Carbonylation

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Borate Esters as Alternative Acid Promoters in the Palladium-Catalyzed Methoxycarbonylation of Ethylene**

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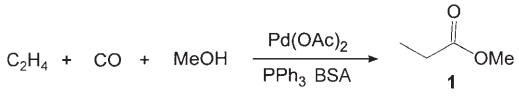
Since the early 1990s there has been considerable interest in the alkoxycarbonylation of olefins, a potentially important reaction for the production of commodity chemicals.[1–5] The attention devoted to this chemistry resulted in the development by Lucite International[6] of a two-step process for the production of methyl methacrylate (MMA) in which the initial step, the carbonylation of ethylene, is catalyzed by a palladium/bidentate phosphine/acid system. The choice of acid in this step is important, as it determines the type of counterion available for the cationic palladium species. A strongly coordinating anion will reduce the rate of the kinetically important addition of CO to C_2H_4, whereas weakly coordinating or noncoordinating anions allow the facile coordination of these reagents.[7,8]

Strong acids, such as methanesulfonic acid (MSA) or *p*-toluenesulfonic acid, which contain weakly coordinating anions, are typically used to achieve the required reaction rates; however, one consequence when using monodentate phosphine ligands is the rapid alkylation thereof.[9] This loss of phosphine inevitably leads to unstable palladium species and subsequent metal plating. Although the utilization of a weak acid, such as trifluoroacetic acid (TFA), can partially decrease the formation of phosphonium salts, significant loss of phosphine still occurs, and hence complex and expensive chelating ligand systems had to be developed for this type of reaction.[10,11]

Our aim was to identify alternative acid promoters to enable the effective use of simple monodentate ligands. We report herein the use of bis(salicylato)boric acid (borosalicylic acid, BSA) as an attractive acid promoter for the palladium-catalyzed methoxycarbonylation of ethylene with triphenylphosphine as the ligand [Eq (1)].



(1)

In the early 1990s British Petroleum[12] described the application of borosalicylic acid as a proton source for the palladium-catalyzed polymerization of ethylene and carbon monoxide, again in the presence of a chelating phosphine ligand. BSA forms during the condensation reaction between salicylic acid and boric acid ($B(OH)_3$) to yield the 1:1 or 1:2 borate complexes.[13] The formation of the 1:2 complex liberates one proton and three water molecules. X-ray crystal structure analyses of borate complexes with salicylic acid[14,15] confirm the existence of these species.

The performance of BSA (formed in situ and preformed) in the palladium/triphenylphosphine-catalyzed carbonylation of ethylene was compared with that of MSA and TFA as benchmarks. The reaction rates in the presence of different acids, as well as the amount of PPh_3 remaining after a TON of 1000 had been reached, are reported in Table 1 (TON = mol methyl propionate (**1**) formed per mol catalyst). MSA at 110 °C showed the highest activity and TFA at 120 °C the lowest activity when the total concentration of acid was identical. The results of a typical reaction promoted by BSA are shown in Figure 1a, and in Figure 1b those of

Table 1: Palladium-catalyzed methoxycarbonylation of ethylene with various acid promoters.[a]

Entry	Acid	*T* [°C]	TOF [h^{-1}][b,c]	STY[d]	PPh_3 remaining [%][e]
1	MSA	110	2130	4.50	28
2	BSA	110	1020	2.15	>99[f]
3	BSA[g]	110	886	2.02	>99
4	TFA	110	572	1.14	72
5	MSA	120	3528	10.64	9
6	BSA	120	1249	3.77	77
7	TFA	120	812	2.45	10

[a] p_{final} = 20 bar (CO/C_2H_4 1:1), MeOH (120 mL); entries 1–4: $Pd(OAc)_2$ (2 mM), PPh_3 (100 mM), acid (200 mM; $[B(OH)_3]$ = 200 mM for BSA, $[B(OH)_3]$/[salicylic acid] 1:2); entries 5–7: $Pd(OAc)_2$ (3 mM), PPh_3 (150 mM), acid (450 mM; for BSA: $B(OH)_3$ (450 mM), salicylic acid (1350 mM)). [b] Calculated after 10 min. [c] Turnover frequency [mol **1** formed per mol Pd and h] calculated according to the gas-uptake curve. [d] Site–time yield [mol **1** consumed per mol active sites and h at low conversion] calculated according to the gas-uptake curve. [e] Calculated after TON = 1000. [f] After 10 h, 94% of PPh_3 remained. [g] Preformed BSA was used.

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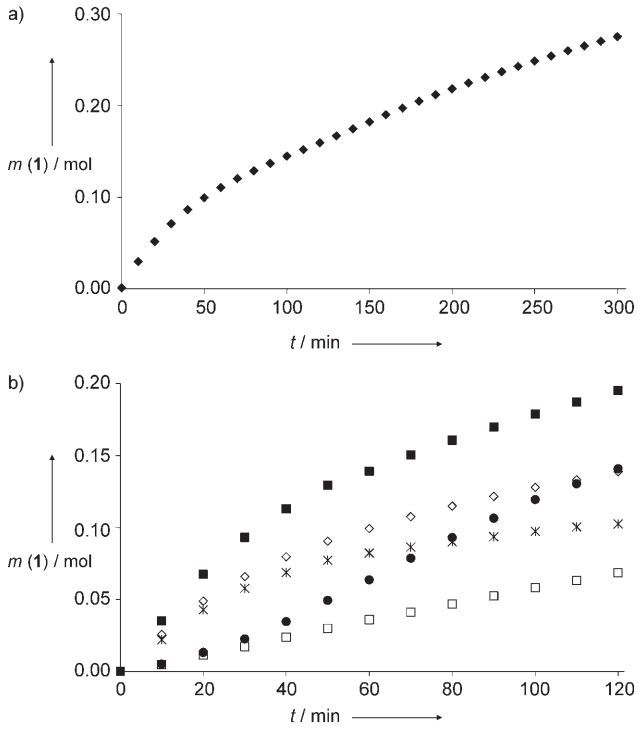

Figure 1. Formation of **1** in the palladium-catalyzed methoxycarbonylation of C_2H_4 with salicylate esters formed from boric acid and salicylic acid ((a) and ◇ in (b)); b) 5-substituted salicylic acid derivatives: ● 5-methylsalicylic acid, □ 5-aminosalicylic acid, ▲ 5-methoxysalicylic acid, ■ 5-chlorosalicylic acid.[16] Reaction conditions: $Pd(OAc)_2$ (2 mM), PPh_3 (100 mM), $B(OH)_3$ (150 mM), salicylic acid derivative (300 mM), p_{final} = 10 bar (CO/C_2H_4 1:1), MeOH (120 mL).

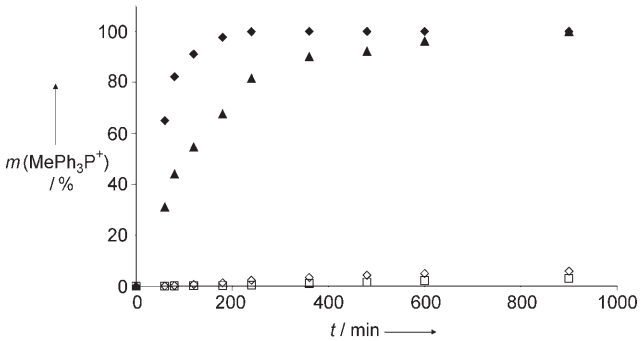

Figure 2. Formation of the methyltriphenylphosphonium salt from the reaction of acid with PPh_3 in MeOH. Reaction conditions: T = 110 °C, p_{final} = 10 bar (CO/C_2H_4 1:1); ◆ PPh_3 (100 mM), MSA (200 mM); ■ PPh_3 (23 mM), MSA (25 mM); BSA prepared in situ (□), preformed BSA (◇) (200 mM: $B(OH)_3$ (200 mM), salicylic acid (400 mM)), PPh_3 (100 mM).

reactions promoted by an extended range of other salicylate promoters.[16] Good initial catalyst activity was observed for all reactions.

A significant observation was how much PPh_3 remained after a TON of 1000 had been reached for the various acids. MSA was the most active acid promoter, but also gave the highest amount of phosphonium salts (72%, 110 °C); TFA produced lower amounts of phosphonium salts (28%, 110 °C). Surprisingly, negligible salt formation was observed with BSA, and an acceptable reaction rate was retained (99% of PPh_3 remained when the reaction was carried out at 110 °C; Table 1, Figure 2).

An increase in the temperature and catalyst concentration resulted in the expected increase in reaction rate; however, the amount of phosphonium salts formed also increased, which led to decreased catalyst stability and thus to the formation of palladium black. The most significant temperature effect on the alkylation of PPh_3 was observed with TFA (28% salt formation at 110 °C versus 90% at 120 °C). Although the catalyst activity was lower with both preformed BSA and BSA formed in situ than with MSA, it is clear that salt formation was retarded significantly in the presence of BSA relative to that observed with the other acids used.

The methyltriphenylphosphonium salt was the major salt formed under the reaction conditions employed. Strong acids, such as MSA, react with MeOH to form, in this case, methyl methanesulfonate. This very strong methylating agent reacts subsequently with PPh_3 to produce the $MePh_3P^+$ cation, which can later be isolated as the sulfonate salt.[10] The formation of $MePh_3P^+$ is therefore not metal-mediated. Minor salts observed, for example, ethyltriphenylphosphonium salt, are usually formed metal-mediated. The metal mediation was confirmed experimentally by the observation of an increase in the amount of ethyltriphenylphosphonium salt formed at increased pressures of C_2H_4.

Assessment of the extent of alkylation of PPh_3 by means of high-pressure NMR spectroscopy under the reaction conditions indicated that with an excess of MSA ([PPh_3]/[MSA] 1:2) all of the PPh_3 was converted into the methyltriphenylphosphonium salt within 6 h (◆ in Figure 2).

Even when only a slight excess of MSA was used, the amount of salt observed was still relatively high compared to that when BSA was used (compare ■ and empty symbols in Figure 2). The rate of formation of the methyltriphenylphosphonium salt was lowest when BSA was produced in situ; this result corresponds to a significant reduction in the unwanted side reaction. Surprisingly, although the BSA-promoted reaction was approximately 2.5 times slower than that with MSA, at least one order of magnitude less phosphonium salt was formed for the same TON.

Some deactivation of the BSA catalyst system was observed as a result of organic side reactions, the most problematic being the formation of methyl salicylate. However, preliminary experiments in a semicontinuous system showed that the initial catalyst activity could be maintained by the addition of excess salicylic acid.

4- or 5-substituted salicylic acid derivatives were also evaluated to determine whether the deactivation of the system could be reduced (see Figure 1b). The use of 5-chlorosalicylic acid led to the best results and the highest reaction rate. Surprisingly, nitro-substituted salicylic acid derivatives were not active (not shown), probably because of poisoning of the palladium catalyst by these compounds.

In conclusion, BSA was found to be an effective alternative acid promoter for the Pd-catalyzed methoxycarbonylation of C_2H_4, and the proof-of-concept has thus been clearly

demonstrated. The reaction rates observed are commercially viable, and significantly less alkylation of the monodentate phosphine ligand occurred than with MSA. This catalytic system also offers unique advantages in the unprecedented regioselectivity of the methoxycarbonylation of alkyl and aryl acetylenes,[17] together with the low cost, low corrosivity, and absence of sulfur as added benefits. Further detailed studies on the fundamental aspects of BSA formation are currently being undertaken.

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