Hydrothermal Chemistry of Silicates. Part XX.† The Question of Phosphorus Substitution for Silicon during Zeolite Synthesis

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Isomorphous replacement of framework silicon (or aluminium) by phosphorus during zeolite synthesis, which has been the subject of conflicting reports, has been investigated under low-temperature hydrothermal conditions. As sources of Al and Si, blends of $AlPO_4$ and silica were prepared from metakaolinite and phosphoric acid, in some instances with further additions of silica. Samples of zeolites A, Na–P (gismondine-type), sodalite hydrate and K–F (edingtonite-type) thus obtained were analysed for phosphorus. The content of this element was extremely low, the maximum possible extents of framework substitution ranging from about 0·00056 to 0·0117 atoms of phosphorus per atom of aluminium. Some or all of this low content could merely represent discrete anions trapped in cavities within the frameworks.

THE structural analogies between certain crystalline silicas and the forms of $AlPO_4$[1] lead one to enquire how far Si and P can replace each other in silicates. A rare natural example of such substitution is reported in viseite which is considered to be isostructural with analcime.[2] It has been pointed out in connection with the similarity between $AlPO_4$ and SiO_2 that radius and electron requirements in the substitution $Al + P \rightleftharpoons 2Si$ are very well balanced. Al has one electron less than Si and P has one more; and the radius of Al exceeds that of Si by about the same amount as the radius of Si exceeds that of P, in all cases as the ions.

First studies of possible isomorphous substitution in aluminosilicates during hydrothermal crystallisations in the system Al_2O_3–SiO_2–P_2O_5–base–H_2O were made by Barrer and Marshall.[3,4] They found that aluminophosphates often co-precipitated with aluminosilicates but could find no evidence of aluminosilicophosphate frameworks. Kuhl[5,6] reported on zeolite synthesis in presence of sodium diphosphate. The phosphate complexed the aluminium so that the zeolites formed tended to be siliceous. Again, however, no evidence of substitution of Si by P was obtained. On the other hand Flanigen and Grose[7] reported the synthesis of phosphorus-substituted zeolites, and suggested as an explanation of the failure of the earlier work[3-6] to form such products that the mere presence of a phosphate salt in the reactants would not result in phosphorus-substituted zeolites. In the synthesis of the zeolites they termed P–W, P–R, and P–G they started from a mixture of $AlCl_3$ and H_3PO_4 which was neutralised with KOH to a pH of 7·5. The product is apparently a mixture of $AlPO_4$ gel with KCl and K_2HPO_4. The gel portion was then blended with colloidal silica and alkali to make the reactant mixture. It seemed from the above procedure of Flanigen and Grose that the active gel should contain $AlPO_4$. In view of the conflicting prior results it was of considerable interest to examine this possibility and to explore further the hydrothermal substitution of Si by P in zeolites.

EXPERIMENTAL

Metakaolinite ($Al_2O_3,2SiO_2$), obtained from kaolinite by heating at 600 °C, is a versatile starting material for zeolite synthesis.[8] It may also be a source of $AlPO_4$ since the Al_2O_3 can be dissolved from it by dilute mineral acids.[9] Preliminary experiments showed that $AlPO_4$ could indeed be made from metakaolinite (MTK) and H_3PO_4 but that the $AlPO_4$ was quite soluble in excess of acid. Accordingly MTK was treated with its exact equivalent of 0·5M-H_3PO_4 at 80 to 100 °C for 24 h. After the reaction

$$Al_2O_3,2SiO_4 + 2H_3PO_4 \longrightarrow 2AlPO_4 + 2SiO_2 + 3H_2O$$

the aqueous phase was almost neutral (pH ~5) and the weights of the initial MTK and of the dried resultant solids corresponded exactly with the above reaction equation. The $AlPO_4$ was identified by its *X*-ray powder pattern. Two reactant mixtures of blended $AlPO_4$ and silica were prepared in this way from the MTK: in the first (P-MTK-100) all the aluminium was present as $AlPO_4$; in the second (P-MTK-50) 50% of the aluminium was present as $AlPO_4$, only 50% of the stoicheiometric amount of H_3PO_4 required by the above reaction equation having been used. In the second sample this $AlPO_4$ was amorphous. When desired the above two mixtures were fortified with dry silica powder.

Aqueous solutions of reagent grade NaOH and LiOH and also the solids were weighed into screw top polypropylene bottles and rotated at 100 °C for periods from 48 to 96 h. With KOH at 150 °C the reactions took place in Teflon-lined stainless-steel vessels. After reaction the solids were filtered off, washed, and air dried. They were identified by *X*-ray powder photography. No significant

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† Part XIX, R. M. Barrer and E. F. Freund, preceding paper.

[1] J. R. van Wazer, ' Phosphorus and its Compounds,' Interscience Publishers, New York, 1968, pp. 552—5.

[2] D. McConnell, *Amer. Min.*, 1952, **37**, 609.

[3] R. M. Barrer and D. J. Marshall, *J. Chem. Soc.*, 1965, 6616.

[4] R. M. Barrer and D. J. Marshall, *J. Chem. Soc.*, 1965, 6621.

[5] G. H. Kuhl in ' Molecular Sieves,' Soc. of Chem. Ind., London, 1968, p. 85.

[6] G. H. Kuhl in ' Molecular Sieve Zeolites,' Advances in Chemistry Series 101, 1971, p. 63.

[7] E. M. Flanigen and R. W. Grose in ' Molecular Sieve Zeolites,' Advances in Chemistry Series 101, 1971, p. 76.

[8] R. M. Barrer and D. E. Mainwaring, *J.C.S. Dalton*, 1972, 1254, 1260, and 2534.

[9] Uhlman Encylopadie de Technischen Chemie, 3rd edn., 1953, vol. 3, p. 400.

difference in the products was observed for experimental reaction times of 48 to 96 h.

TABLE 1

Syntheses * with LiOH and KOH

Parent composition †	Temp. (T/°C)	Time (t/h)	Base and normality	Product (and preparation no.)
P-MTK-50	100	96	1·5N-LiOH	Li-A(BW)
(1·3 g)			2·0N-LiOH	Li-A(BW)
			3·0N-LiOH	Li-A(BW)
P-MTK-100	100	96	1·5N-LiOH	Li-A(BW)
(1·6 g)			2·0N-LiOH	Li-A(BW)
			3·0N-LiOH	Li-A(BW)
MTK (1 g)	150	72	1·5N-KOH	Mixture of species
			3·0N-KOH	Mixture of species
P-MTK-50	150	72	1·5N-KOH	K-F + ? (10-13)
(1·3 g)			3·0N-KOH	K-F + ? (10-14)
P-MTK-100	150	72	1·5N-KOH	K-F (10-15)
(1.6 g)			3·0N-KOH	K-F (10-16)

* Li-A(BW) = lithium zeolite of Barrer and White[10] K-F = zeolite K-F of Barrer and Baynham.[13] † The quantities of aqueous alkali added were in each case 20 cm^3 at the concentrations given in the Table.

The products, after thorough washing, were examined for their phosphorus content in two ways, qualitatively by the molybdenum blue test and quantitatively by the method of Kirkbright, Smith, and West.[10] In the qualitative test, 100 to 200 mg samples of zeolite were decomposed with $HNO_3 + HF$ and the residues filtered and washed with hot water. The total filtrate was transferred to a standard flask, the reagents added, and the solution made up to 100 cm^3. No positive result was obtained in this test, which has a sensitivity limit of about 1 part in 40,000.

The much more sensitive quantitative method was next used on a range of zeolite preparations. 0·25 g Samples of each were treated with 18 cm^3 of conc. HCl, heated gently, and allowed to stand for 1 h. All the zeolites so decomposed were aluminous and broke down readily under the above treatment. The solutions were transferred to 100 cm^3 flasks and diluted to volume with distilled water. 10 cm^3 Aliquots were then treated with molybdate solution and extracted with isobutyl acetate. The aqueous phase was discarded and the acetate phase washed three times with 2M-HCl. The Mo content of the phosphomolybdate extract was determined by atomic absorption spectrophotometry in a nitrous oxide–acetylene flame at 313 nm. Each phosphorus atom is associated with 12 Mo atoms. The procedure is not subject to interference by silicon.

Products.—With LiOH the zeolite Li-A(BW) of Barrer and White[11] was the only product with solutions up to 3N (Table 1). Crystallinity was poor to moderate. Lithium aluminate and phosphate are relatively insoluble and therefore part of the LiOH may be bound and not available and the same may be true of part of the aluminium. In absence of phosphate and with KOH as base a mixture of phases appeared (Table 1). With P-MTK-50 the edingtonite-type[12] zeolite, K–F,[13] was formed, but with an unidentified crystalline impurity. With P-MTK-100 pure K–F was obtained although good crystallites formed only with higher concentrations of KOH.

$AlPO_4$ did not dissolve in 0·7N-NaOH solutions (Table 2)

TABLE 2

Syntheses with NaOH *

Parent composition † (and weights taken)	Time t/h	Products (and preparation no.) 1·4N-NaOH at 80 °C	0·7N-NaOH at 100 °C	1·4N-NaOH at 100 °C	2·5N-NaOH at 100 °C	1·4N-NaOH at 100 °C
MTK (1 g)	48		A + P (6-29)	A + P (6-30)		
P-MTK-50 (1·3 g)	48	A (6-37)	Am (6-12)	A (6-16)	P + A (6-32)	
	72	A (6-38)				
	96	A + P (6-34)				S + ? (6-40)
P-MTK-100	48		$AlPO_4$ (6-11)	A (6-15)	S + A (6-31)	
(1·6 g)	82				A (6-35)	S + (?) (6-39)
	96	Am (6-33)		A (6-17)	S (6-36)	
MTK + SiO_2	48		P (7-29)	P (7-30)		
(1 g) (0·12 g)	96		P (7-27)	P (7-28)		
P-MTK-50 + SiO_2	48		Am (7-12)	P (7-16)		
(1·3 g) (0·12 g)	96		Am (7-14)	P (7-18)		
P-MTK-100 + SiO_2	48		$AlPO_4$ (7-11)	A (7-15)		
(1·6 g) (0·12 g)	96			A (7-17)		
MTK + SiO_2	48		P (8-29)	P (8-30)		
(1 g) (0·24 g)	96		P (8-27)	P (8-28)		
P-MTK-50 + SiO_2	48		Am (8-12)	P (8-16)		
(1·3 g) (0·24 g)	96		Am (8-14)	P (8-18)		
P-MTK-100 + SiO_2	48		$AlPO_4$ (8-11)	Am (8-15)		
(1·6 g) (0·24 g)	96		$AlPO_4$ (8-13)	A (8-17)		

* A = zeolite A; P = zeolite Na-P; S = sodalite hydrate; Am = amorphous. † The quantities of aqueous alkali added were in each case 20 cm^3 at the concentrations indicated in the Table.

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[10] G. F. Kirkbright, A. M. Smith, and T. S. West, *Analyst*, 1967, **92**, 411.

[11] R. M. Barrer and E. A. D. White, *J. Chem. Soc.*, 1951, 1267.

[12] C. Baerlocher and R. M. Barrer, *Z. Krist.*, in the press.

[13] R. M. Barrer and J. W. Baynham, *J. Chem. Soc.*, 1956, 2882.

and therefore no zeolites formed using such solutions. At higher concentrations the phosphate promoted crystallisation of zeolite A in preference to the gismondine-type Na–Pl [14] which appeared as a minor phase with pure MTK. The addition of extra silica promoted synthesis of Na–Pl in place of zeolite A, but with P-MTK-100 this effect was neutralised by the phosphate since zeolite A was obtained under all conditions.

TABLE 3

The phosphorus contents of some zeolites

Zeolite	Nos. of preparations	P content (μg/g)	P atoms per Al *
Zeolite A	7-17	95 ± 8	$0{\cdot}0005_6$
Zeolite A	6-35	482 ± 26	$0{\cdot}0028_4$
Zeolite A	8-17	1100 ± 72	$0{\cdot}006_5$
Zeolite A	6-16	1100 ± 70	$0{\cdot}006_5$
Sodalite hydrate	6-36	2230 ± 50	$0{\cdot}011_7$
Zeolite Na-P	8-18	110 ± 7	$0{\cdot}0006_3$
Zeolite Na-P	7-18	190 ± 10	0·0011
Zeolite K-F	10-16	175 ± 10	0·0011

* Assuming $Al_2O_3 : SiO_2 = 1 : 2$ for each zeolite. This may not be exact for Na-P and K-F, but is a very good approximation for sodalite hydrate and zeolite A.

Phosphorus Contents.—Those zeolites which could be obtained pure had the phosphorus contents given in Table 3. These were zeolites A, Na–P, sodalite hydrate, and K–F. The phosphorus contents of all these are extremely low especially in Na–P and K–F. The phosphorus contents can represent only upper limits to the extent of framework substitution because some or all of the phosphorus could instead be intercalated as discrete phosphate anions in cavities in the frameworks. This is particularly likely in sodalite hydrate and in zeolite A, because the 14-hedral sodalite-type cages in each are known to be able to trap anions.[15]

These results accord with those of Barrer and Marshall [3,4] and of Kuhl [5,6] rather than with those of Flanigen and Grose.[7] One experimental difference is the source of silica, which in ref. 7 was colloidal. The silica component of the mixtures used in our work may have a different reactivity. Nevertheless this seems an insufficient reason for the strikingly different results reported in our work and in that of ref. 7. In particular the presence of $AlPO_4$ in our reaction mixtures did not promote substitution of Si by P in any of the four zeolite types examined.

One of us (M. L.) thanks the Wolfson Foundation for the award of a research fellowship which enabled him to take part in this programme. We are indebted to Drs G. F. Kirkbright and P. J. Wilson for the phosphorus determinations in Table 3.

[4/837 *Received, 25th April*, 1974]

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[14] R. M. Barrer, J. W. Baynham, F. W. Bultitude, and W. M. Meier, *J. Chem. Soc.*, 1959, 195.

[15] R. M. Barrer and J. F. Cole, *J. Chem. Soc.* (*A*), 1970, 1523.