Homogeneous catalytic hydrogenation of organic compounds using orthometallated schiff base complexes of palladium(II)

Deb K Mukherjee, Biman K Palit & Chitta R Saha
Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302
Received 21 August 1991; revised and accepted 3 December 1991

The dinuclear orthometallated schiff base complexes of palladium(II) are efficient catalysts for dihydrogen reduction of organic -NO₂, >C=O, >C=C<, > C=N -, - N=N - and -C=N groups under normal or high pressure conditions. The dependence of the catalytic activity on the nature of the bridging group and the schiff base ligands has been established. The experimental conditions control the nature and number of the reduction products in case of nitroaromatics. Reduction mechanism has been proposed on the basis of the nature of intermediate and final reduction products, change of physico-chemical properties of the catalyst solutions, polarographic data of the ligands and the complexes and the kinetic data.

Numerous methods have been developed for the catalytic reduction of organic nitrocompounds¹⁻⁷, alkenes⁸⁻¹² and alkynes⁸·¹³,¹⁴ in homogeneous phase, but relatively few investigations have been made on the reduction of nitriles¹⁵⁻¹⁷ and aliphatic nitrocompounds¹⁸⁻²². The importance of the reduction lies in the use of the products for the manufacture of dyes, drugs, pharmaceuticals etc. The elucidation of unambiguous reaction mechanism for the reductions was difficult due to several limitations²⁰,²². We have investigated the catalytic activities of various dinuclear orthopalladated complexes with differently C,N-substituted schiff base ligands in order to find out the influence of electron density and steric environment at different points of the complex on their catalytic efficiencies. This may help in the modification of the catalysis system. The present paper reports the results of such investigations.

Materials and Methods

Pure and recrystallised solid reagents, predistilled solvents and pure, dry and deoxygenated hydrogen and nitrogen gases were used for all the experiments. Dimethylformamide (DMF) was dried by storing it over CaH₂ under N₂ for 24 h followed by distillation under reduced pressure. H₂ and N₂ gases were deoxygenated and dried by passing them successively through alkaline pyrogallol, liquid N₂ trap and silica gel tower before introduction into the reaction system.

The complexes used in the present investigation were prepared according to the literature methods²³ and purified by recrystallization from dichloromethane/n-hexane and their purities were checked by physico-chemical means before use as catalysts.

Analyses of the product mixture were done on a Varian 3700 gas chromatograph equipped with a flame ionization detector using a S.S. column packed with 25% SE-30 on Chromosorb W mesh. Temperature programming was done in the range 180° to 300°C with the increase of temperature at the rate of 17°C/min. Vibrational, electronic and PMR spectra were recorded in Perkin-Elmer-883, Shimadzu MPC-3100, and Varian EM-390, 90 MHz spectrometers respectively. Molecular weights of the complexes in C₆H₆ and DMF were determined in a Knauer Dampdruck osmometer.

Preparation of the catalysts

The schiff base ligands were prepared by refluxing equimolar quantities of the appropriate aldehyde or ketone and amine in benzene or xylene²⁴,²⁵. The sterically hindered schiff bases required extended reflux period (2-3 days) in xylene. The preparation of benzophenoneanil using appropriate reagents required the presence of POCl₃ in the medium²⁶. Reaction of the schiff base ligand and Pd(II) acetate in refluxing acetic acid resulted in the precipitation of the corresponding complex which was further purified by repeated crystallization from solvent mixture²³. The purities of the complexes were checked by TLC, IR and electronic spectral data. The metathetical reaction of acetato-bridged complexes with NaCl or NaBr in acetone yielded the corresponding chloro- and bromo-analogues²³.

Another series of orthopalladated complexes was
prepared using the secondary amine LH₂. The latter were obtained by the dihydrogen reduction of the corresponding Schiff base ligand, LH in the presence of the presently investigated catalysts or otherwise. Reaction of Pd(OAc)₂ with LH in refluxing AcOH produced Pd₂(LH₂)₂(OAc)₂. The corresponding chloro- and bromo-analogues were prepared by metathetical reactions. The catalytic activities of the orthometallated complexes, Pd₂(LH₂)₂X₂ (Fig. 1a) towards the reduction processes were found to be comparable to those of Pd₂L₂X₂ (Fig. 1b).

**Reduction procedure**

The procedures for normal and high pressure reductions were mentioned in our earlier papers. In case of normal pressure reduction, the yellow DMF solution of the catalyst turned deep greenish brown within 10 min on stirring under hydrogen at 20°C. The substrate addition at this stage slightly faded the solution colour and hydrogen absorption started at a maximum rate which was measured using a graduated gas reservoir. The intermediate samples (0.20 ml) were withdrawn from the reaction mixture at an interval of 10 min and analysed immediately by GLC. In the case of high pressure reductions, the final reaction mixture was quenched and the components were estimated by GLC using appropriate columns. The intermediate sample analysis in this case was made at an interval of 30 min only.

**Results and Discussion**

The compounds have low solubilities in non-polar solvents like benzene, cyclohexane, etc., and moderate solubilities in mild coordinating solvents like DMF, DMSO, etc. The reduction rate of a given substrate was highest in DMF medium and hence most of the reactions were carried out in this medium. Detailed investigations were made with the acetato-bridged complexes due to their better solubilities and higher catalytic activities (Table 1).

**Reduction of nitroaromatics, alkenes, alkynes and other organic substrates**

The catalytic hydrogenation of nitroaromatics leads to the formation of the corresponding anilines in almost all cases except nitrophenol and m-dinitrobenzene where the final products were only the corresponding hydroxylamines (Table 2). Analysis of the intermediate reaction samples indicated the primary formation of hydroxylamines in the case of substrates which are finally reduced to the corresponding anilines. The formation of coupled products such as azo- or azoxybenzene was not ob-

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**Table 1—Relative catalytic activity of Pd(II) Schiff base complexes in DMF medium at 25°C**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Nitrobenzene</th>
<th>Styrene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cat. Conc. (mol. lit⁻¹ × 10⁻⁴)</td>
<td>Sub. Conc. (mol. lit⁻¹)</td>
</tr>
<tr>
<td>Pd₂(mbi)₂(OAc)₂</td>
<td>4.8</td>
<td>0.32</td>
</tr>
<tr>
<td>Pd₂(BAN)₂(OAc)₂</td>
<td>4.8</td>
<td>0.32</td>
</tr>
<tr>
<td>Pd₂(pTBAN)₂(OAc)₂</td>
<td>4.8</td>
<td>0.32</td>
</tr>
<tr>
<td>Pd₂(mTBAN)₂(OAc)₂</td>
<td>4.8</td>
<td>0.32</td>
</tr>
<tr>
<td>Pd₂(dmBAN)₂(OAc)₂</td>
<td>4.8</td>
<td>0.32</td>
</tr>
<tr>
<td>Pd₂(apkt)₂(OAc)₂</td>
<td>4.8</td>
<td>0.32</td>
</tr>
<tr>
<td>Pd₂(mbpkt)₂(OAc)₂</td>
<td>4.8</td>
<td>0.32</td>
</tr>
<tr>
<td>Pd₂(bpkt)₂(OAc)₂</td>
<td>4.8</td>
<td>0.32</td>
</tr>
</tbody>
</table>

mbi = N-methylbenzaldimine; BAN = N-phenylbenzaldimine; pTBAN = (N-(p-tolyl)benzaldimine); mTBAN = (N-(m-tolyl)benzaldimine); dmBAN = (N-(3,5-dimethyl)benzaldimine); apkt = N-phenylacetophenoneketimine; bpkt = N-phenylbenzophenoneketimine; mbpkt = N-methylbenzophenoneketimine.
Table 2—Optimum conditions and yields of main products at 1 atm pressure of Hydrogen and 25°C using (a) = Pd₂(mbih(OAc))₂, (b) = Pd₂(pTBANMOAc)₂, (c) = Pd₂(apkt)₂(OAc)₂ as catalysts

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Catalyst</th>
<th>Initial rate of H₂-abs. (ml min⁻¹)</th>
<th>Initial turnover number (min⁻¹)</th>
<th>Product %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Nitrobenzene</td>
<td>a</td>
<td>4.8</td>
<td>7.90</td>
<td>14.60</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>4.6</td>
<td>5.50</td>
<td>10.60</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>4.6</td>
<td>5.20</td>
<td>08.80</td>
</tr>
<tr>
<td>2 o-Chloronitrobenzene</td>
<td>a</td>
<td>4.8</td>
<td>2.70</td>
<td>05.00</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>4.6</td>
<td>2.40</td>
<td>04.60</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>4.6</td>
<td>2.15</td>
<td>04.40</td>
</tr>
<tr>
<td>3 p-Chloronitrobenzene</td>
<td>a</td>
<td>4.8</td>
<td>3.40</td>
<td>06.30</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>4.6</td>
<td>2.70</td>
<td>05.20</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>4.2</td>
<td>2.20</td>
<td>04.65</td>
</tr>
<tr>
<td>4 m-Dinitrobenzene</td>
<td>a</td>
<td>4.8</td>
<td>7.82</td>
<td>12.40</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>4.6</td>
<td>6.30</td>
<td>09.80</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>4.2</td>
<td>5.70</td>
<td>07.65</td>
</tr>
<tr>
<td>5 o-Nitrotoluene</td>
<td>a</td>
<td>4.8</td>
<td>2.82</td>
<td>05.20</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>4.6</td>
<td>2.35</td>
<td>04.50</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>4.2</td>
<td>2.20</td>
<td>04.05</td>
</tr>
<tr>
<td>6 Pent-1-ene</td>
<td>a</td>
<td>4.2</td>
<td>5.40</td>
<td>31.40</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>5.6</td>
<td>4.15</td>
<td>18.80</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>5.2</td>
<td>3.15</td>
<td>15.30</td>
</tr>
<tr>
<td>7 Hex-1-ene</td>
<td>a</td>
<td>4.2</td>
<td>5.05</td>
<td>28.60</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>5.6</td>
<td>3.70</td>
<td>15.80</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>5.2</td>
<td>2.70</td>
<td>12.80</td>
</tr>
<tr>
<td>8 Cyclohexene</td>
<td>a</td>
<td>4.2</td>
<td>3.15</td>
<td>19.30</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>5.6</td>
<td>3.30</td>
<td>14.70</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>5.2</td>
<td>2.40</td>
<td>09.80</td>
</tr>
<tr>
<td>9 Benzaldehyde</td>
<td>a</td>
<td>5.7</td>
<td>2.70</td>
<td>14.20</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>4.8</td>
<td>1.15</td>
<td>13.10</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>4.8</td>
<td>1.00</td>
<td>04.55</td>
</tr>
<tr>
<td>10 Benzyldiene aniline</td>
<td>a</td>
<td>5.9</td>
<td>2.55</td>
<td>13.80</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>4.8</td>
<td>1.00</td>
<td>07.80</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>4.8</td>
<td>0.70</td>
<td>02.60</td>
</tr>
</tbody>
</table>

The presence of alkali in low concentration (0.01 M) does not affect the reduction rates or the nature and yields of final products but its presence in high concentration decomposes most of the catalytic species. The addition of acid as expected from the equilibrium reaction (2) (vide infra) decreases the reduction rate and stops hydrogenation if the acid concentration exceeds 0.5 M.

Reduction of alkenes

Alk-1-enes undergo simultaneous reduction and isomerization. The initial rates of reduction of styrene, acrylonitrile or isoprene where the double bond is a part of delocalized system are much higher than those of alk-1-enes or penta-1,4-diene where the double bond is either single or non-conjugated.
Reduction of nitroalkanes, benzonitrile and benzophenone

The reduction of these substrates is possible only under high pressure and high temperature conditions. The reduction rate decreases with increasing molecular weight of the nitroalkanes and increases with increasing branching at the α-carbon atom (Table 3). Relatively higher hydrogen pressure and higher temperature are necessary for the reduction of benzophenone and benzonitrile. The former produced the corresponding alcohol while the latter was reduced to a mixture of benzylamine (15-20%) and dibenzylamine (80-85%).

The DRS and solution spectra of any complex catalyst in benzene solution are almost identical but differ appreciably from those taken in DMF or DMSO. The molecular weight measurements of the complexes in dilute DMF solution indicated nearly 100% dissociation. These facts together with the bridge cleavage of the dinuclear complexes by PPh₃, Py etc.²,²⁸ suggest them to undergo the following reaction in DMF solution.

\[
Pd_2L_2X_2 \rightleftharpoons 2 \text{Pd.L.X.DMF} \quad \text{(1)}
\]

where \(X = \text{OAc, Cl, Br}\).
The passage of H₂ through the yellow DMF solution of the catalyst changed the solution colour to greenish brown. The visible electronic spectra of the greenish brown solution and that of the final solution after catalytic run were identical for any catalyst in both normal and high pressure conditions indicating the formation of the same catalytic species in both the cases. The actual catalytic species could not be isolated from the final solutions as they decompose to Pd⁰ at the final stage of concentration. It was, however, possible to isolate the secondary amine (LH₃) corresponding to reduced schiff base ligand from the decomposed solution. The ¹H NMR spectra of the concentrated solution exhibit a signal at τ 21-22 ppm indicating the presence of metal hydride complexes in them. The liberation of HX during hydrogen activation was inferred from the increase in conductance and decrease in pH of the solution and the liberation of CO₂ from NaHCO₃.

The DMF solution spectra of palladium(II) complexes with schiff bases, their H₂ activated species and the amines corresponding to schiff bases are presented in Table 4. The spectra of hydrogen activated solutions derived from Pd₂L₂(OAc)₂ or Pd₂[LH₂]₂(OAc)₂ are almost identical indicating the formation of same catalytic species in both cases. The actual catalytic species, suggested to be Pd(LH₂)(H)DMF may be formed as follows:

\[
\begin{align*}
R^1\text{-}C_6H_5CH = N - C_6H_5 \quad &\quad \text{LH} = C_6H_5CH = N\text{C}_6H_5CH(p) \\
LH_3 = C_6H_5CH_2 - NH - C_6H_5 \quad &\quad \text{L'H}_3 = C_6H_5CH_2 - NH - C_6H_5CH(p)
\end{align*}
\]

The equilibrium concentration of (A) should depend on the nature of HX as the weaker is the acid HX, the higher will be the concentration of (A). This is in accordance with the observed dependence of the activity of the complex on the nature of the bridging group: OAc > Br > Cl. The higher catalytic activities of the acetato-bridged complexes are due to their greater percentage of conversion to the actual catalytic species (A) during substrate reduction.

The reduction could be carried out only in DMF or DMSO and no reductions occurred in non-coordinating solvents like C₆H₆, C₆H₅CH₃ or in moderate coordinating solvents like CH₃CN or PhCN. In alcohol, the decomposition of the complex to Pd⁰ occurs during hydrogen treatment. The reduction is inhibited in the presence of PPh₃, Py, acacH or Dipy. The strong coordinating agents (reaction medium or added ligands) probably occupy the vacant coordination site and thus prevent substrate coordination to the metal. In alcohol the corresponding catalytic species PdLH₂(H)C₆H₅OH is probably too unstable to withstand the reaction conditions. The activities

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**Table 4—Electronic spectral data of the simple and H₂-activated DMF solution of the complexes**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>ν₁ (cm⁻¹)</th>
<th>ν₂ (cm⁻¹)</th>
<th>ν₃ (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Pd₂L₂(OAc)₂</td>
<td>24,400</td>
<td>33,800</td>
<td></td>
</tr>
<tr>
<td>2 Pd₂[LH₂]₂(OAc)₂</td>
<td>22,700</td>
<td>32,200</td>
<td></td>
</tr>
<tr>
<td>3 Pd₂L₂(OAc)₂ + H₂</td>
<td>22,650</td>
<td>27,700 (sh)</td>
<td>31,200 (sh)</td>
</tr>
<tr>
<td>4 Pd₂[LH₂]₂(OAc)₂ + H₂</td>
<td>22,700</td>
<td>27,700 (sh)</td>
<td>31,160 (sh)</td>
</tr>
<tr>
<td>5 Pd₂[LH₂]₂(OAc)₂</td>
<td>23,800</td>
<td>32,600</td>
<td></td>
</tr>
<tr>
<td>6 Pd₂[LH₂]₂(OAc)₂</td>
<td>24,700</td>
<td>29,400</td>
<td>33,330</td>
</tr>
<tr>
<td>7 Pd₂L₂(OAc)₂ + H₂</td>
<td>25,900</td>
<td>29,700</td>
<td>32,800 (sh)</td>
</tr>
<tr>
<td>8 Pd₂[LH₂]₂(OAc)₂ + H₂</td>
<td>25,580</td>
<td>29,680</td>
<td>32,600 (sh)</td>
</tr>
</tbody>
</table>

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Fig. 3—Reduction of nitrobenzene with Pd₂(apkt)₂(OAc)₂ in DMF at 25°C, under 1 atm. of hydrogen and in presence of pyridine as additive. ○ = nitrobenzene; ♦ = phenylhydroxylamine.
of the complexes decrease in the presence of low concentration of added \( \text{HX} \) \( (X = \text{bridging group}) \) and are lost completely if the concentration exceeds 0.1 \( M \). All these results support the existence of equilibrium (Eq. 2) in the reaction medium.

The complex \( \text{Pd}_2\text{L}_2(\text{OA} \text{c})_2 \) \( (\text{L} = \text{C}_6\text{H}_4\text{CH} = \text{NH}) \) could not be synthesized and hence its catalytic activities could not be studied. The catalytic activities of \( \text{Pd}_2\text{L}_2(\text{OA} \text{c})_2 \) and their corresponding \( \text{Pd}_2(\text{LH})_2(\text{OA} \text{c})_2 \) are almost identical and their yellow DMF solutions undergo the same type of transformations \( (\text{OA} \text{c} \text{H})_2 \) are almost identical and their yellow DMF solutions undergo the same type of transformations 

The polarographic reductions of the Schiff base ligands \( \text{LH} \), the corresponding secondary amines \( \text{LH}_2 \), and their corresponding orthopalladated complexes were studied in DMF solution in the range of \(-0.1 \text{ V} \) to \(-1.7 \text{ V}\). The studies were made using tetraethyl ammonium iodide as the supporting electrolyte and the potentials are referred to the usual saturated calomel electrode. Each of the Schiff base ligands and its corresponding complex showed two well defined reduction steps each involving one electron. The linearity of the plot of \( E \) versus \( \log(i/i_0 - i) \) in each case indicated the reversibility of the process. The \( E_{1/2} \) and \( n \) values and the shape of the polarograms of the ligand and the corresponding complex are almost identical. \( (E_{1/2})_1 \) value of the ligands and the complexes lie within the range \(-0.49 \text{ V} \) to \(-0.54 \text{ V} \) while the corresponding \( (E_{1/2})_2 \) values fall in the range \(-0.715 \text{ V} \) to \(-0.73 \text{ V} \). The corresponding reduced ligands \( \text{LH}_2 \) and their complexes do not exhibit any reduction wave in the given range. The results suggest that the \( E_{1/2} \) and \( n \) values obtained both for the Schiff base ligand and its complex are actually the reduction values of the ligands only. The Schiff base ligand in the complex, therefore, undergoes an overall 2-electron reversible reduction which may be represented as follows (Eq. 3):

\[
\begin{align*}
\text{R} & \quad \text{N} \quad \text{C} \quad \text{Pd} \quad \text{X} \quad \text{R} \quad \text{N} \quad \text{C} \quad \text{Pd} \quad \text{X} \\
\text{R} & \quad \text{N} \quad \text{C} \quad \text{Pd} \quad \text{X} \quad \text{R} \quad \text{N} \quad \text{C} \quad \text{Pd} \quad \text{X} \\
2e & \quad \text{R} & \quad \text{N} \quad \text{C} \quad \text{Pd} \quad \text{X} \quad \text{R} \quad \text{N} \quad \text{C} \quad \text{Pd} \quad \text{X} \\
2e & \quad \text{R} & \quad \text{N} \quad \text{C} \quad \text{Pd} \quad \text{X} \quad \text{R} \quad \text{N} \quad \text{C} \quad \text{Pd} \quad \text{X} \\
\end{align*}
\]

\( \text{(3)} \)

\text{Kinetic studies and mechanism}

Kinetic studies using the two most active complexes as catalytic system and nitrobenzene and styrene as substrates have been made under normal pressure at 25°C. Studies under high pressure conditions were carried out using the same two catalytic systems and \( \text{CH}_3\text{NO}_2 \) as substrate at 110°C. The rate was determined by analysis of the product composition at different time intervals and the initial rates were determined from graphical extrapolation of the rate curve to zero time.
**Variation of catalyst concentration**

Kinetic studies revealed that the initial rates of hydrogenation of nitrobenzene and styrene were first order dependent on [catalyst].

**Variation of hydrogen pressure**

The initial rate of reduction of nitrobenzene and styrene was found to be second order dependent on the hydrogen pressure in the range of 200-1000 mm of Hg (Fig. 4). A first order rate dependence on the hydrogen pressure was observed for the reduction of nitromethane. Variation of substrate concentrations was found to have no appreciable effect on the reduction rate in the range of 0.5 to 3.5 M (Fig. 5).

The average initial rate of nitrobenzene reduction during the first 10 min, as determined from the volume of H$_2$ absorption and the G.C. analysis, lies in the range $1.93 \times 10^{-5}$ to $2.02 \times 10^{-5}$ mol dm$^{-3}$ s$^{-1}$ and the corresponding value of $k_4$ lies in the range $9.9 \times 10^4$ to $11.5 \times 10^4$ dm$^3$ mol$^{-2}$ s$^{-1}$. The above mechanism supports the comparable catalytic activities of Pd$_2$(LX)$_2$ and Pd$_2$(LH)$_2$X$_2$. The actual catalytic species is suggested to be (A) formed as per Eq. 2. Simultaneous hydrogenation and isomerization of alk-1-enes require the presence of monohydride species$^{29}$ like (A) and supports the formation of similar monohydride species like (B), (D) and (F) during $\geq$ C$-$NO$_2$ reduction (Scheme 1). The influence of C, N substituents on the catalytic activities of the complexes suggest step (V) (Scheme 1) to be the rate determining step. Polarographic studies indicate the reversibility of the process PdLX

DMF$\rightleftharpoons$Pd(LH)$_2$X DMF, and thereby indirectly supports the above reaction mechanism. The conversion of C to D is in accordance to $\beta$-hydrogen transfer$^{30}$($R' - C\_i - H$) to the metal atom.

According to Scheme 1

\[
\text{Rate} = k_4[E][H_2]^2
\]

\begin{align*}
[\text{Cat}]_r &= [A] + [B] + [C] + [D] + [E] + [F] \\
\text{Considering the steady state equilibrium of E and D and substituting the concentration of the species, we get:}
\end{align*}

\begin{align*}
[\text{Cat}]_r &= \frac{K_4[E][H_2]^2}{[\text{DMF}]} + \frac{K_5[E][H_2]^2}{[\text{DMF}]} + \frac{K_6[E][H_2]^2}{[\text{DMF}]} \\
&+ \frac{E(K_7 + K_8[H_2]^3)}{[\text{DMF}])} + [E] \\
&+ \frac{K_9[E][H_2]^2[\text{PhNOH}]}{[\text{PhNO}_2]} \\
\end{align*}

where

\[
K_4 = \frac{k_4}{k_1 K_1 K_2}, \quad K_5 = \frac{k_4}{k_1 K_2}, \quad K_6 = \frac{k_4}{k_1}, \quad K_7 = \frac{k_2}{k_3},
\]

\[
K_8 = \frac{k_4}{k_3}, \quad K_9 = \frac{K_4 k_3}{k_3 K_1 K_2}
\]

\begin{align*}
[\text{Cat}]_r &= \frac{[E][K_4[H_2]^2][\text{DMF}] + K_5[H_2]^3}{[\text{DMF}] [\text{PhNO}_2]} \\
&+ \frac{K_7 [\text{PhNO}_2] + [\text{DMF}] [\text{PhNO}_2]}{[\text{DMF}] [\text{PhNO}_2]} \\
&+ \frac{K_8[H_2]^2[\text{PhNO}_2] + K_9[H_2]^3}{[\text{DMF}] [\text{PhNO}_2]} \\
&\times [\text{PhNOH}][\text{DMF}]
\end{align*}
\[ [E] = \frac{[\text{Cat}]_{\text{II}}[\text{DMF}]\text{[PhNO}_2\text{]}\left\{K_7\text{[PhNO}_2\text{]} + [\text{DMF}]\text{[PhNO}_2\text{]} + [H_2]^2 K_4[\text{DMF}]^2 + K_5\text{[PhNO}_2\text{]} + K_6[\text{DMF}]\text{[PhNO}_2\text{]} + K_7^2 \right\}}{K_7\text{[PhNO}_2\text{]} + [\text{DMF}]\text{[PhNO}_2\text{]} + K_7 + [\text{DMF}]} \]

as \([H_2]^2\) is negligibly small; \(\sim 10^{-5}\) mol lit\(^{-1}\)

Now

\[
\text{Rate} = \frac{k_4[\text{Cat}]_{\text{II}}[\text{DMF}]H_2^2}{K_7 + [\text{DMF}]} = K[\text{Cat}]_{\text{II}}[H_2]^2
\]

where \(K = \frac{k_4[\text{DMF}]}{K_7 + [\text{DMF}]}\) as [DMF] is constant.

References