



Experimental and theoretical investigation of the oxidative carbonylation of toluene to toluic acid catalyzed by palladium(II) in the presence of vanadium and molecular oxygen

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ABSTRACT

The mechanism and kinetics of the liquid-phase, oxidative carbonylation of toluene to toluic acid over Pd(II) in the presence of trifluoroacetic acid (TFAH), trifluoroacetic anhydride (TFAA), and molecular oxygen were investigated through a combination of experimental and theoretical approaches. The experimental results are consistent with the previously proposed mechanism for the oxidative carbonylation of arenes. The reaction is initiated by coordination of toluene to the Pd(II) complex and activation of a C–H bond in the benzene ring. This initial step becomes rate limiting when a sufficiently high (NH₄VO₃)/Pd ratio is used for the reoxidation of Pd(0) to Pd(II). Both processes are found to be dependent on the electron withdrawing and donating capability of the anionic ligands. Overall catalyst activity peaks for ligands of intermediate basicity, and diminishes for both more and less basic ligands. Theoretical analysis of the coordination of toluene and activation of the C–H bond on the benzene ring reveals that the basicity of the ligands affects the two processes in opposite ways. Weakly basic ligands promote the coordination of toluene but have the opposite effect on the activation of the C–H bond. The tradeoff in these two effects leads to a maximum in the apparent rate coefficient with pK_a of the conjugate acid of the anionic ligands. The absence of significant product stereoselectivity is due to a lack of steric hindrance in the binding of toluene to the Pd(II) complex.

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1. Introduction

Palladium acetate has been shown to be an active catalyst for a number of reactions involving arene C–H bond activation [1–16]. We note, in particular, that the oxidative carbonylation of arenes to the corresponding aryl carboxylic acid can be catalyzed by Pd(II) in the presence of acetic acid and CO [1–10]. Early studies of this reaction revealed that in the course of this reaction, Pd(II) is reduced to Pd(0) and hence, in the absence of an oxidizing agent, the yield of products is stoichiometric in the initial concentration of Pd(II) [1]. The oxidative carbonylation of arenes can be made catalytic by adding an oxidant to convert Pd(0) to Pd(II) [2]. If BuOOH or K₂S₂O₈ is used as an oxidant, this component is consumed in the course of the reaction [2,3,8]. Molecular oxygen can also be used as the oxidant provided a co-catalyst is added to promote the activation of O₂. Examples of such co-catalysts include Cu(acetate)₂ [4], MnO₂ [6] and NH₄VO₃ [10].

A reaction mechanism has been proposed to rationalize the oxidative carbonylation of toluene to toluic acid [5]. It involves coordination of toluene to the Pd(II) center, activation of a C–H bond in the coordinated toluene at the *para*, *meta*, or *ortho* position of the benzene ring, electrophilic activation of the arene C–H bond, and subsequent insertion of CO into the Pd–C bond of the Pd-toluylyl species formed in the preceding step. The resulting acyl species is envisioned to undergo reductive elimination to form a mixed anhydride of the desired aryl acid and the acid that was used in the reaction system to provide anionic ligands (e.g., trifluoroacetic acid). Pd(0) formed in this latter process is then re-oxidized to close the catalytic cycle. The observation that formation of toluic acid is faster when trifluoroacetic acid is used in place of acetic acid suggests that the activation of the arene C–H bond occurs via an electrophilic mechanism [9]. While the proposed mechanism is plausible, definitive evidence for electrostatic activation of the C–H bond of toluene is very limited as are the effects of changing the electrophilicity of the anionic ligand. Recent theoretical work by Davies et al. on model C–H bond activation systems indicates that the nature of such activation is specific to the metal and ligand environment, which has implications regarding transition state stabilization such as through

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the presence or absence of agostic H–metal interactions [12,13]. Understanding the nature of the ligand and metal interactions in the aforementioned Pd-catalyzed toluene activation is therefore important to developing improved arene oxidative carbonylation catalysts.

In recent studies of the oxidative carbonylation of toluene catalyzed by Rh(III) complexes involving acetate ligands, it was demonstrated that the activity of the catalyst can be tuned through a maximum by substitution of the H atoms of the methyl group in the acetate ligands by Cl or F, or combinations of the elements [17–19]. Experimental studies of the reaction have demonstrated that under conditions where most of the Rh is present as Rh(III), the rate-limiting step is the electrophilic activation of the C–H bond on the benzene ring of coordinated toluene. Theoretical analysis of the process shows that coordination of toluene is a reversible process that is sensitive to the composition of the acetate ligand, as is the activation of the C–H of the benzene ring. In the present study we show that the oxidative carbonylation of toluene to toluic acid catalyzed by Pd(II) also proceeds via electrophilic activation and that the catalyst activity is affected by the composition of the acetate ligand. Theoretical analysis of the coordination of toluene to Pd(II) and the activation of the benzene C–H bond explains why Pd(II) complexes are more active than Rh(III) complexes but less stereoselective toward the formation of *p*-toluic acid.

2. Experimental

Reactions were conducted in a stirred, 50 mL Parr autoclave made of Hastelloy C. Between experiments, the reactor was washed thoroughly with water and acetone and then dried in a vacuum oven overnight to avoid contamination. The reaction temperature was monitored using a thermocouple located inside a Hastelloy C thermowell. During a typical reaction, 3.46 g of anhydrous toluene (99.8%, Aldrich), 1.48 g of CF₃COOH (99%, Aldrich), 0.8 g of (CF₃CO)₂O (≥99%, Aldrich), 0.0016 g of Pd(TFA)₂ (Aldrich) and 0.0604 g of NH₄VO₃ (99+%, Aldrich) were placed into the autoclave, which was then sealed and purged four times with nitrogen or helium. For the kinetic isotope experiment, a similar procedure was performed as described above except that toluene was substituted with 3.76 g d₈-toluene (99.6 atom% D, Aldrich). After purging, the reactor was pressurized at 293 K with 0.345 MPa O₂ (99.993%, Praxair) and 0.345 MPa CO (99.5%, Praxair). The reactor was then heated to 353 K in approximately 10 min and then held at this temperature for 4 h. Upon the completion of the reaction, the reactor was quenched with ice water to 308 K and vented.

The contents of the reactor were emptied into a vial and weighed, after which approximately 12 g of deionized H₂O was added to the organic phase in order to extract the trifluoroacetic acid from it. The vial was inverted 20 times and the aqueous and organic phases were allowed to separate completely. After inverting the vial containing the mixture of aqueous and organic phases 20 times, the two phases were allowed to separate and the aqueous phase was discarded. Solids produced by the reaction were separated from the organic phase by centrifugation and dried overnight in a vacuum oven at 313 K.

The concentration of toluic acid in the organic phase was determined by gas chromatography using an Agilent Technologies 6890N gas chromatograph equipped with an HP-1 capillary column coated with crosslinked methyl siloxane and an FID detector. After washing with H₂O and drying, the product solids were dissolved in toluene and similarly analyzed by gas chromatography. The solid lines shown in all figures represent the average over all replicas.

3. Theoretical methods

Molecular structures, energies, vibrational modes, and rotational constants were calculated with Density Functional Theory [20] in Q-Chem [21]. Geometry optimization of minimum energy structures and vibrational analysis were performed with the B3LYP density functional [22–25] and the 6-31G* basis set. Electronic structure energies of the optimized molecular structures were also computed with the B3LYP density functional, and then refined at the 6-311++G** level. For all calculations, the core basis functions for palladium were replaced with the LANL2DZ effective-core potential [26]. Geometry optimization and single point energy calculations performed with larger basis sets did not significantly change the structure shapes or energies, indicating that the chosen basis sets were sufficient. Estimates of transition state structures were obtained with the Growing String Method [27] and refined within the normal geometry optimization functionality of Q-Chem.

All calculations were performed in the gas phase. No meaningful model of the solvent mixture of toluene and acetic acids was found to be practical, so solvent effects were ignored. Thermochemical calculations were performed at the experimental reaction temperature of 353 K, and invoked the rigid-rotor–harmonic oscillator approximation. The energetics of toluene binding were basis set superposition-error corrected using the counterpoise method. Equilibrium constants were calculated at a standard state of 1 bar and adjusted to molar concentration units according to Eq. (1):

$$K = \left(\frac{RTc^o}{P^o} \right)^{-\Delta\nu} \exp \left(\frac{-\Delta G^o}{RT} \right) \quad (1)$$

where K is the equilibrium constant, R is the gas constant, T is the absolute temperature, c^o is the standard-state concentration in the liquid phase (1 mol/L), P^o is the standard-state pressure (1 bar), $\Delta\nu$ is the difference between the sums of the stoichiometric coefficients of the products and reactants, and ΔG^o is the Gibbs free energy of reaction at the reaction temperature. Rate constants were computed from transition state theory, Eq. (2):

$$k = \frac{k_B T}{h} \exp \left(\frac{\Delta S^\ddagger}{R} \right) \exp \left(\frac{-\Delta H^\ddagger}{RT} \right) \quad (2)$$

4. Results and discussion

A proposed mechanism for the oxidative carbonylation of toluene to toluic acid is shown in Scheme 1. This scheme is very similar to that suggested in earlier work by [4,5,7,10]. The main catalytic cycle is initiated by the electrophilic reaction of toluene with Pd(TFA)₂ to form a methyl aryl complex, Pd(TFA)(C₆H₄CH₃) and TFAH, where TFA is trifluoroacetate. A CO molecule from the reaction mixture then binds to the complex and undergoes a migratory insertion to form Pd(TFA)₂(COC₆H₄CH₃). This species then reacts via reductive elimination to produce Pd(0) and a mixed anhydride. The mixed anhydride then either hydrolyzes to give TFAH and toluic acid, or exchanges a proton with TFAH to produce trifluoroacetic anhydride and the toluic acid. Only the former version is shown in Scheme 1. The reduced Pd catalyst is re-oxidized with NH₄VO₃/O₂ [28] via a sequence of steps, which are taken to be identical to those established for the oxidation of Rh(I) to Rh(III) during the oxidative carbonylation of toluene catalyzed by Rh(III) acetate complexes [17–19].

Scheme 1 suggests that the reaction of Pd(TFA)₂ with toluene will become the rate-limiting step provided that the rate of reoxidation of Pd(0) to Pd(II) and the rates of carbonylation and mixed anhydride formation are rapid and, hence, kinetically insignificant. To test whether the rate of Pd(0) oxidation could be made to satisfy this criterion, experiments were carried out in which the amount of NH₄VO₃ was varied while keeping the quantity of Pd present in

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