

Oxidative carbonylation of toluene to *p*-toluic acid catalyzed by rhodium in the presence of vanadium and oxygen

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Received 3 May 2007; received in revised form 13 June 2007; accepted 14 June 2007

Available online 19 June 2007

Abstract

The mechanism and kinetics of the liquid phase, oxidative carbonylation of toluene to toluic acid were investigated. The catalyst system consisted of $\text{Rh}(\text{acac})_3$, NH_4VO_3 , trifluoroacetic acid (TFAH), and trifluoroacetic anhydride (TFAA). Liquid toluene together with gaseous CO and O_2 was used as the reactant. The effects of temperature, the partial pressures of O_2 and CO, the concentrations of TFAH and TFAA, the concentrations of $\text{Rh}(\text{acac})_3$ and NH_4VO_3 , and time on the activity and selectivity of the catalyst for forming *p*-toluic acid were investigated. The conversion of toluene to toluic acid increased with temperature but the *p/m* and *p/o* isomer ratios decreased. A conversion maximum occurred with CO partial pressure, and conversion increased monotonically with O_2 . The conversion of toluene to toluic acid increased with time. Under optimal conditions, 700 mole of toluic acid were produced per mole of Rh in 4 h. During the course of reaction, Rh(III) is reduced to Rh(I). The latter species is reoxidized by reaction with V(V) in the form of VO_2^+ . The V(IV) produced in this process is then reoxidized by O_2 . The concentration of water, produced during the reoxidation of Rh(I) to Rh(III), in the reaction system must be controlled by reaction with TFAA, since the accumulation of excess water can lead to the generation of H_2 via the water-gas-shift reaction leading to a reduction of Rh(III) to Rh(I). A mechanism for the overall catalytic process is proposed and discussed.

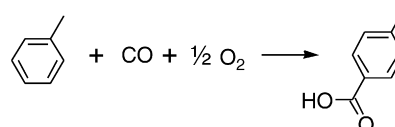
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Keywords: Toluene; Toluic acid; Oxidative carbonylation; Rhodium; Vanadium

1. Introduction

Toluic acid is an intermediate in the manufacture of terephthalic acid, a compound used to produce polyethylene terephthalate (PET) via condensation polymerization with ethylene glycol [1]. The current approach for producing terephthalic acid is the oxidation of *p*-xylene, in the course of which *p*-toluic acid is formed as an intermediate [2]. Given the availability and lower cost of toluene as compared to *p*-xylene, the direct oxidative carbonylation of toluene to form *p*-toluic acid represents an attractive opportunity for reducing the cost of producing terephthalic acid.

Several studies have demonstrated that *p*-toluic acid can be produced by the oxidative carbonylation of toluene:



Fujiwara and coworkers have reported evidence for the oxidative carbonylation of toluene and other arenes using palladium acetate in the presence of trifluoroacetic acid (TFAH) and its anhydride (TFAA) [3–5]. In subsequent studies, Kalinovskii and coworkers have shown that the oxidative carbonylation of arenes can also be catalyzed using rhodium(III) or palladium(II) cations [6–9], and they have proposed a mechanism for the synthesis of toluic acid from toluene [9]. Since Rh(III) is reduced to Rh(I) and Pd(II) is reduced to Pd(0) in the course of the reaction, it was necessary to provide a means for reoxidizing the reduced metal. In the case of Pd, this could be done effectively using Cu(II) cations together with O_2 in a Wacker-type process [6]. FeC_2O_4 , $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$, $(\text{NH}_4)\text{VO}_3$, and V_2O_5 in combination with O_2 were also shown to work effectively as oxidants for both Pd and Rh [7]. The reoxidation of Pd could also be achieved using MnO_2 but in the absence of O_2 [8]. While Pd was found to be more

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active than Rh, the selectivity to *p*-toluic acid was highest for Rh. More recently, Grushin et al. have demonstrated that toluic acid could be produced using [(acac)Rh(CO)₂] in TFAH by first oxidizing rhodium thoroughly with hydrogen peroxide and then conducting the oxidative carbonylation of toluene in the presence of K₂S₂O₈ [10]. About 35–100 mole of toluic acid per mole of Rh could be produced by this means in 16 h. This catalyst system was tolerant to small quantities of water but was poisoned by chloride anions, and the addition of trifluoroacetic anhydride was found to reduce the activity of the catalyst [10,11]. The reoxidation of Rh(I) to Rh(III) was hypothesized to be the rate-limiting step and it was observed that the rate of reaction per Rh atom decreased with increasing Rh concentration, due presumably to the formation of a stable but catalytically inactive [Rh₂(TFA)₄] species [10,11]. Grushin and Thorn also found iridium to be an active catalyst for the oxidative carbonylation of toluene [12]. The use of formic acid instead of CO has also been reported. In this case palladium was used as the catalyst, and a 89% conversion of toluene to toluic acid with an *o*:*m*:*p* = 18:31:51 distribution of toluic acid isomers was observed [13].

The aim of this investigation was to identify the effects of reaction conditions on the oxidative carbonylation of toluene to toluic acid using Rh as the catalyst and NH₄VO₃/O₂ as the oxidant. Rh was chosen over Pd as the catalyst because of its higher selectivity to *p*-toluic acid and NH₄VO₃/O₂ was chosen for reoxidation of the catalyst because of its demonstrated effectiveness [6]. Additional components of the reaction system were trifluoroacetic acid (TFAH) and trifluoroacetic anhydride (TFAA). The influence of the concentration of each component of the catalyst system and of the partial pressures of carbon monoxide and oxygen were examined with the aim of determining more clearly the role of each component and its effect on the activity of Rh for the oxidative carbonylation of toluene and its selectivity for producing *p*-toluic acid.

2. Experimental

Reactions were conducted in a stirred, 50 mL Parr autoclave made of Hastelloy C. Between runs, 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), 1.48 g of (CF₃CO)₂O (≥99%, Aldrich), 0.0039 g of Rh(acac)₃ (97%, 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. 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. The aqueous phase was decanted and analyzed by UV–vis spectroscopy in order to determine the oxidation state of the dissolved vanadium. To remove any residual trifluoroacetic acid from the organic phase it was extracted with approximately 5 g deionized H₂O. 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.

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. Unknown peaks were identified by GC/MS. A sample of the head-space gas was collected and analyzed for O₂, CO, and CO₂ by gas chromatography. An Alltech Hayesep DB 100/120 column was used to separate the gaseous products, which were detected by a TCD. Each reaction was repeated between one and three times. The solid lines shown in all figures represent the average over all replicas.

The oxidation state of vanadium in the aqueous phase extracted from the reaction mixture was determined by UV–vis spectroscopy. A peak at 760 nm attributed to VO²⁺ was used to determine the amount of V(IV) present in solution. The extinction coefficient associated with this absorbance was determined by reference to a standard solution of VO(acac)₂.

To test for the isomerization of *p*- or *m*-toluic acid, 0.3507 g of *p*-toluic acid (98% Aldrich) or *m*-toluic acid (99%, Aldrich), 0.0038 g Rh(acac)₃, and 0.0595 g NH₄VO₃ were dissolved in 2.99 g CF₃COOH and 2.97 g (CF₃CO)₂O. The solution was heated in the autoclave using standard procedures. After cooling, 3.45 g of toluene was added to the solution followed by 12.64 g of deionized water. The sample was inverted 20 times, and after phase separation, the organic phase was analyzed by GC.

3. Results and discussion

3.1. Scoping experiments

Figs. 1(A) and 2(A) show that the total yield of toluic acid and the distribution among the three isomers is independent of the oxidation state of Rh and the composition of the ligands associated with the original complex. For these experiments, the moles of Rh present as Rh(acac)₃ and [Rh(CO)₂Cl]₂ were kept constant at 10 μmol, as was the V/Rh ratio at 51. For both sources of Rh, approximately 350 turnovers were achieved in 4 h. Fig. 1 also demonstrates that both NH₄VO₃ and O₂ must be present in order to achieve high conversion. Only a trace amount of toluic acid is formed if neither NH₄VO₃ and O₂ is used and Rh is initially in the trivalent state, but no products are observed if Rh is introduced as Rh(I). A small amount of toluic acid is produced if O₂ is present alone, but much less product is formed if NH₄VO₃ is used as the sole oxidant. It was also observed that a small amount of toluic acid could be formed in the absence

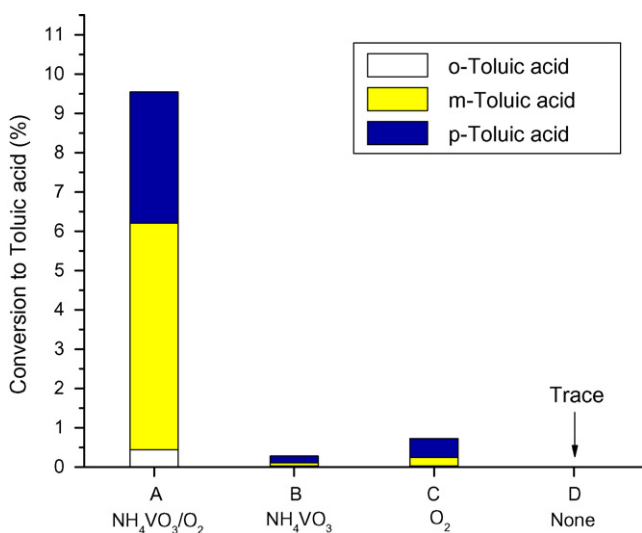


Fig. 1. Conversion of toluene to toluic acid catalyzed by Rh(acac)₃. Reaction conditions: 37.5 mmol toluene (3.46 g); 13.0 mmol CF₃COOH (1.48 g); 7.05 mmol (CF₃CO)₂O (1.48 g); P_{CO} = 1.207 MPa; t = 4 h; T = 398 K. Oxidizing agents: 0.5163 mmol NH₄VO₃ (0.0604 g); P_{O₂} = 0.345 MPa. Rhodium content: 10 μmol Rh(acac)₃ (0.0039 g).

of Rh but in the presence of O₂. Taken together, these results demonstrate that Rh is active as Rh(III) but undergoes reduction to Rh(I) during the course of reaction and must be reoxidized, and that this process occurs most effectively in the presence of NH₄VO₃ and O₂. These findings are in agreement with those reported earlier by Kalinovskii et al. [6].

3.2. Temperature

The influence of temperature on catalyst activity and selectivity was investigated. In nearly all the reactions, the *para* and *meta* isomers were the only products formed in significant

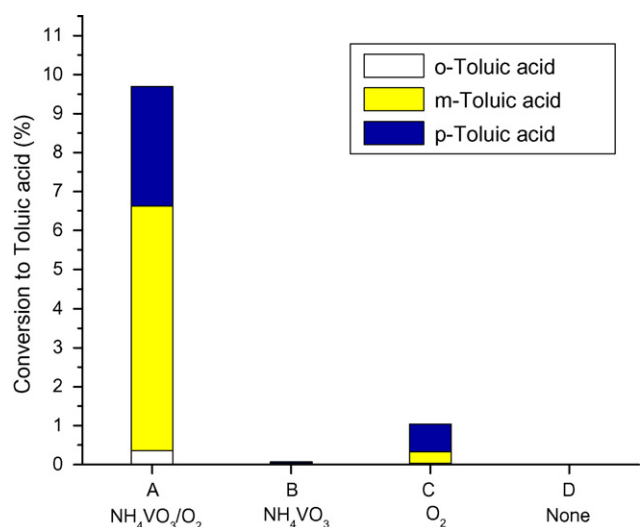


Fig. 2. Conversion of toluene to toluic acid [Rh(CO)₂Cl]₂. Reaction conditions: 37.5 mmol toluene (3.46 g); 13.0 mmol CF₃COOH (1.48 g); 7.05 mmol (CF₃CO)₂O (1.48 g); P_{CO} = 1.207 MPa; t = 4 h; T = 398 K. Oxidizing agents: 0.5163 mmol NH₄VO₃ (0.0604 g); P_{O₂} = 0.345 MPa. Rhodium content: 5 μmol [Rh(CO)₂Cl]₂ (0.0021 g) (10 μmol Rh).

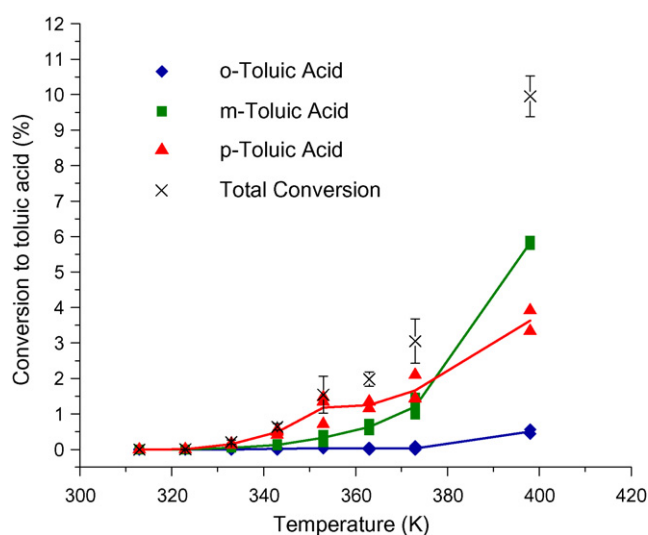


Fig. 3. Effect of temperature on conversion. Reaction conditions: 37.5 mmol toluene (3.46 g); 13.0 mmol CF₃COOH (1.48 g); 7.05 mmol (CF₃CO)₂O (1.48 g); 10 μmol Rh(acac)₃ (0.0039 g); 0.5163 mmol NH₄VO₃ (0.0604 g); P_{CO} = 1.207 MPa; P_{O₂} = 0.345 MPa; t = 4 h.

concentration. The *ortho* isomer was observed at temperatures exceeding 333 K but in significantly smaller quantities compared to the other isomers. As illustrated by Fig. 3, the conversion of toluene to all isomers of toluic acid increased monotonically with increasing temperature, whereas Fig. 4 shows that the *p/o* and *p/m* isomer ratio decreased with increasing temperature. The latter trend indicates that the activation energies for the formation of *o*-toluic acid and *m*-toluic acid are higher than that for the formation of *p*-toluic acid. A significant amount of arene coupling to form 1-methyl-2-(phenylmethyl) benzene and isomers of this product was observed at temperatures above 373 K, and a dark brown solid was also produced. To avoid the formation of these by-products and to obtain higher *p/m* isomer ratios of toluic acid, all subsequent reactions were carried out at 353 K.

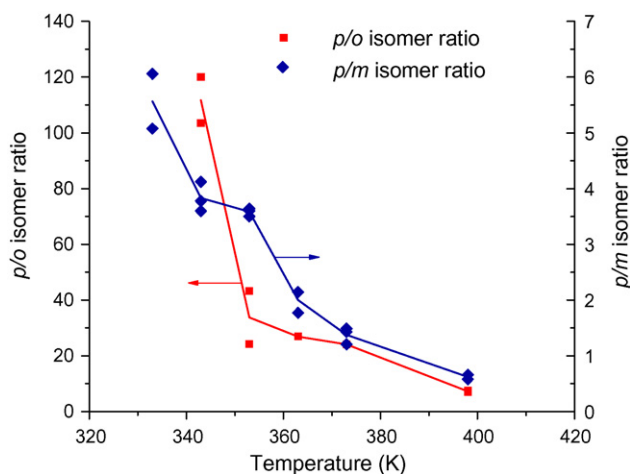


Fig. 4. Effect of temperature on the *p/m* and *p/o* ratio of toluic acid isomers. Reaction conditions: 37.5 mmol toluene (3.46 g); 13.0 mmol CF₃COOH (1.48 g); 7.05 mmol (CF₃CO)₂O (1.48 g); 10 μmol Rh(acac)₃ (0.0039 g); 0.5163 mmol NH₄VO₃ (0.0604 g); P_{CO} = 1.207 MPa; P_{O₂} = 0.345 MPa; t = 4 h.

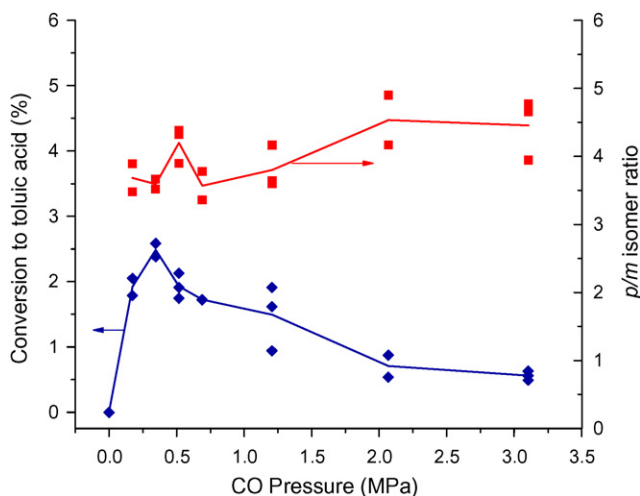


Fig. 5. Effect of carbon monoxide partial pressure on the conversion of toluene and the ratio of *p/m* isomers of toluic acid. Reaction conditions: 37.5 mmol toluene (3.46 g); 13.0 mmol CF_3COOH (1.48 g); 7.05 mmol $(\text{CF}_3\text{CO})_2\text{O}$ (1.48 g); 10 μmol $\text{Rh}(\text{acac})_3$ (0.0039 g); 0.5163 mmol NH_4VO_3 (0.0604 g); $P_{\text{O}_2} = 0.345$ MPa; $T = 353$ K; $t = 4$ h.

3.3. CO and O_2 partial pressures

The partial pressures of the carbon monoxide and the oxygen were varied to determine their influence on the formation of toluic acid and the *p/m* isomer ratio. Fig. 5 shows that no toluic acid is formed in the absence of CO, and that the yield of toluic acid increases up to a maximum at 0.345 MPa, after which the yield declines monotonically. Over the range of CO partial pressures investigated, the *p/m* isomer ratio increased only slightly. These results suggest that at CO partial pressures below 0.345 MPa the solubility of CO may be insufficient to drive the reaction, whereas at higher CO partial pressures CO may contribute to the reduction of Rh(III) to Rh(I).

Oxygen partial pressure was also varied but kept below 0.517 MPa to minimize risk of explosion. In accordance with the scoping experiments, a small quantity of toluic acid product was obtained at 0 MPa and, as shown in Fig. 6, the yield of toluic acid increased monotonically with increasing O_2 partial pressure. Unexpectedly, though, the *p/m* isomer ratio decreased with increasing O_2 partial pressure. The effect of O_2 partial pressure on the yield of toluic acid suggests that the re-oxidation of Rh(I) to Rh(III) is rate limiting, rather than C–H bond activation in agreement with findings of Kalinovskii et al. [6]. Moreover, spectroscopic evidence discussed below suggest that while the oxidation of Rh(I) by VO_x species in solution is rapid, the re-oxidation of the resulting VO_{x-1} species by O_2 is slow.

3.4. Reaction time

The conversion of toluene and the ratio of *p*- to *m*-toluic acid were monitored as a function of reaction time. As seen in Fig. 7, the conversion of toluene to toluic acid increased, but the *p/m* isomer ratio tended to decrease with time. The decrease in the *p/m* isomer ratio is attributed to the time at which the autoclave is at reaction temperature relative to the initial ramp time. As

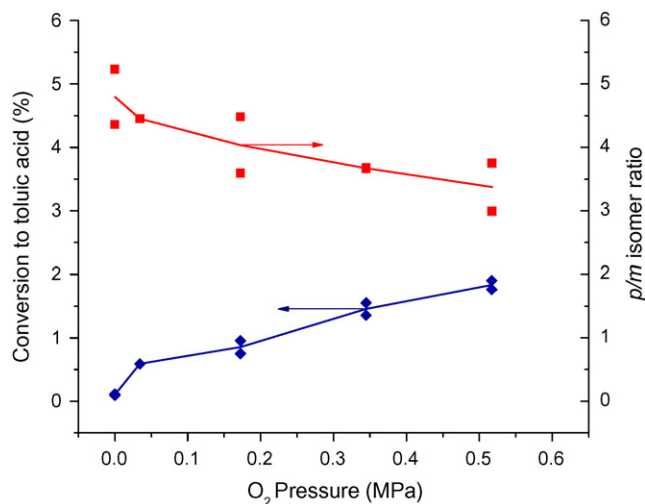


Fig. 6. Effect of oxygen partial pressure on the conversion of toluene and the ratio of *p/m* isomers of toluic acid. Reaction conditions: 37.5 mmol toluene (3.46 g); 13.0 mmol CF_3COOH (1.48 g); 7.05 mmol $(\text{CF}_3\text{CO})_2\text{O}$ (1.48 g); 10 μmol $\text{Rh}(\text{acac})_3$ (0.0039 g); 0.5163 mmol NH_4VO_3 (0.0604 g); $P_{\text{CO}} = 0.345$ MPa; $T = 353$ K; $t = 4$ h.

shown in Fig. 4, higher *p/m* ratios were observed at lower temperatures, so in reactions with a long ramp time relative to run time, the relative lower temperature favored *p*-toluic acid formation. To test for the possibility of isomerization from *p*- to *m*-toluic acid, reactions were carried out starting with *m*-toluic acid or *p*-toluic acid, but without toluene. Analysis of the products formed during the reaction of *p*-toluic acid showed evidence for a very small amount of *m*-toluic resulting in a *p/m* isomer ratio of approximately 42. Additional peaks were observed for products formed by toluic acid coupling. It was also observed that *m*-toluic acid did not undergo isomerization. Therefore, it is concluded that product isomerization is not responsible for the change in the *p/m* ratio with reaction time seen in Fig. 7.

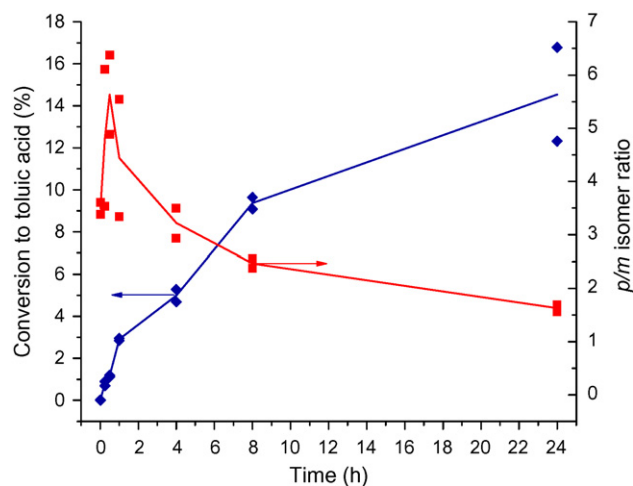


Fig. 7. The conversion of toluene and the ratio of *p/m* isomers of toluic acid vs. time. Reaction conditions: 37.5 mmol toluene (3.46 g); 13.0 mmol CF_3COOH (1.48 g); 7.05 mmol $(\text{CF}_3\text{CO})_2\text{O}$ (1.48 g); 10 μmol $\text{Rh}(\text{acac})_3$ (0.0039 g); 0.5163 mmol NH_4VO_3 (0.0604 g); $P_{\text{CO}} = 0.345$ MPa; $P_{\text{O}_2} = 0.345$ MPa; $T = 353$ K.

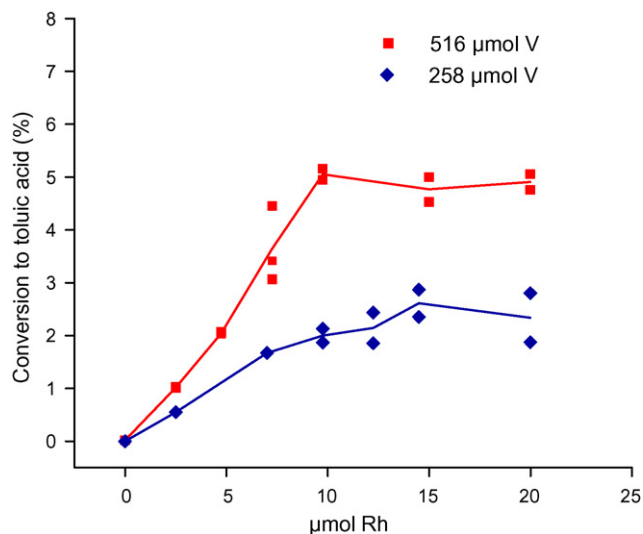


Fig. 8. Effect of rhodium loading on toluene conversion to toluic acid. Reaction conditions: 37.5 mmol toluene (3.46 g); 13.0 mmol CF_3COOH (1.48 g); 3.53 mmol $(\text{CF}_3\text{CO})_2\text{O}$ (0.75 g); 0.5163 mmol NH_4VO_3 (0.0604 g); $P_{\text{CO}}=0.345$ MPa; $P_{\text{O}_2}=0.345$ MPa; $T=353$ K; $t=4$ h.

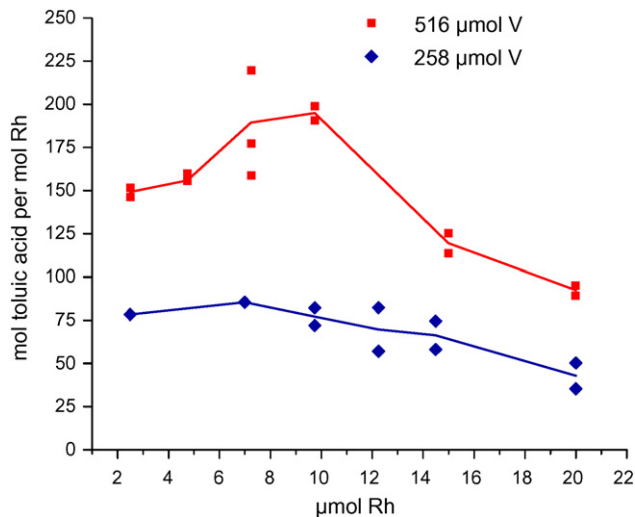


Fig. 9. Effect of rhodium loading on rhodium activity. Reaction conditions: 37.5 mmol toluene (3.46 g); 13.0 mmol CF_3COOH (1.48 g); 3.53 mmol $(\text{CF}_3\text{CO})_2\text{O}$ (0.75 g); 0.5163 mmol NH_4VO_3 (0.0604 g); $P_{\text{CO}}=0.345$ MPa; $P_{\text{O}_2}=0.345$ MPa; $T=353$ K; $t=4$ h.

3.5. Rh and NH_4VO_3 loading

The effect of Rh loading on the yield of toluic acid at high and low vanadium loadings is illustrated in Fig. 8. For Rh loadings below 10 μmol , the yield of toluic acid increases nearly linearly with Rh loading. However, at higher Rh loadings, the yield of toluic acid becomes independent of Rh loading. These results suggest that for loadings below 10 μmol , the oxidizing potential of the reaction mixture is sufficiently high and, therefore, the rate of reaction is limited by the amount of Rh in solution. However, for Rh loadings above 10 μmol , the rate of reoxidation becomes inversely dependent on the Rh loading because more and more of the vanadium is present as V(IV) than V(V). Increasing the vanadium content from 258 μmol V to 516 μmol V resulted in increased activity because more vanadium was present to re-oxidize the Rh. Fig. 9 shows the number of moles of toluic acid formed per mole of Rh present initially in the system. Below 10 μmol Rh, the TON increased slightly with increasing Rh loading; however, beyond 10 μmol Rh, the TON decreased, presumably because the amount of vanadium in the system was insufficient to fully oxidize Rh(I) back to Rh(III). Consistent with this interpretation, the TON was found to increase with the amount of V added to the system for a fixed amount of Rh.

The effect of NH_4VO_3 loading was also investigated. In this case the Rh loading was held constant at 10 μmol . As seen in Fig. 10, the moles of toluic acid formed per mole of Rh in the system increased nearly linearly as the loading of NH_4VO_3 was increased. These results confirm that NH_4VO_3 is essential for the reoxidation of Rh(I) to Rh(III). Moreover, if the ratio of NH_4VO_3 to Rh is too low, then the rate of Rh(I) reoxidation may limit the overall kinetics of toluene conversion to toluic acid (see Fig. 8). Fig. 10 also shows that the moles of toluic acid formed per mole of V added to the system decreases from ~ 6 to ~ 3 as the amount of V added to the system is increased.

The reoxidation of Rh(I) is hypothesized to occur via the reaction process $2\text{VO}_2(\text{TFA}) + \text{Rh}(\text{CO})_2(\text{TFA}) + 4\text{TFAH} \rightarrow 2\text{VO}(\text{TFA})_2 + \text{Rh}(\text{CO})_2(\text{TFA})_3 + 2\text{H}_2\text{O}$. The oxidant for this reaction, $\text{VO}_2(\text{TFA})$, is thought to be formed by the reaction of NH_4VO_3 with TFAH, i.e., $\text{NH}_4\text{VO}_3 + \text{TFAH} \rightarrow \text{VO}_2(\text{TFA}) + \text{NH}_3 + \text{H}_2\text{O}$. Evidence for the presence of VO_2^+ and VO^{2+} cations was obtained from UV–vis spectroscopy. As illustrated in Fig. 11, a solution consisting of NH_4VO_3 in water with TFAH, absorbed strongly in the ultraviolet region but showed no peaks from 900 nm to around 500 nm. The absence of peaks in the visible portion of the spectrum was expected since V(V) has no d electrons to participate in d-to-d transitions. On the other hand, an aqueous solution of $\text{VO}(\text{acac})_2$ containing TFAH absorbed strongly in the UV and at 760 nm. The absorption coefficient for the latter band is $13.53 \text{ L mol}^{-1} \text{ cm}^{-1}$. UV–vis

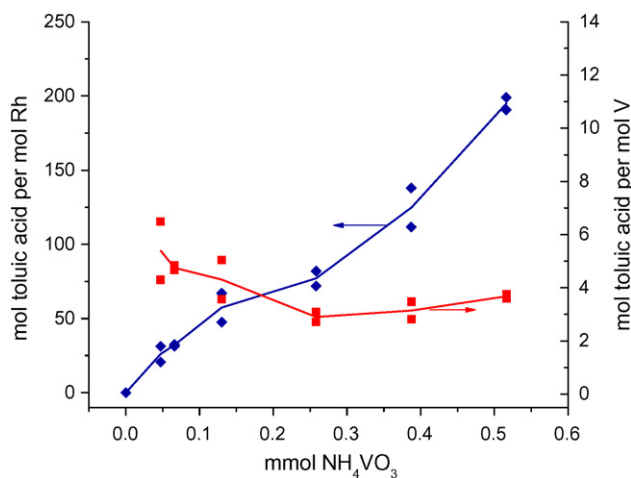


Fig. 10. Effect of vanadium loading on the activity of rhodium and vanadium. Reaction conditions: 37.5 mmol toluene (3.46 g); 13.0 mmol CF_3COOH (1.48 g); 3.53 mmol $(\text{CF}_3\text{CO})_2\text{O}$ (0.75 g); 10 μmol $\text{Rh}(\text{acac})_3$ (0.0039 g); $P_{\text{CO}}=0.345$ MPa; $P_{\text{O}_2}=0.345$ MPa; $T=353$ K; $t=4$ h.

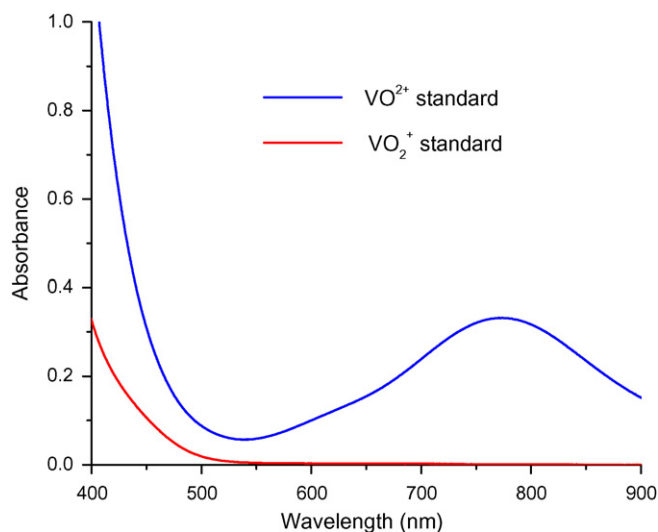


Fig. 11. UV-vis spectrum of vanadium standards in water. VO_2^{2+} standard: 87.49 μmol $\text{VO}(\text{acac})_2$ (0.0232 g); 0.8333 mol deionized H_2O (15.0082 g); 8.9309 mmol CF_3COOH (1.0183 g). VO_2^+ standard: 0.28 mmol NH_4VO_3 (0.0328 g); 0.8347 mol deionized H_2O (15.0337 g); 9.3746 mmol CF_3COOH (1.0689 g). Background: deionized H_2O .

spectroscopy was used to observe the reduction of VO_2^+ to VO^{2+} during oxidation of Rh(I) to Rh(III). The appearance of a small peak at 760 nm in the solution in which $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ was added to NH_4VO_3 indicated the reduction of V(V) to V(IV), while no peak was observed without the addition of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (see Fig. 12). The peak at 760 nm in the first solution indicated a VO^{2+} concentration of 5.0 mM. Complete oxidation of Rh(I) to Rh(III) was expected to yield a VO^{2+} concentration of 4.0 mM based on the measured quantity of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ added. The discrepancy between these numbers is due possibly to experi-

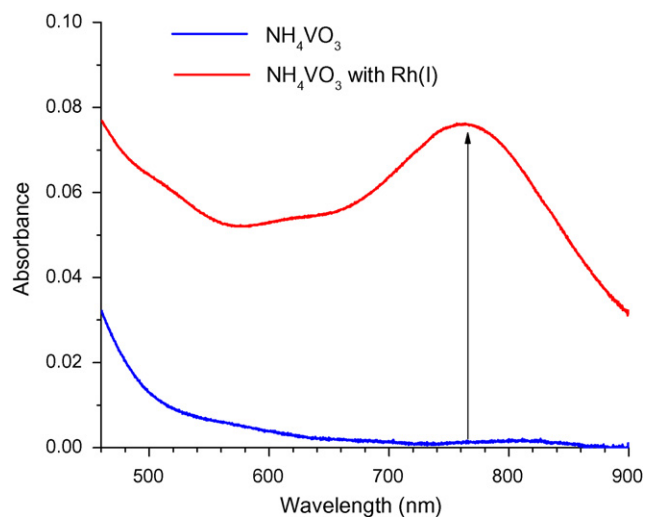


Fig. 12. UV-vis spectrum of Rh(I) reduction of VO_2^+ to VO^{2+} . (a) NH_4VO_3 : [0.0116 g NH_4VO_3 ; 0.5758 g CF_3COOH ; 0.5880 g $(\text{CF}_3\text{CO})_2\text{O}$; 12.4092 g deionized H_2O . Background: deionized H_2O]. (b) NH_4VO_3 with Rh(I): [0.0302 g NH_4VO_3 ; 1.4939 g CF_3COOH ; 1.4996 g $(\text{CF}_3\text{CO})_2\text{O}$; 0.0053 g $[\text{Rh}(\text{I})(\text{CO})_2\text{Cl}]_2$; 11.7915 g deionized H_2O]. Background: [0.0053 g $[\text{Rh}(\text{CO})_2\text{Cl}]_2$; 1.5035 g CF_3COOH ; 1.5040 g $(\text{CF}_3\text{CO})_2\text{O}$; 12.0359 g deionized H_2O].

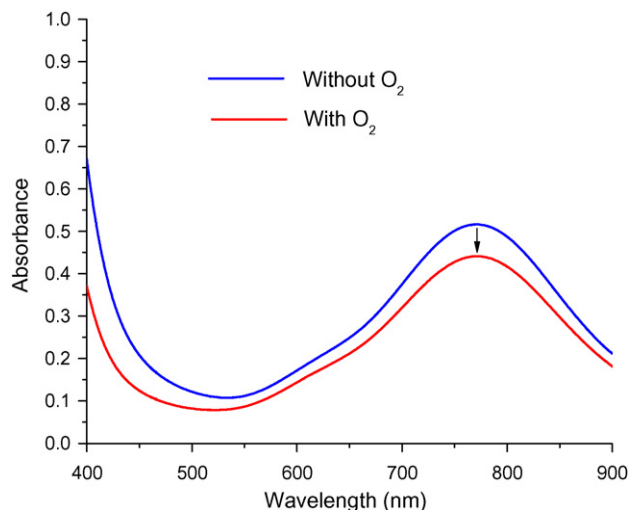


Fig. 13. UV-vis spectrum illustrating the oxidation of VO^{2+} to VO_2^+ . (a) 0.1603 mmol $\text{VO}(\text{acac})_2$ (0.0425 g); 4.6386 mmol CF_3COOH (0.5289 g); $P_{\text{O}_2} = 0.689$ MPa; $T = 323$ K; $t = 4$ h. (b) 0.1603 mmol $\text{VO}(\text{acac})_2$ (0.0425 g); 4.6386 mmol CF_3COOH (1.0578 g); 0.4185 mol deionized H_2O (7.5378 g); $T = 323$ K; $t = 4$ h. Background: deionized H_2O .

mental error. Nevertheless, these results indicate that Rh(I) is oxidized stoichiometrically by V(V) to Rh(III). The oxidation of Rh(I) is rapid since the reaction occurred entirely in the time required to heat the autoclave to 353 K and then cool it to 298 K, about 30 min. By contrast, the oxidation of VO^{2+} to VO_2^+ was slow, as shown by the results presented in Fig. 13. After 4 h of heating at 323 K, only a small fraction, 15%, of VO^{2+} had reacted to VO_2^+ . This process is thought to occur via the reaction $2\text{VO}(\text{TFA})_2 + \text{H}_2\text{O} + 1/2\text{O}_2 \rightarrow 2\text{VO}_2(\text{TFA}) + 2\text{TFAH}$. The role of water in this reaction was confirmed. When the concentration of water in the reaction mixture was reduced significantly by adding excess anhydride the yield of toluic acid decreased dramatically from 2.25 mmol to 0.75 mmol.

Interestingly an excess of H_2O also proved detrimental to the reaction. While the reaction $2\text{VO}(\text{TFA})_2 + 1/2\text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{VO}_2(\text{TFA}) + 2\text{TFAH}$ requires water to proceed, excess H_2O can react with the CO to produce H_2 via the water-gas-shift reaction and, in fact, addition of 0.01 MPa of H_2 to the autoclave resulted in the nearly complete cessation of the oxidative carbonylation of toluene, very likely as a consequence of the reduction of Rh(III) to Rh(I) by the reaction $\text{Rh}(\text{CO})_2(\text{TFA})_3 + \text{H}_2 \rightarrow \text{Rh}(\text{TFA})(\text{CO})_2 + 2\text{TFAH}$.

UV-vis spectra were also taken of solutions immediately after reaction in order to estimate the fraction of V present as VO^{2+} during reaction. As seen in Fig. 14, 94% of the V is present as VO^{2+} when no O_2 is added to the autoclave, but the percentage of VO^{2+} decreased to 67% when the reaction was carried out in the presence of 0.345 MPa of O_2 .

3.6. TFAH and TFAA loadings

The effect of TFAH loading on the conversion of toluene to toluic acid is illustrated in Fig. 15. The conversion increases linearly up to a TFAH loading of 30 mmol, where after the conversion decreases. Since TFAH is consumed in the reoxidation of

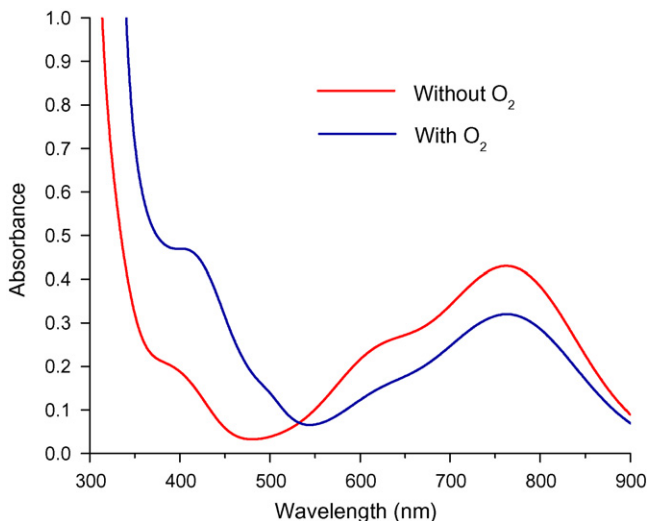


Fig. 14. UV-vis spectrum of aqueous phase following reaction and acid extraction with water. Reaction conditions: 37.5 mmol toluene (3.46 g); 13.0 mmol CF_3COOH (1.48 g); 7.05 mmol $(\text{CF}_3\text{CO})_2\text{O}$ (1.48 g); 10 μmol $\text{Rh}(\text{acac})_3$ (0.0039 g); 0.5163 mmol NH_4VO_3 (0.0604 g); $P_{\text{CO}} = 0.345$ MPa; $T = 353$ K; $t = 4$ h. Reaction with oxygen: $P_{\text{O}_2} = 0.345$ MPa.

Rh(I) to Rh(III) (see above), the rise in conversion with TFAH loading is ascribed to an increase in the driving force for this reaction resulting from the increasing concentration of TFAH. However, above 30 mmol of TFAH, the decrease in toluene conversion may result from the dilution effect of adding additional TFAH.

Fig. 16 shows that the yield of toluic acid is very sensitive to the amount of TFAA present in the reaction mixture. For TFAA loadings below 2.5 mmol, the conversion of toluene to toluic acid was very small. A sharp maximum in toluene conversion occurred for a TFAA loading of approximately 4.1 mmol, after which the conversion decreased slowly with increasing concen-

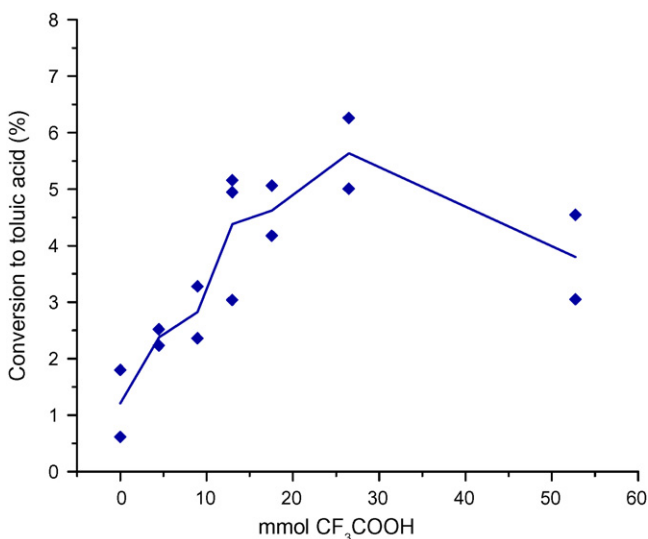


Fig. 15. Effect of CF_3COOH loading on toluene conversion. Reaction conditions: 37.5 mmol toluene (3.46 g); 3.53 mmol $(\text{CF}_3\text{CO})_2\text{O}$ (0.75 g); 10 μmol $\text{Rh}(\text{acac})_3$ (0.0039 g); 0.5163 mmol NH_4VO_3 (0.0604 g); $P_{\text{CO}} = 0.345$ MPa; $P_{\text{O}_2} = 0.345$ MPa; $T = 353$ K; $t = 4$ h.

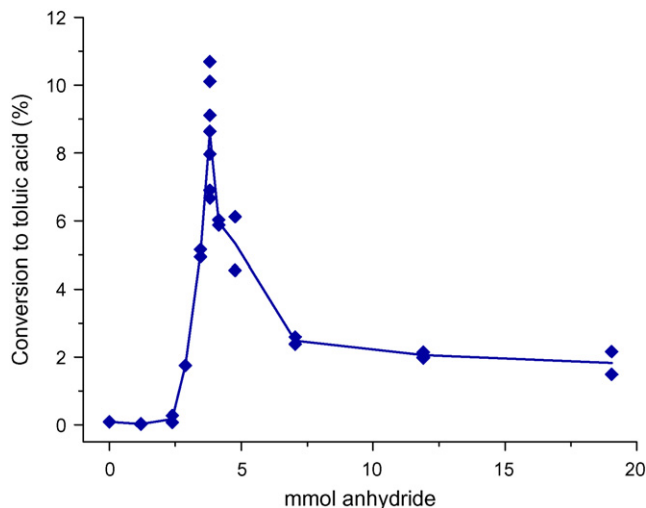


Fig. 16. Effect of $(\text{CF}_3\text{CO})_2\text{O}$ loading on toluene conversion. Reaction conditions: 37.5 mmol toluene (3.46 g); 13.0 mmol CF_3COOH (1.48 g); 10 μmol $\text{Rh}(\text{acac})_3$ (0.0039 g); 0.5163 mmol NH_4VO_3 (0.0604 g); $P_{\text{CO}} = 0.345$ MPa; $P_{\text{O}_2} = 0.345$ MPa; $T = 353$ K; $t = 4$ h.

tration of TFAA. TFAA is thought to serve as a scavenger of water present in the reactor initially or produced during the course of the reaction. As already noted above, while a certain amount of water is required for the oxidation of VO^{2+} to VO_2^+ , excess H_2O can lead to formation of H_2 and the subsequent reduction of Rh(III). This reasoning would suggest that for the conditions shown in Fig. 16, the optimum amount of water is achieved using a TFAA concentration of approximately 4.1 mmol.

3.7. Proposed reaction mechanism

A possible mechanism for *p*-toluic formation is illustrated in Fig. 17. The individual reactions appearing in this scheme are suggested by the experiments described above and by the mechanistic work reported by Kalinovskii and coworkers [9]. The number of carbonyl ligands present on the Rh was chosen such that the complex satisfies the 18-electron rule commonly used in inorganic chemistry. It should be noted that one of the trifluoroacetate ligands acts as a three-electron donor whereas the other trifluoroacetate ligands donate only one electron. The formation of toluic acid is initiated by the reaction of toluene with $\text{Rh}(\text{CO})_2(\text{TFA})_3$ to form a methyl aryl complex, $\text{Rh}(\text{CO})_2(\text{C}_6\text{H}_4\text{CH}_3)(\text{TFA})_2$ and TFAH. The latter product may stay associated with the Rh(III) center or enter into the solution as free acid. CO in the Rh complex then undergoes a migratory insertion into the Rh–C bond of $\text{Rh}(\text{CO})_2(\text{C}_6\text{H}_4\text{CH}_3)(\text{TFA})_2$ to form the 16-electron complex $\text{Rh}(\text{CO})(\text{COC}_6\text{H}_4\text{CH}_3)(\text{TFA})_2$ in reaction 2. This complex then readily binds CO in the reaction solution to form the 18-electron $\text{Rh}(\text{CO})_2(\text{COC}_6\text{H}_4\text{CH}_3)(\text{TFA})_2$ complex. The latter product then releases the mixed anhydride of toluic and trifluoroacetic acid in reaction 4, at the same time that Rh(III) is reduced to $\text{Rh}(\text{CO})_2(\text{TFA})$. As discussed above, Rh(I) cations are reoxidized to Rh(III) cations via reaction 5, with $\text{VO}_2(\text{TFA})$ serving as the oxidizing agent. Since this step involves six species, it is unlikely that reaction 5 occurs exactly

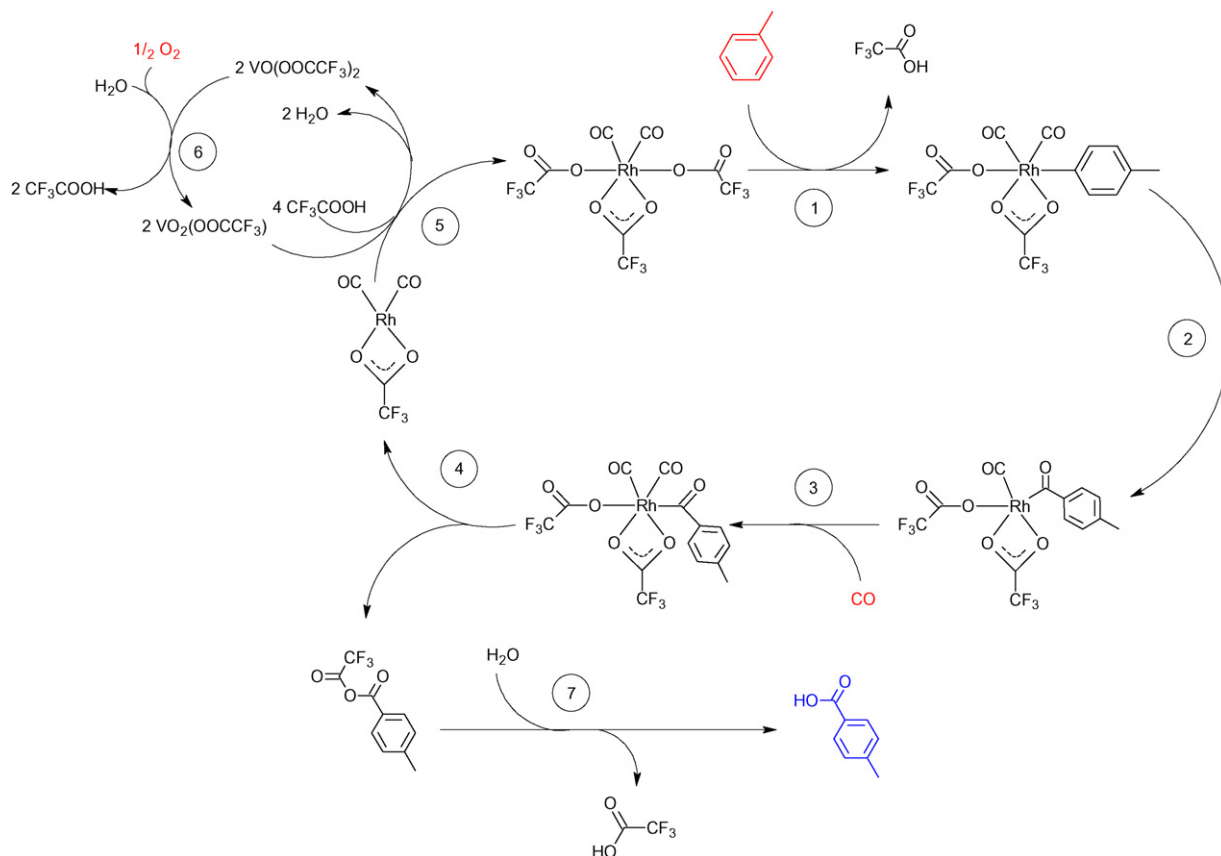


Fig. 17. Proposed reaction pathway.

as written and, in fact, the overall process must involve a series of elementary steps. The V(IV) species produced in reaction 5 are then reoxidized in reaction 6. Here again, it is most likely that reaction 6 is comprised of a series of elementary steps.

The proposed reaction mechanism clearly illustrates the role of V(V) species in the reoxidation of Rh(I) to Rh(III) and the role of O_2 and H_2O in the reoxidation of V(IV) species back to V(V) species. The need to maintain a V/Rh ratio in excess of 10 in order to achieve a reasonable rate of toluic acid formation suggests that the rate of Rh(I) reoxidation by V(V) is relatively slow and must be driven by a large excess of V. Likewise, it is noted that the oxidation of V(IV) back to V(V) by O_2 is relatively slow, as evidenced by the observation that at the end of a typical reaction 67% of the V is present at V(IV). The role of CO is also shown clearly in Fig. 16. The yield of toluic acid increases initially with increasing CO partial pressure as a consequence of the enhanced rate of reaction 3. However, CO can also react with H_2O produced in reaction 5 to form H_2 , which will, in turn, reduce Rh(III) to Rh(I) without forming toluic acid.

4. Conclusion

Results of this study indicated that the oxidative carbonylation of toluene to toluic acid using rhodium-based catalysts and $\text{NH}_4\text{VO}_3/\text{O}_2$ as the oxidizing agent is strongly influenced by the water content in the reactor, gas partial pressures, and the concentration of rhodium. Maintaining an optimum water

content is extremely important because either excess or insufficient water limits the re-oxidation of Rh(I) to Rh(III). The production of water during rhodium re-oxidation exacerbates this step. Without the proper balance of anhydride, water either accumulates in the reactor thereby limiting rhodium re-oxidation or the anhydride consumes the water to the extent that it precludes vanadium re-oxidation by oxygen. It is also found that the moles of toluic acid produced per mole vanadium are nearly constant with increasing vanadium content, whereas rhodium activity increases nearly linearly. Evidence from UV-vis spectroscopy indicates that VO_2^+ cations readily oxidize Rh(I) to Rh(III); however, the re-oxidation of VO^{2+} by O_2 back to VO_2^+ is slow. These results strongly indicate that the re-oxidation of vanadium by oxygen limits the reaction rather than the re-oxidation of rhodium by vanadium (VO_2^+) or Rh C-H bond activation. Increasing the amount of vanadium present at the onset of reaction or the partial pressure of O_2 increases the catalytic activity.

A mechanism for the oxidative carbonylation of toluene to toluic acid is proposed based on the observations reported in this study (see Fig. 17). In this scheme, Rh(III) activates the C-H bond in toluene to produce a methyl benzyl group as a ligand. Migratory insertion of CO into the Rh-C bond of this ligand and a subsequent reductive elimination results in the formation of a mixed anhydride of trifluoroacetic and toluic acid. This product then reacts with water already present in the system or during product work-up to form toluic acid. V(V) in the

form of VO_2^+ re-oxidizes the Rh(I) in the presence of trifluoroacetic acid to Rh(III). Water produced during this process is either consumed by trifluoroacetic anhydride or accumulated in the reaction system. The reduced V(IV) as VO^{2+} is then re-oxidized to V(V) by oxygen. While CO is required to produce the acyl precursor to the mixed anhydride, an excess partial pressure of CO, as well as excess H_2O , contributes to the formation of H_2 , which can reduce Rh(III) to Rh(I). The relatively slow rate of V(IV) re-oxidation to V(V) by oxygen appears to influence the overall rate of reaction to a larger extent than the rate of Rh(I) re-oxidation or the rate of C–H bond activation by Rh(III).

Acknowledgements

The authors wish to thank Mark Zerella and David Sikkenga of BP for many useful discussions along. This work was supported by the Methane Conversion Cooperative, funded by BP.

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