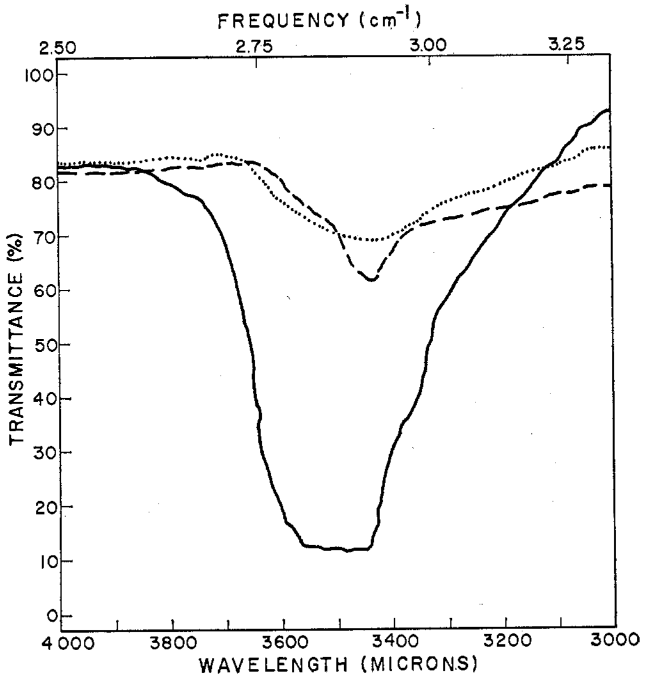

Fig. 2.—The infrared absorption spectra of (a) β-Be(OH)$_2$ (solid line), (b) BeO with enlarged unit cell (dashed line), and (c) well-crystallized BeO formed by dehydration of β-Be(OH)$_2$ during a hydrothermal experiment (dotted line). The presence of the O–H stretching band at 3500 cm.$^{-1}$ suggests that the enlargement of the unit cell in (b) is due to residual water in the crystal lattice.

Samples dehydrated within ±10° of the univariant curve invariably were mixtures of the hydroxide and oxide.

While the conversion of hydroxide to oxide was carried out reproducibly, hydration of the oxide was not realized in these experiments. In other words, BeO is capable of persisting as a metastable phase below its reaction temperature for reasons not well understood at the present time. This difficulty in obtaining equilibrium is not unique to this system and seems to be quite common in oxide–water systems.[13-18] Consequently, the univariant curve as drawn probably does not represent the boundary along which hydroxide, oxide, and water coexist in equilibrium. Therefore, no attempt was made to calculate thermodynamic values, such as heats of reaction, from these data.

Conclusions

It is concluded that the stability region of the BeO phase is well within the capabilities of currently available pressure equipment. Differences in particle size, surface area, and impurity content among starting materials have little effect on the phase relationships in this system. These results confirm the feasibility of growing BeO by hydrothermal techniques; a task recently accomplished for the first time in our laboratory.

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Potassium Dihydrogen Peroxophosphate: Preparation and Characterization[1a]

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Peroxophosphoric acid, H_3PO_5, is the phosphorus analog of the better known peroxosulfuric (Caro's) acid, H_2SO_5. Peroxophosphoric acid was prepared for the first time in 1910 by Schmidlin and Massini[2] by carefully bringing into contact concentrated H_2O_2 (usually 30%) with P_2O_5. The direct addition of concentrated H_2O_2 to P_2O_5 results in an extremely exothermic reaction, and some decomposition of the product was impossible to avoid. Schmidlin and Massini found that the H_3PO_5 prepared was quite unstable; only dilute aqueous solutions of H_3PO_5 could be preserved for any length of time. They attempted to prepare salts: in acid solutions no precipitates were obtained upon addition of silver, iron, nickel, manganese, and other heavy metal salts; in neutral solutions, precipitates were obtained which rapidly evolved oxygen and decomposed into phosphates.

In 1937 Toennies[3] tried to moderate the reaction between concentrated H_2O_2 and P_2O_5 by using acetonitrile as an "inert diluent." He claimed to have prepared solutions containing 56–57% of peracid and 19–20% H_2O_2 which were "relatively stable"—after 3 days at −11° ∽51% peracid was present. No preparation of the salts was attempted. We repeated Toennies' preparation and obtained very low yields of H_3PO_5; apparently acetonitrile is hydrolyzed to acetic acid by H_3PO_5.

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[2] J. Schmidlin and P. Massini, *Ber.*, **43**, 1162 (1910).
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In another chemical preparation of H_3PO_5, Fichter and Bladergroen[4] bubbled elemental F_2 through H_3PO_4 solutions. The reactions that were believed to be taking place are

$$2H_3PO_4 + F_2 \longrightarrow H_4P_2O_8 + 2HF$$

$$H_4P_2O_8 + H_2O \longrightarrow H_3PO_5 + H_3PO_4$$

Again, only dilute solutions of H_3PO_5 were obtained. Fichter and Müller[5] prepared solutions containing the peroxophosphate anion by the anodic oxidation of phosphate solutions. The solutions also contained potassium chromate and potassium fluoride and thus were of limited synthetic use. Further electrolytic work by Fichter and Rius y Miro[6] resulted in the stable solid $K_4P_2O_8$; however, the H_3PO_5 salts could be obtained only in solutions, probably as K_2HPO_5; these solutions were quite unstable. In fact, Fichter and Rius y Miro state "it appears hopeless to obtain solid salts of H_3PO_5." They found that solutions containing the peroxophosphate anion are much more stable in acid media. Husain and Partington[7] studied the action of H_2O_2 on phosphates and the electrolytic oxidation of phosphates. Again, they obtained dilute solutions of peroxophosphates containing also peroxodiphosphates. They found rubidium and cesium peroxophosphate solutions to be quite unstable.

Recently Edwards and co-workers[8] studied the kinetics of oxidation of halide ions by monosubstituted peroxides. In this work, H_3PO_5 solutions were made by acid hydrolysis of $Li_4P_2O_8 \cdot 4H_2O$.

Our work[9] was initiated with the idea of obtaining a stable, preferably pure, source of the peroxophosphate anion. It was decided to use the direct chemical method for the preparation of H_3PO_5, that is, the reaction $P_2O_5 + 2H_2O_2 + H_2O \rightarrow 2H_3PO_5$. It was obvious that some manner must be found to moderate the extremely vigorous reaction between P_2O_5 and H_2O_2. The possibility of finding a solvent in which both P_2O_5 and H_2O_2 would be soluble without undergoing a reaction was explored without success. It was, therefore, decided to moderate the P_2O_5–H_2O_2 reaction by using an inert diluent. The best substances found for this purpose have been the higher boiling fluorocarbons, such as Freon-113 fluorocarbon (1,1,2-trichloro-1,2,2-trifluoroethane). In a typical preparation, powdery P_2O_5 is suspended in Freon-113, previously purified by shaking with concentrated H_2SO_4 and distillation. The suspension is cooled to −10–0° and sufficient 90% H_2O_2 is added with vigorous stirring to provide 1 mole of H_2O per 1 mole of P_2O_5; this results in an excess of H_2O_2. The addition of H_2O_2 is the critical step; if H_2O_2 is added too rapidly, reaction is too violent; if it is added too slowly, P_2O_5 may form a ball. This may allow the buildup of H_2O_2 while unreacted P_2O_5 is still present inside the ball. Then, when the P_2O_5 is cut by the stirrer, a violent reaction takes place, and in the process some of the product is decomposed. The reaction is not complete immediately after the H_2O_2 addition and further stirring or simply storage in the refrigerator overnight is needed. The resulting H_3PO_5–H_2O_2 (15–85%) layer is very unstable due to the reaction between H_3PO_5 and H_2O_2.

$$H_3PO_5 + H_2O_2 \dashrightarrow H_3PO_4 + H_2O + O_2$$

It is believed that with water and H_3PO_4 the equilibrium reactions

$$H_3PO_5 + H_2O \rightleftarrows H_3PO_4 + H_2O_2$$

$$H_3PO_5 + H_3PO_4 \rightleftarrows H_4P_2O_7 + H_2O$$

take place. Rather than try to prepare H_3PO_5 free of H_2O_2, H_2O, and H_3PO_4, it was decided to prepare a peroxophosphate in the hope that it would be stable. The H_3PO_5–H_2O_2 layer was neutralized with 50% KOH at low temperatures and with vigorous stirring. The water and some of the H_2O_2 were removed by freeze-drying. The sticky solid produced contained H_2O_2 and was unstable. It is possible, however, to eliminate H_2O_2 by recrystallization from water–ethanol solutions. In this manner 96–98% KH_2PO_5 is produced containing no H_2O_2. This crystalline material is stable, although hygroscopic.

Potassium dihydrogen peroxophosphate has been characterized by elemental analysis (Table I) and by active oxygen analysis. The total active oxygen content is determined from the iodine formed in an acidic iodide medium by a given weight of the sample; the iodine is titrated with a standard thiosulfate solution. The active oxygen due to hydrogen peroxide is determined by permanganate titration; the titration must be performed rapidly to avoid the oxidation of Mn(II) formed by the peroxo acid. The active oxygen due to H_3PO_5 is the difference between the total active oxygen and that due to H_2O_2.

Table I

Elemental Analysis of KH_2PO_5

	% K	% P	% H
KH_2PO_5 (theor.)	25.71	20.37	1.33
KH_2PO_4 (theor.)	28.73	22.76	1.48
98.0% KH_2PO_5	25.38	20.5	
94.8% KH_2PO_5[a]	25.69	20.59	1.48

[a] Analysis performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Potassium dihydrogen peroxophosphate is a white, crystalline material. J. H. B. has run a single crystal X-ray diffraction study and has found that the KH_2PO_5 crystals are orthorhombic with $a = 4.67$, $b = 5.49$, $c = 8.43$ Å., each within ±0.02 Å. From systematic absences the probable space group was deduced to be $P222_1$. The assumption that there are two formula weights of KH_2PO_5 per unit cell yields a reasonable calculated density of 2.34 g./cm.^{3} (the density has not been measured). The powder pattern of KH_2PO_5 is shown in Table II. It is apparent that the sample contains a small amount of KH_2PO_4 and an unidenti-

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TABLE II

X-RAY POWDER PATTERN OF KH_2PO_5[a]

d (obsd.)	I/I_0	d (calcd.)	hkl
14.8[b]	5		
13.4[b]	4		
10.3[b]	1		
8.7[b]	3		
7.5[b]	2		
6.97[b]	1		
5.45	12	5.49	010
4.67	6	4.67	100
4.59	6	4.56	011
4.21	12	4.22	002
3.92[b]	4		
3.73[c]	8		
3.62[b]	23		
3.55	100	3.56	110
3.34	31	3.33	012
3.29	50	3.28	111
3.16	34	3.13	102
3.02[c]	2		
2.91[c]	7		
2.831[b]	18		
2.748	8	2.745	020
2.729	20	2.718	112
2.647[b]	14		
2.591	15	2.608	021
2.500	8	2.500	013
2.449[b]	4		
2.358	6	2.366 2.337	120 200
2.287	9	2.299 2.277	022 121
2.254	5	2.252	201
2.206	6	2.205	113
2.166	8	2.150	210
2.068	10	2.083	211

[a] Obtained with a Norelco spectrometer and Cu Kα radiation. [b] Unidentified impurity. [c] KH_2PO_4.

fied impurity, believed to be a hydrate of KH_2PO_5 or possibly a potassium peroxodiphosphate. It was possible to distinguish the lines from KH_2PO_5 by indexing them on the basis of the above unit cell.

The infrared spectra of KH_2PO_5 and a related compound, $KHSO_5 \cdot H_2O$, are given in Table III; the tentative assignments of the observed frequencies are included. Comparison of the infrared spectra of KH_2PO_5 with those of $KHSO_5 \cdot H_2O$ provides definite evidence that (1) the band at 2940 cm.$^{-1}$ is due to -OO-H stretching; the shift from 3320 cm.$^{-1}$ in solid hydrogen peroxide[10] is probably due to intramolecular hydrogen bonding to the -P-O group, as can be shown by Stuart-Briegleb atomic models; (2) the band at 770 cm.$^{-1}$ is due to -O-O stretching; this frequency occurs in solid hydrogen peroxide at 878 cm.$^{-1}$.[10]

TABLE III

INFRARED SPECTRA

Frequency, cm.$^{-1}$	Tentative assignment
	KH_2PO_5[a]
2940 m[c]	-OO—H stretching (intramolecular hydrogen bonding to -P=O)
2700 s	-PO—H stretching
1700 m (br)	Combination or overtone band
1450 s (sp)	-OO—H bending
1300 m	-POH deformation mode
1200 m 1100 s 920 s 860 m	-P=O or -P—OH stretching
770 s	-O—O- stretching
	$KHSO_5 \cdot H_2O$[b]
3380 s	-O—H stretching in H_2O
3000 m	-OO—H stretching (intramolecular hydrogen bonding to -S=O)
1615 w	Combination band
1290 w 1090 m	-S=O stretching
725 s	-O—O- stretching

[a] Obtained with a Perkin-Elmer Model 237 spectrophotometer using Irtran-2 windows; Kel-F No. 90 (1450–2940 cm.$^{-1}$ bands) and Apiezon M (770–1300 cm.$^{-1}$ bands) greases were used. [b] Obtained with a Perkin-Elmer Model 112 spectrophotometer using sodium chloride optics; a Nujol mull was used. [c] s, strong; m, medium; w, weak; br, broad; sp, sharp.

So far, chemical properties of the peroxophosphates have not been studied extensively. The discoverers of H_3PO_5, Schmidlin and Massini,[2] reported that H_3PO_5 oxidizes Mn(II) to MnO_4^-, a property that is not shown by H_2SO_5, and, therefore, recommended H_3PO_5 as a reagent for manganese (the solution must, of course, be free of hydrogen peroxide). Fichter and Bladergroen[4] claimed that instead of MnO_4^-, $MnPO_4$ is formed ($MnPO_4$ is also purple), since they could not obtain the absorption spectrum of MnO_4^-. Using spot tests and absorption spectra for identification, we have found that in neutral solution Mn(II) is oxidized to MnO_2 by KH_2PO_5; in 0.1 *N* H_2SO_4 the permanganate ion is formed. Potassium dihydrogen peroxophosphate oxidizes Cl^- to Cl_2; again this oxidation takes place more readily in 0.1 *N* H_2SO_4. No reaction was apparent with $Cr(NO_3)_3$. Further studies of the chemical properties of peroxophosphates will be conducted.

Acknowledgments.—We wish to thank Dr. J. L. Margrave for a sample of $KHSO_5 \cdot H_2O$. A helpful discussion with Dr. W. H. Fletcher is acknowledged.

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The Preparation of Difluoroaminotrifluoromethoxytetrafluorosulfur(VI), $CF_3OSF_4NF_2$

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Trifluoromethyl hypofluorite reacts with sulfur tetrafluoride to form CF_3OSF_5[1,2] and $(CF_3O)_2SF_4$.[2] If oxygen[1] is present the compounds $CF_3OSF_4OSF_5$, $CF_3OSF_4OOSF_5$, and $CF_3OSF_4OOSF_4OCF_3$ are also

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