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Direct Involvement of the Acetato Ligand in the Reductive Elimination Step of Rhodium-Catalyzed Methanol Carbonylation

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Supporting Information

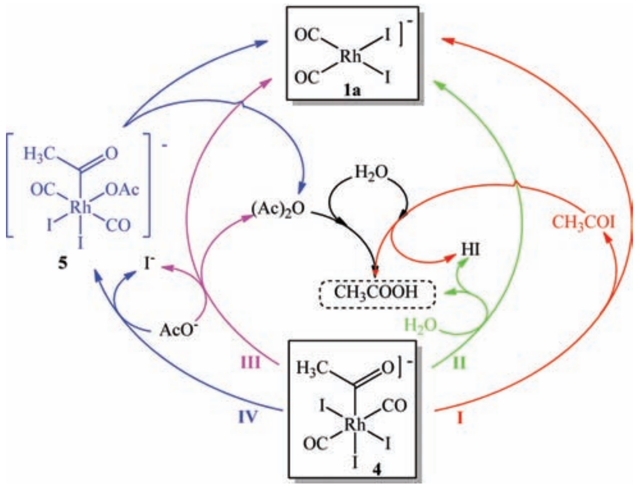
ABSTRACT: For the last step of rhodium-catalyzed methanol carbonylation, high-pressure NMR, and kinetic and experimental data supported by density functional theory calculations are consistent with substitution of I^- by an AcO^- ligand on the $[RhI_3(COCH_3)(CO)_2]^-$ species followed by reductive elimination of acetic anhydride, which immediately reacts with water to afford acetic acid.

Approximately 80% of the 9 million tons of worldwide production of acetic acid (AcOH) is manufactured by rhodium- or iridium-catalyzed carbonylation of methanol. This reaction represents a major industrial application of homogeneous catalysis. The historical rhodium-catalyzed Monsanto process developed in the early 1970s involves the anionic active species *cis*-$[RhI_2(CO)_2]^-$ (**1a**). This process requires more than 14 wt % water in the reactor to maintain a high catalyst activity with acceptable stability of this rhodium(I) complex.[1] Because of the high reactor water content, a significant operating cost is required to separate AcOH from water by distillation. Therefore, many research efforts have been directed toward the design of an active and stable catalytic system able to operate at lower water content. Currently, two industrial processes are operating close to 5 wt % water content. The Cativa process developed by British Petroleum Chemicals involves the more stable anionic species $[IrI_2(CO)_2]^-$ with a ruthenium cocatalyst to maintain high carbonylation rates.[1] A rhodium-catalyzed process developed by Hoechst Celanese uses LiI, as a copromoter and stabilizer. LiI enhances the activity of the catalytic system and precludes the formation of insoluble inactive RhI_3.[1a] Some authors suggested that the use of this salt allows for the formation of a hypothetical pentacoordinated rhodium(I) dianionic species $[RhI_3(CO)_2]^{2-}$, which is more nucleophilic for the oxidative addition of methyl iodide.[1a] Furthermore, the presence of significant amounts of acetate ions (ca. 0.3 M), due to the equilibrium of eq 1, could result in the formation of $[RhI_2(OAc)(CO)_2]^{2-}$.[1a]

$$LiI + CH_3OAc \rightleftharpoons CH_3I + LiOAc \qquad (1)$$

In rhodium-catalyzed carbonylation, the amount of water impacts the nature of the rate-determining step (rds). At high water content, typically >14 wt %, the rds is the oxidative addition of CH_3I to **1a**, producing *cis*-$[RhI_3(CH_3)(CO)_2]^-$ (**2a**), which evolves rapidly toward the acetyl species $[RhI_3(COCH_3)(CO)]^-$ (**3**) by CO migratory insertion and then by coordination of external CO to form $[RhI_3(COCH_3)(CO)_2]^-$ (**4**).[2] In the absence of a CO atmosphere, complex **3** dimerizes into $[Rh_2(\mu\text{-}I)_2I_4(COCH_3)_2(CO)_2]^{2-}$ (**3′**).[2b] Some years ago, Jones proposed that the reductive elimination (RE) could be the rds if the water content is below 8 wt %.[3] The mechanism for the RE has not been explored in detail, unlike the other proposed steps in the catalytic cycle.[4] The elimination of acetyl iodide from **4** followed by its immediate hydrolysis to AcOH is largely accepted as the final step of the catalytic cycle (Scheme 1, path I).[1,2] However, an alternative proposed mechanism involves the direct solvolysis of **4** by water (path II).[2a] The CH_3COI RE has also been proposed for the anhydrous carbonylation of methyl acetate to acetic anhydride (Eastman process) and carbonylation of a MeOH/MeOAc mixture to $AcOH/Ac_2O$ at low water content (BP Chemicals process). Both involve $[RhI_2(CO)_2]^-$ and iodide salts and lead to the formation of Ac_2O from the reaction of CH_3COI with OAc^- (similar to path I).[5]

Scheme 1. Different Proposed Pathways for Reductive Elimination



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In this Communication, we report experimental and theoretical evidence that supports a new alternative mechanism for this final step, which involves (i) substitution of an iodo ligand from **4** by an acetato ligand followed by (ii) reductive elimination of acetic anhydride, which immediately hydrolyzes to afford two molecules of AcOH (path IV).

First, complexes **1a**, **3′**, and *mer,trans*-$[RhI_3(COCH_3)(CO)_2]^-$ (**4a**) have been prepared with bis(triphenylphosphoranylidene)ammonium (PPN^+) as the countercation and fully characterized by infrared and NMR spectroscopies and mass spectrometry (see SI.1 in the Supporting Information, SI). The effect of the water concentration on the rhodium reactivity has been studied by high-pressure NMR, giving direct information on the nature of the rds, the carbonylation reaction operating at 363 K and 15 bar ^{13}CO initial pressure.

The $^{13}C\{^1H\}$ NMR spectra were recorded for ^{13}CO-labeled **1a** in a $CD_3COOD/MeOAc/CH_3I$ solution at three water concentrations (SI.2 5, 10, and 20 wt %). At 20 wt %, water, the main detected rhodium species is **1a**[6] (δ_{CO} = 182.8 ppm and $^1J_{CO-Rh}$ = 69.5 Hz), which is consistent with the rds being the oxidative addition of MeI. When the water content is decreased to 10 wt %, new signals appear which are assigned to the acetyl species **4a** (δ_{CO} = 177.8 ppm and $^1J_{CO-Rh}$ = 54.6 Hz; δ_{COMe} = 216.9 ppm and $^1J_{MeCO-Rh}$ = 18.2 Hz). When the water content is reduced further to 5 wt %, the sole rhodium carbonyl species detected is **4a**. This buildup of a steady-state content of this acetyl rhodium species with the complete disappearance of **1a** points to a shift of the rds as the RE from **4a**. These experimental observations could be interpreted as a direct involvement of water in the last step. Because hydrolysis of acetyl iodide is very fast, its classically proposed RE should be independent of the water concentration. Thus, solvolysis of **4a** (Scheme 1, path II) seems more probable than the direct RE of CH_3COI. However, because different amounts of water should generate different concentrations of acetate anion (arising from AcOH dissociation; see SI.3), its possible role in the RE step must also be considered. The RE from **4a** was followed by FT-IR in CH_2Cl_2 at 298 K under 5 bar of CO in the presence and absence of water (see SI.4). In fact, the reaction operates slowly, independent of the water concentration. However, with 1 equiv of butylmethylimidazolium acetate under anhydrous conditions, the RE is immediate. Similarly, Maitlis et al. have shown that tetrabutylammonium acetate reacts immediately with **4a** to give **1a** and acetic anhydride.[4] Because these results are not consistent with either the direct RE of CH_3COI or solvolysis of **4**, density functional theory calculations, B3PW91 [Rh:SDD+f,I:SDD+d, CHO:6-31G(d,p)], were performed to investigate the reactivity of **4** under various conditions (see SI.5).

Initial computational studies probed the mechanism for the RE of CH_3COI from **4** (see SI.6). It can involve either *mer,trans*-**4a** or its isomer *fac,cis*-**4b**. An endergonic pathway with a Gibbs free energy of +8 kcal·mol^{-1} is obtained for **4a** and a slightly exergonic pathway for **4b** (−1 kcal·mol^{-1}). The corresponding energy barriers are both 26 kcal·mol^{-1}, which agree well with previous calculations reported by Kinnunen and Laasonen (25 kcal·mol^{-1} for **4a** and 23 kcal·mol^{-1} for **4b**).[7] The two proposed mechanisms for RE from **4b** and **4a** are different. The pathway from **4b** is a straightforward intramolecular reaction involving the addition to the $-COCH_3$ group of an adjacent iodide, whereas **4a** requires a two-step process. Decoordination of the iodide trans to $-COCH_3$ occurs first, followed by the attack of I^- at the acetyl carbon. In both cases, CH_3COI is formed. Because these pathways are thermodynamically endergonic for **4a** and slightly exergonic or at best thermoneutral, according to the precision of the calculations, for **4b**, the possible involvement of water was investigated. Its direct attack on the acetyl group has been calculated. The reaction is exergonic by 5 kcal·mol^{-1} but possesses an energy barrier of 44 kcal·mol^{-1}, making it kinetically unlikely (see SI.7). Instead, the observed impact of the water content on the rate of RE from **4a** is most likely due to the change in the acetate anion concentration as a function of the water content in an AcOH medium. This statement is consistent with the experimental observation described above. Consequently, the direct attack of AcO^- on the acetyl group of **4a** must be considered as a probable pathway for the RE (path III). Although it is found to be highly exergonic (see SI.8, 36 kcal·mol^{-1}), the energy barrier is far too high to be competitive (56 kcal·mol^{-1}). Therefore, an alternative pathway that involves an indirect acetate-mediated reaction appears to be more probable (path IV). This mechanism involves the replacement of an iodo ligand on **4** by OAc^- to form $[RhI_2(COCH_3)(AcO)(CO)_2]^-$ (**5**: Figure 1). This species forms acetic anhydride upon RE that rapidly hydrolyzes to produce two AcOH molecules.

There are three possible complexes that can form by substitution of I^- with AcO^- on **4** to obtain an acetate ligand cis to the acetyl group without the highly endergonic replacement of a CO. The reaction of AcO^- with **4a** affords two possible rhodium carbonyl complexes. The first one, **5a**, conserves two iodide ligands trans to each other, with one CO moving trans to the acetyl ligand. The second complex, **5b**, preserves the two CO ligands trans to each other with no other ligand rearrangement. The reaction of AcO^- with **4b** affords only structure **5c**, in which the I^- and CO ligand geometry relative to the acetyl ligand remains unchanged. For all of these cases, the replacement of I^- by AcO^- leads to stabilization of **5a**, **5b**, and **5c** by −14, −24, and −31 kcal·mol^{-1}, respectively.

The comparative difference of these results for **5a**–**5c** can be explained primarily by a closer analysis of their geometries. Specifically the predominant factor that impacts the stabilization energy of **5** is the ligand type trans to the acetyl ligand (Figure 1). As expected, an iodide trans to the acetyl ligand stabilizes **5b** and **5c** by strengthening the Rh–C bond of the acetyl group (push–pull effect). On the other hand, **5a** is less stable because of the presence of two donor ligands trans to each other. Even though the three proposed isomers **5a**–**5c** produce a molecule of acetic anhydride and **1**, the three corresponding transition states of **5** lead to different energy barriers. As was previously observed for **5**, the nature of the ligand trans to the acetyl one of the TS complexes primarily impacts the relative energy barriers to form acetic anhydride. The calculated energy barriers of 14, 23, and 18 kcal·mol^{-1} for TS_A, TS_B, and TS_C, respectively, are consistent with kinetically facile reactions.

Although TS_A is the least stable structure, it leads to the lowest energy barrier because a CO ligand trans to the acetyl affords a weaker acetyl Rh–C bond because of π-back-bonding on CO. TS_B leads to the highest energy barrier (23 kcal·mol^{-1}). Indeed, at TS_B, the anhydride moiety is already formed and the $-COCH_3$ and $-OC(CH_3)O$ groups are loosely interacting with the Rh center (2.26 and 2.73 Å for Rh–O and Rh–C bonds, respectively). Both TS_A and TS_C exhibit short Rh–O bonds (2.15 Å). In addition, the Rh–C bond lengthens from 2.05 to 2.57–2.50 Å for **5a**/**5c** and TS_A/TS_C, respectively. The two transition states TS_A and TS_C are thus better prepared from **5a** and **5c** in line with a lower energy barrier. Finally, the formation of **1a** and acetic anhydride is more favorable than

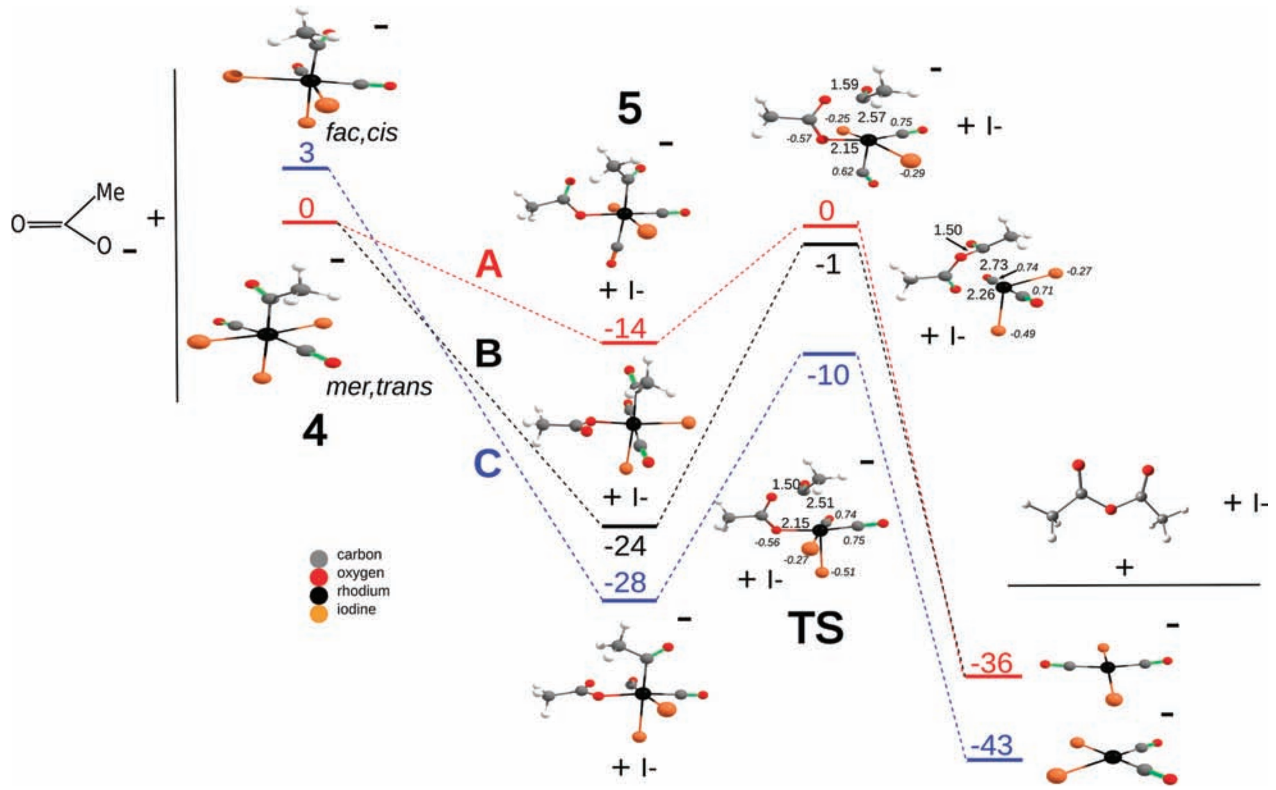

Figure 1. Gibbs free-energy pathways computed for the acetate-mediated reductive elimination (kcal·mol^{-1}).

that of acetic anhydride and *trans*-[$RhI_2(CO)_2$]$^-$ (**1b**) by 7 kcal·mol^{-1}. From the three possible pathways for the RE, A and C can be retained as the most probable mechanistic routes because of their lower energy barriers compared to pathway B. Furthermore, pathway C is far more exergonic than A, thus making it the most feasible way to obtain acetic anhydride.

In conclusion, the present experimental and theoretical studies support a new alternative acetate-mediated mechanism, for the reductive elimination step of rhodium-catalyzed methanol as well as methyl acetate carbonylation reactions. This proposed mechanism proceeds stepwise: substitution of an iodo ligand by an acetate anion on the rhodium acetylcarbonyl complex followed by reductive elimination of acetic anhydride, which is immediately hydrolyzed to AcOH. This result contrasts with the classically proposed mechanism that involves the direct reductive elimination of CH_3COI followed by its hydrolysis or the direct solvolysis of the acetyl ligand of the rhodium complex.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, characterization data, kinetic and conductivity measurements, and computational details (Figures SI.1−SI.9). This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) (a) Torrence, P. In *Applied Homogeneous Catalysis with Organometallic Compounds*, 2nd ed.; Cornils, B., Herrmann, W. A., Eds.; Wiley-VCH: Weinheim, Germany, 2002; pp 104−136. (b) Haynes, A. In *Topics in Organometallic Chemistry*; Beller, M., Ed.; Springer-Verlag: Berlin, 2006; pp 179−205. (c) Haynes, A. *Adv. Catal.* **2010**, *53*, 1−45.

(2) (a) Forster, D. *J. Am. Chem. Soc.* **1976**, *98*, 846−848. (b) Adams, H.; Baily, N. A.; Mann, B. E.; Manuel, C. P.; Spencer, C. M.; Kent, A. G. J. *J. Chem. Soc., Dalton Trans.* **1988**, 489−496.

(3) Jones, J. H. *Platinum Met. Rev.* **2000**, *44*, 94−105.

(4) Maitlis, P. M.; Haynes, A.; Sunley, G. J.; Howard, M. J. *J. Chem. Soc., Dalton Trans.* **1996**, 2187−2196.

(5) Morris, G. In *Mechanism in Homogeneous Catalysis. A Spectroscopic Approach*; Heaton, B., Ed.; Wiley-VCH Verlag: Weinheim, Germany, 2005; pp 195−230.

(6) Merbach, A. E.; et al. *Inorg. Chem.* **2000**, *39*, 304−307, . It was observed by ^{13}C NMR that the CO ligands of [$RhI_2(CO)_2$]$^-$ exchange quickly with ^{13}CO dissolved in CD_2Cl_2 at 363 K, resulting only in a broad single signal. In the present solvent/reactant system (MeOAc, CH_3COOH, CH_3I, and H_2O), the exchange rate becomes slower so that we observed separate signals for dissolved ^{13}CO and **1a**. The signal at ca. 186 ppm could be assigned to [$RhI_2(CO)_3$]$^-$.

(7) Kinnunen, T.; Laasonen, K. *J. Organomet. Chem.* **2001**, *628*, 222−232.