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 $\log p_{mm} = 6.1276 - 0.005092\,T + 1.75 \log T - 2078.8/T$; 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. $\epsilon = 3580$; minimum at 1965 Å., $\epsilon = 650$), 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°; $\log p_{mm} = 8.752 - 1979/T$ 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.; $\log p_{mm} = 8.11 - 1390/T$ 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 $\log p_{mm} = 10.7217 - 2426.1/T$; for the liquid, $\log p_{mm} = 9.6968 - 0.01099T + 1.75 \log T - 2528.3/T$ 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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[3] A. Stock and C. Somieski, *Ber.*, **50B**, 1757 (1917).

[4] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd Edition, John Wiley and Sons, Inc., New York, N. Y., 1958, p. 318.

[5] J. J. Lagowski, *Quart. Revs.*, **13**, 233 (1959).

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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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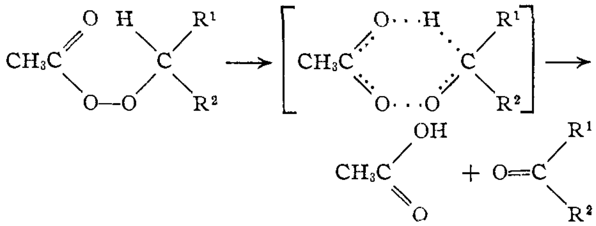
[1] This investigation has been supported in part by National Science Foundation Grant No. 4136 which we gratefully acknowledge.

[2] P. D. Bartlett and R. R. Hiatt, THIS JOURNAL, **80**, 1398 (1958).

sec-butyl peroxyacetate (II) without proposing an entirely different mechanism. Neither steric considerations nor differences in stabilities of *sec*-butoxy *versus* *t*-butoxy radicals developing during the transition state could account for the observed differences. Furthermore, there is no reason to suspect an ionic mechanism.[4]

The formation of *n*-butyl *n*-butyrate, methyl *n*-butyl ether, carbon dioxide and methane as minor products in the decomposition of I indicates that radical reactions are involved. These products are greatly reduced, although not eliminated, when α-methylstyrene is used as a solvent and radical trap, while the amount of *n*-butyraldehyde and acetic acid are not greatly affected. This suggests that the latter are of non-radical origin.

The case of *sec*-butyl peroxyacetate (II) is decisive, the only two major products being acetic acid and methyl ethyl ketone whether the decomposition is of the neat liquid or in α-methylstyrene. The high yield of acetic acid could not arise from acetoxy radicals which are known to decarboxylate almost as rapidly as formed[3] in a variety of solvents including α-methylstyrene.[5] Thus the nature of the products, relative rates, and the effect of inhibitor clearly indicate that the mechanism for the decomposition of *n*- and *sec*-butyl peroxyacetates differs from that of the *tertiary* isomer. We interpret this as indicating a *cyclic concerted process* formally resembling that of the pyrolysis of esters.[6] This type of mechanism has been observed previously in the thermal decomposition of peroxyhemiacetals giving molecular hydrogen.[7]



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[3] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 491–493.

[4] P. D. Bartlett and B. T. Storey, THIS JOURNAL, **80**, 4954 (1958).

[5] M. Levy and M. Szwarc, *ibid.*, **76**, 5981 (1954).

[6] E. R. Alexander and A. Mudrak, *ibid.*, **72**, 1811 (1950).

[7] L. J. Durham, C. F. Wurster and H. S. Mosher, *ibid.*, **80**, 332 (1958).

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CYANOGEN FLUORIDE

Sir:

Cyanogen fluoride, FCN, has been the subject of a number of investigations in other laboratories,[1] but apparently the authentic compound has not been isolated. We have prepared relatively large quantities of FCN and have isolated and characterized this compound.

A number of routes to FCN have been employed successfully. The currently preferred synthesis is the pyrolysis of cyanuric fluoride[2] in a stream of nitrogen at 1300° and *ca.* 50 mm. pressure to give cyanogen fluoride in greater than 50% yield. Of several methods of pyrolysis tried, the most suitable for preparative work employed an induction-heated carbon tube 0.75 in. in inside diameter packed with 4–8 mesh carbon granules. In this equipment, cyanuric fluoride was pyrolyzed at the rate of 50 g./hr. to yield crude cyanogen fluoride. Distillation of this product in a glass column at atmospheric pressure gave pure cyanogen fluoride, b.p. −44°.

Elemental analysis showed 42.32, 42.39% fluorine (calcd., 42.21%). Gas density determination gave a molecular weight of 45.1 (calcd., 45.02). The tabulated mass spectrum was obtained on a Consolidated Electrodynamics Corp. Model 21-103-C Spectrometer and is consistent with the structure FCN.

FRAGMENTATION PATTERN OF FCN

m/e	Ion	Pattern, %
12	C^+	11.5
14	N^+	4.1
19	F^+	1.1
26	CN^+	17.7
31	CF^+	15.3
45	FCN^+	100.0

The nuclear magnetic resonance pattern measured at 40 mc. showed a triplet peak that centered at +3180 cps. to high field of CF_3COOH with 32–34 cps. splitting between adjacent peaks. The splitting, attributed to the N^{14} nucleus, collapsed to a singlet peak on cooling to near the freezing point. This temperature dependence of the F^{19} multiplet structure of FCN is similar to that observed for NF_3[3] and is attributed to the temperature dependence of the quadrupole-dominated relaxation time of the N^{14} nucleus.[4]

The infrared absorption spectrum[5] of gaseous FCN showed three prominent bands indicative of the structure FCN: two doublet bands centered at 2290 cm.$^{-1}$ and at 1078 cm.$^{-1}$, the latter with 24 cm.$^{-1}$ separation between the two branches, and a triplet band centered at 451 cm.$^{-1}$. The positions of these bands correspond satisfactorily with those calculated by Thomas[6] and by Luft[7] and also with those recently observed by Aynsley, Dodd and Little,[1d] which were interpreted to indicate the probable presence of FCN in a mixture obtained by fluorination of cyanogen.

Cyanogen fluoride has been stored without appreciable change for over one year in stainless steel cylinders kept at solid carbon dioxide temperature. At room temperature in the condensed phase it is

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[1] (a) V. E. Cosslett, *Z. anorg. allgem. Chem.*, **201**, 75 (1931); (b) H. J. Callomon, H. W. Thompson, F. A. Andersen and B. Bak, *J. Chem. Soc.*, 3709 (1953); (c) A. A. Woolf, *J. Chem. Soc.*, 252 (1954); (d) E. E. Aynsley, R. E. Dodd and R. Little, *Proc. Chem. Soc.*, 265 (1959).

[2] (a) A. F. Maxwell, J. S. Fry and L. A. Bigelow, THIS JOURNAL, **80**, 548 (1958); (b) D. W. Greisley, Jr., E. W. Gluesenkamp and S. A. Heininger, *J. Org. Chem.*, **23**, 1802 (1958).

[3] E. L. Muetterties and W. D. Phillips, THIS JOURNAL, **81**, 1084 (1959).

[4] J. A. Pople, *Molecular Physics*, **1**, 168 (1958).

[5] More extensive infrared studies of FCN prepared in the present work are being carried out by Professor R. C. Lord of Massachusetts Institute of Technology.

[6] W. J. O. Thomas, *J. Chem. Phys.*, **20**, 920 (1952).

[7] N. W. Luft, *ibid.*, **21**, 1900 (1953).