[CONTRIBUTION FROM THE INORGANIC CHEMICALS DIVISION, MONSANTO CHEMICAL COMPANY]

Structure and Properties of Condensed Phosphates. XV. Viscosity of Ultraphosphate Melts[1]

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RECEIVED AUGUST 13, 1958

The viscosities of sodium, hydrogen and mixed sodium–hydrogen ultraphosphate melts were measured in the temperature range from 300 to 600°. The data were interpreted in terms of reorganization and cross-linking in the melts. At lower temperatures, the contribution of cross-linking to the viscosity of the melt was pronounced, but at 600° and above, the rates of reorganization of the melts were so rapid, the cross-links contributed very little to the viscosity of the melts. In the mixed sodium–hydrogen ultraphosphate systems, a minimum occurs in the composition *versus* viscosity curve at the sodium acid metaphosphate composition. The sodium acid metaphosphate composition is the composition at which all cross-linking has been destroyed, and the $Na_2O + H_2O/P_2O_5$ ratio equals unity.

Introduction

Modern theories of condensed phosphate structure[2] demand that ultraphosphate systems contain molecular structures which are cross-linked to satisfy the bond requirements of the phosphate tetrahedra. No data have been published giving average molecular weights for the ultraphosphate glasses, but they are probably composed of very large molecule-ions exhibiting a network structure. To date, no crystalline sodium or hydrogen ultraphosphate has been prepared. Little is known of ultraphosphate solution properties other than the fact that they hydrolyze rapidly in aqueous media to yield acidic phosphates with an over-all composition near the metaphosphate composition

$$(i.e., (Na_2O + H_2O)/P_2O_5 \approx 1)$$

The viscosity work reported here was done to determine whether the viscosity data were consistent with the theories of the reorganization and structures of condensed phosphates.[2,3]

Experimental

A Brookfield viscosimeter was used to determine the viscosities of the melts. It was equipped with a solid cylindrical platinum spindle which was $^1/_8$ in. in diameter and $1^7/_8$ in. in length. Only 1 in. of the spindle was submerged in the melts during the measurements. In order to easily locate the 1 in. level, the spindle was machined to $^1/_{16}$ in. diameter above the melt line.

The spindle was calibrated with several Bureau of Standards' standard viscosity oils. The platinum bucket which was used to hold the phosphate melts during their measurements contained the standard oils during the calibration.

The sodium ultraphosphates were prepared by heating the required quantities of phosphoric oxide with anhydrous insoluble sodium metaphosphate ($NaPO_3$-II) at 300 to 400° until a clear liquid melt was obtained. The same general procedure was employed to prepare the condensed phosphoric acids except that 85% reagent grade orthophosphoric acid was mixed with the phosphoric oxide and the mixture was heated near 200°. The viscosities of the melts were measured immediately after the melts were made. The phosphate melts were prepared in a standard laboratory furnace and were transferred to a small upright pot type furnace for the viscosity measurements.

The temperature of the pot furnace was controlled by a manually operated transformer. The temperature of the melt within the furnace was continuously recorded. A small platinum–platinum rhodium thermocouple was submerged near the edge in the melt and the thermocouple was connected to a stripchart temperature recorder.

The viscosity measurements on a sample were made at several temperatures over a 4 hr. period while the sample was being heated, and a few measurements were made as the samples cooled. Whether on heating or cooling, the sample was allowed to remain at a constant temperature for about 20 min. before the viscosity was measured. This allowed sufficient time for the measured viscosity to become constant. The heating and cooling technique demonstrated that the sodium ultraphosphate samples were not appreciably changed during the heating cycle. Some difficulties were encountered with the ultraphosphoric acids, however. These acids are hygroscopic and on humid days will absorb atmospheric water during the course of measurements. When the difficulties were extreme, the samples were discarded.

The samples of ultraphosphates were analyzed for phosphoric oxide and water. The sodium oxide content was obtained by difference. Phosphoric oxide was determined by *p*H titrations after the sample had been hydrolyzed to orthophosphate.[4] The water contained in the sample was determined by the weight loss on ignition of about 0.5 g. of ultraphosphate with 2 g. of preignited zinc oxide. The mixture was ignited at 550° for 1 hr.

The phosphoric oxide analysis is usually some more reliable than the water analysis. The M_2O/P_2O_5 ratios of the melts were based upon the phosphoric oxide analyses when possible. The water analysis was used exclusively as a check on the phosphoric oxide analysis except in the mixed Na_2O–H_2O–P_2O_5 systems where both H_2O and P_2O_5 analyses are required to define the system.

Reliable analyses were obtained for the sodium ultraphosphates and the mixed sodium–hydrogen phosphates, but analyses of the ultraphosphoric acids with H_2O–P_2O_5 ratios near unity were never really satisfactory. Errors in duplicate analyses were often as great as 5%. The fact that the analyses were difficult to obtain and the viscosity data were also sometimes erratic in the sodium-free systems means that the data on the ultraphosphoric acids are only semiquantitative.

Discussion and Results

The measured viscosities of the phosphates used in this work were independent of the rates of shear employed (12 to 60 r.p.m.). This is interpreted to mean that the liquids are Newtonian. A graph of logarithm of the viscosity coefficient *versus* the reciprocal of absolute temperature yielded a straight line for all compositions studied. The slopes of the straight lines become greater as the M_2O/P_2O_5 ratio of the melt is decreased. Table I is a compilation of the coefficients relating the viscosity, temperature and M_2O/P_2O_5 ratios of the melts. The activation energy, E_{vis}, is also listed in Table I. It should be noted that as the complexity of the melt increases (lower M_2O/P_2O_5 ratios) the activation energy increases.

Figure 1 shows the change of viscosity of the sodium ultraphosphate and sodium polyphosphate melts as a function of the Na_2O/P_2O_5 ratio at constant temperature. The data for the curves in

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[1] Presented by E. J. Griffith before the 131st Meeting of the American Chemical Society, Miami, Florida, April, 1957.

[2] J. R. VanWazer and E. J. Griffith, THIS JOURNAL, **77**, 6140 (1955).

[3] J. R. Parks and J. R. VanWazer, *ibid.*, **79**, 4890 (1957).

[4] E. J. Griffith, *Anal. Chem.*, **28**, 515 (1956).

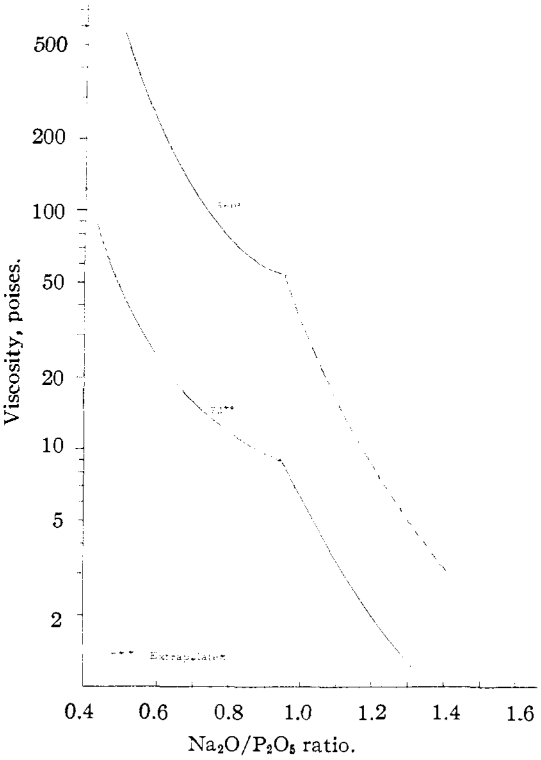

Fig. 1.—Viscosities of sodium phosphates as a function of Na_2O/P_2O_5 ratio and temperature.

Fig. 1 were obtained by first plotting the measured data as logarithm of viscosity *versus* the reciprocal of the absolute temperature and then reading the viscosity for the various Na_2O/P_2O_5 ratios at a constant temperature from the graph. The assumption has been made that the data from the plot of log η *vs.* $1/T$ may be extrapolated to the highly supercooled region. That is to say that the viscosity–temperature relationship of a melt is unchanged even though the temperature of the melt has been lowered many degrees (300° in the most extreme case) below its normal solidification temperature. This is done for the sake of comparing systems which could not otherwise be compared. The solidification temperatures for some of the compositions are not known accurately because of pronounced tendencies toward supercooling. The melts were still fluid at the lowest temperatures given in Table I.

Two important items should be noted about Fig. 1. The first is the abrupt change in the slopes of the curves very near the metaphosphate composition ($Na_2O/P_2O_5 \cong 1$). It is interesting that the break in these curves corresponds reasonably well to the K_2O/P_2O_5 ratio which yields a maximum viscosity in the aqueous solutions of cross-linked potassium Kurrol's salt.[5]

The exact form of the curves at the point of intersection is not known and the experimental techniques employed were not sufficiently precise to determine the exact shape. It is doubtful that the curves intersect sharply; the change of slope is probably continuous.

Table I

Coefficients for Calculating the Viscosities of Phosphate Melts

$$\eta = ae^{E_{vis}/RT}$$

Na_2O/P_2O_5 mole ratio	H_2O/P_2O_5 mole ratio	Temp. range investigated (°C.)	a ($\times 10^3$)	E_{vis} (kcal.)
		Sodium–hydrogen phosphates		
0.0	0.68	375–600	3.076	14.689
.13	.68	325–600	1.548	14.117
.32	.68	400–575	1.250	13.846
.61	.39	400–525	1.945	14.330
		Sodium phosphates		
0.47		600–700	0.071	27.077
.65		550–875	.306	22.160
.72		475–800	.409	20.895
.83		500–800	.981	18.452
.93		450–800	1.164	17.823
1.00		750–1025	1.436	16.543
1.10		700–1000	1.419	15.708
1.30		650–1025	1.572	13.433
		Phosphoric acids		
	0.60	400–600	1.825	17.502
	.68	375–600	3.076	14.689
	.88	275–550	0.681	13.721
	.98	250–350	.619	12.245
	1.05	250–325	.139	12.401
	1.24	75–200	.221	8.494

The second noteworthy property of the curves is the concave upward nature of them both to the left and right of the metaphosphate composition. Starting at the left-hand side of the curves, the addition of sodium oxide lowers the viscosity of the melt by breaking cross-linkages in the melt and thus loosening the network structure of the phosphate molecules. As the metaphosphate composition is approached the number of cross-linkages in the melt decreases until at the metaphosphate composition no cross-linkages exist. Further additions of sodium oxide to the right of the metaphosphate composition break P–O–P linkages in chains and thus the result is that each mole of Na_2O added to the melt breaks one mole of P–O–P, forming two shorter chains from each longer chain that is cleaved. The larger molecules contribute proportionally more to the viscosity compared to similar number of moles of phosphorus contained in smaller molecules.

The phosphoric oxide–water system contains an azeotrope,[6] the composition of which is about 92% (by weight) P_2O_5 and 8% H_2O. The azeotrope boils at *ca.* 870° at atmospheric pressure. The azeotropic phosphoric acid is an ultraphosphate with H_2O/P_2O_5 equal to 0.68. Thirty-two per cent. of the total phosphorus atoms are involved in cross-linkages. The percentage of the phosphorus atoms which are involved in cross-linkages may be calculated by the equation

$$\% P_t = 100(1 - R) \text{ for } R < 1 \qquad (1)$$

where

P_t = branched phosphorus atoms
R = M_2O/P_2O_5

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(5) R. Pfanstiel and R. K. Iler, This Journal, **74**, 6059 (1952); W. Dewald and H. Schmidt, *J. prakt. Chem.*, **44**, 196 (1955).

(6) E. H. Brown and C. D. Whitt, *Ind. Eng. Chem.*, **44**, 615 (1952); G. Tarbutton and M. E. Deming, This Journal, **72**, 2096 (1950).

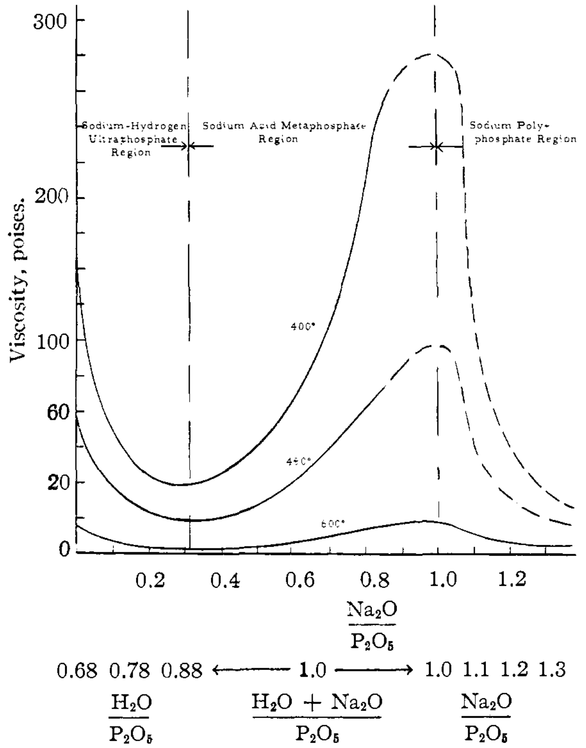
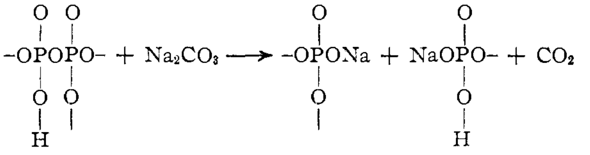


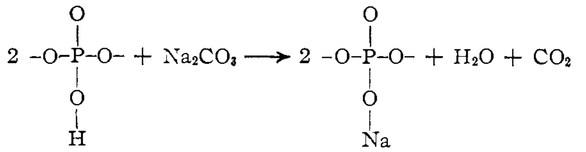
Fig. 2.—Viscosities of sodium–hydrogen phosphates as a function of $Na_2O + H_2O/P_2O_5$ and temperature; - - -, extrapolated data.

The variation of the viscosity of the azeotropic phosphoric acid with temperature may be obtained from the data of Table I.

When sodium carbonate is added to molten azeotropic phosphoric acid, the principal reaction is the breaking of a cross-linkage and the liberation of carbon dioxide. The significant feature of this reaction is the fact that practically no water is liberated from the melt until the acid metaphosphate composition is reached. Once the acid metaphosphate composition is reached, the further addition of sodium carbonate serves to neutralize the hydrogen ions of the melt, thus replacing hydrogen ions with sodium ions. Figure 2 shows the changes of the viscosity of azeotropic phosphoric acid as sodium carbonate is added to the melt. The viscosity of the melt rises as the Na_2O/P_2O_5 ratio approaches unity because the sodium ions contribute more to the viscosity than an equal number of hydrogen ions. It should be understood that the acid metaphosphate region extends from the minimum near Na_2O/P_2O_5 equal to 0.33 to the maximum at Na_2O/P_2O_5 equal to 1.0. When the Na_2O/P_2O_5 ratio reaches 1.0, all of the hydrogen ions of the melt have been neutralized and replaced by sodium ions. To the right of the maximum at Na_2O/P_2O_5 equal to 1.0, the addition of more Na_2CO_3 results in the breaking of P–O–P linkages to form shorter chains from longer chains, thus accounting for the decrease in viscosity at a constant temperature as the Na_2O/P_2O_5 ratio is increased above unity. Portions of the data of Fig. 2 were obtained from extrapolating the viscosity data below the melting point of the phosphates employed.[7] The viscosity data for the polyphosphate region ($Na_2O/P_2O_5 > 1$) of the curve were taken from a previous publication.[8]



$$\text{-O}\underset{\underset{\text{H}}{|}}{\underset{|}{\overset{\overset{\text{O}}{|}}{\text{P}}}}\text{O}\underset{\underset{\text{H}}{|}}{\underset{|}{\overset{\overset{\text{O}}{|}}{\text{P}}}}\text{O-} + Na_2CO_3 \longrightarrow \text{-O}\underset{\text{O}}{\underset{|}{\overset{\overset{\text{O}}{|}}{\text{P}}}}\text{ONa} + \text{NaO}\underset{\underset{\text{H}}{|}}{\underset{\text{O}}{\underset{|}{\overset{\overset{\text{O}}{|}}{\text{P}}}}}\text{O-} + CO_2$$



$$2\ \text{-O-}\underset{\underset{\text{H}}{|}}{\underset{\text{O}}{\underset{|}{\overset{\overset{\text{O}}{|}}{\text{P}}}}}\text{-O-} + Na_2CO_3 \longrightarrow 2\ \text{-O-}\underset{\underset{\text{Na}}{|}}{\underset{\text{O}}{\underset{|}{\overset{\overset{\text{O}}{|}}{\text{P}}}}}\text{-O-} + H_2O + CO_2$$

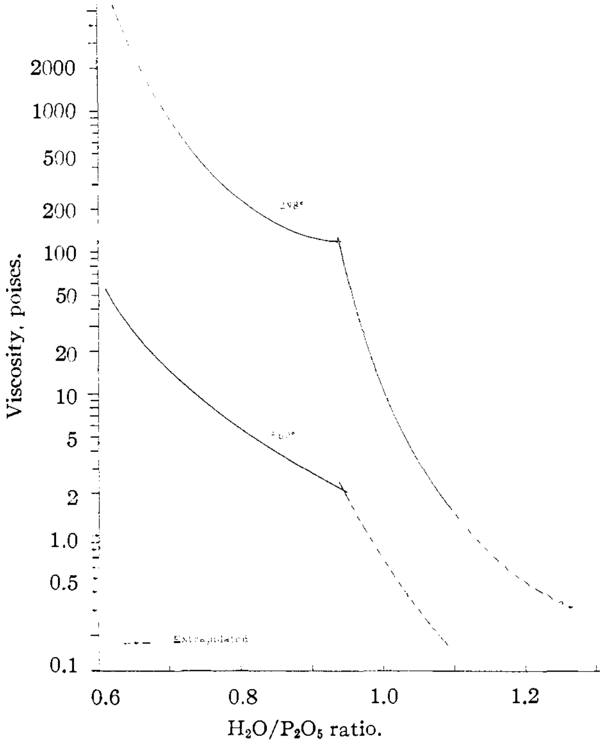
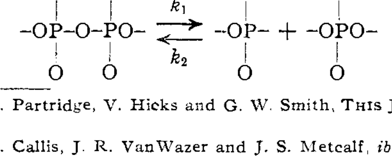


Fig. 3.—Viscosity of the phosphoric acids as a function of H_2O/P_2O_5 ratio and temperature.

As the temperature is raised, the minimum in the curve at $Na_2O/P_2O_5 \approx 0.33$ becomes more and more obscured. The system is continuously reorganizing *i.e.*, there is continuous making and breaking of P–O–P linkages. At any fixed temperature, the ultraphosphate network and the fragments broken away by thermal energy are in dynamic equilibrium. Designating the specific rate constant of breaking as k_1 and the specific rate constant of the making reaction as k_2 then

$$\frac{k_1}{k_2} = K \qquad (2)$$

where K is the equilibrium constant for the reaction



$$\text{-O}\underset{\text{O}}{\underset{|}{\overset{\overset{\text{O}}{|}}{\text{P}}}}\text{-O-}\underset{\text{O}}{\underset{|}{\overset{\overset{\text{O}}{|}}{\text{P}}}}\text{O-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{-O}\underset{\text{O}}{\underset{|}{\overset{\overset{\text{O}}{|}}{\text{P}}}}\text{-} + \text{-O}\underset{\text{O}}{\underset{|}{\overset{\overset{\text{O}}{|}}{\text{P}}}}\text{O-}$$

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[7] E. P. Partridge, V. Hicks and G. W. Smith, THIS JOURNAL, **63**, 454 (1941).

[8] C. F. Callis, J. R. VanWazer and J. S. Metcalf, *ibid.*, **77**, 1471 (1955).

As the temperature of the system is increased, the vibrational component of the thermal energy will become greater and k_1 will increase relative to k_2, thus shifting the equilibrium to favor the broken bonds. This decreases the size of the flow unit and, therefore, the viscosity of the melt.[8]

In Fig. 3 the phosphoric acids are treated in the same way the sodium phosphates were in Fig. 1. The principal difference which should be noted is the fact that the viscosity of the acids are about one order of magnitude lower than the corresponding sodium phosphates at the same temperature. This fact should be considered when interpreting the data of Fig. 2 when on the far left-hand side of the curve the viscosity is decreasing at constant temperature despite the fact that the sodium ions are being added to the system.

The nuclear magnetic resonance spectra of ultraphosphates[9] exhibit only one broad peak at a chemical shift value intermediate between that found for a branched phosphorus and a middle-group phosphorus. When non-equivalent species undergoing reorganization are present in a sample, a single resonance appears at an intermediate chemical-shift value dependent upon the molar concentrations of the non-equivalent species.[10] The average lifetime τ in a given electronic (chemical) environment of a nucleus undergoing reorganization is given by $\tau = 1/4\pi\delta$, where δ is the chemical shift in cycles per second between the exchanging environments.[10,11] For middle-group and branched phosphorus, the average lifetime must be less than *ca.* 2×10^{-4} sec., since the chemical shift between these two phosphorus nuclei is *ca.* 400 cycles per second.[9,12] Additional data are being gathered to check the concentration dependence *versus* the ultraphosphate compositions.

Acknowledgment.—The authors wish to acknowledge the help given by F. K. Fuller in obtaining the data presented in this work.

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[9] J. R. VanWazer, C. F. Callis, J. N. Shoolery and R. C. Jones, THIS JOURNAL, **78**, 5715 (1956).

[10] H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **21**, 1688 (1953).

[11] E. L. Muetterties and W. D. Phillips, paper presented at the 130th meeting of the American Chemical Society in Atlantic City September, 1956.

[12] D. Ames and Leo Groenweghe, Monsanto Chemical Company, private communication.

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The Behavior of Trimeric Nitrilophosphoric Halides Toward Certain Basic Reagents

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RECEIVED AUGUST 21, 1958

Trimethylamine is split by $(NPCl_2)_3$ at room temperature, forming $(CH_3)_4NCl$ and placing an equivalent number of $(CH_3)_2N$ groups on P without disrupting the $(NP)_3$ ring. Triethylamine and pyridine fail to react similarly, only forming limited amounts of tarry material (by reactions possibly influenced by impurities) and permitting nearly complete recovery of $(NPCl_2)_3$. Trimethylamine is virtually inert toward $(NPF_2)_3$ but may have a mild catalytic effect in changing the degree of polymerization. Sodium acetylide attacks $(NPCl_2)_3$ in a suitable solvent, replacing Cl by acetylide, with hints of placement of Cl and P on C and possibly lengthening of the carbon chain, forming an apparently polymeric material.

It was reported by Schäpperkötter[2] that pyridine, quinoline or tribenzylamine acts to depolymerize $(NPCl_2)_n$ ring compounds, to form $NPCl_2 \cdot 2$ amine complexes. Apparently in accord with this, it was found in these Laboratories that trimethylamine reacts with $(NPCl_2)_3$, $(NPCl_2)_4$ or higher polymers, slowly approaching compositions not far from the empirical formula $NPCl_2 \cdot 2(CH_3)_3N$.[3,4]

Actually, however, this reaction is not a depolymerization to form a monomer-adduct but a wholly unpredicted splitting of the tertiary amine—by a type of acid–chloride which usually is regarded as relatively unreactive. The result is a formation of $(CH_3)_4NCl$ and replacement of Cl by $(CH_3)_2N$ on P, without destruction of the $(NP)_n$ ring.

This type of reaction seems to be quite restricted in scope; for $(NPF_2)_3$[5] failed to react with trimethylamine, and $(NPCl_2)_3$ with triethylamine gave only a slight hint of a reversible attachment of the amine to the ring. Our many attempts to make Schäpperkötter's pyridine complex, from $(NPCl_2)_3$ under different sets of conditions, led only to small amounts of tarry material and nearly complete recovery of the trimer.

It was not found possible to methylate $(NPCl_2)_3$ by methyllithium, nor could we form any chloroalkyl derivatives by reaction with either acetylene (in the presence of Al_2Cl_6) or 2-methylpropene. However, sodium acetylide reacted easily with $(NPCl_2)_3$, replacing a considerable part of the chloride. An apparently polymeric material resulted, and the infrared spectrum indicated the formation of C=C bonds.

The Trimethylamine Reaction

Procedure.—Crude $(NPCl_2)_3$ (obtained either by the method of Schenck and Römer[6] or by purchase) was purified by high-vacuum sublimation and then melted in the range 111.5–112.5° (lit. 114.9).[7] Its molecular weight (cryoscopic in benzene) was determined as 350 (calcd., 347.7). It was considered that a trace of the tetramer would not be chemically significant. Trimethylamine was purified by contact with P_4O_{10}.

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[1] This research was supported by the United States Air Force under Contract AF 33(616)-2743, monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air-Force Base, Ohio. It represents the Master of Science Thesis of Aimery P. Caron, University of Southern California Libraries, 1958 (available on microfilm).

[2] H. Schäpperkötter, Dissertation, Münster, 1925.

[3] J. C. Taylor, M.S. Dissertation, University of Southern California Libraries, 1940.

[4] C. L. Randolph, Jr., M.S. Dissertation, University of Southern California Libraries, 1947.

[5] F. Seel and J. Langer, *Angew. Chem.*, **68**, 461 (1956).

[6] R. Schenck and G. Römer, *Ber.*, **57B**, 1343 (1924).

[7] L. F. Audrieth, R. Steinman and A. D. F. Toy, *Chem. Revs.*, **32**, 119 (1943).