Reaction of Gaseous Sulfur Mustard with Zeolite 13X†

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The behaviour of zeolite 13X, both dried and impregnated with H_2O and various amines, when treated with gaseous sulfur mustard, $(ClCH_2CH_2)_2S$, has been studied. The capacity to absorb/react with S-mustard was largest for the dried zeolite 13X (1.24–1.41 mmol S-mustard g^{-1}), with the capacity of the other samples appearing to depend upon the free space within the zeolite rather than upon the type or loading of the potential decontaminant. The product formed from S-mustard within dried zeolite 13X has been investigated by ^1H and ^{13}C NMR spectroscopy and tentatively assigned the structure $HOCH_2CH_2SCH_2CH_2S^+(CH_2CH_2OH)_2$.

Sulfur mustard, $(ClCH_2CH_2)_2S$, a blister agent which attacks the mucous membranes and which can be lethal at high doses, reacts with a variety of nucleophiles/bases *e.g.* hydroxide, fluoride, amines, thiosulfate, sulfide, sulfite, thiocyanate, *etc.*, and some of these reactions have been exploited for the purposes of decontamination.[1] In the present paper we wish to report a study of the interaction between gaseous S-mustard and both zeolite 13X alone, and zeolite 13X after impregnation with water and various amines.

Experimental

Preparation of Zeolite Supported Nucleophiles/Bases.—The zeolites tested as support materials were from the Union Carbide range (supplied by BDH):[2] Type 3A, Type 4A, Type 5A and Type 13X, all used as powders (0.5–5.0 μm). It soon became apparent that Type 3A, with pore size ≈ 3 Å, was rather limited in its ability to absorb any but the smallest reagent molecules. Types 4A and 5A were rather better, and Type 13X, with pore size ≈ 10 Å, gave quite high loadings of nucleophiles/bases. Most of the investigation centred upon amines absorbed onto the Type 13X zeolite. The amines ethanediamine, imidazole, piperazine and hexamethylenetetraamine (hexamine) were incorporated into the zeolite from solutions in acetonitrile. The resultant dried materials were analysed by aqueous extraction, filtration and titration of the filtrate with standard HCl solution. Since S-mustard would need to enter the zeolite pores in order to react with the amine, it was considered prudent also to test samples with less than saturation loadings of the amines. Samples with less than saturation loadings were therefore also prepared. The test materials prepared (all on zeolite 13X) had the following loadings: ethanediamine, 5.8 wt% (0.97 mmol g^{-1}) [saturated had 11.1 wt% (1.85 mmol g^{-1})]; imidazole, 6.6 wt% (0.97 mmol g^{-1}) [saturated had 17.6 wt% (2.59 mmol g^{-1})]; piperazine, saturated 7.0 wt% (0.81 mmol g^{-1}); hexamine, 2.7 wt% (0.19 mmol g^{-1}) and saturated 9.7 wt% (0.69 mmol g^{-1}).

Treatment of Zeolite Test Materials with Gaseous S-Mustard.—Samples of dried zeolite 13X (dried at > 300 °C), or zeolite 13X impregnated with various reagents (dried *in vacuo* over P_2O_5), were treated with gaseous S-mustard in a stream of dry nitrogen (dried by passage through a bed of activated zeolite 3A), as described previously[3] for reactants supported on ion-exchange materials. In a typical experiment, the S-mustard (1.00 mmol, 159 mg) was passed into the test material (usually 1.00 g) in a stream of dry N_2-gas (usually 100 cm^3 min^{-1}) at

60 °C during 5–8 h. S-Mustard which had not reacted or been absorbed by the test material was collected in a trap containing 50.0 cm^3 hexylene glycol (2-methylpentane-2,4-diol). At the end of the experiment, the sample tube was reweighed to determine the increase (or decrease) in weight of the test material and an aliquot of the trap liquid was diluted as necessary for colourimetric determination of S-mustard using DB-3 reagent [4-(p-nitrobenzyl)pyridine–HO$^-$].[4] It was assumed that the difference between the amount of S-mustard introduced into the test material, and that found by analysis in the trap, was the amount that had reacted with and/or been absorbed by the test material. Control experiments showed that no S-mustard was lost from the trap during the course of the experiment, and that, in the absence of test material, the transfer of S-mustard was quantitative.

$^{13}C\{^1H\}$ MAS NMR Spectra.—Spectra were recorded on a Bruker AM 300/WB Fourier transform spectrometer fitted with a Bruker double bearing MAS probe. The 7.1 T magnet gave a carbon resonance frequency of 75 MHz; proton frequency 300 MHz. Spectra were accumulated using proton decoupling with no cross polarisation. Data were accumulated into 400 data points using a pulse width of 3 μs (30°), a sweep width of 20 000 and a relaxation delay of 1 s. These were then transformed with 10.000 Hz line broadening, digital resolution of 2.441 Hz per point and a data memory size of 16 384. Resonances were referenced to external Me_4Si.

Results and Discussion

Treatment of Zeolite Samples with S-Mustard.—The results shown in Table 1 indicate that whilst 1.00 g samples of dried zeolite 13X were capable of absorbing/reacting with only 0.5–0.9 mmol of S-mustard at a flow rate of 100 cm^3 min^{-1}, at lower flow rates (50 cm^3 min^{-1}) the amount absorbed/reacted became essentially quantitative, *i.e.* complete reaction/absorption of the 1.0 mmol S-mustard introduced. Furthermore, when only 0.50 g samples of the dried zeolite 13X were used, the uptake of S-mustard rose to 1.24–1.41 mmol g^{-1} at 50 cm^3 min^{-1} flow rate. Thus the maximum capacity for absorption/reaction is realised when slow flow rates and an excess of S-mustard are used. The increase in weight in the zeolite samples roughly corresponds with the weight of S-mustard which failed to reach the trap liquid. Once the S-mustard had been taken up by the zeolite, it could not be removed, either by purging with N_2 gas at 60 °C, or by washing with solvent (CS_2).

The remaining results reported in Table 1 concern zeolite 13X samples impregnated with either H_2O (saturated), CH_3CN (saturated), or various amines, both saturated and partially

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Table 1 Treatment of zeolite 13X samples (1.00 g) with gaseous S-mustard (1.00 mmol)

Sample	% S-mustard reacted/absorbed[a]	% wt. gain in zeolite	mmol S-mustard reacted/absorbed per g zeolite[b]
Dried zeolite	56	—	0.56
Continued N_2 purge (7 h)	100	—	—
Dried zeolite	91	15	0.92
Dried zeolite[d]	98	19	1.00
Dried zeolite[d]	100	17	1.00
Dried zeolite (0.5 g)[d]	63	20	1.24
Dried zeolite (0.5 g)[d]	64	24	1.26
Dried zeolite (0.5 g)[d]	62	24	1.24
Dried zeolite (0.5 g)[d]	69	28	1.41
Zeolite satd. with 22.0% H_2O	52	—	0.51
Zeolite satd. with 11.8% CH_3CN	67	0[c]	0.65
Zeolite satd. with 11.8% CH_3CN[d]	58	−3	0.57
Zeolite + 5.8% ethanediamine	48	−3	0.49
Zeolite + 6.6% imidazole	47	−2	0.47
Zeolite satd. with 7.0% piperazine	32	−5	0.31
Zeolite satd. with 9.7% hexamine	28	−5	0.28
Zeolite + 2.7% hexamine	77	—	0.77
Zeolite + 2.7% hexamine	—	0	0.85
Zeolite + 2.7% hexamine	41	−4	0.40

[a] Difference between amount of S-mustard introduced and amount collected in the trap liquid. [b] mmol of S-mustard reacted/absorbed (column 2) divided by weight of zeolite sample. [c] 9% weight loss without mustard treatment (N_2 only). [d] N_2 flow-rate 50 cm^3 min^{-1}.
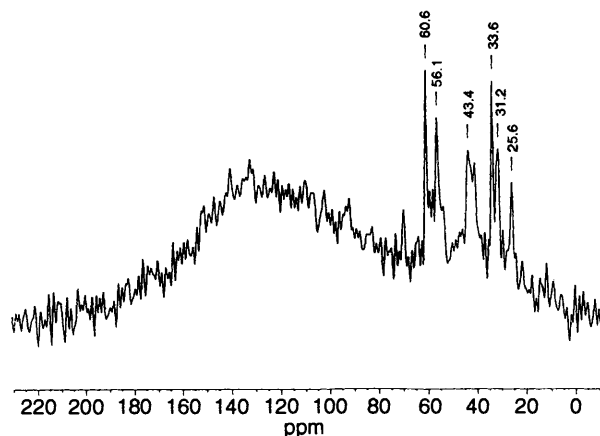
Fig. 1 ^{13}C solid state NMR spectrum of zeolite 13X–S-mustard

saturated. All of these samples exhibited lower capacities for absorption/reaction than the dried, non-impregnated zeolite 13X. Those samples which had less than the maximum loadings of the amines exhibited greater capacities than those which had saturated loadings. It thus appears that it is the free space within the zeolite structure that controls the capacity for absorption/reaction, rather than the amount of a potential reactant present, and that the amines otherwise play a minimal role. The observed changes in weight of the test materials were probably due to a combination of weight gain due to absorption/reaction and weight loss due to partial loss of impregnant.

Variations in the results from apparently duplicate experiments are thought to be due to (i) the moisture content of the non-impregnated zeolite samples (the highest % reaction/absorption values were observed after rigorous drying at > 300 °C) and (ii) errors in pipetting the trap liquid which is very viscous when cold.

Characterisation of Zeolite 13X after Treatment with S-Mustard.—In an attempt to determine whether the S-mustard 'sorbed' by the non-impregnated zeolite 13X remained unchanged or had been chemically modified, samples of the treated zeolite were investigated using IR and NMR spectroscopies.

The IR spectra (KBr disc) exhibited no absorptions characteristic of S-mustard, although control spectra using zeolite 13X saturated with acetone or acetonitrile from the gas phase, showed the characteristic carbonyl and nitrile absorptions respectively. It was concluded that if S-mustard were still present, then it was most probable that its most characteristic absorption at 700 cm^{-1} was being obscured by the absorptions due to the zeolite itself.

The ^{13}C solid state NMR spectrum (Fig. 1) exhibited a broad absorption centred around 140 ppm (also exhibited by the zeolite before treatment with S-mustard and was the only absorption present when the spectrum of the treated material was recorded with cross polarisation) and fine structure typical of more mobile organocarbon species between 25 and 70 ppm; six prominent lines were observed (see Fig. 1 and Table 2).

Samples were also examined by dissolving the zeolite matrix in dilute nitric acid and observing the ^1H NMR spectrum of organic material, either directly, using DNO_3–D_2O to dissolve the zeolite, or after extraction from HNO_3–H_2O solution with $CDCl_3$. Control experiments indicated that S-mustard, if present, would be readily extracted into $CDCl_3$, whilst bis(2-hydroxyethyl) sulfide [$(HOCH_2CH_2)_2S$], a known hydrolysis product, if present would remain predominantly in the aqueous phase. The $CDCl_3$ method gave only a weak spectrum, indicative of small quantities of organic material, but recording the ^1H spectrum directly in DNO_3–D_2O ($Me_3Si[CH_2]_3SO_3Na$ internal reference) produced a much stronger spectrum exhibiting three multiplets (Fig. 2 and Table 2; δ 2.8–3.4, 3.7–4.0 and 4.0–4.3 in the ratio 4:8:3). If it is assumed that all eight of the protons originally present in the 'sorbed' S-mustard are still present and causing the observed absorptions, then comparison of the total integral with that of an internal standard (CH_3CO_2H, δ 2.1) indicated that 65–75% of the 'sorbed' S-mustard is accounted for.

Attempts also to record the ^{13}C spectrum directly from the solution obtained by dissolving the zeolite matrix in HNO_3–H_2O were unsuccessful; the solution gelled (owing to polymerisation of the silicic acid) within 1 h. Whilst this should have given sufficient time for the acquisition of the necessary number of pulses, the changing viscosity of the solution during

Table 2 NMR chemical shift data[a]

Data from ref. 5 (standard: internal or external $Me_3SiCH_2CH_2CH_2SO_3Na$)

	^{13}C				^1H			
	X—CH₂—CH₂—S—CH₂—CH₂—Y				X—CH₂—CH₂—S—CH₂—CH₂—Y			
X = Y = Cl (neat)	45.0	35.8	35.8	45.0	3.69	2.92	2.92	3.69
X = Cl, Y = OH (acetone)	47.0	*37.7*	*38.1*	65.3	—	—	—	—
X = Y = OH (H₂O)	36.2	63.2	63.2	36.2	3.60	2.66	2.66	3.60

^{13}C (D₂O)

63.2	36.3	28.6	44.2	46.4	59.0
HO—CH₂—	CH₂—S—	CH₂—	CH₂—S⁺—	(CH₂—	CH₂—OH)₂
3.6–3.7	2.74	2.96	3.6–3.7	3.6–3.75	4.01

^1H (D₂O)

^1H spectrum, recorded on solution after hydrolysis of zeolite matrix (internal $Me_3SiCH_2CH_2CH_2SO_3Na$, DNO_3–D_2O)
2.8–3.4 (4 H)   3.7–4.0 (8 H)   4.0–4.3 (3 H)

From ref. 5 for $HOCH_2CH_2SCH_2CH_2S^+(CH_2CH_2OH)_2$ (internal $Me_3SiCD_2CD_2COONa$, D_2O)
2.7–3.0 (4 H)   3.6–3.75 (8 H)   4.01 (4 H)

^{13}C spectrum, recorded on solid, S-mustard treated zeolite (external Me_4Si, solid state)
60.6   56.1   43.4   33.6   31.2   25.6

From ref. 5 for $HOCH_2CH_2SCH_2CH_2S^+(CH_2CH_2OH)_2$ (external $Me_3SiCD_2CD_2COONa$, D_2O)
63.2   59.0   46.4   44.2   36.3   28.6

[a] Chemical shifts shown in italics may be reversed.[5]
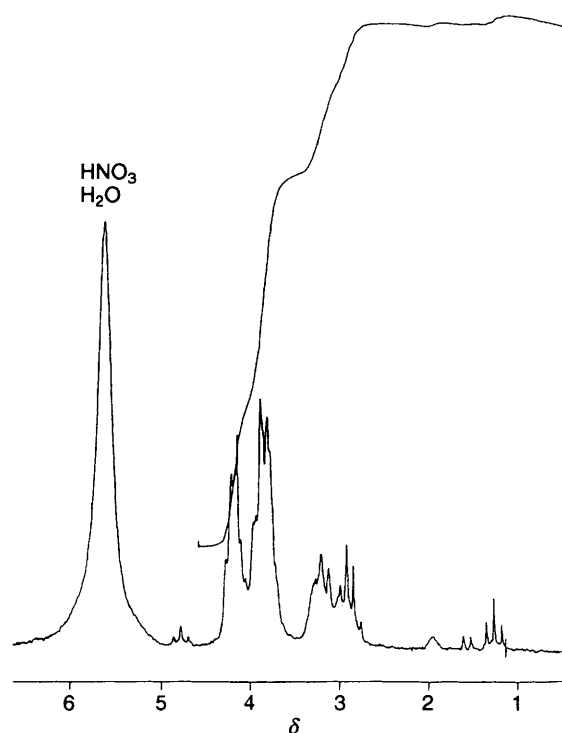
Fig. 2 ^1H NMR spectrum of zeolite 13X–S-mustard after dissolution in DNO_3–D_2O

the acquisition period probably caused the signals to become chemically shifted and thus non-cumulative.

Although the observed solid state ^{13}C and solution ^1H NMR spectra may be consistent with mixtures of 2-chloroethyl 2-hydroxyethyl sulfide ($HO[CH_2]_2S[CH_2]_2Cl$) and bis(2-hydroxyethyl) sulfide, partial and complete hydrolysis products respectively (see Table 2 for reference data),[5] it is tempting to suggest that another reported[5] hydrolysis product of S-mustard

viz. $HO[CH_2]_2S[CH_2]_2S^+([CH_2]_2OH)_2$, is responsible for all of the observed NMR signals, bearing in mind that the spectra reported here and in ref. 5 were recorded in significantly different media, *viz.* solid state *vs.* D_2O for ^{13}C and DNO_3–D_2O *vs.* D_2O for ^1H. This product would exhibit six ^{13}C absorptions and ^1H multiplets in the regions δ 2.7–3.0 (4 H), 3.6–3.75 (8 H) and 4.0 (4 H); it would be expected to be water-, rather than $CHCl_3$-soluble; and it would, on account of its branched structure, be expected to be retained inside the zeolite cavities—all properties consistent with those observed. However, unfortunately, no firm assignment can be made on the basis of the data presently available, except to say that the S-mustard has undergone chemical transformation, most probably hydrolysis, inside the zeolite. If hydrolysis has occurred, the reacting species would be either residual water in the zeolite (even after activation at 300 °C) or free HO sites on the inside surface of the cavities. In the latter case, the free reaction product would not be released until the zeolite structure was itself hydrolysed.

Microflow Calorimetry (MFC) of Zeolite 13X in the Presence of S-Mustard.—The heat of reaction between S-mustard, as a 1.0 wt% (0.043 mol dm⁻³) solution in heptane and dried zeolite 13X was measured by microflow calorimetry. Samples (20 mm³) of the S-mustard solution were injected into a flow of heptane (3.40 cm³ h⁻¹) passing over a 65.5 mg sample of dried zeolite 13X. Large exothermic peaks (average ΔH for eight injections $= -101$ mJ $\equiv -117$ kJ mol⁻¹ S-mustard) were observed. Continuous introduction of the same S-mustard solution (3.40 cm³ h⁻¹) to a 68 mg sample of the zeolite produced a large exotherm which decayed to the base-line during 134 min, typical of a material with a limited capacity for reaction. The integrated heat evolved was equivalent to -65.3 J g⁻¹ zeolite, which, using the above value for the heat of reaction per mol of S-mustard, indicates a reaction capacity (solution/solid) of 0.56 mmol S-mustard/g zeolite. This compares with a value of 1.24–1.41 mmol g⁻¹ in a gas/solid interaction using dried zeolite 13X and 0.57–0.65 mmol g⁻¹ zeolite using CH_3CN saturated zeolite 13X (Table 1).

Conclusions

Potential decontaminating agents for S-mustard such as aliphatic amines, when supported on zeolite 13X appear to be ineffective. Anhydrous zeolite 13X exhibits the greatest capacity for absorption/reaction with S-mustard (1.2–1.4 mmol S-mustard per gram zeolite). Moisture has a marked effect upon this capacity, rendering the use of zeolite 13X itself as a potential decontaminant impractical.

Acknowledgements

References

1 Y.-C. Yang, J. A. Baker and J. R. Ward, Chem. Rev., 1992, 92, 1729.
2 Union Carbide Molecular Sieves for selective adsorption, BDH Publication Prod 57042 1N (3rd edn.).
3 A. J. Bellamy, Reactive Polymers, 1994, 23, 101.
4 A. Stamulis, Modifications in the NRL Colorimetric Method for the Determination of Bis(2-chloroethyl) sulfide with DB-3, NRL Report 5426 (May 16, 1960), US Naval Research Laboratory.
5 Y.-C. Yang, L. L. Szafraniec, W. T. Beaudry and J. R. Ward, J. Org. Chem., 1988, 53, 3293.