

Rhodium-Catalyzed Arene Alkenylation Using Only Dioxygen as the Oxidant

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| ABSTRACT: We | report the oxidative conversion | on of u | nactivated arenes and H | |

alkenes to alkenyl arenes using unpurified air or purified dioxygen as the only oxidant. This method uses RhCl₃ salt as the catalyst precursor and avoids the use of co-oxidants such as Cu(II). The use of dioxygen as the *in situ* oxidant gives water as the only byproduct of the alkenylation reaction. Conditions to achieve >1000 turnovers of alkenyl benzene products have been developed. As the catalysis progresses, oxidation of styrene product to form benzaldehyde becomes competitive. Compared to the Rh catalysis using Cu(II) oxidants, the aerobic reactions give decreased reaction rate and

 $H \\ + R \\ O_{2} \\ HOAc \\ \hline Over 1000 TONs \\ \hline Simple RhCl_{3} catalyst \\ \hline Directing group free \\ \hline HOAc \\ \hline Over 1000 TONs \\$

reduced anti-Markovnikov/Markovnikov selectivity when using α -olefins. For styrene formation, the reaction rate shows a first-order dependence on catalyst concentration, ethylene concentration (with saturation at higher ethylene concentrations), and dioxygen. An intermolecular kinetic isotope effect value of 2.7(6) was determined from parallel reactions with C₆H₆ versus C₆D₆. Synthesis of *trans*-stilbene and pentenyltoluenes has been demonstrated using this Rh-catalyzed aerobic alkenylation reaction.

KEYWORDS: C-H activation, rhodium, aerobic, styrene, arene alkenylation

INTRODUCTION

Alkyl and alkenyl arenes are produced on a large scale for use in the manufacture of commodity and fine chemicals.¹⁻⁴ For example, in 2018, the global consumption of ethylbenzene was \sim 40 million tons with styrene production from ethylbenzene on a scale of \sim 38 million tons.⁵⁻⁸ Commercial synthesis of alkyl arenes, which are often precursors to alkenyl arenes, usually involves either acid-catalyzed Friedel-Crafts or zeolitemediated arene alkylation.¹⁻⁷ Both of these processes involve acidic catalysis, which can result in the generation of polyalkylated arene products.⁹ As a result, energy-intensive distillation and a transalkylation process are often required to increase the yield of monoalkylated products.⁵⁻⁷ Additionally, when using α -olefins, acid catalysts do not produce 1-aryl alkanes (i.e., anti-Markovnikov products) since the formation of carbocationic intermediates from the olefin leads to the exclusive formation of *n*-aryl alkanes (n > 1; i.e., Markovnikovproducts). Palladium-catalyzed aryl-carbon coupling reactions can produce alkyl or alkenyl arenes using aryl halides or pseudo halides, but they require arene halogenation and often a stoichiometric amount of metal-containing reagent.¹⁰⁻¹⁵

Olefin hydroarylation with unfunctionalized hydrocarbons catalyzed by molecular Ni,^{16,17} Ir,^{18–23} Ru,^{24–31} or Pt^{32–40} complexes has been demonstrated for arene alkylation using olefins. In contrast to acid-catalyzed arene alkylation, these transition metal-catalyzed olefin hydroarylation reactions generate both 1-aryl and *n*-aryl alkanes (n > 1) when using α -olefins such as propene and 1-hexene. However, these catalysts have drawbacks including low selectivity for anti-

Markovnikov products (and, in some cases, selectivity for Markovnikov products), limited catalyst longevity, and an inability to selectively produce alkenyl arenes. The recent Ni catalyst reported by Hartwig and co-workers gives exceptionally high selectivity for anti-Markovnikov alkyl arenes (>50:1 in most cases) when using α -olefins.¹⁶

Late transition-metal catalysts have been developed to convert unactivated arenes and olefins to alkenyl arenes using hydrocarbons in the presence of an oxidant (Scheme 1A). Examples of Pd- and Rh-catalyzed arene alkenylation under anaerobic conditions that require stoichiometric consumption of oxidants such as $(NH_4)_2S_2O_{87}^{41}$ AgOAc,⁴² $V_2O_{57}^{43}$ PhCO₃^tBu,⁴⁴ tBuOOH,⁴⁵ or copper(II) carboxylates^{46–50} have been reported. In addition, we previously reported that a cationic Ru(II) complex [(MeOTTM)Ru(P-(OCH₂)₃CEt)(NCMe)Ph][BAr'₄] (MeOTTM = 4,4',4"-(methoxymethanetriyl)-tris(1-benzyl-1H-1,2,3-triazole; BAr'₄ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate)) catalyzes the conversion of ethylene and benzene with 53 turnovers (TOs) of styrene with ethylene serving as an oxidant to form ethane (Scheme 1B).⁵¹ Hong and Yamazaki reported that Rh₄(CO)₁₂ catalyzes the conversion of benzene and ethylene

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Scheme 1. Arene Alkenylation Consuming Stoichiometric Oxidants (A), Ethylene (B), and Dioxygen in the Presence (C) or Absence (D) of Co-Oxidants



in the presence of carbon monoxide to give 472 TOs of styrene and 809 TOs of 3-pentanone.⁵² Recently, we demonstrated the Rh-catalyzed production of alkenyl arenes from benzene and olefins using $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ as the catalyst precursor with high TOs (>800 TOs of styrene and >1470 TOs of propenylbenzene) and near-quantitative yield (>95%) relative to the Cu(II) oxidant.^{53–55}

While the above listed reactions are important advancements, the use of dioxygen as the *in situ* and sole oxidant offers potential advantages since dioxygen is inexpensive (especially when the source is unpurified air) and the only waste is water. However, direct use of dioxygen presents challenges including the following: (1) the radical nature of dioxygen can lead to undesirable odd-electron reactions; (2) dioxygen can react with low-valent metals to generate metal oxo or peroxo products that are incapable of catalysis; and (3) mechanisms for the reaction of dioxygen to sequester reducing equivalents, such as hydrogen in this case, are not well understood.

The Matsumoto, Periana, and Fujiwara groups studied Pdand Rh-catalyzed aerobic benzene ethenylation to form styrene in which Cu(II) or Ag(I) is present as a co-oxidant and is regenerated in situ using air or dioxygen (Scheme 1C).⁵⁶⁻¹ The overall process is akin to the commercialized Wacker-Hoechst process for ethylene oxidation in which the CuCl₂ oxidant is regenerated either in situ by dioxygen or ex situ in a separate reactor by air.^{4,59} Subsequently, examples of aerobic benzene alkenylation using benzoquinone⁶⁰ or polyoxometalates⁶¹⁻⁶³ as the co-oxidant were reported. We reported conditions for the formation of styrene from benzene and ethylene catalyzed by Pd(OAc)₂ using copper(II) pivalate [Cu(OPiv)₂] in the presence of purified dioxygen to yield ~2400 TOs of styrene with >85% selectivity.64 The keys to increase selectivity for styrene are applying low ethylene pressure (20 psig) to reduce the production of undesired vinyl pivalate and high reaction temperature (180 °C) to facilitate the conversion of vinyl pivalate and benzene to styrene.⁶⁴ Also, we recently demonstrated that under optimized conditions, (5-FP)Rh(TFA)(η^2 -C₂H₄) (TFA = trifluoroacetate, 5-FP = 1,2bis(N-7-azaindolyl)benzene) can catalyze aerobic benzene alkenylation in the presence of $Cu(OPiv)_2$ with air as the *in* situ oxidant to produce >13,000 TOs of propenylbenzene products with no evidence of catalyst deactivation.⁶⁵ We developed a Rh-catalyzed aerobic alkenylation reaction for synthesis of stilbene derivatives from simple arenes and styrenes in good to high yields with good functional-group tolerance.⁶⁶ The reaction proceeds with air as a terminal

oxidant in the presence of air-recyclable copper(II) pivalate cooxidant. Unfortunately, the limited stability of the Cu(II) carboxylate co-oxidant gives rise to the formation of side products (*e.g.*, phenyl carboxylate) that result from its thermal degradation.

Pd- and Ru-catalyzed arene alkenylation using electrondeficient acrylates as the alkene source with dioxygen as the direct oxidant was reported (Schemes 1D and 2).^{67–70} Only a

Scheme 2. Metal-Catalyzed Arene Alkenylation Using Only Air or Dioxygen as Oxidant in the Absence of Co-oxidants Previous work:



B) Non-directed aerobic arene alkenylation with electron-deficient olefins

$$R^{2}$$
 + OR^{1} M OR^{1} + $H_{2}O$
Ligand
Additives

C) Non-directed aerobic arene alkenylation with unactivated olefins

$$\begin{array}{c} & & \\ & &$$

This work: Additives

D) Non-directed ligand-free aerobic arene alkenylation catalyzed by Rh(III)

| $ + \neq \frac{\text{RhCl}_{3} \cdot 3\text{H}_2\text{O}}{\text{O}_2} + \text{H}_2\text{O} $ | > 1000 TONs Ligand free Directing group free Unactivated substrates |
|--|---|
|--|---|

few examples exist for aerobic styrene production from benzene and ethylene in the absence of a co-oxidant (Scheme 2C). Shue demonstrated that $Pd(OAc)_2$ can catalyze benzene ethylation under oxygen to yield six TOs of styrene at 80 °C.⁷ Matsumoto, Periana, and co-workers reported that Pd and Rh catalysts with the addition of acetylacetone afford 47 and 23 TOs of styrene, respectively.^{56,57} Milstein and co-workers reported a Ru(II) catalyst that yields 19 TOs of styrene under dioxygen and carbon monoxide.⁷² Despite the significant advancement of these catalytic processes, they give low TOs and require high pressure of pure dioxygen and/or the use of carbon monoxide. Herein, we demonstrate a co-oxidant free aerobic benzene alkenylation with ethylene or propylene using unpurified air (and purified dioxygen) as the only oxidant (Scheme 2D) along with a discussion of limitations of the aerobic process compared to the use of Cu(II) as a co-oxidant. The newly reported aerobic method uses RhCl₃ as the catalyst precursor and does not require additional additives or ligands, and >1000 TOs of alkenyl benzene products are achieved under optimized conditions.

RESULTS AND DISCUSSION

We initially investigated RhCl₃ as a catalyst precursor for the aerobic oxidation of benzene ethenylation (Table 1). For all catalytic reactions shown in Table 1, the TOs are the average of a minimum of three experiments. Heating a 10 mL benzene solution of RhCl₃ (0.112 mM) under 70 psig of ethylene with 1 atm of air at 150 °C reveals no styrene production after 60 h (Table 1, entry1). Under these conditions, the formation of a black precipitate, presumed to be elemental Rh,⁷³ is observed.

Table 1. Optimization of the Rhodium-Catalyzed Aerobic Benzene Alkenylation Using air as an oxidant^a



| entry | volume of benzene (mL) | additives | TOs ^b |
|-------|---------------------------|--|------------------|
| 1 | 10 | | 0 |
| 2 | 10 | 2000 equiv HOAc | 70(8) |
| 3 | 10 | 2000 equiv HOPiv | 40(6) |
| 4 | 10 | 2000 equiv acetic anhydride | 46(5) |
| 5 | 10 | 2000 equiv HTFA | 0 |
| 6 | 10 | 2000 equiv NaOAc | $10(4)^{c}$ |
| 7 | 10 | 2000 equiv KOAc | $8(3)^{c}$ |
| 8 | 10 | 2000 equiv Na ₂ CO ₃ | $11(3)^{c}$ |
| 9 | 10 | 2000 equiv Na ₂ SO ₄ | $3(1)^{c}$ |
| 10 | 10 | 2000 equiv NaCl | 0 ^c |
| 11 | 10 | 2000 equiv KCl | 0 ^c |
| 12 | 5 | 5 mL HOAc | 165(17) |
| 13 | 2 | 8 mL HOAc | 186(21) |
| 14 | 8 | 2 mL HOAc | 159(29) |
| 15 | 5 | 5 mL HOAc | $153(22)^d$ |
| 16 | 5 | 5 mL HOAc | 0 ^e |
| 17 | 5 | 5 mL HOAc + 2000 equiv NaOAc | 84(19) |
| 18 | 5 | 5 mL HOAc + 2000 equiv KOAc | 96(25) |
| 19 | 5 | 5 mL HOAc + 50 equiv acetylacetone | 134(8) |
| 20 | 5 | 5 mL HOAc + 0.05 mL H_2O | 170(18) |
| 21 | 5 | 5 mL HOAc + 1 mL H ₂ O | 151(35) |
| | | | |

^{*a*}Unless otherwise noted, reaction conditions are 0.112 mM RhCl₃, 1 atm air, 70 psig C₂H₄, 60 h, and 150 °C. The reactions were sampled every 12 h until 60 h. Each data point represents the average of three separate experiments. Values in parentheses represent the standard deviations based on a minimum of three independent experiments. ^{*b*}TOs are obtained by GC-FID. ^{*c*}TO is obtained at 96 h. ^{*d*}[Rh(μ -OAc)(η^2 -C₂H₄)₂]₂ (0.112 mM Rh) used. ^{*e*}Without Rh source.

However, the addition of 2000 equiv of HOAc (relative to the Rh) under otherwise identical conditions produces 70(8) TOs of styrene at a constant rate for 60 h (Figure 1 and Table 1, entry 2) coupled with formation of trace amounts of phenyl acetate, vinyl acetate, benzaldehyde, and stilbene (<1 TO for each product) as well as 5(1) TOs of biphenyl (see Table S1). We previously reported that in the absence of a Cu(II) oxidant, the $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ catalyst precursor decomposes to Rh(0) in benzene at 90 °C under ethylene pressure.⁷³ Although the details are unknown, we speculate that HOAc suppresses reductive decomposition of the Rh catalyst to form Rh(s) by serving as a reactive oxidant. Replacing HOAc with the same amount of other carboxylic acids afforded less satisfactory results (Figure 1 and Table 1, entries 3-5). Substituting the carboxylic acid with 2000 equiv of carboxylate salts is partially effective, providing less than 12 TOs of styrene product after 96 h (Table 1, entries 6-9), whereas the use of NaCl or KCl under the identical conditions revealed no styrene production after 96 h (Table 1, entries 10 and 11). These results suggest that a carboxylate group is required for successful reaction, which we attribute to Rh-mediated benzene C-H activation via a concerted metalation-



Figure 1. Comparison of TOs vs time for aerobic benzene alkenylation with ethylene in presence of acids. Reaction conditions: 10 mL of benzene, 0.112 mM RhCl₃, 70 psig ethylene, 1 atm air, and 150 °C. Equivalents of acid or acetic anhydride are relative to RhCl₃. Each data point represents the average of three separate experiments. Error bars represent the standard deviations based on a minimum of three independent experiments.

deprotonation (CMD) mechanism that is facilitated by the presence of Rh–OCOR groups.^{74–78} Increasing the loading of acid by using benzene/acetic acid in a 1:1 (v/v) mixture increases catalytic rate (Figure 2) with 165(17) TOs of styrene



Figure 2. Comparison of TOs vs time for aerobic benzene alkenylation using different volume ratios of benzene and acetic acid. Reaction conditions: 10 mL of a benzene/acetic acid solution, 0.112 mM RhCl₃, 70 psig ethylene, 1 atm air, and 150 °C. Each data point represents the average of three separate experiments. Error bars represent the standard deviations based on a minimum of three independent experiments.

production after 60 h (Table 1, entry 12). For example, the apparent turnover frequency (TOF) after 12 h for the catalysis with 2000 equiv of HOAc is $2.5 \times 10^{-3} \text{ s}^{-1}$, while the apparent TOF at the same time point for the catalysis using a 1:1 (v/v) mixture of benzene/acetic acid is $9.7 \times 10^{-3} \text{ s}^{-1}$. Small quantities of the byproducts phenyl acetate [11(2) TOs], benzaldehyde [22(2) TOs], stilbene [4(2) TOs], and biphenyl [7(1) TOs] were also detected (Table S1). Changing the benzene/HOAc ratio (v/v) from 1:1 to 1:3 and 3:1 did not influence the catalytic performance (Figure 2 and Table 1, entries 13 and 14). Using the Rh(I) complex [Rh(μ -OAc)(η^2 -C₂H₄)₂]₂ (0.112 mM Rh) as the catalyst precursor revealed statistically identical TOs versus time plots compared to RhCl₃ catalysis under the same conditions (Table 1, entry 15, see the Supporting Information, Figure S3). This suggests that the two

Rh catalyst precursors, $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ and RhCl₃, are possibly converted into the same catalytically active Rh species under catalytic conditions. Control reactions in the absence of rhodium reveal no reaction (Table 1, entry 16).

Using 0.112 mM RhCl₃, 1:1 benzene/HOAc (v/v) solution, 70 psig C_2H_4 , and 1 atm of air at 150 °C as a standard set of conditions, the inclusion of additives such as acetylacetone or carboxylate salts does not result in an increased catalytic rate or yield (Figure 3 and Table 1, entries 17–19). Notably, adding



Figure 3. Comparison of TOs vs time for aerobic benzene alkenylation with ethylene in the absence or presence of additives. Reaction conditions: 5 mL C₆H₆, 5 mL HOAc, 0.112 mM RhCl₃, 70 psig ethylene, 1 atm air, and 150 °C. Each data point represents the average of three separate experiments. Equivalents of additives are relative to RhCl₃. Error bars represent the standard deviations based on a minimum of three independent experiments.

0.05 or 1.00 mL of distilled water has negligible impact on the rate of styrene production (Figure S5 and Table 1, entries 20 and 21). These results suggest that the catalytic reaction is not significantly influenced by the formation of water as a byproduct.

The effect of temperature on catalysis was investigated under the standard set of conditions (Figure 4). Generally, catalyst activity is increased by raising the temperature from 120 to 170 °C. However, further increasing the temperature to 180 °C (ethylene pressure was decreased to 50 psig due to the pressure limit of the Fisher–Porter reactor) led to reduced catalyst efficacy [39(9) TOs at 180 °C vs 226(31) TOs at 150 °C after 36 h]. This likely results from low solubility of ethylene in benzene at high temperature. Thus, the optimal temperature appears to be 170 °C.

Under the standard set of conditions, we probed aerobic benzene alkenylation with propylene at 150 and 170 °C (Figure 5). The catalyst is more active at 170 °C than at 150 °C, showing a similar trend to that observed in aerobic catalysis with ethylene. The catalyst is selective for anti-Markovnikov (herein, called linear) 1-phenylpropylene products over Markovnikov (branched) 2-phenylpropylene prod-



Figure 4. Effect of reaction temperature on aerobic benzene alkenylation reaction. Reaction conditions: 5 mL C_6H_6 , 5 mL HOAc, 0.112 mM RhCl₃, and 1 atm air. Each data point represents the average of three separate experiments. Error bars represent the standard deviations based on a minimum of three independent experiments.



Figure 5. Plots of TOs of total products *vs* time (A) and L/B ratio *vs* time (B) for aerobic benzene alkenylation with propylene at 150 and 170 °C. Reaction conditions: 5 mL C₆H₆, 5 mL HOAc, 0.112 mM RhCl₃, 25 psig propylene, 1 atm air, and 170 °C. Each data point represents the average of three separate experiments. Error bars represent the standard deviations based on a minimum of three independent experiments.

ucts, indicating a non-acid-catalyzed process. The linear/ branched product (L/B) ratio increases with reaction time, and the rate of increase is more rapid at 170 °C than at 150 °C. We speculated that the increase of the L/B ratio results from different rates of reaction of the four phenylpropylene products instead of the change of intrinsic catalyst L/B selectivity. To test this hypothesis, we added the four phenylpropylene products (the concentrations are approximately those of phenylpropylene products after 24 h of catalysis at 170 °C) at the beginning of a catalytic reaction using benzene and ethylene to produce styrene. As catalytic styrene production proceeds, the L/B ratio increased from an initial 5.5:1 to 8.3(3):1 after 12 h and was determined to be 35(3):1 after 36 h (Figure 6). This trend is similar to the observations in





Figure 6. Plots of *L/B* ratio of four phenylpropylene products *vs* time under catalytic conditions. Reaction conditions: 5 mL C₆H₆, 5 mL HOAc, 0.112 mM RhCl₃, 70 psig ethylene, 1 atm air, 23 equiv of allylbenzene, 9 equiv of α -methylstyrene, 3 equiv of *cis-β*-methylstyrene, 23 equiv of *trans-β*-methylstyrene, and 170 °C. Each data point represents the average of three separate experiments. Error bars represent the standard deviations based on a minimum of three independent experiments.

aerobic benzene alkenylation with propylene. Next, we speculated that the aerobic benzene alkenylation possibly produces H_2O_2 as a byproduct.^{79–81} Thus, we studied the influence of H_2O_2 on the rate of phenylpropylene consumption. The L/B ratio increases more rapidly in the presence of added H_2O_2 with the L/B ratio increasing from an initial 5.5:1 to 45(4):1 and then 144(27):1 after 36 h when 100 and 500 equiv of H₂O₂ (relative to Rh) was added at the start of the reaction (Figure 6). The isomerization of branched α -methylstyrene to linear products catalyzed by Rh could increase the observed L/B ratio. To study this possible isomerization, we added 50 equiv of α -methylstyrene (relative to Rh) at the beginning of a catalytic reaction using benzene and ethylene to produce styrene. After 36 h of reaction, linear phenylpropylene products were not observed (eq 1), indicating that the isomerization of branched α -methylstyrene to linear phenylpropylene products does not occur under the catalytic conditions.



We speculate that the observed increase in L/B ratio is controlled by the different rates of reaction of the four phenylpropylene products with H₂O₂ (k_{obs1} and k_{obs2} in Scheme 3). If k_{obs1} is smaller than k_{obs2} , α -methylstyrene will

Scheme 3. Explanation for the Increase of Observed L/BRatio during the Aerobic Benzene Alkenylation with Propylene Based on Product Reaction with Hydrogen Peroxide



be consumed more rapidly than the linear products once H_2O_2 is formed. In that case, the unreacted phenylpropylene products give rise to a higher observed *L/B* ratio than the intrinsic catalyst *L/B* selectivity, and the observed *L/B* ratio will increase over time.

When the catalyst loading is reduced to 0.022 mM RhCl_3 , 277(25) TOs of styrene can be reached accompanied by 93(12) TOs of benzaldehyde after 72 h under the standard set of conditions (Figures 7 and S6). Continued reaction for an



• Benzene:HOAc (v:v) = 9:1

Figure 7. Comparison of TOs of styrene *vs* time for aerobic benzene alkenylation with ethylene using different volume ratios of benzene and acetic acid. Reaction conditions: 10 mL of a benzene/acetic acid solution, 0.022 mM RhCl₃, 70 psig ethylene, 1 atm air, and 170 °C. Each data point represents the average of three separate experiments. Error bars represent the standard deviations based on a minimum of three independent experiments.

additional 24 h does not increase the TOs of styrene [268(37) TOs], but higher TOs of benzaldehyde [169(20) TOs] are observed. Increasing the benzene/HOAc ratio (v/v) from 1:1 to 4:1 and 9:1 increases the production of styrene. Performing catalysis with a 9:1 benzene/HOAc ratio (v/v) yields 1031(74) TOs of styrene and 353(37) TOs of benzaldehyde after 192 h (Figures 7 and S6). The formation of 341(45) TOs

of biphenyl, 72(12) TOs of PhOAc, and 119(28) TOs of stilbene were also observed (Table S1). Benzaldehyde likely forms from non-metal-catalyzed oxidative cleavage of styrene by dioxygen.⁸² We believe that as the reaction progresses, under some conditions the benzene alkenylation becomes slow likely due to catalyst deactivation, whereas benzaldehyde production from styrene becomes competitive as the amount of styrene increases.

We performed a series of kinetic studies on three reaction components (ethylene, Rh catalyst, and dioxygen; Figure 8). Under the standard set of conditions at 170 °C, a first-order dependence on ethylene concentration was revealed under ethylene pressure ranging from 25 to 50 psig (Figure 8A), and saturation kinetics were observed when the catalysis was run at ethylene pressure >50 psig (Figure 9). This is in contrast to the previously reported inverse first-order dependence on ethylene concentration for Ir(III)-,¹⁹ Pt(II)-³⁶ or Ru(II)-catalyzed²⁵ ethylene hydroarylation. For the Ir(III), Pt(II), and Ru(II) catalysts, the inverse dependence on ethylene concentration resulted from the formation of off-cycle $M(CH_2CH_2Ph)(\eta^2$ - C_2H_4) (M = cis-(acac-O,O)_2Ir, TpRu(CO) or [(^tbpy)Pt]⁺, acac = acetylacetonate, Tp = hydridotris(pyrazolyl)borate, ^tbpy = 4,4'-di-tert-butyl-2,2'-bipyridine) resting states, which block benzene coordination that is required for C-H bond activation.^{21,29,40} The rate dependence on Rh concentration is near first-order using 0.022-1.121 mM of RhCl₃ (Figure 8B), which is inconsistent with a catalytic pathway that proceeds through a binuclear Rh intermediate or transition state. To study the dependence on dioxygen pressure, we decreased the reaction temperature to 150 °C, which provides a direct comparison to previously reported Rh-catalyzed anaerobic benzene alkenylation using Cu(II) as the oxidant at 150 °C.83 A first-order dependence on dioxygen pressure using 1.0-2.5 atm of dioxygen was observed (Figure 8C). This suggests that the reaction of a Rh intermediate with the dioxygen oxidant is a kinetically relevant step. Performing aerobic catalysis in C₆H₆ and C₆D₆ independently in separate reactors shows a primary kinetic isotope effect (KIE) of 2.7(6)(Scheme 4), which is consistent with the reported values for Rh-mediated C-H activation reactions.⁸³⁻⁸⁵ The KIE result indicates that benzene C-H bond activation likely occurs before or during the rate-limiting step. Catalysis using CD₃CO₂D reveals a statistically identical rate to the catalysis using CH_3CO_2H within 12 h (Figure S11), suggesting that the proton from acetic acid is not involved in kinetically relevant steps.

Based on the experimental results, a plausible catalytic cycle for Rh-catalyzed aerobic styrene production is illustrated in Scheme 5. First, a Rh acetate species is generated through the reaction of a RhCl₃ precursor with HOAc, followed by benzene C-H activation via a CMD mechanism pathway using an acetate ligand. Ethylene coordination and migratory insertion into the Rh-Ph bond forms a Rh-CH₂CH₂Ph intermediate, which undergoes β -hydride elimination to provide styrene and a Rh-H intermediate. Next, dioxygen reacts with the Rh-H intermediate, most likely to form a Rh-OOH complex. Mechanisms for the insertion of dioxygen into late metal-hydrides, such as Pd,^{87–94} Ir,^{95–99} Rh,^{79–81,100,101} and Pt,^{102,103} to generate a metal-hydroperoxo species have been demonstrated. Protonation of Rh-OOH regenerates the catalytically active Rh-OAc intermediate and releases hydrogen peroxide. More detailed studies are needed to probe the oxidation state of the Rh catalyst and characterize possible catalytic



Figure 8. Log-log plots of (A) observed rate constants (k_{obs}) vs concentration of C_2H_4 . Reaction conditions: 5 mL C_6H_{67} 5 mL HOAc, 0.112 mM RhCl₃, 1 atm air, and 170 °C. (B) k_{obs} vs concentration of RhCl₃. Reaction conditions: 5 mL C_6H_6 , 5 mL HOAc, 70 psig C₂H₄, 1 atm air, and 170 °C. (C) k_{obs} vs pressure of O2. Reaction conditions: 5 mL C6H6, 5 mL HOAc, 70 psig C2H4, 0.112 mM RhCl₃, and 150 °C. Each reaction was run in triplicate. The reactions were sampled every 4 h until 12 h. Each trial produces styrene at a constant rate within 12 h (Figures S7-S9). Observed rate constants (k_{obs}) were extracted from the initial rate regime (from 0 to 4 h) of styrene TOs vs time plots (Figures S7-S9). The concentration of ethylene dissolved in benzene under various ethylene pressures at 170 °C was determined according to a reported method.⁸⁶ Each data point represents the average of three separate experiments. Error bars represent the standard deviations based on a minimum of three independent experiments.

intermediates, although under the oxidizing conditions, it seems likely that the Rh(III) oxidation state is maintained.

Under anaerobic conditions for Rh-catalyzed styrene production, catalysis using Cu(II) as an oxidant shows a first-order dependence on ethylene concentration over a concentration ranging from 79 to 237 mM and a near zero-

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Figure 9. Plot of k_{obs} vs $[C_2H_4]$. Reaction conditions: 5 mL C_6H_6 , 5 mL HOAc, 0.112 mM RhCl₃, 1 atm air, and 170 °C. Each data point represents the average of three separate experiments. Error bars represent the standard deviations based on a minimum of three independent experiments.

Scheme 4. Kinetic Isotope Experiment Using Two Parallel Reactions with $C_6H_6 vs C_6D_6^a$



^{*a*}Each reaction was run in triplicate. The reactions were sampled every 4 h until 12 h. Each trial produces styrene at a constant rate within 12 h (Figure S10). $k_{\rm H}$ and $k_{\rm D}$ values were determined using average initial rates (from 0 to 4 h) of three separate experiments. The reported error represents the propagated standard deviation of all values.

Scheme 5. Proposed Mechanism for Aerobic Styrene Production Using RhCl₃ as a Catalyst Precursor in the Presence of HOAc



order kinetic dependence on the concentration of Cu(II).⁸³ In addition, for comparative conversion of C_6H_6 and C_6D_6 , a primary KIE value >2.5 was observed. Based on these kinetic data, for the Cu(II) process we proposed that benzene C–H activation occurs before the rate-determining olefin insertion step, whereas the reaction of Rh with Cu(II) likely occurs after the olefin insertion step. Hence, the C–H bond activation and the reaction with ethylene are kinetically relevant to the overall catalytic process, whereas the reaction of a Rh intermediate,

likely a Rh–H, with Cu(II) is kinetically irrelevant. This also explains why the rate of catalysis is independent of the concentration of Cu(II). Similar to catalysis using Cu(II) oxidant under anaerobic conditions, Rh catalysis under aerobic conditions without Cu(II) shows a first-order dependence on ethylene concentration under ethylene pressure below 50 psig and primary KIE when comparing reaction rate using of C_6H_6 and C_6D_6 . However, a first-order dependence on the concentration of dioxygen is observed, which is in contrast with a near zero-order dependence on the concentration of Cu(II) oxidant under anaerobic conditions. These observations indicate that benzene C–H activation and the reaction of a Rh intermediate with dioxygen and with ethylene are all kinetically relevant steps. The kinetic studies are in agreement with our proposed mechanism (Scheme 6) in which C–H

Scheme 6. Comparison of Mechanistic Pathway (Top) and Reaction Coordinate (Bottom) of Rh-Catalyzed Benzene Ethylation under Aerobic and Anaerobic Conditions



activation and olefin insertion occur before the ratedetermining step, which is proposed to be the reaction of Rh-H with O2. The different kinetic dependence on the oxidant under aerobic conditions using O2 and anaerobic conditions using Cu(II) are consistent with the possibility of a slower reaction of a Rh-H intermediate with dioxygen than the analogous reaction using Cu(II) under anaerobic conditions. This could lead to a shift of rate-limiting steps from olefin insertion (under anaerobic conditions)⁸³ to net dioxygen insertion (regardless of specific mechanism) into a Rh-H bond after olefin insertion (under aerobic conditions) (Scheme 6). Assuming that changing the oxidant from Cu(II) to O2 does not affect the rate of C-H activation, olefin insertion, and β -hydride elimination (which is likely a simplification), a reduced TOF when using O_2 as the sole oxidant is expected. Consistent with this expectation, at 150 °C in the presence of 0.112 mM Rh catalyst, the maximum apparent TOF ($2.1 \times 10^{-3} \text{ s}^{-1}$, calculated based on TO after 12 h) achieved under aerobic conditions using 2.5 atm O₂ is lower than the optimized TOF ($2.8 \times 10^{-3} \text{ s}^{-1}$, calculated when maximum apparent TOF is achieved after the induction period) under anaerobic conditions using a Cu(OAc)₂ oxidant.⁷³

We recently demonstrated that anaerobic benzene propenylation catalyzed by $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ produces phenylpropylene products with ~8:1 ratio of linear 1phenylpropylene products to branched α -methylstyrene when $Cu(OAc)_2$ or $Cu(OPiv)_2$ is used as the *in situ* oxidant,⁵⁴ which is a higher L/B selectivity than Rh-catalyzed aerobic benzene propenylation presented herein. Under Curtin–Hammett conditions, the equilibrium constant between two interconverting insertion products and the relative rates of product formation after the olefin insertion step determine the selectivity between linear and branched products.⁵⁵ Based on our hypothesis that the reaction involves the dioxygen oxidant after the olefin insertion step is the rate-limiting step under aerobic conditions, we speculate that L/B selectivity is controlled by K_{eq} in Scheme 7 and the relative ΔG^{\ddagger} for the

Scheme 7. Possible Explanation for Different Linear/ Branched Product Selectivity of Aerobic and Anaerobic Rh Catalysis



rates of subsequent steps (Scheme 7; L/B ratio = $k_1 K_{eq}/k_2$). In contrast, under anaerobic conditions, L/B ratio is likely governed by the kinetic selectivity of rate-limiting olefin insertion (Scheme 7; L/B ratio = k_3/k_4). Therefore, the change in rate-limiting steps is likely responsible for the decreased L/B selectivity under aerobic conditions.

We explored the versatility of the Rh-catalyzed aerobic alkenylation by probing substituted olefins and arenes. We have reported a Rh-catalyzed alkenylation reaction for synthesis of stilbene derivatives from arenes and styrenes using a sub-stoichiometric amount of Cu(II) carboxylate as a co-oxidant, which is regenerated by air.⁶⁶ Using this aerobic alkenylation protocol, *trans*-stilbene can be prepared from benzene and styrene in 43(1)% yield after 60 h (Scheme 8).

Scheme 8. Rh-Catalyzed Aerobic Benzene Alkenylation with Styrene to Produce *trans*-Stilbene^{*a*}



"Reaction conditions: 9 mL benzene, 1 mL acetic acid, 0.5 mmol styrene, 0.560 mM RhCl₃, 1 atm air, and 170 °C. Yields, which were determined by GC, represent the average of three separate experiments based on the amount of styrene. The standard deviations given in parentheses are based on three independent experiments.

For this aerobic reaction, 24(1)% of styrene was converted to benzaldehyde, which limits the yield of the stilbene product. Also, we have demonstrated Rh-catalyzed alkenylation of toluene with 1-pentene using Cu(II) oxidant to form *meta-* and *para-*substituted 1-pentenyltoluenes and 2-pentenyltoluenes.⁴⁸ Under the aerobic alkenylation conditions, 1-pentene and toluene were transformed into the desired 1-pentenyltoluenes and 2-pentenyltoluenes. Upon hydrogenation, 108(8) TOs of pentyltoluenes with *L/B* ratio (*i.e.*, 1-pentyltoluenes/2pentyltoluenes) of 7(1):1 and a *meta/para/ortho* ratio of ~15:7:1 (Scheme 9) were obtained.

Scheme 9. Rh-Catalyzed Aerobic Alkenylation of Toluene with 1-Pentenea



^{*a*}Reaction conditions: 9 mL toluene, 1 mL acetic acid, 2000 equiv of 1-pentene relative to Rh, 0.112 mM RhCl₃, 1 atm air, and 170 °C. Hydrogenation was achieved using 10% Pd/C under hydrogen atmosphere. The reaction was run in triplicate. The standard deviations given in parentheses are based on three independent experiments. The L/B ratio in the graphic is the ratio of anti-Markovnikov to Markovnikov products.

SUMMARY AND CONCLUSIONS

In conclusion, we have developed a Rh-catalyzed stepeconomical aerobic benzene alkenylation reaction that produces H₂O as the sole byproduct from the oxidation step. Notable hallmarks include the following: (1) the catalysis uses commercially available RhCl₃ salt as catalyst precursor in the absence of additional additives and ligand, (2) the catalysis can use unpurified air or oxygen as the sole oxidant and does not require other co-oxidants, (3) the Rh catalysts can achieve a TON >1000 under optimized conditions. A first-order dependence on O2 oxidant was observed, which is indicative of a kinetically relevant O2 oxidation step. Based on this hypothesis, the reduced L/B selectivity relative to the anaerobic Rh catalysis using Cu(II) oxidants is likely a result of Curtin-Hammett conditions. The aerobic alkenylation protocol is successfully applied to synthesis of trans-stilbene from benzene and styrene and conversion of toluene and 1pentene to pentenyltoluenes. Targets for future catalyst improvement include enhancing catalyst reactivity, which would allow a lower reaction temperature to potentially inhibit benzaldehyde formation.

EXPERIMENTAL SECTION

General Considerations. Glovebox purity was maintained by periodic nitrogen purges and was monitored by an oxygen analyzer (O_2 concentration was <15 ppm for all reactions). Benzene was dried by passage through columns of activated alumina. Benzene- d_6 was used as received and stored under a N₂ atmosphere over 4 Å molecular sieves. Ethylene, propylene, hydrogen, and dioxygen were purchased in gas cylinders from GTS-Welco and used as received. Rhodium trichloride trihydrate was purchased from Pressure Chemical and used as received. All other reagents were purchased from commercial sources and used as received. [Rh(μ -OAc)(η^2 - $(C_2H_4)_2]_2$ was prepared according to a literature procedure.⁵ GC-FID was performed using a Shimadzu GC-2014 system with a 30 m \times 90.25 mm HP5 column with 0.25 μ m film thickness. Gas chromatography-mass spectrometry (GC-MS) was performed using a Shimadzu GCMS-QP2010 Plus instrument with a 30 m × 0.25 mm SHRXI-5MS column with a 0.25 μ m thickness using electron impact ionization was used. The mixture of hydrocarbons and air is flammable and potentially explosive. We advise taking proper safety precaution (e.g., blast shield, burst valves for pressure relief) and avoiding any possible ignition source.

To analyze reaction mixture samples by GC-FID, the reactors were cooled to room temperature, sampled under N_{2} , recharged with gases, and reheated. For reaction mixtures containing the internal standard hexamethylbenzene, aliquots of the reaction mixture (<100 μ L) were sampled, diluted with benzene (0.25 mL), and washed with saturated sodium carbonate solution (0.25 mL). The aqueous and organic layers were separated. The resulting organic layers were analyzed by GC-FID. The reaction mixtures without the internal standard hexamethylbenzene required addition of external hexamethylbenzene while sampling. A stock solution containing hexamethylbenzene (0.0364 g, 0.2243 mmol) and benzene (100 mL) was prepared in a volumetric flask. 100 μ L of the reaction mixture and 0.5 mL of stock solution were measured by microsyringes and combined together. Aliquots of the resulting solution (<100 μ L) were washed with saturated sodium carbonate solution (0.25 mL). The aqueous and organic layers were separated. The resulting organic layers were analyzed by GC-FID.

Vinyl acetate, styrene, benzaldehyde, phenyl acetate, biphenyl, *trans*-stilbene, allylbenzene, α -methylstyrene, *cis-\beta*-methylstyrene, and *trans-\beta*-methylstyrene production were quantified using linear regression analysis of gas chromatograms of standard samples of authentic products. A plot of peak area ratios versus molar ratios gave a regression line using hexamethylbenzene as the internal standard. The slopes and correlation coefficients of the regression lines were 5.83 and 0.99 (vinyl acetate), 1.78 and 0.99 (styrene), 2.24 and 0.99 (benzaldehyde), 1.67 and 0.99 (phenyl acetate), 1.07 and 0.99 (biphenyl), 0.87 and 0.99 (*trans*-stilbene), 1.40 and 0.99 (allylbenzene), 1.23 and 0.99 (α -methylstyrene), 1.47 and 0.99 (*cis-\beta*-methylstyrene), and 1.38 and 0.99 (*trans-\beta*-methylstyrene), respectively.

To analyze reaction mixture samples by GC-MS, plots of peak areas versus molar ratios gave regression lines using

cyclooctane as the internal standard. 1-Tolyl-1-pentane production was quantified using linear regression analysis of gas chromatograms of standard samples of authentic products. The slope and correlation coefficient of the regression lines were 1.34 and 0.998 (1-*m*-tolyl-1-pentane), 1.85 and 0.997 (1*p*-tolyl-1-pentane), and 1.84 and 0.998 (1-*o*-tolyl-1-pentane), respectively. The production of 2-tolyl-2-pentenes was quantified by using the slope and correlation coefficient for a fit of cumene versus *n*-propylbenzene, which enabled an approximation of the ratio of 1-tolyl-1-pentenes to 2-tolyl-2pentenes. The slope and correlation coefficient of the regression line were 1.24 and 0.98 for cumene versus *n*propylbenzene, respectively.

Catalytic Alkenylation of Benzene with Ethylene and Propylene Using RhCl₃ as the Catalyst Precursor and Air or Dioxygen as the Oxidant. A representative catalytic reaction is described here. Under air, a stock solution containing rhodium chloride trihydrate (0.0118 g, 0.0449 mmol) and distilled water (2 mL) was prepared in a volumetric flask. Fisher-Porter reactors were charged with 0.05 mL of stock solution (contains 0.0011 mmol Rh) and placed under dynamic vacuum at 40 °C for 2 h to remove water. The Fisher-Porter reactors were then brought into the glovebox and charged with hexamethylbenzene (0.0182 g, 0.1121 mmol), additives (2000 equiv of relative to per Rh), and benzene (10 mL) or a benzene (5 mL)/acetic acid (5 mL)mixture. The vessels were sealed, purged with air or dioxygen, and pressurized with ethylene (70 psig) or propylene (25 psig). For the reaction under 60, 50, 40, 30, or 20 psig ethylene, after being charged with air and ethylene, the vessels were subsequently pressurized with N₂ up to 80 psig as the top pressure. Then the reactors were stirred and heated to 150 or 170 °C. The reaction mixtures without the internal standard hexamethylbenzene required addition of external hexamethylbenzene while sampling. Since the mixture of hydrocarbon gas and air/O₂ is flammable and explosive, it is important to be aware of explosive limits. The lower and upper explosive limits (LEL and UEL) of ethylene and propylene in air are 2.7 and 36.0 for ethylene and 2.0 and 11.1 for propylene (concentrations in percent by volume), respectively.¹⁰⁴ In our reactions with air, ethylene in the reactors is at a concentration in air higher than the UEL. Thus, the mixture of hydrocarbon gas and air under our conditions will be outside the explosive region. We advise taking proper safety precaution (e.g., blast shield, burst valves for pressure relief) and avoiding any possible ignition source in reactions with air or O2. The reactions were sampled every 12 h until 60 h or every 4 h until 12 h. The resulting product mixture was analyzed by GC-FID.

Catalytic Alkenylation of Benzene with Ethylene and Propylene Using $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ as the Catalyst Precursor and Air or Dioxygen as the Oxidant. In the glovebox, a stock solution containing $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ (0.0111 g, 0.0224 mmol), hexamethylbenzene (0.3640 g, 2.2430 mmol), and benzene (100 mL) was prepared in a volumetric flask. Fisher–Porter reactors were charged with the stock solution (5 mL) and acetic acid (5 mL). The vessels were sealed, purged with air (1 atm) and pressurized with ethylene (70 psig), and subsequently stirred and heated to 150 °C. The mixture of hydrocarbon gas and air is flammable and explosive; we advise taking proper safety precaution (*e.g.*, blast shield, burst valves for pressure relief) and avoiding any possible ignition source. The reactions were sampled every 12 h until 60 h. The resulting product mixture was analyzed by GC-FID.

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Notes

The authors declare no competing financial interest.

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Catalytic Alkenylation of Benzene with Styrene Using RhCl₃ as the Catalyst Precursor and Air as the Oxidant. Under air, a stock solution containing rhodium(III) chloride trihydrate (0.059 g, 0.224 mmol) and distilled water (2 mL) was prepared in a volumetric flask. Fisher–Porter reactors were charged with 0.05 mL of the stock solution (0.0056 mmol Rh) and placed under dynamic vacuum at 40 °C for 2 h to remove water. The Fisher–Porter reactors were then brought into the glovebox and charged with benzene (9 mL), styrene (0.5 mmol), and acetic acid (1 mL). The vessels were sealed, purged with air, and pressurized with dinitrogen. The mixtures were stirred and heated to 170 °C. The reactions were sampled at 60 h. The resulting product mixture was analyzed by GC–FID.

Catalytic Alkenylation of Toluene with 1-Pentene Using RhCl₃ as the Catalyst Precursor and Air as the **Oxidant.** Under air, a stock solution containing rhodium(III) chloride trihydrate (0.0118 g, 0.0449 mmol) and distilled water (2 mL) was prepared in a volumetric flask. Fisher-Porter reactors were charged with 0.05 mL of the stock solution (0.0011 mmol Rh) and placed under dynamic vacuum at 40 °C for 2 h to remove water. The Fisher-Porter reactors were then brought into the glovebox and charged with toluene (9 mL), 1-pentene (2000 equiv relative to Rh), and acetic acid (1 mL). The vessels were sealed, purged with air, and pressurized with dinitrogen. The mixtures were stirred and heated to 170 °C. The reactions were sampled at 36 h. A stock solution containing cyclooctane (63 μ L, 50 equiv relative to Rh) and benzene (10 mL) was prepared in a volumetric flask. Next, 200 μ L of the reaction mixture and 200 μ L of the stock solution were measured and combined. Aliquots of the resulting solution (<200 μ L) were washed with saturated sodium carbonate solution (0.25 mL). The aqueous and organic layers were separated. The resulting organic layers were subjected to hydrogenation.

Hydrogenation Procedure. A Fischer–Porter reactor was charged with aliquots of the reaction mixture, 8 mg of 10% Pd/C and 4 mL of ethanol. The vessels were sealed and pressurized with 100 psi of H_2 after the headspace was evacuated. The reactor was stirred at room temperature overnight. The resulting product mixture was analyzed by GC–MS.

ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.0c03439.

Details of catalyst studies including kinetic plots (PDF)

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