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Activation Volume Measurement for C–H Activation. Evidence for Associative Benzene Substitution at a Platinum(II) Center

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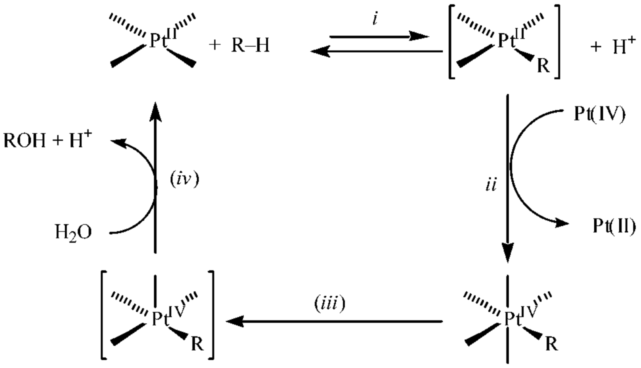
The reaction of the platinum(II) methyl cation $[(N\text{-}N)Pt(CH_3)(solv)]^+$ ($N\text{-}N = ArN{=}C(Me)C(Me){=}NAr$, $Ar = 2{,}6\text{-}(CH_3)_2C_6H_3$, solv $= H_2O$ (**1a**) or TFE $= CF_3CH_2OH$ (**1b**)) with benzene in TFE/H_2O solutions cleanly affords the platinum(II) phenyl cation $[(N\text{-}N)Pt(C_6H_5)(solv)]^+$ (**2**). High-pressure kinetic studies were performed to resolve the mechanism for the entrance of benzene into the coordination sphere. The pressure dependence of the overall second-order rate constant for the reaction resulted in $\Delta V^{\ddagger} = -(14.3 \pm 0.6)$ cm^3 mol^{-1}. Since the overall second order rate constant $k = K_{eq}k_2$, $\Delta V^{\ddagger} = \Delta V^{\circ}(K_{eq}) + \Delta V^{\ddagger}(k_2)$. The thermodynamic parameters for the equilibrium constant between **1a** and **1b**, $K_{eq} = [\mathbf{1b}][H_2O]/[\mathbf{1a}][TFE] = 8.4 \times 10^{-4}$ at 25 °C, were found to be $\Delta H^{\circ} = 13.6 \pm 0.5$ kJ mol^{-1}, $\Delta S^{\circ} = -10.4 \pm 1.4$ J K^{-1} mol^{-1}, and $\Delta V^{\circ} = -4.8 \pm 0.7$ cm^3 mol^{-1}. Thus $\Delta V^{\ddagger}(k_2)$ for the activation of benzene by the TFE solvento complex equals -9.5 ± 1.3 cm^3 mol^{-1}. This significantly negative activation volume, along with the negative activation entropy for the coordination of benzene, clearly supports the operation of an associative mechanism.

Activation of hydrocarbon C−H bonds by organo−transition metal complexes has attracted much attention as a route to directly utilize alkanes as chemical feedstocks.[2] The Shilov system, which consists of aqueous solutions of Pt(II) and Pt(IV) salts that convert alkanes to mixtures of the corresponding chlorides and alcohols under mild conditions, has been extensively studied. Results from several groups support the multistep catalytic mechanism depicted in Scheme 1, where the key first step, the actual C−H bond activation, involves reaction of alkane with a Pt(II) complex.[3]

Scheme 1



A key question concerns how the reacting hydrocarbon enters the Pt(II) coordination sphere. Ligand substitution reactions of square planar d^8 metal complexes in general follow an associative mechanism, but since hydrocarbons are expected to be very weak nucleophiles, the general rule might not apply here. The pentafluoropyridine complex $[(tmeda)Pt(CH_3)(C_5F_5N)]^+$, which activates C−H bonds,[4] appears to undergo dissociative substitution of pentafluoropyridine.[5] Johansson and Tilset have reported evidence for associative methane loss following protonation of (diimine)-$Pt^{II}(CH_3)_2$ complexes.[6] The principle of microscopic reversibility implies associative hydrocarbon coordination, which was also inferred from detailed mechanistic studies of the benzene activation reaction,[7] but some of the evidence is subject to significant experimental uncertainty (e.g., a negative activation entropy) and/or alternative interpretation (see Supporting Information).

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(2) (a) *Selective Hydrocarbon Activation*; Davies, J. A., Watson, P. L., Liebman, J. F., Greenberg, A., Eds.; VCH: New York, 1990. (b) *Activation and Functionalization of Alkanes*; Hill, C. L., Ed.; John Wiley & Sons: New York, 1989. (c) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 2180. (d) Crabtree, R. H.; *Chem. Rev.* **1995**, *95*, 987. (e) Bengali, A. A.; Arndsen, B. A.; Burger, P. M.; Schultz, R. H.; Weiller, B. H.; Kyle, K. R.; Moore, C. B.; Bergman, R. G. *Pure Appl. Chem.* **1995**, *67*, 281. (f) Shilov, A. E.; Shulpin, G. B. *Chem. Rev.* **1997**, *97*, 2879. (g) Sen, A. *Acc. Chem. Res.* **1998**, *31*, 550. (h) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154. (i) Shilov, A. E.; Shul'pin, G. B. *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*; Kluwer: Boston, 2000. (j) Periana, R. A.; Taube, J. D.; Gamble, S.; Taube, H.; Satoh, T., Fujii, H. *Science* **1998**, *280*, 560.

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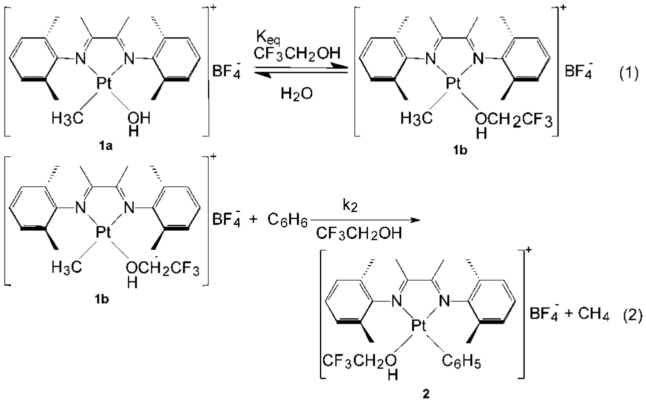
Activation volumes offer a powerful tool for resolving such ambiguities. Associative reactions are usually characterized by significantly negative activation volumes, demonstrating a volume collapse during the substitution process in going from the reactant to the transition state.[8] However, electronic factors can cause a changeover in mechanism from associative to dissociative, involving the participation of a 14-electron three-coordinate transition state; in such cases the activation volume changes sign and becomes positive.[9] We report here the first example of an activation volume measurement for C−H activation.

The reactions studied are shown in eqs 1 and 2. The equilibrium mixture of aqua and solvento methyl cations **1a**/**1b**, generated by protonolysis of the corresponding Pt(II) dimethyl complex by aqueous HBF_4 in deuterated trifluoroethanol (TFE-d_3), reacts with benzene at 25−45 °C to give **2** and methane. The observed rate law, $k_{obs} = k[C_6H_6]/[H_2O]$, is consistent with either a preequilibrium dissociative pathway via a coordinatively unsaturated 14-electron intermediate or a solvent-assisted associative pathway.[7]



We performed kinetic studies under the same conditions but at pressures up to 180 MPa, following the reaction by UV−vis spectroscopy. There is a linear dependence of (ln *k*) on the applied pressure, in the accessible pressure range (Figure 1). The activation volume, obtained from the relationship $[\delta(\ln k)/\delta p]_T = -\Delta V^{\ddagger}/RT$, where $k = k_{obs}[H_2O]/[C_6H_6]$, is $\Delta V^{\ddagger} = -14.3 \pm 0.6\ cm^3\ mol^{-1}$.

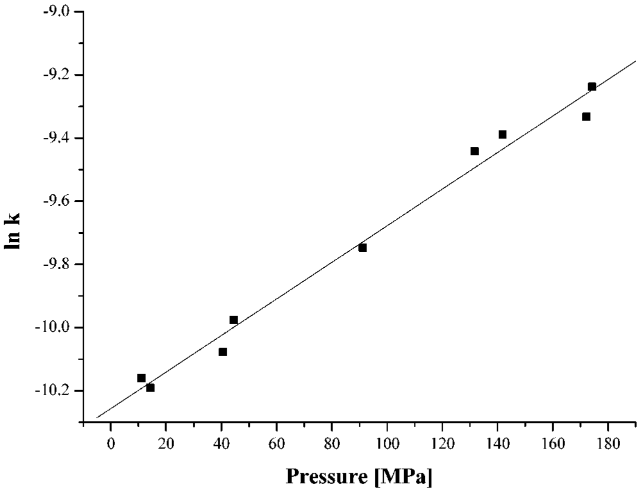


Figure 1. Pressure dependence of the reaction of benzene with a mixture of **1a** and **1b** in TFE. The measurements were done at 24.8 °C. The water concentration was kept sufficiently high that the aqua adduct accounts for >90% of the total Pt(II) species.

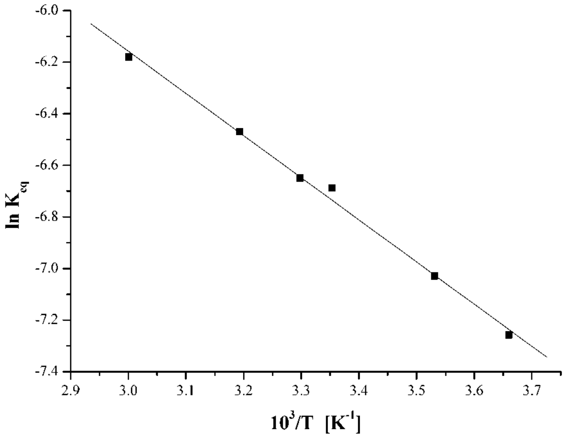


Figure 2. Plot of ln K_{eq} versus $1/T$ for reaction 1.

That the reaction with benzene is accelerated by pressure and characterized by a significantly negative volume of activation favors an associative mechanism for reaction 2. Hence the activation parameters are for the overall second order rate constant $k = K_{eq}k_2$, i.e., the observed activation volume $\Delta V^{\ddagger} = \Delta V^{\circ}(K_{eq}) + \Delta V^{\ddagger}(k_2)$, where $\Delta V^{\circ}(K_{eq})$ represents the reaction volume for the displacement of coordinated water by TFE and $\Delta V^{\ddagger}(k_2)$ represents the volume of activation for the activation of benzene by the TFE solvento complex. Similar relationships will hold for the thermal activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. The ratio of [**1a**]/[**1b**] as a function of temperature and pressure was measured by ^1H NMR spectroscopy. The equilibrium constant $K_{eq} = [\mathbf{1b}][H_2O]/[\mathbf{1a}][TFE] = (8.4 \pm 0.4) \times 10^{-4}$ at 25 °C and atmospheric pressure, in good agreement with the value reported previously, $(1.2 \pm 0.3) \times 10^{-3}$ at 25 °C.[7]

From the temperature dependence of the equilibrium constant over the range 273−333 K (see Figure 2), the enthalpy and entropy changes associated with this equilib-

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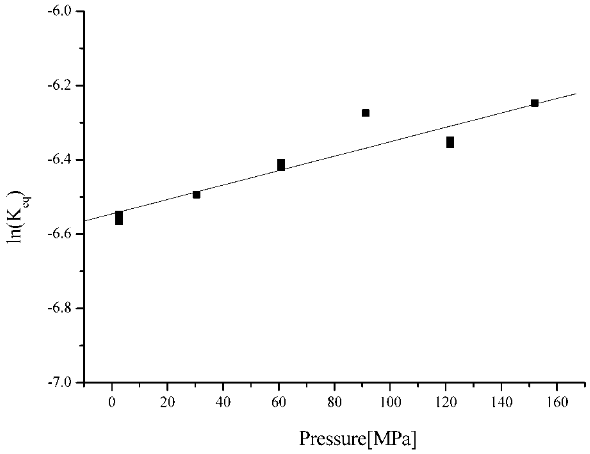

Figure 3. Pressure dependence of ln K_{eq} for the displacement of coordinated water by TFE. The measurements were done at 40 °C.

rium were calculated to be $\Delta H° = 13.6 \pm 0.5$ kJ mol^{-1} and $\Delta S° = -10.4 \pm 1.4$ J K^{-1} mol^{-1}. Combined with the previously determined activation parameters for the overall reaction ($\Delta H^{\ddagger} = 79.5 \pm 1.2$ kJ mol^{-1}, $\Delta S^{\ddagger} = -67 \pm 4$ J K^{-1} mol^{-1}),[7] those for the actual rate-determining step k_2 are calculated to be $\Delta H^{\ddagger} = 65.9 \pm 1.7$ kJ mol^{-1} and $\Delta S^{\ddagger} = -57 \pm 5$ J K^{-1} mol^{-1}.

The plot of ln K_{eq} vs pressure at 40 °C is shown in Figure 3, from which $\Delta V°(K_{eq}) = -4.8 \pm 0.7$ cm^3 mol^{-1}. This means that there is a significant volume decrease on displacing water by TFE, in line with the negative value reported for $\Delta S°$ above. It follows that the volume of activation for the activation of benzene by the TFE solvento complex $\Delta V^{\ddagger}(k_2) = \Delta V^{\ddagger}_{exp} - \Delta V°(K_{eq}) = -9.5 \pm 1.3$ cm^3 mol^{-1}. This result is very typical for associative substitution reactions for square planar Pt(II) complexes.[8,10]

These high-pressure kinetic and thermodynamic results provide the first report of an activation volume for C−H activation, and permit dissection of the apparent activation parameters for the reaction of benzene with a Pt(II) complex into their component parts. The significantly negative value for the activation volume, as well as the significantly negative activation entropy determined previously, clearly supports the operation of an associative mechanism and clarifies the nature of the mechanism for the C−H activation step in a model for the Shilov alkane oxidation system.

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Supporting Information Available: Mechanistic considerations, a table, and three Figures giving details of the NMR characterization and the equilibrium constant between **1a** and **1b** as a function of temperature. This material is available free of charge via the Internet at http://pubs.acs.org.

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