactive species in this benzene and toluene amination chemistry is, most likely, the $\cdot NH_3^+$ protonated amino radical cation, which is generated by reduction of NH_2OH by transition metal redox species in the acidic media. Reaction of $\cdot NH_3^+$ with the aromatic substrates results in protonated aminocyclohexadienyl and aminomethylcyclohexadienyl radical cation species, which are oxidatively aromatized to yield, respectively, aniline and a non-regioselective mixture of toluidines.

Acknowledgements

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