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Transfer Hydrogenation of Nitro Compounds with Heteropolyacid Catalysts

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12-Molybdophosphoric acid-catalyzed transfer hydrogenation of nitroaromatics in homogeneous phase under mild conditions with hydrazine as hydrogen donor is described. Lower yields were observed with *ortho*- and *meta*-substituted than with *para*-substituted nitrobenzenes. IR, ESR, NMR, and X-ray photoelectron studies indicated that Mo^{6+} is reduced to Mo^{5+}, which is the active species, and coordinates with the electron-deficient nitro compound; in the process Mo^{5+} is reoxidized. © 1997 Academic Press

INTRODUCTION

Heteropolyacids (HPAs) are strong protonic acid catalysts and are used both in the heterogeneous solid phase (1) and in the homogeneous solution phase (2). 12-Tungstophosphoric acid has been used as a catalyst for oxidation, hydration of olefins, isomerization of alkanes, and conversion of methanol to ethylene and propylene, in both liquid and gas phases (1, 2). 12-Tungstosilicic acid has been used for the vapor-phase esterification of acetic acid with ethanol (3). 12-Molybdophosphoric acid has been employed for the production of furan from butadiene and the oxidative dehydrogenation of isobutyric acid (4, 5). HPA-catalyzed fine chemical synthesis and organic chemical synthesis has recently been reviewed by Kozhevnikov (6).

In this paper homogeneous liquid-phase transfer hydrogenation of nitro compounds using hydrazine as the hydrogen donor and 12-molybdophosphoric acid (12-MPA: $H_3PMo_{12}O_{40} \cdot 28H_2O$) as the catalyst is reported. The reactions are carried out at ambient pressure and temperature. Reduction of nitroarenes to aminoarenes with hydrazine as hydrogen donor has been reported for a wide range of catalysts such as palladium, copper, iron, Raney nickel, rhodium, and ruthenium (7, 8). Dehalogenation of substrates and substitution reactions are normally observed with these catalysts. These side reactions might be avoided by using a HPA catalyst. The need to use a large excess of hydrazine is a drawback of transfer hydrogenation. Hydrazine has also been used for the reduction of nitroaromatics with montmorillonite clay under reflux conditions and long reaction times (9) and without catalyst, at 160°C (10).

METHODS

Two-hundreths mole of the organic reactant, 0.2 g of the 12-MPA catalyst, and 15 ml of methanol as solvent were taken in a round-bottom flask. Eight grams (0.2 mol) of hydrazine hydrate (80% solution in) was added slowly to the stirred contents over about 30 min. The flask was maintained at 40 to 50°C. The product was separated from the reaction mixture by extracting it with dichloromethane or ethyl acetate, purified by column chromatography, and analyzed by gas chromatography (capillary column with flame ionization detector) or HPLC (Bondapak C_{18} column with acetonitrile and water at 60 : 40 ratio as the solvent mixture). The reactants and the catalyst were obtained from S.D. Fine Chemicals Ltd, India, and were of 99.5% purity.

IR, ESR, proton NMR, and X-ray photoelectron spectra studies of fresh and used catalyst were obtained to determine the active species and the state of the catalyst. In the XPS (Vacuum Generators, ESCA 3 MK II) measurements, a charging correction was applied using the C 1*s* peak at 285.8 eV as the reference. The peaks were deconvoluted assuming Gaussian-type distribution, using a standard statistical package.

IR (Perkin–Elmer 781) spectra were recorded in KBr by preparing pellets from a well-ground and well-mixed mixture of 0.002 g of 12-MPA and 0.1 g of KBr.

12-MPA catalyst (0.28 g, 0.1 mmol) was thoroughly mixed with nitrobenzene (0.5 g, 4.17 mmol) and warmed with *n*-hexane. *n*-Hexane was chosen because it is an aprotic, nonpolar, and noncoordinating solvent. Excess nitrobenzene was removed by successive washes with a mixture of *n*-hexane/chloroform. The solid was filtered and vacuum-dried (complex A) and its IR spectrum was recorded with KBr as described above. The absence of nitrobenzene in the solid was confirmed by thin-layer chromatography.

12-MPA (0.28 g) and nitrobenzene (0.5 g) were homogenized in acetonitrile. Hydrazine hydrate (80%, 1 μl) was added in drops. Excess nitrobenzene was removed and the IR spectrum of the product was recorded as mentioned before.

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Complex A (0.05 g) was dissolved in $CDCl_3$ (0.5 ml) and the proton NMR spectrum was recorded on a Fourier transform 80-MHz Bruker instrument with trimethylsilane as internal standard.

ESR investigations of the solid catalysts were carried out at room temperature with a Varian E-112 instrument.

RESULTS AND DISCUSSION

Table 1 shows the results of the transfer hydrogenation reaction. The reaction conditions are mild. The yield of aniline from nitrobenzene remained only about 60% when 1.75 g (0.04375 mol of hydrazine) of hydrazine hydrate was used, even when the amount of catalyst was tripled, whereas the yield reached 100% with 8 g (0.2 mol of hydrazine) of hydrazine hydrate. There was no loss in the activity of recycled 12-MPA. When 12-tungstophosphoric acid or ammonium molybdate was used as catalyst for the reduction of nitrobenzene, very little aniline was observed, signifying the positive role of molybdenum as present in the 12-MPA. Also, Mo^{6+} is easily reducible, unlike W^{6+}. Reduction of *p*-nitrotoluene was more facile than that of *o*-nitrotoluene, and similarly, reduction of *p*-dinitrobenzene was more facile than that of *m*-dinitrobenzene, indicating steric effects. Dehalogenation was not observed in the case of *p*-nitrochlorobenzene. Very high conversions were observed with 4-nitrodiphenylamine (100%) and *o*-nitroanisole (93%).

Hydrazine Decomposition

Under ideal conditions 1 mol of hydrazine should give 2 mol of hydrogen per the equation

$$N_2H_4 \rightarrow N_2 + 2H_2. \qquad [1]$$

TABLE 1

12-Molybdophosphoric Acid-Catalyzed Transfer Hydrogenation of Nitro Compounds[a]

Substrate	Yield of amine (%)
Nitrobenzene	100 (60% conversion with 1.75 g hydrazine hydrate)
p-Nitrochlorobenzene	100
4-Nitrodiphenylamine	96
o-Nitrotoluene	66
p-Nitrotoluene	100
o-Nitroanisole	93
p-Dinitrobenzene	83 (monoamino) 5 (diamino)
m-Dinitrobenzene	30 (monoamino) 2 (diamino)

[a] Solvent = methanol, reaction temperature = 50°C, time = 30 min, hydrogen donor = hydrazine.

In the presence of finely divided metals like platinum it is known that 1 mol of hydrazine decomposes to give only 0.5 mol of H_2 and 1 mol of ammonia (11):

$$2N_2H_4 \rightarrow 2NH_3 + N_2 + H_2. \qquad [2]$$

In the presence of Raney nickel, 1 mol of hydrazine decomposes to give 1 mol of H_2 (12):

$$N_2H_4 \rightarrow 2N_2 + 3H_2 + 2NH_3. \qquad [3]$$

In the present study, during nitrobenzene reduction with 0.04375 mol of hydrazine, 0.012 mol of the substrate was reduced to aniline (60% conversion), indicating the generation of 0.036 mol of hydrogen. According to Eqs. [2] and [3], 0.0218 and 0.04375 mol of hydrogen, respectively, are expected to be produced by the decomposition of 0.04375 mol hydrazine. In fact, however, the amount of hydrogen generated lies between these two values, indicating that both steps [2] and [3] are operating for hydrazine decomposition with 12-MPA catalyst, probably depending on the oxidation state of Mo^{6+} and the acidity of the HPA.

Reaction Mechanism and Catalytically Active Species

12-Molybdophosphoric acid has the Keggin structure with T_d symmetry, as ascertained by numerous X-ray structural studies (2). 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 bonds Mo–O–Mo that are pseudolinear but with angled bonds for P–O–Mo and Mo=O.

Figure 1 shows the IR spectra of the fresh and used 12-MPA catalyst. The P–O bond is assigned absorption at a wavenumber of 1065 cm^{-1}, Mo=O (terminal oxygen) at 965 cm^{-1}, and Mo–O–Mo (bridged oxygen) at 800 and 875 cm^{-1}. These values match the literature well (13). The area of the band corresponding to Mo=O in the used catalyst is less than that corresponding to fresh catalyst (by 5–6%), indicating that terminal oxygen is lost during reduction. This leads to the formation of Mo^{5+} which was also confirmed by ESR spectroscopy. The *g* value of the ESR spectrum is estimated to be 1.951, which matches the literature data (14). Mo^{6+} is diamagnetic and has no ESR signals. Mo^{5+} is a coordinating site for the electron-deficient nitro compound. During the reduction process Mo^{5+} becomes reoxidized to Mo^{6+}, completing the catalytic cycle. The oxidation–reduction properties of 12-MPA and its alkali salts have been well documented by Misono (15). Loss of only the terminal oxygen allows the Keggin structure to be retained. Stronger reducing conditions are known to remove the bridged oxygen and hence destroy the structure (13). The fresh catalyst, which is soluble in the reaction mixture, is yellow, whereas the reduced catalyst is blue and

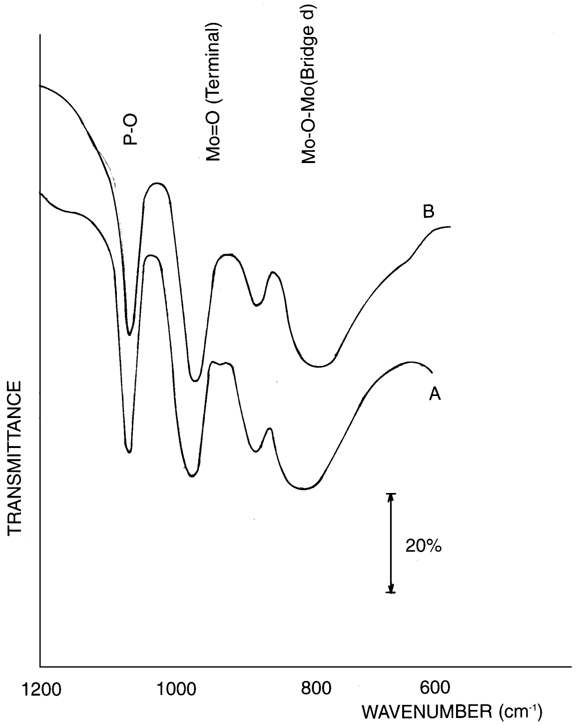

FIG. 1. IR spectra of (A) fresh and (B) used catalyst.

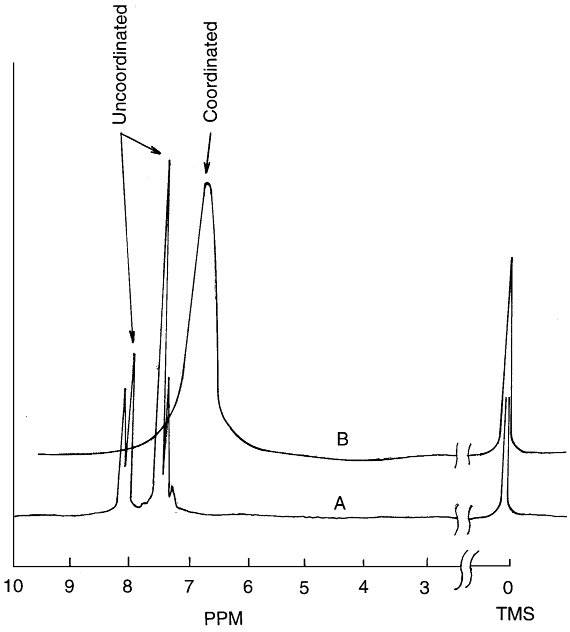

FIG. 2. NMR spectra of (A) nitrobenzene and (B) catalyst–substrate complex.

precipitates out. Also, ESR studies indicate the absence of Mo^{4+}.

Figure 2 shows the ^1H NMR spectra of nitrobenzene and the catalyst–substrate soluble complex. Free nitrobenzene exhibits two sets of peaks, one corresponding to the *ortho* protons at 8.2 ppm. Coordination of nitrobenzene through the nitro group to the catalytic site induces the ring to donate electrons to the catalyst (paramagnetic coupling), resulting in loss of characteristic *ortho, meta,* and *para* protons and giving rise to one single broad peak at 6.82 ppm.

Coordination of the nitro group with the catalyst is also confirmed by IR spectroscopy (Fig. 3). Free nitrobenzene shows peaks at 1530 and 1355 cm^{-1}, corresponding to the asymmetric vibrations of the NO_2 group and C−N bond, respectively. The IR spectra of the fresh (yellow) and used (blue) catalyst complexed with nitrobenzene show two new peaks, one at 1450 cm^{-1} and the other at 1390 cm^{-1}, indicating that the substrate coordinates with both catalysts. The intensities of the 1530 and 1355 cm^{-1} peaks are reduced with the yellow catalyst.

The application of HPAs in homogeneous oxidation and reduction catalysis is due to the redox reversibility of Mo^{5+} under reaction conditions. XPS studies were carried out to investigate formation of the Mo^{5+} state and the redox cycle. Figure 4 shows the X-ray photoelectron spectrum of the fresh (yellow) catalyst. The Mo 3*d* spectrum consists of the doublet of Mo $3d_{3/2}$ and Mo $3d_{5/2}$ as shown in the figure. The binding energy values of these two levels are 235.5 and

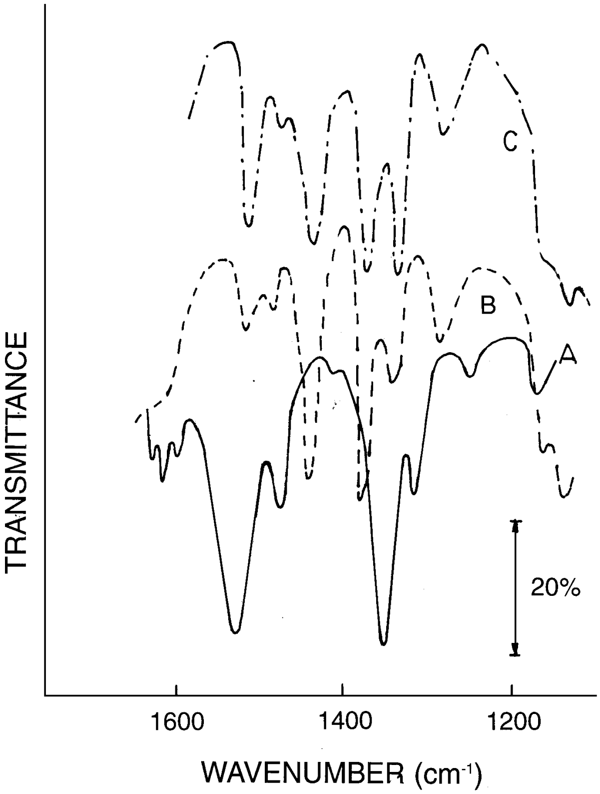

FIG. 3. IR spectra of (A) nitrobenzene, (B) fresh catalyst–substrate complex, and (C) used catalyst–substrate complex.

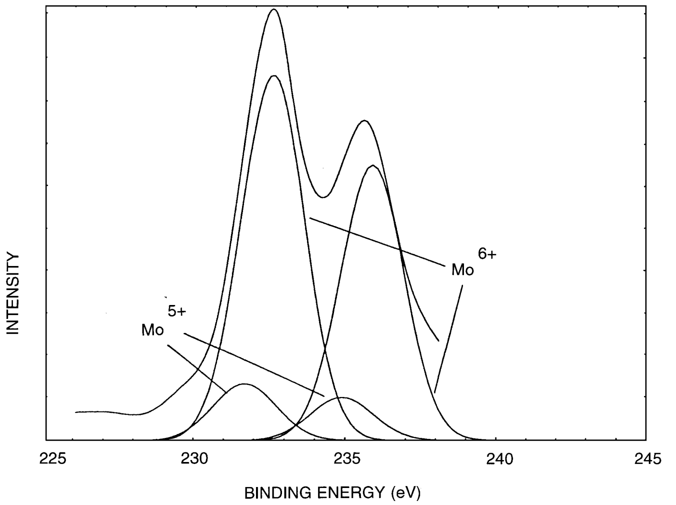

FIG. 4. X-ray photoelectron spectrum of the fresh catalyst and the deconvoluted spectra of Mo^{5+} and Mo^{6+} at $3d_{3/2}$ and $3d_{5/2}$.

232.4 eV, respectively, and are in good agreement with those reported in the literature of $H_3PMo_{12}O_{40}$ and $K_3PMo_{12}O_{40}$ (13, 16). The figure also shows four deconvoluted components, consisting of two signals for Mo^{5+}, namely, Mo^{5+} $3d_{3/2}$ and Mo^{5+} $3d_{5/2}$ at 234.8 and 231.7 eV, respectively, and two signals for Mo^{6+}, namely, Mo^{6+} $3d_{3/2}$ and Mo^{6+} $3d_{5/2}$, at 235.8 and 232.6 eV, respectively. XPS data also indicate the absence of Mo^{4+} formation during reduction.

Figure 5 shows the X-ray photoelectron spectra of Mo after various treatments. The area fractions of Mo^{5+} and Mo^{6+} after deconvolution of these spectra are listed in Table 2. The fresh (yellow) catalyst has a large proportion of Mo in the 6+ state. The reduced and used (blue) catalyst, on the other hand, is soluble in the reaction medium and has a higher proportion of Mo in the lower (5+) oxidation state. It is, however, generally agreed that the blue catalysts have the same structure as parent HPA, in the case of low reductions (2).

TABLE 2

Effect of Catalyst Treatment on Area Fraction of Mo^{5+} and Mo^{6+} in the Deconvoluted X-Ray Photoelectron Spectra

	Fraction of Mo^{5+}	Fraction of Mo^{6+}
(a) Fresh catalyst	0.132	0.868
(b) After hydrazine reduction	0.64	0.36
(c) Nitrobenzene added to hydrazine-prereduced catalyst	0.342	0.658
(d) 12-MPA + nitrobenzene + hydrazine *in situ*	0.56	0.44
(e) Nitrobenzene + 12-MPA (no hydrazine)	0.378	0.622
(f) Used catalyst (blue)	0.644	0.356
(g) H_2-reduced catalyst	0.743	0.256

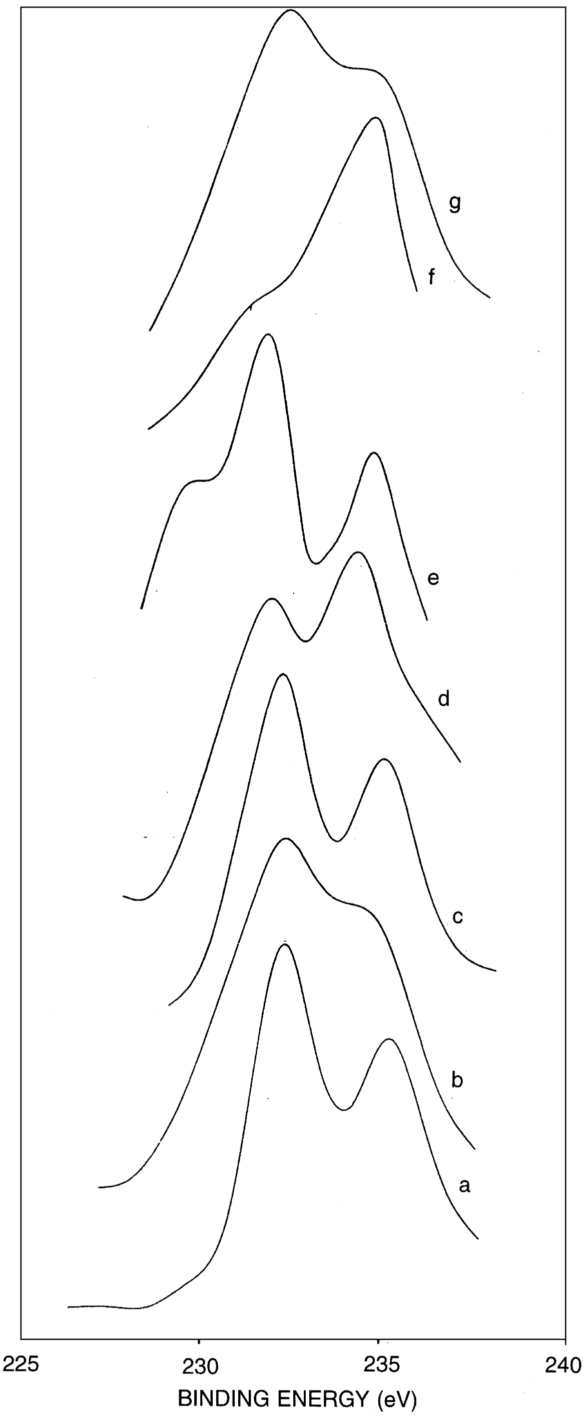

FIG. 5. Effect of various treatments on the XPS signal of the catalyst: (a) fresh catalyst, (b) after hydrazine reduction, (c) nitrobenzene added to hydrazine-prereduced catalyst, (d) 12-MPA + nitrobenzene + hydrazine *in situ*, (e) nitrobenzene + 12-MPA (no hydrazine), (f) used catalyst (blue), (g) H_2-reduced catalyst.

On reduction with hydrazine or hydrogen gas, the ratio of Mo^{5+} to Mo^{6+} increases, indicating the formation of additional Mo^{5+}. Addition of nitrobenzene to prereduced catalyst shifts the oxidation state to a higher value. When both nitrobenzene and hydrazine are present together with the catalyst, the ratio of Mo^{5+} to Mo^{6+} is found to be 0.56 : 0.44. In the absence of the reducing agent, a larger fraction of Mo is in the higher oxidation state (6+).

These studies clearly indicate the operation of a redox cycle during the transfer hydrogenation reaction and show that the catalyst retains the Keggin structure. The catalyst, on contact with hydrazine, is reduced to Mo^{5+}. The reduced catalyst reverts to the higher oxidation state (Mo^{6+}) when it coordinates with nitrobenzene and loses its hydrogen to the latter.

CONCLUSION

This paper describes the transfer hydrogenation of a large number of nitro compounds with 12-MPA as catalyst and hydrazine as hydrogen donor. The reaction takes place at 50°C and has a reaction time of 30 min. IR, NMR, XPS, and ESR studies indicate the loss of terminal oxygen leading to the formation of Mo^{5+}, the active species, which is reoxidized to Mo^{6+} during the course of reaction. Coordination of the nitro compound with the active species is also shown by spectroscopy. Reduction of the catalyst does not disturb the Keggin structure. XPS studies indicate the operation of the redox cycle.

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