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# Phosphovanadomolybdic acid catalyzed desulfurization—oxygenation of secondary and tertiary thioamides into amides using molecular oxygen as the terminal oxidant<sup>†</sup>

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In the presence of phosphovanadomolybdic acids, e.g.,  $H_6PV_3Mo_9O_{40}$ , desulfurization-oxygenation of various kinds of structurally diverse secondary and tertiary thioamides proceeded efficiently using molecular oxygen as the terminal oxidant, affording the corresponding amides in moderate to excellent yields. In addition, <sup>18</sup>O-labeled amides could readily be synthesized using  $H_2^{18}O$  as the oxygen source.

Thioamides have attracted considerable attention in a wide range of fields.<sup>1-6</sup> In the fields of pharmaceuticals and biochemistry, they have been utilized as an important class of drugs, e.g., for thyrotoxicosis control, and for incorporation into peptides as isosteres for the amide linkages.<sup>2</sup> In the field of organic synthesis, they have often been utilized as versatile synthons due to their unique reactivities and wide availability; for example, a variety of important chemicals, such as amides,<sup>3,4</sup> nitriles,5 and sulfur-containing heterocycles,1a,6 have been synthesized through oxidative transformations of thioamides in the presence of various kinds of oxidants. The choice of oxidant determines the efficiency and practicability of the systems, and molecular oxygen (O2) is regarded as the "greenest" oxidant. With a strong awareness of that, we have recently developed catalytic aerobic oxidative transformations of thioamides (Scheme 1, upper): (i) manganese oxide-catalyzed oxidative dehydrosulfurization of primary thioamides to nitriles<sup>5a</sup> and (ii) phosphovanadomolybdic acid-catalyzed oxidative dimerization of primary thioamides to 3,5-disubstituted 1,2,4-thiadiazoles.<sup>6a</sup> The key to realizing these transformations as the efficient catalytic ones was that the catalysts possessed both acidic and oxidation properties to promote the de(hydro)sulfurization and the oxidation of S<sup>2-</sup> species to elemental sulfur (S<sup>0</sup> species).<sup>5a,6a</sup> It was also



**Scheme 1** Transformations of thioamides using  $O_2$  as the terminal oxidant (R, R' = alkyl, aryl; R'' = H, alkyl, aryl).

crucial that  $O_2$  could be utilized for the re-oxidation of the reduced catalysts.<sup>5a,6a</sup>

During the course of our investigations on aerobic oxidative thioamide transformations, we found that phosphovanadomolybdic acids efficiently catalyzed desulfurization-oxygenation of various kinds of structurally diverse secondary and tertiary thioamides using  $O_2$  as the terminal oxidant, giving the corresponding amides (Scheme 1, lower). In addition, <sup>18</sup>O-labeled amides could readily be synthesized by this catalytic system using  $H_2^{18}O$  as the oxygen source. Despite the numerous efforts towards the development of desulfurization-oxygenation of thioamides, challenges still remain because previously reported systems frequently employ metal-, halogen-, or organic-based oxidants or hydrogen peroxide,<sup>3</sup> and there have been only a few catalytic systems utilizing O<sub>2</sub> as the terminal oxidant.<sup>4</sup> Although phosphovanadomolybdic acids have been reported to be catalytically active for various kinds of oxidation reactions,<sup>7,8</sup> their use for this kind of transformation has never been reported so far, to the best of our knowledge.

Our initial experiments focused on the transformation of *N*-phenylthiobenzamide (**1a**) to *N*-phenylbenzamide (**2a**) under various reaction conditions. The reaction did not proceed at all

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Table 1 Effect of solvents on the desulfurization-oxygenation of  ${\bf 1a}$  to  ${\bf 2a}^a$ 

Entry	Solvent	Conv. of <b>1a</b> (%)	Yield of 2a (%)
1	Acetonitrile	>99	98
2	1,4-Dioxane	44	40
3	Chloroform	29	29
4	Tetrahydrofuran	19	17
5	2-Propanol	8	8
6	Ethanol	6	6
7	Methanol	3	3
8	<i>N</i> , <i>N</i> -Dimethylformamide	3	2
9	Dimethyl sulfoxide	2	1
10	Water	1	1

<sup>*a*</sup> Reaction conditions: **1a** (0.125 mmol),  $H_6PV_3Mo_9O_{40}$  (2 mol% with respect to **1a**), solvent (2 mL), 60 °C,  $O_2$  (1 atm), 0.5 h. Yields were determined by HPLC using naphthalene as the internal standard.

in the absence of catalysts. The results of solvent screening are summarized in Table 1.<sup>9</sup> Among the solvents examined, acetonitrile was the best solvent for the transformation and gave 98% yield of **2a** (Table 1, entry 1). 1,4-Dioxane, chloroform, and tetrahydrofuran gave moderate yields of **2a** (Table 1, entries 2–4). In contrast, highly polar solvents, such as water, alcohols, *N*,*N*-dimethylformamide, and dimethyl sulfoxide, were not suitable for the present transformation likely because of their strong coordination to the catalyst (Table 1, entries 5–10). As shown in Table 2, the desired amide product **2a** was significantly obtained when the reaction was performed using vanadium-containing heteropoly acids (HPAs). In these cases, **2a** was selectively obtained without the formation of any byproducts. The catalytic activities increased with an increase in

Table 2Effect of catalysts on the desulfurization-oxygenation of  $\mathbf{1a}$  to $\mathbf{2a}^a$ 

Entry	Catalyst	Conv. of <b>1a</b> (%)	Yield of 2a (%)
1	H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	9	6
2	$H_4PVMo_{11}O_{40}$	64	59
3	TBA <sub>4</sub> PVMo <sub>11</sub> O <sub>40</sub>	4	<1
4	$H_5PV_2Mo_{10}O_{40}$	88	84
5	H <sub>6</sub> PV <sub>3</sub> Mo <sub>9</sub> O <sub>40</sub>	>99	98
$6^b$	H <sub>6</sub> PV <sub>3</sub> Mo <sub>9</sub> O <sub>40</sub>	84	80
7 <sup>c</sup>	H <sub>6</sub> PV <sub>3</sub> Mo <sub>9</sub> O <sub>40</sub>	11	8
8	H <sub>7</sub> PV <sub>4</sub> Mo <sub>8</sub> O <sub>40</sub>	99	94
9	H <sub>4</sub> SiMo <sub>12</sub> O <sub>40</sub>	8	8
10	H <sub>5</sub> SiVM0 <sub>11</sub> O <sub>40</sub>	65	63
11	$H_{3}PW_{12}O_{40}$	5	5
12	$H_4PVW_{11}O_{40}$	11	8
13	$H_5PV_2W_{10}O_{40}$	45	45
14	$H_6PV_3W_9O_{40}$	81	74
15	$H_4SiW_{12}O_{40}$	7	7
16	$H_5SiVW_{11}O_{40}$	6	5
$17^d$	V <sub>2</sub> O <sub>5</sub>	<1	<1
$18^d$	NaVO <sub>3</sub>	<1	<1
$19^d$	$VO(acac)_2$	<1	<1
$20^e$	$V_2O_5 + H_3PMO_{12}O_{40}$	15	15
$21^e$	$NaVO_3 + H_3PMO_{12}O_{40}$	21	20
$22^e$	$VO(acac)_2 + H_3PMO_{12}O_{40}$	6	6
23	w/o	<1	<1

<sup>*a*</sup> Reaction conditions: **1a** (0.125 mmol), catalyst (2 mol% with respect to **1a**), acetonitrile (2 mL), 60 °C,  $O_2$  (1 atm), 0.5 h. Yields were determined by HPLC using naphthalene as the internal standard. <sup>*b*</sup> Air (1 atm). <sup>*c*</sup> Ar (1 atm). <sup>*d*</sup> Vanadium (10 mol%). <sup>*e*</sup> Vanadium (10 mol%) + H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> (1 mol%). w/o = without.

the vanadium content, *i.e.*,  $H_4PVMo_{11}O_{40} < H_5PV_2Mo_{10}O_{40} < H_6PV_3Mo_9O_{40} \approx H_7PV_4Mo_8O_{40}$  for phosphomolybdic acids (Table 2, entries 2, 4, 5, and 8);  $H_4PVW_{11}O_{40} < H_5PV_2W_{10}O_{40} < H_6PV_3W_9O_{40}$  for phosphotungstic acids (Table 2, entries 12–14). With regard to the polyatoms of vanadium-containing HPAs, molybdenum was better than tungsten (Table 2, entries 2, 4, and 5 *vs.* entries 12–14). It is well known that molybdic acids possess higher oxidation potentials in comparison with tungstic acids.<sup>10</sup> Air could be utilized for the transformation, while the reaction was somewhat slower than that in O<sub>2</sub> (Table 2, entry 6 *vs.* entry 5). Under Ar atmosphere, an almost stoichiometric amount of **2a** with respect to the vanadium species employed (6 mol%) was produced (Table 2, entry 7), thus indicating that O<sub>2</sub> can act as the terminal oxidant for the present desulfurization–oxygenation.

When using vanadium-free HPAs, such as  $H_3PMo_{12}O_{40}$ , H<sub>4</sub>SiMo<sub>12</sub>O<sub>40</sub>, H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, and H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>, the reaction hardly proceeded and gave 2a in only 5-8% yields (Table 2, entries 1, 9, 11, and 15). Although these results and the above-mentioned reaction in Ar suggest that vanadium is an indispensable component for the present desulfurization-oxygenation, simple vanadium compounds, such as  $V_2O_5$ , NaVO<sub>3</sub>, and VO(acac)<sub>2</sub> (acac = acetylacetonate), hardly catalyzed the desulfurization-oxygenation (Table 2, entries 17-19). Furthermore, the catalytic activities of phosphovanadomolybdic acids were much superior to those of simple mixtures of vanadium compounds and H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> (Table 2, entries 20-22). Therefore, the substitution of vanadium into HPA frameworks is important to obtain a high catalytic performance.<sup>6a,7,8</sup> It has been reported that vanadium-containing HPAs can efficiently catalyze single-electron oxidation of various kinds of substrates (including  $S^{2-}$  species) and that the vanadium sites play important roles.<sup>6a,7,8</sup> Moreover, the reduced HPAs can readily be re-oxidized by O<sub>2</sub>.<sup>6a,7,8</sup> The acid function of the catalysts was also very important for the present desulfurization-oxygenation; acid-type H<sub>4</sub>PVMo<sub>11</sub>O<sub>40</sub> efficiently catalyzed the desulfurization-oxygenation (Table 2, entry 2), whereas no production of the desired 2a was observed when the reaction was carried out using the corresponding tetra-n-butylammonium (TBA) salt (Table 2, entry 3).

Next, the scope of the present phosphovanadomolybdic acidcatalyzed desulfurization-oxygenation was investigated. As shown in Fig. 1, various kinds of structurally diverse secondary and tertiary thioamides could be converted into the corresponding amides in the presence of H<sub>6</sub>PV<sub>3</sub>Mo<sub>9</sub>O<sub>40</sub>. The amide products could readily be isolated by simple column chromatography on silica gel, and the isolated yields of several products are reported in Fig. 1. N-Substituted thiobenzamides were quantitatively converted into the desired amides. The larger scale reaction was also effective; when the H<sub>6</sub>PV<sub>3</sub>Mo<sub>9</sub>O<sub>40</sub>-catalyzed 2.5 mmol-scale reaction (twenty-fold scale-up) of 1a was carried out, the desired amide 2a was obtained in 99% yield at 60 °C for 0.5 h. The transformations of N-aryl thioacetamides, which contain electron-donating as well as electron-withdrawing substituents on the phenyl rings, proceeded efficiently. The chloro- and bromo-substituted substrates selectively afforded the corresponding amides without occurrence of dehalogenation. It should be noted that linear and cyclic aliphatic thioamides could also be converted into the corresponding aliphatic amides.



**Fig. 1** Scope of the present desulfurization–oxygenation of secondary and tertiary thioamides. Reaction conditions: **1** (0.125 mmol),  $H_6PV_3Mo_9O_{40}$  (2 mol% with respect to **1**), acetonitrile (2 mL),  $O_2$  (1 atm).<sup>a</sup> Isolated yields. <sup>b</sup> Yields were determined by HPLC or GC using naphthalene as the internal standard. <sup>c</sup> $H_6PV_3Mo_9O_{40}$  (4 mol%).

As mentioned above, the acid function of the catalysts was very crucial for the present desulfurization–oxygenation, and no formation of the amide product was observed when using the TBA salt (Table 2, entry 3). We have previously reported that phosphovanadomolybdic acids can catalyze the aerobic oxidation of the S<sup>2–</sup> species in primary thioamides to elemental sulfur.<sup>6a</sup> In the present system, elemental sulfur was isolated after the reaction (ESI<sup>†</sup>).<sup>11</sup> Notably, when the transformation of thioamides was performed in a mixed solvent of acetonitrile/ $H_2^{18}O$ , the corresponding <sup>18</sup>O-labeled amides were significantly produced (Scheme 2),<sup>12</sup> suggesting that the oxygen atoms in these amides mostly come from water. We emphasize that this



**Scheme 2** Synthesis of <sup>18</sup>O-labeled amides. Reaction conditions: **1** (0.125 mmol), catalyst (2 mol% with respect to **1**), acetonitrile/ $H_2^{18}$ O (1.9 mL/0.1 mL), 60 °C, O<sub>2</sub> (1 atm), 4 h for **1a**, and 1 h for **1b**. Yields were determined by HPLC using naphthalene as the internal standard. The <sup>18</sup>O contents were determined by GC-MS analysis.



Scheme 3 A tentatively proposed possible reaction mechanism for the present desulfurization-oxygenation of thioamides into amides (R, R' = alkyl, aryl; R'' = H, alkyl, aryl).

reaction will be one of the most useful procedures for the synthesis of <sup>18</sup>O-labeled amides.

Based on the above-mentioned experimental results, we here proposed a possible reaction mechanism for the present desulfurization-oxygenation (Scheme 3). The present transformation is possibly composed of the following four elementary steps. Steps 1 and 2 are equilibrium reactions to generate the intermediate A. When the reaction is carried out in the presence of H<sub>2</sub><sup>18</sup>O, the <sup>18</sup>O atom is incorporated into the substrate in step 2 (Scheme 2).<sup>12</sup> If catalysts do not possess acidic properties, the intermediate A is hardly generated, thus resulting in no production of the desired amide product, as mentioned above (Table 2, entry 3). In step 3, the oxidative desulfurization takes place through the HPA-catalyzed oxidation of the S2- species in the intermediate **A**,<sup>6a,11</sup> and then the reduced HPA is re-oxidized by  $O_2$ .<sup>6a,7,8</sup> The oxidation ability should be required to effectively promote this step, and thus phosphovanadomolybdic acids which possess relatively high oxidation potentials in comparison with other HPAs are suitable catalysts for the present transformation. Finally in step 4, the deprotonation proceeds to afford the corresponding amide.

In conclusion, we have successfully developed for the first time the efficient catalytic desulfurization-oxygenation of secondary and tertiary thioamides into amides using  $O_2$  as the terminal oxidant and water as the oxygen source. Various kinds of structurally diverse thioamides could be applied to this catalytic system. Moreover, it should be noted that <sup>18</sup>O-labeled amides could readily be synthesized by utilizing H<sub>2</sub><sup>18</sup>O. The key to realizing this transformation as the efficient catalytic one was the use of phosphovanadomolybdic acids which possess both acidic and oxidation properties.

## Experimental

#### General

HPLC analyses were performed on a Shimadzu Prominence system using a UV detector (Shimadzu SPD-20A, 220 nm or 254 nm) equipped with a Shiseido CAPCELL PAK UG80 column (4.6 mm ID  $\times$  250 mm length) using a mixed solvent of acetonitrile/water as an eluent (3/1 or 4/1 v/v). GC analyses were performed on a Shimadzu GC-2014 with a FID equipped with an InertCap 1 capillary column. GC-MS spectra were recorded on a Shimadzu GCMS-QP2010 at an ionization voltage of 70 eV equipped with an InertCap 5MS/Sil capillary column. NMR spectra were recorded on a JEOL ECA-500 (<sup>1</sup>H, 500.0 MHz; <sup>13</sup>C, 125.0 MHz) by using 5 mm tubes. Chemical shifts ( $\delta$ ) were reported in ppm downfield from tetramethylsilane (TMS). H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>, H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, and H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> were obtained from Wako, and other heteropoly acids were obtained from Nippon Inorganic Colour & Chemical. The number of water of crystallization in HPAs was 20-30 per polyanion, and the molecular weights of HPAs were calculated as triacontahydrates. TBA4PVMO11O40 was prepared using the cation-exchange method. H<sub>2</sub><sup>18</sup>O was obtained from Aldrich (<sup>18</sup>O content: >97%). Solvents, amides, several thioamides (1a, 1b, 1k, and 1o), and Lawesson's reagent were obtained from Kanto Chemical, TCI, Wako, Aldrich, or Acros (reagent grade), and used as received. The other thioamides were synthesized starting from the corresponding amides using Lawesson's reagent.<sup>13</sup>

#### Catalytic reaction

H<sub>6</sub>PV<sub>3</sub>Mo<sub>9</sub>O<sub>40</sub> (2 mol%), 1 (0.125 mmol), naphthalene (ca. 0.1 mmol, internal standard), and acetonitrile (2 mL) were placed in a Pyrex-glass tube reactor with a magnetic stir bar, and the reaction solution was vigorously stirred at 60 °C or 90 °C in 1 atm of O<sub>2</sub>. The reaction system was homogeneous. The operations under anaerobic conditions (Ar atmosphere) were carried out in a glove box. During the reaction, a small volume of the reaction solution was periodically sampled, and then the conversion of 1 and the yields of amide products 2 were determined by HPLC or GC analysis. As for product isolation, naphthalene was not used. After the reaction was completed, the reaction mixture was directly subjected to column chromatography on silica gel using a mixed solvent of *n*-hexane/diethyl ether as an eluent (typically 1/1 or 1/2 v/v), giving the analytically pure amide products. The products were confirmed by comparison of their GC retention times, GC-MS patterns, and/or <sup>1</sup>H and <sup>13</sup>C NMR spectra with those of the authentic samples (ESI<sup>†</sup>).

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