Whatever is the explanation, it seems that this is the first observed case of an association (other than coagulation of electrically charged colloidal particles) that requires an activation energy.

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GLUCOSE, A CONSTITUENT OF ALKALINE PHOSPHATASE[1]

Sir:

Alkaline phosphatase of swine kidney, found in the ribonucleoprotein particles of the microsomes[2] and released as an active fragment by proteolysis,[2,3] has been isolated in an apparently homogeneous condition by application of the procedures previously described[3] plus ion-exchange chromatography with Ecteola cellulose.[4] In a typical purification 2,000,000 units activity[2] with a specific activity of over 100,000 units per mg. total N (micro-Kjeldahl) was placed on a column of Ecteola 5 × 100 cm. and, after thorough washing with water, was eluted with a gradient of barium acetate at *p*H 9 varying from 0.01 to 0.05 *M* in 10 liters of solution. The active material was eluted symmetrically near 0.03 *M* and was concentrated by the barium procedure[3] to yield about 1,500,000 units material with a specific activity of 295,000 to 310,000 on the basis of total N. Rechromatography on Ecteola-cellulose, on Deae-cellulose[4] or on Dowex-2[3], paper electrophoresis and paper chromatography (ethanol–1 *M* ammonium acetate, 70–30) revealed no dissociation of absorbancy at 280 mμ from activity. The material was free of peptidase and diesterase activity when tested undiluted, amino acids were without effect on the activity and at no time was it possible to demonstrate dialyzable cofactors other than magnesium ion. The absorbancy in the ultraviolet was characteristic of protein with a maximum at 278 and a minimum at 250 mμ. However, in the course of treatment with dilute acid (0.1 to 1.0 *M* at 100°) the absorbancy was found to increase remarkably and, at the end of 2 hr., the absorbancy at 278 was nearly tripled. There was a parallel release of reducing material,[5] of ninhydrin reactive material,[6] and of material reacting with phosphomolybdate.[7] Paper chromatography (propanol–water, 80–20) separated a phosphomolybdate and ninhydrin reactive material from a ninhydrin negative but aniline hydrogen phthalate positive[8] (brown color) material with the same R_f as glucose. The untreated material in the cysteine methods of Dische[9] gave in the general reaction a product identical with the aldohexoses and in the secondary reaction of hexoses gave a product identical with glucose. A solution of alkaline phosphatase containing 30 μg. N per ml. after 2 hr. at 100° with 1 *N* HCl was found to contain 38 μg. glucose as determined by the reducing sugar method as determined by the cysteine reaction on the untreated material. The hydrolysate was found to contain approximately 25 μg. glucose as determined with glucose oxidase.[10]

The ninhydrin–phosphomolybdate positive material was found to migrate as a cation at *p*H 8 and to be unstable in more alkaline solutions. Other reactions of the compound were an immediate reaction with K_3FeCN_6 and $FeCl_3$ (blue) and an immediate reaction with K_3FeCN_6 alone (blue). Both these reactions were destroyed by previous treatment with traces of cupric ion with exposure to air. In a study of model compounds, phenolic compounds appear to have been eliminated but similar reactions have been observed with tri- and tetra-substituted pyrimidines; from the absorbancy in the ultraviolet, from studies of the model pyrimidines and from analogy with the proposed structure for vicine,[11] it is suspected that the material may be a diamino-5-hydroxypyrimidine attached, in the active material, to the glucose by a glycosidic linkage at the 5-hydroxy position.

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[1] These studies were supported by grants from the U. S. Public Health Service. Detailed studies of the purification, the effects of amino acids and of divalent metal ions will be described by C. Lea.

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THE PHOSPHINOUS ACID $(CF_3)_2POH$ AND THE DIPHOSPHOXANE $(CF_3)_2POP(CF_3)_2$[1]

Sir:

We have recently isolated the new-type compounds $(CF_3)_2POH$ and $(CF_3)_2POP(CF_3)_2$ as stable liquids contrasting with the apparently complete instability of the corresponding hydrocarbon derivatives.[2] Evidently the highly electronegative CF_3 groups lower the power of phosphorus lone-pair electrons to bond either H^+ or $(CF_3)_2P^+$ coming from O. Thus these new $(CF_3)_2P$ compounds do not undergo the rearrangements $R_2POH \rightarrow R_2\overset{H}{P}OH$ and $R_2POPR_2 \rightarrow R_2P\text{-}\overset{O}{P}R_2$ which probably represent the first stages of decomposition when R is a hydrocarbon group.

Synthesis and Characterization of the Diphosphoxane.—The reaction $2(CF_3)_2PI + Ag_2CO_3 \rightarrow CO_2 + 2AgI + (CF_3)_2POP(CF_3)_2$ (room temperature, repeated shaking with fresh silver carbonate) gave yields above 79%. The unused $(CF_3)_2PI$ (1%) was converted by AgCl to the easily

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[2] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 144. We also have found that reactions expected to form $(CH_3)_2POH$ give nearly quantitative yields of $(CH_3)_2PH$ and $(CH_3)_2POOH$; and attempts to make $(CH_3)_2POP(CH_3)_2$ also give products suggesting disproportionation.

removable $(CF_3)_2PCl$. The pure diphosphoxane melted at −53.1 to −52.6°. Its vapor tensions (*e.g.*, 24.4 mm. at 0° and 89.5 mm. at 24.2°) conformed, with an average deviation of 0.25%, to the equation $\log p_{\text{mm}} = 6.1276 - 0.005092\,T + 1.75 \log T - 2078.8/T$; b.p. 78.3° and Trouton constant 22.0 cal./deg. mole. Thus it is slightly more volatile than $P_2(CF_3)_4$ (22.0 mm. at 0°, obsd. by W. Mahler) just as Si_2H_6 and $(SiH_3)_2O$ are almost equally volatile.[3]

The formula $(CF_3)_2POP(CF_3)_2$ was proved by the vapor-phase molecular weight (354.2 *vs.* calcd. 354.0) and the basic hydrolysis of a 42.0 mg. sample to give 32.7 mg. of HCF_3, corresponding to 3.94 CF_3 per molecule. The infrared spectrum showed very strong bands at 1230, 1185, and 1145 cm.$^{-1}$ (C–F stretching), and medium bands at 755 and 715 (C–F bending) and at 885 (unidentified). Two P–O–P stretching frequencies (950 strong and 925 very strong), taken with the strict absence of any P=O bands,[4] verify the P–O–P structure. The ultraviolet spectrum showed a single maximum at 2110 Å. (molar ext. coeff. ϵ = 3580; minimum at 1965 Å., ϵ = 650), qualitatively explained by a set of P_{3d}–O_{2p}–P_{3d} molecular orbitals for the oxygen lone-pair electrons. Such delocalization would partly explain the failure of the oxygen to bond Lewis acids.

Chemistry of the Diphosphoxane.—The compound $(CF_3)_2POP(CF_3)_2$ remained stable at 150° (sealed tube, 66 hr.) but at 250° it was 25% decomposed during 60 hr. and another sample was nearly all gone after 14 days, giving 0.5 CO, 0.7 PF_3, 0.87 $(CF_3)_2PF$ and 0.3 $(CF_3)_3P$ per mole. It was inert toward the Lewis acids BF_3 and SO_2; indeed it is itself a Lewis acid, easily forming the adduct $(CF_3)_2POP(CF_3)_2\cdot(CH_3)_3N$ (0.04 mm. dissociation pressure at −78°; $\log p_{\text{mm}} = 8.752 - 1979/T$ up to −20°, above which it loses identity). This electron-acceptor action is actually stronger than in $PF_3\cdot(CH_3)_3N$ (dissoc. at −78.5°, 9.1 mm.; $\log p_{\text{mm}} = 8.11 - 1390/T$ up to −76°) which was observed in these laboratories many years ago. In general, one may expect Lewis-acid action by PX_3 compounds when X is sufficiently electronegative and does not pi-bond too strongly to the P-3d orbitals.

No evidence of rearrangement to a phosphine oxide could be seen in the reactions of $(CF_3)_2POP(CF_3)_2$ with $(CH_3)_3N$ and HCl, or in its thermal decomposition.

Synthesis and Properties of the Phosphinous Acid.—The compound $(CF_3)_2POH$ was made in 92% yield by the reaction $(CF_3)_2POP(CF_3)_2 + HCl \rightarrow (CF_3)_2PCl + (CF_3)_2POH$ (86 hr., 100°). The vapor-tension equation for the solid was $\log p_{\text{mm}} = 10.7217 - 2426.1/T$; for the liquid, $\log p_{\text{mm}} = 9.6968 - 0.01099T + 1.75 \log T - 2528.3/T$ up to 15.3° (av. deviation, 0.17%; example, 50.6 mm. at 0°). Hence b.p. = 61.4°; Trouton constant = 21.4 cal./deg. mole; enthalpy of fusion = 1910 cal./mole; predicted m.p. = −20.8° (obsd., −21.3 to −21.1°). The molecular weight determination was made difficult by absorption into vacuum greases and waxes, but the value 184.8 (calcd., 186.0) seemed dependable.

The presumed $(CF_3)_2POH$ structure was supported by the infrared spectrum, recorded by a Perkin–Elmer Model 13 instrument using NaCl and KBr prisms. The O–H stretching frequency at 3620 cm.$^{-1}$ was very strong. The $(CF_3)_2PHO$ form was eliminated by the absence of P=O stretching, which would be expected near 1285 by comparison with 1328 for $(CF_3)_3PO$ and 1415 for POF_3.[5] In the region characteristic of P–H stretching (near 2300) there was no band not directly attributable to an overtone.

We could not convert $(CF_3)_2POH$ to the phosphine-oxide form $(CF_3)_2PHO$ by contact with phosphoric anhydride. The acidity of $(CF_3)_2POH$ was tested by forming the salt $(CH_3)_3NH^+(CF_3)_2PO^-$, which proved too stable and non-volatile at room temperature, but from which 81% of the original $(CF_3)_2POH$ was recovered by treatment with hydrogen chloride.

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DECOMPOSITION OF *n*- AND *sec*-BUTYL PEROXYACETATE[1]

Sir:

The uncatalyzed thermal decomposition of *n*- and *sec*-butyl peroxyacetates differs markedly from that of the *tert*-butyl isomer both in rate and products as shown in Table I.

TABLE I

DECOMPOSITION RATES AND PRODUCTS FROM ISOMERIC BUTYL PEROXYACETATES: CH_3COOOR at 64.6°

R =	Half life^a (min. × 10^{-3})	Major products^f
n-C_4H_9 (I)	3.1^b 3.2^c	Butyraldehyde,^{h} acetic acid,^{h} butanol, methyl *n*-butyl ether, butyl acetate, butyl formate, CO_2,^{c} CH_4^{c}
sec-C_4H_9 (II)	0.9^b	Methyl ethyl ketone,^{g} acetic acid^g
t-C_4H_9 (III)	$280^{d,e}$	Carbon dioxide (77), acetone (73), methane (47), HAc (23)

^{a} The rates for I and II, as well as that for III reported in ref. 2, were measured from the decrease of the 5.63 μ infrared absorption band for peroxyesters. ^{b} α-Methylstyrene solvent. ^{c} Bromobenzene solvent. ^{d} Chlorobenzene solvent. ^{e} This value is extrapolated from the data in ref. 2. ^{f} The products from I and II were determined by gas–liquid partition chromatography and infrared spectroscopy. The numbers in parentheses represent yields expressed as moles per 100 moles of starting peroxide. ^{g} The absolute yield was not obtained but the products were formed in the ratio of ketone to acid of two to one. A residue of 34 mg./g. perester remained upon distillation of the decomposition mixture. ^{h} Major products by gas-liquid chromatography.

Whether *t*-butyl peroxyacetate decomposed by a linear concerted mechanism[2] or by a simple homolytic cleavage of the O–O bond,[3] it is difficult to explain the 310-fold greater rate for the isomeric

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