

In-situ degradation of sulphur mustard and its simulants on the surface of impregnated carbon systems

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Abstract

Bis-2-chloroethyl sulphide (sulphur mustard or HD) is an extremely toxic and persistent chemical warfare agent. For in situ degradation of HD and its analogues (simulants), i.e., dibutyl sulphide (DBS) and ethyl 2-hydroxyethyl sulphide (HEES), different carbon systems such as 11-molybdo-1-vanadophosphoric acid impregnated carbon (V_1/C), ruthenium chloride impregnated carbon (Ru/C) and combination of these two ($V_1/Ru/C$) were prepared. These carbons were characterized for cumulative micropore volume and surface area by N_2 BET. The kinetics of the in situ degradation of HD and its simulants were studied and found to be following the first order kinetics. Kinetic rate constants and $t_{1/2}$ values were determined. Products were characterized using NMR, IR and GC–MS. Reaction products were found to be sulphoxide and sulphone. The combined system, i.e., 11-molybdo-1-vanadophosphoric acid plus ruthenium chloride ($V_1/Ru/C$) was found to be best for in-situ degradation of HD and its simulants. In-situ degradation by polyoxometalate based system was found to be stoichiometry based while Ru/C oxidized HD in presence of chemisorbed oxygen. In combined system of $V_1/Ru/C$ ruthenium worked as a catalyst and polyoxometalate acted as a source of oxygen. Effect of moisture was also studied in combined system. Rate of degradation of HD was found to be increasing with increased percentage of moisture content.

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1. Introduction

Porous activated carbon is an universal adsorbent and widely used for the purification of air and water streams [1–4] using different kinds of air and water filtration systems due to its economical viability, ease of availability and high adsorptive potential. It only physisorbs toxic vapours from contaminated environment but do not degrade them. So there is a chance of cross-contamination due to desorption of physisorbed toxic vapours when these filtration systems containing physisorbed CW agents are thrown carelessly or are not disposed off properly. To achieve the toxic chemical degradation, activated carbon is impregnated with suitable impregnants. Activated carbon impregnated with silver, chromium and copper is used in NBC filtration system and this carbon system is known as ASC whet-

lerite by the name of its researcher. This system removes gases such as hydrogen cyanide, cyanogen chloride, phosgene, etc. [5–13]. All of these gases are highly volatile and fall in the category of non-persistent chemical warfare agents (CW). There is one more category of CW agent, i.e., persistent CW agent which are high boiling liquids and are not degraded over ASC whetlerite, only a little hydrolysis of sulphur mustard (HD) has been reported on it [6]. Therefore, there is a need to develop new adsorbent system which can degrade persistent CW agents in-situ. The aim of persistent study was also the degradation of HD/simulants over suitable adsorbent systems.

In order to degrade HD and its simulants over adsorbent systems different polyoxometalates [14–16] impregnated carbon systems were used by different researchers. Damico et al. (1997) studied the detoxification reactions of thioether (mustard analogue) with carbon-supported polyoxometalate [17]. Heteropolyanion salt ($Na_5PV_2Mo_{10}O_{40}$) was supported on microporous carbons and tested against chloroethyl ethyl sulphide (half sulphur mustard) and tetrahydrothiophene [18]. Polyoxometal-

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lates reactions were also studied with tropical skin protectant cream [19]. Polyoxometalates were not only used for degradation of the half sulphur mustard but also used for detecting the presence of toxic chemical based on color change of the cream. Gall (1996) showed that the oxidation of the HD simulant tetrahydrothiophene (THT) to tetrahydrothiophene oxide (THTO), catalysed by $\text{Na}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ impregnated carbon, is of first order type reaction in substrate and proportional to the concentration of the active sites on the $\text{Na}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ impregnated carbon [20]. Singh et al. studied the reaction of thiodiglycol (a hydrolysis product of sulphur mustard) on impregnated carbon [21]. 1,4-Oxathiane and 1,4-oxathiane, 4-oxide were observed as reaction products. All these studies indicated that the impregnants in the detoxification reactions add reactivity to carbon to make it useful for the reactive removal of CW agents. Inspired by these studies we have prepared and studied the reaction of HD and its simulants on 11-molybdo-1-vanadophosphoric acid impregnated carbon (V_1/C), ruthenium chloride impregnated carbon (Ru/C) and combination of these two impregnants ($\text{V}_1/\text{Ru}/\text{C}$). Degradation products were characterized by NMR, IR and GC–MS techniques.

2. Experimental

2.1. Materials

Activated carbon of surface area $1250 \text{ m}^2/\text{g}$ of coconut shell origin, particle size 12×30 BSS (British sieve size) was procured from M/S Active carbon India Ltd., Hyderabad. Sulphur mustard was obtained from Synthetic Chemistry Division of our establishment. Chloroform (AR grade), ruthenium chloride, sodium molybdate, disodium hydrogen phosphate, sulphuric acid, sodium metavanadate dibutyl sulphide, ethyl 2-hydroxyethyl sulphide were obtained from E-Merck, India Ltd., SD fine, India and Lancaster, UK. 11-Molybdo-1-vanadophosphoric acid was prepared using standard method [22].

2.2. Neutralization of active carbon

Procured active carbon was basic in nature. It was treated with 2% nitric acid and washed with distilled water until the extract did not show pH near 7. Nitric acid washed carbon was dried and surface area was determined that was found to be $1313 \text{ m}^2/\text{g}$.

2.3. Impregnated carbon

Activated carbon was impregnated with aqueous solution of ruthenium chloride (5.0%, w/w) and 11-molybdo-1-vanadophosphoric acid (5.0%, w/w) using incipient wetness technique. Three types of impregnated carbon systems were prepared for the kinetics of degradation of HD. These were 11-molybdo-1-vanadophosphoric acid (V_1/C) impregnated carbon, ruthenium chloride (Ru/C) impregnated carbon and 11-molybdo-1-vanadophosphoric acid plus ruthenium chloride ($\text{V}_1/\text{Ru}/\text{C}$) impregnated carbon. The 11-molybdo-1-vanadophosphoric acid plus ruthenium chloride impregnated

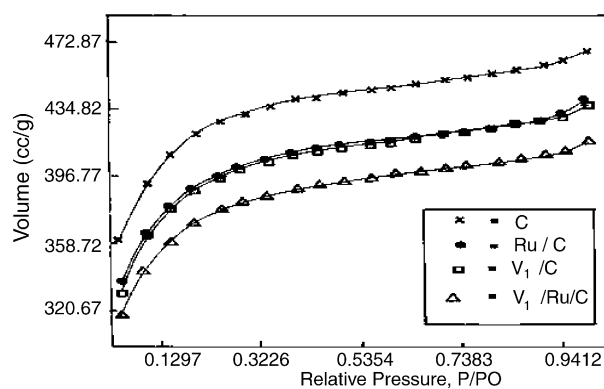


Fig. 1. N_2 adsorption isotherm of carbon systems.

carbon system was prepared by taking 5.0% (w/w) of each impregnants. These systems were dried at 110°C for 6 h.

2.4. Surface area analysis

Surface area of impregnated and unimpregnated carbons were determined by using Autosorb 1C from Quantachrome, USA. Fig. 1 describes the adsorption isotherms. Cumulative micropore volume was determined by using Howarth Kawasaki method.

2.5. Reaction procedure

All the reactions were carried out in glass tubes. One hundred milligrams of impregnated carbon was placed in glass tube with $100 \mu\text{L}$ solution containing $5 \mu\text{L}$ sulphur mustard or dibutyl sulphide or ethyl 2-hydroxyethyl sulphide in chloroform. The tubes containing the reaction mixture were maintained at constant temperature (37°C) in an oven and each tube was taken out for kinetic studies at regular intervals of time. For kinetics of degradation, residual toxicants were extracted in chloroform and the solutions were subjected to GC/FID analysis using splitless injection technique. All gas chromatography analysis was performed on a chemito 8610 gas chromatograph equipped with BP5 column (5% phenyl methyl silicon capillary column of 30 ft. length, 0.3 mm i.d.) and FID detector. Isothermal method was adopted for GC analysis, the oven, injection port and detector were kept at 120, 220 and 250°C , respectively. The experiments were performed carefully using applicable safety procedures. All the experiments were performed in the fume cupboard.

2.6. Effect of moisture

Ninety percent relative humidity was created in a desiccator by using a fixed composition of 90.2 mL water plus 9.8 mL sulphuric acid. One hundred milligrams of carbon samples were taken in Petri dishes and placed in the desiccator for different interval of times to obtain variable moisture content in the adsorbents. In order to study the effect of moisture content, the carbon samples with different moisture contents were subjected for HD degradation.

2.7. Characterization of reaction products

In order to investigate the reaction products, simulants/HD exposed carbon systems were extracted with 2 mL of chloroform for 3 h in well stoppered test tubes. The extracts were concentrated by N_2 purging. Concentrated extracted reaction products were characterized using GC–MS, NMR and GC–FTIR Perkin Elmer model 1720X with light-pipe sampling device. The spectra were recorded in the range of $4000\text{--}700\text{ cm}^{-1}$ using narrow band liquid nitrogen cooled MCT (mercury cadmium telluride) detector. All the NMR spectra were recorded on Bruker 400 MHz NMR spectrometer using magnetic field frequency 400 MHz for proton nuclei and 100 MHz for ^{13}C nuclei. Chemical shift scale was set by using the internal reference TMS (tetra methyl silane) for both the nuclei. Proton–proton homocosity was recorded using cosy gp pulse programme.

3. Results and discussion

The carbon systems such as V_1/C , Ru/C , and $V_1/Ru/C$ were prepared and characterized for surface area and cumulative micropore volume. The surface area and cumulative micropore volume of nitric acid treated active carbon were found to be $1313\text{ m}^2/\text{g}$ and 0.63 cc/g and for V_1/C system $1223\text{ m}^2/\text{g}$ and 0.59 cc/g , respectively. For Ru/C system the same value was determined for micropore volume as for V_1/C system and surface area was $1224\text{ m}^2/\text{g}$. The surface area and micropore volume for $V_1/Ru/C$ system was found to be $1161\text{ m}^2/\text{g}$ and 0.56 cc/g . These values indicated that after impregnation there was reduction in the values of surface area and micropore volume. It is quite evident from the fact that impregnants occupied the porous structure partly and resulted in the decrease of surface area.

Obtained carbon systems were subjected to study the degradation of HD and simulants along with active carbon. Kinetics of reaction was studied. Reaction products were extracted and characterized using NMR, GC–FTIR and GC–MS techniques.

3.1. Kinetics of degradation of DBS

Fig. 2 shows the plot of $\log(a-x)$ against time in hours for active carbon, 11-molybdo-1-vanadophosphoric acid

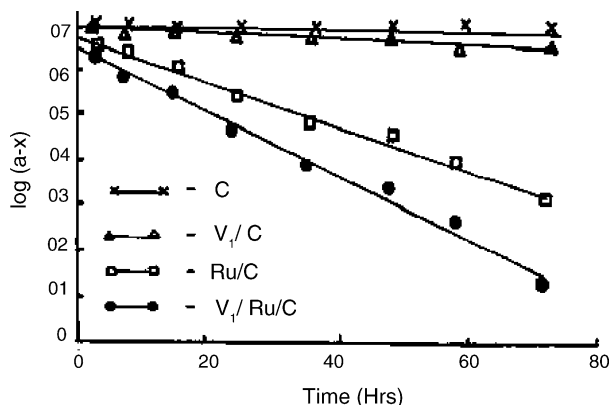


Fig. 2. Kinetics of degradation of DBS on carbon systems.

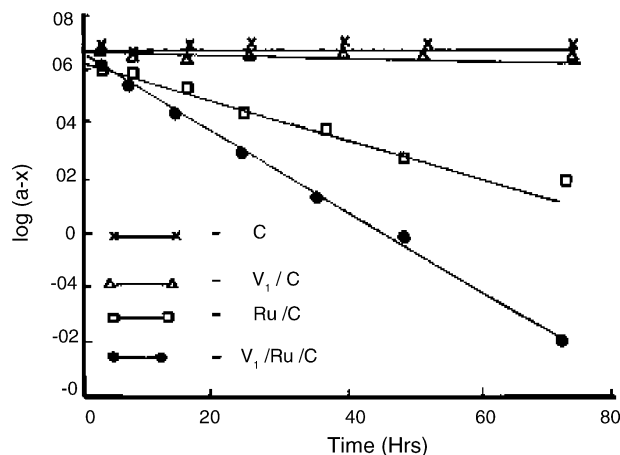


Fig. 3. Kinetics of degradation of HEES on carbon systems.

acid, ruthenium chloride and ruthenium chloride plus 11-molybdo-1-vanadophosphoric acid carbon systems. This reaction was found to follow the pseudo-first-order kinetics. The rate constant values and half life for ruthenium chloride carbon system were found to be $9.2 \times 10^{-3}\text{ h}^{-1}$ and 75.2 h and for combined system ($V_1/Ru/C$) were found to be $1.4 \times 10^{-3}\text{ h}^{-1}$ and 50.15 h. The 11-molybdo-1-vanadophosphoric acid carbon system degraded DBS upto 8% in 72 h.

3.2. Kinetics of degradation of HEES

Fig. 3 shows the plot of $\log(a-x)$ against time in hrs for active carbon, 11-molybdo-1-vanadophosphoric acid, ruthenium chloride and ruthenium chloride plus 11-molybdo-1-vanadophosphoric acid carbon systems. Kinetics of degradation followed the pseudo-first-order kinetics. Rate constant was calculated from slope of straight line drawn in Fig. 3. The rate constant values and half life for ruthenium chloride (Ru/C) carbon system were found to be $2.3 \times 10^{-2}\text{ h}^{-1}$ and 30 h and for the combined system ($V_1/Ru/C$) were found to be $3.4 \times 10^{-2}\text{ h}^{-1}$ and 20 h. The 11-molybdo-1-vanadophosphoric acid carbon system degraded HEES 16% in 48 h.

3.3. Kinetics of degradation of HD

Linear plots of $\log(a-x)$ on Y-axis and time in hours on X-axis were obtained. The linear curves (Fig. 4) indicated that the reactions follow pseudo-first-order kinetics in the case of all the carbon systems. Rate constant was calculated using the slope of the straight line drawn. $t_{1/2}$ values of reactions were calculated from $0.6932/k$. The rate constant and half life values were found to be $1.8 \times 10^{-2}\text{ h}^{-1}$ and 37.61 h for combined system. The ruthenium chloride, 11-molybdo-1-vanadophosphoric acid and ruthenium chloride plus 11-molybdo-1-vanadophosphoric acid carbon system degraded HD upto 40, 21 and 73% in 72 h, respectively.

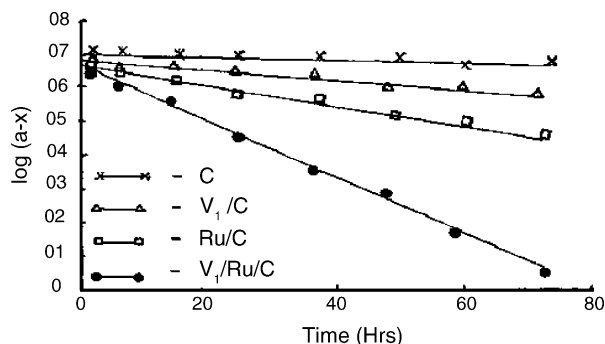


Fig. 4. Kinetics of degradation of HD on carbon systems.

3.4. Product analysis

Products were analysed by NMR, GC–FTIR and GC–MS. GC–FTIR and GC–MS indicated the products to be sulphoxide. However, NMR indicated products to be the sulphoxide and sulphone.

The degradation reaction of most reactive system, i.e., $V_1/Ru/C$ was analysed for products. In proton NMR dibutyl sulphoxide peaks were observed at 2.62, 1.63, 1.43, 0.91 and in ^{13}C NMR peaks at 52.0, 30.1, 22.1 and 14.2 ppm. Peaks of sulphur mustard sulphoxide and sulphone were observed at 55.14, 37.03 and 56.39, 36.46 ppm, respectively for ruthenium chloride plus 11-molybdo-1-vanadophosphoric acid carbon systems (Fig. 5) in ^{13}C NMR spectra. ^{13}C NMR peak values for ethyl 2-hydroxyethyl sulphoxide and sulphone were observed respectively at 14.43, 32.91, 51.97, 62.86 and 6.74, 46.23, 57.36, 61.65 ppm (Fig. 6). The NMR data was found to be in agreement with the reported information published elsewhere [19,23]. The NMR data was also matched with the pure compounds (sulphoxide and sulphone). Some other peaks were also observed which are yet to be identified. The product formation for $V_1/Ru/C$ and Ru/C with all the toxic reactants were studied using NMR (both proton and carbon) technique which confirmed that sulphoxide formation is more in $V_1/Ru/C$ system than Ru/C . Proton–proton homocosity experiment was done to observe the intraprotonic relationship between the protons of the products and reactants (Fig. 7). (A–B), (B–C), and (C–D) contours were for dibutyl sulphide and (1–2), (2–3) and (3–4) were for the dibutyl sulphoxide protons. This also confirmed the formation of sulphoxide.

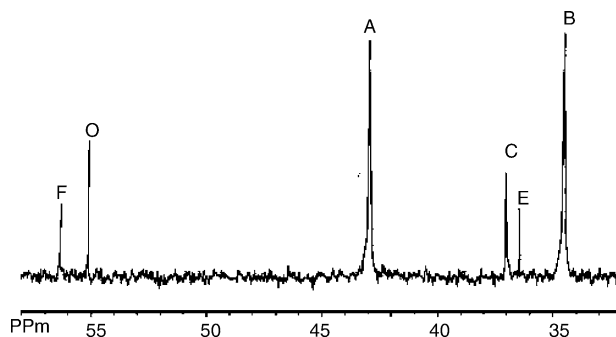


Fig. 5. ^{13}C NMR of HD, sulphoxide and sulphone on $V_1/Ru/C$ system (A, B: HD, C, D: sulphoxide and E, F: sulphone).

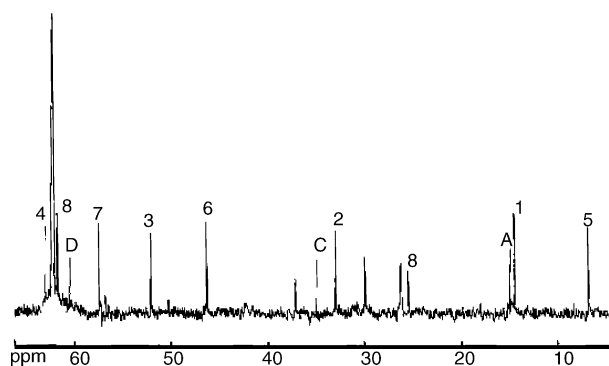


Fig. 6. ^{13}C NMR of HEES, HEESO and HEESO₂ on $V_1/Ru/C$ system (A, B, C, D: HEES, 1, 2, 3, 4: HEESO, 5, 6, 7, 8: HEEO₂).

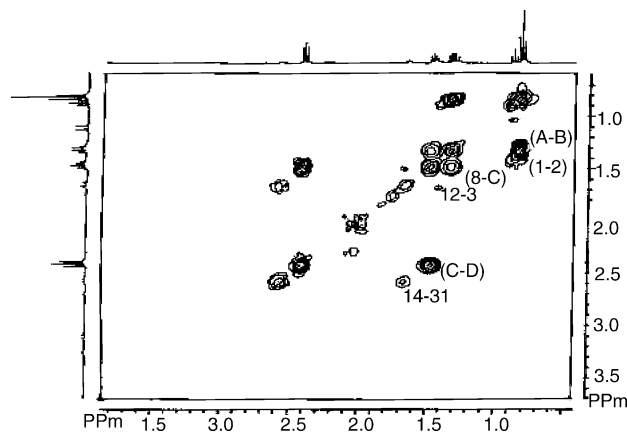


Fig. 7. 1H – 1H Homocosity spectrum of mixture of DBS and sulphoxide on $V_1/Ru/C$ system.

IR spectra showed strong absorption band at 1027 cm^{-1} due to S=O group in dibutylsulphoxide (Fig. 8). This absorption peak was absent in the IR spectra of dibutylsulphide. The IR spectra of HD and HEES were very complex due to overlapping frequencies, which could not provide much information. The formation of dibutylsulphoxide was also confirmed by GC–MS. The m/z values were 162, 145, 106, 89, 57 and 41.

Active carbon did not show degradation and approximately 95% HD was extracted. The 11-molybdo-1-vanadophosphoric acid carbon system degraded 21% HD, 8% DBS in 72 h, respec-

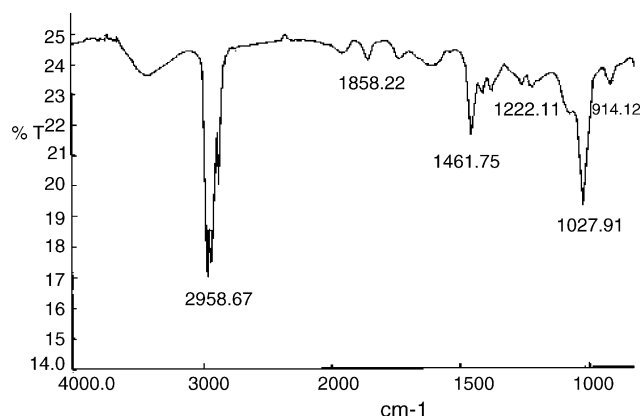
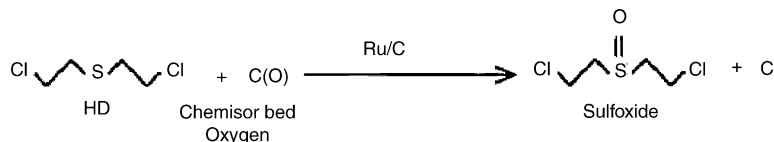


Fig. 8. GC–IR spectra of dibutyl sulphoxide on $V_1/Ru/C$ system.



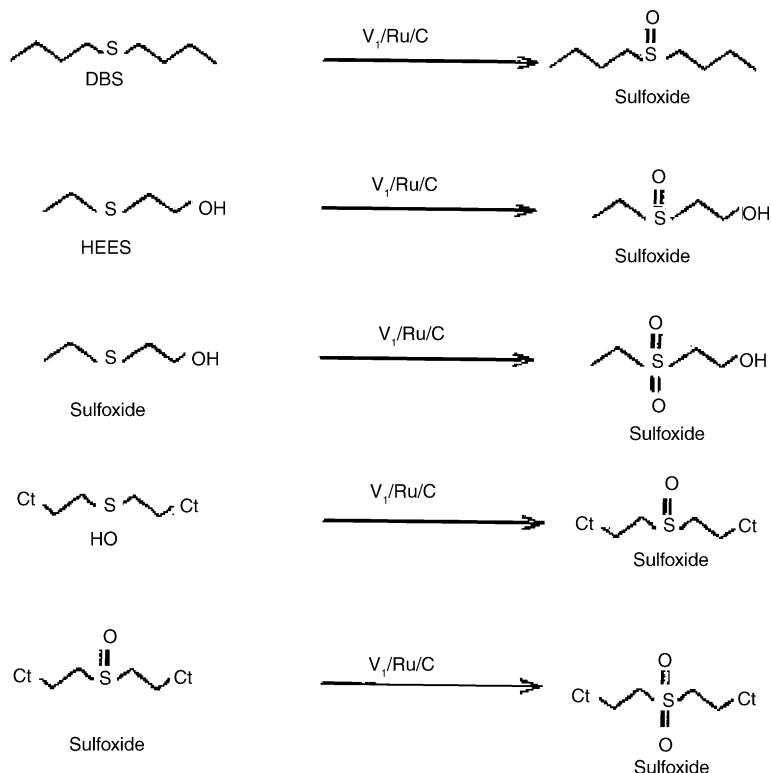
Scheme 1.

tively and 16% HEES in 48 h. No further degradation after 72 and 48 h, respectively for HD, DBS and HEES was observed indicating the reaction ceased or no reactive impregnants were available for further degradation. This was studied by increasing percentage of the impregnants from 5 to 20. As the percentage of impregnants was increased, the degradation of HD and simulants were also found to be increasing. The percentage of degradation of HD was 21, 30, and 58%, respectively for 5, 10, and 20% impregnants. Another experiment was also performed for determination of stoichiometry reaction. In this experiment amount of HD was varied from 1 to 10 μL . In all the three case same percentage of degradation was observed. The reaction was found to be taking place, indicating the reaction was stoichiometry based. The kinetics of DBS and HEES were not observed because reaction was very slow and initially no observable degradation was noticed.

The kinetics of HD reaction with 11-molybdo-1-vanadophosphoric acid indicate that POM probably showed dual character. It could oxidize and hydrolyse the HD as HD has the active groups for hydrolysis. However, no hydrolysis product could be identified. In case of DBS and HEES only oxidation reaction is possible but with HD several pathways are possible that is why kinetics of HD degradation could be

observed. The ruthenium chloride carbon system, however, alone degraded 40% HD, 59% DBS and 70% HEES in 72 h, respectively. The 11-molybdo-1-vanadophosphoric acid carbon system showed very less degradation but in combination with ruthenium chloride, it was found to be degrading significantly. The observed degradation was 73, 75 and 94% in 72 h, respectively for HD, DBS and HEES. Initially the rate of degradation for combined system ($V_1/\text{Ru/C}$) was observed to be fast which slowed down with time. The rate constant values of HD degradation were found to be $1.8 \times 10^{-2} \text{ h}^{-1}$ and half life of reaction to be 37.61 h for combined system. Ru/C system alone oxidized the HD, DBS and HEES probably due to chemisorbed or atmospheric oxygen. In order to confirm this, the in situ degradation of HD on Ru/C was also studied in N_2 atmosphere. No decrease was observed in the degradation of HD in absence of atmospheric air indicating that the Ru/C system oxidizes HD in presence of chemisorbed oxygen only. Scheme 1 shows the probable reaction of HD degradation by Ru/C system.

In the combined system ($V_1/\text{Ru/C}$), extent of degradation was found to be enhanced due to the availability of oxygen from polyoxometalate indicating that ruthenium chloride catalysed the reaction and polyoxometalate acted as a source of oxygen. However, the possibility of supply of oxygen by carbon



Scheme 2.

as chemisorbed oxygen also cannot be ruled out. This can be inferred from the study that if a proper oxygen source is provided to Ru/C system, 100% degradation of HD can be achieved. This will be explored in future.

Keggin-type POMs are sensitive to water [24,25]. So effect of moisture was studied on combined system i.e., V_1 /Ru/C on the degradation of HD as this was found to be the most reactive system. The carbon system was exposed to the humid atmosphere 90% RH (relative humidity) for different time intervals for obtaining different values of moisture, which was created in a dessicator. V_1 /Ru/C system adsorbed 5.09, 16.2 and 22.9% additional moisture in 5, 10 and 60 min. Carbon system (V_1 /Ru/C) with different moisture contents was studied their degradation capability against HD. The rate of degradation was found to be increasing with increasing moisture content in the V_1 /Ru/C system. The observed percentage of degradation was 19.8, 28.5, 49.4 for V_1 /Ru/C system in 24 h having 11.09, 22.2 and 28.9% moisture content, respectively. The reason may be that, in case of V_1 /Ru/C system having less moisture content, HD is strongly attracted to the carbon surface rather than POM sites because of lipophilic nature of carbon surface. This results in the less degradation of HD. However, in case of carbon system with high moisture content, HD molecules migrate to the POM sites rather than carbon surface which is already saturated with water molecules and behaves as lipophobic surface. HD molecules, which reach to POMs sites are degraded to sulphoxide.

In the case where moisture content is high in carbon, POM is also saturated with moisture, which is a favourable condition for POM to regain its geometry and become more efficient species for degradation of HD. No hydrolysis product was observed in carbon system with and without impregnants. It indicated further that probably water enhances degradation of HD due to the change in POM (present over carbon) by interacting with the water molecules in case of V_1 /Ru/C system containing high moisture content.

Scheme 2 shows the plausible proposed reactions for degradation of HD and its simulants by the systems containing polyoxometalate.

4. Conclusion

Ru/C, V_1 /C and V_1 /Ru/C were made and studied the in-situ degradation of HD, DBS and HEES. Kinetics of degradation was found to be following the pseudo-first-order kinetics. Combined system (V_1 /Ru/C) was found to be most efficient system amongst all studied systems for the degradation of simulants/HD. It showed the percentage of degradation of HD, DBS and HEES to 73, 75 and 94%, respectively in 72 h. Study indicated that the V_1 /C system worked on stoichiometry bases and showed slow degradation of HD while Ru/C and V_1 /Ru/C systems were found to be working as a catalytic systems, oxidizing HD in presence of chemisorbed oxygen of carbon of Ru/C system and polyoxometalate oxygen of V_1 /Ru/C system respectively. Effect of moisture on HD degradation on V_1 /Ru/C was also studied and increased degradation was observed with increase in moisture content. The study depicted that if a proper oxygen source is provided to Ru/C system or if V_1 /Ru/C sys-

tem is properly modified with a co-oxidant for oxygen supply, 100% degradation of HD can be achieved and this can lead to the development of efficient NBC filtration system.

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