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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ST. LOUIS, MISSOURI

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

The Behavior of Trimeric Nitrilophosphoric Halides Toward Certain Basic Reagents

BY ANTON B. BURG AND AIMERY P. CARON[1]

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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).

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For the amine reaction, the $(NPCl_2)_3$ sample was resublimed under high-vacuum within a seal-off tube; then an excessive amount of the amine was brought in and the tube sealed off. The reaction times and temperatures varied from one experiment to another, as shown in Table I. Each tube was opened *in vacuo* and the excess amine measured to determine the amount consumed. The non-volatile white solid products were investigated as described below.

TABLE I

THE $(CH_3)_3N$-$(NPCl_2)_3$ REACTION

Expt. no.	Reactants, mmoles $(CH_3)_3N$	$(NPCl_2)_3$	Time, days	Temp., °C.	Recovered amine, mmoles	Reacn. ratio amine/ $NPCl_2$
1	2.53	0.305	0.88	100	1.79	0.81
2	17.10	1.358	10	100	7.17	2.44
3	15.32	1.098	30	25	9.31	1.82

Nature of the Product.—The product of expt. 1, after removal of the excess amine at room temperature, gave off no more amine during a 7.5 hr. period of heating to 220°. At 240° gas evolution was barely detectable and progressed to completion as the material was heated *in vacuo* to 350°. The gas was collected in a trap cooled by liquid nitrogen and shown to consist of 0.33 mmole each of CH_3Cl and $(CH_3)_3N$. The amine was removed as the hydrochloride, using 0.33 mmole of HCl; and the CH_3Cl was identified by its vapor tensions and m.p. The equimolar formation of $(CH_3)_3N$ and CH_3Cl indicated the dissociation of $(CH_3)_4NCl$ in an amount representing slightly less than half of the originally absorbed $(CH_3)_3N$ (0.74 mmole). The remaining amine material had to be in the form of $(CH_3)_2N$ groups, replacing Cl on P. As a check on the character of the dissociation, an authentic sample of $(CH_3)_4NCl$ was heated in the same manner, decomposing similarly.

Experiment 2 was pushed beyond the amine:$NPCl_2$ ratio corresponding to replacement of half of the chloride. The mixed solid product was shaken with a benzene-water mixture, dissolving the aminated NP ring material into the benzene layer while the $(CH_3)_4NCl$ dissolved in the water. The aqueous solution was evaporated and portions dried at 180 and 280°; then chloride analyses showed that the weight per mmole of chloride would be 111.2 or 111.3 mg. (calcd. for Me_4NCl, 109.6 mg.) Partial decomposition *in vacuo* at 280° gave the usual 1:1 mixture of $(CH_3)_3N$ and CH_3Cl. The yield of $(CH_3)_4NCl$ was 4.92 mmoles (calcd., 4.96).

The benzene solution was evaporated, leaving a colorless, semi-crystalline, non-hygroscopic solid; wt. 515.1 mg. (calcd., 515.0). It showed a wide melting range, beginning at 40°. Its average mol. wt. (cryoscopic in benzene) was 370; calcd. 379 for the 61% amino-substitution indicated by the stoichiometry. Hence it appears that the average molecular formula was $[NPCl_{0.78}(NMe_2)_{1.22}]_3$; the $(NP)_3$ ring was not disrupted, and substitution went beyond one Cl per P.

Experiment 3 was done in order to learn whether the same amine-splitting occurs at room temperature. The water-benzene partition method was employed again, giving 3.07 mmoles of $(CH_3)_4NCl$ (calcd., 3.02); the chloride titration of this gave 112.6 mg. per mmole of Cl. The benzene extract was not less than 375 mg. (calcd., 408 mg.); mol. wt. 390. There was an attempt to isolate a pure component by vacuum sublimation; but the sublimate always was a mixture.

All three experiments demonstrated the same main fact: trimethylamine attacks $(NPCl_2)_3$, substituting a $(CH_3)_2N$ group for each Cl^- removed as $(CH_3)_4NCl$, while the ring is undisturbed.

The Tetramer Case.—In the work of Taylor[3] and Randolph[4] it was shown that $(NPCl_2)_4$ absorbs $(CH_3)_3N$ in essentially the same manner as the trimer does. Although not so thoroughly studied, the tetramer product doubtless also represents formation of the $(CH_3)_2N$-P bond.

Attempts at Other Amination Reactions

The Trimeric Chloride with Triethylamine.—By very close observation, $(NPCl_2)_3$ could be seen to dissolve completely in triethylamine and then very soon form a fine precipitate—as though forming an amine adduct. However, a very slow high-vacuum distillation at −23° gave back virtually all of the amine; and at no point in the process was it possible to show a lowered amine pressure corresponding to the dissociation of an adduct. If an adduct was present, its bond energy must have been very slight.

On longer standing in a high-vacuum system, mixtures of thoroughly dried and carefully purified $(NPCl_2)_3$ and $(C_2H_5)_3N$ formed some tar-like material, chiefly at the expense of the amine. Thus 3.967 mmoles of $(NPCl_2)_3$ and 19.21 mmoles of $(C_2H_5)_3N$, after some hours at 0°, had turned yellow to red-brown; then only 16.87 mmoles of amine could be recovered, but the recovery of $(NPCl_2)_3$ (by high-vacuum sublimation at 80°) was 3.876 mmoles (97.7%). In another experiment, 3.215 mmoles of $(NPCl_2)_3$ and 16.65 mmoles of $(C_2H_5)_3N$ (recovered from the preceding experiment) were kept in a sealed tube for 22 hr. at 100°; this time all but 0.28 mmole of the amine was recovered and little brown material was formed. Upon exposure to moist air, such mixtures quickly turned red-brown. The effect seems parallel to the formation of buff-colored or darker solids when triethylamine is dried by P_4O_{10}.

It is concluded that strictly pure $(NPCl_2)_3$ and $(C_2H_5)_3N$ would be mutually inert,[8] certainly undergoing no such reaction as with trimethylamine.

The Trimeric Chloride with Pyridine.—Solutions of $(NPCl_2)_3$ in pyridine were heated at 75, 99 and 115° for periods of time ranging from 66 to 187 hr. Even though the $(NPCl_2)_3$ had been resublimed within the reaction tube and the pyridine thoroughly dried by KOH, P_4O_{10} or metallic calcium in the high-vacuum system, the solution invariably turned black within 6 to 12 hr. It was considered possible that the limited blackening reaction might be due to a reactive impurity which the reaction would destroy; however, the effect persisted with full vigor when vacuum-recovered pyridine was used again. In a number of cases the average molecular weight of the solute was determined from time to time (method; lowering of the vapor tension of the pyridine in a special immersible differential tensimeter); although there was considerable deviation in both directions from the calculated values for $(NPCl_2)_3$, there never was any approach to the complete depolymerization indicated by Schäpperkötter.[2] Instead, the pyridine was partially converted to variable yields of tar, and nearly all of the $(NPCl_2)_3$ could be recovered. The tar had an orange-colored component, separable by paper chromatography and apparently increased by moisture.

Some experiments were run with either pure or crude coal-tar benzene as solvent, never forming any such precipitates as reported by Schäpperkötter. Thus pyridine evidently is like triethylamine in its failure to form any compound with $(NPCl_2)_3$.[8]

The Trimeric Fluoride with Trimethylamine.—A sample of $(NPF_2)_3$ was made by a modification of the KSO_2F-$(NPCl_2)_3$ process.[5] A stainless-steel pressure cylinder was loaded with carefully dried KF and $(NPCl_2)_3$; then dry SO_2 was distilled in. It was expected that KSO_2F would form upon heating and at once react to fluorinate the $(NPCl_2)_3$. The method was not developed to such a point as to give high yields, but a sufficient sample of $(NPF_2)_3$ was obtained.

In one experiment 14.34 mmoles of $(CH_3)_3N$ and a sample of $(NPF_2)_3$ equivalent to 3.17 mmoles of NPF_2 monomer were kept in a sealed tube for 38 days at 100°. The recovery of $(CH_3)_3N$ was 14.24 mmoles; and 2.84 mmoles of NPF_2 units appeared in volatile form (mol. wt. 257; originally 252). The remaining 0.33 mmole of NPF_2 represented the non-volatile white solid product. Possibly there was a little conversion of the trimer to higher polymers (including the tetramer), but no amination occurred.

When $(NPF_2)_3$ was heated alone in a sealed glass tube, again for 38 days at 100°, there seemed to be no effect; the recovery of the unchanged sample was 99.2%. It appeared that trimethylamine had exerted a mild catalytic effect in the preceding experiment.

The Acetylide Reaction

Preparation of Sodium Acetylide.—A stream of dry acetylene was bubbled into 200 ml. of liquid ammonia containing 5 g. of sodium, with stirring in the absence of air, at −78°. As soon as the blue color disappeared, the solution was evaporated and the last of the ammonia was pumped

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[8] The same conclusion was reached independently by Dr. Jan Konecny in equally careful experimentation at the Naval Ordnance Laboratory, Corona, California. We gratefully acknowledge his highly coöperative interest in the main problem represented by this paper.

off at room temperature. It was not possible to bring the product to reaction with $(NPCl_2)_3$ in triethylamine, ether or benzene; but in diglyme (β,β′-dimethoxy-diethyl ether) the reaction was quite extensive even though the NaC_2H itself seemed nearly insoluble.

Replacement of Chloride by Acetylide.—Ten grams each of $(NPCl_2)_3$ and NaC_2H in 200 ml. of diglyme (previously dried by sodium under reflux for 24 hr.) turned black during ten minutes of stirring at room temperature. After 70 min. the mixture was filtered to remove a solid containing chloride but no phosphorus compounds. The diglyme was distilled from the filtrate, under reduced pressure at 70°. Then the oily residue was placed under high vacuum for 6 hr. at 80°, driving out the last of the diglyme and delivering the unused $(NPCl_2)_3$ as a sublimate. This was identified by the mixed melting point method. The final product was a brown, non-crystalline material which began to decompose near 150°. It proved to be insoluble in benzene, nitrobenzene, carbon tetrachloride, acetone, ethanol or ether, as though it were more highly polymeric than the soluble $(NP)_3$-ring compounds. However, it was redissolved by diglyme, indicating no high degree of cross-linking.

Analysis of the Product.—The brown solid product was analyzed for all components in an effort at interpretation of the reaction.

Chloride.—Two roles played by chloride were indicated by the difference of results when chloride was determined after basic hydrolysis at 100° and after a complete breakdown by the Parr peroxide–nitrate bomb method. In each case the final titration was by the Volhard method. The basic hydrolysis gave 42.1% Cl; the Parr-bomb, 50.5% Cl.

Phosphorus and Carbon.—The sample was destroyed by a boiling mixture of sulfuric, nitric and perchloric acids. The resulting carbon dioxide was drawn off, freed of oxidizing gases by shaking with mercury and measured as a gas; % C, 11.1 ± 0.3. The phosphate now was determined by the molybdate method; % P, 25.9 ± 0.4.

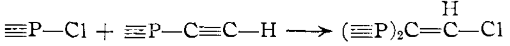
Hydrogen.—It is assumed that no H was removed from C in the acetylide reaction; then from the result for C the % H is calculated as 0.46.

Nitrogen.—The Kjeldahl method gave the % N as 12.18 ± 0.02.

Summary.—Adding the % of the elements here determined gives a total of 100.1 ± 1.2%. If it be assumed that the basic hydrolysis gave all and only the P-bonded chloride, the formula would be written as $[N_3P_{2.88}Cl_{4.10}(C_{3.19}H_{1.59}\text{-}Cl_{0.81})]_x$.

Infrared Spectrum of the Product.—A sample of the acetylide product was pelleted in potassium bromide and the infrared spectrum observed. A medium peak at 871 cm.$^{-1}$, a strong one at 1200 and a weak one at 1990 were essentially the same as for $(NPCl_2)_3$, indicating that the original ring was present. A peak at 3040 was assignable to C–H stretching and another at 770 would be C–H bending. A peak at 1588 would correspond to the literature values for the C=C bond in conjugated systems. The presence of C–C and C=C could not be determined because they would be in a region where the $(NP)_3$ ring produces a wide spectrum without specific peaks.

Interpretation.—The polymerization of a partially acetylided $(NPCl_2)_3$ might occur in at least two ways without disturbing the ring: (1) by the reaction-type



$$\equiv P{-}Cl + \equiv P{-}C{\equiv}C{-}H \longrightarrow (\equiv P)_2C{=}\overset{H}{C}{-}Cl$$

or (2) by direct polymerization of the acetylide unit. The spectroscopically indicated C=C bond would be explained on either basis. The empirical formula suggests some occurrence of (1); however there are too few phosphorus valences available to account for conversion of the 0.81Cl to C-Cl bonds in the manner of (1) alone. Full consistency would seem to require at least a limited occurrence of (2) as well. A full understanding of this polymer might require a more extensive study than is possible within our plans for the future.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, OLIN MATHIESON CHEMICAL CORPORATION]

Exchange Sites in the Deuteration of Decaborane

BY I. SHAPIRO, MAX LUSTIG AND ROBERT E. WILLIAMS

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The progress of the hydrogen–deuterium exchange between decaborane and deuterium oxide in dioxane has been followed by nuclear magnetic resonance spectroscopy. The most rapid exchange occurs with the bridge hydrogens; slower rates of exchange take place at the terminal sites. The preferential order of terminal hydrogen exchange is (a) two equivalent sites, each adjacent to two bridge positions, (b) four equivalent sites, each adjacent to one bridge position, (c) two apical sites and the two remaining sites located furthest from the bridge positions. When a sample of decaborane is separated from the deuterium oxide after becoming bridge-deuterated and is aged in dioxane, H–D exchange occurs involving only the bridge deuterons and the neighboring hydrogens on the four identical terminal sites. A mechanism accounting for these exchanges is proposed.

Decaborane can be deuterated by exchange with deuterodiborane[1] or with deuterium oxide.[2] In the former case the exchange takes place preferentially at the terminal sites of decaborane while in the latter case there is a rapid exchange in the bridge positions followed by a slower exchange at the terminal sites. In either case the exchange is complicated by interaction[3] or hydrolysis[4] with resultant loss of decaborane.

Since a position analysis of decaborane can be made by nuclear magnetic resonance spectroscopy,[5] this technique was applied to the study of the exchange of decaborane with deuterium oxide. In addition to confirming the previous work,[2] it has been possible to observe the relative rate and preferential order in which deuterium atoms replace the various terminal hydrogen atoms in decaborane.

Experimental

Decaborane was prepared by the pyrolysis of diborane[6] and purified by sublimation in standard high vacuum equipment. Deuterium oxide of 99.5% purity was obtained from Stuart Oxygen Co. Dioxane was purified by distillation.

The B^{11} and proton n.m.r. spectra were obtained with a Varian High Resolution Spectrometer operating at 12.8 and 40 mc., respectively. Mass spectra were obtained with a Consolidated Model 21-103 mass spectrometer operating at 70 volts.

The procedure was similar to that described by other workers.[2] Weighed amounts of decaborane and deuterium oxide were condensed with dioxane to give the following concentrations: $B_{10}H_{14}$, 0.08 *M;* D_2O, 3.10 *M*. These ma-

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[4] Ref. 2 did not disclose that decaborane also undergoes hydrolysis; in the course of 3 hr. exposure to water in dioxane an appreciable loss in decaborane occurs.

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