

Catalytic Cycle during Heteropoly Acid Catalyzed Transfer Hydrogenation Reaction

M. V. Joshi, S. Vaidya, R. Pandey, and D. Mukesh¹

ICI India Research and Technology Centre, P.O. Box 155, Thane-Belapur Road, Thane 400601, India

Received September 22, 1998; revised December 8, 1998; accepted December 8, 1998

12-Molybdophosphoric acid catalyzed transfer hydrogenation of nitrobenzene by hydrazine in a homogeneous phase is studied using UV VIS, ESR, P³¹ NMR, FTIR, and XPS. The role of nitrobenzene and solvents on the oxidation state of molybdenum and hence the catalytic activity is elucidated. Breakdown of the Keggin structure leads to a loss in catalytic activity. While hydrazine reduces the catalyst to form the active Mo(V) species, nitrobenzene reoxidizes the catalyst to the Mo(VI) state, thereby completing the catalytic cycle. Nitrobenzene also maintains part of the catalyst in the (VI) state, thus preventing deep reduction and hence structural degradation. © 1999 Academic Press

Key Words: 12-Molybdophosphoric acid; catalytic cycle; redox reaction; solvent effect; ESR; P³¹ NMR.

INTRODUCTION

Heteropolyacids which are super acids have proved to be potential acid and redox bifunctional catalysts in homogeneous and heterogeneous systems. Various types of heteropoly acids (HPAs) used are 12-tungstosilicic acid, 12-molybdophosphoric acid, and 12-molybdosilicic acid. A few reactions such as the hydration of isobutene (1) and the hydrolysis of an ester (2) have been reported earlier. Kozhevnikov (3) recently reviewed different homogeneous and heterogeneous catalytic reactions carried out employing HPAs.

In the present work 12-molybdophosphoric acid (12-MPA) catalyzed transfer hydrogenation of nitrobenzene to aniline by hydrazine in a homogeneous phase is studied and the catalytic cycle is elucidated using various analytical tools. The fresh catalyst (HPA yellow) is predominantly in the Mo(VI) state, whereas the used or pre-reduced catalyst has molybdenum predominantly in the (V) state. The role of the substrate nitrobenzene and the solvent in the catalytic cycle is studied in detail using spectroscopic techniques.

¹ To whom correspondence should be addressed at: ICI India Research and Technology Centre, Thane Works, P.O. Box 155, Thane Belapur Road, Thane 400 601, Maharashtra, India. Fax: 022-763-28-89. E-mail: research.icirt@gems.vsnl.net.in.

EXPERIMENTAL

HPA yellow (S. D. Fine Chemicals Ltd., India) was first purified by dissolving in acetonitrile, the residue (white color) was discarded, and the pure HPA yellow recovered by evaporating the solvent in a rotavapor. The resulting product was used in all the following experiments.

About 200 mg (8.9×10^{-5} M) HPA yellow, nitrobenzene 196.96 mg (1.6×10^{-3} M), and 15 ml of methanol (solvent) were taken in a round bottom flask. Then, 8.0 g (2.0×10^{-1} M) hydrazine hydrate (80%) was added slowly to the stirred contents over a period of 30 min. The flask was maintained at 40–50°C. The product was separated from the reaction mixture by extracting it with dichloromethane or ethylacetate, purified by column chromatography, and analyzed by gas chromatography (capillary column with flame ionization detector). The used catalyst was blue in color.

To examine the reoxidizing capacity of nitrobenzene in the presence of alcohols as well as acetonitrile, the kinetics of reoxidation of HPA blue (from HPA(V) to HPA(VI)) was studied using spectrophotometry. To a solution containing 30 mg of HPA blue, 15 ml of different solvents such as methanol, *n*-butanol, and acetonitrile and 5.5 g nitrobenzene was added. The decrease in the intensity of a peak at 740 nm (corresponding to HPA blue) was recorded after every 15 min.

The various oxidation states of the catalyst samples (HPA blue, HPA yellow, and HPA blue mixed with nitrobenzene (1 : 1 and 1 : 10)) were studied using XPS and P³¹ NMR. The ESR technique was used to ascertain the reoxidation of HPA blue to HPA yellow. HPA blue with nitrobenzene samples was analyzed to determine the effect of nitrobenzene on the changes of the oxidation state of HPA blue.

SPECTROSCOPY

UV-VIS analysis was carried out on a Shimadzu UV-VIS recording spectrophotometer UV-160. A Varian E-line century series E-112 EPR spectrometer which utilizes 100-kHz field modulation was used for recording ESR.

TCNE (tetracyano ethylene) $g=2.00277$ was used as a standard for g -factor calculations. The ESR spectra were recorded at room temperature and at liquid nitrogen temperature. Sharp signals at liquid nitrogen temperature are observed due to Boltzmann's law of distribution of molecules among the ground state and the excited state. Doppler broadening increases with temperature because the molecules acquire a wider range of kinetic energy. Therefore, to obtain spectra of maximum sharpness it is best to work with cold gaseous surroundings. P^{31} NMR analysis was carried out by using a 300-MHz Varian NMR spectrometer and phosphoric acid was used to calibrate the NMR signal. IR measurements were done by using a Perkin Elmer IR spectrophotometer 781, using KBr pellets. In the XPS (Vacuum Generators, ESCA 3 MK II) measurements, a charging correction was applied using the C 1s peak at 285.8 eV as the reference. The peaks were deconvoluted assuming Gaussian-type distribution, using a standard statistical package.

RESULTS AND DISCUSSION

The fresh catalyst contains 12-MPA with Mo predominantly in the (VI) state, while the catalyst recovered after the reduction reaction is blue in color. Decomposition of hydrazine hydrate produces about 1–3 moles of H_2 per mole of hydrazine (5). The reduction process also involves formation of NH_3 gas and is highly exothermic in nature (5). If the HPA yellow is reduced using hydrazine hydrate in the absence of nitrobenzene, a black composition is obtained.

In 12-MPA the Keggin structure has T_d symmetry. This structure is represented by a central PO_4 tetrahedron surrounded by 12- MoO_6 octahedra which share corners and edges with each other. The O atoms are almost close-packed, with chemical Mo–O–Mo bonds that are pseudo-linear but with angled bonds for P–O–Mo and Mo=O (4). The different types of oxygen bonds mentioned above are clearly seen from the IR spectra of HPA yellow and HPA blue catalysts (Fig. 1, curves a and b). Excitation of the P–O bond is assigned to the absorption at $\nu = 1065\text{ cm}^{-1}$, excitation of the Mo=O (terminal) bond to $\nu = 965\text{ cm}^{-1}$, and excitation of the Mo–O–Mo bond (bridged) to bands at 800 and 875 cm^{-1} . A P=O bond is not observed in the IR spectrum probably because of its low intensity. A large reduction in the intensity of Mo=O and Mo–O–Mo peaks is observed in the IR spectrum of deeply reduced HPA, i.e., HPA black (curve c), indicating a disturbance of the Keggin structure. From this figure it is seen that the IR spectrum of a mixture of HPA black and nitrobenzene (1 : 1) does not show the revival of the bonded oxygen atoms (curve d) as seen in case of HPA blue, indicating that the addition of nitrobenzene to a deeply reduced catalyst does not reconstruct the Keggin structure.

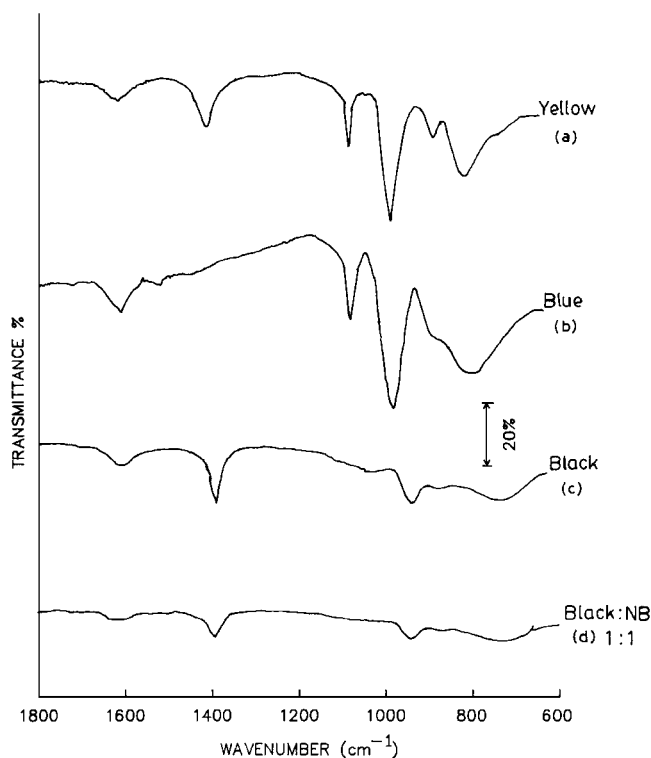


FIG. 1. IR spectrum of (a) HPA yellow, (b) HPA blue, (c) HPA black, (d) HPA black : nitrobenzene (1 : 1).

Reoxidation Kinetics

Kinetics of reoxidation of the HPA blue catalyst (30 mg HPA blue in 5.5 g nitrobenzene) in various solvents was carried out using UV-VIS spectroscopy. The UV-VIS spectrum of HPA yellow shows only one peak at 377 nm (Fig. 2, curve b) while HPA blue shows two peaks at about 351 and 747 nm (Fig. 2, curve a). In Fig. 3 these absorbance values at 747 nm are plotted as a function of time for different solvents. The slope is a measure of the reoxidation rate of HPA blue to HPA yellow. It is found that the rate constant of reoxidation depends on the solvent, namely, $2.5 \times 10^{-4}\text{ min}^{-1}$ in methanol, $3.5 \times 10^{-4}\text{ min}^{-1}$ in *n*-butanol, and $9.5 \times 10^{-4}\text{ min}^{-1}$ in acetonitrile. In the absence of nitrobenzene no reoxidation was observed. This blank run was performed to check whether atmospheric oxygen oxidizes the Mo(V).

It is observed from spectrophotometric data that a reducing solvent such as methanol (Fig. 3, curve b) and *n*-butanol (Fig. 3, curve c) slows the oxidation process down when compared to an oxidizing solvent such as acetonitrile (Fig. 3, curve d). This is because protic solvents such as alcohols stabilize the lower oxidation states of Mo in 12-MPA (namely, Mo(V)). On the other hand acetonitrile enhances the reoxidation of HPA blue (Fig. 3, curve d) since it stabilizes the higher oxidation state of 12-MPA (namely, Mo(VI)).

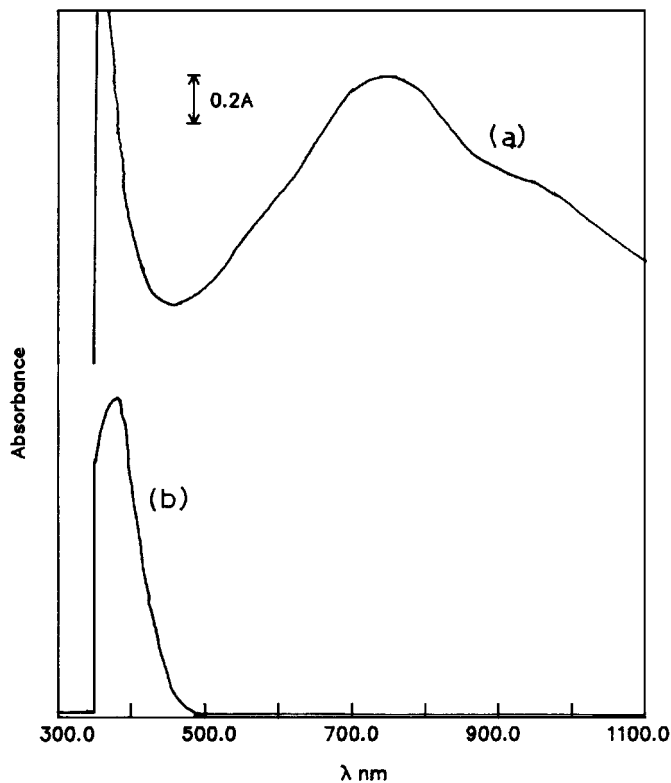


FIG. 2. UV-VIS spectrum of (a) pure HPA blue and (b) pure HPA yellow.

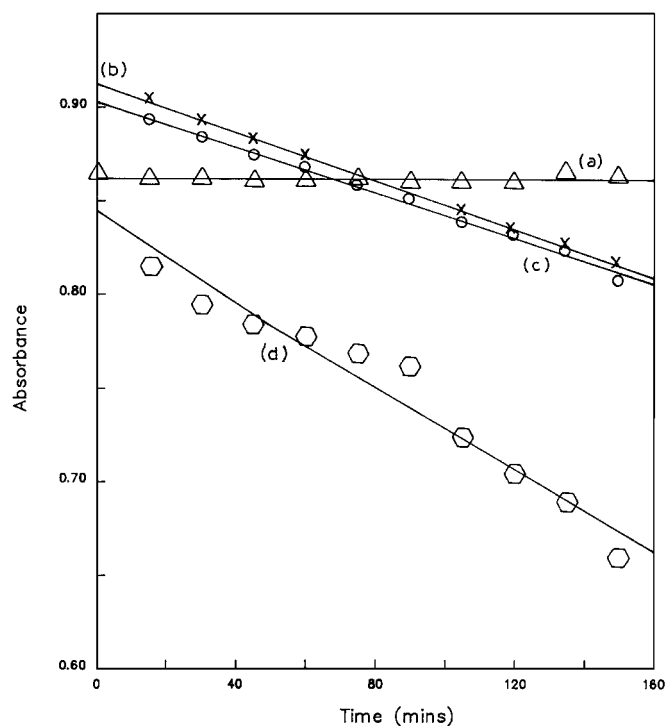


FIG. 3. The effect of solvents on kinetics of reoxidation of HPA blue (as measured at 747 nm): (a) without nitrobenzene, (b) methanol, (c) *n*-butanol, (d) acetonitrile.

Thus, from UV-VIS data it can be easily concluded that Mo in a lower oxidation state is preferred in a reducing solvent medium, whereas Mo in a higher oxidation state is preferred in an oxidizing solvent. When HPA blue is kept in methanol no aerial oxidation of blue has been observed even after a long period of time (Fig. 3, curve a).

ESR Measurements

The ESR signal is an important characteristic for the Mo(V) state in 12-MPA (6–10). Figure 4 shows ESR signals of HPA yellow, pure HPA blue, and HPA blue : nitrobenzene (1 : 1). HPA blue which has a single paramagnetic electron shows a single sharp peak. The g -values obtained for HPA blue match those reported in the literature; i.e., $g_{\parallel} = 1.956$ and $g_{\perp} = 1.87$. When nitrobenzene is added to HPA blue, a decrease in the intensity of the ESR signal is observed (which is seen by the increase in receiver gain). Since HPA yellow is an ESR inactive species, the addition of nitrobenzene to HPA blue converts HPA blue partly to HPA yellow and is indicated by a decrease in the intensity

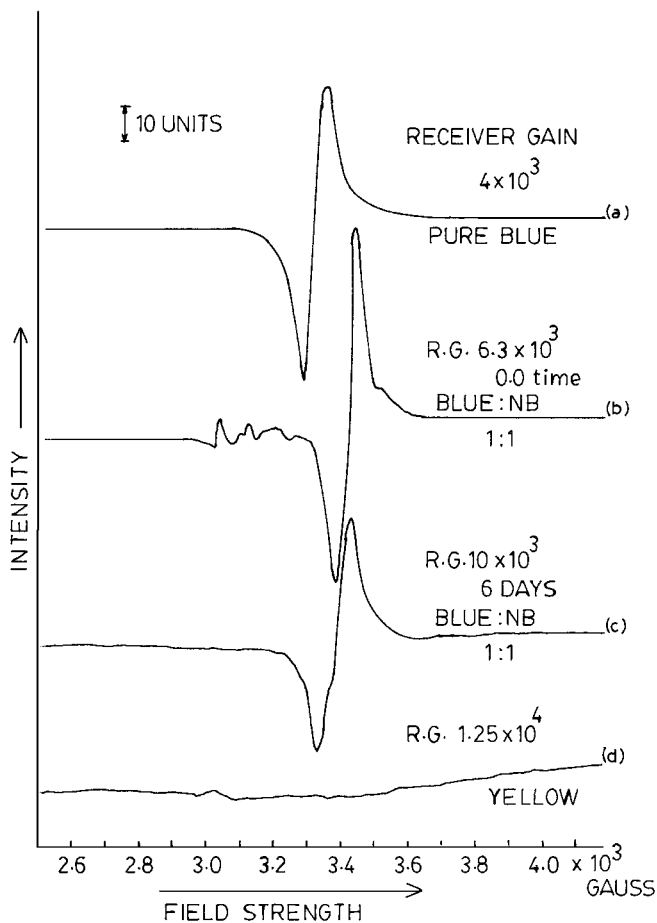


FIG. 4. ESR spectrum (at liquid N₂ temperature) of (a) HPA blue, (b) HPA blue : nitrobenzene (1 : 1) at 0.0 time, (c) HPA blue : nitrobenzene (1 : 1) after 6 days, (d) HPA yellow.

of the ESR signal. In the absence of a solvent even after 6 days a small amount of blue remains in the mixture, as shown in Fig. 4, curve c. An increase in receiver gain from curve a to c of Fig. 4 in order to get the same peak area is an indication that Mo(V) concentration is depleted due to its reoxidation to Mo(VI).

P^{31} NMR Spectra

The environment of phosphorous is indicated by P^{31} NMR (13). Kanda *et al.* (11) have reported P^{31} NMR spectral investigation of $H_3PW_{12}O_{40} \cdot nH_2O$ and $H_3PW_{12}O_{40} \cdot nH_2O$. Black *et al.* (12) have used P^{31} NMR spectroscopy to study acroline oxidation over 12-MPA. Figure 5 shows the P^{31} NMR obtained for HPA blue, HPA yellow, and a mixture of HPA blue and nitrobenzene (1 : 10). All the chemical shifts obtained in the spectrum are on the negative side of the reference material, i.e., phosphoric acid. This indicates that the phosphorous nucleus is highly shielded inside the Keggin structure. Mo(VI) does not have any free electron, whereas Mo(V) has one free electron and hence shielding is larger for HPA blue than for HPA yellow. A peak at ~ -2.0 ppm is due to HPA yellow, whereas a peak at ~ -11.2 ppm stands for HPA blue. Pure HPA blue and pure HPA yellow show intense and sharp signals. When nitrobenzene is mixed with HPA blue (blue : nitrobenzene = 1 : 10) a decrease in the signal for HPA blue at ~ -11.0 ppm and the simultaneous appearance of a peak at ~ -2.0 ppm in-

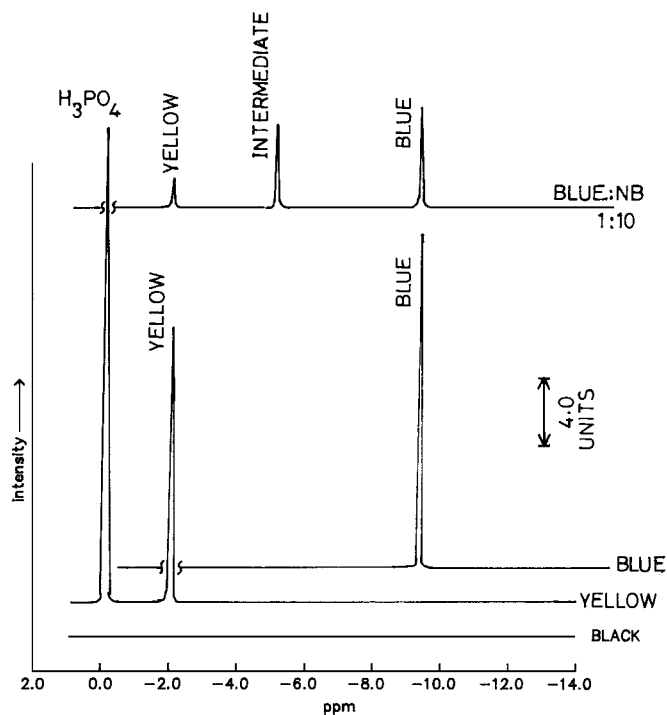


FIG. 5. P^{31} NMR spectrum of (a) HPA yellow, (b) HPA blue, (c) HPA blue : nitrobenzene (1 : 10), (d) HPA black.

TABLE 1

Effect of the Solvent on the Yield of Reduction Reaction with HPA Yellow

Solvent	% Aniline	% Nitrobenzene	% Intermediate
Acetonitrile (r.t.) ^a (12 h)	50	29	21
<i>n</i> -Butanol (r.t.) (12 h)	75	22	2
<i>n</i> -Butanol (reflux) (after 45 min.)	69	30	—
Methanol (r.t.) (12 h)	100	—	—
Methanol (reflux) (after 45 min.)	100	—	—

^a r.t., room temperature = 25°C.

icates the reoxidation of the catalyst without losing the Keggin structure. An intermediate peak obtained during reoxidation has not been identified. The deeply reduced HPA black (curve d) shows that the absence of any peak is probably due to the destruction of Keggin structure of 12-MPA.

Effect of Oxidation State of Molybdenum and Nature of Solvent on the Yield of Reduction of Nitrobenzene

Table 1 shows the effect of different solvents on the reduction of nitrobenzene when HPA yellow is used as a catalyst. An oxidizing solvent such as acetonitrile results in a low yield of aniline. This is due to the fact that a smaller amount of HPA blue gets converted to the Mo(V) state. When methanol and *n*-butanol are used as solvents the yield of aniline is 100% (in 12 h at room temperature), because these solvents reduce the catalyst from Mo(VI) to Mo(V) easily, which is required for the catalytic cycle and to stabilize the lower oxidation state of Mo.

Table 2 shows the effect of the oxidation state of Mo on the reduction of nitrobenzene. Methanol being a protic solvent destabilizes HPA yellow, leading to complete conversion of nitrobenzene, whereas it stabilizes HPA blue leading to a lower conversion. Conversion is very low with the deeply reduced HPA black catalyst, indicating a loss of catalytic activity due to a possible breakdown of structure.

TABLE 2

Effect of the Oxidation State of Molybdenum on Yield of Reduction Reaction

Catalyst	% Aniline	% Nitrobenzene	% Side products
HPA yellow	100	—	—
HPA blue	70	30	—
HPA black	12	68	20

Note. Solvent-methanol.

TABLE 3

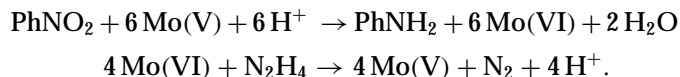
Fraction of Mo(V) and Mo(VI) for Various Catalysts Based on the Deconvolution of XPS Spectra

	Mo(V)	Mo(VI)
HPA yellow	0.132	0.86
HPA blue	0.64	0.35
HPA black	0.7	0.3
HPA black : nitrobenzene (1 : 10)	0.58	0.42

XPS Analysis

XPS studies of the HPA yellow, HPA blue, HPA black, and HPA black with nitrobenzene (1 : 10) were carried out to investigate the formation of the Mo(V) state and the redox cycle. The Mo_{3d} peak consist of the doublet $\text{Mo } 3d_{3/2}$ and $3d_{5/2}$. The four components of the Mo(V) and Mo(VI) signals were deconvoluted using a standard software, and the fractions of the Mo(V) and Mo(VI) are estimated for the various catalysts and are listed in Table 3. As expected the fraction of Mo(VI) is maximum in HPA yellow, while the deeply reduced catalyst HPA black has the highest Mo(V) fraction. Although the addition of nitrobenzene to HPA black increases the Mo(VI) fraction, the NMR and FTIR studies indicate that the Keggin structure which has been destroyed during deep reduction is not regenerated. So from the loss of catalytic activity of HPA black it could be concluded that the Keggin structure is needed for catalyzing this reaction and the mere presence of Mo in the (VI) state is not sufficient. This is also in line with our studies with ammonium molybdate, which exhibited poor activity for the reduction reaction (5).

The catalytic transfer hydrogenation of nitrobenzene via Mo(VI) to Mo(V) can be summarized by following ionic mechanism:



That is the reason why water or protic solvents are preferable. A great excess of hydrazine shifts the pH toward basic range, so the intermediates of the reduction are bimolecular products. The increase of the reaction rate with the acetonitrile found might be because of the increase of the amount of water (one of the products) in the reaction mixture.

CONCLUSIONS

The study indicates that the oxidation state of Mo affects the HPA catalyzed transfer hydrogenation of nitrobenzene.

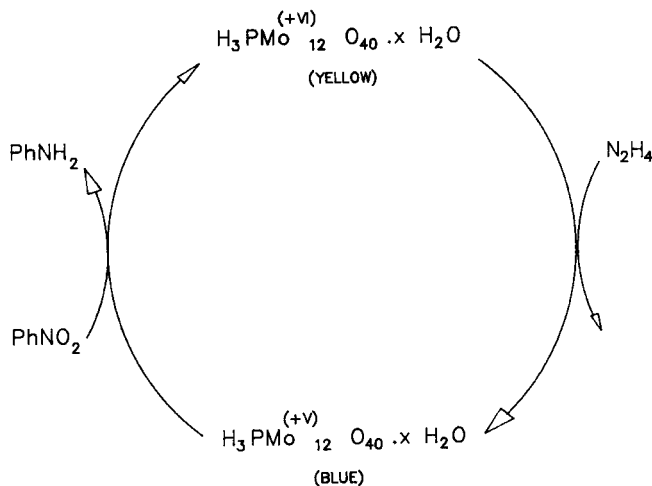


FIG. 6. Catalytic cycle of 12-MPA using hydrazine hydrate as hydrogen donor and nitrobenzene (substrate) as an oxidizing agent.

While hydrazine reduces the catalyst to form the active species, nitrobenzene reoxidizes Mo(V) to Mo(VI). The catalytic cycle is shown in Fig. 6. Protic solvents or water enhance the reduction reaction since they take part in the ionic reaction stabilizing the lower oxidation state. An ESR signal is only obtained when Mo(V) is present; so, as the catalyst is reoxidized with nitrobenzene, the signal decreases. P^{31} NMR confirms that Mo(VI) is less shielded than Mo(V) and it also indicates reoxidation of the 12-MPA catalyst. In the catalytic cycle of the Mo(VI)/Mo(V) redox reaction, the corresponding HPA ($\text{PMo}_{12}\text{O}_{40}^{-3}$) is $\text{H}_4\text{PMo}_{11}^{(\text{VI})}\text{Mo}^{(\text{V})}\text{O}_{40}$.

REFERENCES

- Izumi, Y., Urabe, K., and Onaka, M., "Zeolite, Clay and Heteropoly Acid in Organic Reactions," Kodansha/VCH, Tokyo, 1992.
- Hu, C., Hashimoto, M., Okuhara, T., and Misono, M., *J. Catal.* **143**, 437 (1993).
- Kozhenikov, I. V., *Chem. Rev.* **98**, 171 (1998).
- Misono, M., *Catal. Rev.-Sci. Eng.* **29**, 269 (1987).
- Joshi, M., and Mukesh, D., *J. Catal.* **168**, 273 (1997).
- Fricke, R., and Ohlmann, G., *J. Chem. Soc. Faraday Trans.* **82**, 273 (1986).
- Ohtsuka, R., and Kobayashi, J., *Bull. Chem. Soc. Jpn.* **63**, 2076 (1990).
- Prados, R., Ronald, A., and Pope, M., *Inorg. Chem.* **15**, 2547 (1976).
- Fournier, M., Sanchez, C., Livage, J., Launay, J., and Jeannin, Y., *J. Am. Chem. Soc.* **104**, 3194 (1982).
- Fournier, M., Sanchez, C., Livage, J., and Launay, J., *J. Am. Chem. Soc.* **105**, 6817 (1983).
- Kanda, Y., Lee, Kwan Y., Nakata, S., Asaoka, S., and Misono, M., *Chem. Lett.* 139 (1988).
- Black, J., Clayden, N., Gai, P., Scott, J., Serwicka, E., and Goodenough, J., *J. Catal.* **106**, 1 (1987).
- Massart, R., Contant, R., Fruchart, J., Ciabrini, J., and Fournier, M., *Inorg. Chem.* **16**, 2916 (1977).