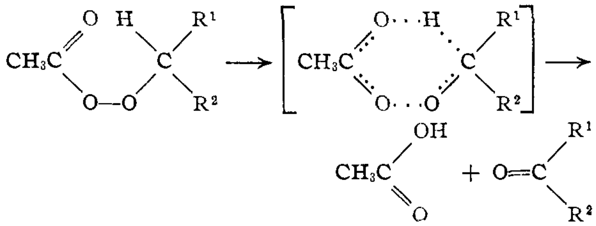
sec-butyl peroxyacetate (II) without proposing an entirely different mechanism. Neither steric considerations nor differences in stabilities of *sec*-butoxy *versus* *t*-butoxy radicals developing during the transition state could account for the observed differences. Furthermore, there is no reason 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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RECEIVED FEBRUARY 8, 1960

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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[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).

converted rapidly to polymeric materials, but in the gas phase it has been recovered partially after several weeks. In certain instances, *e.g.*, in the presence of boron trifluoride or hydrogen fluoride, cyanogen fluoride has undergone violent reaction, and accordingly precautions should be taken in working with this compound.

Cyanogen fluoride, like cyanogen chloride, reacted with benzene in the presence of aluminum chloride to form benzonitrile in 20% conversion.

We are indebted to Drs. W. C. Smith, J. E. Castle, and D. D. Coffman for helpful discussions and suggestions during the course of this investigation. A more detailed account of the syntheses, properties, and chemistry of cyanogen fluoride will be given in forthcoming publications.

CONTRIBUTION NO. 596 FROM
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RECEIVED JANUARY 27, 1960

THE PREPARATION AND PROPERTIES OF ReF$_7$[1]

Sir:

In the course of an attempt to prepare the compound ReF$_6$, certain observations were made which lead us to believe that we have succeeded in preparing the hitherto unknown compound ReF$_7$. In addition we have succeeded in obtaining a considerably purer preparation of ReF$_6$ than those reported previously.[2–4]

Our original preparation, made by the action of fluorine on rhenium metal at 400°, exhibited a vapor pressure of 68 mm. at 0°. This differed from vapor pressures reported in the literature for ReF$_6$. Moreover, it was much lower than the vapor pressure observed for samples of ReF$_6$ that had been prepared previously at this laboratory.

Upon further treatment with fluorine at several atmospheres and 400° the compound absorbed fluorine and became less volatile (vapor pressure 25 mm. at 0°).

Experiments were carried out to determine the nature of this compound and the results are listed below: (1) only fluorine and rhenium are present. (2) Chemical analysis implies an empirical formula of ReF$_{6.9}$ (Given, 1.929 g. compound: Found: 1.106 g. Re, 0.771 g. F; Calculated for ReF$_7$: 1.126 g. Re, 0.804 g. F). (3) Measurement of fluorine absorption by authentic ReF$_6$ at 400° shows that approximately $^1/_2$ mole of fluorine is absorbed per mole of ReF$_6$ to yield ReF$_7$. (4) Reaction of ReF$_7$ with Re metal at 400° results in the formation of ReF$_6$. (5) Vapor density determinations on both compounds give molecular weights of 322.7 for ReF$_7$ and 300.9 for ReF$_6$. (6) The infrared spectrum of ReF$_7$ exhibits markedly different features from the spectrum of ReF$_6$ over the region studied, 600 cm.$^{-1}$ to 2000 cm.$^{-1}$ The two strong combination bands, $\nu_2 + \nu_3$, and $\nu_1 + \nu_3$, which are observed at 1316 cm.$^{-1}$ and 1469 cm.$^{-1}$ in the ReF$_6$ spectrum[4] are absent in the ReF$_7$ spectrum and are replaced by four less intense absorption bands in this region. ReF$_7$ has a very intense absorption band, presumably a fundamental, that coincides with the fundamental, ν_3, observed for ReF$_6$ at 716 cm.$^{-1}$.

The melting points of ReF$_7$ and ReF$_6$ have been determined on gram amounts of these compounds. Preliminary vapor pressure measurements were made on both compounds using a high sensitivity quartz sickle gauge.

ReF$_7$ is a pale yellow solid with a melting point of 48.3°. ReF$_6$ is a yellow solid, melting at 18.6°. Some preliminary vapor pressure measurements for solid ReF$_7$ and for liquid and solid ReF$_6$ are shown in Table I.

TABLE I

VAPOR PRESSURES OF ReF$_6$ AND ReF$_7$

t, °C.	Pressure, mm.	*t*, °C.	Pressure, mm.
Vapor pressure of ReF$_6$		Vapor pressure of ReF$_7$	
Solid		Solid	
0.0	167	0.0	25
9.4	272	10.1	46
14.9	356	15.2	61
Liquid		25.2	106
20.3	454	34.2	165
26.9	590		
30.9	686		

Comparison of the infrared spectra[4] as well as the wide variations in properties reported for ReF$_6$,[2–4] and the ease with which both ReF$_6$ and ReF$_7$ can be prepared lead us to believe that previous workers have been working with mixtures of these two compounds.

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RECEIVED JANUARY 21, 1960

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] O. Ruff, W. Kwasnick and E. Ascher, *Z. anorg. allgem. Chem.*, **209**, 113 (1932).

[3] O. Ruff and W. Kwasnick, *ibid.*, **219**, 65 (1934).

[4] J. Gaunt, *Trans. Faraday Soc.*, **50**, 209 (1954).

A NEW PREPARATION OF TRIPHENYLPHOSPHINEMETHYLENES BY THE REACTION OF CARBENES WITH TRIPHENYLPHOSPHINE[1]

Sir:

Many examples of the reaction of halocarbenes with olefins, which yields halogen-substituted cyclopropanes, have been reported since the first communication on this subject by Doering and Hoffmann.[2] Also, the kinetics of the reaction of halocarbenes with halide ions, hydroxide ion and water have been studied.[3] The electrophilic nature of the carbenes in these reactions has been clearly demonstrated.[3,4] Accepting the description[4] of halocarbenes in terms of carbon in the singlet state in which an electron pair fills one orbital, leaving one orbital unoccupied, one might expect to find reactions of halocarbenes with other nucleophiles besides olefins and halide ions.

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[1] Presented in part at the Fifteenth Southwest Regional Meeting of the American Chemical Society, Baton Rouge, December 4, 1959.

[2] W. v. E. Doering and A. K. Hoffmann, THIS JOURNAL, **76**, 6162 (1954).

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[4] P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956); W. v. E. Doering and W. A. Henderson, *ibid.*, **80**, 5274 (1958).