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The Nature of the Catalytically Active Species in Olefin Dioxygenation with $PhI(OAc)_2$: Metal or Proton?

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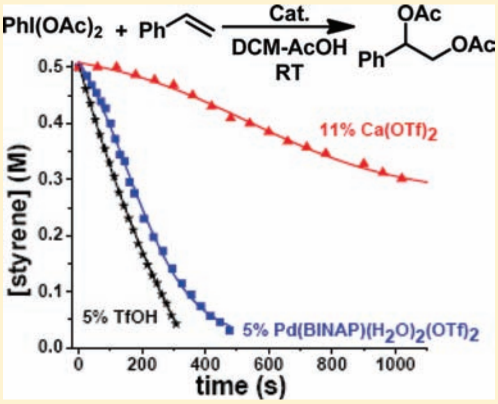
S *Supporting Information*

ABSTRACT: Evidence for the protiocatalytic nature of the diacetoxylation of alkenes using $PhI(OAc)_2$ as oxidant is presented. Systematic studies into the catalytic activity in the presence of proton-trapping and metal-complexing agents indicate that protons act as catalysts in the reaction. Using triflic acid as catalyst, the selectivity and reaction rate of the conversion is similar or superior to most efficient metal-based catalysts. Metal cations, such as Pd(II) and Cu(II), may interact with the oxidant in the initiation phase of the catalytic transformation; however, 1 equiv of strong acid is produced in the first cycle which then functions as the active catalyst. Based on a kinetic study as well as in situ mass spectrometry, a mechanistic cycle for the proton-catalyzed reaction, which is consistent with all experimental data presented in this work, is proposed.

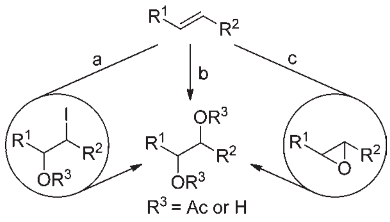


INTRODUCTION

There are several classical methods for the dioxygenation of alkenes that are still widely used in organic synthesis. These include two-step-reactions, such as the Woodward−Prevost reaction (pathway a, Scheme 1)[1] and the epoxidation followed by ring-opening (pathway c).[2] Both operate under relatively mild reaction conditions, even though the former is not a catalytic reaction. The one-step dioxygenation of alkenes catalyzed by OsO_4,[3] along with its asymmetric version, the Sharpless dihydroxylation,[4] are among the most widely used methods but involve an expensive and highly toxic catalyst (pathway b). The development of new efficient catalytic dioxygenation methods for alkenes has therefore remained a challenge.

In recent years, there has been considerable interest in the development of alternative dihydroxylation protocols involving other metal catalysts. With the emergence of palladium(IV) chemistry in catalysis,[5−13] the dioxygenation of alkenes has been reinvestigated using Pd- or Cu-catalysts instead of the very toxic osmium.[14] Very recently, Dong et al. reported a $Pd(OTf)_2$-catalyzed diacetoxylation of alkenes using $PhI(OAc)_2$[15−18] as oxidant.[14a] In this case, a cationic palladium complex with electron-rich diphosphines as ligands as well as the use of the anionic triflato ligand were claimed to be essential for the reaction because, for instance, $Pd(OAc)_2$ itself was found to be inert. Although a Pd^{IV} intermediate was invoked in the proposed catalytic cycle for this reaction, no detailed mechanistic investigations were carried out. Related diacetoxylations were also observed as leading to undesired side products in Pd-catalyzed amino acetoxylations.[6h] It is notable that Chai and co-workers reported the same type of reaction for a copper(II) catalyst, in which the triflate counterion also proved to be essential. In this case, all other copper salts tested, such as $Cu(OAc)_2$ and $CuCl_2$, were catalytically inert.[14b] Claims for a mechanism involving Cu^{III} intermediates were based on in situ high resolution mass spectrometry. However, closer inspection of the data revealed significant discrepancies between the expected and observed data, along with the observation of many other unassigned ion peaks, which make this interpretation questionable.

Scheme 1. Approaches for Dioxygenation or Diacetoxylation of Alkenes



R^3 = Ac or H

a. Woodward-Prevost, I_2 or I^-, [O].

b. OsO_4, $KMnO_4$ or RuO_4, *etc.*

c. [O], Cat., AcOH

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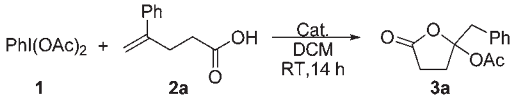
Table 1. Catalyst Screening of Metal Salts and Brønsted Acids[a]



(1)

entry	catalyst	loading (mol %)	% conv[b]	entry	catalyst	loading (mol %)	% conv[b]
1	$Ni(ClO_4)_2 \cdot 6H_2O$	1	100	17[d]	$Pd(OAc)_2$	1	6
2	$Ni(ClO_4)_2 \cdot 6H_2O$	0.1	94	18[d]	$Cu(OAc)_2$	1	2
3	$Ni(ClO_4)_2 \cdot 6H_2O$	0.05	88	19[d]	$CuCl_2$	1	7
4	$Ni(ClO_4)_2 \cdot 6H_2O$	0.01	10	20[g]	$Ca(ClO_4)_2 \cdot 4H_2O$	10	99
5	$Ni(ClO_4)_2 \cdot 6H_2O$	0.001	3.8	21[g]	$Ca(OTf)_2$	10	99
6	$Ni(ClO_4)_2 \cdot 6H_2O$	0.0001	1	22[d]	$CaCl_2$	10	2
7[c]	$Ni(Cl)_2 \cdot$ glyme	5	6	23	$Mg(OTf)_2$	10	100
8[d]	$Cu(OTf)_2$	0.5	99	24	$Mg(ClO_4)_2 \cdot 6H_2O$	10	100
9[e]	$Co(BF_4)_2$	10	99	25[d,g]	$Ba(ClO_4)_2$(99.999%)	1	100
10[f,d]	$Pd(L)(H_2O)_2(OTf)_2$	1	99	26[d,g]	$Ba(ClO_4)_2$(99.999%)	0.1	23
11[f,d]	$Pd(L)(H_2O)_2(OTf)_2$	0.5	96	27	acetic acid (>99.99%)	175	7
12[f,d]	$Pd(L)(H_2O)_2(OTf)_2$	0.25	95	28[g]	$HClO_4$(99.999%)	0.1	93
13[f,d]	$Pd(L)(H_2O)_2(OTf)_2$	0.1	95	29[g]	triflic acid (99%)	0.1	88
14[f,d]	$Pd(L)(H_2O)_2(OTf)_2$	0.03	43	30	trifluoroacetic acid	0.1	2
15[f,d]	$Pd(L)(H_2O)_2(OTf)_2$	0.01	3	31	HCl	0.1	2
16[f,d]	$Pd(L)(H_2O)_2(OTf)_2$	0.001	2	32	4-CF_3-benzoic acid	0.1	2

[a] Reaction conditions: **1** (0.13) mmol; **2a** (0.1 mmol); CH_2Cl_2 (1 mL). **3a** forms after a rearrangement of phenyl group in the reaction (see ref 19 for details). [b] Determined by 600 MHz ^1H NMR. [c] Refers to $NiCl_2{-}CH_3OCH_2CH_2OCH_3$. [d] Reaction time: 20 min. [e] $Co(BF_4)_2 \cdot 6H_2O$ was used. [f] (*R*)-BINAP-$Pd(H_2O)_2(OTf)_2$ was used. [g] ICP-OES measurements show the trace amount of metals: Cu <1 ppm and Pd <5 ppm; see Supporting Information for details.

The nature of the active catalyst in both the palladium- and copper-catalyzed diacetoxylations thus remains to be resolved. However, this point is essential for the further development of the method as a synthetic tool. In view of this uncertainty, we set out to further explore the mechanism of dioxygenation reaction of alkenes using $PhI(OAc)_2$ as oxidant and to identify the active catalyst(s). In this work, we provide new mechanistic insight into this reaction, both its intramolecular and intermolecular version, the catalytically active species involved, and the key role that triflate may play as a weakly coordinating anionic ligand or counterion.

RESULTS AND DISCUSSION

Screening of Metal Salts for Catalytic Activity in the Intramolecular Diacetoxylation of Alkenes. As indicated, both palladium and copper salts have been reported as catalysts for the diacetoxylation of alkenes. It was thus essential to establish to which degree these two metals were necessary, or in fact, whether a metal-based catalyst in general was an indispensible prerequisite. The results of the screening of metal salts and complexes for the intramolecular diacetoxylation represented in eq 1 are summarized in Table 1. Besides $Cu(OTf)_2$ and $Pd(OTf)_2$, other transition metal Lewis acids such as $Ni(ClO_4)_2$ and $Co(BF_4)_2$ were also found to be efficient catalysts, while the corresponding salts with more basic or strongly coordinating counterions, such as $Pd(OAc)_2$, $Cu(OAc)_2$, $CuCl_2$, and $NiCl_2$, proved to be inactive.

Surprisingly, we found that alkali earth metal salts also displayed catalytic activity (entries 20−26). For instance, using 0.1 mol % of extremely pure $Ba(ClO_4)_2$, a full conversion of **2a** was obtained within 20 min (entry 26). ICP-OES analysis of the calcium and barium salts established that traces of copper and palladium in these salts, if present, were well below the 1 and 5 ppm level, respectively (Supporting Information). Since at these concentrations none of the transition metal salts was found to be active, "hidden" catalysis by these metals may be ruled out.

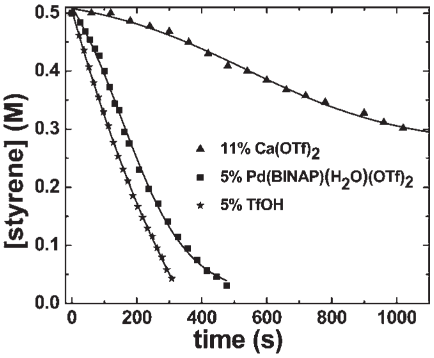


Figure 1. The comparison of the conversion curves for the Pd-, Ca-, and TfOH-catalyzed diacetoxylation of styrene. Note that no inflection point was seen for the triflic acid-catalyzed transformation.

A similar behavior was observed for the intermolecular diacetoxylation of styrene with $PhI(OAc)_2$ (eq 2). For comparison the conversion curves for the Pd-, Ca-, and TfOH-catalyzed reaction are displayed in Figure 1, using 5 mol % of HOTf and [(*R*)-BINAP-$Pd(H_2O)_2(OTf)_2$] as well as 11 mol % of $Ca(OTf)_2$. First of all, we note that the $Ca(OTf)_2$ catalysis occurs with much lower activity and that [(*R*)-BINAP-$Pd(H_2O)_2(OTf)_2$] and HOTf display very similar activities at the same catalyst loading. However, the metal-catalyzed reactions are characterized by sigmoidal conversion curves which may indicate the (reversible) generation of the catalytically active species in the initial stages of the reaction and its gradual disappearance near the end.

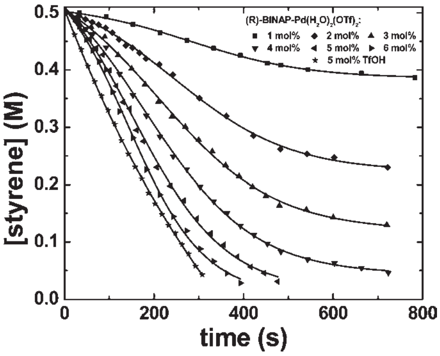


Figure 2. The comparison of the catalytic conversion curves for the diacetoxylation of styrene with $PhI(OAc)_2$ as oxidant, obtained for different amounts of $[(R)\text{-BINAP-Pd}(H_2O)_2(OTf)_2]$ and compared to 5% of TfOH as catalyst.

It is clear from these results that high valent Pd^{IV} or Cu^{III} are not necessarily involved in the catalytic diacetoxylation with $PhI(OAc)_2$. Remarkably, several Brønsted acids proved to catalyze the reaction, albeit under very specific conditions. We note that in a previous study of a noncatalytic version of this reaction[19] no conversion had been observed in the presence of a dilute acidic solution. In our investigations of the reaction, very low activity and conversion was found in the presence of AcOH (175 mol %, entry 27), while 0.1 mol % of $HClO_4$ or HOTf gave rise to complete conversion (entries 28 and 29). Again, ICP-OES analyses of the acids established levels of Cu and Pd of below 1 and 5 ppm, thus again ruling out hidden metal catalysis. However, under the same reaction conditions, other strong acids only induced very low conversions (entries 30−32), thus raising the question as to the specificity of the observed acid catalysis.

Both metal salts as well as triflic and perchloric acid thus appear to catalyze the diacetoxylation. The nature of the actual catalytically active species in these reactions therefore remains to be resolved and, in particular, whether there might be a common underlying principle. In Figure 2 the conversion curves of the $[(R)\text{-BINAP-Pd}(H_2O)_2(OTf)_2]$-catalyzed diacetoxylation of styrene with $PhI(OAc)_2$ as oxidant (eq 2) are compared for different Pd catalyst loadings (and with HOTf). At all catalyst loadings, the sigmoidal characteristics of the conversion curves, already noticed in Figure 1, are found. At the point of inflection, the activity of the Pd catalyst is essentially the same as that of HOTf at an equal catalyst loading (in this case: 5 mol %). It appears that for the Pd catalyst, the active species, which we propose to be the "excess" proton, is being formed initially, an aspect that will be further discussed below.

Proton-Trapping Study. To investigate the possible catalytic role of protons in this dioxygenation reaction, proton-trapping agents were added to the reaction in eq 1 for various catalysts. As shown in Table 2, the intramolecular reference reaction catalyzed by HOTf was effectively inhibited by either 5 mol % of proton sponge (*N*,*N*,*N*′,*N*′-tetramethyl-1,8-naphthalenediamine) or 100 mol % of Bu_4NOAc (entries 2 and 4).

On the other hand, EDTA as neutral tetracarboxylic acid, which was added as a metal complexation agent, had no inhibitive effect on the $Cu(OTf)_2$, $Ba(ClO_4)_2$, and $(R)\text{-BINAP-Pd}(H_2O)_2(OTf)_2$-catalyzed dioxygenation (entries 9, 15, and 21), while the ligand EDTA itself (in its neutral, protonated form) was inactive (entry 6). This indicated that the scavenging of the metal by a complexone did not impede the activity of the system. On the other hand, both proton-sponge and Bu_4NOAc were efficient inhibitors for the $Cu(OTf)_2$-, $Pd(OTf)_2$-, and $Ba(ClO_4)_2$-catalyzed reaction (entries 10−13, 16−19, 22−24) in the presence or absence of EDTA.

Table 2. Proton-Trapping Study on the Intramolecular Reaction[a]

entry	catalyst	additive	% conv[b]
1	HOTf	–	99
2	HOTf	5% H-sponge	<4
3	HOTf	20% Bu_4NOAc	33
4	HOTf	100% Bu_4NOAc	11
5	HOTf	200% Bu_4NOAc	1
6	EDTA	–	0
7	AcOH	–	0
8	$Cu(OTf)_2$	–	99
9[c]	$Cu(OTf)_2$	1% EDTA	99
10[c]	$Cu(OTf)_2$	1% EDTA+5% H-sponge	0
11	$Cu(OTf)_2$	5% H-sponge	0
12	$Cu(OTf)_2$	20% Bu_4NOAc	7
13	$Cu(OTf)_2$	100% Bu_4NOAc	0
14	$Ba(ClO_4)_2$	–	99
15[c]	$Ba(ClO_4)_2$	1% EDTA	99
16[c]	$Ba(ClO_4)_2$	1% EDTA+5% H-sponge	0
17	$Ba(ClO_4)_2$	5% H-sponge	0
18	$Ba(ClO_4)_2$	20% Bu_4NOAc	23
19	$Ba(ClO_4)_2$	50% Bu_4NOAc	<1
20[d]	$Pd(L)(H_2O)_2(OTf)_2$	–	99
21[c,d]	$Pd(L)(H_2O)_2(OTf)_2$	1% EDTA	99
22[c,d]	$Pd(L)(H_2O)_2(OTf)_2$	1% EDTA+5% H-sponge	<1
23[d]	$Pd(L)(H_2O)_2(OTf)_2$	5% H-sponge	<1
24[d]	$Pd(L)(H_2O)_2(OTf)_2$	20% Bu_4NOAc	6

[a] Reaction conditions: **1** (0.13 mmol); **2a** (0.1 mmol); catalyst (1 mol %); CH_2Cl_2 (1 mL); 20 min. Proton sponge refers to *N*,*N*,*N*′,*N*′-tetramethyl-1,8-naphthalenediamine. [b] Determined by 600 MHz ^1H NMR. [c] Added as neutral tetracarboxylic acid. [d] $(R)\text{-BINAP-Pd}(H_2O)_2(OTf)_2$ was used.

Analogous proton-trapping experiments were carried out for the intermolecular dioxygenation of styrene with iodobenzene diacetate (eq 2). This reaction proceeded smoothly in the presence of 5 mol % of HOTf to give 97% conversion at room temperature within 6 h (Table 3, entry 1). When proton sponge or Bu_4NOAc were added at the outset, no conversion was observed even after 24 h. In the cases of $Cu(OTf)_2$ and $Pd(OTf)_2$, the proton traps also efficiently suppressed the reaction, and $Cu(OAc)_2$ as well as $Pd(OAc)_2$, containing the basic acetate as counteranion, were found to be inactive as noted in previous studies.[14]

In Figure 3 the conversion curves of the $[(R)\text{-BINAP-Pd}(H_2O)_2(OTf)_2]$-catalyzed diacetoxylation of styrene with or without an equivalent amount of $Bu_4N(OAc)$ are displayed. We note that 1 mol of added base essentially quenches 1 mol of Pd catalyst. This would be consistent with a mechanistic scenario, in which the catalytically active proton is generated in a first reaction step of the metal complex with the oxygenation agent $PhI(OAc)_2$ (vide infra) and is trapped if additional acetate is present.

Substrate Scope of the Metal Catalysts and the Proton. The observations made in the catalyst screening suggested the possibility of the proton alone acting as a catalytically active

Table 3. Proton-Trapping Study on the Intermolecular Reaction of Styrene with Iodobenzene Diacetate

entry	catalyst	additive (mol %)	t, h	% conv
1	HOTf (5 mol %)	–	6	97
2	HOTf (5 mol %)	6 mol % H-sponge	24	0
3	HOTf (5 mol %)	100 mol % Bu_4NOAc	24	0
4	HOTf (5 mol %)	6 mol % Bu_4NOAc	24	0
5	$Cu(OTf)_2$ (5 mol %)	–	4	44
6	$Cu(OTf)_2$ (5 mol %)	6 mol % Bu_4NOAc	4	32
7	$Cu(OTf)_2$ (5 mol %)	12 mol % Bu_4NOAc	24	0
8	$Cu(OTf)_2$ (5 mol %)	6 mol % H-sponge	4	36
9	$Cu(OTf)_2$(5 mol %)	12 mol % H-sponge	24	0
10	(R)BINAP-$Pd(H_2O)_2(OTf)_2$ (5 mol %)	–	4	66
11	(R)BINAP-$Pd(H_2O)_2(OTf)_2$ (5 mol %)	6 mol % H-sponge	24	0
12	(R)BINAP-$Pd(H_2O)_2(OTf)_2$ (5 mol %)	6 mol % Bu_4NOAc	24	0
13	$Pd(OAc)_2$ (5 mol %)	–	4	0
14	$CuCl_2$ (5 mol %)	–	4	0
15	$Cu(OAc)_2$ (5 mol %)	–	4	0

[a] Reaction conditions: **1** (0.5 mmol); **2** (0.25 mmol); CH_2Cl_2 (0.5 mL); AcOH (12.5 μL). [b] Determined by 600 MHz ^{1}H NMR.

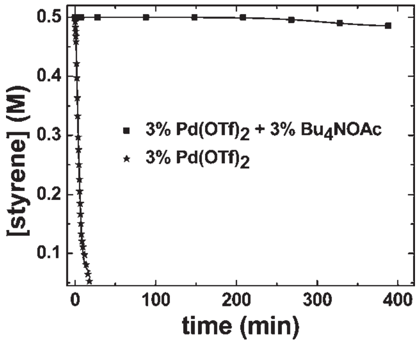


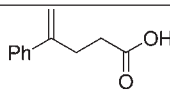
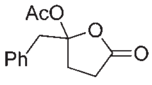
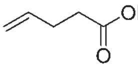
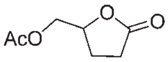
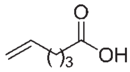
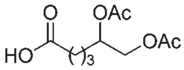
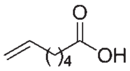
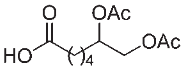
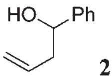
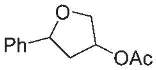
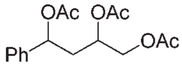
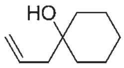
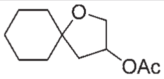
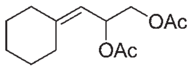
Figure 3. The comparison of the [(*R*)-BINAP-$Pd(H_2O)_2(OTf)_2$]-catalyzed (3 mol %) diacetoxylation of styrene with or without an equivalent amount of Bu_4NOAc: 1 mol of added base essentially quenches 1 mol of Pd catalyst.

species in the diacetoxylation of alkenes with iodobenzene diacetate. Therefore, the generality of the catalytic capability of protons in this type of reaction had to be established and compared to previous observations made in the apparent metal catalysis.[14] As shown in Table 4, both copper triflate and triflic acid itself were efficient, the latter possessing only trace amounts of transition metals (<1 ppm of Co, Cu, and Ni, <5 ppm of Pd). The less reactive substrates required acetic acid as solvent and elevated reaction temperatures (entries 3−9). For the substrates in entries 4 and 5 possessing longer chains between the carboxyl and acetyloxy groups, both cyclic and acyclic products were observed by ^{1}H NMR. To avoid this problem, water was added to the reaction mixture, which was subsequently worked up by treatment with acetic anhydride to obtain clean diacetoxylations of the terminal alkenes. By tuning the reaction conditions with or without addition of water, both the cyclic ethers and the acyclic diacetoxylation products were obtained, respectively (entries 6 and 7). The cyclizations involving carboxyl groups, giving lactones, proceeded more cleanly compared to those of hydroxyl groups, yielding cyclic ethers that may be due to the elimination of water as a side reaction. Notably, the latter occurred exclusively in the diacetoxylation of 1-allylcyclohexanol **2f** in the presence of water (entry 9).

As far as the *intermolecular* version of this reaction is concerned, triflic acid was efficient for a variety of alkenes. In a comparative study, HOTf gave the same or better yields and diastereoselectivities than the $Pd(OTf)_2$ or $Cu(OTf)_2$ catalysts (entries 1−4, Table 5). The reactions were carried out with or without water in glacial acetic acid, giving the same yields but quite different diastereoselectivities (entries 3 and 4). As discussed below, a possible explanation is the reaction of a nonmetalated cyclic cationic intermediate with water, generating a nonacetylated hydroxyl group, which in turn is transformed to OAc after treatment with acetic anhydride in the workup (vide infra).[14a] Both *cis*- and *trans*-stilbene gave the syn-diastereomer as the major product (entries 1−6), which may be due to an intramolecular rotation within the cationic intermediate. Cyclic and terminal aliphatic alkenes also gave good yields and diastereoselectivities (entries 7 and 8 and entries 14 and 15) as did styrene itself and its derivates (entries 9 and 10). The reaction in wet acetic acid gave the 2-hydroxyl derivative (entries 11 and 13), underscoring the interpretation of the role of water given above. In the presence of water in acetic acid, very similar diastereoselectivites were obtained as reported in ref 14a. However, in dry acetic acid, diastereoselectivities decreased, probably due to the change in the attacking nucleophile. For example, *cis*-stilbene afforded the diacetoxylation products with the ratio of syn/anti of 10/1 and 6/1 in our case (entry 4, Table 5) and in ref14a, respectively. When the reactions were carried out in dry acetic acid, in contrast, very low diastereoselectivities were observed both with the palladium catalyst or triflic acid (entries 2 and 3). Finally, the dioxygenation of α,*β*-unsaturated ester **4k** also gave the corresponding reaction product in moderate yield (entry 16).

It is instructive to compare the results obtained in this study for the intra- and intermolecular diacetoxylations/dioxygenations summarized in Tables 4 and 5 using triflic acid as catalyst to those obtained previously as well as in our own study as a result of

Table 4. Intramolecular Diacetoxylations of Alkenes with Iodobenzene Diacetate[a]

entry	substrate	product	catalyst	solvent	t/h	T/°C	%yld[b]
1[c]	 **2a**	 **3a**	$Cu(OTf)_2$(1%)	DCM	1	RT	99
2[c]			HOTf(1%)	DCM	1	RT	99
3	 **2b**	 **3b**	HOTf(5%)	AcOH	17	80	99
4	 **2c**	 **3c**	HOTf(5%)[d]	AcOH	24	80	99
5	 **2d**	 **3d**	HOTf(5%)[d]	AcOH	24	80	94
6	 **2e**	 **3e**	HOTf(5%)	AcOH	72	50	72 (dr1.2/1)
7		 **3f**	HOTf(5%)[d]	AcOH	5	50	82 (dr1.6/1)
8	 **2f**	 **3g**	HOTf(5%)	AcOH	5	50	83[e]
9		 **3h**	HOTf(5%)[d]	AcOH	5	50	81

[a] Reaction conditions: **1** (0.65 mmol); **2** (0.50 mmol); solvent (1 mL). [b] Isolated yield. [c] Reaction product **3a** is formed by a rearrangement step following the initial diacetoxylation; see ref 19. [d] With 3 equiv of H_2O; after reaction, if treated with acetic anhydride, OH was transformed to OAc. [e] Using 1.0 mmol of **2** and 0.2 mL of AcOH.

catalysis by a palladium triflato complex[14a] as well as copper triflate.[14b] The *intramolecular* dioxygenation of **2e** with triflic acid (entry 7, Table 4) gave the reaction product in 72% yield compared to 78% and 80% yield reported in the literature using phosphine palladium triflate and copper triflate as catalysts, respectively.[14a,b] Furthermore, the dioxygenation of **2f** catalyzed by triflic acid led to almost the same yield of the reaction product as the Pd(dppp)$(H_2O)_2(OTf)_2$ catalyst reported by Dong et al.[14a] For the *intermolecular* diacetoxylation reaction, very similar results were obtained under the same reaction conditions. For example, the diacetoxylation of styrene catalyzed by Pd(dppp)-$(H_2O)_2(OTf)_2$, copper triflate, and triflic acid (entry 9, table 5) at room temperature gave the corresponding reaction products in 90%, 80% (at 40 °C), and 91% yields, respectively. The diacetoxylations of **4b**, **4i**, and **4j** catalyzed by triflic acid (Table 5) gave the same or higher yields and diastereoselectivities (same major diastereomers) as those catalyzed by the palladium and copper triflate catalysts.[14a,b] In conclusion, in both the intra- and intermolecular diacetoxylations, triflic acid always gave comparable yields and diastereoselectivities to those obtained with the metal triflato complexes. Assuming a general catalytic principal for this transformation, this further supports the aforementioned hypothesis that the diacetoxylation of alkenes with iodobenzene diacetate is a proton-catalyzed reaction.

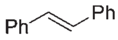
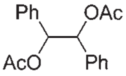
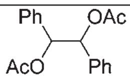
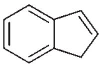
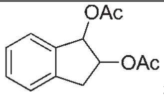
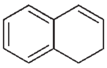
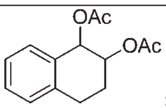
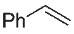
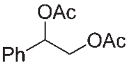
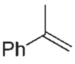
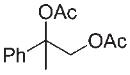
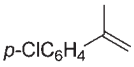
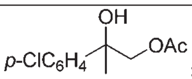
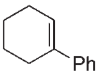
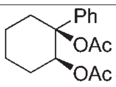
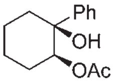
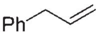
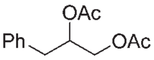
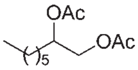
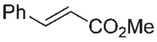
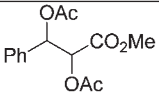
Kinetic Study of the HOTf-Catalyzed Diacetoxylation of Styrene with Iodobenzene Diacetate. The diacetoxylation of styrene with iodobenzene diacetate may be conveniently followed by ^{1}H NMR which was employed in a kinetic study using added 2-bromo-1,3-xylene as internal standard. This established a first-order dependence of the reaction rate on both the concentration of HOTf (Figure 4) and the oxidant $PhI(OAc)_2$ (Figure5).

Remarkably, zeroth order dependence on the reaction rate was established for the substrate styrene (Figure 6), indicating a mechanism in which the rate-determining step precedes the interaction of the oxidant with the olefin.

In Situ Mass Spectra and Discussion of a Potential Reaction Mechanism. In situ high resolution ESI mass spectra recorded during the diacetoxylation of styrene and α-methylstyrene are depicted in Figure 7A and 7B, respectively. Samples were taken 1−5 min after mixing of the reagents and diluted with CH_3CN prior to the injection into the mass spectrometer.

First of all, we note the presence of peaks at m/z = 262.95635, 344.95942, and 260.93336, which are assigned to the ions $[PhI(OAc)]^+$, $[PhI(OAc)_2 - Na]^+$, and $[PhI(OAc)_2 - K]^+$, respectively. All three species are derived from the oxidizing agent alone and were also found previously in ESI mass spectra of $PhI(OAc)_2$.[20] Notably, an additional mass peak in Figure 7A at

Table 5. Intermolecular Diacetoxylations of Alkenes with Iodobenzene Diacetate [a]

entry	substrate	product	cat.(5%)	t/h	T/°C	%yld[b]	dr(syn/anti)
1	 **4b**	 **5b**	$Cu(OTf)_2$	2	50	66	1.4/1
2			$Pd(OTf)_2$[c]	2	50	79	1/1
3			HOTf	2	50	80	1.5/1
4			HOTf[d]	2	50	80	10/1
5	 **4c**	 **5b**	HOTf	2	50	99	1.7/1
6			HOTf[d]	2	50	99	4/1
7	 **4d**	 **5c**	HOTf	1	RT	86	1/5.3
8	 **4e**	 **5d**	HOTf	1	RT	86	1/4
9	 **4a**	 **5a**	HOTf	2	RT	91	-
10	 **4f**	 **5e**	HOTf	1	RT	61	-
11	 **4g**	 **5f**	HOTf[d]	2	RT	65	-
12	 **4h**	 **5g**	HOTf	2	RT	74	>99/1
13		 **5h**	HOTf[d]	2	RT	62	>99/1
14	 **4i**	 **5i**	HOTf[d]	5	50	99	
15	1-octene **4j**	 **5j**	HOTf[d]	5	50	100	
16	 **4k**	 **5k**	HOTf	48	70	52	1/0.7

[a] Reaction conditions: **1** (0.65 mmol); **4** (0.50 mmol); AcOH (1 mL). [b] Isolated yield. [c] (*R*)-BINAP-$Pd(H_2O)_2(OTf)_2$ was used. [d] With 3 equiv of H_2O; after reaction, if treated with acetic anhydride, OH was transformed to OAc.

m/*z* = 306.99782 and the corresponding peak in Figure 7B at *m*/*z* = 321.01347 are assigned to $[PhCCH_2(IPh)]^+$ and $[Ph(Me)CCH_2(IPh)]^+$, respectively, which are species generated by the interaction of the oxidant with styrene and α-methylstyrene. They are thought to be derived from one of the key intermediates in the catalytic cycle for the proton-catalyzed diacetoxylation of alkenes.

The proposed mechanism of the catalytic cycle for the diacetoxylation of styrene (as example of alkene substrates in general) is represented in Scheme 2. Upon protonation of iodobenzene diacetate, one molecule of AcOH is eliminated, giving rise to the cationic intermediate **A**. The possibility of the protolytic formation of **A** has been previously demonstrated and is supported by a series of X-ray crystal structure determinations

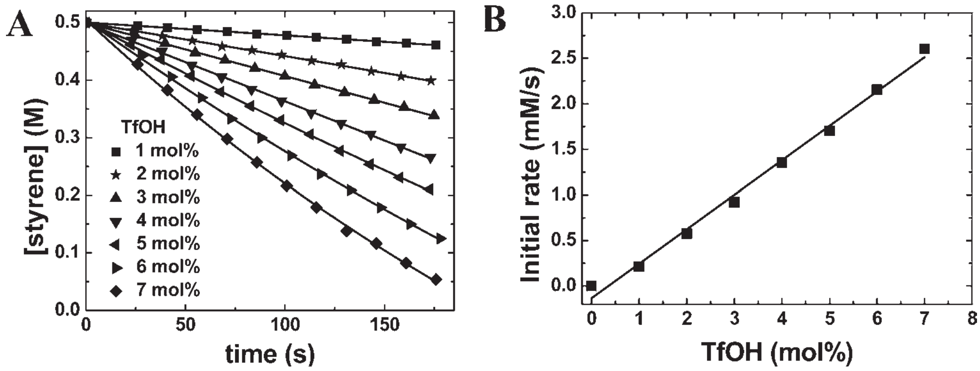


Figure 4. Dependence of the initial rate on TfOH: (A) Plots of [styrene] vs time using TfOH; (B) initial rate vs TfOH (mol %). Initial rates were calculated as the slopes of time zero using Originlab software. Reaction conditions (initial): [styrene] = 0.50 M (0.25 mmol), $[PhI(OAc)_2]$ = 0.7 M, TfOH (1−7 mol %), AcOH (5.0 M), CD_2Cl_2, RT, recorded on 600 MHz ^1H NMR.

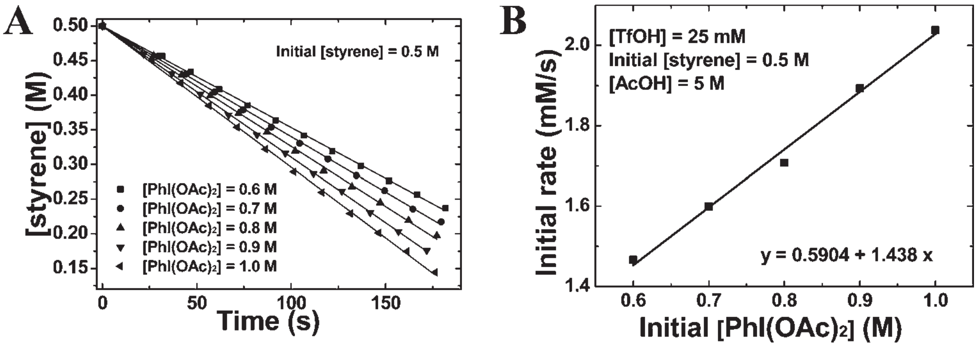


Figure 5. Dependence of initial rate on initial $[PhI(OAc)_2]$: (A) Plots of [styrene] vs time and (B) initial rate vs initial $[PhI(OAc)_2]$. Initial rates were calculated as the slopes of time zero using Originlab software. Reaction conditions: [styrene] = 0.50 M, $[PhI(OAc)_2]$ = 0.6−1.0 M, [TfOH] = 25 mM, AcOH (5.0 M), CD_2Cl_2, RT, recorded on 600 MHz ^1H NMR.

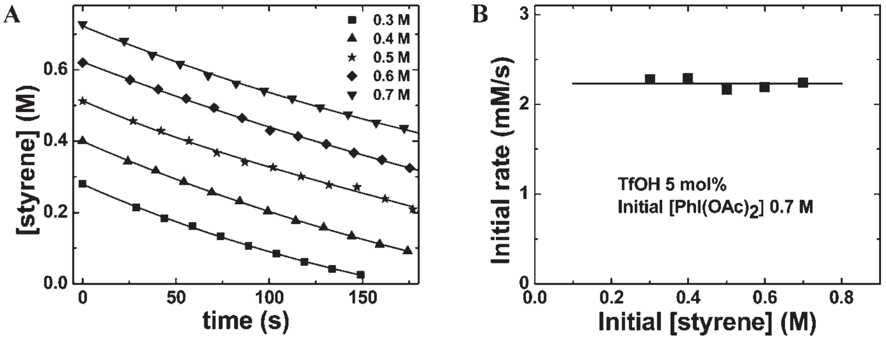


Figure 6. Dependence of initial rate on initial [styrene]: (A) Plots of [styrene] vs time, (B) initial rate vs initial [styrene]. Initial rates were calculated as the slopes of time zero using Originlab software. Reaction conditions: [styrene] = 0.30−0.70 M, $[PhI(OAc)_2]$ = 0.7 M, [TfOH] = 25 mM, AcOH (5.0 M), CD_2Cl_2, RT, recorded on 600 MHz ^1H NMR.

of such species reported by Ochiai and co-workers.[21] The cation **A** was also observed in the HRMS-ESI study discussed above and was previously found in the HRMS-ESI mass spectra of $PhI(OAc)_2$.[20] Our kinetic study established first-order dependence of the reaction rate on the concentration of added triflic acid as well as oxidant but zeroth order dependence on the concentration of the alkene. This suggests that the formation of **A** is the rate-determining step in the catalytic cycle and that the cationic iodoso reagent is rapidly trapped by the alkene (in this case styrene) to form **B**. As indicated in the previous section, the formation of **B** is supported by the observation of the peak m/z = 306.99782 and the corresponding peak at m/z = 321.01347 in the in situ recorded HR mass spectra from the diacetoxylation of styrene and α-methylstyrene. These mass peaks are assigned to $[PhCCH_2(IPh)]^+$ and $[Ph(Me)CCH_2(IPh)]^+$, respectively, which are probably formed by elimination of AcOH from **B** under the conditions of the HRMS experiments.

In the following step, intermediate **B** could be attacked by acetate either from acetic acid attacking externally (pathway b) or, in an intramolecular rearrangement, from OAc in **B** (pathway a), and both intermediates could form the cyclic intermediate **E**,

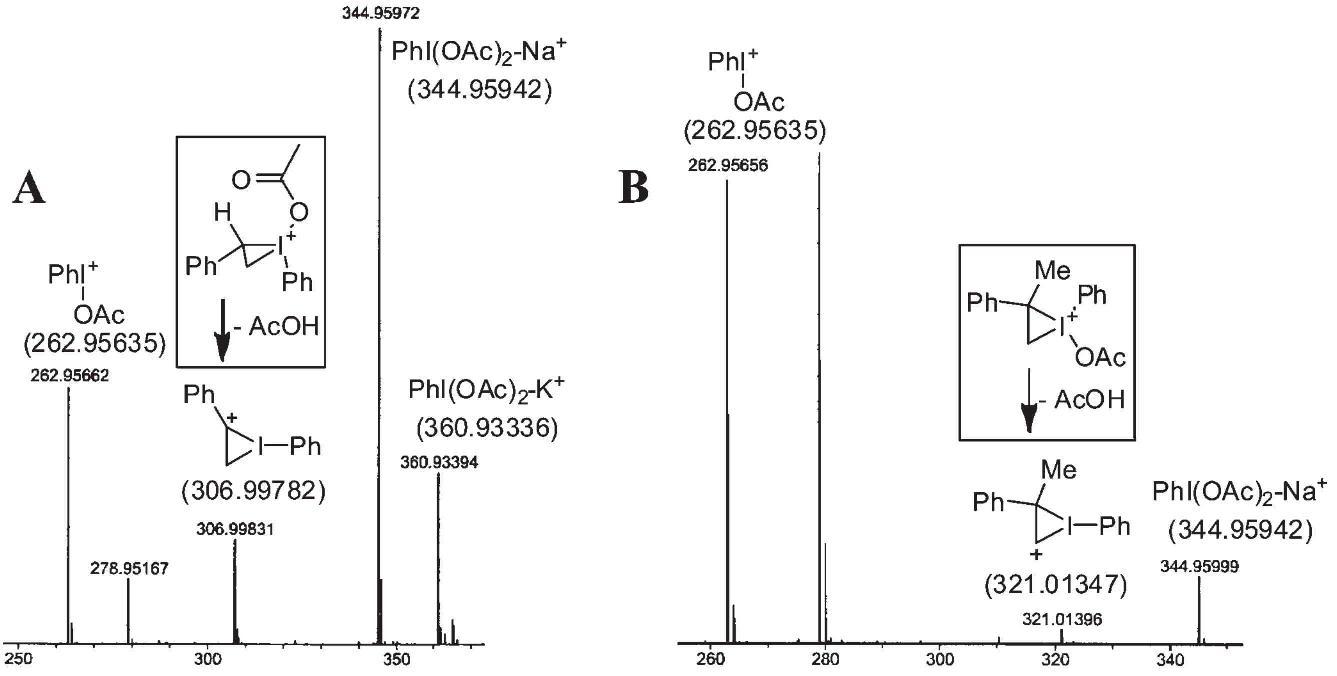
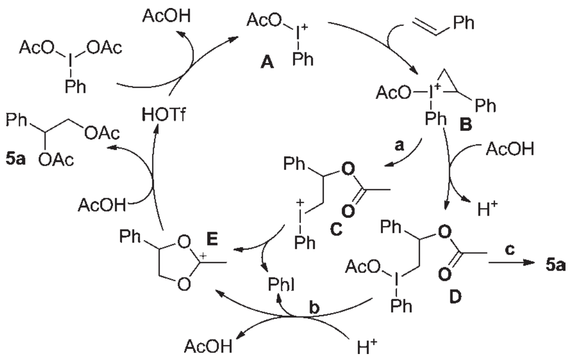


Figure 7. HRMS-ESI experiments for reaction solutions. Reaction conditions: styrene or α-methylstyrene (0.125 mmol), $PhI(OAc)_2$ (0.25 mmol), TfOH (1 M in AcOH, 50 μL), AcOH (0.45 mL), RT, 1−5 min, diluted with CH_3CN before HRMS-ESI tests.

Scheme 2. Proposed Mechanism for the TfOH-Catalyzed Intermolecular Diacetoxylation of Styrene Based on the Evidence Presented in This Work



which had also been proposed by Dong et al. in the published catalytic cycle based on a Pd^{II}/Pd^{IV} catalytic system.[14a] Finally, the cyclic cation is attacked by AcOH to afford the diacetoxylation product along with with the liberation of a proton which then acts as catalyst in the next cycle.

What remains to be addressed is the role played by the metal dications/metal complexes which catalyze the diacetoxylation of alkenes. The sigmoidal behavior of the conversion curves and the observation of a point of inflection provide an indication that the catalytically active species is being generated during an initiation step. This may be the formation of the cationic key intermediate **A**, the generation of which is initially catalyzed by the Lewis acidic metal dications. In the following reaction steps, one excess proton is generated provided that the metal salt or metal complex does not contain a basic counterion such as acetate. The excess proton(s) then act as (more active) catalyst in the subsequent reaction cycle, thus making the proton the effective catalyst also in these cases as demonstrated by the absence of any catalytic activity in the presence of proton-capturing agents. Finally, the presence of chlorido or other potentially coordinating ligands, in turn, will suppress the formation of **A** due to recombination with the cation and thus deactivation of the actual oxidizing agent.

■ CONCLUSION

In this work, we have provided evidence for the protiocatalytic nature of the diacetoxylation of alkenes using $PhI(OAc)_2$ as oxidant. Metal cations, such as Pd(II) and Cu(II), may interact with the oxidant in the initiation phase of the catalytic transformation; however, 1 equiv of strong acid is produced in the first cycle which then functions as the active catalyst. A mechanistic cycle for the protiocatalytic reaction, which is consistent with all experimental data presented in this work, has been proposed. Based on this discovery of proton catalysis for the reaction at hand, we developed the intra- and intermolecular triflic acid-catalyzed dioxygenation for a range of alkene substrates.

On the basis of our observations, particular care has to be taken in the interpretation of metal catalysis involving $Ph(OAc)_2$ as a substrate. It is clear that Pd-catalyzed reactions[6] performed under basic conditions are not explicable by a simple protolytic scheme as put forward in this work.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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