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Volume Profile Analysis of Oxidative Addition to Palladium(II) and Reductive Elimination from Palladium(IV)

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The oxidative addition of MeI to Pd(II) in the complex $PdMe_2(bpy)$ to produce $PdIMe_3(bpy)$ was studied as a function of [MeI] and pressure. The $\Delta V^{\ddagger}$ of -11.9 ± 0.6 cm^3 mol^{-1} for the addition process underlines the validity of the proposed S_N2 mechanism in the literature. The reductive elimination from $PdIMe_3(bpy)$ to form PdIMe(bpy) and C_2H_6 was studied as a function of pressure and [NaI]. The complex was prepared in situ via oxidative addition of MeI to the Pd(II) complex. $\Delta V^{\ddagger}$ is $+17 \pm 1$ cm^3/mol for the reductive elimination process. If NaI is added to the Pd(IV) compound, the rate slows down, but it did not affect the activation volume. The large positive value of $\Delta V^{\ddagger}$ for the elimination reaction suggests bond cleavage and/or the partial reduction from Pd(IV) to Pd(II) in the transition state. A volume profile for the overall oxidative addition and reductive elimination reactions is presented.

Introduction

In recent years volume profiles have been constructed for a wide range of inorganic, organometallic, and bioinorganic reactions in an effort to improve the understanding of the underlying reaction mechanism.[2] A volume profile presents the change in partial molar volume of the reactant species along the reaction coordinate to the product species, where the position of the transition state is determined by the volume of activation for the reaction. The latter quantity can only be determined from kinetic measurements at elevated pressures, usually up to 200 MPa, i.e. 2 kbar. Volume profiles have now been reported for solvent exchange, complex formation, aquation, base hydrolysis, ligation, addition/elimination, isomerization, and, most recently, electron-transfer reactions.[2,3]

As far as we know this study is the first to construct a volume profile for a combined oxidative addition and reductive elimination reaction involving a palladium(II/IV) system. Canty and collaborators[4-6] have performed a series of detailed kinetic studies on such systems. They[4] found that the oxidative addition of MeI and $PhCH_2Br$ to $[PdMe_2(bpy)]$ (bpy = 2,2′-bipyridine) is characterized by a significantly negative entropy of activation, which is in line with an associative (S_N2) mechanism. Reductive elimination from $[PdIMe_3(bpy)]$ to give ethane and [PdIMe(bpy)] mainly involves Pd–C bond cleavage accompanied by C–C coupling, but surprisingly is also characterized by a significantly negative entropy of activation.[4] Thus a volume profile for this combined process may assist the elucidation of the underlying mechanism, for which different alternatives were suggested.[4]

Earlier studies have demonstrated that oxidative addition reactions of Rh(I) and Ir(I) complexes are characterized by significantly negative volumes of activation that result from bond formation, partial oxidation of the metal center, and charge creation due to the polar nature of the transition state.[7-9] In fact, such data show a strong dependence on the nature of the solvent as expected for a polar transition state.[10] Up to now only a single volume of activation has been reported for a reductive elimination reaction, that of hydrogen from $[H_3Ru_3(\mu_3\text{-}COMe)(CO)_9]$.[11] The present study extends the range of such data and contributes toward a mechanistic clarification of the reductive elimination process.

Experimental Section

$[PdMe_2(bpy)]$ was prepared and characterized as described before.[12] Solutions of this complex were prepared shortly before use in order to avoid slow decomposition reactions. Acetone and NaI were of analytical reagent quality and used without further purification. MeI was destilled before use.

UV–vis spectra and slow kinetic experiments were measured in the thermostated cell compartments of Varian Cary 1 and Hewlett-Packard 8452A spectrophotometers. Fast kinetic experiments were performed on a Durrum D110 stopped-flow instrument at ambient pressure and on a homemade high-pressure stopped-flow system[13] at elevated pressure. Both instruments were thermostated to within ±0.1 °C, and an on-line data acquisition system employing OLIS KINFIT software was used to fit the kinetic traces. Slow kinetic experiments at elevated pressure were performed on a modified Zeiss PMQ II spectro-

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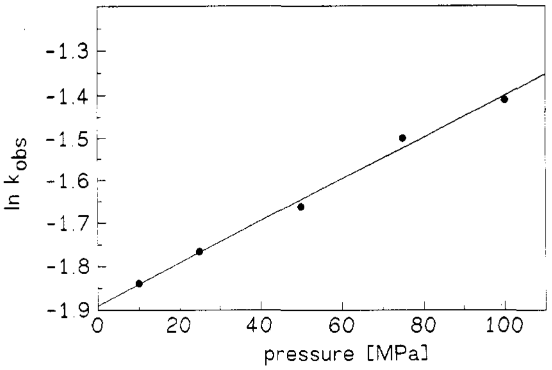


Figure 1. Effect of pressure on the reaction [PdMe$_2$(bpy)] + MeI → [PdIMe$_3$(bpy)]. Experimental conditions: [Pd] = 3×10^{-4} M; [MeI] = 0.04 M; solvent = acetone; temperature = 20.0 °C; each data point is the average of six kinetic runs.

photometer equipped with a two-window, thermostated (±0.1 °C) high pressure cell.[14]

At least a 10-fold excess of MeI was used in the oxidative addition reactions to ensure pseudo-first order conditions. The reaction was monitored at 440 nm. The reductive elimination reaction was followed at 380 nm by preparing the [PdIMe$_3$(bpy)] complex in solution via the oxidative addition reaction. In both cases the kinetic traces resulted in good first-order plots.

Results and Discussion

The oxidative addition of MeI to [PdMe$_2$(bpy)] was studied as a function of [MeI] at ambient pressure. Plots of k_{obs} versus [MeI] exhibited good linear behavior and resulted in a second-order rate constant k_1 = 3.79 ± 0.06 M^{-1} s^{-1} at 20 °C, which is in close agreement with the value

$$[\text{PdMe}_2(\text{bpy})] + \text{MeI} \xrightarrow{k_1} [\text{PdIMe}_3(\text{bpy})] \tag{1}$$

3.23 ± 0.08 M^{-1} s^{-1} reported in the literature.[4] The effect of pressure was studied at 0.04 M MeI and the results in Figure 1 clearly demonstrate the acceleration of this reaction under pressure. The corresponding volume of activation is −11.9 ± 0.6 cm^3 mol^{-1}.

The reductive elimination reaction (2) was studied as a subsequent step to the oxidative addition reaction in the present study. The presence of 0.04 MeI caused a

$$[\text{PdIMe}_3(\text{bpy})] \rightarrow \text{C}_2\text{H}_6 + [\text{PdIMe}(\text{bpy})] \tag{2}$$

slight deceleration of the reductive elimination reaction, which can account for the lower rate constants found in this study compared to those reported in the literature for the reaction performed on an isolated sample of [PdIMe$_3$(bpy)].[4] Addition of 0.04 M NaI caused as significant deceleration of the reaction as found before[4] and our data are once again slower due to the presence of MeI. The latter species presumably has a similar but significantly smaller decelerating effect on the reductive elimination reaction than NaI. The results reported in Figure 2 demonstrate a significant decrease in k_2 with increasing pressure in both cases, which results in $\Delta V^\ddagger$ values of +17.5 ± 0.8 and +17.3 ± 1.4 cm^3 mol^{-1} in the absence and presence of NaI, respectively. By way of comparison, reductive elimination of H$_2$ from [H$_3$Ru(μ_3-COMe)(CO)$_9$] resulted in a $\Delta V^\ddagger$ value of +20 ± 2 cm^3 mol^{-1}.[11] It follows that elimination of C$_2$H$_6$ in reaction 2 is accompanied by a large volume increase and must include considerable bond cleavage in the transition state.

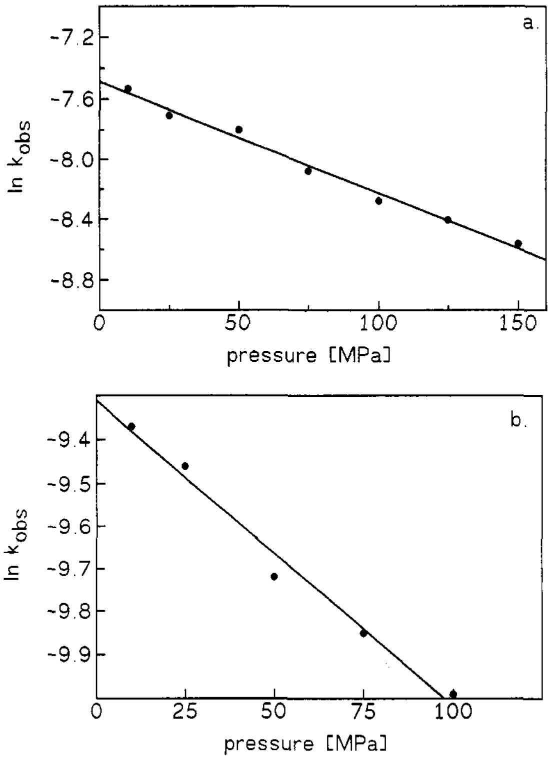
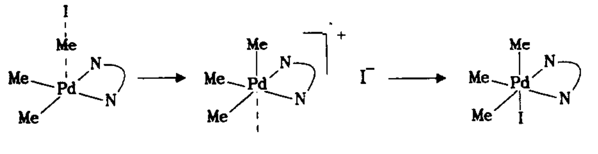


Figure 2. Effect of pressure on the reaction [PdIMe$_3$(bpy)] → C$_2$H$_6$ + [PdIMe(bpy)]. Experimental conditions: [Pd] = 3×10^{-4} M; [MeI] = 0.04 M; [NaI] = 0 (a, top), 0.04 M (b, bottom); solvent = acetone; temperature = 11.8 (a), 20.0 °C (b); each data point is the average of at least three kinetic runs.

Oxidative addition reactions of MeI to Ir(Cl)(CO)PPh$_3$[10] and Rh(L-L)(CO)PR$_3$,[8,9] where L-L = acetylacetone, trifluoroacetylacetone, thioacetylacetone and cupferron and R = OPh and Ph, are characterized by $\Delta V^\ddagger$ values that vary between −14 and −28 cm^3 mol^{-1}, depending on the nature of L-L and the polarity of the solvent. It was concluded[9,10] that oxidative addition in these systems is accompanied by an intrinsic volume collapse of ca. −17 cm^3 mol^{-1}, which results from bond formation accompanied by oxidation of the metal center. The solvent dependence of $\Delta V^\ddagger$ was interpreted as evidence in favor of a concerted three-center reaction route. In the present case the oxidative addition of MeI in reaction 1 is suggested to follow an S$_N$2 mechanism as outlined in (3), that involves the end-on interaction between Pd and MeI. Such a reaction will involve a significant volume collapse due to bond formation and partial charge creation. NMR spectra recorded at −50 °C have led to the detection of the intermediate [PdMe$_3$(bpy)(solvent)]$^+$ I^{15} suggested to participate in reaction 3. The $\Delta V^\ddagger$ value does not allow us to distinguish between an S$_N$2 or side-on attack of MeI, but in the light of the kinetic and spectroscopic observa-



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tions mentioned above, the S_N2 mechanism is clearly favored in the present case.

The reductive elimination reaction 2 is less well understood. Important observations are that the reaction is decelerated by the presence of NaI (and to a minor degree by the presence of MeI), it exhibits $\Delta S^{\ddagger}$ values of −66 ± 34 and −53 ± 25 J K^{-1} mol^{-1} in the absence and presence of NaI, respectively,[4] and is characterized by large positive $\Delta V^{\ddagger}$ values of +17 ± 1 cm^3 mol^{-1}. To account for the first two observations, Canty and collaborators[4] concluded that at least partial ionization of iodide must occur before reductive elimination of ethane from $[PdIMe_3(bpy)]$. The precursor state to reductive elimination could be a polar species $[Me_3(bpy)Pd^{\delta+}\text{- - -}I^{\delta-}]$, or it could be a tight ion pair $[Me_3(bpy)Pd]^+I^-$. This would not account for the inhibition of the reaction by iodide, but the higher polarity of these species could account for the significantly negative $\Delta S^{\ddagger}$ values.[4] It should however be kept in mind that although the $\Delta S^{\ddagger}$ values found for reductive elimination are negative, they are considerably more positive than the values found for oxidative addition, which could mean that charge creation is not that well developed in the transition state as expected. From a detailed study of the effect of the NaI concentration on the reductive elimination reaction the following mechanism was suggested.[4]

$$\begin{tikzcd}
{[PdIMe_3(bpy)]} \arrow[r, shift left] \arrow[d, "k_a"] & {[PdMe_3(bpy)]^+ + I^-} \arrow[l, shift left] \arrow[d, "k_b"] \\
{C_2H_6 + [PdIMe_3(bpy)]} & {[PdMe_3(bpy)]^+ + C_2H_6} \arrow[l, "I^-"']
\end{tikzcd} \tag{4}$$

The mechanism in (4) involves the participation of a solvated cation $[PdMe_3(bpy)]^+$ or $[PdMe_3(bpy)(acetone)]^+$, of which the concentration is controlled by the iodide concentration in solution. In the absence of iodide the reaction mainly follows the k_b path, whereas under limiting conditions (i.e. high NaI concentration) the reaction proceeds via the slower k_a path, where $k_b \approx 40k_a$ at 20 °C.[4] Both reaction paths are characterized by similar $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ values, indicating that the transition state for the reductive elimination paths must involve the same degree of charge distribution and bond cleavage as compared to the ground state in both cases. These very similar effects would suggest both ground-state Pd(IV) species to be six coordinate, viz. $[PdIMe_3(bpy)]$ and $[PdMe_3(bpy)(acetone)]^+$, with the more labile solvento complex being more capable to convert to the square planar Pd(II) product state. The large volume increase can only arise from significant bond cleavage and/or the formal reduction from Pd(IV) to Pd(II). The actual reductive elimination

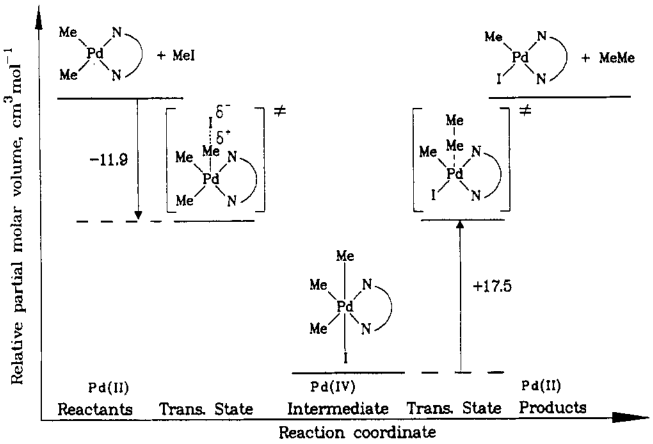

Figure 3. Volume profile for the combined oxidative addition and reductive elimination reaction $[PdMe_2(bpy)] + MeI \rightarrow [PdIMe_3(bpy)] \rightarrow C_2H_6 + [PdIMe(bpy)]$. For experimental conditions see Figures 1 and 2. The diagrams of the transition states are not meant to represent the configurations of those states.

is most probably a concerted process as suggested for the platinum(IV) case,[16] which involves C–C bond formation accompanied by Pd–C bond cleavage and a formal reduction of the metal center, followed by the release of C_2H_6.[4]

The volumes of activation found in this study can be used to construct an overall volume profile for the combined oxidative addition and reductive elimination reactions as shown in Figure 3. It has been assumed that the partial molar volumes of the reactant and product states are very similar since it follows from density data that the partial molar volumes of MeI and C_2H_6 are 62.3 and 52.4 cm^3 mol^{-1}, respectively. This also applies to the partial molar volume of the two transition states indicated in Figure 3. The fact that both the oxidative addition and reductive elimination reactions exhibit rather similar absolute volumes of activation indicates that the corresponding transition states must be rather similar in terms of bonding properties, charge distribution, and polar effects. Although the electronic nature and the relative energies of these transition states could be rather different, the close agreement in the partial molar volume data suggests this not to be the case. The intermediate $[PdIMe_3(bpy)]$ species has a partial molar volume ca. 30 cm^3 mol^{-1} lower than either the reactant and final product states. This is due to the coordination of either MeI or C_2H_6 and the change in formal oxidation state from Pd(II) to Pd(IV).

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