mally stable. Dta–tga analysis shows endotherms during decomposition at 242, 292, and 336°.

The infrared spectrum (Nujol mull) of K_2ZnH_4 shows two strong broad bands at 1400 and 650 cm^{-1}. These bands are consistent with octahedral coordinated zinc, since in the related system of magnesium hydrides (MgH_2 and $KMgH_3$) where the magnesium is known to be octahedrally coordinated, broad infrared bands occur at 1160 and 650 cm^{-1}.[6]

Although we have not indexed the powder pattern, the most likely structure of K_2ZnH_4 would seem to be that of K_2ZnF_4[7] which is the K_2NiF_4[8] structure.

We observed that NaH and di-*sec*-butylzinc do not react in hydrocarbon; however a 1:2 complex of NaH:(*sec*-C_4H_9)$_2$Zn [$NaZn_2R_4H$] was formed in dimethoxyethane. Although NaH was used in excess, a 1:1 ($NaZnR_2H$) or 2:1 ($Na_2ZnR_2H_2$) complex was not observed. Hydrogenation of this complex produced a black solid. The X-ray powder diffraction pattern (Table II) indicated that the solid was a mixture of zinc metal and another compound with a similar pattern to K_2ZnH_4, probably Na_2ZnH_4. When the black solid was subjected to dta–tga, a decomposition pattern similar to that observed for K_2ZnH_4 was obtained. The stepwise endothermic decomposition occurs at slightly lower temperatures: 190, 220, and 265°. A fourth endotherm is observed at 322° with no weight loss that is associated with the melting of zinc metal. On the basis of the X-ray powder pattern and the dta–tga, the existence of Na_2ZnH_4 seems likely.

An attempt to prepare $LiZnH_3$ or Li_2ZnH_4 by hydrogenolysis of the reaction production of *sec*-C_4H_9Li and (*sec*-C_4H_9)$_2$Zn in benzene solvent was not successful. Instead, a solid product was produced which exhibited an X-ray powder pattern characteristic of LiH. It was hoped that reaction of Li-*sec*-C_4H_9 and Zn(*sec*-C_4H_9)$_2$ would take place to produce LiZn(*sec*-C_4H_9)$_3$ which then would be hydrogenalyzed to form either $LiZnH_3$ or Li_2ZnH_4

$$\text{Li-}sec\text{-C}_4\text{H}_9 + (sec\text{-C}_4\text{H}_9)_2\text{Zn} \longrightarrow \text{LiZn}(sec\text{-C}_4\text{H}_9)_3 \overset{\text{H}_2}{\not\longrightarrow} \text{LiZnH}_3 \text{ or } \text{Li}_2\text{ZnH}_4 \quad (5)$$

Work is in progress to prepare other complex metal hydrides of zinc.

Acknowledgment.—We are indebted to the Office of Naval Research (Grant NOO14-67-A-0159-0005) for support of this work.

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High-Silica Analogs of Zeolite A Containing Intercalated Phosphate

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Extension of the phosphate-complexing technique to the mixed tetramethylammonium–sodium system led to the crystallization of high-silica zeolites of type A structure as well as a high-silica sodalite. The products of zeolite A crystal structure were found to contain intercalated phosphate, in amounts up to 1 phosphorus per sodalite cage, whereas the high-silica sodalite did not contain phosphorus. Two types of zeolites of the same crystal structure were distinguished: one type, classified as zeolite ZK-21, crystallized in the sodium form; the other, zeolite ZK-22, had an exchangeable cation to aluminum ratio of less than 1 because of the presence of nonexchangeable tetramethylammonium ions trapped during crystallization. As all materials of zeolite A structure, these two zeolites sorb straight-chain hydrocarbons if the number of cations per unit cell is not greater than 10. The more siliceous of the ZK-21's and ZK-22's, in their lanthanum and hydrogen forms, are stable, shape-selective cracking catalysts with an interconnected three-directional channel network.

The use of phosphate as a complexing agent for aluminate in the preparation of zeolite Y has been reported previously.[1] The study disclosed that the equilibrium

$$\text{Al(PO}_4)_2{}^{3-} + 4\text{OH}^- \rightleftarrows \text{Al(OH)}_4{}^- + 2\text{PO}_4{}^{3-}$$

is responsible for the increase in the silica to alumina ratio of the product when phosphate is present in the reaction mixture. The complex was identified as a diphosphatoaluminate.[2]

The phosphate-complexing technique yielded a variety of high-silica zeolites with faujasite,[1] chabazite,[1] and phillipsite structures.[1,3] It has also been applied successfully to the gallosilicate system,[1,4] yielding a high-silica gallosilicate zeolite of faujasite structure.

So far, only sodium and potassium had been used as cations in mixtures containing phosphate. When a combination of sodium and tetramethylammonium was used, high-silica, phosphate-containing zeolites of type A structure were obtained. (For a detailed description of zeolite structures see ref 5.) Preparations and properties of these materials are described in this paper.

A zeolite of type A structure containing organo-substituted ammonium ions was first synthesized by Barrer and Denny.[6] The yield was low, and a complete

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analysis was not published, but the authors surmised from the low nitrogen content that the SiO_2/Al_2O_3 ratio was high; the lattic parameter of $a_0 = 12.13$ Å supports this assumption. The principal cation in this zeolite was reported to be $(CH_3)_2NH_2^+$.

Kerr and Kokotailo[7] described the composition and properties of a high-silica form ($SiO_2/Al_2O_3 = 3.33$) of zeolite A, designated zeolite ZK-4. This zeolite was crystallized from a mixed sodium–tetramethylammonium system.[8] The SiO_2/Al_2O_3 molar ratio of ZK-4 was in the range of 2.8–3.4. Zeolite ZK-4 contained sodium and $(CH_3)_4N^+$ cations.

The preparation of still more siliceous forms of zeolite A was reported by Barrer, Denny, and Flanigen[9] (zeolite N-A) and Kühl,[10] as well as Wadlinger, Rosinski, and Plank[11] (zeolite α).

Zeolites ZK-21 and ZK-22 can be distinguished from each other as well as from zeolites ZK-4, N-A, and α as shown in Table I.

TABLE I

	ZK-21	ZK-22	ZK-4	N-A	α
SiO_2/Al_2O_3	2–4.5	2–7	2.7–3.4	2.5–6	4–7
Na_2O/Al_2O_3	≥ 1.0	<1.0	<1.0	<1.0	<1.0
Contains phosphate	Yes	Yes	No	No	No
Cokes upon calcination	No	Yes	Yes	Yes	Yes

Zeolite ZK-21 has the advantage over the other four that it is completely in the sodium form as crystallized and can, therefore, be exchanged directly into other cationic forms.

While zeolite α crystallizes from reaction mixtures having very high SiO_2/Al_2O_3 ratios (15–60), both zeolites ZK-21 and ZK-22 of all SiO_2/Al_2O_3 ratios can be prepared with the assistance of phosphate from mixtures whose silica to alumina ratio is in the range of 2–6.

Experimental Section

A. **Chemicals.**—The chemicals used are as follows, along with their sources, and/or descriptions: sodium aluminate, reagent grade from Allied Chemical, General Chemical Division; 43.3% Al_2O_3, 37.7% Na_2O; sodium metasilicate, reagent grade from Allied Chemical, General Chemical Division; 21.9% SiO_2, 24.55% Na_2O; waterglass, Q-brand from Philadelphia Quartz Co.; 28.7% SiO_2, 8.9% Na_2O; colloidal silica sol, Ludox LS, containing 31.5% SiO_2; tetramethylammonium hydroxide, 25% aqueous solution from Matheson Coleman and Bell; phosphoric acid, 85% aqueous solution; aluminum phosphate dihydrate, Amend Drug and Chemical Co., New York, N. Y.; tetramethylammonium bromide, Eastman Organic Chemicals.

B. **Preparation of Zeolites ZK-21 and ZK-22.**—The reaction mixtures were prepared in the following way. Aluminum phosphate was dissolved in the mixture of tetramethylammonium hydroxide and phosphoric acid at a temperature not exceeding 70° (or in the hydroxide only with the acid being added later). Sodium aluminate was dissolved in water at room temperature and tetramethylammonium hydroxide and phosphoric acid were added. The phosphatoaluminate solution prepared by either method was diluted to a known volume and the silicate solution—made by dissolving sodium metasilicate in a known amount of water or by diluting waterglass or Ludox with a known volume of water—was added with stirring. Usually a gel did not form immediately. Stirring was discontinued as soon as a uniform mixture was obtained, and the polypropylene flask with the reaction mixture was placed in a constant-temperature bath. The progress of the crystallization was followed by microscopic examination. When all the gel had disappeared, the mixture was filtered on a Büchner funnel. The zeolite was washed with water and dried at 110°.

C. **X-Ray Investigation and Sorption Measurements.**—The crystal structures of the products were determined by X-ray diffracton. Debye–Scherrer photographs were taken with a Siemens Kristalloflex II and compared with the patterns of known materials.

The lattice parameter measurements of the hydrated samples were made on a Siemens Kristalloflex IV X-ray diffractometer equipped with scintillation counter, pulse height analyzer, and strip-chart recorder. A scan speed of 0.125°/min was used with a 1 cm/min chart speed. The cubic lattice parameters, a_0, were measured by the double-scanning diffractometry technique[12] which minimizes zero 2θ errors. The 731 peak was used for this measurement.

For the sorption measurements, the reaction products were calcined at 550° and, after cooling to ambient temperature, exposed to the vapor of the sorbate at 25°.[13] A pressure of 20 mm was used for *n*-hexane and cyclohexane; 12 mm, for water sorption.

For the thermogravimetric investigations, a Du Pont 950 thermogravimetric analyzer was used.

Results and Discussion

A. **General Considerations.**—The size of the anionic species in solution during the crystallization of a zeolite is dependent on the pH of the solution. The higher the pH, the smaller are the anionic species; the lower the pH, the larger are the anionic species. Also, the lower the pH, the more different anionic species are present in significant amounts and in equilibrium with one another (for solutions of constant concentrations and constant silicate to aluminate ratios).

It is hypothesized that the basic unit for the zeolite A structure is a double-four-ring aluminosilicate anion and that for the faujasite structure is a double six ring.[14] If this hypothesis is valid, it can be expected that the zeolite A structure is formed at a higher pH than the faujasite structure under otherwise identical conditions. Since aluminate does not condense with aluminate under the conditions of a zeolite crystallization, but more easily with silicate than silicate with silicate, the double four rings are most readily formed in a mixture containing silicate and aluminate in a ratio close to 1:1. If phosphate is present in such a mixture containing sodium as cations, then zeolite Y is formed at low pH, zeolite X at somewhat higher pH values, zeolite A at still higher alkalinity, and sodalite at very high pH, where presumably single four rings are the predominant species. When the crystallizing structure changes from X to A, the pH is so high that the silica to alumina ratio of the resulting zeolite is low. A higher SiO_2/Al_2O_3 ratio of the zeolite A structure has not been obtained by this procedure.

When a zeolite crystallizes, the number of cationic charges incorporated in the zeolite structure is equal to the number of aluminum atoms in the zeolite framework. Obviously, if only a small number of cations (*e.g.*, Na) are available, the amount of aluminum being included in the zeolite framework is limited.

So, by using cations whose size prevents them from being as easily incorporated as sodium, one can limit the number of cations effectively available for the zeolite crystallization without affecting the pH of the reaction mixture.

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If some of these large cations are incorporated in the crystallizing zeolite, they provide an additional advantage: because of their size, they limit the number of cationic charges per unit cell and thus cause further increase of the silica to alumina ratio of the product (see also ref 6 and 8). It is important, of course, that the size and shape of the large cations be compatible with the zeolite structure desired. Typical examples are the preparations of zeolites ZK-4[8] and ZK-5.[15] Tetramethylammonium ions have previously been shown to be incorporated in zeolite A-type structures.[6,8-11]

B. Preparation of Zeolite ZK-21.—As initially prepared from the reaction mixture, zeolite ZK-21 crystallizes in the sodium form. Sodium metasilicate is a preferred source of silica; however, other silica sources, such as colloidal silica sol and waterglass, may be used satisfactorily. Aluminum, introduced as sodium aluminate, is complexed by phosphate ions in order to decrease the concentration of hydroxoaluminate ions.[1] As cations, a combination of sodium and tetramethylammonium ions is employed.

Zeolite ZK-21 may be prepared from a reaction mixture having the following reactants expressed in mole ratios: SiO_2/Al_2O_3 between about 2 and 10, P_2O_5/Al_2O_3 at least about 2, $Na_2O/(Na_2O + [(CH_3)_4N]_2O)$ between about 0.10 and 0.55, and $(Na_2O + [(CH_3)_4N]_2O)/P_2O_5$ at least about 2.5. Preparations of zeolite ZK-21 are summarized in Table II.

TABLE II
PREPARATION OF ZEOLITE ZK-21
(P_2O_5/Al_2O_3 = 3.99; METASILICATE)

Expt	SiO_2/Al_2O_3	$Na_2O/(Na_2O + [(CH_3)_4N]_2O)$	$(Na_2O + [(CH_3)_4N]_2O)/P_2O_5$	$H_2O/(Na_2O + [(CH_3)_4N]_2O)$	Final pH	Product X-Ray	Product SiO_2/Al_2O_3
1	2.0	0.291	3.08	*Ca.* 54	11.95	ZK-21	2.06
2	3.0	0.359	3.26	*Ca.* 51	12.35	ZK-21	3.09
3	4.0	0.406	3.52	*Ca.* 47	12.8	ZK-21	3.26
4	6.0	0.486	4.06	*Ca.* 44	13.3	ZK-21+ Y	3.89
5	4.0	0.315	4.56	*Ca.* 46	13.9	ZK-21	2.79
6	6.0	0.386	5.1	*Ca.* 46	13.8	ZK-21	3.16

In the first four experiments, the amount of sodium metasilicate has been varied, which means that the three significant mixture ratios increase simultaneously. Under these conditions, the silica to alumina ratio of the product increases steadily. However, the high $Na_2O/(Na_2O + [(CH_3)_4N]_2O)$ ratio of example 4 results in the crystallization of some faujasite-type material. The steady rise of $(Na_2O + [(CH_3)_4N]_2O)/P_2O_5$ partially offsets the higher SiO_2/Al_2O_3 ratio of the mixture.

In experiments 5 and 6, an attempt was made to lower the ratio $Na_2O/(Na_2O + [(CH_3)_4N]_2O)$ by using more tetramethylammonium hydroxide in order to reduce the chance of faujasite-type zeolites to crystallize. The expected effect has been observed, but the simultaneous increase of $(Na_2O + [(CH_3)_4N]_2O)/P_2O_5$ results in lower SiO_2/Al_2O_3 ratios of the products, compared with experiments 3 and 4.

In order to increase the amount of tetramethylammonium ions, but not the concentration of OH^- ions, tetramethylammonium bromide was used in the experiments summarized in Table III. In experiments 7–10, tetramethylammonium bromide was added, in addition to the greater amounts of tetramethylammonium hydroxide. The influence on the SiO_2/Al_2O_3 ratio of the product is only slight, whereas the crystallization of the faujasite structure is effectively hindered, so that greater amounts of sodium metasilicate can be used. The pH, however, is so high that the phosphate is inactive for complexing aluminum and raising the silica to alumina ratio of the product. When the SiO_2/Al_2O_3 molar ratio of the reaction mixture was raised to 12, the ratio of sodium to total cations increased to a value that permitted crystallization of faujasite-type material again. While in all the previous examples of this table, tetramethylammonium hydroxide and phosphoric acid were used in the molar ratio of 3:1, corresponding to the tertiary phosphate, the secondary salt was used in examples 11 and 12, which results in lower pH values and products of higher SiO_2/Al_2O_3 ratios. The appearance of faujasite-type material in example 11 appears to be attributable to the greater dilution of the reaction mixture.

TABLE III
PREPARATION OF ZEOLITE ZK-21 (P_2O_5/Al_2O_3 = 3.99)

Expt	SiO_2[a]$/Al_2O_3$	$Na_2O/(Na_2O + [(CH_3)_4N]_2O)$	$(Na_2O + [(CH_3)_4N]_2O)$[b]$/P_2O_5$	$H_2O/(Na_2O + [(CH_3)_4N]_2O)$	Final pH	Product X-Ray	Product SiO_2/Al_2O_3
7	4.0	0.189	4.58	*Ca.* 40	13.9	ZK-21	2.93
8	8.0	0.384	5.64	*Ca.* 36	14.0	ZK-21	3.34
9	10.0	0.382	6.17	*Ca.* 30	>14	ZK-21	3.45
10	12.0	0.411	6.56	*Ca.* 37	14.0	ZK-21 + Y	3.47
11	4.0	0.257	3.53	*Ca.* 62	12.55	ZK-21 + Y	3.23
12	6.0	0.386	4.06	*Ca.* 39	13.05	ZK-21	3.82
13	4.0	0.174	3.80	*Ca.* 56	Nd[c]	ZK-21	3.09
14	6.0	0.206	3.94	*Ca.* 45	13.5	ZK-21	3.73

[a] In 7–12, metasilicate; in 13 and 14, waterglass Q. [b] Includes only the portion of $(CH_3)_4N^+$ added as hydroxide. [c] Not determined.

In examples 13 and 14, waterglass was employed as the silicate source, thus reducing the amount of sodium introduced into the reaction mixture.

Table IV shows the influence of the concentration on the type of crystallizing structure. The composition of the reaction mixtures was the same, except for the amount of water used. The highest dilution yields mainly faujasite-type material. Intermediate concentrations cause the zeolite A structure to crystallize. The sodalite structure crystallizes from the reaction mixture of the highest concentration.

TABLE IV
EFFECT OF CONCENTRATION ON CRYSTALLIZING STRUCTURE
(SiO_2/Al_2O_3 = 8.0; $Na_2O/(Na_2O + [(CH_3)_4N]_2O)$ = 0.256; $(Na_2O + [(CH_3)_4N]_2O$[a]$)/P_2O_5$ = 3.40)

Expt	Reacn mixt $H_2O/(Na_2O + [(CH_3)_4N]_2O)$	Temp, °C	Final pH	Product X-Ray	Product SiO_2/Al_2O_3	Product Na_2O/Al_2O_3
15	53	90	12.3	Y + 5% ZK-22	6.0	0.62
16	43	90	12.95	ZK-22 + 10% Y	4.9	0.82
17	26	95	12.6	Sodalite + 15% ZK-22	7.4	0.46
18	26	90	12.3	Sodalite	8.1	0.56

[a] Includes only the portion of $(CH_3)_4N^+$ added as hydroxide.

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(15) G. T. Kerr, *Inorg. Chem.*, **5**, 1539 (1966).

Attempts have been made to eliminate the phosphate from the reaction mixture. Two moles of tetramethylammonium bromide was substituted for 1 mol of secondary tetramethylammonium phosphate. This substitution does not change $Na_2O/(Na_2O + [(CH_3)_4N]_2O)$ nor significantly affect the pH. The zeolite A structure did not crystallize from these mixtures in spite of seeding with zeolite A. Instead, zeolites X and B were obtained. When the tetramethylammonium ions in a phosphate-containing reaction mixture were replaced by sodium, again no zeolite A structure was obtained.

It thus appears that the combination of phosphate and tetramethylammonium ions is of particular advantage for the crystallization of high-silica zeolite A materials from such mixtures.

C. Preparation of Zeolite ZK-22.—When attempts were made to increase the silica to alumina ratio of zeolite ZK-21, products of Na/Al ratios below 1.0 (ZK-22) were obtained. In examples 19 and 20 in Table V, metasilicate was used as the silica source and aluminum was introduced as aluminum phosphate. The pH, indicated as the ratio of cation oxides to P_2O_5, is lower than for the preparation of ZK-21. When the ratio of Na_2O over total cation oxides increased significantly above 0.4, zeolite Y was obtained as an impurity along with zeolite ZK-22.

TABLE V

PREPARATION OF ZEOLITE ZK-22

						Product	
Expt	SiO_2/Al_2O_3	$Na_2O/(Na_2O + [(CH_3)_4N]_2O)$	$(Na_2O + [(CH_3)_4N]_2O)/P_2O_5$	$H_2O/(Na_2O + [(CH_3)_4N]_2O)$	Final pH	X-Ray	SiO_2/Al_2O_3
19	4.0	0.338	2.54	*Ca.* 49	11.2	ZK-22	3.94
20	6.0	0.435	2.97	*Ca.* 42	12.1	ZK-22 + Y	5.64
21	8.0	0.234	4.10	*Ca.* 44	13.6	ZK-22	4.06
22	8.0	0.234	2.56	*Ca.* 45	11.7	ZK-22 + sodalite	6.16
23	6.0	0.404	2.94	*Ca.* 38	11.75	ZK-22	6.15
24	6.0	0.368	2.66	*Ca.* 40	11.8	ZK-22 + sodalite	5.66
25	6.0	0.330	2.51	*Ca.* 43	11.4	ZK-22	5.34
26	6.0	0.286	2.35	*Ca.* 45	No crystallization		. . .

In order to increase further the SiO_2/Al_2O_3 ratio of the type A structure, the amount of sodium has to be lowered, which can be achieved by using waterglass as the silica source, as demonstrated in the next two examples. With secondary tetramethylammonium phosphate, the reaction mixture did not crystallize. Tertiary phosphate (example 21) gave ZK-22, but the pH was quite high. A decrease of the pH by addition of more phosphoric acid resulted in the crystallization of a high-silica ZK-22 contaminated with some high-silica, sodalite-type material (example 22). Attempts to lower the sodium to total cation ratio of example 20 by employing mixtures of sodium metasilicate and waterglass without using more tetramethylammonium hydroxide were successful and yielded the best samples of high-silica ZK-22 (examples 23–25). In example 26, the pH dropped finally to such a low value that a crystallization did not occur.

Low silica to alumina ratio forms of zeolite ZK-22 were obtained with colloidal silica sol as the source of silica (Table VI). Examples 30 and 31 supply further evidence that high silica to alumina ratios and/or low pH values favor simultaneous crystallization of a high-silica sodalite material.

TABLE VI

PREPARATION OF ZEOLITE ZK-22[a]

						Product	
Expt	SiO_2/Al_2O_3	$Na_2O/(Na_2O + [(CH_3)_4N]_2O)$	$(Na_2O + [(CH_3)_4N]_2O)/P_2O_5$	$H_2O/(Na_2O + [(CH_3)_4N]_2O)$	Final pH	X-Ray	SiO_2/Al_2O_3
27	3.0	0.103	3.49	*Ca.* 54	13.0	ZK-22	2.38
28	4.0	0.103	3.49	*Ca.* 51	13.1	ZK-22	2.71
29	6.0	0.103	3.49	*Ca.* 51	12.9	ZK-22	3.05
30	8.0	0.103	3.49	*Ca.* 51	12.5	ZK-22 + sodalite	4.86
31	4.0	0.147	2.45	*Ca.* 59	Nd	ZK-22 + sodalite	3.68

[a] Silica source: colloidal silica sol.

The crystallization of example 25 required more than 10 weeks to be complete. Attemps have been made to decrease the crystallization time. The experiments are summarized in Table VII. The reaction mixtures of examples 32–35 were seeded with a small amount of the product of example 25. The best material was obtained at 125° in about 1 week.

TABLE VII

PREPARATION OF ZEOLITE ZK-22[a]

	Crystallization			Product	
Expt	Temp, °C	Time, days	Final pH	X-Ray	SiO_2/Al_2O_3
25	90	74	11.41	ZK-22	5.34
32	95	34	Nd	ZK-22	5.70
33	100	35	11.42	ZK-22	5.70
34	125	8	11.46	ZK-22	6.24
35	150	<7	10.95	ZK-22	6.82

[a] Compositions of all reaction mixtures are the same as in experiment 25.

D. Properties of Zeolites ZK-21 and ZK-22. 1. Composition and Crystal Structure.—Zeolite ZK-21 has a crystal structure like zeolite A, but with a somewhat contracted lattice, due to the higher silica to alumina ratio. The molar SiO_2/Al_2O_3 ratio can vary from 2 to 4 or slightly higher. The X-ray diffraction pattern of the product of example 3 (SiO_2/Al_2O_3 = 3.26) is given in Table VIII. In Figure 1, the lattice parameters of four samples of zeolite ZK-21 are plotted as a function of the number of aluminum atoms per unit cell (uc). The straight line has been drawn through the

TABLE VIII

X-RAY DIFFRACTION DATA OF ZEOLITE ZK-21

d, Å	I/I_0	*hkl*	*d*, Å	I/I_0	*hkl*
12.16	100	100	2.348	6	511
8.65	68	110	2.227	3	521
7.07	63	111	2.154	10	440
5.48	29	210	2.122	4	441
5.02	4	211	2.093	3	530
4.33	15	220	2.061	3	531
4.07	63	300	2.033	9	600
3.86	3	310	1.904	7	621
3.675	83	311	1.881	5	541
3.389	30	320	1.839	2	622
3.264	59	321	1.818	2	630
2.952	77	410	1.740	2	632
2.878	15	411	1.722	14	710
2.732	10	420	1.706	2	711
2.664	5	421	1.674	8	641
2.601	32	332	1.659	2	721
2.491	9	422	1.615	4	722
2.441	4	430,500	1.586	5	731
2.395	2	510	1.560	5	650

TABLE IX
PROPERTIES OF ZEOLITE ZK-21

	Composition, wt %										Sorption, g/100 g of sample			
	Ignited weight basis			Hydrated weight basis										
Expt	SiO_2	Al_2O_3	Na_2O	Ash	C	N	P	SiO_2/Al_2O_3	Na_2O/Al_2O_3	P/uc	c-C_6H_{12}	n-C_6H_{14}	H_2O	Remarks
1	40.9	33.7	20.6	80.5	2.52	0.58	1.41	2.06	1.00	1.00	0.90	1.92[a]	21.5	
2	50.4	27.8	17.55	78.5	n.d.	1.11	1.00	3.09	1.03	0.71	1.30	12.1	21.6	
3	53.2	27.6	17.0	79.0	2.72	0.68	1.05	3.26	1.01	0.74	1.32	12.2	23.0	$a_0 = 12.17 \pm 0.02$
4	57.4	25.1	15.0	78.9	3.06	0.78	0.73	3.89	0.98	0.49	2.78	12.4	24.3	Contains Y
5	48.1	29.4	18.7	79.5	2.08	0.55	0.92	2.79	1.04	0.66	1.03	11.0	21.7	
6	52.2	28.0	18.45	78.1	Nd	0.56	1.00	3.16	1.08	0.70	0.40	11.9	22.2	
7	48.9	28.4	18.1	83.4	2.56	0.61	1.13	2.93	1.05	0.76	0.19	11.2	22.0	$a_0 = 12.185 \pm 0.02$
8	51.7	26.4	18.0	79.8	1.05	0.62	1.08	3.34	1.12	0.76	0.75	11.9	22.4	
9	52.3	25.8	18.5	79.4	2.46	0.59	1.04	3.45	1.18	0.74	1.29	12.2	23.0	$a_0 = 12.15 \pm 0.02$
10	53.7	26.3	16.45	78.7	1.95	0.61	0.95	3.47	1.03	0.66	2.71	12.7	24.6	Contains Y
11	52.6	27.7	17.1	79.3	4.88	0.72	0.85	3.23	1.02	0.58	2.71	12.0	22.7	Contains Y
12	56.6	25.2	16.3	80.0	2.76	0.77	1.02	3.82	1.06	0.68	1.54	12.5	24.4	$a_0 = 12.125 \pm 0.02$
13	51.0	28.5	18.4	81.0	3.27	0.77	0.85	3.04	1.06	0.58	n.d.	11.3	24.1	
14	56.0	25.5	15.8	79.1	3.65	0.97	0.79	3.73	1.02	0.54	1.15	13.2	24.6	

[a] 11.9 Na/uc.

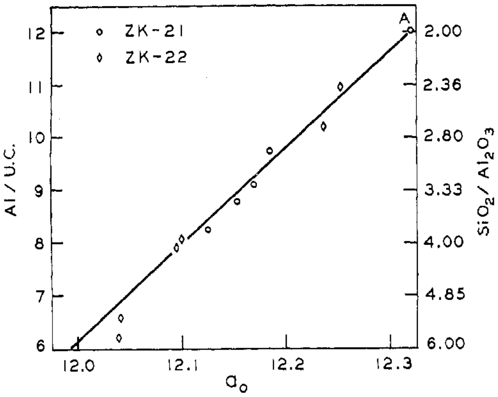

Figure 1.—Lattice parameters of zeolites ZK-21 and ZK-22.

point for zeolite A (SiO_2/Al_2O_3 = 2.0, a_0 = 12.32 ± 0.02 Å) and the calculated value for a sample containing 6 Al's per unit cell using the distances Si–O = 1.60 Å and Al–O = 1.78 Å and assuming that the angles do not change with the silica content.[16]

The analytical data are summarized in Table IX. As crystallized, zeolite ZK-21 is completely in the sodium form and differs in this respect from zeolites ZK-4, ZK-22, N-Q, and α. Zeolite ZK-21 contains up to 1 phosphate per unit cell. The lower limit appears to be about 0.5 P/uc. This phosphate cannot be washed out, as will be shown later, and is assumed to be intercalated within the sodalite cages. Since there is 1 sodalite cage per unit cell, the theoretical upper limit for the phosphate content is 1 P/uc, if the sodalite cage cannot accommodate more than one phosphate ion. Some nitrogenous material is apparently associated with the phosphate. The carbon to nitrogen and the nitrogen to phosphorus ratios vary within a wide range so that the nature of this material is unknown. In contrast to zeolites ZK-4, α, N-Q, and ZK-22, which contain zeolitic nitrogenous cations, zeolite ZK-21 does not coke upon calcination.

The nitrogenous material in zeolite ZK-21 does not constitute zeolitic cations. The sodium ions present are sufficient to balance the negative charges of the framework aluminum. In order to determine whether all the sodium ions are zeolitic, the product of example 3 was exchanged with calcium ions. The composition of the product was as shown in Table X. Refluxing with calcium nitrate solution eventually reduced the sodium content to 0.05% Na_2O while the nitrogen content remained constant within the analytical tolerance (0.65% N). This experiment demonstrates that all the sodium in ZK-21 is zeolitic. Since Na_2O/Al_2O_3 is 1 (within the analytical accuracy), the nitrogenous material cannot be zeolitic.

TABLE X

	Wt %	
SiO_2	53.1	Ignited weight basis
Al_2O_3	27.6	
Na_2O	0.61	
CaO	15.5	
N	0.68	Hydrated weight basis
	Ratio	
SiO_2/Al_2O_3	3.27	
$(Na_2O + CaO)/Al_2O_3$	1.04	

The phosphate would be precipitated as calcium phosphate if it were removed from the zeolite and so remain in the sample. The calcium-exchange experiment does, therefore, not distinguish between phosphate adsorbed on the surface of the crystals and that intercalated within the zeolite. Treatment of the product of example 3 with sodium chloride, however, showed that the phosphate was not removed (see Table XI).

TABLE XI

	Wt %	
	Washed with hot H_2O	Equilibrated with 2 batches of 2 N NaCl
	Ignited Weight Basis	
SiO_2	53.2	51.9
Al_2O_3	27.6	27.1
Na_2O	17.0	16.6
	Hydrated Weight Basis	
C	2.72	2.58
N	0.68	0.70
P	1.05	1.05
Ash	79.0	79.2

Thus it has to be assumed that a nitrogenous phosphate is intercalated. The general formula of calcined ZK-21 is $M_2O \cdot Al_2O_3 \cdot YSiO_2 \cdot ZP_2O_5$, where Z is a value not exceeding $(Y + 2)/48$.

The molar SiO_2/Al_2O_3 ratio of zeolite ZK-22 can vary from 2 to about 7, but ratios above 6.0 have yet to be firmly established. The sodium to aluminum ratio is always below 1.0. Some of the cationic charges are

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(16) J. V. Smith, *Acta Crystallogr.*, **7**, 479 (1954).

TABLE XII

PROPERTIES OF ZEOLITE ZK-22

	Composition, wt %													
	Ignited wt basis			Hydrated wt basis							Sorption, g/100 g of sample			
Expt	SiO_2	Al_2O_3	Na_2O	Ash	C	N	P	SiO_2/Al_2O_3	Na_2O/Al_2O_3	P/uc	c-C_6H_{12}	n-C_6H_{14}	H_2O	Impurity
19	58.5	25.2	14.7	81.1	3.65	0.94	0.87	3.94	0.96	0.58	1.28	12.4	24.2	
20	69.3	20.9	8.5	79.7	5.15	1.38	0.13	5.64	0.67	0.08	3.45	11.6	21.7	Y
21	58.6	24.5	13.4	77.4	3.57	1.04	0.73	4.06	0.90	0.50	0.92	13.7	25.9	
22	73.7	20.3	6.3	79.4	7.25	1.86	0.28	6.16	0.51	0.17	Nd	8.74	20.2	Sodalite
23	70.9	19.6	7.95	79.7	6.00	1.51	0.33	6.15	0.67	0.21	0.87	12.4	22.6	
24	69.8	20.9	8.28	78.2	6.03	1.33	0.20	5.66	0.65	0.13	Nd	11.2	21.8	Sodalite
25	66.9	21.3	10.1	79.1	5.92	1.41	0.58	5.34	0.78	0.38	Nd	14.2	25.4	
27	46.9	33.6	18.6	83.4	3.17	0.75	0.45	2.38	0.91	0.29	Nd	9.82[a]	24.6	
28	49.9	31.3	17.65	80.7	3.23	0.87	0.44	2.71	0.93	0.29	0.58	13.5[b]	27.0	
29	53.5	29.8	16.0	77.0	4.37	1.05	0.41	3.05	0.88	0.28	Nd	13.4	26.3	
30	67.0	23.4	9.8	78.2	6.26	1.15	0.39	4.86	0.69	0.25	0.74	9.85	21.4	Sodalite
31	57.6	26.6	11.45	78.4	5.54	1.14	1.43	3.68	0.71	0.95	Nd	9.58	23.2	Sodalite
32	69.5	20.7	6.74	80.8	6.20	1.53	0.21	5.70	0.54	0.13	0.48	14.0	25.3	
33	70.8	21.1	7.95	76.9	6.15	1.58	0.26	5.70	0.62	0.16	0.84	13.8	25.7	
34	70.9	19.3	7.4	80.2	6.48	1.74	0.19	6.24	0.63	0.12	0.68	14.8	26.6	
35	72.3	18.0	5.8	80.8	6.73	1.65	0.16	6.82	0.53	0.10	0.38	13.2	24.2	

[a] 10 Na/uc. [b] 9.5 Na/uc.

provided by tetramethylammonium ions. These ions decompose during calcination and form coke. Thus, zeolites ZK-21 and ZK-22 can easily be distinguished by a calcination test. Only if Na_2O/Al_2O_3 is close to 1.0, it may be sometimes difficult to recognize the discoloration. Like zeolite ZK-21, ZK-22 contains intercalated phosphate. The composition of the ZK-22 samples is summarized in Table XII. The number of phosphorus atoms per unit cell can be as low as 0.10. The even lower value of 0.08 in the sample of experiment 20 is attributed to the contamination with zeolite Y, which does not contain phosphorus.

The C/N atomic ratio in zeolite ZK-22 varied widely between 3.4 and 4.8, but mostly above 4.0. It appears that the principal nitrogenous cation is $(CH_3)_4N^+$; some amine is lost during the crystallization, probably leaving behind some carbonaceous decomposition product, which accounts for the usually high C/N ratio. The crystal structure of zeolite ZK-22 is identical with that of zeolite ZK-21, the high-silica material having an even more contracted lattice. This contraction is partially compensated by the expanding effect of the large tetramethylammonium ions if they represent a substantial portion of the cation population. The lattice parameters of several samples are shown in Figure 1 and Table XIII. The data indicate that, for Na/Al atomic ratios of about 0.8 and higher, the tetramethylammonium ions do not significantly affect the lattice parameter. The compound of experiment 32, with only 0.54 Na/Al, has a somewhat expanded lattice. The lattice parameter of the sodium form, prepared by sorbing ammonia after thermal decomposition of the organic cations and exchange with sodium ions, suggests that the SiO_2/Al_2O_3 ratio of the zeolite is about the same as that of experiment 25 and that a small percentage of amorphous silica is present. The hydrogen form, prepared by calcination of the NH_4–$(CH_3)_4N$ form of the zeolite, had the smallest lattice parameter.

TABLE XIII

LATTICE PARAMETERS OF ZEOLITE ZK-22

Expt	SiO_2/Al_2O_3	No. of Al/uc	Na/Al	a_0, Å
27	2.38	10.95	0.91	12.25 ± 0.02
28	2.71	10.20	0.93	12.24 ± 0.02
19	3.94	8.08	0.96	12.10 ± 0.02
21	4.06	7.92	0.90	12.095 ± 0.02
25	5.34	6.54	0.78	12.04 ± 0.02
32	5.70	6.23	0.54	12.07 ± 0.02
32, calcined			0.54	12.03 ± 0.02
32, Na form			0.89	12.04 ± 0.02
32, La form, 0.38 La/Al			...	12.02 ± 0.02
32, H form			0.01	11.98 ± 0.02

2. **Sorption Properties.**—The zeolite A structure sorbs straight-chain hydrocarbons if the number of cations per unit cell is not greater than 10.[17,18] For the sodium form of the zeolite, this corresponds to a Si:Al ratio of 14:10 or $SiO_2/Al_2O_3 = 2.8$. Zeolite ZK-21 sorbs n-hexane if the molar ratio SiO_2/Al_2O_3 is higher than 2.8. Samples having ratios below this figure do not sorb straight-chain hydrocarbons, as experiment 1, Table IX, demonstrates. If the SiO_2/Al_2O_3 molar ratio is close to 2.8, the rate of sorption is significantly lower than for the high-silica forms of the same zeolite. The product of example 5 sorbed only 9.85 g of n-hexane/100 g of zeolite within 1 hr; by the next morning the sorbed amount had reached 11 g/100 g of zeolite. Branched-chain and cyclic hydrocarbons are not admitted to the zeolite supercages because the ports are only about 5 Å wide. Nevertheless, a cyclohexane sorption capacity of somewhat over 1% has frequently been observed, although no X-type material could be detected in the sample. When the sorption capacity for cyclohexane was above 2%, faujasite-type material was always easily found by X-ray diffraction.

Zeolite ZK-22 sorbs straight-chain hydrocarbons, if the number of thermally stable cations per unit cell is not greater than 10. In contrast to zeolite ZK-21, this limit cannot be expressed in terms of SiO_2/Al_2O_3, because ZK-22 contains zeolitic tetramethylammonium ions, which are not thermally stable and are removed upon calcination. The rate of hydrocarbon sorption is reduced in samples containing close to 10 Na^+/uc. The compound of experiment 27 (10 Na/uc) sorbed only 9.82 g of n-hexane/100 g of zeolite in 18 hr. Although the compound of experiment 28 (9.5 Na/uc) sorbed the major portion of n-hexane relatively fast, it required a long time to reach equilibrium, as the following data demonstrate: 3 hr, 11.4; 5 hr, 11.9; 6 hr, 12.3; 23 hr, 13.5 g/100 g of zeolite. The framework structure of zeolite ZK-22 excludes branched-chain and cyclic hydrocarbons.

3. **Ion-Exchange and Cracking Activity.**—The sodium ions can easily be exchanged with calcium. The

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[17] T. B. Reed and D. W. Breck, *J. Amer. Chem. Soc.*, **78**, 5972 (1956).

[18] G. T. Kerr, *J. Phys. Chem.*, **66**, 2271 (1962).

product of experiment 12, 5 g, was treated with three batches of 500 ml of 0.1 *N* $Ca(NO_3)_2$ solution at room temperature for 1 day each, then with a fourth batch at refluxing temperature. The composition and properties of the starting material and the exchanged product compare as in Table XIV.

Table XIV

	Na form	Ca form
	Wt %	
SiO_2	56.6	58.1
Al_2O_3	25.2	26.0
Na_2O	16.3	0.35
	Ratio	
CaO	. . .	14.7
SiO_2/Al_2O_3	3.82	3.80
Cation equiv/Al	1.06	1.06

The ratio of cation equivalents to aluminum is retained at a somewhat high level, suggesting that the intercalated phosphate may contribute to the exchange capacity. The sorption properties of the calcium form are the same as for the sodium form.

All the sodium ions of zeolite ZK-22 can be exchanged with other cations without prior removal of the tetramethylammonium ions. The latter are too big to pass the 5-Å ports. They can be removed by calcination under anhydrous conditions.

The sodium ions of a sample of zeolite ZK-22 (experiment 32) were removed by treatment with ammonium sulfate solution at 80°. The mixed ammonium tetramethylammonium zeolite ZK-22 was calcined in air at a heating rate of 10°/min (Figure 2). The tga curve shows first a loss of adsorbed water. When the decomposition and oxidation of the tetramethylammonium ions started at about 200°, the temperature of the sample increased beyond the temperature of the furnace. At 350° it returned to the furnace temperature. The following weight loss is attributed to the loss of ammonia and oxidation of carbon deposited during the decomposition of the tetramethylammonium ions. At 900°, constant weight is attained for the dehydroxylated form of the zeolite. Calculated from this value, the weight of the hydrogen zeolite is 41.9 mg, which was reached with a distinct step at 650° under the conditions of the experiment.

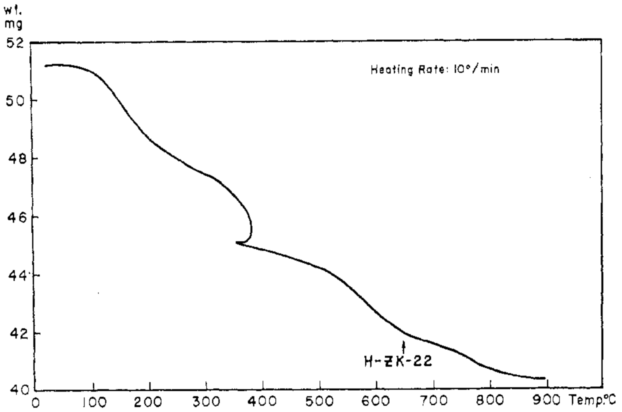

Figure 2.—Calcination of NH_4-$(CH_3)_4N$–ZK-22 in air.

As Figure 2 suggests, the hydrogen form of ZK-22 can be obtained by prolonged heating of the zeolite in air at 550° after initial decomposition at lower temperatures. A sample prepared in such manner was cooled to 100° (Figure 3). During this process, it gained 0.6 mg, most likely by sorption of water. Then ammonia was admitted. In an exothermic reaction, ammonia was sorbed (about 10%). The physically adsorbed ammonia was removed in a stream of dry helium at 100° Constant weight of 45.85 mg was reached after about 50 min. No significant further weight loss was observed when this treatment was continued for another 40 min.

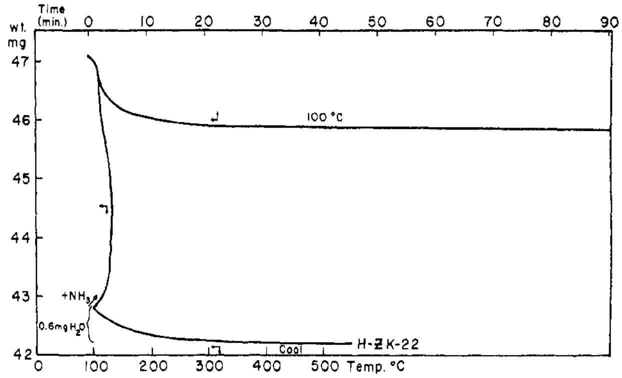

Figure 3.—Formation of NH_4–ZK-22.

The theoretical weight of the NH_4–ZK-22 is 45.25 mg. To this has to be added the amount of water sorbed upon cooling of the hydrogen zeolite (= 0.6 mg). Thus the theoretical value agrees with the experimentally found one. Upon recalcination at 10°/min, the original weight of 42.2 mg was attained at 600°. The ammonium form of the zeolite can be exchanged with other cations. A sample having a $([(CH_3)_4N]_2O + Na_2O)/Al_2O_3$ molar ratio of 0.89 and a Na_2O/Al_2O_3 ratio of 0.54 was calcined under anhydrous conditions in order to avoid hydrolysis of framework Al. The product was treated with ammonia and the excess ammonia desorbed as described above. Subsequent exchange with NaCl solution yielded a product with Na_2O/Al_2O_3 = 0.89, indicating that all original tetramethylammonium ions were replaced by sodium ions. The results are evidence that the crystallinity of the zeolite was retained. This was also shown by X-ray diffraction and sorption measurements.

Thermally stable hydrogen and rare earth forms of zeolites are generally known to be very active cracking catalysts.[19] The Ce, La, H form of synthetic faujasite, for example, is more than 10,000 times as active for cracking *n*-hexane than conventional silica–alumina.

In contrast to the faujasite structure, the zeolite A framework admits only straight-chain hydrocarbons resulting in a shape-selective cracking of such hydrocarbons from a mixture.[20] The cracking activities increase with the silica to alumina ratio. Thus, the calcium form of example 12 (SiO_2/Al_2O_3 = 3.82) had an *n*-hexane cracking activity of α = 0.9 compared with 0.6 for CaA[19] and approached that of conventional silica–alumina.

High-silica zeolites are more stable in their acid forms than their low-silica analogs. Calcination of am-

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(19) P. B. Weisz and J. N. Miale, *J. Catal.*, **4**, 527 (1965).

(20) P. B. Weisz, V. J. Frilette, R. W. Maatman, and E. B. Mower, *ibid.*, **1**, 307 (1962).

monium zeolite A, in an attempt to prepare the hydrogen form, causes a complete collapse of the crystal structure. As shown above, the structure of high-silica acid ZK-22 is thermally stable. Table XV contains α values of hydrogen zeolite ZK-22. It is evident that the activity increases with the silica content and with decreasing sodium content. After severe steam treatment, the material was still 200 times as active as fresh silica–alumina compared with 20 for steamed Ce, La, H faujasite.[18] The highest activity sample gave only 0.1% conversion of methylpentane, thus proving shape-selectivity of the zeolite.

TABLE XV

CRACKING ACTIVITY OF HYDROGEN ZEOLITE ZK-22

Expt	SiO_2/ Al_2O_3	Residual Na, wt %	α	*n*-Hexane sorption, g/100 g of zeolite
19	3.94	0.21	160	Nd
24	5.66	0.39	850	11.9
32	5.70	0.14	55,000	13.5
	After steaming		200	. . .

Table XVI shows the activities of lanthanum hydrogen forms of zeolites ZK-21 and ZK-22. Again the most siliceous sample with the lowest percentage of residual sodium shows the highest activity.

TABLE XVI

CRACKING ACTIVITY OF LANTHANUM HYDROGEN ZEOLITE ZK-22

Expt	SiO_2/ Al_2O_3	Residual Na, wt %	Equiv of La^{3+}/Al	α	*n*-Hexane sorption, g/100 g of zeolite
19	3.94	1.1	0.71	46	11.6
21	4.06	0.79	0.87	26	14.5
32	5.70	0.18	0.47	4100	12.6

Acknowledgment—The assistance of Mr. A. E. Schweizer in the experimental work and of Mr. J. N. Miale, who measured the α activities, is gratefully acknowledged.

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Phosphonitrilic Compounds. XI.[1] Electroreduction and Electron Spin Resonance Spectra of Phosphazenes[2]

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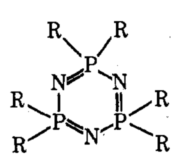
Electrolytic reduction of several organocyclophosphazenes in nonaqueous media has generated phosphazene radical anions, and electron spin resonance spectra of these species have been observed. The data suggest that the organic ligands are the primary reduction sites.

Introduction

The reduction of organic aromatic compounds to radical anions has been widely investigated, and the reduction potentials and electron spin resonance spectra of the products have provided valuable structural information. Considerably less information is available about inorganic "pseudoaromatic" systems. Reduction potentials have been reported for borazines,[3] and radical anions have been obtained from tetrasulfur tetranitride,[4] but no prior electrolytic reduction studies have been described for cyclo- and polyphosphazenes (phosphonitriles).

We have undertaken an electrolytic reduction and electron spin resonance examination of a number of phosphazene derivatives. The compounds studied included cyclic trimers of general structure I where R is C_6H_5, OC_6H_5, *p*-$OC_6H_4NO_2$, OCH_2CF_3, OCH_3, NHC_6H_5, F, Cl, and Br, cyclic tetramers of structure II where R is C_6H_5, OC_6H_5, and OCH_2CF_3, spirocyclic trimers of structure III where O_2R is 2,3-$O_2C_{10}H_6$ (dioxynaphthyl), 1,8-$O_2C_{10}H_6$ (dioxynaphthyl), 1,2-$O_2C_6H_4$ (*o*-dioxyphenyl, and 2,2′-$O_2C_{12}H_8$ (dioxybiphenyl), and linear high polymers of structure IV where R is OC_6H_5 and OCH_2CF_3. The mixed-substituent cyclic trimers, V and VI, were also examined.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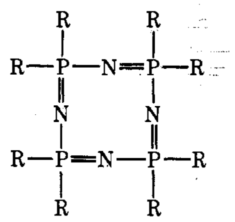
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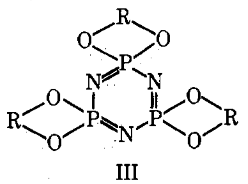
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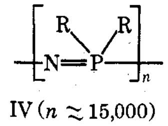
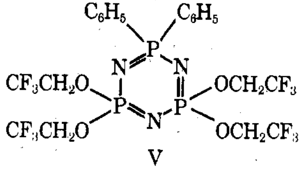

IV ($n \approx 15{,}000$)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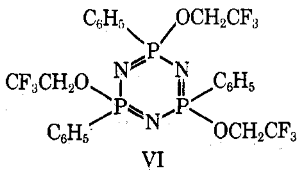
VI

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(1) Part X: H. R. Allcock and E. J. Walsh, *Inorg. Chem.*, **10**, 1643 (1971).

(2) A preliminary report on this work has appeared: H. R. Allcock and W. J. Birdsall, *J. Amer. Chem. Soc.*, **91**, 7541 (1969).

(3) D. F. Shriver, D. E. Smith, and P. Smith, *ibid.*, **86**, 5153 (1964).

(4) D. Chapman and A. G. Massey, *Trans. Faraday Soc.*, **58**, 1291 (1962).