Kinetics of degradation of sulphur mustard on impregnated carbons

G.K. Prasad [*], Beer Singh, M.V.S. Suryanarayana, B.S. Batra

Defence Research and Development Establishment, Jhansi Road, Gwalior 474002, Madhya Pradesh, India

Abstract

Kinetics of degradation of sulphur mustard (HD) on the surface of $NaOH/CrO_3/C$, $NaOH/CrO_3/EDA/C$ and $RuCl_3/C$ systems has been examined by using gas chromatography technique by extracting and analyzing the residual HD periodically. The carbons were prepared by impregnating activated carbon with 4% sodium hydroxide plus 3% Cr(VI) as CrO_3 with and without 5% ethylene diamine (EDA) and 5% ruthenium chloride by using their aqueous solutions. Obtained carbons were characterized for surface area analysis by BET conventional method. Kinetic plots reveal that the observed reactions are fast at the initial stages, slow at the later stages and progress to a steady state indicating the first order behavior. Effect of moisture on kinetic rate is also observed. In the case of $NaOH/CrO_3/C$ system the rate constant is decreased from 13.36 to $5.53 \times 10^{-2} \, h^{-1}$ and half life is increased from 5.2 to 12.54 h while moisture content is increased from 1.9% to 11.2%. Whereas, the rate constant of HD degradation reaction is decreased from 10.4 to $4.14 \times 10^{-2} \, h^{-1}$ and half life is increased from 6.7 to 16.72 h while moisture content is increased from 2.1% to 10.8% on $NaOH/CrO_3/EDA/C$. Reaction on $RuCl_3/C$ system also behaves in the similar manner. Extracted reaction products were characterized by GC/MS and it is found that on $NaOH/CrO_3/C$, HD degrades to hemisulphur mustard, thiodiglycol and 1,4-oxathiane. Whereas, on $NaOH/CrO_3/EDA/C$, HD is degraded to 1,4-thiazane and it is degraded to divinyl sulphone on $RuCl_3/C$. All these investigations reveal that above mentioned carbons can be used in nuclear, biological and chemical (NBC) filtration systems for protection against sulphur mustard.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Activated carbon; Adsorption; Chemical warfare agent; Impregnation; Sulphur mustard

1. Introduction

Disposal of carbon based filtration systems [1–4] after their use is of great concern due to several reasons. Of them, cross contamination of the environment due to desorption of adsorbed agents is considered to be the important aspect which should be taken care off due to the possible threat after the disposal of filtration systems. Such task is performed efficiently by the filtration system containing reactive carbons and they are prepared by impregnating activated carbon with various metal salts. ASC whetlerite [5] is one such im-

pregnated carbon which is used in NBC filtration systems for the reactive removal of hydrogen cyanide, cyanogen chloride and phosgene [6–21]. Activity of such impregnated carbons to degrade the above agents is quite dependent on ingredients present on the surface of active carbon. However, it was found to be deteriorating due to weathering, aging, exposure to high temperatures and storage for long time. This deactivation of the active catalyst is caused owing to the change in oxidation state of the ingredient and also due to drastic reduction in surface area. This reduction of surface area arises due to the formation of large crystallites within the pores owing to the dissolution of active species in water present on the surface of the adsorbent. On the other hand, reactions [22] of many gases on impregnated carbons were reported to be strongly influenced by the presence of water. In this regard, Hall et al. [23] studied the hydrolysis reaction of perfluoro isobutene on charcoal (PFIB). PFIB [24] was hydrolyzed as

[*] Corresponding author. Present address: Center for Crystal Science and Technology, Faculty of Engineering, Yamanashi University, Miyamae 7, Kofu, Yamanashi 4008511, Japan. Tel.: +81 552541094; fax: +81 298587190.

E-mail address: gkprasad@lycos.com (G.K. Prasad).

per the following reaction to hexafluoro isobutyric acid and hydrofluoric acid:

$$(CF_3)_2C=CF_2 + 2H_2O \rightarrow (CF_3)_2CHCOOH + 2HF$$
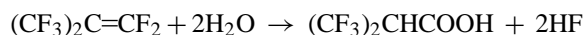
Moreover, Gall et al. [25] reported the detoxification reactions of thioether (mustard analogue) with poly oxo metallate on carbon supports and Prasad and coworkers [26a] have studied the reaction of thiodiglycol (a hydrolysis product of sulphur mustard) on impregnated carbon. Such type of carbons can be used suitably in NBC filtration systems for irreversible adsorption and in situ degradation of sulphur mustard leaving no scope for cross contamination due to desorption [26b]. Hence, it was thought to obtain the information regarding the kinetics of degradation and the extent of degradation of sulphur mustard on various impregnated carbons which will be helpful to predict their behavior in real conditions. Further, it will also give information regarding the time needed for complete degradation of the adsorbed HD after the disposal of the filter cartridge and also regarding the scope of desorption of the agent in to the environment which is indispensable for the safety of the user of filter cartridge and the personnel living in the premises.

For this purpose, we have studied the kinetics of degradation of sulphur mustard and the effect of moisture content on the rate of degradation on reactive carbon systems such as NaOH/CrO$_3$/C, NaOH/CrO$_3$/EDA/C and RuCl$_3$/C. Kinetic parameters are reckoned by first order rate equation and reaction products were characterized by GC/MS.

2. Experimental

2.1. Materials

Activated carbon of surface area 1100 m^2/g of coconut shell origin, with a particle size of 12 × 30 of British sieve size was procured from Active Carbon (India) Ltd., Hyderabad. Pure sulphur mustard (99%) was obtained from the Process Technology Development Division of our establishment. Dichloromethane, acetonitrile, NaOH, RuCl$_3$·3H$_2$O, CrO$_3$ and EDA were obtained from E Merck (India) Pvt. Ltd.

2.2. Impregnated carbons

Activated carbon was impregnated with aqueous solutions of NaOH (4%), Cr(VI) oxide (3% Cr(VI)), EDA (5%) and RuCl$_3$3H$_2$O (5%) (Table 1). Incipient wetness technique [27]

was used for impregnation. These impregnation experiments on active carbon were carried out at room temperature by slowly mixing above solutions and activated carbon. Obtained metal impregnated carbons were dried at 110 °C for 6 h and stored in air tight bottles.

2.3. Estimation of impregnants

Chromium was extracted in basic media from carbons and estimated iodometrically. NaOH was extracted by boiling carbon in distilled water and estimated by titrating with dilute hydrochloric acid. Whereas, RuCl$_3$ was extracted by using hydrochloric acid and estimated by spectrophotometric method [28].

2.4. Surface area analysis

Impregnated and unimpregnated carbons were characterized for surface area (N$_2$ BET) using Gemini 2765 surface area analyzer (Micromeritics). Micropore volume was determined by using Dubinin equation [29]. The results were described in Table 1.

2.5. Apparatus used for adsorption of carbons

Adsorption of sulphur mustard has been carried out in the assembly fabricated by us. Fig. 1 shows the outline diagram of adsorption assembly. The system contains sample cell, purge cell to keep the agent (HD) and the circulating pump. The total system volume, consisting of the cell, tubing, fittings and circulating pump is approximately 300–400 ml. The unique feature of the apparatus is that the sample is gently fluidized during adsorption, thus providing uniform contact between the particles and HD vapor. The sample (2.0 gm) was loaded from the top of the cell and once the loading is over, the sample was purged with HD/air mixture at room temperature (36 °C) with valve placed in recycle position (moisture free air was not used for this purpose). After the HD loading on carbons, they were placed in closed glass viols at room temperature. Subsequently, 100 mg of carbon was taken out from the glass viol at kinetic intervals of time and the remaining HD was extracted from it. For this purpose, it was treated with 5.0 ml acetonitrile for five times in order to ensure the complete extraction and the obtained solutions were analyzed by gas chromatograph. Gas chromatograph equipped with flame ionization detector, i.e., Chemito 8610 with BP1 column of 30 ft length was used for the analysis at isothermal conditions. Oven temperature was kept at 120 °C, injection port temper-

Table 1
Recipie of impregnants and systems prepared

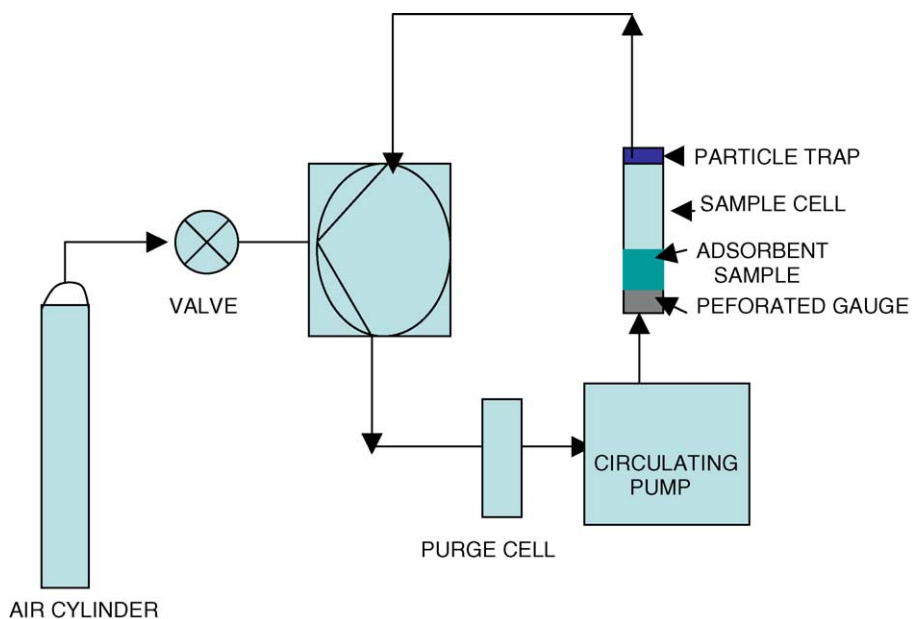| Serial no.	Amount of impregnants loaded on carbon	System	Surface area (m^2/g)	Pore volume (ml/g)
1	NaOH (4%), CrO$_3$ (3.0%)	NaOH/CrO$_3$/C	912	0.53
2	NaOH (4.0%), CrO$_3$ (3.0%), EDA (5%)	NaOH/CrO$_3$/EDA/C	855	0.5
3	RuCl$_3$/C	RuCl$_3$/C	950	0.51
4	Cu(II) (6.0%), Cr(VI) (3.0%), Ag(I) (0.2%), NaOH (2%)	Whetlerite	1050	0.52

Fig. 1. Adsorption assembly.

ature was kept at 220 °C and detector temperature was kept at 180 °C. Quantitative analysis was done by calibrating the concentrations.

2.6. Characterization of reaction products

Reaction products were characterized by extracting the analytes by acetonitrile and analyzed by GC/MS of Hewlett Packard 5739 equipped with BP 5 column of 30 ft length and 0.33 mm i.d. using temperature programmer from 50 to 280 °C at the rate of 20 °C/min. The electron impact ion source temperature was 230 °C with electron impact energy of 70 eV and the quadruple analyzer temperature was 150° C. The injection port and GC/MS interface temperature was 280 °C, respectively. Obtained mass spectra of the analytes/reaction products extracted from carbons were compared to the original spectra of compounds to confirm the presence of the reaction products.

3. Results and discussion

The prepared impregnated carbons were characterized for surface area and micropore volume (Table 1). The results show that the surface area and micropore volume decrease after impregnation. This observation can be attributed to the fact that the N_2 molecules could not enter the pores as some pores are blocked by the impregnant material [19].

Kinetics of degradation of HD on $NaOH/CrO_3/C$, $NaOH/CrO_3/EDA/C$ and $RuCl_3/C$ was studied by monitoring the residual HD concentration by GC/FID. Kinetic plots are made by taking $\log(a/a-x)$ on Y-axis and time on X-axis [32] and are illustrated in Figs. 2–4; where a, is the

initial concentration and x is the degraded amount. Figs. 2–4 show the kinetics of degradation of HD on $NaOH/CrO_3/C$, $NaOH/CrO_3/EDA/C$ and $RuCl_3/C$ and also the effect of moisture content on kinetics.

They show that the reaction is fast at the initial stages and slowed down after several hours to achieve a steady state exhibiting first order behavior. At the initial stages of the reaction, concentration of the active sites is expected to be large hence the rate of reaction is high and the slope of the initial portion (linear) of the curve is also high. As the time progresses, i.e., after several hours the number of available active sites is negligible and the rate is very low, obviously the slope is also negligible leading to a steady state. Wagner

(-○- 1.9 % ;   -▼- 4.8 % ;   -□- 11.2 %)
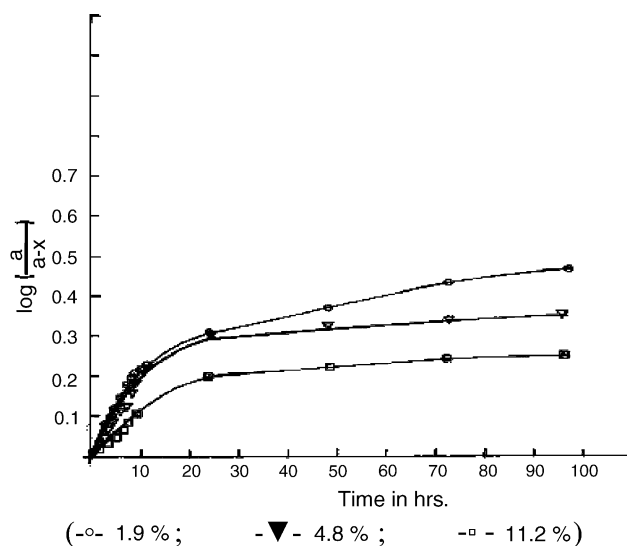
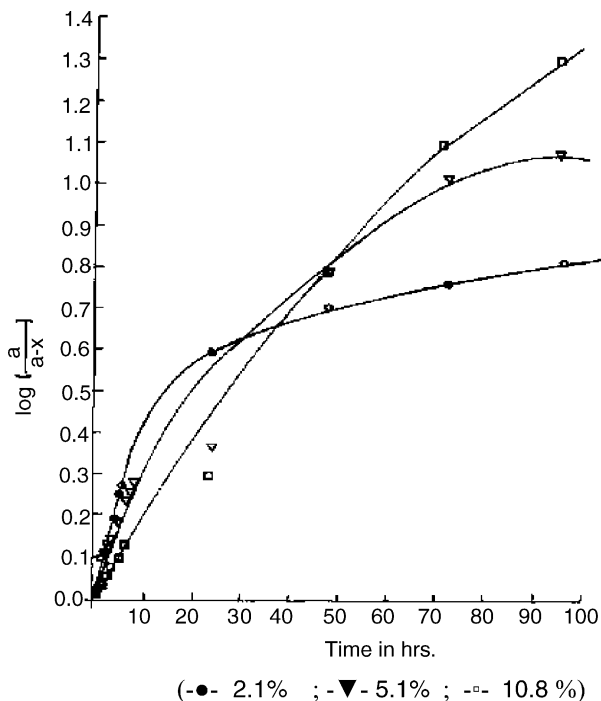Fig. 2. Effect of moisture content on kinetics of degradation of HD on $NaOH/CrO_3/C$.

Fig. 3. Effect of moisture content on kinetics of degradation of HD on NaOH/CrO$_3$/EDA/C.

et al. [30] and Stark et al. [31] observed the same pattern for the degradation of chemical warfare agents on nano-size particles and zeolites. Rate constant values are calculated by using the first order rate equation. The rate constant value is found to be 13.3×10^{-2}, 10.3×10^{-2}, 5.9×10^{-2} h^{-1}, respectively for NaOH/CrO$_3$/C, NaOH/CrO$_3$/EDA/C, and RuCl$_3$/C. Whereas, half life values are found to be 5.2, 6.7, 11.6 h, respectively for NaOH/CrO$_3$/C, NaOH/CrO$_3$/EDA/C, RuCl$_3$/C. Tables 2–4 describe the effect of moisture con-
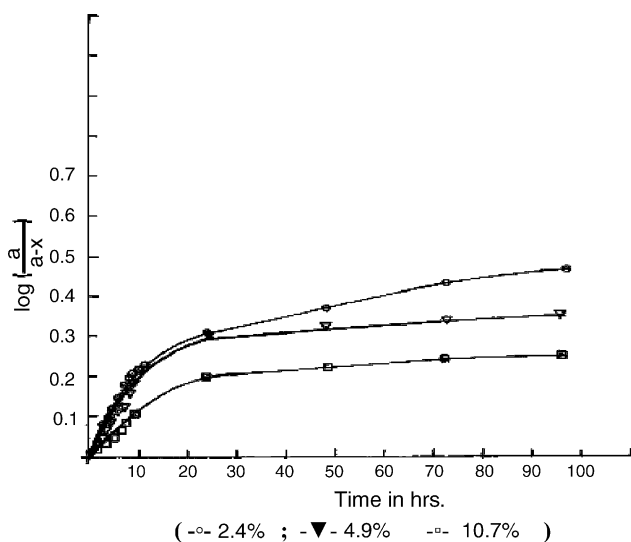

Fig. 4. Effect of moisture content on kinetics of degradation of HD on RuCl$_3$/C.

Table 2
Effect of moisture content on kinetic parameters of degradation reaction of HD on NaOH/CrO$_3$/C system

Moisture content in carbon system (%)	Rate constant of reaction ($\times 10^{-2}$ h^{-1})	Half life of reaction, $t_{1/2}$
1.9	13.36	5.2
4.8	9.90	7.0
11.2	5.53	12.5

tent on reaction kinetics. It is found that in the case of NaOH/CrO$_3$/C system, rate constant decreases from 13.36 to 5.53×10^{-2} h^{-1} and half life is found to increase from 5.2 to 12.54 h while moisture content is increased from 1.9% to 11.2%. Where, in the case of NaOH/CrO$_3$/EDA/C, it decreases from 10.4 to 4.14×10^{-2} h^{-1} and half life of the reaction increases from 6.7 h to 16.72 h where the moisture content is increased from 2.1% to 10.8%. RuCl$_3$ impregnated carbon also behaves in similar manner. It indicates that with the increase in moisture content, number of active sites for reaction between HD and metal impregnated carbon decreases thereby, the reaction was slows down. Possibly, moisture form a surrounding of the impregnant thereby not allowing the HD molecule to come into contact of impregnant for reaction or poisons the catalyst for degradation.

3.1. Reaction of HD with NaOH/CrO$_3$/C

Sulphur mustard reacts with NaOH/CrO$_3$/C to give hemisulphur mustard, 1,4-oxathiane and thiodiglycol. Cr(VI), being a better oxidizing agent could not oxidize HD on the surface of NaOH/CrO$_3$/C. It can be due to predominant formation of sulphonium ion on the surface of NaOH/CrO$_3$/C.

Table 3
Effect of moisture content on kinetic parameters of degradation reaction of HD on NaOH/CrO$_3$/EDA/C system

| Moisture content in carbon system (%)	Rate constant of reaction ($\times 10^{-2}$ h^{-1})	Half life of reaction, $t_{1/2}$
2.1	10.34	6.7
5.1	8.30	8.4
10.8	4.14	16.7

Table 4
Effect of moisture content on kinetic parameters of degradation reaction of HD on RuCl$_3$/C system

Moisture content in carbon system (%)	Rate constant of reaction ($\times 10^{-2}$ h^{-1})	Half life of reaction, $t_{1/2}$
2.4	6.00	11.6
4.9	3.92	17.7
10.7	2.50	27.4

Table 5
Reaction products and GC/MS data

System	Reaction products	m/z values
NaOH/CrO$_3$/C	Hemisulphur mustard	140/142, 109/111, 73, 45
	Thidiglycol	122, 104, 61, 43
	1,4-Oxathiane	104, 74, 46, 15
NaOH/CrO$_3$/EDA/C	1,4-Thiazane	117, 103, 88, 75, 57, 45
RuCl$_3$/C	Divinyl sulphone	75, 47, 27

Probably, in the presence of impregnants HD undergoes transformation to form sulphonium ion by release of HCl. In the presence of a water molecule the sulphonium ion converts into hemisulphur mustard. Formation of 1,4-oxathiane may occur in two ways from hemisulphur mustard. The former is that it undergoes direct transformation to form 1,4-oxathiane by the release of HCl. In the later reaction hemisulphur mustard, undergoes transformation to sulphonium ion, which hydrolyses to thiodiglycol and then undergoes dehydration reaction in the presence of NaOH on carbon to from 1,4-oxathiane. The same is observed by GC/MS (Table 5). Sulphur mustard, hemisulphur mustard, thiodiglycol and 1,4-oxathiane were eluted at 6.9, 7.2, 7.57 and 4.43 min.
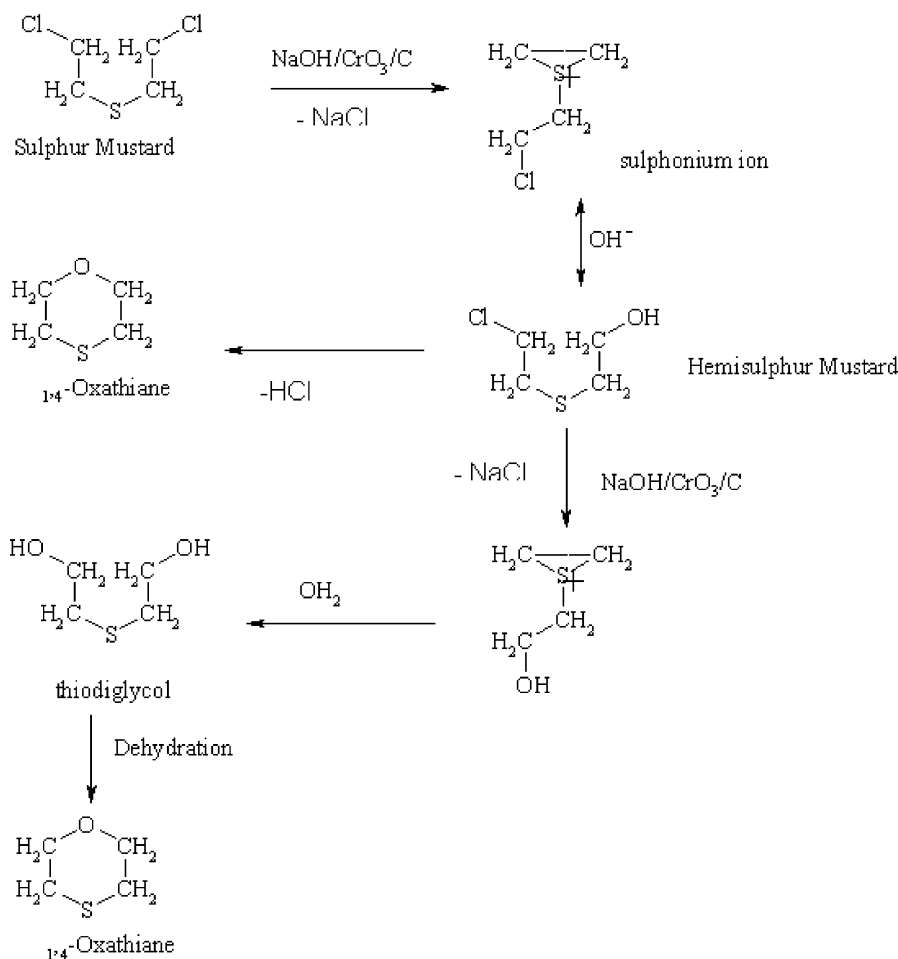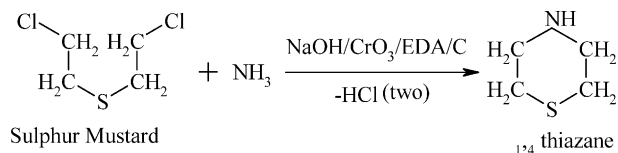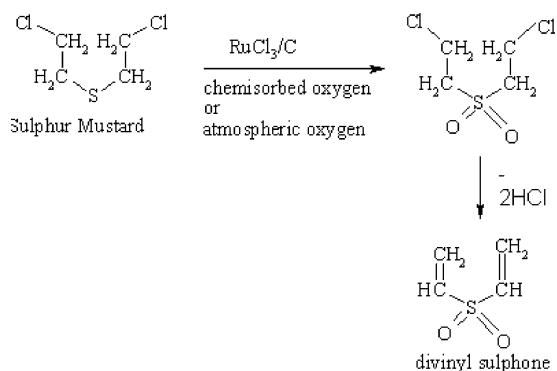

Scheme 2.

Most probably, the following is the reaction path way (Scheme 1) for HD to undergo detoxification on NaOH/CrO$_3$/C:

3.2. Reaction of HD with NaOH/CrO$_3$/EDA/C

Sulphur mustard reacts with impregnants present on NaOH/CrO$_3$/EDA/C to form 1,4-thiazane. The following is the most possible reaction pathway (Scheme 2):

NaOH/CrO$_3$/EDA/C was observed to be giving NH$_3$ on storage, probably it reacts with HD to form 1,4-thiazane. The same is confirmed by GC/MS data (Table 5) and 1,4-thiazane was eluted at 4.13 min.

Scheme 1.

Scheme 3.

3.3. Reaction of HD with RuCl₃/C

Sulphur mustard is found to be converted to divinyl sulphone on RuCl₃/C probably due to oxidation on the surface of carbon. The following are the possible reactions (Scheme 3):

Probably, sulphur mustard reacts with impregnants present on the surface of RuCl₃/C in the presence of atmospheric oxygen or chemisorbed oxygen to give divinyl sulphone. The same is supported by GC/MS data (Table 5) and the divinyl sulphone was eluted at 4.83 min.

No reaction product was observed in the solution extracted from HD exposed active carbon. Reaction was extended to 96 h in order to study the extent of degradation of HD on these impregnated carbons. However, 73% of HD on NaOH/CrO₃/C, 91% of HD on NaOH/CrO₃/EDA/C and 65.6% of HD on RuCl₃/C has been found to get degraded. RuCl₃/C system seems to be suitable adsorbent for in-situ degradation of HD as reaction products is non-toxic. NaOH/CrO₃/EDA/C system can also be used but it decomposes while releasing ammonia loses its efficiency. NaOH/CrO₃/C system degrades HD to give toxic hemisulphur mustard. Hence, the RuCl₃/C can be used in futuristic NBC filtration systems provided 100% HD degradation could be achieved.

4. Conclusion

Kinetics of degradation of sulphur mustard on the surface of NaOH/CrO₃/C, NaOH/CrO₃/EDA/C and RuCl₃/C systems has been examined. HD degradation reaction on these systems is found to follow the first order behavior. Reaction is observed to be fast initially and slows down towards a steady state as time progresses. Kinetic rate constants are calculated for NaOH/CrO₃/C, NaOH/CrO₃/EDA/C and RuCl₃/C carbon systems. On NaOH/CrO₃/C, HD degrades to hemisulphur mustard, thiodiglycol and 1,4-oxathiane. On NaOH/CrO₃/EDA/C it is degraded to 1,4-thiazane and it degrades to divinysulphone on RuCl₃/C.

References

[1] L.A. Jonas, J.A. Rehrmann, Predictive equations in gas adsorption kinetics, Carbon 11 (1973) 59–64.
[2] G.O. Wood, J.F. Stampfer, Adsorption rate coefficients for gases and vapors on activated carbon, Carbon 31 (1) (1993) 195–200.
[3] B. Singh, S. Madhusudanan, V. Dubey, Rabinder Nath, N.B.S.N. Rao, Activated carbon for removal of toxic chemicals from contaminated water, Carbon 34 (3) (1996) 327–330.
[4] M. Smisek, S. Cerny, Activated Carbon, Manufacture, Properties and Applications, Elsevier Publishing Company, London, 1970.
[5] N.A. Noyes, National Research Committee Report vol. 1, Division 10, Military Problems with Aerosols and Non-persistent Gases, Washington, DC, 1946.
[6] R.E. Wilson, J.C. Whetzel, Impregnated carbon for use as gas adsorbent, Chem. Abstr. 19 (1925) 564.
[7] A.J. Jallmand, R. Chaplin, Adsorption of hydrogen cyanide and carbon dioxide at low temperature by activated carbon, Proc. R. Soc. A 132 (1931) 460–479.
[8] D.H. Moreau, Activated carbon for purification of toxic atmospheres, Chem. Abstr. 72 (6) (1970) 58838.
[9] Z. Barnir, C. Aharoni, Adsorption of cyanogen chloride on impregnated carbon, Carbon 13 (5) (1975) 363–366.
[10] F.A.P. Maggs, Respiratory protection against hydrogen cyanide, Chem. Abstr. 84 (1979) 168895.
[11] C.T. Chiou, P.J. Reucroft, Adsorption of phosgene and chloroform by activated carbon and impregnated carbon, Carbon 15 (2) (1977) 49–53.
[12] P.J. Reucroft, C.T. Chiou, Adsorption of cyanogen chloride and hydrogen cyanide by activated and impregnated carbons, Carbon 15 (5) (1977) 285–290.
[13] C. Aharoni, Z. Barnier, Efficiency of adsorbents for removal of cyanogen chloride, J. Am. Hyg. Ind. Assoc. 39 (4) (1978) 334–339.
[14] G.B. Freemann, P.J. Reucroft, Adsorption of hydrogen cyanide and water vapour mixtures by activated and impregnated carbons, Carbon 17 (4) (1979) 313–316.
[15] E.G. Poziomek, R.P. Barret, R.A. Mackay, ESR a quantitative tool in studying reactivity of copper/chromium/silver impregnated charcoals, Carbon 13 (4) (1975) 259–262.
[16] J.A. Baker, E.J. Poziomek, Effect of amine treatment on the chemical reactivity of copper/chromium/silver impregnated charcoals, Carbon 13 (4) (1975) 347–348.
[17] E.G. Poziomek, R.P. Barret, R.A. Mackay, ESR a quantitative tool in studying reactivity of copper/chromium/silver impregnated charcoals, Ext. Abstr. Prog. Bienn. Conf., Carbon 12 (1975) 179–180.
[18] R. Stostak, A.H. Weiss, A. Sacco, EDX analysis of whetlerite, Ext. Abstr. Prog. Bienn. Conf., Carbon (1983) 373–374.
[19] P. Ehrburger, J. Dentzer, J. Lahaye, P. Dziedinl, R. Fangeat, Thermal behaviour of chromium trioxide deposited on carbon, Carbon 28 (1) (1990) 113–118.
[20] L. Zhigang, Z. Mingrong, C. Kuixue, The investigation for the deactivation of copper–chromium impregnated carbon by XPS, Carbon 31 (7) (1993) 1179–1184.
[21] C.J. Karwacki, G.A. Stickel, Influence of moisture content on breakthrough behaviour of perfluoro isobutene, in: Proceedings of the 20th Biennial Conference on Carbon, American Carbon Society, Santa Barbara, 1991, p. 74.

[22] C.J. Karwacki, J.H. Buchanan, J.J. Mahle, L.C. Buettner, G.W. Wagner, Effect of temperature on the desorption and decomposition of mustard from activated carbon, Langmuir 15 (25) (1999) 8645–8650.

[23] C.R. Hall, I.W. Lawston, A.M. Tinsley, Protection provided by activated carbon vapour filter against perfluorroisobutene, Chem. Ind. 5 (1989) 145–146.

[24] M.C. Beisinger, N.S. McIntyre, S.J. Splinster, S. Liang, Studies of reactions on metal impregnated charcoal: characterization and the thermal desorption of water, Carbon 35 (4) (1997) 475–482.

[25] R.D. Gall, Destruction of thioether of mustard analogues by divanado decamolybdophosphonic acid, Chem. Abstr. 126 (1997) 224933.

[26] (a) B. Singh, G.K. Prasad, M.V.S. Suryanarayana, S. Banerjee, The reaction of thiodiglycol on metal-impregnated carbon, Carbon 39 (14) (2001) 2131–2142;
(b) G.K. Prasad, B. Singh, Reactions of sulphur mustard on impregnated carbons, J. Haz. Mater. B 116 (2004) 213–217.

[27] B. Singh, S. Madhusudanan, C.G. Padma Kumar, S.R.S. Sachan, S.K. Pandey, S. Agarwal, Determination of copper, total chromium and Silver in impregnated carbon, Def. Sci. J. 48 (4) (1998) 365–369.

[28] A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, in: The English language Book Society and Longmans, 3rd ed., 1961, 450 pp.

[29] M.M. Dubinin, Generalization of the theory of volume filling of micropores to nonhomogeneous microporous structures, Carbon 23 (4) (1985) 373.

[30] G.W. Wagner, P.W. Bartram, O. Koper, K.J. Klabunde, Reactions of VX, GD, and HD with Nanosize MgO, J. Phys. Chem. B 103 (1999) 3225–3228.

[31] J.V. Stark, D.G. Park, I. Lagadic, K.J. Klabunde, Nanoscale metal oxide particles/clusters as chemical reagents. Unique surface chemistry on magnesium oxide as shown by enhanced adsorption of acid gases (sulphur dioxide and carbon dioxide) and pressure dependence, Chem. Mater. 8 (8) (1996) 1904–1912.

[32] S.H. Maron, C.F. Prutton, Principles of Physical Chemistry, 4th ed., Amerind Publishing Co. Pvt. Ltd., New Delhi, 1972.