936. *Intracrystalline Oxidation of Hydrogen Sulphide.*

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Hydrogen sulphide reacts with oxygen within the channels of zeolites to form products which vary according to experimental conditions and to the zeolite used. Direct oxidation to sulphur trioxide occurs at a temperature of 100° c in molecular sieve 4A or at 200° in the calcium form of sieve 13X.

A NUMBER of reactions has been found to proceed in zeolitic channels and this illustrates that such an intracrystalline environment can promote unexpected chemical behaviour. Addison and Barrer [1] found that nitric oxide sorbed in zeolites disproportionates to form other nitrogen oxides, and, under conditions which prevent the complete disproportionation of nitric oxide, the sorbed gas does not react with subsequently sorbed oxygen. Beachell and John [2] found that sorption of diborane on several zeolites is irreversible and suggested that this was due to chemical reaction leading to the attachment of boron to the aluminosilicate framework by a boron–oxygen bond. Cannon [3] found that the sorption of chlorodifluoromethane in zeolites initiates a reaction in which carbon dioxide is formed. Further examples of unexpected intracrystalline behaviour are given in reference 1.

The oxidation of hydrogen sulphide within zeolitic channels has now been investigated and it has been shown that zeolites promote this oxidation and that the course of the oxidation depends upon both the particular zeolite used and the experimental conditions.

EXPERIMENTAL AND RESULTS

Oxygen was supplied pure by the British Oxygen Co. Ltd. Hydrogen sulphide was prepared by the action of dilute hydrochloric acid on zinc sulphide and was dried with calcium chloride and then fractionated until no impurity was detected in its infrared spectrum.

The zeolites used were the Linde molecular sieves 4A, 5A, and 13X and the calcium and potassium modifications of the last, prepared by treating the zeolite with saturated solutions of the appropriate metal chloride. Before being used for gas sorption each sample of zeolite was outgassed overnight at 300°/10^{-6} mm.

Gas sorption was measured by volumetric methods.

Method.—Hydrogen sulphide was admitted to the zeolite at 200° (after it had been demonstrated that no decomposition of hydrogen sulphide occurs under these conditions), and the whole was cooled to the appropriate temperature during 24 hr. before oxidation was started. This procedure should minimise the tendency for sorbate molecules to form clusters and should produce a more uniform distribution throughout the zeolite crystals.[4] The volume of hydrogen sulphide used was in all cases such that no pressure could be detected in the gas phase when equilibrium had been reached. Successive doses of oxygen were admitted to the system and each was left until no further change in pressure was detected during a period of 24 hr.

Results.—Runs were carried out at 0°, 100°, and 200° c with different zeolites and different concentrations of hydrogen sulphide within each zeolite. A considerably greater volume of oxygen was always sorbed than was expected by comparison with the same system in the absence of hydrogen sulphide. After 24 hr. at 100° and 200° no gas, and at 0° only a small volume of gas could be desorbed although the sorption of oxygen by zeolites is normally completely reversible. Some desorption could be effected by raising the temperature above 200°. These features indicate that chemical reaction took place between hydrogen sulphide and oxygen within the zeolitic channels. (Hydrogen sulphide and the possible products of its oxidation would be sorbed more strongly than oxygen and would not be desorbed readily.)

In Table 1 are presented the data for the two zeolites which have been studied most completely, *i.e.*, sieve 4A and the calcium form of sieve 13X. The ratio of the volume of oxygen sorbed to the volume of hydrogen sulphide pre-sorbed (v_{O_2}/v_{H_2S}) increases with increase of temperature and with decrease in the concentration of hydrogen sulphide within the sorbent.

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[1] Addison and Barrer, *J.*, 1955, 757.

[2] Beachell and John, *J. Chim. phys.*, 1958, **55**, 280.

[3] Cannon, *J. Phys. Chem.*, 1959, **63**, 160.

[4] Barrer and Rees, *Trans. Faraday Soc.*, 1954, **50**, 852.

Under comparable conditions the ratio v_{O_2}/v_{H_2S} is greater in sieve 4A than in the calcium form of sieve 13X.

TABLE 1.

H_2S sorbed per g. of zeolite (c.c. at N.T.P.)	Temp.	v_{O_2}/v_{H_2S} at p_{O_2} 0 cm.	v_{O_2}/v_{H_2S} at p_{O_2} 70 cm.	H_2S sorbed per g. of zeolite (c.c. at N.T.P.)	Temp.	v_{O_2}/v_{H_2S} at p_{O_2} 0 cm.	v_{O_2}/v_{H_2S} at p_{O_2} 70 cm.
	Sieve Ca13X				Sieve 4A		
14·29	0°	0·51	0·58	6·21	0°	0·93	1·01
16·53	100	0·46	0·65	5·03	100	1·65	1·70
15·46	100	0·49	0·64	1·17	100	1·24	2·00
4·32	100	0·67	0·89	1·08	200	1·95	1·95
1·12	100	0·80	1·13				
7·79	200	1·49	1·50				
3·80	200	1·61	2·00				
1·02	200	1·80	2·00				

In those runs in which some oxygen was desorbed, such a volume is considered to have been physically sorbed and the ratios quoted in the last column above have been corrected for this and represent the amount of chemisorption.

Values for v_{O_2}/v_{H_2S} are quoted for two different pressures of oxygen in the gas phase; by comparing the pairs of columns of Table 1 it can be seen that in each run at least 60% (and in many cases appreciably more) of the oxygen was sorbed before any pressure of gas could be detected in the gas phase. The pressure of 70 cm. was chosen to indicate the extent of reaction at a pressure which approximates to atmospheric.

Identification of Reaction Products.—Evidence of the products formed in the various reactions was obtained after completion of the oxidation by pumping off the excess of oxygen, hydrothermally extracting the zeolite, and testing the resultant solutions qualitatively. The results are shown in Table 2, and are for sieve 4A, except that for the ratio 0·58, which is for the calcium form of sieve 13X. When the zeolite was heated to effect complete desorption, gaseous sulphur dioxide was evolved where the ratio was $<2{\cdot}0$ and identified by measurement of its infrared spectrum. The presence of sulphur formed within the zeolitic channels as an oxidation product in samples where the ratio was between 0·5 and 1·0 has been inferred from two observations: first, that the zeolite after an oxidation experiment and subsequent outgassing showed a measurable paramagnetism that was not detected in the fresh zeolite; and, secondly, after the zeolite had been outgassed at 300° to remove any volatile products of reaction, further sorption of oxygen could be effected which was irreversible, appreciable in amount, and extremely slow; subsequent desorption on heating released sulphur dioxide which was detected as above.

The formation of sulphur as a product of the oxidation of hydrogen sulphide when a gaseous mixture was streamed over sieve 13X has recently been reported by Kerr and Johnson.[5]

TABLE 2.

v_{O_2}/v_{H_2S}	0·58	1·01	1·35	1·70	2·00
Test for SO_3^{2-}	+	+	+	+	–
SO_4^{2-}	–	–	+	+	+

DISCUSSION

Hydrogen sulphide can react with oxygen to give different products:

$$H_2S + \tfrac{1}{2}O_2 \longrightarrow H_2O + S \qquad (1)$$

$$H_2S + O_2 \longrightarrow H_2O + SO \qquad (2)$$

$$H_2S + \tfrac{3}{2}O_2 \longrightarrow H_2O + SO_2 \qquad (3)$$

$$H_2S + 2O_2 \longrightarrow H_2O + SO_3 \qquad (4)$$

The ratios of v_{O_2}/v_{H_2S} obtained when these reactions proceed stoicheiometrically are 0·5, 1·0, 1·5, and 2·0, respectively. The ratios obtained in the oxidation experiments seldom correspond with these ideal values and such a ratio is no guide to the products which have been formed, unless it be 2·0; in that case sulphur trioxide must have been formed quantitatively in accordance with reaction (4) since no further oxidation, and thus

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[5] Kerr and Johnson, *J. Phys. Chem.*, 1960, **64**, 381.

greater ratio, can occur. If the ratio in a given experiment were 1·5, this could mean that 75% of the hydrogen sulphide molecules had reacted completely to form sulphur trioxide while the remaining 25% did not react at all, or that 100% of the molecules had reacted to form either sulphur dioxide or a mixture of sulphur, sulphur dioxide, and sulphur trioxide.

Since an appreciable quantity of sulphur dioxide was detected in a sample on which the ratio of 0·58 was obtained, and an appreciable amount of sulphur trioxide for a ratio of 1·35, it is clear that reaction does not proceed in such a way that reaction (1) above is complete before reaction (2) commences, etc. Further evidence of this was obtained by treating hydrogen sulphide in a zeolite with oxygen under conditions which had been shown to lead to complete formation of sulphur trioxide, but now only half the required volume of oxygen was admitted. A considerable amount of sulphate was detected after hydrothermal extraction.

It is postulated that the initial step in the intracrystalline reaction is the bimolecular one (2), since it is unlikely that any zeolitic cage could contain more than two molecules under the conditions used. There is evidence that when hydrogen sulphide is sorbed in sieve 4A one molecule is situated at the centre of a cage in the aluminosilicate framework,[6] and it seems likely that a similar situation could apply to sieve 13X. Under conditions which cause the sorbed species to have a low mobility, the molecules of water and sulphur monoxide formed in the initial reaction would remain in the one cage; this would prevent the access of a further oxygen molecule to react with the molecule of sulphur monoxide and lead to further oxidation. When several cages have become blocked by molecules of the reaction products in this way the access of a first molecule of oxygen to some cages which contain hydrogen sulphide molecules would be prevented. (The effect of water molecules in decreasing the sorption capacity of zeolites has been discussed by Barrer.[7]) Thus the complete oxidation of hydrogen sulphide to this stage resulting in the overall ratio of 1·0 is not reached. The prevention of complete reaction would be more likely the higher the concentration of presorbed hydrogen sulphide in the zeolite, since the number of blocked cages must be related to the number of hydrogen sulphide molecules present. The v_{O_2}/v_{H_2O} ratio can be seen always to decrease with an increase in the amount of presorbed hydrogen sulphide when other conditions are maintained constant (Table 1).

When no attempt was made to distribute hydrogen sulphide uniformly, as described above, the volume of oxygen taken up under otherwise comparable conditions was reduced. The higher local concentrations of hydrogen sulphide molecules would make it more possible for blocked cages to stop access to further hydrogen sulphide molecules.

When reaction was complete and the excess of oxygen had been pumped off, heating the sorbent caused the more strongly sorbed sulphur-containing gases to be desorbed. It is postulated that as the temperature is increased the sulphur monoxide molecules become mobile, and in the absence of oxygen would be likely to react together to form sulphur dioxide and sulphur, $2SO \longrightarrow SO_2 + S$. The sulphur dioxide would be desorbed and the sulphur would remain in the channels of the zeolite. Conditions of low mobility appear to be temperatures of $<100°$ for the calcium form of sieve 13X and 0° or less for sieve 4A. This difference in behaviour can be attributed to the greater force of attraction between sorbent and sorbed molecules when the interstitial ions are bivalent rather than univalent.

Replacement of sodium ions by calcium ions without change in the aluminosilicate framework or in experimental conditions leads to a decrease in the v_{O_2}/v_{H_2S} ratio and this has been demonstrated by a change from sieve 4A to sieve 5A and from the sodium to the calcium form of sieve 13X. A change of univalent cation, *e.g.*, of sodium for potassium, had little effect.

Under conditions where adsorbed sulphur monoxide is mobile, reaction can proceed by

[6] Lewis, *J. Phys. Chem.*, 1959, **63**, 527.

[7] Barrer, *Ann. Reports*, 1944, **41**, 31.

collision with another molecule of the same species or with a molecule of oxygen to form sulphur trioxide. When the original hydrogen sulphide concentration and hence the sulphur monoxide concentration is low, reaction to form sulphur trioxide should be more likely. The results in Table 1 show that the higher the initial concentration of hydrogen sulphide, the lower is the final v_{O_2}/v_{H_2S} ratio.

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