tored with a copper–constantan thermocouple. The sample compartment of the spectrometer was continuously swept with dry nitrogen to prevent condensation of moisture on the cell windows.

Since these solutions are not stable for long periods of time (*vide infra*), and their concentrations at any time are therefore not well known, it was not possible to obtain accurate values for the molar extinction coefficients.

Discussion of Results

The absorptions in divalent europium are ascribed to transitions between the $^8S_{7/2}$ ground state with its seven "optical" electrons in the 4f shell and excited states having one of these 4f electrons in a 5d, 6s, or 6p, etc., state. The lowest excited state in divalent europium is the $^6P_{7/2}$ state.[5] The absorption at 4050 Å. is assigned to this transition.

If we use the energy separation between the $^6P_{7/2}$ state and the $^8S_{7/2}$ ground state thus obtained in conjunction with the g value of 1.990 ± 0.002 observed in the paramagnetic resonance experiments[3] we can calculate the spin–orbit coupling constant for divalent europium. This calculation assumes that only the $^6P_{7/2}$ state mixes appreciably with the ground state.

$$g_{\text{exptl}} = (1 - \epsilon^2)g(^8S_{7/2}) + \epsilon^2 g(^6P_{7/2})$$

where ϵ^2 is the fraction of $^6P_{7/2}$ character in the ground state and g is the theoretical Lande g factor corrected for relativistic and diamagnetic effects.[6] The extent of the admixture in the case of divalent europium in liquid ammonia amounts to about $\epsilon^2 = 3.5\%$. Using this value for the per cent $^6P_{7/2}$ character of the ground state in conjunction with the theoretical relation

$$\epsilon^2 = \frac{14\zeta^2}{(E_p - E_s)^2}$$

where ζ is the spin–orbit coupling constant and $(E_p - E_s)$ the energy separation of the $^6P_{7/2}$ and the $^8S_{7/2}$ states, we obtain a value of $\zeta = 1230 \pm 20$ cm.$^{-1}$ for the spin–orbit coupling constant of divalent europium in liquid ammonia. This value is in reasonably good agreement with that estimated for gaseous divalent europium, namely 1250 ± 50 cm.$^{-1}$.[6]

The ground state of divalent ytterbium is $^1S_0$ ($4f^{14}$). The excited states have one of these electrons in a 5d, 6s, etc., shell as with divalent europium. These allowed excited states include ^{1}(P, D, F, G, H) and ^{3}(P, D, F, G, H). The transitions observed are probably between $^1S_0$ and ^1P or ^3P states.[4]

There is no evidence for an appreciable concentration of trivalent metal ions in either solution. The fact that we did not observe the sharp lines characteristic of the visible spectrum of trivalent europium and ytterbium is not, however, truly conclusive evidence that there are no trivalent ions in solution. The visible transitions of these trivalent ions are forbidden by the Laporte selection rule, and therefore their molar extinction coefficients are small.[7] Since the total metal concentrations studied were quite small, it would be difficult to observe spectra from trivalent ions.

The two broad bands observed in the visible and near-ultraviolet are, we feel, characteristic of both divalent europium and ytterbium. We have not as yet explained the magnitudes of the shifts in the peaks with respect to those of the aqueous divalent chloride solutions observed by Butement. There is evidence, however, that at least the spectrum of divalent europium depends rather markedly on the nature of its environment in crystals—much more so than typical rare earths.[8] Differences between the effective crystalline fields at the europium and ytterbium ions in ammonia solution and those in aqueous chloride solutions may be sufficient to account for the observed shifts of the visible and near-ultraviolet bands in ammonia with respect to the corresponding bands observed in aqueous chloride solutions.

The gradual disappearance of the blue color arising from the tail of the near-infrared absorption of the solvated electron species was monitored at −31° and 11,200 Å. In moderately dilute solutions, the optical density decreased linearly with time. The integrated intensities of the paramagnetic resonance signals of both the europium species and the solvated electron species show similar linear decays with time. The zero-order chemical kinetics of decomposition are in qualitative agreement with the zero-order kinetics observed by Warshawsky for the decomposition of alkali metal–ammonia solutions.[9] A full discussion of the kinetics of decomposition of these solutions is forthcoming.[3]

Acknowledgment.—This work was supported in part by the Joint Services Electronics Program under Contract DA-36-039-AMC-03200(E) and in part by the National Science Foundation.

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[6] B. R. Judd and I. Lindgren, *Phys. Rev.*, **122**, 1802 (1961).

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF FLORIDA, GAINESVILLE, FLORIDA,
AND THE WASHINGTON RESEARCH CENTER,
W. R. GRACE AND COMPANY, CLARKSVILLE, MARYLAND

The Synthesis of Polymeric Dimethylphosphonitrile by Pyrolytic Condensation of Dimethyldiaminophosphonium Chloride

BY HARRY H. SISLER, STEPHEN E. FRAZIER, RIP G. RICE, AND M. G. SANCHEZ

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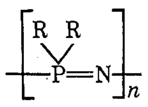
An intriguing feature of phosphonitrilic chemistry is the ability of certain cyclic derivatives to undergo decyclization and linear polymerization to form rubbery or elastomeric materials generally formulated as



This process was discovered by Stokes[1] while investigating the phosphonitrilic chlorides. Upon heating the cyclic trimer or tetramer to about 300° Stokes noted the formation of a material with properties similar to natural rubber. Similarly, the cyclic phosphonitrilic fluorides have been polymerized to rubbery materials at 350°,[2] the trimeric and tetrameric bromides give an air-sensitive elastomer when heated to 250–300,°[3,4] and the cyclic isothiocyanates polymerize when heated to 150°.[5,6] With R groups other than halogens or pseudohalogens, the process of simple thermal polymerization has not been observed. However, several new synthetic methods of various types have been recently developed for the synthesis of macromolecular phosphonitriles in which the groups on phosphorus are aryl, alkyl, or N-substituted amino. For example, it has been shown that lithium azide and sodium azide react with halophosphines to produce intermediates which undergo thermal polymerization to high-molecular-weight phosphonitriles.[7,8] Diphenylphosphinyl azide has been shown[9] to undergo a similar reaction producing linear phosphonitriles. Further, recently published results[10] indicate that the pyrolysis of certain hydrazinophosphines produces polymeric phosphonitrilic species, presumably by an Arbuzov-type rearrangement. Finally, polymeric phosphonitrilic chloride has been successfully methylated by slurrying the chloride with a solution of methylmagnesium bromide or methyllithium.[11] The products of this reaction, however, were not fully characterized.

This communication reports the synthesis of macromolecular dimethylphosphonitrile by a new method, *viz.*, the pyrolytic condensation of dimethyldiaminophosphonium chloride.

Experimental Section

Materials.—Solvents used were dried over calcium hydride. Dimethyldiaminophosphonium chloride was synthesized by the method of Sisler and Frazier.[12] Finely divided ammonium chloride was prepared by the gas-phase reaction of ammonia and chlorine.

TABLE I[a]

INFRARED ABSORPTION DATA FOR POLY(DIMETHYLPHOSPHONITRILE) (CM.$^{-1}$)

2975 (m), 2900 (m), 1410 (m), 1290 (s), 1270 (s), 1200 (s, sh), 1160 (vs), 1010 (w, sh), 965 (m), 940 (m), 915 (s), 880 (s), 855 (vs), 751 (m), 720 (s), 685 (m), 630 (w), 560 (m), 490 (m), 420 (s), 370 (w).

[a] s, strong; m, medium; w, weak; sh, shoulder; v, very.

TABLE II

EFFECT OF AMMONIUM CHLORIDE ON PRODUCT DISTRIBUTION

Wt. % NH_4Cl in starting matl.	Recovered yield of polymer, %	Recovered yield of $[(CH_3)_2PN]_{3,4}$, %
0	4.5	82
Trace	4.2	82
Trace	6.9	79
5.6	13.6	56
9.9	32	42
10.4	32	...
17.4	14.4	44
20	11.2	68

Analyses.—Elemental analyses were carried out by Galbraith Microanalytic Laboratories. Several nitrogen analyses were obtained by us using a Coleman Model 27 nitrogen analyzer. Melting points were observed in a Thomas-Hoover capillary melting point apparatus and are uncorrected. Molecular weights were determined in benzene or chloroform solution using a Mechrolab vapor pressure osmometer. The infrared spectrum of polymeric dimethylphosphonitrile was determined on a Beckman Model IR-10 spectrophotometer, using a KBr disk. The thermogravimetric analyses of the polymer were carried out using an Aminco Thermograv (American Instrument Company, Silver Spring, Md.). A summary of the spectral bands of the polymeric mixture between 3.4 and 30 μ is found in Table I.

Synthesis of Polymeric Dimethylphosphonitrile.—In a typical experiment, dimethyldiaminophosphonium chloride was transferred in a drybox to a semimicro sublimation apparatus. A measured weight of ammonium chloride was then added to the solid phosphonium chloride and the mass thoroughly mixed. This mixture was then heated for a period of from 1 to 4 days at about 200° and at a pressure of from 1 to 0.1 mm. At the completion of the reaction a white sublimate was observed on the cold finger and a gray-black, glassy residue remained in the sublimation pot. The sublimate was extracted with 30–60° petroleum ether and shown to consist of a mixture of ammonium chloride and dimethylphosphonitrilic trimer and tetramer. The residue was scraped from the pot or removed by dissolving it in hot benzene. The melting range of the crude residual material was typically 136–146°. *Anal.* Calcd. for $[(CH_3)_2PN]$: C, 32.01; H, 8.06; N, 18.66; P, 41.28; mol. wt./$(CH_3)_2PN$ unit, 75. Found: C, 31.81; H, 8.16; N, 18.79, P, 41.14; mol. wt., 7640.

The high polymers thus formed were usually soluble in hot benzene and chloroform. In some cases a residue was observed which swelled in benzene but did not dissolve. Extraction of the crude material with cyclohexane produced, upon evaporation of the solvent, a white powder melting at 139–146° and having a molecular weight of from 3500 to 9000 depending on the sample used. The residue from the cyclohexane extraction was soluble in benzene, melted at 136–138°, and had a molecular weight of 12,500.

Thermal gravimetric analysis of a sample with an average molecular weight between 8000 and 9000 was obtained using a 100 cc./min. flow of helium at a rate of temperature increase of 3°/min. This analysis showed no weight loss up to 300° and a rapid loss of weight from 300 to 500° during which essentially all of the sample sublimed from the apparatus as low-molecular-weight cyclic material, principally trimer and tetramer.

A film of polymeric dimethylphosphonitrile having a molecular weight of between 8000 and 9000 was examined by X-ray using Cu Kα radiation and was found to have the following interplanar spacings: 6.85 Å. (strong), 5.94 Å. (strong), 5.21 Å. (weak), and 4.50 Å. (medium). Differential thermal analysis was carried out on this material in helium using a heating rate of 3°/min. with Al_2O_3 as reference. A sharp endotherm was observed at 142° (measured m.p. 143–145°) and broad exotherm starting at a little under 300°, the latter presumably resulting from the onset of thermal decomposition.

A sample of the polymer having a molecular weight of from 11,000 to 12,000 was subjected to 40 Mrads of radiation from a

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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°.

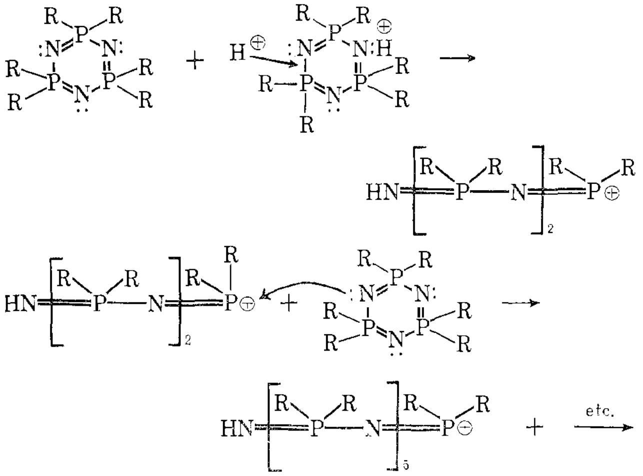
Discussion

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.

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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.