

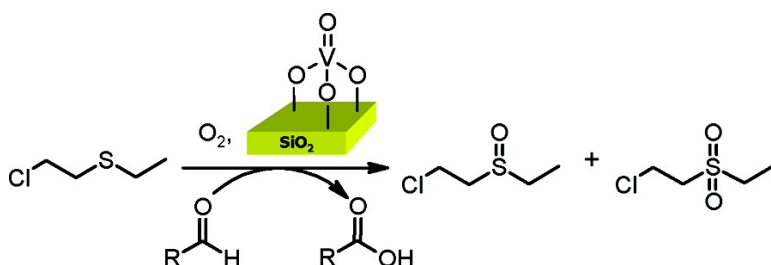
Communication

**Oxidation of a Mustard Gas Analogue Using an Aldehyde/O System Catalyzed by V-Doped Mesoporous Silica**

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## Oxidation of a Mustard Gas Analogue Using an Aldehyde/O<sub>2</sub> System Catalyzed by V-Doped Mesoporous Silica

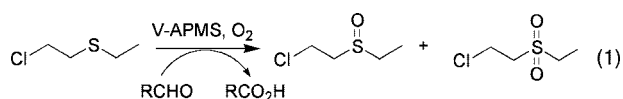
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Oxidation of the chemical warfare agent mustard gas, bis(2-chloroethyl) sulfide, using strong oxidants is one way in which mustard gas decontamination can be accomplished.<sup>1,2</sup> The desired product is the partially oxidized, nontoxic sulfoxide rather than the fully oxidized, toxic sulfone.<sup>3</sup> Although many catalysts exist that can perform sulfide oxidation using hydrogen peroxide or *tert*-butyl hydroperoxide, only a few catalytic systems directly use molecular O<sub>2</sub> as the oxidant under ambient conditions.<sup>4</sup> Another possibility that has not been explored extensively for mustard gas oxidation is the generation of oxidants in situ from O<sub>2</sub>. For example, aldehydes are known to undergo autoxidation by a free radical chain mechanism that involves the oxidation of the aldehyde to the corresponding acyl radical.<sup>5</sup> The acyl radical then reacts with O<sub>2</sub> to form the corresponding peracid, which is capable of oxidizing an additional aldehyde molecule to the corresponding acid. Although the autoxidation of aldehydes occurs at ambient conditions, the reaction rate can be increased by the use of metal catalysts.<sup>6</sup> Other species present in the reaction solution can also be oxidized by the generated peracid, resulting in the oxidation of sulfides to sulfoxides and sulfones.<sup>7</sup>

Supported vanadium oxide catalysts are commonly used in the oxidation of organic substrates.<sup>8</sup> We have recently shown that vanadium oxide supported on acid prepared mesoporous spheres (V-APMS) is an effective catalyst for the oxidation of the mustard gas analogue 2-chloroethyl ethyl sulfide (CEES) by *tert*-butyl hydroperoxide.<sup>9</sup> We now report the use of V-APMS as a catalyst in the room temperature oxidation of CEES using molecular oxygen from the air in the presence of aldehydes (eq 1).



V-APMS with a vanadium loading of 0.6 wt% (**1**) was prepared via wet impregnation of APMS with NH<sub>4</sub>VO<sub>3</sub> following a previously described procedure.<sup>10</sup> The surface areas of undoped APMS and **1** were 888 and 794 m<sup>2</sup>/g; the lack of XRD peaks corresponding to crystalline V<sub>2</sub>O<sub>5</sub> indicated that isolated VO<sub>4</sub> tetrahedra were the predominant vanadium oxide species.<sup>10</sup>

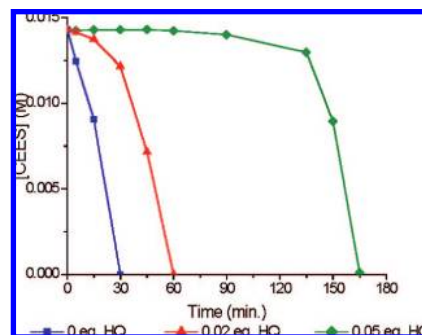
Initial studies of the room temperature oxidation of CEES in neat acetaldehyde, trimethylacetaldehyde, and propionaldehyde showed that the oxidation of CEES occurred even in the absence of a catalyst, resulting in 100% conversion of CEES within 75 min. This oxidation is attributed to the autoxidation of acetaldehyde at ambient temperatures as described above.<sup>11,12</sup> In the presence of **1**, complete conversion of CEES was observed in less than 15 min, indicating the catalytic nature of V-APMS.

We also studied the oxidation of CEES catalyzed by **1** in a system of aldehyde and the fluorinated solvent HFE-7100 (C<sub>4</sub>F<sub>9</sub>OCH<sub>3</sub>). HFE-7100 is of practical interest because it is nontoxic and nonflammable and can be used to rinse polymeric and electronic

**Table 1.** Oxidation of CEES by **1** in the Presence of Aldehydes/O<sub>2</sub><sup>a</sup>

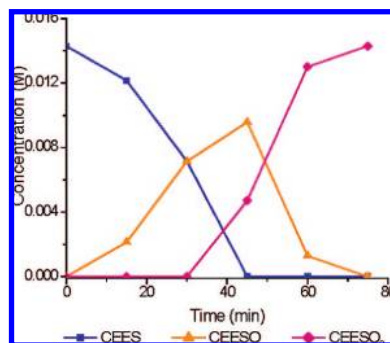
aldehyde	equiv of aldehyde	time (min) <sup>b</sup>
acetaldehyde	10	> 1440 <sup>c</sup>
acetaldehyde	20	50
acetaldehyde	neat <sup>d</sup>	15
trimethylacetaldehyde	10	> 1440 <sup>c</sup>
trimethylacetaldehyde	20	35
trimethylacetaldehyde	neat <sup>d</sup>	15
propionaldehyde	10	45
propionaldehyde	20	15
propionaldehyde	neat <sup>d</sup>	10

<sup>a</sup> Reaction conditions: CEES (42.9 μmol), aldehyde (429 or 858 μmol), **1** (20 mg) in HFE-7100 (3.0 mL), 21 °C. <sup>b</sup> Time required for 100% conversion of CEES. <sup>c</sup> An induction period was observed prior to CEES oxidation. <sup>d</sup> Reactions performed in neat aldehyde (3.0 mL).



**Figure 1.** Effect of hydroquinone on CEES oxidation in propionaldehyde (25 equiv)/CH<sub>3</sub>CN, catalyzed by **1** at 21 °C.

equipment contaminated with mustard gas without causing damage. The results given in Table 1 show that CEES oxidation occurred most rapidly with propionaldehyde/O<sub>2</sub>. Interestingly, the oxidation rate increased as a function of time, and a long induction period was observed with 10 equiv of propionaldehyde and trimethylacetaldehyde. This behavior has been observed in similar reaction systems and has been attributed to the ability of sulfides to act as free radical scavengers, inhibiting the oxidation by forming radical species with low reactivity.<sup>7b</sup> To confirm that radicals were also present in the propionaldehyde/O<sub>2</sub> system, we repeated the reaction in propionaldehyde (25 equiv)/CH<sub>3</sub>CN in the presence of hydroquinone, which would be expected to inhibit a free radical reaction until it has been consumed.<sup>12,13</sup> CH<sub>3</sub>CN was used for these experiments due to the insolubility of hydroquinone in HFE-7100. An induction period was observed for the reactions that contained hydroquinone (0.02 and 0.05 equiv with respect to CEES) that lengthened in duration as the hydroquinone concentration increased (Figure 1). Similar results were obtained in the absence of CEES, indicating that the oxidation of aldehydes by O<sub>2</sub>, catalyzed by



**Figure 2.** Concentration of CEES, CEESO, and CEESO<sub>2</sub> for **1** catalyzed oxidation of CEES by propionaldehyde (10 equiv)/O<sub>2</sub> in HFE-7100 at 21 °C.

V-APMS, occurs by a radical mechanism and that radicals are present in the CEES oxidation reactions.

Figure 2 shows the products formed during CEES oxidation with **1** in the propionaldehyde/HFE-7100 system. CEES was initially exclusively oxidized to the corresponding sulfoxide (CEESO), and formation of the sulfone (CEESO<sub>2</sub>) only occurred after CEES had been completely consumed. This is consistent with a two-step oxidation process in which CEESO<sub>2</sub> is formed from CEESO, not directly from CEES.<sup>1</sup> It also indicates that the oxidation of the sulfide is faster than the sulfoxide, which is a consequence of the reduced nucleophilicity of the sulfur atom in the sulfoxide.<sup>14</sup>

There are two possible capacities in which V-APMS could act as a catalyst in this reaction: (1) the oxidation of the aldehyde to the corresponding peracid by O<sub>2</sub> and (2) the oxidation of CEES and CEESO by the peracid. The possibility that V-APMS catalyzed the oxidation of propionaldehyde was studied by quantifying the amount of propionic acid formed in the presence and absence of **1** in HFE-7100. After 60 min, the propionic acid concentration was 0.05 M in the presence of **1** and the acid concentration was only 0.002 M when it was absent, showing that V-APMS was catalyzing the oxidation of propionaldehyde to the acid. The ability of V-APMS to catalyze the oxidation of CEES by a peracid was also studied by reacting CEES and peracetic acid in the presence and absence of **1** in HFE-7100. In either case, when equimolar amounts of peracetic acid and CEES were used, the reaction was extremely rapid; however the product distributions were measurably different. In the absence of **1**, the conversion of CEES was 97% after 1 min, and the product ratio of CEESO to CEESO<sub>2</sub> was 24:1. When **1** was present, CEES conversion was only 67% after 1 min, but the product ratio was now 1.9:1. The increased concentration of CEESO<sub>2</sub> indicates that the role of the catalyst is not exclusively to form the peracid; it also participates in sulfide and sulfoxide oxidations. The amount of sulfone in the catalyzed reaction indicated that the catalyst enhanced the oxidation of both substrates. The formation of CEESO<sub>2</sub> was found to be dependent on the initial peracid concentration; decreasing the concentration of peracetic acid increased the selectivity for CEESO. This accounts for the initial sulfoxide selectivity observed with **1** (Figure 2); the concentration of peracid remained low, since it was being generated and then consumed in the oxidation of CEES.

Finally, leaching of V from solid substrates has also been a recent concern.<sup>15</sup> To examine this effect, the amount of V in **1** was

determined by chemical analysis as synthesized, after stirring in pure aldehydes, and after stirring in HFE-7100 containing 10 equiv of aldehydes. It was found that between 5 and 41 wt% V leached from the support in the neat aldehydes after 1 h. However, there was no significant V leaching in HFE-7100, indicating that under these conditions V-APMS acts as a heterogeneous catalyst, not a source of solvated V, and it could easily be recovered by filtration for repeated use.

In summary, we have shown that CEES can be oxidized under ambient conditions using several aldehydes and O<sub>2</sub> from air, with V-APMS acting as a heterogeneous catalyst for both the in situ generation of the corresponding peracid and the oxidation of CEES and CEESO by the peracid. Although this work was limited to the oxidation of CEES and aldehydes, additional work may reveal other applications of V-APMS/aldehyde/O<sub>2</sub> systems in aerobic oxidations.

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

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