Effects of Ligand Composition on the Oxidative Carbonylation of Toluene to Toluic Acid Catalyzed by Rh(III) Complexes

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Abstract: Experimental and theoretical studies were conducted to investigate the influence of anionic ligands (e.g., CF_3COO^-, $CH_3SO_3^-$) on the catalytic activity and selectivity of Rh(III) in the oxidative carbonylation of toluene to toluic acid. The catalyst activity was found to pass through a maximum as the pK_a of the conjugate Brønsted acid decreases from 4.63 to −2.00, with the maximum activity occurring at pK_a = 0.35, corresponding to $CClF_2COOH$. The theoretical analysis showed that the strength of toluene coordination increases with decreasing basicity of the anion (i.e., decreasing pK_a of the corresponding acid). In contrast, the activation barrier for C−H activation increases with decreasing ligand pK_a. The experimentally observed effect of anion composition on catalyst activity can be explained using calculations of the apparent rate coefficient for toluene activation based on density functional theory and transition state theory. The ratio of *p*- to *m*-toluic acid formed increases with decreasing acid pK_a and passes through a maximum for pK_a = 0, corresponding to CF_3COOH. The effect of anion composition on the isomer selectivity is attributed to changes in the charge density on the Rh(III) cation, which in turn affect the distribution of charge on the para and meta carbon atoms of the aromatic ring.

Introduction

The oxidative carbonylation of aromatic hydrocarbons to produce carboxylic acids was first demonstrated by Fujiwara and co-workers using Pd(II) cations in acetic acid.[1−5] In subsequent work, it was shown that oxidative carbonylation of aromatic hydrocarbons, particularly benzene and toluene, could also be catalyzed by Rh cations and that for both Pd(II) and Rh(III) cations, the use of trifluoroacetic acid resulted in significantly higher reaction rates than the use of acetic acid.[6−17]

In their investigation of the oxidative carbonylation of alkanes, Fujiwara and co-workers[6] noted that acids more or less acidic than trifluoroacetic acid, such as trifluoromethanesulfonic and methanesulfonic acids or dichloroacetic and acetic acid, respectively, are ineffective in promoting the formation of carboxylic acids in the presence of Pd cations. Zakzeski and Bell[18] have recently demonstrated that acid composition has a considerable effect on the activity and selectivity of Rh(III) and Pd(II) in the oxidative carbonylation of benzotrifluoride to trifluoromethylbenzoic acid.

Attempts to explain the effect of acid composition on the catalytic activity of Rh(III) and Pd(II) complexes in the oxidative carbonylation of arenes have focused on the impact of the anionic ligands derived from acids on the electrophilicity of the cation. Thus, for example, Fujiwara and co-workers[8] and Kalinovski and co-workers[13] have attributed the higher rate of oxidative carbonylation in trifluoroacetic acid than in acetic acid to the greater electrophilicity imparted to the metal cation by trifluoroacetate anions than by acetate anions. Implicit in this interpretation is the assumption that the rate-limiting step in the oxidative carbonylation of aromatic compounds is electrophilic activation of a C−H bond on the aromatic ring. Recent theoretical work indicates that C−H activation of aromatic compounds can also occur by other mechanisms. For example, Ziatdinov and co-workers[19] have concluded that the C−H bond

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Scheme 1. Proposed Mechanism for the Oxidative Carbonylation of Toluene by Rh(III) in the Presence of Trifluoroacetic Acid: Reoxidation of Rh(I) to Rh(III) is Illustrated for the Case Where VO_2^+ Serves as the Oxidizing Agent
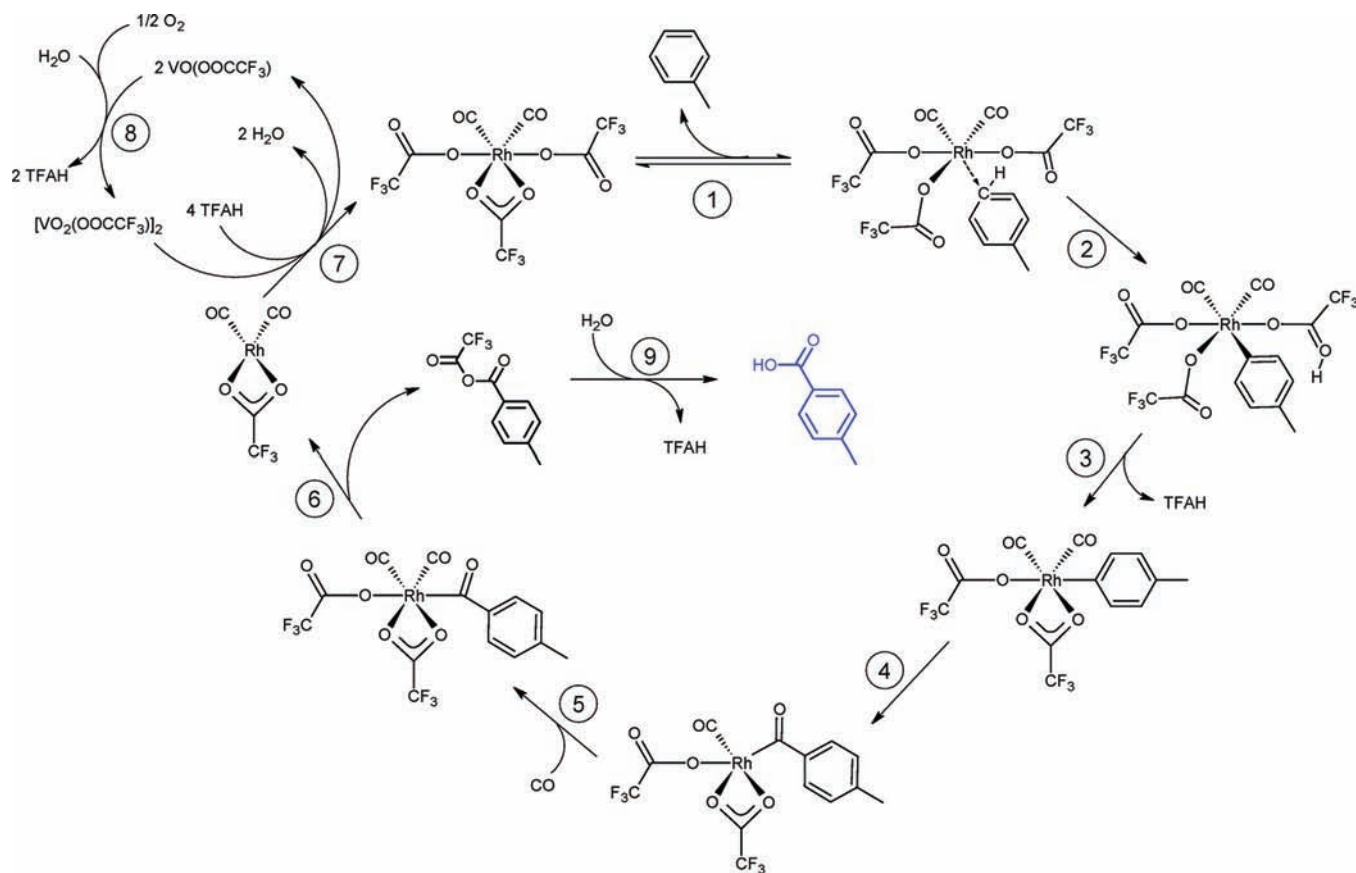
activation of benzene by the complex $Pt(pic)(TFA)_2^-$ (pic = picolinate, TFA = trifluoroacetate) is best described as an electrophilic substitution proceeding via addition of the Pt center to the arene ring as opposed to σ-bond metathesis. Work by Davies et al. on the cyclometalation of dimethylbenzylamine (DMBA-H) with $Pd(OAc)_2$ and $Ir(OAc)Cp$ (OAc = acetate) showed that C−H bond activation in the case of $Pd(OAc)_2$ proceeds via an agostic C−H complex,[20] whereas in the case of $Ir(OAc)Cp$, C−H bond activation proceeds by an electrophilic mechanism.[21]

The objective of the present investigation was to develop a systematic understanding of the effects of ligand composition on the oxidative carbonylation of toluene to toluic acid catalyzed by Rh(III) complexes. Previous investigations of the mechanism and kinetics of this reaction have suggested that when the solvent is the reactant itself, the Rh(III) cation is stable as a cation−anion pair.[8,18,22] This view is supported by a theoretical study of the oxidative carbonylation of toluene by Rh(III) cations in the presence of trifluoroacetic acid (TFAH).[23] This work suggested that the species responsible for the activation of toluene is $Rh(CO)_2(TFA)_3$. In the course of the reaction, Rh(III) is reduced to Rh(I), and the latter cation must be reoxidized in order to complete the catalytic cycle. When NH_4VO_3 is used as the oxidant, the rate of reoxidation is much more rapid than the

rate of reduction, and hence, Rh in its resting state is present as Rh(III).[22] The composition and structure of the catalytically active species have recently been investigated by combined spectroscopic and theoretical work, and this effort has confirmed that the resting state of the catalyst is $Rh(CO)_2(TFA)_3$.[24]

Scheme 1 illustrates the mechanism for the oxidative carbonylation of toluene to toluic acid catalyzed by $Rh(CO)_2(TFA)_3$ when $[VO_2]^+$ cations serve as the oxidizing agent for the reoxidation of Rh(I) to Rh(III).[23,24] Both experimental and theoretical studies have suggested that the first step in the oxidative carbonylation of toluene is the coordination of the toluene by Rh(III), which is followed by C−H bond activation of the arene to produce a Rh−arene complex and TFAH. Theoretical and experimental analysis of the process suggests that the coordination of toluene to the Rh complex, $Rh(CO)_2(TFA)_3 + C_6H_5CH_3 \rightleftharpoons Rh(CO)_2(TFA)_3(C_6H_5CH_3)$, is equilibrated and that C−H bond activation is the rate-limiting step.[23,24] Thus, it is of interest to establish the roles of anion composition in promoting the coordination of toluene and the activation of the C−H bond associated with the aromatic ring. With this aim in mind, we have investigated the effects of ligand composition on the rate of oxidative carbonylation of toluene both experimentally and theoretically.

Experimental and Computational Details

Experiments. Reactions were conducted in a stirred 50 mL Parr autoclave made of Hastelloy C. Between runs, the reactor was

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washed thoroughly with water and acetone and then dried in a vacuum oven. 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), 13 mmol of either CF_3COOH (99%, Aldrich), $CF_2ClCOOH$ (98%, Aldrich), C_2F_5COOH (97%, Aldrich), CCl_3COOH (99%, Alfa Aesar), CCl_2HCOOH (99%, Alfa Aesar), $CClH_2COOH$ (99%, Alfa Aesar), CH_3COOH (99.7%, EMD), CF_3SO_3H (98%, Aldrich), or CH_3SO_3H (≥99.5%, Aldrich), 3.8 mmol of either $(CF_3CO)_2O$ (≥99%, Aldrich), $(CF_2ClCO)_2O$ (98%, Aldrich), $(C_2F_5CO)_2O$ (99%, Aldrich), $(CCl_3CO)_2O$ (96%, Alfa Aesar), $(CCl_2HCO)_2O$ (Aldrich, 96%), $(CClH_2CO)_2O$ (Alfa Aesar, 96%), $(CH_3CO)_2O$ (99%, EM Science), $(CF_3SO_2)_2O$ (99+%, Aldrich), or $(CH_3SO_2)_2O$ (97%, Aldrich), respectively, 0.0039 g of $Rh(acac)_3$ (97%, Aldrich), and 0.0604 g of NH_4VO_3 (99+%, Aldrich) were placed into the autoclave, which was then sealed and purged four times with nitrogen. Next, the reactor was pressurized at 293 K with 0.345 MPa O_2 (99.993%, Praxair) and 0.345 MPa CO (99.5%, Praxair). The reactor was then heated to 353 K in ~10 min and held at this temperature for 4 h. Upon completion of the reaction, the reactor was quenched with ice water to 308 K and vented. The quantity of toluic acid was determined by gas chromatography using an Agilent Technologies 6890N gas chromatograph equipped with an FID detector and an HP-1 capillary column coated with cross-linked methylsiloxane.

Calculations. Electronic structures and energies of reactants, products, and transition states were determined using density functional theory (DFT) as implemented in Q-Chem.[25] The B3LYP functional was used to describe electron exchange and correlation, and the 6-31G* basis set was used to locate optimized ground-state and transition-state structures. The LANL2DZ effective core potential was used to describe the Rh atom. After a particular molecular structure was optimized to a stationary point (transition-state or minimum-energy structure), its energy was further refined at a higher level of theory using the 6-311G**/LANL2DZ basis set (also see the Supporting Information). All of the stationary and transition-state points were found on the basis of gas-phase calculations. The growing string method (GSM) was used to locate the transition state (TS) connecting two minimum-energy structures.[26] In this method, a minimum-energy path connecting the reactant and product is estimated without making an initial guess for the reaction path. The geometry at the point with the highest energy on this minimum-energy path is taken as an estimate of the transition-state geometry, which is then converged to the exact saddle point by the transition-state-finding algorithm implemented in Q-Chem. Vibrational analyses were performed to verify the nature of the energy minima and transition states as well as to generate thermochemical data. All of the reported energies and free energies are for the gas phase at 353 K, the experimental reaction temperature. Vibrational, rotational, and translational entropy values were computed using standard statistical-mechanical methods within the rigid-rotor–harmonic-oscillator approximation. The energetics of toluene binding were corrected for basis-set superposition error 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:

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

where K is the equilibrium constant, R is the gas constant, T is the absolute temperature, $c°$ is the standard-state concentration in the liquid phases (1 mol/L), $P°$ 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 $\Delta G°$ is
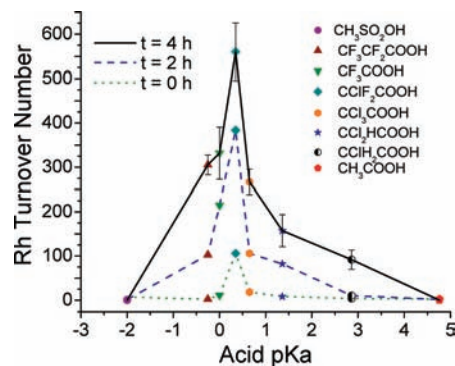
Figure 1. Turnover number for Rh-catalyzed oxidative carbonylation of toluene to toluic acid as a function of acid pK_a. Reaction conditions: 37.5 mmol (3.46 g) of toluene, 13.0 mmol of the designated acid, 3.8 mmol of the corresponding anhydride, 10 μmol (0.0039 g) of $Rh(acac)_3$, 0.5163 mmol (0.0604 g) of NH_4VO_3, $P_{CO} = 0.345$ MPa, $P_{O_2} = 0.345$ MPa, $T = 353$ K.

the Gibbs free energy of reaction at the reaction temperature. Rate coefficients were computed from transition state theory, as described by eq 2:

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

where k is the elementary rate coefficient, k_B is Boltzmann's constant, h is Planck's constant, and $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ are the entropy and enthalpy of activation, respectively, at the reaction temperature. Energy decomposition analysis (EDA) was performed using the method of Khaliullin et al.,[27] as implemented in Q-Chem.

Results and Discussion

Figure 1 shows the effect of acid pK_a on the number of turnovers obtained for Rh(III) at various reaction times. The reactions for $t = 4$ h were repeated in triplicate. Comparison of the turnover numbers for reactions at different times indicates that the relative order of catalytic activity with respect to acid pK_a remained constant. In each case, the total reaction time includes the time required to heat and cool the autoclave (see the Supporting Information). As indicated by Figure 1, only acids with pK_a's between −2 and 3 were effective in producing toluic acid, and the most effective acids were those with pK_a's between 0 and 0.5.[28–30] Within this range, $CClF_2COOH$ (pK_a = 0.35) yielded the largest number of turnovers. Reduced catalytic activity was observed for acids with pK_a values greater than that of $CClF_2COOH$ (such as CCl_3COOH, CCl_2HCOOH, $CClH_2COOH$, and CH_3COOH) as well as acids with pK_a's smaller than that of $CClF_2COOH$ (such as C_2F_5COOH and CH_3SO_2OH). The data shown in Figure 1 also confirm that both very strong and very weak acids are ineffective in promoting the oxidative carbonylation of toluene to toluic acid, consistent with the observations of Fujiwara and co-workers for the oxidative carbonylation of alkanes.[6]

The oxidative carbonylation of toluene to toluic acid involves several important steps in which ligands play an integral role. These include coordination of toluene to the Rh complex and

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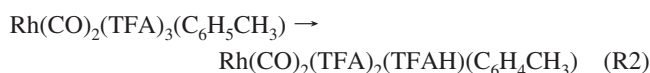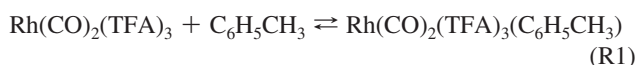(29) Gelb, R. I.; Alper, J. S. *J. Chem. Eng. Data* **1998**, *43*, 1068–1071.
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subsequent C−H bond activation, reductive elimination of toluic−trifluoroacetic mixed anhydride, and reoxidation of the Rh(I) species to complete the catalytic cycle.[12,22] In the case of trifluoroacetic acid, the rate of reoxidation is rapid, and C−H bond activation is the rate-limiting step.[22,24] To ascertain whether the reduced activity observed for acids that are more or less acidic than CClF$_2$COOH resulted from the toluene C−H bond activation rate and not from a decrease in Rh reoxidation rate, experiments were conducted to determine the resting state of the catalyst in a manner similar to that used for the case of trifluoroacetic acid.[24] In all cases except for CH$_3$COOH, the rate of reoxidation was rapid, and the resting state of the catalyst was found to be Rh(III). Spectroscopic analysis suggests that in the presence of acetic acid, the majority of Rh was present as Rh(I).

The kinetics of the oxidative carbonylation of toluene can be represented in terms of the two reactions shown below, illustrated for the case in which TFA anions derived from TFAH serve as the ligands:

$$Rh(CO)_2(TFA)_3 + C_6H_5CH_3 \rightleftarrows Rh(CO)_2(TFA)_3(C_6H_5CH_3) \quad (R1)$$

$$Rh(CO)_2(TFA)_3(C_6H_5CH_3) \rightarrow$$
$$Rh(CO)_2(TFA)_2(TFAH)(C_6H_4CH_3) \quad (R2)$$

Reaction R1 represents the reversible coordination of toluene to the complex Rh(CO)$_2$(TFA)$_3$, and Reaction R2 represents the irreversible activation of the para C−H bond in the coordinated toluene to form the complex Rh(CO)$_2$(TFA)$_2$(TFAH)(C$_6$H$_4$CH$_3$). The rate of toluene activation, r, can then be written as:

$$r = k_{app}[Rh][CH_3C_6H_5] \quad (3)$$

where

$$k_{app} = K_{coord}k_{act} \quad (4)$$

In eqs 3 and 4, k_{app} is the apparent rate coefficient for the oxidative carbonylation of toluene, k_{act} is the intrinsic rate coefficient for activation of the C−H bond, K_{coord} is the equilibrium constant for the coordination of toluene to the complex Rh(CO)$_2$(TFA)$_3$, and [Rh] and [CH$_3$C$_6$H$_5$] are the concentrations of Rh(CO)$_2$(TFA)$_3$ and toluene, respectively. The turnover number (TON) based on the formation of toluic acid can then be expressed as follows, assuming that the reaction occurs in a well-stirred batch reactor:

$$TON = \frac{[CH_3C_6H_4COOH]}{[Rh]_0} = \frac{[CH_3C_6H_5]_0}{[Rh]_0} \times \{1 - \exp(-k_{app}[Rh]_0t)\} \quad (5)$$

In this expression, [Rh]$_0$ and [CH$_3$C$_6$H$_5$]$_0$ represent the concentrations of Rh and toluene, respectively, that were loaded into the reactor, and t is the reaction time. Since the rate of reoxidation of Rh(I) to Rh(III) is very rapid relative to the rate of reduction of Rh(III), the concentration of Rh(III) is assumed to be equivalent to the concentration of Rh placed into the reactor at the start of an experiment.

Equation 4 suggests that ligand composition can affect the kinetics of toluic acid formation in two ways: through the effect of the anion in the ligand on the coordination of toluene and through the effect of the ligands on C−H bond activation. As suggested by earlier work, weakly basic anions promote the
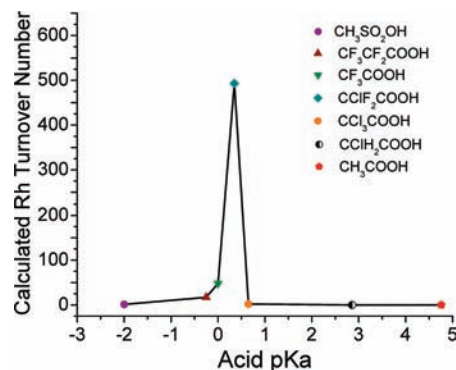

Figure 2. Turnover numbers calculated from eq 4 using apparent rate coefficients determined theoretically.
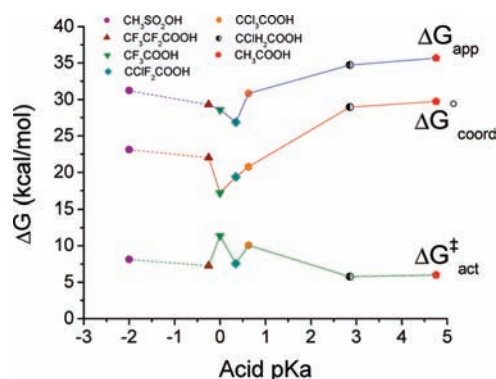
Figure 3. Gibbs free energies of toluene coordination (ΔG°_{coord}) and C−H bond activation ($\Delta G^{\ddagger}_{act}$) and the apparent Gibbs free energy of activation (ΔG_{app}) as functions of the pK_a of the acid from which the anionic ligand is derived.

coordination of toluene by enhancing the electrophilicity of the Rh(III) cation;[12] however, the anions must be sufficiently basic to accommodate the proton from the aromatic ring of toluene in the rate-limiting step of C−H activation. This interpretation is supported by our quantum-chemical calculations discussed below.

Figure 2 shows the number of turnovers predicted from eq 4 after 4 h of reaction. Consistent with experimental observations, the highest turnover number occurs for CClF$_2$COOH, and this value is in good agreement with that observed experimentally (see Figure 1). It is noted, though, that the decrease in turnover number for acids with larger or smaller pK_a's than CClF$_2$COOH (pK_a = 0.35) is more rapid than that observed in Figure 1. The variation in the number of turnovers with the pK_a of the acid from which the anionic ligand is derived can be interpreted in terms of the value of ΔG_{app}, defined as $\Delta G_{app} = \Delta G^{\circ}_{coord} + \Delta G^{\ddagger}_{act}$, since k_{app} is exponentially dependent on ΔG_{app}. The dependence of ΔG_{app} on the pK_a of the acid from which the anionic ligand is derived is shown in Figure 3. This figure shows that the lowest value of ΔG_{app} is for CClF$_2$COOH. Consistent with this, the value of k_{app} is largest for CClF$_2$COOH, as is the turnover number determined from eq 5 (see Figure 2). The sharpness of the change in the turnover number with acid pK_a can be ascribed to the variation in the value of $\Delta\Delta G_{app}$, the change in apparent Gibbs free energy of activation relative to the value of ΔG_{app} calculated for CClF$_2$COOH, with acid composition. For example, the values of $\Delta\Delta G_{app}$ are 3.9 and 1.7 kcal/mol for CCl$_3$COOH and CF$_3$COOH, respectively. Reference to Figure 1 suggests that $\Delta\Delta G_{app}$ should be approximately ±1 to obtain the experimentally observed results. Thus, while the theoretically
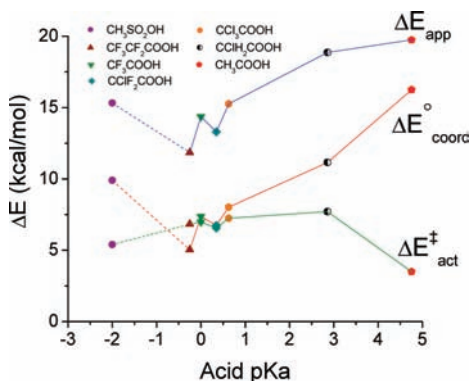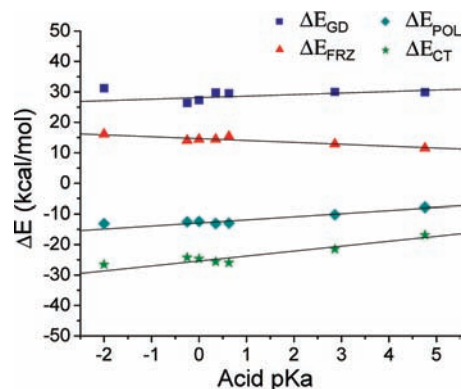
Figure 4. Energies of toluene coordination (ΔE_{coord}) and C−H bond activation ($\Delta E_{\text{act}}^{\ddagger}$) and the apparent energy of activation (ΔE_{app}) as functions of the pK_a of the acid from which the anionic ligand is derived.

Figure 5. Values of ΔE_{GD}, ΔE_{FRZ}, ΔE_{POL}, and ΔE_{CT} for toluene coordination derived from EDA as functions of the pK_a of the acid from which the anionic ligand is derived.[27]

derived values of ΔG_{app} reproduce the trends seen experimentally, differences in the value of this quantity are not calculated accurately enough to capture the magnitude of the observed changes in turnover number. Solvent interactions with the catalyst may also contribute to charge delocalization, which could result in the gradual decrease observed experimentally.

The cause of the variation in the magnitude of ΔG_{app} with pK_a can be understood more completely by examining the effects of anionic ligand composition on the component parts of ΔG_{app}, namely, $\Delta G_{\text{coord}}^{\circ}$ and $\Delta G_{\text{act}}^{\ddagger}$. As seen in Figure 3, the magnitude of $\Delta G_{\text{coord}}^{\circ}$ goes through a minimum at a pK_a of ∼0, corresponding to CF₃COOH, but the effect of pK_a on $\Delta G_{\text{act}}^{\ddagger}$ is more complex. This component of ΔG_{app} tends to increase with decreasing pK_a of the acid from which the anionic ligand is derived; however, this trend is not completely monotonic in the pK_a range from 1 to 0. It is as a consequence of these small variations that the minimum value of ΔG_{app} occurs for CClF₂COOH.

Figure 4 shows the internal energies of toluene coordination (ΔE_{coord}) and C−H bond activation ($\Delta E_{\text{act}}^{\ddagger}$) as well as ΔE_{app}, defined as $\Delta E_{\text{app}} = \Delta E_{\text{coord}} + \Delta E_{\text{act}}^{\ddagger}$. The value of ΔE_{coord} decreases more or less monotonically with decreasing pK_a down to $pK_a = 0$, corresponding to CF₃COOH, but then suddenly increases for CH₃SO₂OH, which has a pK_a of −2. The decrease in the magnitude of ΔE_{coord} with decreasing pK_a for the carboxylate anions is a direct consequence of the increasing electronegativity of the anion, which causes the positive charge on the Rh cation to increase. The latter effect makes the cation more electrophilic and hence strengthens the coordination of toluene (see below for further details). By extension of this logic, one would expect the value of ΔE_{coord} for CH₃SO₂O⁻ anions derived from CH₃SO₂OH to be lower than that for C₂F₅COO⁻ anions derived from C₂F₅COOH; however, Figure 4 shows that this is clearly not the case. The reason for the anomalous behavior of CH₃SO₂OH is discussed below. Figure 4 also shows that $\Delta E_{\text{act}}^{\ddagger}$ increases as the pK_a decreases from 5 to 3, but thereafter the value of this component of ΔE_{app} decreases slightly. Finally, it is interesting to observe that ΔE_{app} is smallest for C₂F₅COOH, from which it might be concluded purely on the basis of energetic considerations that the anionic ligands derived from this acid (C₂F₅COO⁻) should produce the highest catalyst activity. That this is not the case is a result of the effect on ΔG_{app} caused by variations in $\Delta S_{\text{app}}^{\ddagger}$, the apparent entropy of activation, arising from differences in composition of the anionic ligands. Thus, to summarize, the minimum in ΔG_{app} with respect to pK_a, as seen in Figure 3, is a consequence of

the combined effects of anionic ligand composition on the apparent energy and entropy of activation.

The abnormally high toluene coordination energy, ΔE_{coord}, for the case of CH₃SO₂OH can be understood on the basis of an energy decomposition analysis (EDA) of ΔE_{coord}.[27] EDA represents ΔE_{coord} as the sum of four terms: ΔE_{GD}, ΔE_{FRZ}, ΔE_{POL}, and ΔE_{CT}. ΔE_{GD} is the geometric distortion contribution, which accounts for the energy required to take the reactants from their equilibrium geometries (i.e., free toluene and free Rh complex) to the geometry they assume in the complex (in this case, the state in which toluene is coordinated to the rhodium complex). ΔE_{FRZ}, the frozen density interaction, is defined as the electrostatic repulsion of the reactants (i.e., the toluene and the Rh complex). ΔE_{POL} is the polarization energy lowering attributed to relaxation of the molecular orbitals due to the presence of toluene coordinated to the Rh complex. Finally, ΔE_{CT}, the charge transfer energy lowering, is defined as the stabilization that results from moving charge from one reactant to the other (in this case, primarily from toluene to the Rh complex).

The results of the EDA are shown in Figure 5. Trend lines are fitted to the ligands derived from carboxylic acids and then extrapolated to methanesulfonic acid. This analysis provides general insight into the effect of ligands on toluene binding. ΔE_{FRZ} tends to increases as pK_a decreases. The slightly negative slope of this trend indicates that the electrostatic repulsion of the electrons in the Rh complex increases as the electron density on the complex increases. The value of ΔE_{POL} tends to decrease as pK_a decreases, indicating that as the pK_a of the acid used to derive the ligands decreases, the complex is better able to redistribute charge. The trend in ΔE_{POL} strongly resembles that for ΔE_{FRZ}. The value of ΔE_{CT} also tends to decrease with decreasing pK_a. This trend is a consequence of the increase in the electropositive character of the Rh cation, which in turn increases the extent of charge transfer from the coordinated toluene. The magnitude of ΔE_{GD} results from distortions in both the complex and the toluene molecule but is dominated by the distortion of the complex, and it tends to increase with decreasing pK_a. Specifically, in the course of coordinating toluene, the catalyst must break one of the Rh−O bonds associated with a bidentate-ligated acetate anion in order to accommodate toluene into the coordination sphere.[22,23] The increase in ΔE_{GD} shows that ligands derived from acids with smaller pK_a values require more energy to make the transition from bidentate to monodentate ligation of the anion.

The EDA for methanesulfonic acid shows that while most terms follow the trends with pK_a seen for the carboxylic acids,
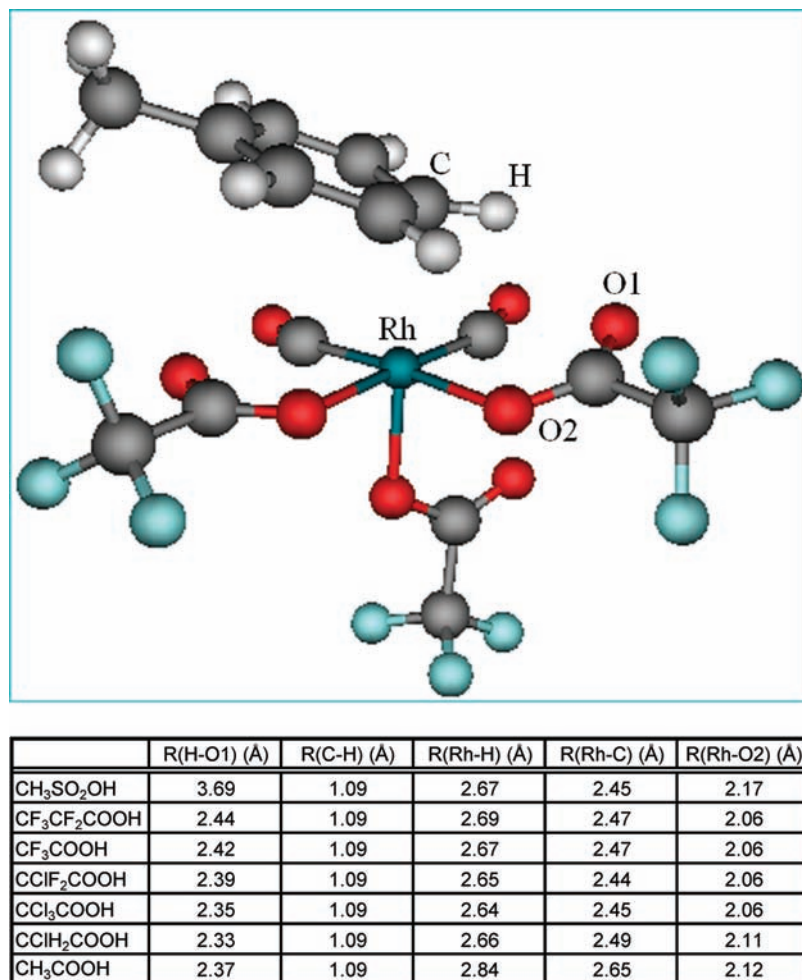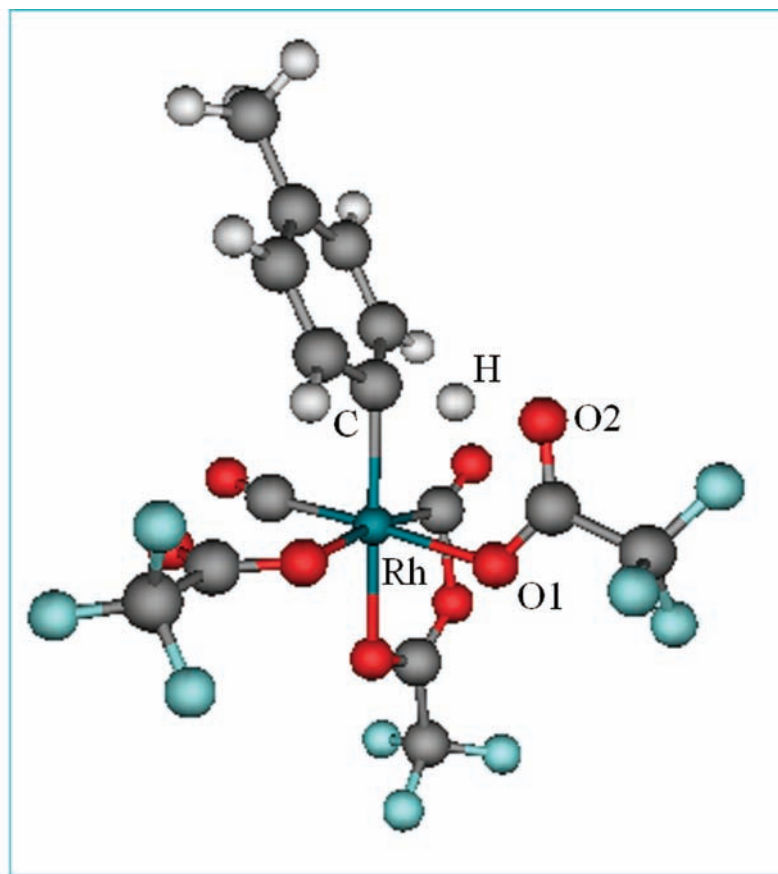
	R(H-O1) (Å)	R(C-H) (Å)	R(Rh-H) (Å)	R(Rh-C) (Å)	R(Rh-O2) (Å)
CH₃SO₂OH	3.69	1.09	2.67	2.45	2.17
CF₃CF₂COOH	2.44	1.09	2.69	2.47	2.06
CF₃COOH	2.42	1.09	2.67	2.47	2.06
CClF₂COOH	2.39	1.09	2.65	2.44	2.06
CCl₃COOH	2.35	1.09	2.64	2.45	2.06
CClH₂COOH	2.33	1.09	2.66	2.49	2.11
CH₃COOH	2.37	1.09	2.84	2.65	2.12

Figure 6. Structure of coordinated toluene. Selected bond distances are shown in the table.

there are some notable differences. The value of ΔE_{FRZ} for CH₃SO₂OH is consistent with that for the carboxylic acids, which indicates that the electrostatic repulsion of the electrons in the complex does not contribute disproportionately to the higher value of ΔE_{coord}. ΔE_{POL} for CH₃SO₂OH is slightly above the carboxylic acid trend line, indicating that methanesulfonate anions cannot redistribute charge quite as well as carboxylate anions. The value of ΔE_{CT} for CH₃SO₂OH is again slightly higher than that projected by the trend line for carboxylic acids, indicating that the ability of methanesulfonic acid to accept and redistribute charge contributes to its weak binding. However, most importantly, the magnitude of ΔE_{GD} for CH₃SO₂OH lies considerably above the trend line for the carboxylic acids. This deviation indicates that the energy required to convert the CH₃SO₂O⁻ ligation from bidentate to monodentate (to allow the Rh cation to coordinate toluene) is notably higher than that projected for a carboxylate anion of equivalent basicity, and it is this effect that reduces the overall binding strength of toluene when CH₃SO₂O⁻ anions are coordinated to Rh. The combined influence of the four terms constituting ΔE_{coord} results in a less favorable binding energy for the Rh−methanesulfonate complex than would be expected for a Rh complex involving a carboxylate anion derived from an acid with a pK_a equivalent to that of CH₃SO₂OH.

Examination of the geometry of the coordinated toluene complex and the transition state involved in the activation of the C−H bond at the para position provide additional insights

into the chemistry by which the oxidative carbonylation of toluene occurs. Figure 6 shows the geometries of coordinated toluene and the relevant bond distances for the various ligands. Since methanesulfonate ligands have two oxygens with which to receive the abstracted H atom, each methanesulfonic acid catalyst reaction possesses two possible transition states. Only the lower-energy transition state of methanesulfonic acid was considered in this study. In the minimum-energy configuration for coordinated toluene, two of the three anions and the two CO ligands lie in the equatorial plane, whereas toluene and the third anion are axially coordinated. As the pK_a of the conjugate acid decreases, going from CH₃COOH to CH₃SO₂OH, the length of the Rh−C bond tends to decrease, and the most dramatic shortening occurs when progressing from CH₃COOH to CClH₂COOH. The decrease in the Rh−C distance is a consequence of the increasingly electropositive character of the Rh cation as the pK_a of the conjugate acid decreases, which leads to tighter coordination of the arene. Similarly, the decrease in the H−O1 distance occurs because the more basic acetate ligand is better able to interact with the proton at the para position of toluene. The electronegativity of the anionic ligand, however, has no effect on the length of the C−H bond. The length of the Rh−H bond is greater than 2.64 Å in all cases, and hence, there is no evidence for the formation of an agostic C−H interaction with the Rh cation, which would be characterized by a Rh−H distance of 1.9 Å or less.[20]

	R(H-O1) (Å)	R(C-H) (Å)	R(Rh-H) (Å)	R(Rh-C) (Å)	R(Rh-O2) (Å)
CH₃SO₂OH	1.35	1.31	2.40	2.17	2.23
CF₃CF₂COOH	1.34	1.31	2.42	2.21	2.10
CF₃COOH	1.38	1.28	2.40	2.17	2.11
CClF₂COOH	1.38	1.28	2.40	2.17	2.11
CCl₃COOH	1.38	1.28	2.40	2.16	2.11
CClH₂COOH	1.40	1.27	2.32	2.19	2.16
CH₃COOH	1.43	1.26	2.28	2.21	2.16

Figure 7. Structure of transition state for C−H bond activation in coordinated toluene. Selected bond distances are shown in the table.

Figure 7 shows the geometry of the transition state for the C−H bond activation step (Reaction R2), and the associated table gives the interatomic bond distances as a function of the anion composition. In all cases, the length of the C−H bond undergoing activation increases from 1.09 Å in the coordinated toluene to 1.26 Å or greater in the transition state, the length of this bond decreasing with increasing pK_a of the associated acid. The increased basicity of the ligand results in an earlier transition state during the C−H bond activation step, and hence, a smaller C−H bond distance is observed with more basic ligands. It is also evident that the distance between the activated Rh cation and the H atom decreases from 2.42 to 2.28 Å with increasing pK_a. Again, the possible contribution of agostic interactions to C−H bond activation can be eliminated because the Rh−H distance is large (2.28−2.42 Å) relative to that seen in agostic interactions (~1.9 Å).[20] These results suggest that the activation of the C−H bond in the systems studied is best described as electrophilic activation or, alternatively, as oxidative hydrogen transfer.[19]

Further evidence for the structure of the arene intermediate is supplied by the strong preference for C−H activation at the para position of toluene. Charge stabilization by the electron-donating methyl substituent on the aromatic ring favors C−H bond activation at the ortho and para positions, but significant formation of the ortho isomer is precluded by the steric bulk of the Rh complex. Consistent with this reasoning, the major reaction products were *p*-toluic acid and *m*-toluic acid, and only traces of *o*-toluic acid were observed. The para/meta (p/m) isomer ratio is shown in Figure 8 as a function of acid pK_a. As the pK_a decreases, the p/m ratio increases from 1.5 to 3.8 and then decreases to 2.3. The overall trend in selectivity reflects the inverse of the trend for $\Delta G°_{coord}$ shown in Figure 3. The maximum in the p/m ratio occurs for CF₃COOH, which also binds toluene most strongly. It has been shown previously that the preferred formation of *p*-toluic acid when the anionic ligand is CF₃COO⁻ can be attributed to the stronger coordination of toluene via the para position on the benzene ring than that via the meta position.[23] Calculations of the Mulliken charge on the C atoms at the para and meta positions on the benzene ring indicate that coordination of toluene to the Rh(III) cation in the complex enhances the difference in negative charge on the para and meta positions relative to that observed for uncoor-
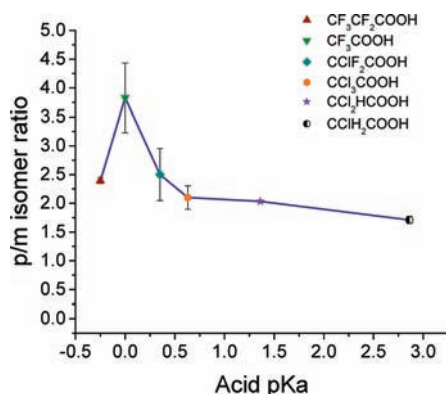
Figure 8. Acid pK_a dependence of the p/m ratio of toluic acid observed for the Rh-catalyzed oxidative carbonylation of toluene to toluic acid. Reaction conditions: 37.5 mmol (3.46 g) of toluene, 13.0 mmol of the designated acid, 3.8 mmol of the corresponding anhydride, 10 μmol (0.0039 g) of Rh(acac)$_3$, 0.5163 mmol (0.0604 g) of NH$_4$VO$_3$, P_{CO} = 0.345 MPa, P_{O_2} = 0.345 MPa, T = 353 K, t = 4 h.

dinated toluene. Similar calculations done for ligands derived from CH$_3$COOH and CF$_3$CF$_2$COOH show a smaller difference in the Mulliken charge on the C atoms in the para position relative to those in the meta position, suggesting that the difference in energies for coordination of toluene via the para and meta C atoms is smaller for catalysts that bind toluene more weakly. This reasoning leads to the conclusion that the maximum in the p/m ratio of toluic acid observed for CF$_3$COOH can be ascribed to the effect of the anion composition on the electrophilicity of the Rh cation and, in turn, the effect of the cation charge on the relative energies of toluene coordination via the para and meta C atoms of the benzene ring.

Conclusions

The results of this investigation demonstrate that the composition of the anion associated with Rh(III) can be tuned to obtain an optimum activity of the cation for oxidative carbonylation of toluene. Anions derived from acids with pK_a's between 0.0 and 0.5 exhibit the highest activities.

Theoretical analysis of the reaction for Rh(III) cations reveals that the coordination of toluene is favored by decreasing the acid pK_a; however, the activation energy and free energy for aromatic ring C–H bond activation are only weakly affected over the same range of pK_a. The difference in toluene binding strength for methanesulfonic and carboxylic acids was attributed mostly to geometric effects, with smaller contributions from polarization and charge transfer. Bond distances during the toluene–Rh coordination and in the transition state indicate the absence of an agostic interaction in the course of the reaction, which proceeds instead through an electrophilic mechanism. The identity of the ligands influences the charge density of the metal complex, which slightly alters the selectivity of the rhodium complex in favoring coordination via the para position over the meta position. Altering the characteristics of the ligands on the Rh complex therefore influences not only the activity (by balancing the ability of the complex to coordinate toluene, activate the C–H bond, and abstract the activated proton) but also the isomer selectivity (by altering the charge on the metal center relative to the carbon atoms in free toluene).

Supporting Information Available: Autoclave operation for t = 0 h; effect of quantum-mechanical theory and basis set level on calculated thermodynamic values; optimization of toluene-coordinated intermediates; Gibbs energy, rate coefficients, predicted turnover numbers, and experimental turnover numbers for anionic ligands derived from various acids; optimized geometries of toluene, catalysts, toluene-coordinated complexes, and transition states; and complete ref 25. This material is available free of charge via the Internet at http://pubs.acs.org.

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