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# Sodium metavanadate catalyzed one-step amination of benzene to aniline with hydroxylamine

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## Abstract

The direct amination of benzene to aniline with hydroxylamine catalyzed by sodium metavanadate in acetic acid water under mild conditions took place more efficiently in open air than in a closed system. The presence of oxygen significantly enhanced the yield of aniline. Satisfactory aniline yield (64%) and turnover number (48 mol of aniline per mol of vanadium) were obtained under optimized reaction conditions. The decomposition of hydroxylamine was studied to understand its function during the amination process. A computational study on the UV–vis spectra of some typical vanadium complexes was carried out by the time-dependent DFT method. A free-radical mechanism is proposed based on the results of EPR, $^{51}$V NMR, and UV–vis characterizations.

*Keywords:* Catalytic amination; Hydroxylamine; Aniline; Vanadium; EPR; $^{51}$V NMR; UV–vis; Free radical mechanism

## 1. Introduction

Aniline is an important organic chemical that is widely used in industry. Traditional aniline production involves multiple reactions, which has many disadvantages. The production is highly energy- and time-consuming, has low atomic efficiency, requires strict operational conditions, generates a large amount of byproducts, and causes serious environmental pollution, all of which contradict the "greening" trends of global chemical manufacturing [1]. One-step production of aniline by the direct amination of benzene is an attractive and challenging method from the standpoint of both green chemistry and synthetic chemistry. Numerous attempts for this intriguing reaction have been made [2–13]. Among them, ammonia was generally used as the aminating agent, and gaseous oxygen was used as the oxidant. These methods generally suffer from critical operation conditions of high temperature (ca. 373–1273 K), high pressure (10–1000 atm), relatively low aniline yield, and/or relatively low selectivity to aniline. In our previous work, aniline was catalytically synthesized directly from benzene and aqueous ammonia in the presence of hydrogen peroxide over Ni–Zr–Ce/$Al_2O_3$ [14], V–Ni/$Al_2O_3$ [15], Mo–Ni/$Al_2O_3$, and Mn–Ni/$Al_2O_3$ [16] catalysts under mild conditions, but only modest yields were obtained. Recently, Mantegazza et al. [17] reported the direct synthesis of hydroxylamine with high yield by the oxidation of ammonia with hydrogen peroxide in the presence of Ti-silicalite at low temperature under atmospheric pressure. With suitable selection of solvent, no potential deep oxidation of ammonia occurs, and no byproduct forms. Thus, it provided a potential benign supply of hydroxylamine for the amination of benzene. Although the use of hydroxylamine in amination is not economically advantageous or environmentally benign at present, the study of the direct amination of benzene with hydroxylamine will help discern such amination chemistry and provide information for synthesizing aniline-like molecules with ammonia and hydrogen peroxide in the future. The latter is promising in the replacement of the traditional aniline production. Notably, Kuznetsova et al. [18] investigated the amination of benzene and toluene with hydroxylamine sulfate in the presence of transition metal redox catalysts in a closed system. The reaction was carried out in acetic acid–water or

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sulfuric acid–acetic acid–water media, and a maximum aniline yield of about 27 mol% was obtained. However, to the best of our knowledge, no detailed information about the variation of the metallic atoms during the amination process has been reported.

This paper reports the direct amination of benzene to aniline with hydroxylamine hydrochloride homogeneously catalyzed by sodium metavanadate in open air. The variation of the state of the vanadium catalyst during the reaction was studied by $^{51}$V NMR, EPR, and UV–vis techniques. A time-dependent DFT (TD-DFT) calculation on the typical intermediate species was also carried out to help understand the UV–vis spectra. The amination chemistry was investigated mechanistically.

## 2. Experimental and computational details

### 2.1. Catalytic amination reaction

Analytical-grade $NaVO_3 \cdot 2H_2O$, $VOSO_4$, and $NH_2OH \cdot HCl$ were commercially obtained. The glacial acetic acid and benzene were of analytical grade and used without further purification.

The catalytic amination reaction was carried out in a thermostatted two-necked round-bottomed flask at atmosphere pressure in open air. Before the reaction, a catalyst solution was prepared by dissolving the required amount of $NaVO_3$ in 15 mL of acetic acid–water mixture. For comparison, $VOSO_4$ was used as the catalyst instead of $NaVO_3$. A typical procedure for the amination was as follows: The catalyst solution and a weighed portion of $NH_2OH \cdot HCl$ were loaded into the glass flask; after stirring for about 20 min at 303 K, 22.5 mmol benzene was introduced, and the mixture was heated to the required temperature under intensive agitation and reflux in air. It should be noted that the use of $NH_2OH \cdot HCl$ should be handled carefully to prevent heating in the dry state due to its potentially explosive nature. After the reaction was carried out for the required period, the reaction was stopped, and the resulting mixture was cooled to room temperature and neutralized by a 30% solution of NaOH. The organic compounds were extracted with ether and analyzed by gas chromatography (Varian, GC-960 equipped with hydrogen flame detector and a capillary column). *M*-toluidine was used as an internal standard to quantify the aniline produced. The main product of the catalytic amination was identified by coupled gas chromatography and mass spectroscopy (GC-MS, Agilent, 5973 Network 6890N) to be aniline. Comparatively, the same amounts of reactants and catalyst were used for the amination reaction in a closed system performed in an autoclave under about 2.0 atm. Unless specified otherwise, the amination reaction was carried out in an open system under atmospheric pressure.

The mol% yield of aniline was calculated as (mol aniline)/(mol initial benzene). The selectivity to aniline based on benzene was calculated as (mol aniline)/(mol benzene consumed). The selectivity to aniline based on hydroxylamine was calculated as (mol aniline)/(mol initial hydroxylamine). The turnover number was calculated as (mol aniline)/(mol initial $NaVO_3$).

### 2.2. Catalyst characterization

The samples removed from the reaction mixture at specified time intervals were characterized by $^{51}$V NMR, UV–vis, and EPR. The $^{51}$V NMR spectra of the samples were recorded on a Bruker DRX-300 spectrometer operating at 78.9 MHz using a 10-mm broad-band probe, at 295 ± 0.5 K. Chemical shifts were externally referenced to $VOCl_3$ at 0 ppm. To quantify the vanadium concentrations in the samples, a $H_2O$–$D_2O$ solution containing $4.5 \times 10^{-3}$ mol/L of $NaVO_3$ was prepared and used as an external reference. The $^{51}$V NMR acquisition parameters were 98 kHz of spectral width, 0.15 s of acquisition time, and 30 Hz of line broadening.

The X-band EPR spectra were obtained on a Bruker EMX-8 spectrometer, operating at 9.81 GHz at 295 ± 0.5 K. The parameters used were microwave power, 10.01 mW; modulation frequency, 100.00 kHz; modulation amplitude, 1.00 G; time constant, 20.48 ms; and sweep time, 20.97 ms. The frequency was calibrated with strong pitch. The *g* values were determined by simulating the spectra using Bruker Win-EPR Version 4.33.

A fixed volume of the reaction mixture diluted with HOAc–$H_2O$ (4:1, v/v) solution was studied by UV–vis spectroscopy. The electronic spectra of the samples in the range of 200–900 nm were collected at 295 ± 0.5 K using a TU-1901 UV–vis spectrophotometer. The sample cells were quartz with a 10-mm path length. All UV–vis spectra were background-substituted from a reference sample of HOAc–$H_2O$–$C_6H_6$ solution.

### 2.3. Computational details

The UV–vis spectra of some typical vanadium complexes proposed to be present in the amination process were modeled by the time-dependent density functional theory (TD-DFT) method. Geometry optimizations, as well as frequency calculations for all the stationary points considered, were performed at B3LYP level of theory [19–21], together with the TZVP basis set [22,23]. For each optimized stationary point, vibrational analysis was performed to determine its character (minima). After optimization of the geometries, the electronic spectra were computed using TD-DFT at PBE1PBE (the 1997 hybrid functional of Perdew, Burke and Ernzerhof, which uses 25% exchange and 75% correlation weighting)/TZVP level with IEF-PCM nonequilibrium solvent model [24–26], because the PBE1PBE hybrid functional can provide excitation energies across the board, not only for valence, but also Rydberg excitations close to the ionization threshold [27]. Calculated electronic spectra were transformed, using the SWizard program [28], into simulated UV–vis spectra using Gaussian functions with half-widths of 3000 $cm^{-1}$. All of the calculations reported in the present work were carried out with the Gaussian 03 package [29].

### 2.4. Decomposition of hydroxylamine

Studies on the decomposition of hydroxylamine were carried out at atmospheric pressure in argon with a flow rate of 25 mL/min. The gas product formed during the decomposition was analyzed by GC (SP-6800A, 3 m × 2.3 mm Porapak Q column, TCD detector) after being dried by CaO.

## 3. Results and discussion

### 3.1. *Decomposition of hydroxylamine*

Hydroxylamine has been widely used in several organic reactions as a kind of aminating agent [18]. It exists as $HONH_3^+$ in weak acid solution and normally acts as a reducing agent [30]. The protonated hydroxylamine is prone to undergo a disproportionation as follows:

$$4HONH_3^+ \rightarrow N_2O + 2NH_4^+ + 2H^+ + 3H_2O. \qquad (1)$$

In addition, the chemical structure of $NH_2OH$ is suitable for interacting with vanadium to form a complex and makes the $NH_2OH$ unstable. Furthermore, the quinquevalent vanadium species can oxidize the reducing agent $NH_2OH$ according to

$$2HONH_3^+ + xV^{5+} \rightarrow N_2O + 6H^+ + xV^{4+,3+} + H_2O, \qquad (2)$$

where $x$ is determined by the final valence of vanadium. Thus, the present catalytic amination carried out in HOAc–$H_2O$ medium is likely accompanied by the decomposition of hydroxylamine, by either its disproportionation and/or its interaction with vanadium species. In both reactions, gaseous $N_2O$ would be produced. Therefore, we could obtain information about the decomposition of hydroxylamine by measuring the amount of gaseous $N_2O$ produced over time during the reaction period.

The effect of the temperature and the acetic acid concentration, as well as the amount and the valence of vanadium used on the decomposition of hydroxylamine, were studied. It was found that hydroxylamine decomposed slowly below 343 K, and more rapidly above 353 K (see Fig S1 in the supplementary material). Adding water to the glacial acetic acid made the system homogeneous, and hydroxylamine decomposed faster than in glacial acetic acid or water (Fig. 1). As the HOAc/$H_2O$ volume ratio was increased from 0 to 4, the pH of the solution decreased sharply from 7 to 0.22, whereas a further increase of the HOAc/$H_2O$ (v/v) ratio increased the pH slightly (Fig. S2). Thus, it is clear that the decomposition of hydroxylamine is affected by both the solubility and the acidity of the system under the conditions investigated. In the medium with a HOAc/$H_2O$ volume ratio of 4, which exhibits good solubility and the highest acidity, the highest decomposition rate was observed. However, no $N_2O$ was detected in the absence of vanadium in HOAc–$H_2O$ (4:1, v/v) medium (Fig. S3), indicating that the decomposition of hydroxylamine was catalyzed by vanadium. Kuznetsova et al. [18] attributed the decomposition of hydroxylamine to its disproportionation. Our work shows that the decomposition also may result from the oxidation of hydroxylamine by vanadium. For comparison, the decomposition of hydroxylamine was carried out in the presence of the tetravalent vanadium compound $VOSO_4$. The amount of $N_2O$ produced in the presence of $V^V$ is much larger than that in the presence of $V^{IV}$ (Fig. S4), which is probably due to the higher oxidative power of $V^V$ compared with $V^{IV}$. The foregoing results also indicate that the $V^V$ species are more active than the $V^{IV}$ species for the catalytic decomposition of hydroxylamine.

### 3.2. *Catalytic amination of benzene*

#### 3.2.1. *Effect of the acidity of the reaction medium*

Different concentrations of the HOAc–$H_2O$ media resulted not only in a different decomposition behavior of hydroxylamine, but also different aniline yields (Fig. 2). No aniline was

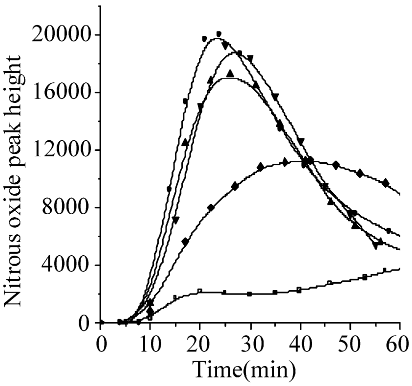
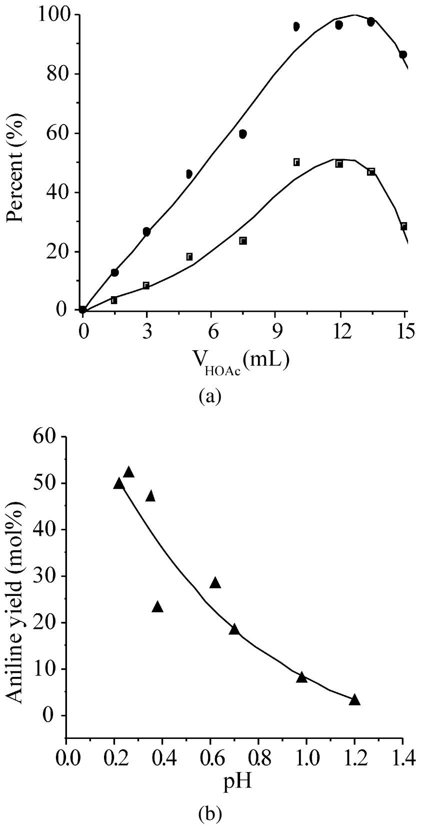


Fig. 1. Peak height of $N_2O$ produced over time in various concentrations of HOAc–$H_2O$ media: (■) HOAc:$H_2O$ = 15:0, (●) HOAc:$H_2O$ = 4:1, (▲) HOAc:$H_2O$ = 1:1, (▼) HOAc:$H_2O$ = 1:4, (□) HOAc:$H_2O$ = 0:15. Experimental conditions: 22.5 mmol $NH_2OH{\cdot}HCl$, 1 mmol $NaVO_3$, 15 mL HOAc–$H_2O$ solution, 353 K.



(a)

(b)

Fig. 2. Influence of the concentration of acetic acid on the amination: (a) aniline yield (■) and selectivity (●) as a function of the concentration of acetic acid; (b) aniline yield (▲) as a function of pH values of the solutions. Experimental conditions: 22.5 mmol benzene; $n_{benzene}:n_{NH_2OH{\cdot}HCl} = 1:1$; 0.2 mmol $NaVO_3$; 15 mL HOAc–$H_2O$ solution; 353 K; 4 h.

obtained in the absence of acetic acid, indicating zero activity of the vanadium species formed in water for the titled amination. The data collected in Fig. 2a show that with increasing $HOAc/H_2O$ ratio, the aniline yield as well as the turnover number based on vanadium first increase, reach a maximum value (50 mol%, 56 mol aniline per mol V) at the $HOAc/H_2O$ (v/v) ratio of 4, and then decrease. Moreover, the turnover number obtained in the $HOAc/H_2O$ (v/v = 4) medium is about two times larger than that in the glacial acetic acid medium. This may be due to the better dissolution of sodium metavanadate and hydroxylamine hydrochloride in water. The selectivity to aniline showed the same tendency [Fig. 2a, upper curve]. The higher aniline yields and turnovers were obtained in the reaction media with pH values below 0.7, especially in the range of 0.22–0.35 [Fig. 2b]. Thus, a relatively acidic reaction medium is advantageous for the amination of benzene to aniline. The coincidence of the higher amination activity and higher decomposition rate of hydroxylamine makes it reasonable to presume that the amination process is related to the decomposition of hydroxylamine.

In an attempt to further investigate the acidity of the medium on the yield of aniline, acetone, anhydrous ethanol, and acetonitrile were used as the reaction media and HCl (0.10 M) or $HNO_3$ (0.10 M) were selected to adjust the pH values of the reaction media to below 1.0. A homogeneous system was observed after all of the reactant was introduced. No or only a trace amount of aniline was obtained in these systems. Thus, we conclude that the role of acetic acid is not limited to aiding in dissolving the aromatic compound and supplying an acidic surrounding. Acetic acid perhaps coordinates with the vanadium center and affects the mechanism of the amination.

### 3.2.2. *Effect of oxygen*

The effect of the presence of air or oxygen on the amination reaction was studied by carrying out the reaction in open and closed systems. The turnover number based on vanadium and selectivity to aniline were much higher in the open-air system than in the closed system. Trace amounts of phenol and biphenyl were detected as the main byproducts in the open-air system, whereas in the closed system more of these two byproducts was formed, with chlorobenzene and some other *N*-substituted aromatic compounds also detected. They further resulted in decreased selectivity to aniline. As stated before, the amination is associated with the decomposition of hydroxylamine, resulting in the formation of gaseous $N_2O$. At this rate, the open system is reasonably advantageous for the escape of gaseous $N_2O$ and further favors the amination progress. On the contrary, a closed system blocks the escape of gaseous $N_2O$ and the presence of $N_2O$ may further lead to side-reactions such as the hydroxylation of benzene to phenol [31–35]. Similar results were obtained in our previous work [36]. That is, higher toluidine yields were obtained in the open-air system than in the closed system for the amination of toluene with hydroxylamine. Thus, all of the results indicate that open air favors the amination reaction.

When the reaction was carried out in flowing nitrogen, a much lower aniline yield was obtained. While using oxygen instead of nitrogen, the turnover number obtained was slightly higher than that obtained in open air, further indicating that the presence of oxygen promotes amination. Thus, the present amination probably occurs concomitantly with the $V^{IV} \leftrightarrow V^{V}$ equilibrium, and the presence of oxygen favors the reoxidation of lower valent vanadium species to higher valent ones in the acidic medium [37,38]. Based on this assumption, it is deduced that the existence of the higher valent vanadium species ($V^{V}$) must be essential for the amination process.

If 5 mL hydrogen peroxide (64.5 mmol, 30%), about three times the amount of hydroxylamine (22.5 mmol) added, was dropped in slowly, a trace amount of aniline and a small amount of chlorobenzene, nitrobenzene, phenol, and some other multisubstituted aromatic compounds were detected. This may mean that the excess of hydrogen peroxide leads to the accelerated oxidation of the lower valent vanadium formed earlier to higher valent vanadium, and that the remaining excess hydrogen peroxide further results in the deep oxidation of aniline produced earlier in the system. Furthermore, the lack of the lower valent vanadium disfavors the aniline formation. Thus, the presence of $H_2O_2$ in the system is disadvantageous for the selective amination of benzene to aniline.

### 3.2.3. *Effect of the amount of vanadium*

No aniline was detected without the use of $NaVO_3$. As vanadium is essential for the catalytic performance, a set of experiments using various amounts of $NaVO_3$ was carried out and the results are shown in Fig. 3. The aniline yield as well as the turnover number based on vanadium increased with the amount of $NaVO_3$ up to the maximal levels (0.3 and 0.2 mmol, respectively), beyond that they started to decrease. The selectivity to aniline in this set of experiments varied from 82 to 98%, and stayed above 95% when the amount of $NaVO_3$ varied from 0.1 to 0.5 mmol. The main byproducts detected were chlorobenzene and biphenyl. With further increases in the amount of $NaVO_3$, the amount of byproducts increased, and the selectivity to aniline decreased but stayed stable at >85%. The decrease of the aniline yield and selectivity, as well as the turnover number

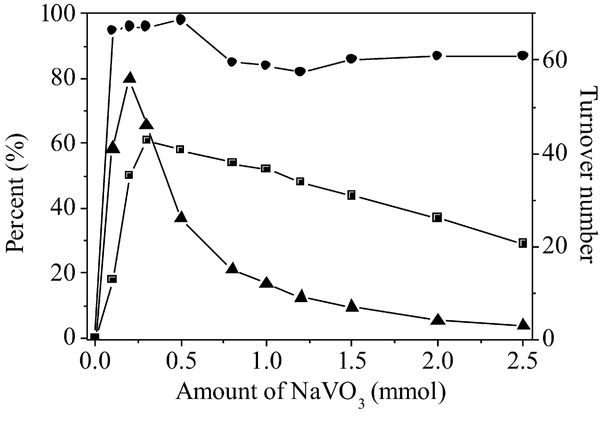


Fig. 3. Influence of the amount of initial $NaVO_3$ on the catalytic amination of benzene: (■) yield of aniline; (●) selectivity to aniline based on benzene; (▲) turnover number. Experimental conditions: 22.5 mmol benzene; $n_{\text{benzene}}:n_{NH_2OH\cdot HCl} = 1:1$; 15 mL $HOAc–H_2O$ (v/v = 2:1) solution; 353 K; 4 h.

with increasing $NaVO_3$ amount over 0.5 mmol, may be due to the accelerated decomposition of hydroxylamine by vanadium, which further leads to the loss of active aminating species. Obviously, the present amination is a vanadium-catalyzed process, and a catalytic amount of 0.3 mmol vanadium is suitable for the production of aniline. The vanadium species present in the system are involved not only in the catalytic decomposition of hydroxylamine, but also in the formation of active aminating species. The cooperative action of these two competitive reactions further leads to the formation of aniline.

### *3.2.4. Effect of the amount of hydroxylamine*

When the $n_{\mathrm{NH_2OH}}/n_{\mathrm{benzene}}$ molar ratio was increased from 1:1 to 2:1, the aniline yield increased slightly from 64% (48 mol aniline per mol V) to 69% (52 mol aniline per mol V) (Fig. 4), and byproducts such as 4-chlorotoluene and biphenyl were detected, which further decreases the selectivity to aniline based on benzene. In addition, the selectivity to aniline based on the initial $NH_2OH$ decreased with increasing $n_{\mathrm{NH_2OH}}/n_{\mathrm{benzene}}$ ratio. That is, a relatively larger initial concentration of hydroxylamine in the solution led to the accelerated decomposition of hydroxylamine by vanadium. The greatest selectivity to aniline based on initial $NH_2OH$ was 64% at $n_{\mathrm{NH_2OH}}/n_{\mathrm{benzene}}$ ratio of 1:1. If another 22.5 mmol hydroxylamine was added to the resulting mixture, then the aniline yield increased to about 81 mol%, and the turnover number increased to 61, suggesting that the resulting catalyst solution was still active for amination. Because some amount of benzene remained in the resulting mixture, the turnover number based on vanadium could be increased by adding an appropriate amount of fresh hydroxylamine.

### *3.2.5. Effect of reaction temperature and reaction time*

No aniline was produced at 323 K, and no decomposition of hydroxylamine was observed, suggesting that the amination process is associated with the decomposition of hydroxylamine. The yield of aniline increased sharply from 333 to 353 K and decreased at 363 K (Fig. 5). The optimal reaction temperature was 353 K with a yield of 64 mol% and a turnover number of 48. The decomposition rate of hydroxylamine showed the same tendency (Fig. S1), indicating that an appropriate decomposition rate of hydroxylamine favors the amination progress. The decrease of aniline yield at 363 K may due to the accelerated decomposition of hydroxylamine, leading to loss of the active aminating species. The aniline yield reached only 25 mol% after a reaction time of 2 h, then increased sharply after 3 h of reaction to about 60 mol% (Fig. 6). However, when the reaction time exceeded 4 h, the aniline yield decreased slightly. The selectivity to aniline decreased over time but remained >85%. These data indicate that 4 h was sufficient for the amination reaction. When adding 22.5 mmol fresh benzene to the resulting reaction mixture ($n_{\mathrm{NH_2OH}}/n_{\mathrm{benzene}} = 1{:}1$), no increase of the aniline yield was obtained, suggesting that all of the hydroxylamine in the system was exhausted. Thus the amination was stopped by the consumption of hydroxylamine.

### *3.3. Initial state of the catalyst*

Using 0.3 mmol $NaVO_3$ as the catalyst, the initial state of the vanadium species before the amination was characterized by combined $^{51}V$ NMR, UV–vis, and EPR spectroscopy. Before the addition of hydroxylamine and benzene, the $^{51}V$

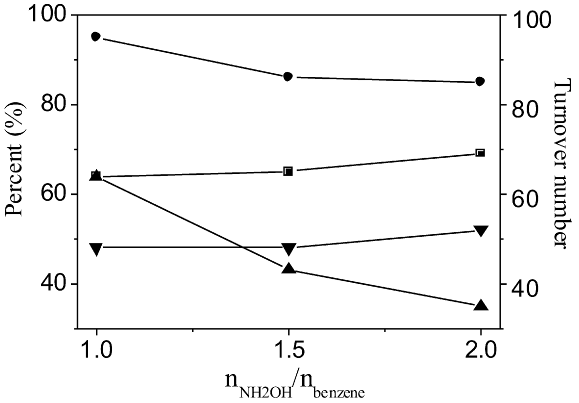


Fig. 4. Influence of the feed ratios on the catalytic amination of benzene: (■) yield of aniline, (●) selectivity to aniline based on benzene, (▲) selectivity to aniline based on hydroxylamine, (▼) turnover number. Experimental conditions: 22.5 mmol benzene; 0.3 mmol $NaVO_3$; 15 mL $HOAc–H_2O$ (v/v = 4:1) solution; 353 K; 4 h.

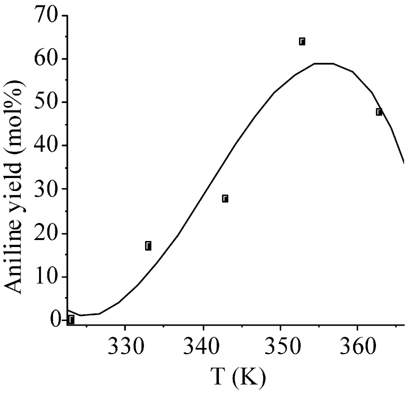


Fig. 5. Influence of the reaction temperature on the mol% yield of aniline. Experimental conditions: 22.5 mmol benzene; $n_{\mathrm{benzene}}:n_{\mathrm{NH_2OH\cdot HCl}} = 1{:}1$; 0.3 mmol $NaVO_3$; 15 mL $HOAc–H_2O$ (v/v = 4:1) solution; 353 K; 4 h.

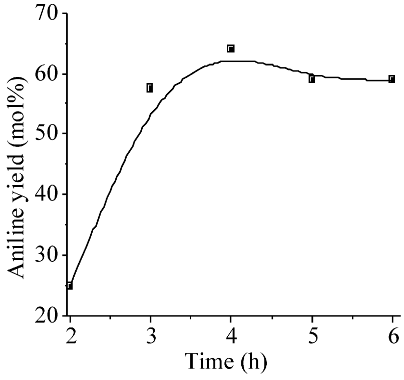
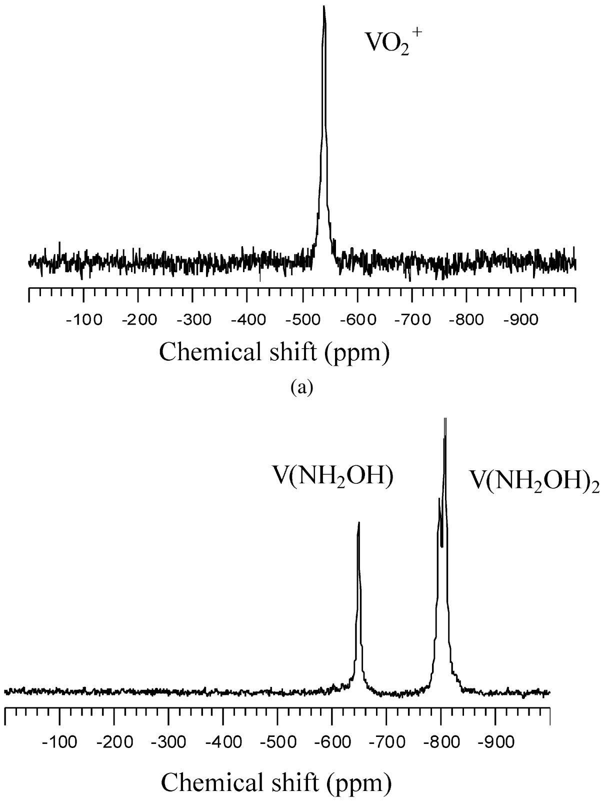


Fig. 6. Influence of the reaction time on the mol% yield of aniline. Experimental conditions: 22.5 mmol benzene; $n_{\mathrm{benzene}}:n_{\mathrm{NH_2OH\cdot HCl}} = 1{:}1$; 0.3 mmol $NaVO_3$; 15 mL $HOAc–H_2O$ (v/v = 4:1) solution; 353 K.



(a)

(b)

Fig. 7. $^{51}V$ NMR signals of (a) solution of $HOAc–H_2O$ (4:1, v/v) containing $NaVO_3$ (below 0.02 mol/L); (b) solution of $HOAc–H_2O$ (4:1, v/v) containing 0.02 mol/L $NaVO_3$ and 1.5 mol/L $NH_2OH{\cdot}HCl$.

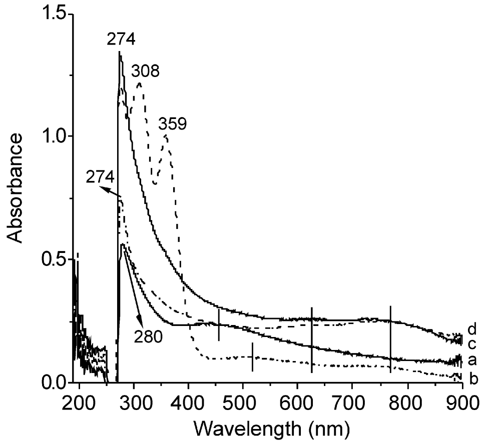


Fig. 8. UV–vis spectra of (a) solution containing $NaVO_3$ (below 0.02 mol/L); (b) solution containing 0.02 mol/L $NaVO_3$ and 1.5 mol/L $NH_2OH{\cdot}HCl$, octuply diluted; (c) solution containing 0.02 mol/L $VOSO_4$ and 1.5 mol/L $NH_2OH{\cdot}HCl$, quadruply diluted; (d) solution containing 0.02 mol/L $VOSO_4$, quadruply diluted.

NMR of the solution containing a small amount of $NaVO_3$ (<0.02 mol/L) exhibited one peak at −540 ppm [Fig. 7a], attributed to the $VO_2^+$ cation [39]. The UV–vis spectrum of this sample shows an intense absorption band maximum at 280 nm and a broad band at 420–550 nm (Fig. 8, curve a), which are believed to be $O^{2-} \rightarrow V^{5+}$ charge transfer (CT) transitions [40], confirming the presence of $VO_2^+$. This sample was EPR silent.

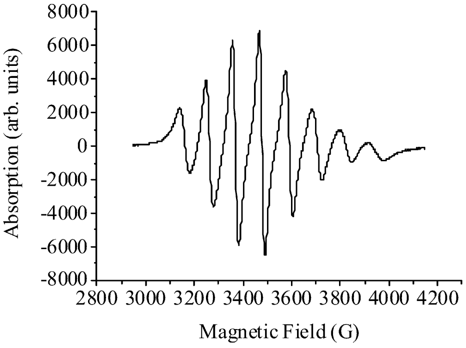


Fig. 9. Room temperature X-band EPR spectrum of the solution containing 0.02 mol/L $NaVO_3$ and 1.5 mol/L $NH_2OH{\cdot}HCl$ in $HOAc–H_2O$ (4:1, v/v) medium.

When hydroxylamine was added to the foregoing system and the mixture was heated until dissolved, a transparent bluish-green solution was obtained. This color change indicates the reduction of $V^V$ to lower-valent vanadium species. The bluish-green solution shows an EPR spectrum typical of a vanadyl ion in liquid solution (Fig. 9) [41]. The isotropic $g$ and hyperfine coupling constants are estimated to be 1.971 and 111.4 G, respectively. The $^{51}V$ NMR spectrum of this sample exhibited three peaks at around −648, −796, and −806 ppm [Fig. 7b]. These signals can be assigned to the complexes resulting from the coordination of hydroxylamine, $H_2O$, and HOAc with quinquevalent vanadium. The condensation reaction between hydroxylamine and vanadate occurs at both nitrogen and oxygen atoms [42]. The observed peak at −648 ppm corresponds to the monoligand product $[V^V(NH_2OH)]$, and the other two peaks are due to the bisligand products $[V^V(NH_2OH)_2]$. Quantitative results showed that the coordinating $V^V$ complexes in the solution were about 6% of the initial vanadium. It should be noted that the peaks appearing in the current $^{51}V$ NMR chemical shift are shifted by about +20 to +30 ppm compared with the values reported previously [42] (pH = 6.9). This may be due to the effect of solvent and the much more acidic medium than that reported in the literature [42], indicating that the chemical environment around the vanadium center of the complexes is influenced by solvent molecules and protons in the solution. Thus, the monohydroxamido and bishydroxamido vanadium complexes formed may undergo protonation under the current experimental conditions. No detailed information was obtained on the protonation from this work. The UV–vis spectrum of the same sample also reveals the presence of the vanadyl complex from the observation of the absorption band centered at 274 nm, assigned to the $O^{2-} \rightarrow V^{4+}$ CT transitions, and two broad bands centered at 620 and 760 nm due to the d–d electronic transitions of $VO^{2+}$ in a distorted octahedral symmetry (Fig. 8, curve b) [40]. Besides the aforementioned three bands, two additional intense absorption bands appeared at around 308 and 359 nm, which may be associated with the hydroxamido vanadium species. Because no corresponding absorption peaks were observed in the $VOSO_4–NH_2OH/HOAc–H_2O$ solution (Fig. 8, curve c) and the $VOSO_4/HOAc–H_2O$ solution (Fig. 8, curve d), no obvious direct coordination of hydroxylamine with the $VO^{2+}$ cation occurred, insofar as UV–vis allows this interpretation. Thus, it could be assumed that the bands at 308 and 359 nm belong to the monohydroxamido and bishydroxamido vanadium(V) complexes, respectively, in accordance with the $^{51}$V NMR results. The remaining broad absorption band in the region of 450–600 nm may be tentatively assigned to the solvent-coordinated $V^{IV}$ species (Fig. 8, curve b) [40]. The presence of $V^{III}$ is obscure from the UV–vis spectra, because its absorption peaks are generally overlapped with the $V^{IV}$ bands [40]. But the existence of $V^{III}$ in the present oxygen-enriched system is excluded due to the fact that $V^{IV}$ is known to be the most stable species in the oxygen-rich acidic solution. Thus, about 94% of the initial vanadium was present as $V^{IV}$ in the solution.

Based on the foregoing results, we can deduce that part of the hydroxylamine added in the system is oxidized by quinquevalent vanadium to form gaseous $N_2O$, accompanied by the partial reduction of $V^V$ to lower-valent vanadium ($V^{IV}$). This redox readily occurs in an acidic medium with a pH value <1 above 353 K. On the other hand, hydroxylamine coordinates with quinquevalent vanadium species, which probably further participates in the following amination process.

### 3.4. Calculation of the electronic spectra

To relate the experimentally determined λ values to given vanadium species, a computational study on the UV–vis spectra of some typical vanadium complexes was carried out. The structures of these vanadium species were optimized before calculating the electronic spectra (Table S1). The UV–vis spectra of the vanadium(V) complexes exhibited intense ligand-to-$V^V$ charge-transfer (CT) transitions in the 160–350 nm region (Fig. S5). The vanadium(IV) complexes exhibited intense CT bands in the 150–360 nm region and weak d–d transitions in the 500–1000 nm range (Fig. S6). The intensities of the d–d transitions were very low with respect to that of the intense CT transitions and always lay in the same region, making them hard to distinguish. The computation shows that hydroxylamine cannot coordinate with vanadium(IV) directly, but aniline can. The calculated electronic spectrum of the $V^{IV}O(AcO)_2(PhNH_2)$ complex shows more intense CT transitions centered at 228 and 299 nm, with weak d–d transitions centered at 594 nm, which lie in the same region as those of the other $V^{IV}$ complexes. It should be pointed out that the computationally obtained λ values are blue-shifted by about 85–100 nm compared with the experimental values.

### 3.5. State variation of the catalyst during the amination process

The reaction mixtures withdrawn at certain intervals were simultaneously analyzed by $^{51}$V NMR, UV–vis, and EPR to investigate the state of the homogeneous vanadium catalyst as a function of time during the reaction period. The $^{51}$V NMR spectra of the samples show elimination of both the monohydroxamido and bishydroxamido vanadium compounds during the reaction period (Fig. S7). The $V^V(NH_2OH)_2$ species disappeared quickly within 15 min (Fig. 10). It is interesting that aniline was detected to form within this reaction time. The $V^V(NH_2OH)$ species slowly decreased and vanished after 4 h of reaction. Comparing these data with the variation of the yield of aniline over time, it is reasonable to assume that the decrease of the hydroxamido vanadium complexes in the reaction mixture was responsible for the progress of the amination.

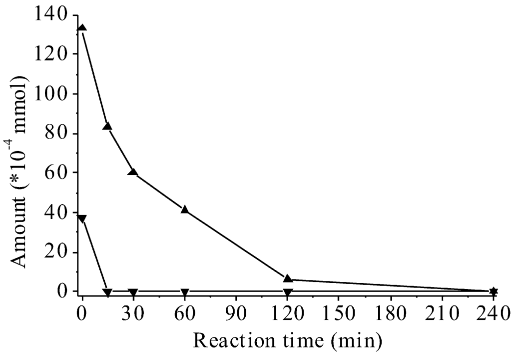


Fig. 10. Variation of the amount of the hydroxamido vanadium complexes as a function of time based on $^{51}$V NMR spectra. (▼) $V^V(NH_2OH)_2$, (▲) $V^V(NH_2OH)$. Experimental conditions: 22.5 mmol benzene; $n_{\text{benzene}}$: $n_{NH_2OH\cdot HCl}$ = 1:1; 0.3 mmol $NaVO_3$; 15 mL HOAc–$H_2O$ (v/v = 4:1) solution; 353 K.

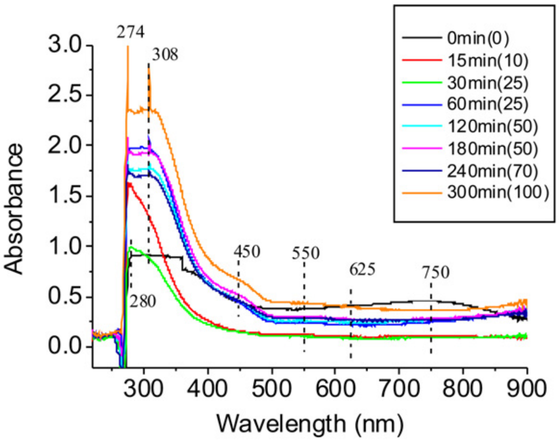


Fig. 11. UV–vis spectra of the samples removed from the reaction mixture at specified time intervals. The experimental conditions are the same as stated in Fig. 10. The values in the parentheses show the diluted times of the samples.

The UV–vis spectra of these samples showed complicated results (Fig. 11). At the beginning of the reaction (0 min), an intense and broad absorption band in the 270–460 nm region (LCT transitions) and two weak broad bands centered at around 615 and 740 nm (d–d transitions) were observed, confirming the coexistence of $V^V$ and $V^{IV}$ species in the solution. The vanadium species existed in several complexes forms at this time. Just after 15 min of reaction, these broad CT bands became sharp and showed maxima at 274 and 280 nm, with an additional band centered at 308 nm and a weak broad band at around 550 nm. Comparing this spectrum with Fig. 8 (curve b), the disappeared 359-nm absorption band was tentatively associated with the disappearance of $V^V(NH_2OH)_2$ species, and the observed 308-nm absorption band was attributed to the remaining $V^V(NH_2OH)$ species, in agreement with the $^{51}$V NMR results. However, as indicated by the computational study, aniline can coordinate with $VO^{2+}$ in solution and results in much more intense absorption bands (Fig. S6). Thus the appearance of the band at 308 nm also may indicate the formation of aniline. As the amination proceeded, the absorption band at 280 nm (CT transitions for $V^V$) gradually disappeared or was masked by the more intense CT transitions of $O^{2-} \rightarrow V^{4+}$ (274 nm). That is, it is difficult to measure the decrease in the amount of $V^V$ in the reaction mixture by UV–vis spectra. Furthermore, as Fig. 10 suggests, about 94% of the vanadium existed as $V^{IV}$ at 0 min of the reaction, so the increase of the intensities of the UV–vis spectra for the $V^{IV}$ species would be inconspicuous. Thus, the significant increase in the intensities of the absorption bands seen at 274, 308, and 550 nm suggest the increase in the amount of aniline-coordinated $V^{IV}$ complexes. That is, the UV–vis spectra revealed the increase in the amount of aniline formed. The UV–vis spectra showed an additional shoulder peak in the 400–500 region from the 60-min sample, which also belongs to the aniline-coordinated $VO^{2+}$ species. In all cases, d–d transitions were observed between 600 and 800 nm, but their intensity was very low with respect to that of the major bond, making then difficult to distinguish.

The EPR signals of these samples indicate the presence of the vanadyl ion in solution in all cases. But different $g_{iso}$ and $A_{iso}$ values were obtained. Within 30 min, a $g_{iso}$ value of $1.972 \pm 0.001$ with an $A_{iso}$ value of $111.4 \pm 0.2$ G was established. After 30 min, the $A_{iso}$ value of this paramagnetic species increased to 113.7 G, indicating changes in the tetravalent vanadium complex geometry. A higher value for $A_{iso}$ reveals higher symmetry at the site of vanadium and lower delocalization of electron density onto the ligands. Interestingly, a signal corresponding to a new species with a $g_{iso}$ value of $2.0041 \pm 0.0005$ appeared after 30 min, just after the disappearance of the bishydroxamido $V^V$ species. This new species may be assigned to an organic free radical. A representative spectrum is shown in Fig. 12. The presence of the organic free radical reveals a radical mechanism for the present amination.

### 3.6. Reaction mechanism

Several free-radical mechanisms have been proposed for amination reactions using *N*-chloroalkylamines, hydroxylamine-*O*-sulfonic acid, and alkylhydroxylamines as the aminating agents catalyzed by redox metal ions such as $Ti^{3+}$, $Fe^{2+}$, and $Cu^+$ [43,44]. Kuznetsova et al. [18] proposed a free-radical mechanism, considering the protonated amino radical ($^{\bullet}NH_3^+$) as the active aminating species, by ab initio quantum mechanical calculations for the amination of benzene and toluene. In the present work, based on the literature and the obtained spectroscopic observations as well as the activity measurement, we propose a similar free-radical mechanism for the vanadium-catalyzed amination of benzene to aniline, as shown in Scheme 1.

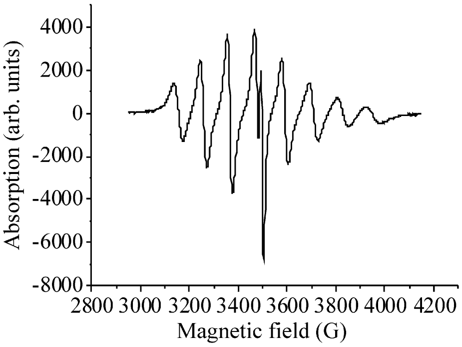
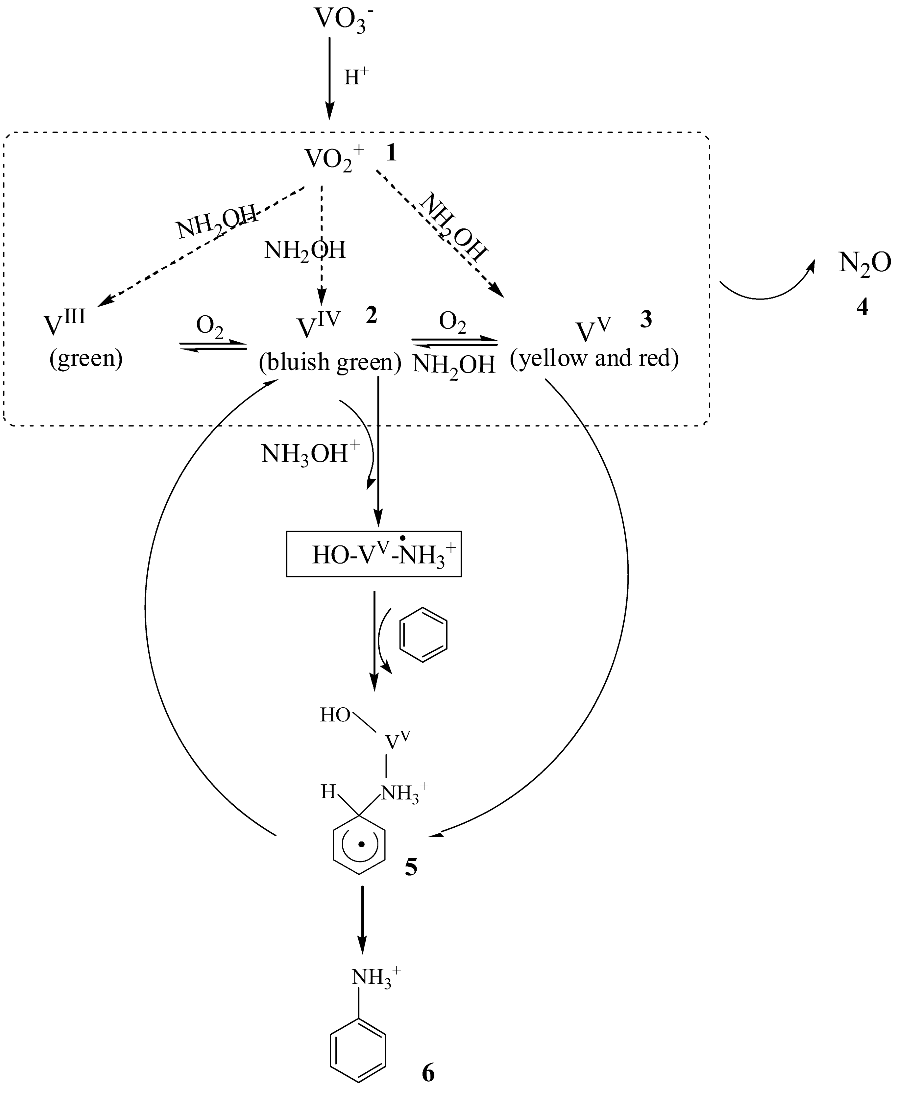


Fig. 12. Room temperature X-band EPR spectrum of the reaction mixture (120 min). The experimental conditions are the same as stated in Fig. 10.

The proposed mechanism involves the interaction of a $VO_2^+$ cation (species **1**) with hydroxylamine to form the lower-valent vanadium species, mainly $V^{IV}$. Gaseous $N_2O$ (species **4**) is evolved during this redox course. The $V^{III}$ species likely formed is unstable in open air and is oxidized to the relatively stable $V^{IV}$ (species **2**). But the $V^{IV}$ species also probably would be partially oxidized to $V^V$ (species **3**) in the presence of hydroxylamine, acetic acid, and atmospheric oxygen. On account of the relatively stronger reductive power of lower-valent vanadium species, the hydroxylamine present in the system then acts as oxidative agent and is reduced to a protonated amino radical ($^{\bullet}NH_3^+$). The $^{\bullet}NH_3^+$ species, existing as a protonated amino-vanadium complex ($HO–V^V–{}^{\bullet}NH_3^+$), then attacks the benzene ring to give a protonated aminocyclohexadienyl radical intermediate (species **5**), which is subsequently oxidized by $V^V$ species to form a protonated aniline (species **6**) accompanying the regeneration of lower-valent vanadium species in a catalytic cycle. The exhaustion of hydroxylamine stops the formation of $HO–V^V–{}^{\bullet}NH_3^+$, which further results in the termination of the amination process. In addition, it is clear that the presence of the $V^V$ species (**1** and **3**) is essential for the amination process, because they are involved not only in the production of lower-valent vanadium species, but also in the rearomatization of the aminocyclohexadienyl radical intermediate to form aniline [44]. The lower-valent vanadium species are further involved in the formation of the active protonated amino-vanadium radical species. Atmospheric air favors the coexistence of $V^V$ (**3**) and $V^{IV}$ (**2**), which is crucial for the amination progress.

The presence of species **1** was been detected by $^{51}V$ NMR [Fig. 7a, −540 ppm]. The $V^V$ species **3** refers to its bishydroxamido and monohydroxamido complexes, especially the latter, and their existence was confirmed by their $^{51}V$ NMR signals [Fig. 7b, −796, −806, and −648 ppm]. The $^{51}V$ NMR signals also indicate the decrease in the amount of species **3** (Fig. 10). EPR signals give information on the formation of the $V^{IV}$ species **2** (Fig. 9) and the aminocyclohexadienyl radical intermediate **5** (Fig. 12). Gaseous product **4** was observed by monitoring the decomposition of hydroxylamine. No information is obtained on whether a coordination change occurs during the reduction of $V^V$ species to lower-valent ones, but this process is possible.

To verify the validity of the proposed mechanism, the amination was also carried out using 0.3 mmol $VOSO_4$ as the catalyst under the aforementioned optimized conditions. An aniline yield of about 37%, with a selectivity of 90% to aniline, was obtained. The UV–vis spectra of the samples withdrawn at specific time intervals during the amination exhibited similar



Scheme 1. Proposed mechanism.

values as the $V^V$ catalyzed ones (Fig. S8); that is, both $V^{IV}$ and $V^V$ species existed in the solution during the amination, suggesting that a small amount of the $V^{IV}$ species were oxidized by atmospheric oxygen and hydroxylamine to $V^V$ species. The protonated amino-vanadium radical species ($HO–V^V–{}^{\cdot}NH_3^+$), evolved from the reduction of hydroxylamine by $V^{IV}$, then participated in the subsequent amination process to produce aniline. However, the intensities of UV–vis of the $V^{IV}$ catalyzed system were relatively weaker than those of the $V^V$ catalyzed ones, indicating that less aniline was formed in the $V^{IV}$ system compared with the $V^V$ system. This may be explained by the fact that the $V^V$ species has a greater oxidative power than the $V^{IV}$ species, and the higher oxidizing character is obviously favorable for rearomatization of the aminocyclohexadienyl radical intermediate [44].

To clearly determine whether the phenol intermediate had been generated during the amination, the reaction was comparatively carried out using phenol as the starting material in the presence of $NaVO_3$. Both $NH_2OH{\cdot}HCl$ and ammonia were used as "aminating agents." The results showed that no aniline or hydroxy-substituted anilines were produced in these two systems, suggesting that the titled amination proceeded through a direct ring attack by protonated amino-vanadium radical species to form aniline, but not through an attack at the hydroxy-group of the phenol intermediate.

In addition, our previous work [36] also favors the present mechanism. That is, the amination of toluene with hydroxylamine in acidic media catalyzed by supported vanadium catalysts resulted in an unselective formation of *o*-, *p*- and *m*-toluidines. It is well known that if the amination progressed by an electrophilic mechanism, then *o*- and *p*-toluidines would be predominant in the products. The unselective product formation suggests that the amination occurred through a radical mechanism, as proposed above.

## 4. Conclusion

In summary, it is shown that aniline can be directly synthesized from benzene and hydroxylamine hydrochloride catalyzed by sodium metavanadate in acidic reaction media under mild conditions. A relatively acidic reaction medium—especially an organic acid such as acetic acid–water medium—is advantageous for the present homogeneously catalyzed amination. We have shown that the amination reaction occurs more efficiently in an open-air system than in a closed system. The optimized reaction conditions investigated in the present work were $n_{\mathrm{benzene}}/n_{\mathrm{NH_2OH}}$ 1:1, HOAc:$H_2O$ (v/v) 4:1, conducted at 353 K for 4 h under atmospheric pressure. These conditions proved to be more favorable than those reported previously [18], with a much longer reaction time, higher reaction temperature, higher reaction pressure, and more acidic reaction media used and a lower aniline yield obtained. Satisfactory aniline yield and turnover (64 mol%, 48 mol aniline/mol V) were obtained under the optimized reaction conditions. This approach shows promise for the further development of a direct amination process with hydroxylamine as the aminating agent.

Based on the results of spectroscopic and activity measurements, as well as quantum chemical calculation, a free-radical mechanism has been proposed. The decomposition of hydroxylamine is highly related to the amination process, resulting in the production of lower-valency vanadium species that are further involved in creation of the active aminating species ($\mathrm{HO{-}V^{V}{-}{}^{\bullet}NH_3^+}$). The presence of the $V^{V}$ species is essential for the amination process, because they are involved not only in the production of lower-valency vanadium species, but also in the rearomatization of the aminocyclohexadienyl radical intermediate to form aniline. The atmospheric air favors the coexistence of $V^{V}$ and $V^{IV}$, which is crucial for the amination progress. The acetic acid used in the present study not only acts as a good solvent for mixing the reactants into one phase, but also supplies an acidic surrounding, perhaps even coordinating with the vanadium center and affecting the mechanism of the titled amination reaction.

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## Supplementary material

The on-line version of this article contains additional supplementary material.

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