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Improved Reduction on Amines of Dihydrophenophosphazine System

JIN-HAI CUI[1,2,*], SHU-FEN ZHANG[1], LEI ZHANG[2] and ZHI-GANG YIN[3]

[1]State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, P.R. China
[2]School of Chemical Engineering, Kaifeng University, Kaifeng 475001, P.R. China
[3]Henan Provincial Key Laboratory of Surface and Interface Science, Zhengzhou Institute of Light Industry, Zhengzhou 450002, P.R. China

*Corresponding author: Fax: +86 371 23810622; Tel: +86 371 23810032, +86 15039025857; E-mail: navyclark71@aliyun.com

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With the addition of 15-20 % more of water in absolute methanol dissolvent, the hydrogenation reduction on four of nitro-derivatives of 5,10-dihydro-phenophosphazine system was improved from 75 to 95 %, yet with reduced time and more efficiency. Both the adsorption and desorption of nitro-derivative on the surface of Pd/C and the concentrate of methanol aqueous solution were proved to be the dominating factors for the reaction rate of hydrogenation reduction, the optimistic concentrate of methanol aqueous solution were fitted by nonlinear Gaussian function and be verified by experiments also.

Keywords: Amines of dihydrophenophosphazine, Hydrogenation reduction, Reduction mechanism.

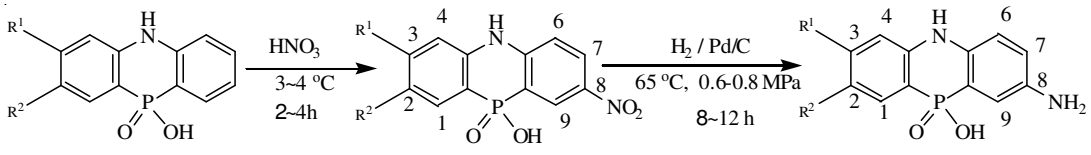
INTRODUCTION

Ever since it was proved that the amines of 5,10-dihydro-phenophosphazine, a series of important eco-friendly-hetero-cyclic intermediates, can be used to synthesize non-mutagenic azo dyes in place of carcinogenic aromatic amines such as diphenyl-amine, 2-naphathyl amine, *etc.*[1]. Several studies[2-6] reported the synthetic route of nitrates and amines of phenophosphazine.

The amines of 5,10-dihydrophenophazine-10-oxide (**3a-d**) can be synthesized by the corresponding nitrates (**2a-d**) at 65 °C through 10 h of reacting process. Hereinto, hydrogen was used as reducing agent at 6 to 8 atmospheric pressure, with palladium on the carbon, 5 % in total weight, being used as catalyst, and alcohol or methanol as solvent, after the acidity of turbid solution was adjusted to pH 7.0-7.2. The hydrogenation reduction reaction on nitro-derivatives (**2a-d**) is given in **Scheme-I**.

As a matter of fact, although the reduction process can clearly be observed in catalytic hydrogenation mentioned above all, mono-nitrates (**2a, 2b**) and di-nitrates (**2c, 2d**) can not be reduced completely within 8 to10 h, and nitrates (**2a-d**) can be detected out from their amines easily by mass spectrum even if the reaction time exceeds 12 h. The amino-derivatives (**3a-d**) ,with less than 75 % of maximum yields detected by HPLC, varied their colour from light blue, dark blue to dark which were in conflict with that of pale grey as described previously[7].

Surprisingly, when the solvents were changed from alcohol or methanol to alcohol or methanol aqueous solution in reduction mentioned above, both mono-nitrates of 5,10-dihydro-phenophosphazine (**2a**, **2b**) and di-nitrates of 5,10-dihydro-phenophosphazine (**2c**, **2d**) can be reduced easily within 8 to12 h and the reduced-products identified with those in their studies.



1a $R^1=R^2=H$
b $R^1=Me$; $R^2=H$

2a $R^1=R^2=H$
b $R^1=Me$; $R^2=H$;
c $R^1=H$; $R^2=NO_2$
d $R^1=Me$;$R^2=NO_2$

3a $R^1=R^2=H$
b $R^1=Me$; $R^2=NH_2$
c $R^1=H$; $R^2=NH_2$
d $R^1=Me$;$R^2=NH_2$
e $R^1=H$; $R^2=NO_2$
f $R^1=Me$;$R^2=NO_2$

Scheme-I

From Figs. 1 and 2, it can be seen that although mono-nitrates **2a** and **2b** can be reduced into **3a** ([M-H]$^-$, 245.1; [2M-H]$^-$, 491.1) and **3b** ([M-H]$^-$, 259.0; [2M-H]$^-$, 519.1) when the reaction time was extended to 12 h, the di-nitrates **2c** and **2d** can only be reduced completely to **3c** ([M-H]$^-$, 261.1)and **3d** ([M-H]$^-$, 274.1) with the part-reduced products **3e** ([M+Cl$^-$]$^-$, 291.0) and **3f** ([M+Cl$^-$]$^-$, 339.2) even if the reaction time was extended to 12 h.

While in Figs. 3 and 4, it is clear that not only can mono-nitrates **2a** and **2b** be reduced to **3a** and **3b**, the di-nitrates **2c** and **2d** can also be reduced completely to **3c** ([M-H]$^-$, 261.1) and **3d** ([M/Z]$^-$, 274.1) when solvent was changed from methanol to 80 % methanol in aqueous solution solely.

By analyzing the different speeds of absorption and desorption between nitrates of 5,10-dihydro-phenophosphazine (**1a -1d**) and hydrogen on the surface of catalyst, this paper attempts to find out the appropriate solvent, dose of Pd/C catalyst, pressure of hydrogen and reaction time to optimize the reaction conditions. It was found out that with the addition of 15-20 % water in absolute methanol dissolvent, the hydrogenation reduction on four of nitro-derivatives of 5,10-dihydro-phenophosphazine system was improved from 75 to 95%, yet with decreased time and more efficiency. The inner salt and polymer of nitrates of phenophosphazine were thought as the key factor to retard the catalytic hydrogenation, and the measure how to decrease the self-polymerization of nitrates of phenophosphazine accordingly.

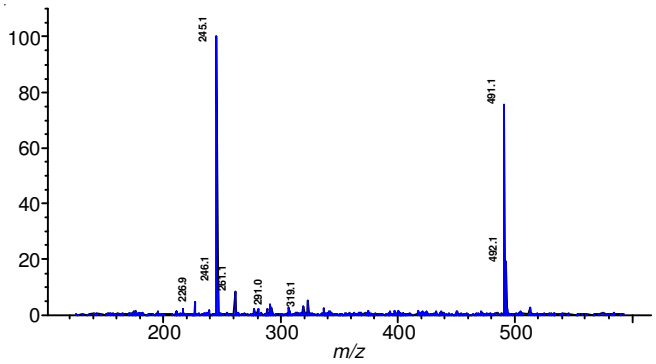


Fig. 1. MS of reduced nitro-derivative (**2a** and **2c**); nitro-derivatives (**2a-d**) were reduced in methanol solution

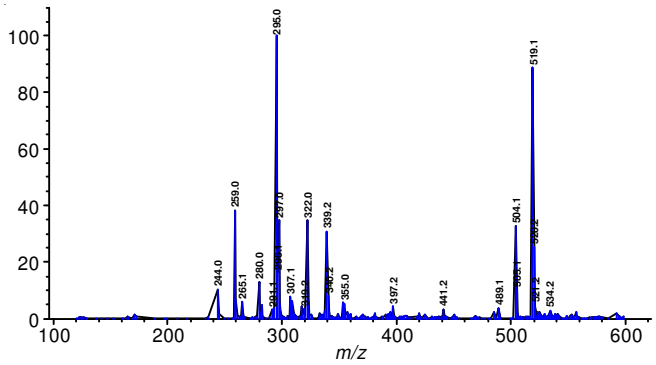


Fig. 2. MS of reduced nitro-derivative (**2b** and **2d**); nitro-derivatives (**2a-d**) were reduced in methanol solution

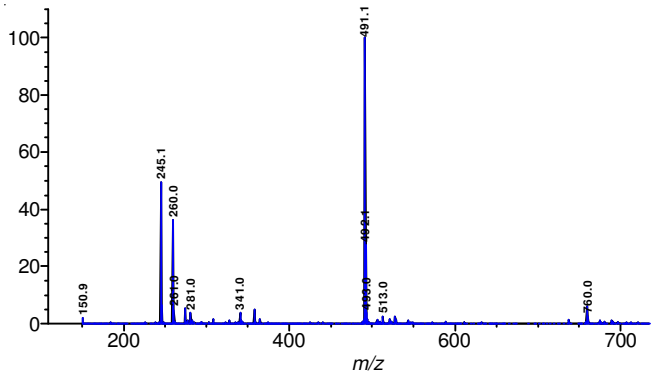


Fig. 3. MS of nitro-derivatives (**2a** and **2c**); nitro-derivatives (**2a-d**) were reduced in aqueous methanol solution

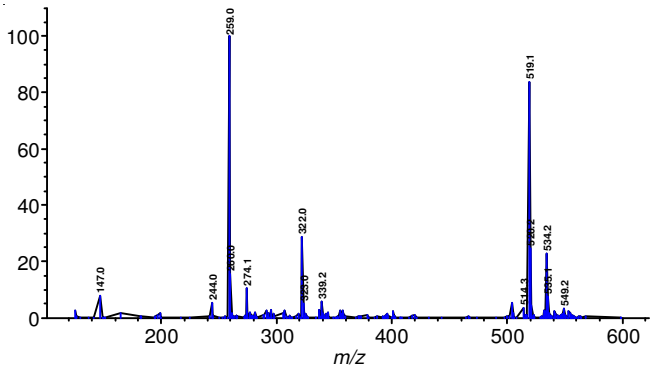


Fig. 4. MS of nitro-derivative (**2b** and **2d**); nitro-derivatives (**2a-d**) were reduced in aqueous methanol solution

EXPERIMENTAL

The MS spectra were measured on HP1100 high efficiency liquid chromatography spectrometer/mass spectrometer system and ^{1}H NMR spectra were measured on the Varian INOVA-400 spectrometer, using DMSO-d_6 as solvent and tetramethylsilane (TMS) as the internal standard, and the melting points were measured on X-6 micromelting point apparatus.

Phenophosphazine-10-oxide derivatives (1a and **1b):** 5,10-dihydro-phenophosphazine (**1a**) and 7-methyl-5,10-dihydro-phenophosphazine (**1b**) were synthesized successfully in the previous studies[1]. The detecting results on relative contents and melting points were analyzed by high efficiency liquid chromatography spectrometer and micro-melting point apparatus showed that **1a** and **1b** have melting points of 264-268 °C (97.5 %, w/w) and 284-287 °C (98.5 %), respectively which were consistent with the results of previous studies[10,11].

Mono-nitrates of phenophosphazine-10-oxide (2a and 2b): 7 g of **1a** and 150 mL of ice acetic acid were added into three-neck bottle with which electric agitator, thermograph and reflux condenser were matched. The mixture was heated up to reflowing to guarantee **1a** dissolved in acetic as best as could be, and then the temperature was dropped to 4 °C. After that nitryl agent (nitrate, 63-68 %, (w/w): acetic acid = 1:1.5 (v/v)), which is 4 times of reagent in mole ratio, was added dropwise into reaction bulb from dropping funnel, and with the reaction temperature kept less than 4 °C within 3 h of reaction time. Then orange-red product solution were poured into 200 mL of ice-water mixture, and the yellow precipitation was filtered from water solution by Büchner funnel, washed with distilled water and dried to obtain the yellow powder solid **2a** in the yield of 60-80 %. The relative content of **2a** is 98% and final melting point is more than 300 °C.

The product had m.p. >300 °C (dec.); MS (API-ES) *m/z* (% rel. int.):275.0 ([M-H]$^-$, 98), 551.1 ([2M-H]$^-$, 100); ^{1}H NMR

δ: ~4.8 (broad peak), 7.20 (t, 1H, ^3J = 7.2, 6.7), 7.27 (t, 1H, ^3J = 7.4, $^4J_{P-H}$ = 6.3), 7.31 (q, 1H, ^3J = 9.2, $^4J_{P-H}$ = 6.0), 7.55 (q, 1H, ^3J = 6.7, 7.4), 7.78 (q, 1H, ^3J = 7.2, $^3J_{P-H}$ = 12.7), 8.25 (q, 1H, ^3J = 9.2, ^4J = 2.5), 8.56 (q, 1H, ^4J = 2.5), 10.80 (s, 1H).

The yellow powder product (**2b)** which has 98 % of relative content and more than 300 °C in melting point can be obtained when the mole ratio of nitryl agent and reagent **1b** were decreased to 3:1 and the same synthesizing procedure and purifying method were employed.

The product had m.p. >300 °C (dec.); MS (API-ES) *m/z* (% rel. int.):289.0 ([M-H]$^-$, 100), 579.1 ([2M-H]$^-$, 46); ^{1}H NMR δ: 2.62 (s, 3H), ~4.32 (broad peak), 7.07 (d, 1H, $^4J_{P-H}$ = 3.7), 7.13 (d, 1H, $^4J_{P-H}$ = 3.8), 7.22 (t,1H, ^3J = 7.4, $^4J_{P-H}$ = 4.3),7.78 (t, 1H, ^3J = 8.0, $^4J_{P-H}$ = 12.0), 8.38 (q, 1H, ^3J = 8.0, $^3J_{P-H}$ = 12.0), 8.52 (d, 1H, ^3J = 12), 10.80 (s, 1H).

Di-nitrates of phenophosphazine-10-oxide (2c and 2d): Di-nitrates of phenophosphazine-10-oxide (**2c** and **2d**) were synthesized and purified successfully according to the methods as reported in the previous studies[2,12] and the detecting results on the structures of **2c** and **2d** are also in accordance with the literature.

The product **2c** had m.p. > 300 °C (dec.); MS (API-ES) *m/z* (% rel. int.): 320.0 ([M-H]$^-$, 90), 641.0 ([2M-H]$^-$, 100). ^{1}H NMR δ: 7.48 (q, 2H, ^3J_H = 9.2, $^4J_{P-H}$ = 6.5); 8.38 (d, 2H, ^3J_H = 9.2); 8.60(d, 2H, $^3J_{P-H}$ = 13.6); 10.90 (s, 1H).

The product **2d** had m.p. > 300 °C (dec.); MS (API-ES) *m/z* (% rel. int.):334.1 ([M]$^-$, 100), 669.2 ([2M-H]$^-$, 28); ^{1}H NMR δ: 2.89 (s, 3H, ~4.32 (broad peak), 7.34 (d, 1H, $^4J_{P-H}$ = 6.9); 7.85 (t,1H, $^4J_{P-H}$ = 6.5); 8.36(d, 1H, ^3J = 8.0); 8.47 (d, 1H,$^3J_{P-H}$ = 12); 8.52 (d, 1H, $^3J_{P-H}$ = 12); 10.90 (s, 1H).

Amines of phenophosphazine-10-oxide (3a and 3b): 2 g of **2a** and 50 mL of 80 % methanol in aqueous solution were added into 200 mL of Erlenmeyer flask and adjusted the pH of suspension in 10 % of potassium hydroxide solution to 8 to assure its dissolvent. The reduction was performed in a 100 mL of high pressure reactor where 0.16 g of Pd/C were used as catalyst, 0.8 MPa of hydrogen was used as reducer during the 8 h of reducing course. The rough reducing solution was diluted with 50 mL of deionized water, acidified to pH 5-6 in weak acidification with 10 % of HCl. The formed precipitation thereof was collected with sand core funnel, washed with a little deionized water to remove the salt formed during acidification. 1.7-1.8 g of **3a** was obtained in 98 % of purity.

The product **3a** had m.p. > 300 °C (dec.); MS (API-ES) *m/z* (% rel. int.): 245.2 ([M-H]$^-$, 25), 281.0 ([M+Cl$^-$]$^-$, 75), 491.9 ([2M-H]$^-$, 100); ^{1}H NMR δ: ~4.8 (broad peak) 4.6 (broad peak), 6.82 (q, 1H, ^3J = 8.8, ^4J = 2.2), 6.91 (t, 1H, ^{3} J = 6.9, 6.3), 6.93 (q, 1H, ^3J = 8.8, $^4J_{P-H}$ = 6.8), 6.99 (d, 1H, ^4J = 2.2), 7.05 (t, 1H,^{3} J = 8.0, $^4J_{P-H}$ = 6.4), 7.35 (t, 1H, ^3J = 6.3, 8.0), 7.65 (q, 1H, ^3J = 6.9, $^3J_{P-H}$ = 12.6), 9.58 (s, 1H).

The similar reaction conditions and method of purifying were used in the course of reduction to 7-methyl-3-nitro-5,10-dihydrophenophosphazine-10-oxide (**2b)** apart from prolonging reactive time to 9 h and the light grey amine of **3b** was obtained in 97.5 % of purity.

The product **3b** had m.p. > 300 °C (dec.); MS (API-ES) *m/z* (% rel. int.): 259.0 ([M-H]$^-$, 100), 519.1 ([2M-H]$^-$, 84); ^{1}H NMR δ: 2.27(s, 3H), 4.6 (broad peak),6.51(d, 1H, ^3J = 12.6), 6.79 (d, 1H, ^3J = 3.8), 6.89 (d, 1H, $^4J_{P-H}$ = 2.1), 6.98 (d, 1H, $^3J_{P-H}$ = 12.5), 7.15 (t, 1H, ^3J = 8.2,$^4J_{P-H}$ = 6.4), 7.52 (q, 1H, ^3J = 4.6, $^3J_{P-H}$ = 12.4), 9.44 (s, 1H).

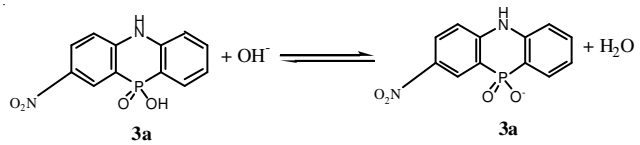
Synthesis to diamino phenophosphazine-10-oxide (3c and 3d): The same reaction conditions and method of purifying as they were used in the course of reduction to dinitro nitrates of 5,10-dihydrophenophosphazine-10-oxide **2c** and **2d** apart from prolonging reactive time to 12-14 h. The silver grey amines of **3c** and **3d** were obtained in 95.5 and 97.0 % of purity.

The quaternary ammonium chloride of product **3c** had m.p. > 300 °C (dec.); MS (API-ES) *m/z* (% rel. int.): 259.0 ([M-H]$^-$, 38), 295.0 ([M+Cl$^-$]$^-$, 100) 519.1 ([2M-H]$^-$, 90); ^{1}H NMR δ: ~4.8 (broad peak), 4.6 (broad peak), 7.50 (q, 2H, ^3J = 8.9, $^4J_{P-H}$ = 6.4), 7.63 (t, 2H, ^3J = 8.9, 2.2), 7.80 (d, 2H, $^3J_{P-H}$ = 12.8), 9.38 (s, 1H).

The product **3d** had m.p. > 300 °C (dec.); MS (API-ES) *m/z* (% rel. int.): 274.1 ([M-H]$^-$, 100), 549.3 ([2M-H]$^-$, 11); ^{1}H NMR δ: 2.27 (s, 3H), ~4.14(broad peak) 7.09 (d, 1H, $^4J_{P-H}$ = 3.6), 7.25 (q, 1H, ^3J = 8.2, $^4J_{P-H}$ = 7.6), 7.66 (d, 1H, ^3J = 11.8), 7.71 (d, 1H, $^3J_{P-H}$ = 8.2), 7.96 (d, 1H,$^3J_{P-H}$ = 3.2), 9.75 (s, 1H).

RESULTS AND DISCUSSION

The reduction reaction proceeds smoothly when the nitrates of 5,10-dihydro-phenophosphazine was in excellent solvency in methanol in basic condition other than in acidific.. This fact indicated that not only did the whole reduction take place on the surface of Pd/C, but also the speed of absorption and desorption on reagent in methanol went with the whole course of reduction. The interaction of nitrates of 5,10-dihydrophenophosphazine with basic solution is given in **Scheme-II**.



3a Poor solubility in alcoholic solution

3a Excellent solubility in alcoholic solution

Scheme-II

In order to study the effects of the dosage of catalyst in reduction, the dosage of catalyst of Pd/C was changed to 6, 8, 10 and 12% of substrate's weight, respectively in each experiment while the same reactive conditions and method of purifying were unchanged during the reduction of **3c**. The results of the experiment showed that the suitable dosage of catalyst may be 8% o f substrate's weight, which is consistent with the analytical result of MS as well as high efficiency liquid chromatography.

The effects of different pressure of hydrogen on nitrates of **2a** and **2b** were also examined, and the results of reduction are depicted in Table-1. The pressure of hydrogen was changed at 7, 8, 9 and 10 atm, respectively in each experiment while the other reaction conditions and method of purifying were unchanged.

Table-1 indicates that no more than 76 % of **2a** and **2b** can be reduced into **3a** and **3b** under 7 atmospheres of hydrogen and the yield of amines do not increase proportionally when the hydrogen pressure is more than 9 atm. This phenomenon indicates that there is suitable proportional relationship between

TABLE-1
REDUCING RESULT OF **3a** WITH H_2 OVER 8 % Pd/C CATALYST UNDER DIFFERENT REACTION PRESSURE

No.	R·P (atm)	U.A.P* (nm)	Result by HPLC of product (%)	
			3a	**3b**
1	7	283	74.30	75.43
2	8	278	98.48	97.62
3	9	278	96.82	96.35
4	10	278	94.17	95.49

*Detecting wavelength of HPLC: 283 and 278 nm; chromatographic column: Hypersil ODS2 (5 μ, 2.5 × 150); flowing phase: 50/50 MeOH -1 % of aqueous HOAc (v/v); flowing velocity: 0.6 mL/min

hydrogen and nitro derivatives on the surface of Pd/C catalyst, in which the largest yield of reduction product can be obtained. The concentration balance between reduction agent and nitro derivatives was destroyed when the higher hydrogen pressure such as 9 atm. were used, and the decrease in the yield of amines of phenophosphazine will be inevitable when the pressure of hydrogen is more than 8 atm.

The effect of different dissolvent on reduction yield of nitrates of **2a-2d** was also examined. Water, 25 % of MeOH, 50 % of MeOH, 75 % of MeOH and absolute MeOH were used in each experiment while the other reactive conditions and method of purifying remained unchanged. The purity of amino derivatives, detected by high pressure liquid chromatography, was the same as those under the detecting condition of Table-1, and the results were as Table-2.

TABLE-2
REDUCING RESULT OF **3a** WITH H_2 OVER 8 % Pd/C CATALYST IN DIFFERENT SOLVENT

Solvent	Result by HPLC of product in different solvent (%)*			
	3a	**3b**	**3c**	**3d**
H_2O	50.60(8)	45.20(9)	55.31(10)	62.11(12)
25 % MeOH	60.30(8)	61.33(9)	70.58(10)	80.48(12)
50 % MeOH	80.13(8)	78.73(9)	86.55(10)	90.35(12)
75 % MeOH	95.75(8)	94.15(9)	92.10(10)	94.19(12)
Absolute MeOH	91.38(8)	91.38(9)	91.40(10)	93.20(12)

*The detecting condition is as same as Table-1, and different figures enclosed in parentheses mean reaction time (h)

Experiments showed that reducing effect in methanol aqueous solution is more positive than in water or in absolute methanol. No doubt, this will provide an alternative synthetic method, and with more conciseness, efficiency and lower cost. The experimental results on reducing yields of **3a**-**3d** were fitted in non-linear Gaussian function, the fitting curves are shown in Figs. 5-8 and fitting plots areas are given in Table-3. It can be seen from Fig. 5 that the suitable temperature of reduction depends on both the reduction of the time of reaction and the decrease of the by-product.

It was obvious that the highest yields of 97, 95, 93 and 95 % on **3a**, **3b**, **3c** and **3d** can be figured out respectively when the maximum concentrations of 82.6, 82.6, 82.8 and 79.5 % were substituted to x in their own fitting plots. The fitting curves have the ideal goodness of fit in 0.99961, 0.99388, 0.98972 and 0.99067.

It is very interesting to find that the ideal reduction yields can be obtained in the methanol aqueous solution other than in absolute methanol solution. From the variable reduction

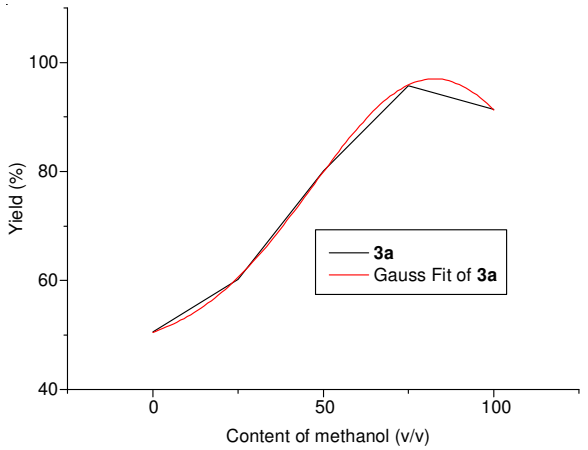


Fig. 5. Yield of **3a** in different content methanol in aqueous solution

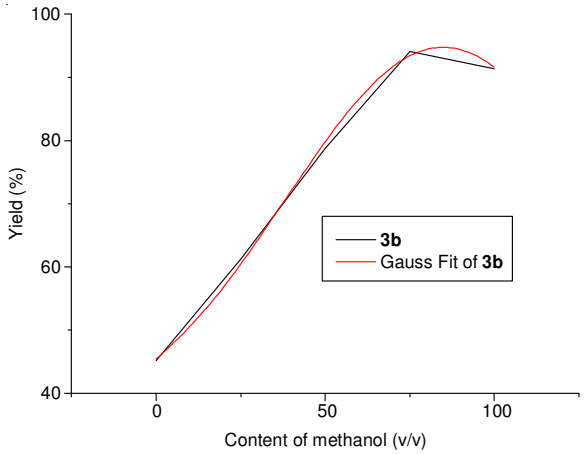


Fig. 6. Yield of **3b** in different content methanol in aqueous solution

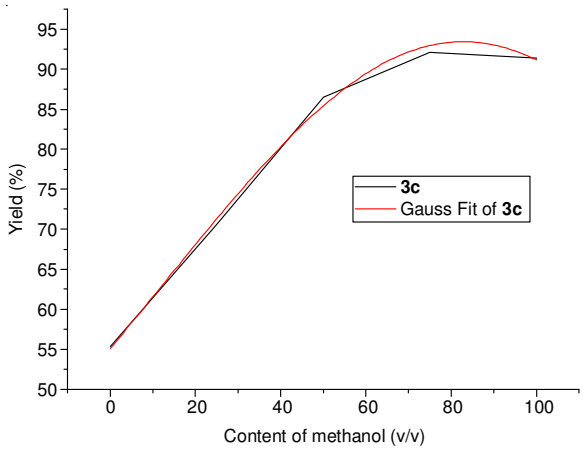


Fig. 7. Yield of **3c** in different content methanol in aqueous solution

yield in different dissolvent it can be deduced that the catalytic reduction rate was determined by the rate of absorption and desorption of nitro-derivatives of 5,10-dihydro-phenophosphazine system on the surface of catalyst.

As both acidic hypo-phosphorous group and basic imino group coexisted in the nitro-derivatives of 5,10-dihydro-phenophosphazine system, neutralization reaction would inevitably occur between nitro-derivatives. As a result of their neutralization reaction, dimmer and polymer of nitro-derivatives can be seen in **Scheme-III** in the form of inner salt thereof.

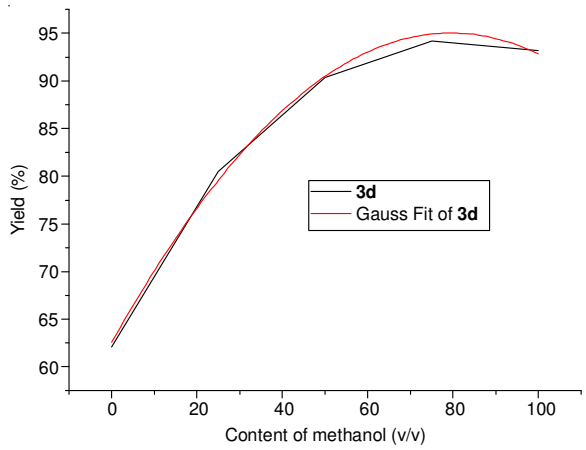
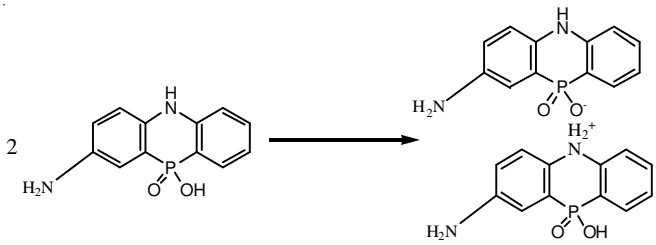


Fig. 8. Yield of **3d** in different content methanol in aqueous solution

TABLE-3
FITTING PLOTS ON AMINES (**3a**-**3d**)

Amino-products	Fitting plots*	Adj. R^2
3a	$y = 47.1728 + 49.8378 \times e^{-\frac{(x-82.5452)^2}{2517.0151}}$	0.99961
3b	$y = 34.2030 + 60.5706 \times e^{-\frac{(x-82.5452)^2}{4283.7323}}$	0.99388
3c	$y = 19.4822 + 73.9420 \times e^{-\frac{(x-82.8237)^2}{9404.0327}}$	0.98972
3d	$y = -665.2857 + 760.3064 \times e^{-\frac{(x-79.4896)^2}{144747.9328}}$	0.99067

*Plots were fitted by nonlinear Gaussian function where 'x' is the concentration of methanol aqueous solution and 'y' is the yield of reducing products correspondingly



Scheme-III

The existence of dimmer and polymer of nitro-derivatives which bulked their molecular volume would retard the absorption and desorption of nitro-derivatives on the surface of catalyst, prolong the reaction time, and decrease the reducing yield. Therefore, the reduction of nitro-derivatives of 5,10-dihydrophenophosphazine system will depend on the extent to which the auto polymerization of the nitro-derivatives can be decreased.

It is well known that water has high dielectric constant (ε = 78.4) as compared to methanol (ε = 30), and it can be used as an excellent ionizing and dissociative medium and the electrolyte in water will not have association-reaction unless at very high concentration[5]. Meanwhile, as the electrolyte, the association of nitro-derivatives of 5,10-dihydrophenophosphazine system would be suppressed, and sole ions of nitro-derivatives would increase when absolute methanol was changed into suitable concentration of methanol aqueous solution. Therefore, the existence of large amount of sole ions of nitro-derivatives in methanol aqueous solution would no doubt accelerate the process of reduction and enhance the efficiency of reduction.

However, suitable concentration of water in methanol must be considered. Not only that water would be generated from the hydrogenation reduction reaction while the nitro groups were reduced to amino groups in 5,10-dihydrophenophosphazine system, but that superfluous water added in methanol will decrease the synthesized amino-derivatives of **3a-3d** in accordance with Le Chatelier's principle on chemical equilibrium. These effects indicated that water added would decrease the generation of polymer on nitro-derivatives and accelerate the rate of reaction, while water generated would slow its rate of desorption from the surface of catalyst, and retard the whole rate of hydrogenation reduction reaction thereof[9].

According to Haber's mechanism[13], the normal route for hydrogenation of nitrobenzene to aniline takes place through bimolecular coupling of aniline and nitrosobenzene, forming azo benzene as intermediate, which is then rapidly hydrogenated into two anilines. Given this, the adsorption and desorption of nitro-derivatives **2a**-**2d**, nitroso intermediates, hydroxylamines and azo benzene intermediates of phenophosphazine system on the surface of catalyst, as well as the desorption of the generated H_2O.

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