Co-60 source at 150° (slightly above its melting point). The molecular weight dropped to 6000 to 7000 and the melting range changed from 139–142° to 137–145°.

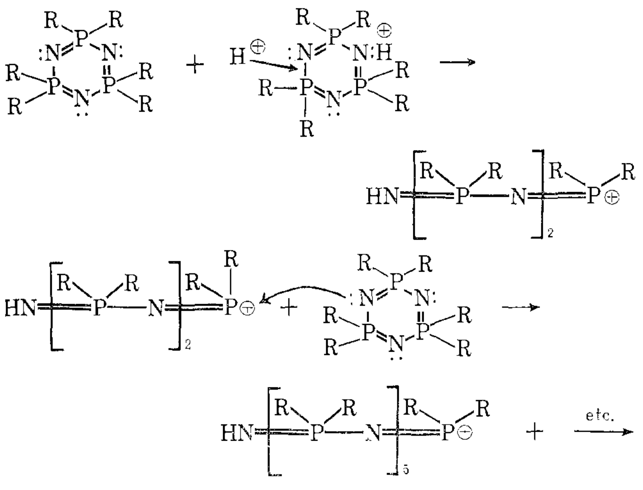
Discussion

The pyrolytic conversion of $[(CH_3)_2P(NH_2)_2]Cl$ to $[(Cl_3)_2PN]_n$ involves the loss of one mole of ammonium chloride per mole of phosphonium salt reacted. It is interesting to note, however, that the yield of high polymer from this reaction seems to depend on the amount of ammonium chloride mixed with the starting material (Table II) under similar conditions of temperature, pressure, and time. The postulated first step of the condensation process

$$2[(CH_3)_2P(NH_2)_2]Cl \longrightarrow [(CH_3)_2P(NH_2)—N{=}P(NH_2)(CH_3)_2]Cl + NH_4Cl$$

has been confirmed in the pyrolysis of diethyldiaminophosphonium chloride.[12] Since the actual mechanism of condensation is not clearly known, any statement concerning the mechanism of the effect of ammonium chloride on the first reaction step or subsequent intermolecular condensations would be highly speculative.

However, in view of the fact that the cyclic dimethylphosphonitriles are weak bases,[13] it is conceivable that in the molten reaction mixture a proton transfer could occur between ammonium chloride and a ring nitrogen. This could result in the breaking of a P—N bond and the formation of a $=\overset{\oplus}{P}<$ species which could attack other ring-nitrogen atoms and lead to linear products. For instance, the attack could occur on a cyclic trimer



This is similar to the mechanism postulated by Allcock and Best[14] for the polymerization of $[PNCl_2]_{3,4}$.

The dimethylphosphonitrile polymers formed are isoelectronic with the dimethylsilicones, $[(CH_3)_2SiO]_n$, and contain very little, if any, cross linking. This probably accounts for the fact that complete depolymerization to cyclic derivatives occurs in the 300–500° range.

The dimethylphosphonitrile polymer was shown by its X-ray pattern and its relatively sharp melting point to have a considerable degree of crystallinity.

Acknowledgments.—We are pleased to acknowledge the generous support of the Florida portion of this work by W. R. Grace and Co. through a contract with the University of Florida. We also wish to thank Mr. Don McElwee of the University of Florida for his help in obtaining some of the molecular weight data.

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[13] D. Feakins, W. A. Last, N. Neemuchwala, and R. A. Shaw, *J. Chem. Soc.*, 2804 (1965).

[14] H. R. Allcock and R. J. Best, *Can. J. Chem.*, **42**, 447 (1964).

CONTRIBUTION FROM THE RESEARCH INSTITUTE OF
TEMPLE UNIVERSITY, PHILADELPHIA, PENNSYLVANIA 19144

Photochemical Formation of Krypton Difluoride from Krypton and Fluorine or Oxygen Difluoride[1]

BY L. V. STRENG AND A. G. STRENG

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It was reported recently that xenon reacts with fluorine at room temperature and ordinary pressure when exposed to sunlight, forming xenon difluoride.[2] Similar results have been obtained now in similar experiments with $Kr–F_2$ and $Kr–OF_2$ mixtures.

Equimolar mixtures of krypton and fluorine or krypton and oxygen difluoride have been exposed to sunlight for 5 weeks in dry 2-l. Pyrex glass flasks at room temperature and at a total pressure of 1 atm. absolute. Under these conditions, a slow reaction proceeds between krypton and fluorine,[3] and, if a tubular extension of the flask (a "finger" 10 in. long and about 1 in. in diameter) is cooled with Dry Ice (see Figure 1), small colorless crystals begin to appear on the cold walls of the tube. The formation of crystals was noticed on the third day of standing. The amount of crystals increased with time. The crystals have been analyzed and were found to be krypton difluoride, KrF_2.

However, when the same flasks with $Kr–F_2$ or $Kr–OF_2$ mixtures were kept in the dark for the same period of time there was no formation of any noticeable traces of krypton fluorides.

For analysis, the product was thermally decomposed by warming it to about 80° and by measuring and analyzing the gas evolved. The fluorine was determined by allowing it to react with dry mercury and the krypton was identified by its melting point and vapor pressure.

A 76-mg. sample of the compound obtained in the $Kr + F_2$ experiment evolved 27.8 cm.^{3} of gas, measured at N.T.P. The gas contained 13.7 cm.^{3} of fluorine and 14.1 cm.^{3} of krypton, *i.e.*, the $Kr:F_2$ ratio was 1.03:1.00 and the empirical formula of the product KrF_2. A 27-mg. sample of the product obtained in the $Kr + OF_2$

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[1] This note describes a part of work performed for the Air Force Rocket Propulsion Laboratory, Edwards, Calif., Contract AF 04(611)-9555, and for the Office of Naval Research, Washington, D. C., Contract Nonr 3085(01).

[2] L. V. Streng and A. G. Streng, *Inorg. Chem.*, **4**, 1370 (1965).

[3] Oxygen difluoride probably decomposes first to oxygen and fluorine under the action of ultraviolet light and the liberated fluorine then reacts with krypton.

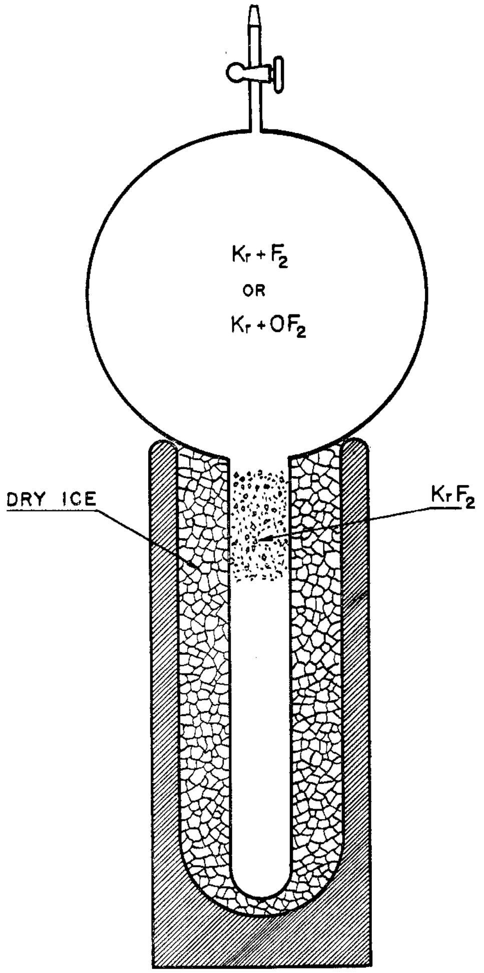

Figure 1.—Reaction flask.

experiment evolved 10.06 cm.^{3} of gas which consisted of equal volumes of krypton and fluorine. Thus, the product was also KrF_2.

Both krypton tetrafluoride and krypton difluoride are known to be unstable at room temperature. Therefore, under the conditions of our experiments only those portions of krypton difluoride formed which got into the cooled extension tube of the flask were entrapped (quenched) and remained undecomposed. The amount of the KrF_2 produced depends, therefore, not only upon the amount of radiation energy absorbed but, to a very large extent, upon the effectiveness of cooling.

In the experiments with $Kr-F_2$ mixtures the total amount of KrF_2 formed in a 2-l. flask during 5 weeks of standing varied from 70 to 100 mg.; *i.e.*, the average rate of production was 2–3 mg. of KrF_2 per day. In the experiments with $Kr-OF_2$ mixtures the rate of formation was about 1 mg. of KrF_2 per day.

The yield of KrF_2 may probably be increased by use of a wider tubular extension of the flask and by lowering the cooling temperature (to the boiling point of krypton, 120°K.).

Acknowledgment is due to Dr. A. V. Grosse for valuable suggestions.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE PENNSYLVANIA STATE UNIVERSITY,
UNIVERSITY PARK, PENNSYLVANIA

Preparation and Properties of The Monoborane Adduct of N,N,N′,N′-Tetramethylethylenediamine

BY A. R. GATTI AND THOMAS WARTIK

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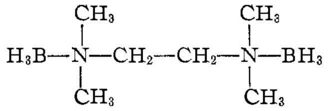
Generally, when a simple monofunctional Lewis acid is treated with a simple difunctional Lewis base, only one of the two possible adducts is observed and, in most cases, regardless of the proportions of reactants, this is the one involving two moles of the acid per mole of difunctional base. Presumably this rather unexpected preference for the diadduct is due to lattice stabilization effects resulting from considerations of symmetry.

In the case of simple boron acids, only a few monoadducts of simple difunctional bases have been reported,$^{1-4}$ and, of these, only one appears to have been isolated in reasonably pure condition. We now wish to report the preparation, isolation, and identification of the monoborane adduct of N,N,N′,N′-tetramethylethylenediamine (hereafter referred to as TMED).

Miller and Muetterties, in 1964, reported the preparation of the bis-borane adduct of TMED,[5] a white solid which our B^{11} n.m.r. studies indicate to be a symmetrical molecule with the structure



$$\begin{array}{ccccccc} & CH_3 & & & & CH_3 & \\ & | & & & & | & \\ H_3B- & N & -CH_2- & CH_2- & & N & -BH_3 \\ & | & & & & | & \\ & CH_3 & & & & CH_3 & \end{array}$$

We found that $TMED{\cdot}2BH_3$, although virtually insoluble in TMED at room temperature, was quite soluble in this liquid at 60°. (The resulting solution showed a strong tendency to supersaturate on cooling, and 3 days at room temperature passed before precipitation of $TMED{\cdot}2BH_3$ commenced.) When a portion of the supersaturated solution was cooled to $-23°$ and subjected to pumping, a white crystalline solid remained which, on being warmed slowly, melted to a clear, colorless liquid at $-3°$ to $-1°$. The clear melt almost immediately became turbid and, after 1 hr., the sample had decomposed to a new white solid (shown by its infrared spectrum[6] to be $TMED{\cdot}2BH_3$) and a colorless liquid (shown by its infrared spectrum and vapor pres-

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(1) S. V. Urs and E. S. Gould, *J. Am. Chem. Soc.*, **74**, 2948 (1952).

(2) C. A. Brown, E. L. Muetterties, and E. G. Rochow, *ibid.*, **76**, 2537 (1954).

(3) E. L. Muetterties, *Z. Naturforsch.*, **12b**, 265 (1957).

(4) A. K. Holliday and W. Jeffers, 16th International Congress of Pure and Applied Chemistry, Paris, 1957, Section on Inorganic Chemistry, p. 541.

(5) N. E. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 1033 (1964).

(6) The infrared spectrum of $TMED{\cdot}2BH_3$, which does not appear to have been previously reported, showed the following absorption (cm.$^{-1}$): 2955 (m), 2905 (m), 2390 (vs), 2280 (sh), 2250 (s), 2170 (w), 2055 (w), 1470 (vs), 1435 (s), 1405 (m), 1350 (m), 1310 (m), 1250 (w), 1205 (s), 1168 (vs), 1148 (s), 1010 (s), 875 (s), 800 (m), 725 (w), 685 (w).