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Introduction

During the last few decades, research interests in the field of nano particles have swung enormously resulting in an upsurge in our knowledge bank about the fundamentals at sub-molecular level physics and chemistry. Numerous efforts have been put to prepare different nano particles of various morphologies with newer techniques¹⁻⁸ to discover their physical and potential chemical properties.⁹⁻¹⁵ A considerable attention have also been cast towards nano particles prepared from the novel metals, like platinum, due to its high stability and catalytic efficiencies. Platinum based nano particles play a crucial

PVP stabilized Pt nano particles catalyzed de-oxygenation of phenoxazine group by hydrazine in physiological buffer media: surfactant competes with reactants for the same surface sites[†]

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PVP capped platinum nano particles (PNP) of 5 nm diameter were prepared and characterized as homogeneous and of spherical nature. At physiological pH range (6.0-8.0), these PNP catalyze the deoxygenation of phenoxazine group containing resazurin (1) by hydrazine. The observed rate constants (k_o) , increase linearly with [PNP] at constant [1] and [Hydrazine]; but first increase and then after reaching a maximum it decrease with increase in [1] as well as in [Hydrazine]. The k_{0} values increase linearly with $1/[H^+]$ indicating N₂H₄ as the reducing species that generates from the PNP assisted deprotonation of $N_2H_5^+$. The kinetic observations suggest Langmuir–Hinshelwood type surface reaction mechanism where both 1 and hydrazine are adsorbed on nano particles surface and compete for the same sites. Interestingly, the surfactant molecules, polyvinylpyrrolidone (PVP), though do not take part into reduction reaction but having same type of functional groups as reactants, competes with them for the same surface sites. Adsorption on PNP with same type of functional group is further supported by the FTIR spectra of Pt-PVP and Pt-1. Thus on increasing [PVP], k_o decreases linearly and only when [PVP] is held constant, the plot of k_o vs. [PNP] passes through the origin indicating the insignificance of uncatalyzed reaction. The plot of $\ln k_o vs.$ [1] or [Hydrazine] shows two different linear zones with different exponent values with respect to [1] and [Hydrazine]. This indicates that along with the complex heterogeneous surface adsorption processes, the mutual interactions between the reactants are also changing with the relative concentrations of reactants or, in general, with the molar ratio ([Hydrazine]/[1]).

role in the hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) in fuel cells and chemical reactions.^{16–20} Since platinum itself remains an inert metal in biological systems, platinum based nano particles are promising tools in this field. Recent studies have shown such potentiality in treatment of cancerous cell^{21,22} and in destruction of harmful radicals.²³

Motivated by this, we have synthesized homogenous PVP stabilized platinum nano particles (PNP) by a fast and easier but efficient single pot method and studied the catalyzed deoxygenation reaction of phenoxazine group.

Phenoxazine group, present in resazurin (7-hydroxy-3*H*-phenoxazin-3-one-10-oxide) (1) contains a heterocyclic *N*-oxide group that on reduction loses its oxygen and produces fluorescent resorufin (7-hydroxy-3*H*-phenoxazin-3-one) (2). Resazurin, also known as Alamar Blue,^{24,25} had been used over last half of the century to determine bacterial or yeast contamination in biological fluids and in milk.^{26,27} Moreover, since resazurin is nontoxic to cells it has been in profuse use for the

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[†]Electronic supplementary information (ESI) available: Fig. S1–S7, Tables S1–S7 and explanation of effects of surface restructuring on k_0 are provided. See DOI: 10.1039/c2dt32007j

assessment of cell proliferation and cytotoxicity.^{28–30} In metabolically active cells, resazurin is reduced to resorufin and dihydroresorufin by mitochondrial enzymes activity by accepting electrons from NADPH, FADH, FMNH, NADH as well as from numerous cytochromes.^{31–33} A great deal of photochemical studies have also been carried out on resazurin because the deoxygenation of *N*-oxide has a close resemblance to the enzyme mediated oxygen atom transfer involving monooxygenases.^{34,35} Due to these importance, in recent times nano particles catalyzed reduction of resazurin have also been studied by laser and single molecule fluorescence microscopy.^{36–38}

Following the importance of nano particles in biological field,^{21–23} the detailed kinetics of PNP catalyzed reduction of resazurin by hydrazine was studied in physiological pH condition. The study shows that the reaction takes place on the very nano particle surface and molecules with similar functional groups compete for the same reaction sites.

Experimental section

Materials

Potassium tetrachloroplatinate(II) (Aldrich), sodium citrate dihydrate (Rankem, India), polyvinylpyrrolidone (k-30, avg. MW = 40 000, Fluka), resazurin (Loba Chemie, India), hydrazine hydrate (Loba Chemicals), sodium nitrate (Merck), potassium dihydrogen phosphate (SRL, India) and sodium hydroxide (SRL) were used as received. Milli-Q water and double distilled water was used for the preparation of PNP and kinetic experiments respectively. All other chemicals used were of analytical grade.

Preparation PVP stabilized platinum nano particles (PNP)

Preparation of stable polymer capped platinum nano particles was proposed long back in 1940s by Rampino and Nord.³⁹ Since then platinum nano particles have been prepared by wide and different varieties of techniques both in aqueous and in organic medium which is very well documented.⁴⁰ Different types of surfactants were also used to stabilized the nano particle.^{41–45} Nevertheless, a necessity of simple and quick preparation method of stable platinum nano particles from corresponding Pt(II) salt in pure aqueous medium is undeniable from the viewpoint of effectiveness, intricate setups and costly materials.

Herein, we developed a rapid, one-pot, two step, efficient synthetic procedure for polyvinylpyrrolidone (PVP) capped platinum nano particles (PNP). Platinum nano particles were prepared by the reduction of aqueous Pt(n) ions with tri sodium citrate. Citrate ions act as both the reducing agent and the primary stabilizing agent. Though it is generally believed that a metal salt like Pt(n) is reduced first to zero-valent metal atom as Pt(0) at its embryonic stage and then forms metal clusters after reaching a critical concentration of Pt(0), an alternative mechanism with initial formation of Pt(n)-Pt(n)bond has also been proposed.⁴⁶ However, citrate ions primarily stabilize the nano particles electrostatically by forming electrical double layer at the particle interfaces.⁴⁷ After the complete reduction and thus formation of nano particles, aqueous solution of PVP was added to Pt nano particles solution to cap them for enhanced stability. PVP, a colorless, non-ionic, non-toxic and water soluble, polymeric compound of high molecular weight has been used abundantly to stabilize different kinds of metal nano particles.^{48–51}

The general procedure for the preparation of platinum nano particles (PNP) was as following: 50 mL of an aqueous K_2 PtCl₄ solution (2.5 × 10⁻⁴ M) was heated to boiling with vigorous stirring. Then 2 mL of 1% (w/v) aqueous tri sodium citrate solution was quickly injected in this solution to reduce $Pt(\pi)$ to Pt nano particles. The solution was allowed to boil for one hour with vigorous stirring when the transparent light brownish-yellow colored solution turned to brown and finally to opaque black indicating the formation of Pt nano particles. At this stage, 5 mL of 1% (w/v) aqueous PVP solution was added to this Pt nano particles solution and the boiling was continued for another 30 minutes with stirring. Finally, the opaque black PNP solution was cooled to room temperature and was stored in a cold, dry and dark place. This PNP solution, which was treated as the stock is stable for months and was always used after sonication.

Instrumentation

Absorbance and UV-VIS spectra were recorded using a Shimadzu spectrophotometer (UV-1700) with 1.00 cm quartz cuvettes. Transmission electron microscopic (TEM) analyses were performed in a Hitachi (H-9000 NAR) instrument on samples prepared by placing a drop of PNP solution on Cu grid, precoated with carbon films, followed by solvent evaporation under vacuum. PNP solution was centrifuged in Heraeus, Biofuge primo R machine and Fourier Transform Infrared Spectroscopy (FTIR) data were collected using a Shimadzu FT-IR 8400S. PNP solution was regularly sonicated in Rivotek ultrasonic bath (50 Hz) before any experimentation.

The buffer solutions were prepared following literature method⁵² and were measured with a Toshniwal pH-meter (CL-54, India), calibrated as usual using standard buffers.

Characterization of PNP

The formation of PNP was characterized by TEM imaging and UV-VIS spectroscopy. The TEM images of the PNP are shown at two different magnifications (Fig. 1). The size and the shape of the nano particles ware determined from enlarged images and it can be seen that the sample contains solid nano particles of spherical nature. The % size distribution plot (Fig. 2) shows that the extent of heterogeneity in nano particles sizes lie in a very narrow range. Whereas the nano particles of size of 5 nm diameter alone consists about 50% of the total population, the other nano particles with diameters of 3, 4 and 6 nm contributes for the rest of the part.

Fig. 3 presents the UV-VIS spectrum of aqueous solution of Pt(n) complex and stock PNP solution. Spectrum of the aqueous solution of the precursor Pt(n) complex shows three distinct absorbance peaks at 322, 384 and 472 nm which



Fig. 1 (a, b) HR-TEM image of PVP stabilized platinum nano particles (PNP)

become absent in the UV-VIS absorption spectrum of stock PNP solution. The absence of peaks confirm the formation of the platinum nano particles.^{53–56}

The presence of PVP molecules on platinum surface was confirmed by FTIR spectral analysis. The FTIR spectrum of PNP (Fig. 4) shows an intense absorption band at 1643 cm⁻¹ which is attributed to the presence of C=O bond in pyrrolidone ring of PVP. Other peaks at ~3400 (s, w), 1400 (m) and 1288 (m) and 1099 (m) are assigned to C-H and O-H stretching (from residual water molecules), C-H bending, N-OH and C-N stretching respectively.⁵⁷⁻⁵⁹ PVP molecules have both a carbonyl group and a heterocyclic nitrogen atom and it can coordinate to nano particles in either or combined way.^{58,60} Since the platinum nano particles are of very small sizes (~5 nm) and the electronegativity of nitrogen atom is less than the oxygen atom, a weak coordination of PVP molecules to



Fig. 2 The % distribution of different sizes of PNP shows a predominance of 5 nm nano particles.



Fig. 3 Characteristic UV-VIS spectrum of K_2PtCl_4 complex (brown) and PNP, after formation (grey).

platinum surface through the nitrogen of heterocyclic ring apart from the carbonyl group is also feasible. But, whatever be the mode of coordination, it is evident that PVP is present and is capping the nano particles surface through charge transfer interaction.

Here it is worthwhile to mention that though the role of PVP is to protect the nano particles surface, the interaction of PVP with platinum surface is not very strong^{61,62} and it does not passivate the surface like other capping agents (for example, –SH).⁶³

Deoxygenation reaction of 1

The UV-visible absorption spectrum of resazurin in aqueous phosphate buffer solutions shows a characteristic strong absorption band at 602 nm and a weak one at 380 nm which arises due to the π - π * transition of the phenoxazin-3-one and the weak n- π * transitions of the *N*-oxide, respectively. When



ig. 4 FTIR spectrum of PVP capped Pt nano particles (PNP)



resazurin is catalytically reduced by hydrazine, resorufin is produced which shows its characteristic visible absorption at 572 nm with a shoulder at 535 nm (Fig. S1, ESI[†]).⁶⁴ Here it is worth mentioning that resorufin, which was produced on deoxygenation of **1** is also catalytically reduced to colorless protonated resorufin anion (**3**) at pH 7.0.⁶⁵ Thus there are two catalyzed reaction (**R1** and **R2**) and visibly the whole reduction process is accompanied with a distinct color change from blue to pink to colorless (Scheme 1). The reduction of resorufin can be followed spectrophotometrically at 572 nm (Fig. S2[†]). But here we have only contended our study to the detailed kinetics of catalyzed reduction of **1**.

Kinetics

The reduction of resazurin (1) by hydrazine is strongly catalyzed by PVP stabilized platinum nano particles (PNP). The uncatalyzed reaction between 1 and [Hydrazine] ([Hydrazine] is the analytical concentration of added hydrazine) in absence of PNP (other conditions being the same as in general kinetic experiments) is very slow (Fig. S3⁺). Also, when measured amount of PNP or aqueous PVP solution ([PVP] $\leq 0.0018\%$) alone was added to the buffered solution of 1, the absorbance at 602 nm does not change at least for two hours. It ensures that platinum nano particles alone ($\sim 10^{-10}$ M, vide infra) or the stabilizing agent PVP molecules present in the final reaction mixture cannot reduce 1 under similar kinetic condition. Moreover, it has also been ensured that the addition of mere PVP solution ([PVP] \leq 0.0018%) cannot catalyze the reduction of 1 by hydrazine. During the preparation of final reaction mixture, measured amount of PNP solution from the stock solution and sodium nitrate solution (to maintain ionic strength, μ) were added to the buffered solution of 1 followed by the final quick addition of hydrazine solution. The final volume of the reaction mixture was 3.0 mL. A typical UV-VIS spectral change of 1 with time for the catalyzed reaction is shown in Fig. 5. Kinetics was measured in phosphate buffer (pH 6.0–8.0) *in situ* in an electrically controlled thermostat.

Kinetic experiments for reduction of **1** were performed in the presence of a large excess of hydrazine over [1] to ensure pseudo first-order conditions. The rate constants (k_0) were determined from the plots of decrease in absorbance with time at 602 nm, the visible absorption peak of **1**, where no other species in the reaction mixture absorbs. Non-linear, standard least-squares fit to a first-order equation of such decay with time, yielded the observed first-order rate constants, k_0 (Fig. 6). However, it can be noted that there is an induction period (t_0) in catalyzed reaction and which was not considered in the determination of k_0 values. Presence of arial oxygen or the impurities in the reaction medium cannot explain the induction period because on passing argon or on addition of



Fig. 5 Spectral change for PVP capped platinum nano particles (PNP) catalyzed reduction of **1** by hydrazine at 60 s time interval. Condition: [**1**] = 0.025 mM; [Hydrazine] = 5.0 mM; [PNP] = 5.46×10^{-11} M; μ = 0.25 M; pH = 7.0; T = 25.0 ± 0.1 °C.



Fig. 6 PNP catalyzed reduction of **1** by hydrazine at 602 nm. Condition: [**1**] = 0.025 mM; [Hydrazine] = 5.0 mM; [PNP] = 5.46×10^{-11} M; $\mu = 0.25$ M; pH = 7.0; $T = 25.0 \pm 0.1$ °C.

chelating agent, like dipicolinic acid, the induction period remains as usual.⁶⁶ This induction period can be attributed to the nano particles surface restructuring and will be discussed again later.

Here, it is worth mentioning that in our previous work⁶⁶ we have shown that all the nano particles with different sizes followed the same reaction mechanism and gives a first-order reaction. The effect of size of nano particles is manifested in the rate of the reactions which usually decrease with the increase in the nano particles size. With larger size distribution, the difference in rate constants will also be large. In this study, as we have mentioned earlier that the differences between the size of nano particles are limited within a very narrow range, the difference in rate constant values derived

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Fig. 7 Variation of k_o with the increase of [1] at fixed [Hydrazine] and [PNP]. Condition: [Hydrazine] = 5.0 mM (A), 10.0 mM (B); [PNP] = 5.46 × 10⁻¹¹ M; μ = 0.25 M; pH = 7.0; T = 25.0 ± 0.1 °C.

from the reactions catalyzed by nano particles of different sizes (reactions performed under similar conditions) are supposed to be also too small to be differentiated. Hence, we can assume that the rate constant of the catalyzed reaction is virtually unaffected by the insignificant amount of heterogeneity in nano particles sizes.

However, to minimize the impacts of the unavoidable errors, we have tried to put more emphasis on the trends of different variations to draw conclusions rather than the numerical value of any particular data.

Results and discussion

Concentration of PNP

The approximate concentration of PNP was calculated using eqn $(1)^{67}$

$$[PNP] = [Pt2+ ions]/(V_{PNP}/V_{Pt atom})$$
(1)

where, *V* refers to the corresponding volumes. Calculations with effective ionic radii for Pt(II) as 0.080 pm⁶⁸ and sizes of PNP assigned from TEM imaging as ~5 nm gives the concentration of stock PNP solution to be approximately 8.2×10^{-9} M. Similar formulation, based on ion and particle diameters also gives about the same order of value.⁶⁹ Different amounts of PNP solution from stock were used to catalyze the reaction and in reaction media the concentration of PNP was in the order of 10^{-11} M.

Variation of k_o with [1] and [Hydrazine]

When concentration of **1** is increased at fixed [Hydrazine] and [PNP] (Table S1[†]), the observed first-order rate constant, k_0 , first increases with the increase in [**1**]; then reaching a maxima it decreases with further increase in [**1**] (Fig. 7).

Similar type of variation of k_0 is observed when [Hydrazine] at fixed [1] and [PNP] is increased. The observed rate

Dalton Transactions



Fig. 8 Dependency of k_{\circ} on [Hydrazine] at fixed [1] and [PNP]. Condition: [1] = 0.025 mM (A), 0.04 mM (B); [PNP] = 5.46 × 10⁻¹¹ M; μ = 0.25 M; pH = 7.0; T = 25.0 ± 0.1 °C.

constants, k_0 first increase and then it decrease with the increase in [Hydrazine] (Table S2,[†] Fig. 8).

These kinetic observations are in firm support of surface catalytic reaction. In general, heterogeneous surface reaction can be explained either by Eley-Rideal or by Langmuir-Hinshelwood mechanism. In Eley-Rideal mechanism, one of the reactants, present in gas or solution phase interacts with the surface adsorbed reactant whereas in Langmuir-Hinshelwood mechanism both reactants are adsorbed on the catalyst surface. If the reduction of 1 proceeds through Eley-Rideal mechanism, then with increase of [1] or [Hydrazine] values of k_0 should have reached saturation. But since the rate constant values first increases and then decreases, it is more plausible that the catalytic reduction follows Langmuir-Hinshelwood mechanism where both resazurin and the reductant hydrazine molecules compete to sit on the surface sites.^{38,70–73} Thus, at fixed [PNP], when [1] or [Hydrazine] is increased, the reaction sites on PNP are more occupied by the corresponding molecules. This results in increased reaction rate up to an optimum value and then due to the paucity of other reactants ([Hydrazine] or [1], respectively) the observed rate constants decrease. Both the observations are in accord with the recent observations made by Chen et al.38

Here the effect of variation of [1] and hydrazine is noteworthy. While for [1], after the optimum concentration ~0.015 mM the decrease of k_0 starts, for hydrazine the decrease takes place at high concentration as ~20 mM. Apparently, it seems that at comparatively lower concentration of 1 the surface of platinum nano particles appears to be covered to such extent that the reductant molecule hydrazine lacks the sitting place. This effect probably arises from the bulky nature of the molecule 1. The aromatic ring moiety of 1 has a planner structure and it has been proposed to be oriented in parallel way to the surface during adsorption.⁷¹ Due to this steric hindrance, even at low [1], it covers up the other adsorption sites. Hydrazine molecule, on the contrary being a much smaller and flexible species require much less space and thus only at high [Hydrazine] k_0 values commence to decrease.

Here it will be very interesting to consider that how the reactant molecules occupy the sites on platinum surface. In case of hydrazine it is well established that being a symmetrical molecule it only uses lone pair of electron of nitrogen atoms to be adsorbed on platinum surface.^{74,75} However, to the best of our effort, we could not find any report regarding any possible mode of attachment between Pt and resazurin in the literature. We studied the FTIR of pure resazurin and PNPresazurin mixture to understand the mode of coordination through which it is adsorbed on nano particles surface (Fig. S4 and S5[†] respectively). It can be seen that peaks both at 1354 cm⁻¹, which can be assigned to N⁺-O⁻ bond⁷⁶ and peaks at 1606 cm⁻¹, attributed to carbonyl group, have red shifted. Since peaks ~1350 cm⁻¹ are more diminished and more red shifted, it can be assumed that the probability that resazurin uses N⁺-O⁻ end to sit on platinum surface is more than the C=O end.

The different nature of interaction of **1** and hydrazine with the platinum surface also results in different adsorption strengths. Between **1** and hydrazine, literature report shows that the adsorption coefficient of **1** is much more stronger than hydrazine.³⁸ This preferential adsorption of **1** over hydrazine is probably another reason that why even at small increase in [**1**] compared to that in [Hydrazine], the surface tends to saturate and the reaction rate starts to fall.

Effect of [PNP] and [PVP] on k_0

The observed rate constants, k_0 , for catalyzed reaction not only depend upon the concentration of PNP but it is also affected by the concentration of capping agent, PVP in the media. At fixed [1] and [Hydrazine], with increasing [PNP] ([PVP] vary approximately as 0.0006–0.0018% only, Table S3†) the observed rate constants increase linearly. This trend is consistent with our previous findings and reveals only the typical behavior of the catalyst.⁶⁶ But, whereas, at zero concentration of catalyst, it was also expected that the rate should have been zero as the uncatalyzed reaction between 1 and hydrazine is very slow, the plot yields an intercept value about $1 \times 10^{-3} \text{ s}^{-1}$ (Fig. 9). This large intercept value alone cannot be explained by the much lower uncatalyzed reaction rate constant value $(2.4 \times 10^{-4} \text{ s}^{-1})$.

Interestingly, at fixed [PNP] and other kinetic conditions, when total [PVP] is increased by additional PVP solution the observed rate regularly falls (Fig. 10, Table S4[†]). Thus increasing [PNP] and [PVP] have the mutually opposite effect on the observed rate and this complexity results in the aforesaid large intercept value. Thus, true dependence of the catalyzed rate constants on [PNP] can only be observed when the [PVP] is kept constant. So, when [PVP] is kept fixed at 0.01% through calculated addition of extra PVP solution, the observed rate constants, k_o not only linearly increases with the increase with [PNP] but also passes through origin (Fig. 11, Table S3[†]).

Thus the observed rate constants depend both on the relative concentrations of PNP and PVP. PVP molecules themselves



Fig. 9 Variation of k_o with [PNP] is a straight line but with intercept. Condition: [**1**] = 0.025 mM; [Hydrazine] = 5.0 mM; μ = 0.25 M; pH = 7.0; T = 25.0 ± 0.1 °C.



Fig. 10 Variation of k_0 with [PVP]. Condition: [**1**] = 0.025 mM; [Hydrazine] = 5.0 mM; [PNP] = 5.46×10^{-11} M; $\mu = 0.25$ M; pH = 7.0; $T = 25.0 \pm 0.1$ °C.

do not take part in reduction reaction or their presences in large amount do not disturb the diffusion behavior of reactants in solution. The later can be confirmed from the fact that uncatalyzed reaction rates are not affected by the absence or presence of PVP in large concentration (0.02%). These observations lead us to the possibility that PVP molecules not only cap the platinum surface but also occupy the same sitting sites as resazurin and hydrazine does. It is more plausible because PVP molecules possess similar coordinating groups like both hydrazine and resazurin. Again it is also supported by the earlier mentioned fact, that there is evidence^{58,60} for PVP for using both types of coordination mode. Since PVP has no role in the main reduction reaction of 1, the concentration of PVP does not appear in the reaction mechanism and the extra occupation of reaction sites is only manifested in the decrease in reaction rates.



Fig. 11 Plot of k_o vs. [PNP] at fixed [PVP] is straight line passing through origin. Condition: **[1]** = 0.025 mM; [Hydrazine] = 5.0 mM; μ = 0.25 M; [PVP] = 0.01%; pH = 7.0; T = 25.0 ± 0.1 °C.



Fig. 12 Variation of k_{\circ} with [H⁺]. Condition: [1] = 0.025 mM; [Hydrazine] = 5.0 mM; [PNP] = 5.46 × 10⁻¹¹ M; μ = 0.25 M; T = 25.0 ± 0.1 °C.

Effect of $[H^+]$ on k_0

PNP catalyzed reaction rates increases fairly linearly with $1/[H^+]$ in the pH range 6.0–8.0 (Table S5,[†] Fig. 12) which indicates that the reactive reducing species is hydrazine, not the hydrazinium (N₂H₅⁺) ion. Since the p K_a value for N₂H₅⁺ is 7.95, at lower pH most of the hydrazine will remain protonated and free hydrazine (N₂H₄) will only be available at higher pH. Thus, the production of free N₂H₄ molecules at lower pH will require an assisted deprotonation of N₂H₅⁺ molecules. Assisted deprotonation may result from the adsorption of hydrazinium ion on PNP surface.⁶⁶

Effect of ionic strength (μ) on k_0

The observed rate constants of catalyzed reactions increases linearly with the ionic strength of the media (Table 1). Ionic

Table 1 Representative k_o values at different ionic strength (μ)



strength of the reaction medium was maintained by the calculated addition of NaNO₃ solution. The positive slope indicates that the reacting species are of same charge.

Proposed mechanism for R1

On the basis of the kinetic observations the catalyzed reaction steps can most simply be presented by Scheme 2. The possible products that are formed from 1 and hydrazine are well reported in literature. On deoxygenation of 1, along with 2, mainly water is produced^{32,77} and on oxidation of hydrazine, mainly N₂ is formed along with little H₂.^{74,78-81} Though recent studies have shown that metal-catalyzed hydrogen production from the decomposition of hydrazine takes place only under certain reaction conditions,⁸² the possibility of formation of small amount of hydrogen, however, cannot be neglected. Thus separate experiments were conducted where pure hydrogen gas was passed through the reaction mixture under similar reaction condition. It has been found that no reaction takes place at least for 2 hours. Thus we can firmly eliminate the possibility of reduction of 1 by hydrogen, if any generated.

In Scheme 2, the aromatic side rings of **1** and **2** have been omitted for simplicity. The scheme is only representative and protons may not come from a particular hydrazine but from other neighboring hydrazine molecules also.

During the adsorption on the platinum surface (step 1), resazurin (1) is adsorbed through the N^+ – O^- bond (from FT-IR data, as previously mentioned) and hydrazine molecules are adsorbed through the nitrogen atoms. Since during the self decomposition of hydrazine on metal films, it has been found that at initial stage the hydrogen atoms are ruptured, we can assume that this hydrogen can be transferred to 1 in step 2.^{83–85} With this hydrogen, 1 is reduced and 2 is produced (step 3). The adsorbed OH species then receives another proton from the hydrazine residue (step 3) and departs as water molecule. The remaining hydrazine residue reacts further with another molecule of 1 or itself decomposes to produce N₂, NH₃ and little H₂ (step 4).

Since the kinetic observations support the Langmuir–Hinshelwood surface mechanism, the rate of the reaction can simply be expressed as follows⁷⁰

$$\begin{aligned} \text{Rate} &= -d[\mathbf{1}]/dt = k_{\text{o}}[\mathbf{1}] \\ &= (kK_{\text{R}}[\mathbf{1}]^{\alpha}K_{\text{H}}[\text{Hydrazine}]^{\beta})/(\mathbf{1} + K_{\text{R}}[\mathbf{1}]^{\alpha} \\ &+ K_{\text{H}}[\text{Hydrazine}]^{\beta})^2 \end{aligned} \tag{2}$$

where, *k* is the true rate constant and $K_{\rm R}$ and $K_{\rm H}$ are the adsorption coefficients of **1** and hydrazine respectively. The exponents α and β are the corresponding reaction order with respect to [**1**] and [Hydrazine]⁸⁶ which can also be correlated with the heterogeneity of the nano particles surface, that is the adsorption energy of the adsorption sites is not homogeneous.⁸⁷

The above equation can be rearranged as

$$([\mathbf{1}]^{\alpha}/k_{o}[\mathbf{1}])^{1/2} = (\mathbf{1}$$

$$+ K_{H}[Hydrazine]^{\beta})/(kK_{R}K_{H}[Hydrazine]^{\beta})^{1/2}$$

$$+ [\mathbf{1}]^{\alpha}(K_{R}/kK_{H}[Hydrazine]^{\beta})^{1/2}$$
(3)

Or,
$$([\text{Hydrazine}]^{\beta}/k_{o}[\mathbf{1}])^{1/2} = (\mathbf{1} + K_{R}[\mathbf{1}]^{\alpha})/(kK_{H}K_{R}[\mathbf{1}]^{\alpha})^{1/2} + [\text{Hydrazine}]^{\beta}(K_{H}/kK_{R}[\mathbf{1}]^{\alpha})^{1/2}$$

(4)

If, both $\alpha = \beta = 1$, then both the equation reduces to classical Langmuir–Hinshelwood equation,

$$([\mathbf{1}]/k_{o}[\mathbf{1}])^{1/2} = (\mathbf{1}$$

$$+ K_{H}[Hydrazine])/(kK_{R}K_{H}[Hydrazine])^{1/2}$$

$$+ [\mathbf{1}](K_{R}/kK_{H}[Hydrazine])^{1/2}$$
(5)

Or,
$$([\text{Hydrazine}]/k_{\text{o}}[\mathbf{1}])^{1/2} = (\mathbf{1} + K_{\text{R}}[\mathbf{1}])/(kK_{\text{H}}K_{\text{R}}[\mathbf{1}])^{1/2} + [\text{Hydrazine}](K_{\text{H}}/kK_{\text{R}}[\mathbf{1}])^{1/2}$$
 (6)

So, the plot of $([1]/k_0[1])^{1/2} \nu s$. [1] or $([Hydrazine]/k_0[1])^{1/2} \nu s$. [Hydrazine] should have been be a continuous straight line.⁸⁸ But we have found that none of the plot is a single straight line (Fig. 13 and 14).

It can be seen that both in Fig. 13 and 14 that though some experimental points consists a linear zone but it deviates from linearity over the wide concentration range and more importantly there are unexpected breaks in the graph. The appearance of the breaks cannot be related to any inhomogeneity in nano particles size because for any first-order reaction, the plots should have been a straight line. These breaks in the plots tell that the interaction between the adsorbate molecules and the adsorption sites are not very homogenous. Thus, it is reasonable that the exponent values are not constant over the total reactant concentrations or in general, at different molar ratio ([Hydrazine]/[1]). If we assume that the adsorption of [1] and [Hydrazine] is not so strong, then the eqn (2) can be

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Fig. 13 Plot of $([1]/k_0[1])^{1/2}$ vs. [1]. Condition: [Hydrazine] = 10.0 mM; [PNP] = 5.46 × 10⁻¹¹ M; μ = 0.25 M; pH = 7.0; T = 25.0 ± 0.1 °C.



Fig. 14 Plot of ([Hydrazine]/ k_o [**1**])^{1/2} vs. [Hydrazine]. Condition: [**1**] = 0.04 mM; [PNP] = 5.46 × 10⁻¹¹ M; μ = 0.25 M; pH = 7.0; T = 25.0 ± 0.1 °C.

simplified to

$$Rate = k_{o}[\mathbf{1}] = kK_{R}[\mathbf{1}]^{\alpha}K_{H}[Hydrazine]^{\beta} \text{ or,}$$

$$k_{o} = kK_{R}[\mathbf{1}]^{\alpha-1}K_{H}[Hydrazine]^{\beta}$$
(7)

If we plot $\ln k_o vs. \ln[1]$ or $\ln k_o vs. \ln[Hydrazine]$ (Fig. S6 and S7[†] respectively) keeping [Hydrazine] or [1] constant respectively, clearly in each case, we get two distinct array of points which can be fitted to straight lines. From the slope values of different linear zones the corresponding exponent values with respect to reactants can be obtained (Table 2).⁸⁵ This type of adsorption profile with multiple linear section may result from irregular energy distribution associated with adsorption processes.⁸⁹

It can be seen from Table 2 that both the exponents with respect to **1** (α) and hydrazine (β) change over different molar ratios. Also, the large exponent values are noteworthy, which actually indicates the favorable surface adsorption processes.⁹⁰

Table 2 Change in α and β values with molar ratio

	Exponent value	Molar ratio ^a	Exponent value	Molar ratio ^a
α^b α^c	$\begin{array}{c} 1.76 \pm 0.0 \\ 1.37 \pm 0.0 \end{array}$	500–333 2000–1000	2.55 ± 0.14 2.43 ± 0.21	333–125 666–250
β^{d} β^{e}	$\begin{array}{c} 1.54 \pm 0.4 \\ 0.53 \pm 0.25 \end{array}$	200–600 125–375	$\begin{array}{c} 0.62 \pm 0.09 \\ 0.33 \pm 0.09 \end{array}$	800–1400 500–1125

^{*a*} Molar ratio = [Hydrazine]/[1]. ^{*b*} [Hydrazine] = 5.0 mM; [PNP] = 5.46 × 10^{-11} M; $\mu = 0.25$ M; pH = 7.0; $T = 25.0 \pm 0.1$ °C. ^{*c*} [Hydrazine] = 10.0 mM; [PNP] = 5.46×10^{-11} M; $\mu = 0.25$ M; pH = 7.0; $T = 25.0 \pm 0.1$ °C. ^{*d*} [1] = 0.025 mM; [PNP] = 5.46×10^{-11} M; $\mu = 0.25$ M; pH = 7.0; $T = 25.0 \pm 0.1$ °C. ^{*e*} [1] = 0.04 mM; [PNP] = 5.46×10^{-11} M; $\mu = 0.25$ M; pH = 7.0; $T = 25.0 \pm 0.1$ °C.



Fig. 15 Plot of ln k_o vs. ln[Hydrazine] at different temperature. Condition: [**1**] = 0.025 mM; [PNP] = 5.46×10^{-11} M; $\mu = 0.25$ M; pH = 7.0.

It is conceivable since with the change in molar ratio the extent of surface occupation by the reactants also changes. Thus the interaction between a reactant molecule with its adsorption site or even with the neighboring reactants also changes and that should profoundly affect the observed catalytic rate value. This gives the validation of the overall nonlinearity of Fig. 13 and 14. The calculated changes in exponent values are over a wide molar ratio range and thus they are only representative data to support the findings. In reality the change may be more continuous with each smaller change in molar ratio values. It has also been found that the exponent values are more or less temperature independent (Table S6⁺) which can be seen from the plot of $\ln k_0 vs. \ln[\text{Hydrazine}]$ at different temperatures (Fig. 15). Since it will be very much erroneous to assume certain α or β value, further attempt to evaluate $K_{\rm R}$ or $K_{\rm H}$ was not put forward.

Role of induction period, t_0

The induction period, t_0 , had been suggested as a measure of surface restructuring of the PNP and $1/t_0$ can be treated as the rate of restructuring process.^{70,73} Surface restructuring is an inevitable phenomena occurring at the surfaces due to the



Fig. 16 Plot of $1/t_0$ vs. [Hydrazine]. Condition: [**1**] = 0.025 mM; [PNP] = 5.46 × 10^{-11} M; μ = 0.25 M; pH = 7.0; T = 25.0 ± 0.1 °C.



Fig. 17 Plot of $(1/t_0 - 1/t_{0.sp})$ vs. [Hydrazine]. Condition: [**1**] = 0.025 mM; [PNP] = 5.46×10^{-11} M; $\mu = 0.25$ M; pH = 7.0; $T = 25.0 \pm 0.1$ °C.

relative instability of surface atoms in comparison to the bulk of the materials.91 The restructuring process consists of both spontaneous as well as adsorbate induced which are well documented in literatures.⁹¹⁻⁹³ For nano particles formed by 5d elements, like platinum, where the relativistic effects favors the incident,⁹² restructuring is more important and along with the spontaneous restructuring process, adsorbate induced restructuring also demands an attention. The initial induction period, t_0 , during the catalyzed de-oxygenation reaction of 1 includes both of the spontaneous and reactants induced restructuring effect.^{70,73} Fig. 16 shows the variation of $1/t_0$ against [Hydrazine] and the intercept of the plot gives a measure of spontaneous restructuring $(t_{0,sp})$.^{70,73} Thus we can have the only effect of adsorbate induced restructuring by calculating the $(1/t_0 - 1/t_{0.sp})$, which not only increase linearly with [Hydrazine] but also passes through the origin (Fig. 17). The confirmation whether the induction period is really a result of surface restructuring also comes from the plot of $1/t_0$



Fig. 18 Variation of $1/t_0$ vs. [PNP] (A) in absence and (B) in presence of excess PVP (for Condition, see Fig. 9 and Fig. 11 respectively).



Fig. 19 Plot of $ln(1/t_0)$ vs. $10^3/T$ gives. Condition: [1] = 0.025 mM; [Hydrazine] = 5.0 mM; [PNP] = 5.46×10^{-11} M; $\mu = 0.25$ M; pH = 7.0.

vs. [PNP] (Fig. 18). As expected in absence of PNP, $1/t_0$ is also zero.

From the above discussions it is also noteworthy that the rate of spontaneous surface restructuring is really small and this probably results from the relative stability of platinum surface than the others, like, gold surface. The findings are in accordance with literature reports.³⁸ Moreover, since both of k_0 and $1/t_0$ varies linearly with [Hydrazine], even if we subtract the contribution of restructuring (however small it may be) from the rate constants, the nature of different plots will remain same (see ESI[†] for a detail explanation). Thus the conclusions derived from the variations from different trends still holds in spite of the presence of surface restructuring effects.

The energy of surface restructuring can be calculated from $1/t_0$ following the simple Arrhenius law. Thus from the slope of the plot of $\ln(1/t_0) \nu s$. $10^3/T$ (Fig. 19), the surface restructuring energy can be obtained as approximately 58 ± 4 kJ M⁻¹. This is in close similarity with literature reports.^{71,72}



Fig. 20 The Arrhenius plot of $\ln k_0$ vs. 10³/*T*. Condition: [1] = 0.025 mM; [Hydrazine] = 5.0 mM; [PNP] = 5.46×10^{-11} M; $\mu = 0.25$ M; pH = 7.0.

Effect of temperature on catalysis

The activation energy for the PNP catalyzed reduction of **1** by hydrazine can be calculated from simple Arrhenius equation, ln $k_0 = \ln A - E_a/RT$ where k_0 and A are the observed rate constant and pre-exponential constant respectively. The plot of ln $k_0 vs$. $10^3/T$ is linear as expected (Table S7,[†] Fig. 20) and the approximate activation energy, E_a is 77 ± 9 kJ M⁻¹. The surface restructuring energy and the reaction activation energy, E_a are very close.⁷⁰

Conclusions

We have prepared homogenous spherical 5 nm sized PVP capped platinum nano particles (PNP) and studied the kinetics of catalyzed reduction and hence deoxygenation of 1 by hydrazine. The reaction takes place on nano particle surface and follows Langmuir–Hinshelwood mechanism where both reactants 1 and hydrazine competes for the same reaction sites. Since, PVP molecules, present as capping agent, have the same type of functional groups like 1 and hydrazine, compete for the same surface sites as the reactants though do not take part in reduction process. The reaction rate depends on the mutual interaction between the reactants as well as between reactants and adsorption sites but this interaction continuously changes as the ratio of concentration of hydrazine and 1 is varied.

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