

Oxidative coupling of methyl benzoate with palladium/heteropolyacid catalysts

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Abstract

The oxidative coupling of methyl benzoate in the presence of a catalyst system comprising of Pd(OAc)₂ and a vanadium-containing heteropolyacid produced 2,2'-biphenic acid dimethyl ester with a high selectivity. The mode of coordination of methyl benzoate to palladium and the non-coordinating nature of the heteropolyacid appeared to be responsible for the unusual selectivity. Addition of Hg(OAc)₂ or triphenyl phosphine increased greatly the conversion of methyl benzoate without impairing the selectivity to the 2,2'-isomer. The catalyst deactivated with reaction time, mainly due to water produced from the reaction.

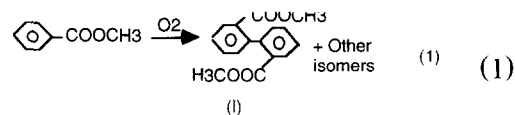
Keywords: Oxidative coupling; Methyl benzoate; Palladium/heteropolyacid catalyst; Selectivity

1. Introduction

The oxidative coupling of aromatic compounds is a useful route to the synthesis of biphenyl derivatives [1–14]. Ube Industries [12–15] have been operating the commercial production of tetramethyl 3,4,3',4'-biphenyltetracarboxylate by the oxidative coupling of dimethyl phthalate under the presence of a homogeneous catalyst system composed of palladium acetate Pd(OAc)₂, copper acetate Cu(OAc)₂, and 1,10-phenanthroline (phen). The addition of phen as a ligand (Pd:phen = 1:1) enhanced the catalytic activity and suppressed the formation of by-products, namely 2,3,3',4'

and 2,3,2',3' isomers. The tetramethyl 3,4,3',4'-biphenyltetracarboxylate is a building block of polyimides which are used as a thermostable film.

In a study of Pd-catalyzed oxidative coupling of various aromatic compounds, we found that a catalyst system of Pd(OAc)₂–heteropolyacid (HPA) promoted the selective conversion of methyl benzoate into 2,2'-biphenic acid dimethyl ester (I).



The compound has been produced commercially from phenanthroline in a stoichiometric reaction

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with potassium permanganate or chromate [16]. The high price of the materials and the toxicity of the oxidants have posed problems in the process. There have been a number of reports on the oxidative coupling of aromatic compounds catalyzed by Pd/HPA catalysts [9–11,17,18]. Heteropolyacids with the composition of $H_{(3+n)}PMo_{(12-n)}V_nO_{40}$ ($n = 2–6$) were found to be the most efficient, like in other cases where, in order to make use of their reversible oxidizability, HPA was employed as a reoxidant of palladium in a catalytic cycle similar to the Wacker chemistry [17–19]. $Hg(OAc)_2$ was often employed as a promoter in these homogeneous, liquid phase catalytic systems in order to improve activity and/or selectivity to 4,4'- and 3,4'-isomers [8,10]. Yet, to the best of our knowledge, there has been no report of unusual selectivity to the 2,2'-isomer in the oxidative coupling of aromatic compounds in the presence of Pd/HPA catalysts. This paper discusses the characteristics of this interesting catalytic system.

2. Experimental

Reagents employed for reactants and catalysts were used as received. Heteropolyacids were synthesized according to the standard procedure described by Tsigdinos and coworkers [20]. As a typical synthetic procedure to prepare $H_9PMo_6V_6O_{40} \cdot nH_2O$, 26.8 g $Na_2HPO_4 \cdot 2H_2O$ and 145.2 g $Na_2MoO_4 \cdot 2H_2O$ were dissolved in 700 ml water by mixing at 60°C for 0.5 h, and combined with a solution prepared by dissolving $NaVO_3$ (81.3 g) and $NaOH$ (25.3 g) into 500 ml water. The resulting solution was stirred vigorously at 80°C for 1 h, and 271 g of 35% HCl solution was added dropwise over 4 h to obtain a dark red solution. The solution was filtered to remove impurities and cooled to room temperature. The heteropolyacid was then extracted with 400 ml diethyl ether and 10 ml 35% HCl in a 1 l separating funnel. In this extraction, the heteropolyetherate was present as

a middle layer. After separation, a 80 ml water was added and a stream of He was passed through the heteropolyetherate layer to free it of ether. 131.3 g of $H_9PMo_6V_6O_{40} \cdot nH_2O$ was obtained as orange crystals in a desiccator over concentrated H_2SO_4 . Different HPA were prepared by employing different reagents or composition. The Keggin structure of the synthesized HPA was confirmed by the presence of the characteristic twin infrared peaks at 600–1100 cm^{-1} [21].

The coupling reaction was conducted in a 50 ml three-necked round flask equipped with a magnetic stirrer, a reflux condenser cooled by cooling water at $-10^\circ C$, a thermocouple inside a thermowell, and a gas inlet tube immersed into the reaction solution. The reaction temperature was regulated within $\pm 1^\circ C$ with a PID temperature controller. The reaction solution containing catalysts and reactants was heated to a desired reaction temperature within 0.5 h while O_2 was continuously bubbled through the reaction mixture. The products were analyzed by a gas chromatograph (HP 5890 II) equipped with an FID and a DB-1 capillary column (0.25 mm ID, 50 m). The identification of each isomer was accomplished with NMR (Bruker AC80) after separation with HPLC and column chromatography. The identification for 2,2'- and 4,4'-isomers was also confirmed by the gas chromatography analysis of commercial authentic samples (Tokyo Kasei)

3. Results

The oxidative coupling of methyl benzoate in the presence of Pd/HPA produced the expected six isomers of biphenyl dicarboxylic acid dimethyl esters without significant formation of other compounds. All these isomers were positively identified by NMR analysis of each isomer isolated, by HPLC and column chromatography. When either $Pd(OAc)$ or HPA was omitted from the reaction mixture, the reaction did not proceed. The same was true when O_2 bub-

Table 1

Effect of heteropolyacids in the oxidative coupling of methyl benzoate to biphenyl dicarboxylic acid dimethyl esters catalyzed by palladium acetate^a

Heteropolyacid	Conv. (%)	Isomer distribution (%) ^b					
		2,2'-	2,3'-	2,4'-	3,3'-	3,4'-	4,4'-
H ₃ PMo ₁₂ O ₄₀	0.48	67.4	22.6	5.0	—	5.0	—
H ₅ PMo ₉ V ₃ O ₄₀	3.28	76.2	14.6	5.3	0.8	2.2	—
H ₅ PMo ₁₀ V ₂ O ₄₀	3.69	77.2	14.3	3.5	2.3	2.7	—
Ditto (120°C)	5.26	67.2	22.3	3.2	2.7	3.5	1.1
Ditto (150°C)	6.93	53.1	30.2	7.4	5.0	2.1	2.2
H ₄ PMo ₁₁ AsO ₄₀	0.76	80.7	16.5	2.8	—	—	—
H ₄ SiMo ₁₂ O ₄₀	0.78	66.3	12.8	1.3	—	19.6	—
H ₅ SiMo ₁₁ VO ₄₀	2.51	75.1	7.1	1.5	—	16.3	—
H ₅ PW ₁₀ V ₂ O ₄₀	0.05	58.0	—	—	—	42.0	—
H ₄ AsMo ₁₂ O ₄₀	1.49	83.5	10.2	2.4	—	3.9	—

^aMethyl benzoate, 122.6 mmol; Pd(OAc)₂, 0.08 mmol; HPA, 1 g; T = 100°C unless otherwise specified; 1 atm; air flow 100 ml/min; reaction time 12 h.

^bIsomers of biphenyl dicarboxylic acid dimethyl ester.

bling was replaced with N₂ bubbling. Thus, the reaction described in Eq. (1) was indeed occurring in the presence of Pd/HPA catalysts.

The effect of different HPA in Pd(OAc)₂-catalyzed oxidative coupling of methyl benzoate was studied at 100°C and the results are shown in Table 1. For all HPA, the 2,2'-isomer of biphenyl dicarboxylic acid dimethyl esters (I) was the main product with a selectivity of 53–84% and a substantial amount of 2,3'-isomer was produced. The concentration of 4,4'-isomer was negligible. Different HPA exhibited different catalytic activity as reflected in different conversions of methyl benzoate. All active catalysts contained both vanadium and molybdenum. The effect of heteroatoms (P, Si, or As) was not significant. Under the present conditions, 1% conversion of methyl benzoate corresponds to a turnover number with respect to Pd (molecules of methyl benzoate converted per molecules of Pd(OAc)₂ introduced) of 15.3. Since the amount of employed HPA was ca. 0.12 mmol, the catalysts had turned over enough times with respect to HPA to establish the fact that the reaction was catalytic. As the reaction temperature increased, the selectivity to 2,2'-isomer decreased as exemplified for H₅PMo₁₀V₂O₄₀.

The effect of the quantity of HPA is shown for H₅PMo₁₀V₂O₄₀ in Fig. 1. The methyl benzoate conversion increased initially with increasing amounts of HPA, but did not show any further effect once its quantity went above ca. 0.1 mmol for 0.08 mmol of Pd(OAc)₂. The selectivity to the 2,2'-isomer showed an initial decrease and then was stabilized with increasing amounts of HPA.

In order to understand the salient features of the present reaction system, some control experiments described in Table 2 were performed. In experiment 1, the oxidative coupling of methyl benzoate was carried out in the presence of Pd(OAc)₂/Cu(OAc)₂/phen catalyst. As mentioned earlier, this catalyst system is known to be employed by Ube Industries in the commercial production of biphenyltetracarboxylate by the oxidative coupling of dimethyl phthalate [12–15]. Compared to a typical result of methyl benzoate coupling with Pd(OAc)₂/HPA catalyst (experiment 2a), this catalyst system showed a similar methyl benzoate conversion, but completely different product distribution. The 3,4'-, 4,4'-, and 3,3'-isomers were dominant products with the Pd(OAc)₂/Cu(OAc)₂/phen catalyst whereas Pd(OAc)₂/HPA catalyst produced mostly 2,2'- and 2,3'-isomers. When Hg(OAc)₂ or triphenyl phosphine was added to Pd(OAc)₂/HPA catalyst, a marked improve-

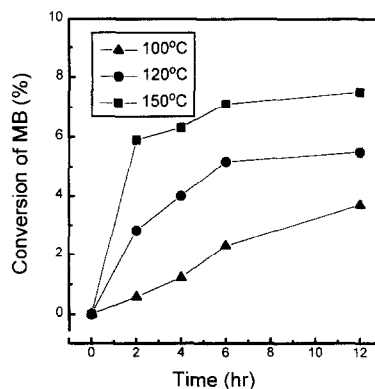


Fig. 1. The effect of the amount of H₅PMo₁₀V₂O₄₀ on the conversion of methyl benzoate and selectivity to 2,2'-biphenic acid dimethyl acid. Pd(OAc)₂: 0.08 mmol; initial charge of methyl benzoate: 123 mmol; air flow: 100 ml/min; 120°C; 6 h.

Table 2
Some control experiments for aryl coupling catalyzed by palladium acetate

Experiment No. ^a	Conv. (%)	Isomer distribution (%)					
		2,2'-	2,3'-	2,4'-	3,3'-	3,4'-	4,4'-
1	4.04	—	3.2	1.4	16.3	53.2	25.9
2a	5.33	79.6	18.2	0.8	0.9	0.5	—
2b	15.3	72.1	18.3	8.6	0.4	0.6	—
2c	12.9	75.6	10.2	4.2	4.3	5.7	—
3	0.31	9.9	12.1	5.4	13.2	36.3	23.1
4	0.18	n.a. ^b	n.a. ^b	n.a. ^b	n.a. ^b	24.7	40.5

^aDescription of experiments: (1) Pd(OAc)₂ (0.4 mmol)/Cu(OAc)₂ (0.12 mmol)/1,10 Phenanthroline (0.4 mmol) catalyst system. Methyl benzoate, 122.6 mol; 195°C; 1 atm; air flow 200 ml/min; reaction time 12 h. (2a) Pd(OAc)₂ (0.08 mmol)/H₆PMo₉V₃O₄₀ (0.4 g) catalyst system. Methyl benzoate, 122.6 mmol; 120°C; 1 atm; air flow 100 ml/min; reaction time 6 h. (2b) (2a)+0.32 mmol of Hg(OAc)₂. (2c) (2a)+0.08 mmol of triphenyl phosphene. (3) Toluene (87 mmol) coupling. Pd(OAc)₂ (0.04 mmol)/H₆PMo₉V₃O₄₀ (0.2 g) catalyst system. 80°C; 1 atm; air flow 150 ml/min; reaction time 6 h. (4) Anisole (200 mmol) coupling. Pd(OAc)₂ (0.08 mmol)/H₆PMo₉V₃O₄₀ (0.4 g) catalyst system. 120°C; 1 atm; air flow 150 ml/min; reaction time 6 h.

^bNot available due to unresolved GC peaks (total area 34.8%).

ment in methyl benzoate conversion was observed without significant change in the isomer distribution (experiments 2b and 2c). When toluene or anisole was employed as a substrate in the presence of Pd(OAc)₂/HPA catalyst, the conversion was lower and the product distribution shifted towards 3,4'- and 4,4'-isomers (experiments 3 and 4).

Fig. 2 shows the change with time of the reaction in the conversion of methyl benzoate

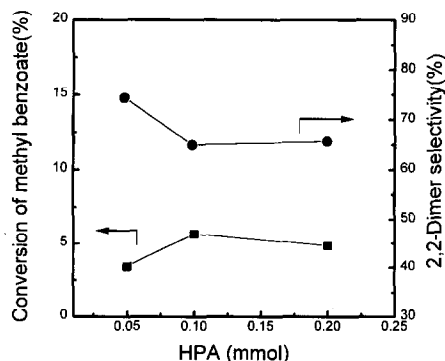


Fig. 2. The effect of reaction temperature on the conversion of methyl benzoate. Pd(OAc)₂: 0.08 mmol; H₅PMo₁₀V₂O₄₀: 0.11 mmol; initial charge of methyl benzoate, 123 mmol; air flow: 100 ml/min.

Table 3
Effects of added benzoic acid and water on the oxidative coupling of methyl benzoate

Additive	Conv. (%)	Isomer distribution (%)					
		2,2'-	2,3'-	2,4'-	3,3'-	3,4'-	4,4'-
None ^a	5.68	68.5	14.3	3.5	2.3	2.7	—
Benzoic acid ^b	1.89	49.9	35.1	9.5	5.2	0.3	—
Water ^c	0.0	—	—	—	—	—	—

^aPd(OAc)₂ (0.08 mmol)/H₆PMo₁₀V₂O₄₀ (0.4 g) catalyst system. Methyl benzoate, 122.6 mmol; 120°C; 1 atm; air flow 150 ml/min; reaction time 6 h.

^b24 mmol of benzoic acid added under otherwise the same conditions as in a.

^c30 mmol of water added under otherwise the same conditions as in a.

for Pd(OAc)₂/HPA catalyst. The rates of the reaction which is represented by the slopes of this plot showed a gradual decrease with time. In the cases of 120°C and 150°C, in particular, the conversion reached a plateau. This is not due to the equilibrium limitation since the reaction is far from equilibrium under the present conditions. The consumption of methyl benzoate by the reaction does not appear to be responsible for the reduction in rates with time at those low conversions observed here. Hence, the deactivation of the catalyst due to reaction products was suspected. Table 3 shows the effects of added benzoic acid and water into the reaction mixture. Addition of benzoic acid reduced drastically the methyl benzoate conversion and the selectivity to 2,2'-isomer. Water stopped the reaction completely.

4. Discussion

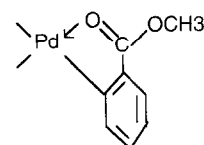
The application of HPA as a homogeneous, liquid phase catalyst is an emerging field of research with a great deal of practical implications. In particular, the Pd/HPA redox system has been the subject of the most serious interest due to its excellent activity and selectivity in the oxidation of many organic substances including oxidation and acetoxylation of olefins, oxidation of alcohols, and oxidative coupling of arenes [17–19]. Because of the higher activity and the

absence of the Cl^- ion, the catalyst system has been considered to have potential to replace the conventional $\text{Pd(II)}-\text{CuCl}_2$ system. The HPA, efficient as an oxidation catalyst, usually has the Mo-based Keggin structure, in which 1–3 of 12 Mo atoms are replaced by V. This could also be confirmed in Table 1. It is known that the substitution of Mo by V in the polyanion results in an increase of the oxidation potential of HPA and that HPA based on Mo has a higher oxidation potential than HPA based on W [18]. Heteroatoms (P, As or Si) did not exert significant effects.

The most salient feature of the oxidative coupling of methyl benzoate with the Pd/HPA catalyst is the high selectivity to 2,2'-isomer of biphenyl dicarboxylic acid dimethyl ester. The activation of aromatic C–H bonds by Pd(II) usually starts from the formation of Pd–Ar complex intermediates by electrophilic substitution of C–H aromatic bonds with Pd(II) [22]. In case of aryl coupling, the intermediate should be a diarylpalladium species, Ar–Pd–Ar, and the intramolecular reductive elimination would yield the coupling product, Ar–Ar. It is well established that the formation of the C–C linkage between two phenyl rings occurs exclusively at the carbon atoms bound directly to the metal atom [23,24]. Hence, the kinetic isomer distribution should be determined by the mode in which methyl benzoate attaches itself to Pd.

The oxidative addition of an aromatic compound to a metal center belongs to the aromatic electrophilic substitution in which the metal is the electrophile [25]. When electron-donating groups are attached to the benzene ring, the reaction is ortho–para directing and the reaction rate increases. Electron-withdrawing groups, on the contrary, are meta-directing and decrease the rate. The predominant formation of 2,2'-isomer in the present case with an electron withdrawing substituent ($-\text{COOCH}_3$) indicates that these general rules of the aromatic electrophilic substitution does not apply. Instead, the methyl benzoate appears to bond preferentially ortho to the methoxy group. The driving force for this

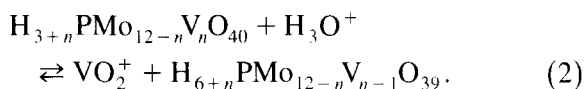
preference may be the coordination of carbonyl oxygen through its unshared pair of electrons forming the intermediate (II).



(II)

This bidentate structure has been proposed for dimethyl phthalate coordinated to various divalent cations [14,26]. The second methyl benzoate molecule may be bonded through ortho (primarily) and meta positions to account for the observed isomer distribution.

If the argument made above to explain the isomer distribution is indeed true, the Pd/HPA system does not show any significant steric effect. In the Pd/Cu/phen system of Ube Industries, the major coupling product was 3,4,3',4'-biphenyltetracarboxylate derived from the para coordination of dimethyl phthalate [14]. Obviously, this is attributable to a strong steric hindrance that strongly coordinating phen exerts around the Pd center. It has been shown that HPA retains its Keggin structure in a concentrated solution and yet undergoes destructive dissociation to some extent in diluted solutions ($< 10^{-2} \text{ mol l}^{-1}$). Our reaction conditions belong to the latter and the following dissociation has to be considered [17,18]:



None of these product species and HPA itself are strongly coordinating to Pd. This nature of Pd–HPA interaction appears to be responsible for the apparent absence of any steric hindrance.

In case of toluene or anisole as a substrate of the oxidative coupling, the isomer distribution for Pd/HPA catalyst was similar to the one observed for Pd/acetylacetonone [3] or Pd/NaOAc catalyst [8]. Both of these substrates with an electron donating substituent would form

monodentate intermediates with Pd and the preference of para coordination is apparent. Another interesting point is that the reaction rates for toluene and anisole are slower than that for methyl benzoate. This is opposite to what is expected from the general rule that electron donating substituents activate the electrophilic aromatic substitution and that electron withdrawing substituent deactivate it [25]. It is believed that methyl benzoate coupling has been facilitated due to the extra coordination of carbonyl oxygen to Pd, forming a more stable bidentate intermediate.

The addition of $\text{Hg}(\text{OAc})_2$ or triphenyl phosphine improves the conversion of methyl benzoate substantially without any significant effect on the isomer distribution. The effect of triphenyl phosphine is a usual ligand effect, observed previously for phen as well. $\text{Hg}(\text{OAc})_2$ has been reported to improve both the reaction rate and the selectivity of para isomers [8,10]. In our case, the effect on the selectivity was almost none.

When practical application of the Pd/HPA catalyst system is considered for the oxidative coupling of methyl benzoate, the most significant problem seems to be the loss of the catalyst activity with time. As shown in Table 3, both water and benzoic acid would contribute to the deactivation. Since the source of benzoic acid is probably the hydrolysis of methyl benzoate and its concentration under the real reaction condition would be much less than introduced in the control experiment shown in Table 3, water is the major cause of the catalyst deactivation.

Acknowledgements

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