

# Unprecedented Molecular 'VPO' assembly with Catalytic Activity under Mild Conditions

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- The conversion of butane into maleic anhydride (MA) is one of the most complex catalytic processes utilized by the petrochemical industry. Industrial catalysts are based on vanadium-phosphorous-oxide (VPO) systems, which consist of a suitable *precursor* and a derived *active species* formed *in-situ* at high temperatures (~700 K).
- We have sought to prepare an active catalyst phase directly, at room temperature, as a discrete molecular assembly
- We have successfully built such a systems (see Figure 1) and studied it's crystalline phases (figure 1) and basic catalytic activity (see Figure 2 and table 1)

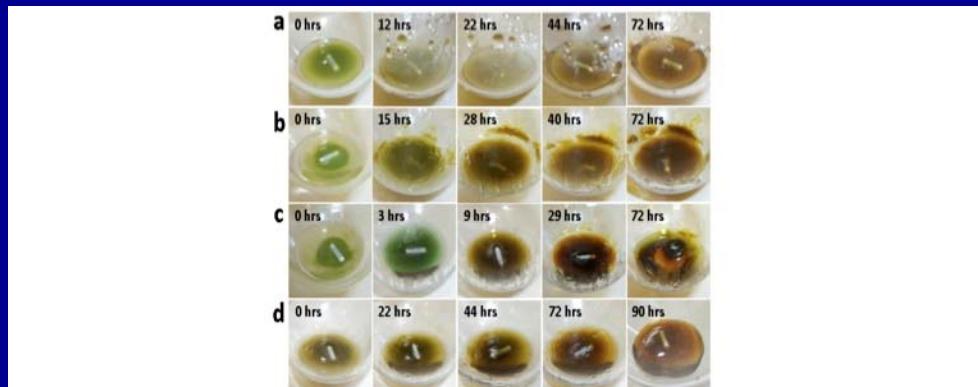


Figure 2. Snapshots of the reaction course at various time-points (only selected examples): (a) BA (1ml) + TEA (10mol%) + 1 (1mol%) under argon at 100°C; (b) BA (1ml) + pyridine (10mol%) + 1 (1mol%) under air at 100°C; (c) BA (1ml) + TEA (10mol%) + 1 (1mol%) under air at 100°C; (d) BA (1ml) + TEA (10mol%) + 1-anhyd (1mol%) under air at RT.

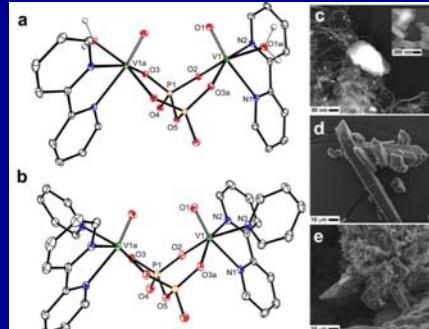


Figure 1. (a,b) ORTEP plots (20% probability level) of the vanadyl-pyrophosphate dimeric unit in 1 (a) and 1-pyr (b) with the atom labeling scheme (bipy and pyridine-H atoms are omitted for clarity). Vanadyl (V=O) units are evidenced with the open-type bond. Selected bond lengths (Å) in 1: V1-O1 = 1.611(3), V1-O2 = 1.979(3), V1-O3a = 1.960(3), V1-O1w = 2.038(3), V1-N1 = 2.294(4), V1-N2 = 2.143(3)

Table 1. Aerobic oxidation of benzyl alcohol (route 1) or pinacol (route 2) catalyzed by complex 1.<sup>[a,b]</sup>

Entry	Substrate	mol% 1	atm	additive	% conversion
1		none	argon	Et <sub>3</sub> N	<1
2		none	air	Et <sub>3</sub> N	<2
3		1	argon	pyr	<2
4		1	argon	Et <sub>3</sub> N	<2
5		1	air	none	9
6		1	air	pyr	10
7 <sup>[c]</sup>	benzyl alcohol	1	air	Et <sub>3</sub> N	16
8 <sup>[c,d]</sup>	alcohol	1	air	Et <sub>3</sub> N	42
9		1	air	Et <sub>3</sub> N	35 ± 4
10		0.5	air	Et <sub>3</sub> N	33 ± 6
11		0.25	air	Et <sub>3</sub> N	30 ± 4
12		0.1	air	Et <sub>3</sub> N	10
13		2	air	Et <sub>3</sub> N	50
14		5	air	Et <sub>3</sub> N	46
13	pinacol	none	air	Et <sub>3</sub> N	49
14	pinacol	1	air	Et <sub>3</sub> N	70
15	pinacol	0.25	air	Et <sub>3</sub> N	67

[a] Reaction conditions, unless otherwise stated: 1 ml substrate, no solvent (*neat*); [b] % conversion determined from <sup>1</sup>H NMR analysis (see the Experimental Section for further details); [c] Reaction conditions: 5 ml substrate, no solvent, 3 days at 100 °C under air; [d] % conversion after 11 days.