

**Application of NMR and EPR Spectroscopy to the Analysis of  
the Reaction of Phosphovanadomolybdate Polyoxometalate  
( $H_5PV_2Mo_{10}O_{40}$ ) with Chloroethyl Sulfides (Half-Sulfur  
Mustard and Sulfur Mustard)**

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## Abstract

Magnetic resonance spectroscopy, nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR) techniques support the oxidation of sulfur mustard (bis- (2-chloroethyl) sulfide; military designation, HD) and its analogous compound (2-chloroethyl ethyl sulfide; H-MG) by the vanadium-substituted heteropoly acid,  $H_5PV_2Mo_{10}O_{40}$ , readily accessible and significantly selective. All detected reaction products were characterized by  $^{13}C$ -NMR spectroscopy. The detected products are the reductively dehalogenated 2-ethylthioethanol, an organosulfur oxyacid, a cyclic sulfoxide, and the sulfone.  $^{31}P$ -NMR spectra exhibited significant up-field chemical shift changes in the presence of the sulfur mustard and its analogous compound. The distinction in the up-field chemical shift was modest in the  $^{31}P$ -NMR spectra; however, the up-field chemical shift in the  $^{51}V$ -NMR spectra was exceptionally conspicuous.  $V_2P$  resonance at  $\delta -523.12$  ppm was shifted up-field by more than twice the amount of any other  $PV_2Mo_{10}O_{40}^{-5}$  resonances. The fact that an up- field shift was observed in the presence of the sulfur mustard or its analogous compound supports the presence of the  $V^{+4}$  paramagnetic cation. The presence of the paramagnetic  $V^{+4}$  ion was verified by EPR since the reduced form of the polyoxometalate,  $PV^{IV}_2Mo_{10}O_{40}^{7-}$  was detected. It was noted that the most characteristic and distinctive feature of  $H_5PV^V_2Mo_{10}O_{40}$  consists of its propensity for easy O-atom transfer to the donor substrate (S) yielding oxidation product SO. Decamolybdodivanadophosphate ( $H_5PV^V_2Mo_{10}O_{40}$ ) directly oxidizes the substrate (HD or H-MG) and a terminal oxidant reoxidizes the reduced form of the polyoxometalate ( $PV^{IV}_2Mo_{10}O_{40}^{-7}$ ):

*Keywords:* phosphovanadomolybdate; sulfur mustard; heteropoly acids; oxidation; polyoxometalates; reoxidation

## Introduction

Polyoxometalates (POMs) have been used to catalyze the oxidative breakdown of halogenated organic compounds and are good candidates to

inactivate chemical warfare agents (CWAs) (Khenkin et al., 2001). Many of the POMs undergo rapid, reversible redox changes. In 1999, Hill (Johnson & Hill, 1999) introduced the concept that POMs could be used as a reactive component in the existing topical skin protectant (TSP) (McCreery, 1997), or barrier cream, against chemical warfare agents (CWAs).

Sulfur mustard (HD) received its name from its smell (onion, garlic, mustard) (Medema, 1986). When mustard was first used by the Germans, the Allies called it Hun Stoffe (German stuff), abbreviated HS; later it became known as H (Medema, 1986). Distilled, or near pure, sulfur mustard is known as HD. The aim of the present was to apply magnetic resonance techniques, namely nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR), to obtain a more complete picture on the mechanism of the chemical reaction of a selected POM with sulfur mustard and its analogous compound.

Here, we present evidence that vanadium containing polyoxometalates of Keggin (Haimov & Neumann, 2002; Neumann & Dahan, 1997; Neumann & Dahan, 1998; Khenkin & Neumann, 2000; Pope, 1983) structure  $H_5PV^V_2Mo_{10}O_{40}$  (Figure 1) can activate sulfides and oxidizes such substrates yielding the product and reduced catalyst. Reoxidation of the catalyst by dioxygen and formation of water then follows. The regeneration of the original oxidized form of the catalyst by reaction with molecule of oxygen is very fast suggesting that  $H_5PV^V_2Mo_{10}O_{40}$  could be used as catalyst for the decontamination of sulfur mustard and its analogous compound.

## **Experimental Section**

### **Materials and Instruments:**

NMR solvents, available from commercial sources (Sigma Chemical Company and Aldrich Chemical Company, St. Louis, MO, USA), were of the highest purity available, and were used without additional purification. The metal-free water was obtained from a Millipore water purification system (Quantum EX Ultrapure Organex cartridge, Bedford, MA, USA). Half-sulfur mustard (2-chloroethyl ethyl sulfide; H-MG) was obtained from Sigma Chemical Co. (St. Louis, MO, USA). Sulfur mustard (bis- (2-chloroethyl) sulfide; HD) was

acquired from the United States Army Soldier and Biological Chemical Command (Aberdeen Proving Ground, MD, USA). Professor Craig L. Hill, Department of Chemistry, Emory University, Atlanta, GA, USA provided the  $H_5PV_2Mo_{10}O_{40}$  polyoxometalate.  $H_5PV_2Mo_{10}O_{40}$  polyoxometalate was used as received. No further purification was made. Hydrated  $PV_2Mo_{10}O_{40}^{-5}$  was prepared by drying the POM at 120° C for 24 h. The quaternary ammonium salt  $[(C_4H_9)_4N]_5PV_2Mo_{10}O_{40}$  was prepared by mixing 10 equiv of tetrabutylammonium bromide  $[(C_4H_9)_4NBr]$ ; Sigma Chemical Co.; T 2390] dissolved in water and an aqueous solution of  $H_5PV_2Mo_{10}O_{40}$ . The precipitate was removed by filtration and dried overnight in a vacuum oven at 85° C. The thermogravimetric analysis showed the absence of water (data not shown).

#### **Nuclear Magnetic Resonance (NMR):**

$^{13}C$ -NMR (150.81 MHz, internal standard) and  $^{31}P$ -NMR (242.78 MHz, 85%  $H_3PO_4$  external standard) measurements were taken on a VARIAN 600 MHz *INOVA* high-resolution spectrometer (VARIAN Nuclear Magnetic Resonance Instruments, Palo Alto, CA, USA), equipped with an Oxford Instruments LTD magnet. The  $^{13}C$  and  $^{31}P$  NMR measurements were obtained on a 600 MHz 5mm PENTA PFG probe.  $^{51}V$ - NMR [157.66 MHz, vanadium (V) oxytrichloride ( $VOCl_3$ ) used as external standard] measurements were taken using a 600 MHz SWITCHABLE probe. All one-dimensional experiments were performed at temperatures ranging from 25° - 37° C. Data acquisition, processing, display, and analysis were performed on SUN ULTRA 10 using VNMR 6.1C software.

#### **Electron Paramagnetic Resonance (EPR):**

Fifty microliters ( $\mu L$ ) of a stock solution of  $H_5PV_2Mo_{10}O_{40}$  (4 mM) in 950  $\mu L$  of metal-free water were transferred under  $N_2$  gas at 37° C into an EPR quartz capillary tube (50  $\mu L$ ; dimensions: o.d. 3 mm; i.d. 1.99 mm; wall 0.48 mm; Wilmad Glass, Buena, NJ, USA). The EPR spectrum was immediately recorded at room temperature. The EPR powder spectra were obtained from 35 mg of hydrated  $PV_2Mo_{10}O_{40}^{-5}$ , transferred into an EPR quartz tube at 25 ° C. All EPR spectra were recorded on a Bruker ESP 300E X-band EPR spectrometer at 100-

KHz magnetic field modulation and a microwave frequency 9.78 GHz. The magnetic field was set at 348.0 mT, the microwave power at 5.02 mW, the modulation amplitude at 0.1 mT (unless otherwise indicated), the time constant at 655 ms, the sweep time at 335 s, the receiver gain at  $5.0 \times 10^4$ , and the sweep width at 300.0 mT. The Bruker EPR software tools were used for the computer simulation.

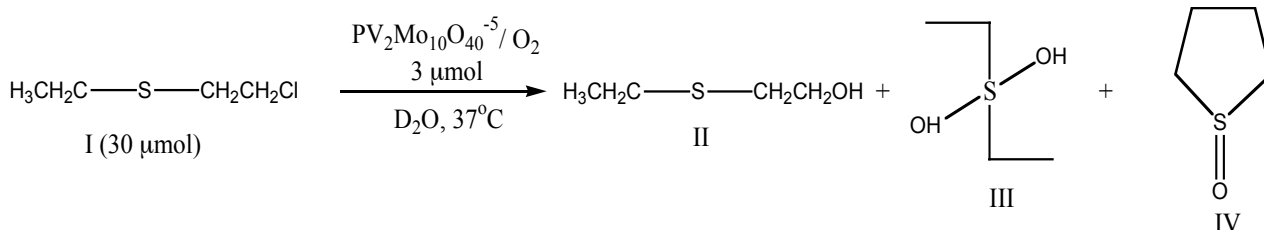
#### **Determination of Rate Law for the Reaction of the HD with $\text{H}_5\text{PV}^{\text{V}}_2\text{Mo}_{10}\text{O}_{40}$ :**

The initial-rate method was employed to determine the reaction order. The initial rate was obtained by following spectrophotometrically the formation of the reduced form of  $\text{H}_5\text{PV}^{\text{V}}_2\text{Mo}_{10}\text{O}_{40}$  ( $\lambda_{\text{max}} = 780 \text{ nm} / \epsilon = 1430 \text{ M}^{-1} \text{ cm}^{-1}$  in  $\text{CD}_3\text{CN}$ ). For the determination of the order with respect to HD, six vials each with 0.0280 g of  $\text{H}_5\text{PV}^{\text{V}}_2\text{Mo}_{10}\text{O}_{40}$ , 40  $\mu\text{L}$  of  $\text{D}_2\text{O}$  and 4 mL of  $\text{CD}_3\text{CN}$ , were allowed to stand overnight to ensure complete equilibration. Six vials each with 1 mL of  $\text{CD}_3\text{CN}$  and varying amounts of HD from 0.25 - 4.5  $\mu\text{L}$  were prepared. The reactions were conducted in a 1-cm pathlength quartz cuvette with an affixed glass stopcock. Immediately before the experiment, both the  $\text{H}_5\text{PV}^{\text{V}}_2\text{Mo}_{10}\text{O}_{40}$  and HD solutions were degassed by a repeated vacuum/nitrogen gas cycle three times. Next, 1.0 mL of the solution was injected through a rubber septum stopper into a nitrogen-filled cuvette, and then the cuvette was placed into a UV-Vis (Varian) spectrometer. The reaction was initiated by adding 0.25 to 4.50  $\mu\text{L}$  of HD solution into the cuvette, in which the contents were magnetically stirred. The timer was started on the addition of the HD. The absorbance was measured every 30 s for 8 min and then less frequently until it leveled off. The final concentrations of the reactants in the cuvettes were as follows:  $\text{H}_5\text{PV}^{\text{V}}_2\text{Mo}_{10}\text{O}_{40}$ ,  $1.60 \times 10^{-4} \text{ M}$ ;  $\text{D}_2\text{O}$ ,  $2.20 \times 10^{-1} \text{ M}$ ; 0.40% by volume; HD from  $4.40 \times 10^{-1}$  to  $1.70 \times 10^{-1} \text{ M}$ .

## Results

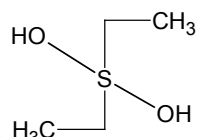
### NMR Spectroscopy:

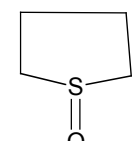
The oxidation of half sulfur mustard (I) catalyzed by the heteropolyacid,  $H_5PV_2Mo_{10}O_{40}$ , was monitored by NMR. This reaction was performed in deuterated water at 37° C generating several products given in *Scheme 1*. Figure 2 represents a continuous  $^{13}C$ -NMR 1-D experiment recorded for 15-hrs and shows a time averaged product distribution.



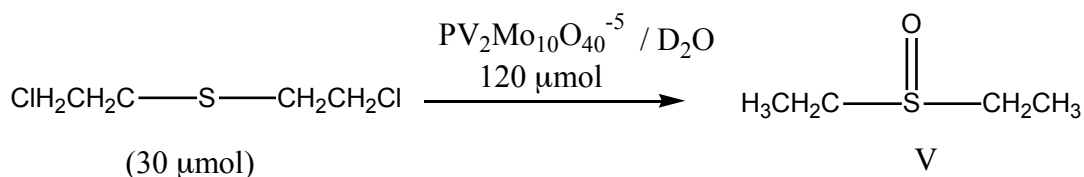
### *Scheme 1.*

In addition to the excess 2-chloroethyl ethyl sulfide (I), with the characteristic  $^{13}C$ -NMR resonances  $\delta$  C<sub>4</sub> 42.31, C<sub>3</sub> 34.89, C<sub>2</sub> 25.40 and C<sub>1</sub> 14.24 ppm (Figure 2), the 2-ethylthioethanol (II) was observed at  $\delta$  C<sub>4</sub> 60.52, C<sub>3</sub> 33.04, C<sub>2</sub> 25.27 and C<sub>1</sub> 13.98 ppm. An organosulfur oxyacid, a sulfenic acid, was detected displaying chemical shifts of 8.34

and 40.08 ppm assigned to be  III. As the reaction proceeded for 15-hrs the  $^{13}C$ -NMR spectrum exhibited resonance peaks at 25.44 and 56.34 ppm corresponding

to a cyclic sulfoxide product  IV. The yield of the reaction was 99.9% with the final relative product distribution of 10% for compound I, 20% for compound II, 20% for compound III and 50% for compound IV.

When the reaction with the sulfur mustard was carried out in deuterated water at 37°C a sulfone V was the only product observed after 18 hrs (*Scheme 2*).



### *Scheme 2.*

Figure 3 shows the  $^{13}\text{C}$ -NMR spectrum of the sulfone V with resonances at  $\delta$  6.99 and  $\delta$  33.97 ppm. Since each  $\text{H}_5\text{PV}^{\text{V}}_2\text{Mo}_{10}\text{O}_{40}$  molecule can be formally considered as a two-electron oxidant, the conversion into sulfone was 99.9 %.

Multiple  $^{31}\text{P}$  and  $^{51}\text{V}$  NMR resonances for the decamolybdodivanadophosphate in deuterated aqueous solutions evidence the coexistence of multiple positional isomers. These positional isomers exhibit, among them, five resolvable  $^{31}\text{P}$  NMR resonances, and six resolvable  $^{51}\text{V}$  NMR resonances, Figure 4 and Figure 6, respectively. Equilibrated solutions containing decamolybdodivanadophosphate exhibited identical  $^{31}\text{P}$  and  $^{51}\text{V}$  NMR spectra, when at the same concentration and  $\text{pH} \geq 2$ .

The five- $^{31}\text{P}$  NMR chemical shifts varied over HD concentrations that ranged from 0.0 to  $4.4 \times 10^{-4}$  M; no additional resonances corresponding to  $\text{H}_5\text{PV}^{\text{V}}_2\text{Mo}_{10}\text{O}_{40}$  species were revealed.  $^{31}\text{P}$ -NMR resonances at  $\delta$  -3.64 ppm and  $\delta$  -3.47 ppm exhibit significant chemical-shift changes in the presence of HD (Figure 4). The up-field shift of  $\delta$  -3.64 ppm fits the normal expectation that a decreased electron density on phosphorus increases shielding, decreases *p*-orbital unbalancing, and decreases deshielding (downfield shift) of the phosphorus nucleus (Gorenstein, 1984). These shift variations may also relate to O – P – O torsional-angle changes with increasing HD concentrations (Gorenstein, 1984). The detected up-field shift in the presence of H-MG or HD supports the presence of  $\text{V}^{+4}$  cations.

A typical  $^{51}\text{V}$ -NMR spectrum of  $\text{H}_5\text{PV}^{\text{V}}_2\text{Mo}_{10}\text{O}_{40}$  in  $\text{D}_2\text{O}$  is shown in Figure 5. In the  $^{31}\text{P}$ -NMR spectra of the reaction of  $\text{H}_5\text{PV}^{\text{V}}_2\text{Mo}_{10}\text{O}_{40}$  with HD, the up-field chemical-shift change is moderate (Figure 4), but in the  $^{51}\text{V}$ -NMR spectra (Figure 6) of the reaction of  $\text{H}_5\text{PV}^{\text{V}}_2\text{Mo}_{10}\text{O}_{40}$  with HD, it is exceptionally evident. The  $^{51}\text{V}_2\text{P}$

resonance at  $\delta -523.12$  ppm is shifted up-field by more than twice the amount of any other  $\text{H}_5\text{PV}^{\text{V}}_2\text{Mo}_{10}\text{O}_{40}$  resonance, as shown in Figure 6. The  $^{51}\text{V}$  chemical shifts are not measurably dependent on the concentration of the decamolybdodivanadophosphate, but the  $^{31}\text{P}$  chemical shifts are. Presumably, this is a bulk susceptibility effect. The  $^{31}\text{P}$  chemical shifts are also dependent on the ionic medium concentration, which is held constant in the present study.

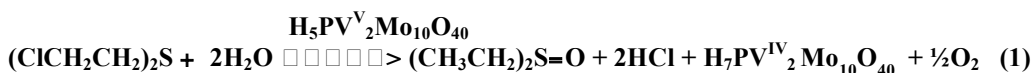
### EPR spectroscopy:

The  $\text{V}^{+4}$  cation has a single unpaired electron in its lowest lying  $d_{xy}$  orbital and its interaction with the  $^{51}\text{V}$  nucleus (99.7% abundance,  $I = 7/2$ ) yields a sharp eight-line EPR isotropic spectrum in solution at room temperature (Bolton, 1972). The fifteen-line EPR spectrum illustrated in Figure 7 shows the anisotropic hyperfines of the hydrated powder of  $\text{PV}^{\text{V}}_2\text{Mo}_{10}\text{O}_{40}^{-5}$ . In the aprotic dimethyl sulfoxide (DMSO) solvent, the EPR spectrum of the decamolybdodivanadophosphate shows the lowest intensity (Figure 8A), which indicates the presence of a small amount of  $\text{V}^{+4}$  cations. The reaction of the  $\text{H}_5\text{PV}^{\text{V}}_2\text{Mo}_{10}\text{O}_{40}$  polyoxometalate with the sulfur mustard increases the quantity of  $\text{V}^{+4}$  cations, since the EPR signal intensity is raised by 1.6 fold (Figure 8B). Evidence for the appearance of the reduced species  $\text{PV}^{\text{IV}}_2\text{Mo}_{10}\text{O}_{40}$ .

We attempted to detect the ethylenesulfonium radical cation *in situ* by applying EPR-spin trapping techniques (Arroyo, 1999); however, we were unable to observe the ethylene sulfonium radical cation under these experimental conditions used. Also previously, we showed that the radical cation of the half-sulfur mustard (I) or sulfur mustard could not be observed by EPR-spin trapping techniques (Arroyo, 1999).

### The Reaction Rate of the Sulfur Mustard with $\text{H}_5\text{PV}^{\text{V}}_2\text{Mo}_{10}\text{O}_{40}$ :

The course of the reaction



### Scheme 3.

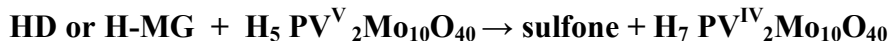
was evaluated by using the integrated first-order rate law (Eq. 1) under pseudo-first-order conditions.

$$A_t = A_{\infty} + (A_0 - A_{\infty}) \exp(-k_{\text{obs}}t) \quad (1)$$

The concentrations of HD, H<sub>2</sub>O, and H<sub>5</sub>PV<sup>V</sup><sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> were 4.4 x 10<sup>-1</sup> M, 2.0 x 10<sup>-1</sup> M and 4.61 x 10<sup>-4</sup> M, respectively. The following values were determined experimentally: A<sub>∞</sub> = 3.366, A<sub>0</sub> = 1.110 and slope = 0.016; the calculated rate constant from Eq. 1 was 3.40 ± 0.05 s<sup>-1</sup>. The reaction in eq 1 take place by initial thioether reduction of polyoxometalate and subsequent reoxidation of the reduced polyoxometalate by the terminal oxidant. This reaction has been previously reported by Hill (Johnson & Hill, 1999), which indicates that the polyoxometalate directly oxidizes the substrate and a terminal oxidant reoxidizes the reduced form of the polyoxymetalate.

## Discussion

Sulfide oxidation by  $\text{H}_5\text{PV}^{\text{V}}_2\text{Mo}_{10}\text{O}_{40}$  was monitored via  $^{13}\text{C}$ -NMR to determine the identity of the products. The oxidation was observed by the change in the  $^{13}\text{C}$ -NMR spectra of the sulfide and the changes the complexes  $^{51}\text{V}$ -NMR spectra. It was noted that the most characteristic and distinctive feature of  $\text{H}_5\text{PV}^{\text{V}}_2\text{Mo}_{10}\text{O}_{40}$  consists of its propensity for easy O-atom transfer to the donor substrate (S:) yielding oxidation product SO. Decamolybdodivanadophosphate ( $\text{H}_5\text{PV}^{\text{V}}_2\text{Mo}_{10}\text{O}_{40}$ ) facilitates the oxidation of sulfur mustard by directly oxidizing the substrate (HD or H-MG) and an oxidant reoxidizes the reduced form of the polyoxometalate ( $\text{PV}^{\text{IV}}_2\text{Mo}_{10}\text{O}_{40}^{-7}$ ):

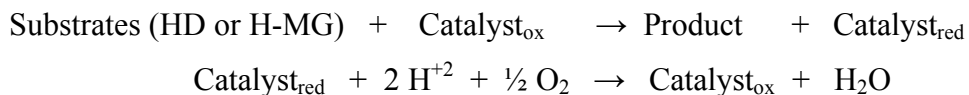


This was verified by the  $\text{V}^{5+} \leftrightarrow \text{V}^{4+}$  transformation, this transformation was observed by EPR spectroscopy. The  $\text{V}^{5+} \leftrightarrow \text{V}^{4+}$  is actually responsible for the redox activity of the heteropolyacid,  $\text{H}_5\text{PV}^{\text{V}}_2\text{Mo}_{10}\text{O}_{40}$  (Khenkin & Neumann, 2000). Furthermore, the vanadium substituted heteropolyanions have a fairly high value of oxidation potential (0.7 relative to normal hydrogen electrode (NHE)) and are capable of oxidizing substrates ranging from organic to inorganic compounds. They are reversibly acting oxidants i.e., their reduced forms can be reoxidized to the original form by oxygen in mild conditions.

Our magnetic resonance data indicate that the reaction under study takes place by initial reduction of polyoxometalate with chloroethyl sulfide, to afford the reduced form  $\text{PV}^{\text{IV}}_2\text{Mo}_{10}\text{O}_{40}^{-7}$ , as was observed by EPR. In accord with reported work on the reduction of polyvanadomolybdic acids (Sharer et al, 1991; Kozhevnikov, 1998; Muller et al., 1998; Petterson et al., 1994; Weinstock, 1998) and the known redox potentials, only the  $\text{V}^{\text{V}}$  and not the  $\text{Mo}^{\text{VI}}$  ions are reduced (Khenkin & Neumann, 2000). The observed chemical up-field shift for the  $^{31}\text{P}$  or  $^{51}\text{V}$  metal centers most likely results from the paramagnetic  $\text{V}^{4+}$  cations of the reduced form of the polyoxometalate,  $\text{PV}^{\text{IV}}_2\text{Mo}_{10}\text{O}_{40}^{-7}$  when HD or H-MG are present. This observation was confirmed by the appearance of a

reduced blue species,  $PV^{IV}_2Mo_{10}O_{40}^{-7}$ , at 750 nm in the visible spectrum (data not shown).

Aerobic heterogeneous catalytic oxygenation of sulfides with transition metal oxides involves activation of S-R<sub>2</sub> bond and transfer of lattice oxygen from the polyoxometalate to yield the product and the reduced catalyst. Re-oxidation of the catalyst by dioxygen and formation of water then follows.



The experiments described above indicate that oxygenation occurred by oxygen transfer from a lattice oxygenation of the  $H_5PV^V_2Mo_{10}O_{40}$  to the sulfide substrate. Further aspects of the oxidation mechanism and catalytic cycle will be studied in the near future.

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**Figure Legends:**

**Figure 1.** Ball-and-stick representation of the  $\text{H}_5\text{PV}^{\text{V}}_2\text{Mo}_{10}\text{O}_{40}$  polyoxometalate; center pink sphere represents the phosphorous (P) atom, the two black spheres the vanadium (V) atoms, the ten brown spheres the molybdenum (Mo) atoms, and the forty white spheres the oxygen (O) atoms.

**Figure 2.**  $^{13}\text{C}$ -NMR spectrum of the reaction between  $\text{H}_5\text{PV}^{\text{V}}_2\text{Mo}_{10}\text{O}_{40}$  and 2-chloroethyl ethyl sulfide (half-sulfur mustard, H-MG); reaction conditions: 3.0  $\mu\text{mol}$   $\text{H}_5\text{PV}^{\text{V}}_2\text{Mo}_{10}\text{O}_{40}$  and 30.0  $\mu\text{mol}$  of the H-MG in 1.0 mL of deuterated water ( $\text{D}_2\text{O}$ ) at 37° C under aerobic conditions ( $\text{O}_2$  gas). The NMR acquisition parameters were: number of transients 74000 scans, acquisition time 1.29 s, first delay (d1) 1.00 s, pulse width (pw) 4.75  $\mu\text{sec}$  and 90° pulse width (pw90) 9.50  $\mu\text{sec}$ ; the recording time was 15 h.

**Figure 3.**  $^{13}\text{C}$ -NMR spectrum of the reaction of  $\text{H}_5\text{PV}^{\text{V}}_2\text{Mo}_{10}\text{O}_{40}$  with bis-2-chloroethyl sulfide (sulfur mustard, HD); reaction conditions: 30.0  $\mu\text{mol}$  of HD in deuterated water with  $\text{H}_5\text{PV}^{\text{V}}_2\text{Mo}_{10}\text{O}_{40}$  (120  $\mu\text{mol}/\text{mL}$ ) at 37° C under aerobic conditions. The NMR acquisition parameters were: number of transients 8075 scans, acquisition time 3.8 s, first delay (d1) 2.0 s, pulse width (pw) 7.3  $\mu\text{sec}$  and 90° pulse width (pw90) 14.60  $\mu\text{sec}$ ; recording time was 13:60:46 h.

**Figure 4.** A)  $^{31}\text{P}$ -NMR spectrum of a solution of 3.0  $\mu\text{mol}$   $\text{H}_5\text{PV}^{\text{V}}_2\text{Mo}_{10}\text{O}_{40}$  and 30.0  $\mu\text{mol}$  of HD in 1.0 mL of  $\text{D}_2\text{O}$  at 37° C under aerobic conditions with resolution enhancement. The NMR acquisition parameters were: number of transients 512 scans, acquisition time 1.6 s, first delay (d1) 1.0 s, pulse width (pw) 10.65  $\mu\text{sec}$  and 90° pulse width (pw90) 27.40  $\mu\text{sec}$ ; the recording time was 00:30:48 h. Inserts are  $^{31}\text{P}$ -NMR spectra windows at various concentrations of  $\text{H}_5\text{PV}^{\text{V}}_2\text{Mo}_{10}\text{O}_{40}$  after reaction with HD ( $4.4 \times 10^{-4}$  M): a) 5.0 mg/600  $\mu\text{L}$  in  $\text{D}_2\text{O}$ ; b) 10.0 mg/600  $\mu\text{L}$

in D<sub>2</sub>O, and c) 15.0 mg/600 μL in D<sub>2</sub>O at 37° C under aerobic conditions.

**Figure 5.** <sup>51</sup>V-NMR spectrum of phosphovanadomolybdate polyoxometalate, H<sub>5</sub>PV<sup>V</sup><sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> (35.0 mg/ 600 μL D<sub>2</sub>O); the <sup>51</sup>V-NMR spectrum was referenced to pure vanadium (V) oxytrichloride (VOCl<sub>3</sub>, 99.99%). The NMR acquisition parameters were: number of transients 4096 scans, acquisition time 0.10 s, first delay (d1) 1.0 s and pulse width (pw) 9.2 μsec; the recording time was 00:37:51 h. The large linewidth of the signal at δ -535 ppm is indicative of an equilibrium mixture of α- and β-Keggin structural isomers.

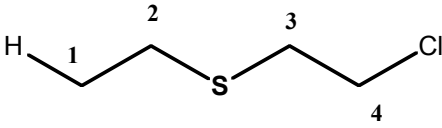
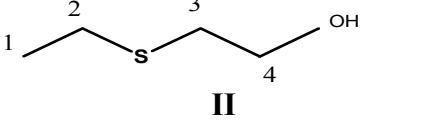
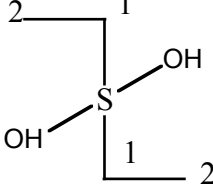
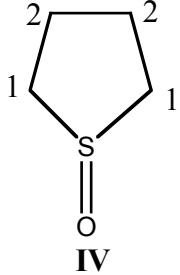
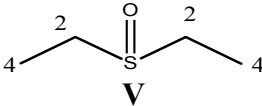
**Figure 6.** Progressive <sup>51</sup>V-NMR spectra of a solution of H<sub>5</sub>PV<sup>V</sup><sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> (25.0 mg/600 μL D<sub>2</sub>O) with HD (4.40 x 10<sup>-4</sup> M) at 37° C as a function of time; the NMR spectra were recorded immediately after the reaction started and then every hour for 12 h. The NMR acquisition parameters were: number of transients 4096 scans, acquisition time 0.1 s, first delay (d1) 1.0 s and pulse width (pw) 9.2 μsec . An external reference VOCl<sub>3</sub> was used.

**Figure 7.** First-derivative powder EPR spectrum of phosphovanadomolybdate, PV<sup>V</sup><sub>2</sub>Mo<sub>10</sub>O<sub>40</sub><sup>-5</sup> (35.0 mg), at 25° C; the graph shows the decay of the anisotropic hyperfine splitting of the vanadyl transition metal in PV<sup>V</sup><sub>2</sub>Mo<sub>10</sub>O<sub>40</sub><sup>-5</sup> (35.0 mg) for the reaction with 0.0 mg/mL, 1.7 mg/mL, 3.4 mg/mL, and 5.1 mg/mL of H-MG under aerobic condition for 20 min at 37° C; the EPR parameters are given in the Experimental Section.

**Figure 8.** A) EPR spectrum of a solution PV<sup>V</sup><sub>2</sub>Mo<sub>10</sub>O<sub>40</sub><sup>-5</sup> polyoxometalate (35.0 mg) in 1.0 mL of dimethyl sulfoxide (DMSO) under aerobic conditions at 37° C; B) EPR spectrum of the reaction of PV<sup>V</sup><sub>2</sub>Mo<sub>10</sub>O<sub>40</sub><sup>-5</sup> polyoxometalate with HD (4.5 μL of 9.35 mg/mL) in DMSO under aerobic conditions at 37° C. The EPR spectrum (A) of the polyoxometalate in DMSO shows a small contribution of the <sup>51</sup>V<sup>+4</sup>

paramagnetic cation. The presence of HD (B) increases the quantity of  $^{51}\text{V}^{+4}$  cation by 1.6 fold. The eight hyperfine lines are due to specific transitions of  $^{51}\text{V}^{+4}$  cation ( $I = 7/2$ ). The EPR parameters were: receiver gain  $5 \times 10^4$ , time constant 655.36 ms, sweep time 335.54 s, sweep width 300.0 mT and microwave power 50.2 mW.

**Table I**  
<sup>13</sup>C -NMR Chemical Shifts of the Half Sulfur Mustard and the Identified Reaction Products

Chemical Structure	Identified <sup>13</sup> C atoms	Observed $\delta_{\text{TMS}}$ Scale (ppm)*	Predicted $\delta$ ( <sup>13</sup> C) Values	Configuration Limits (calculated error)
 <b>I</b>	C <sub>3</sub> C <sub>4</sub> C <sub>2</sub> C <sub>1</sub>	33.04 42.31 25.40 14.24	35.60 42.76 26.38 15.11	1.10 1.10 1.10 1.10
 <b>II</b>	C <sub>3</sub> C <sub>4</sub> C <sub>2</sub> C <sub>1</sub>	34.89 60.52 25.27 13.98	34.30 61.00 26.00 14.68	0.50 0.50 0.50 0.50
 <b>III</b>	C <sub>2</sub> C <sub>1</sub>	25.44 34.89	24.23 34.25	1.02 1.00
 <b>IV</b>	C <sub>2</sub> C <sub>1</sub>	25.44 56.34	1.12 1.43	1.27 1.10
 <b>V</b>	C <sub>2</sub> C <sub>4</sub>	42.25 8.34	44.30 7.03	2.10 1.30

\*  $\delta_{\text{TMS}}$  scale (ppm) with tetramethylsilane (TMS) as internal reference.