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Chloramination of Trimethylhydrazine

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The reaction of chloramine with trimethylhydrazine, $(CH_3)_2NNH(CH_3)$, has been investigated. The principal product formed when this reaction is carried out in ether is the dimethylhydrazone of formaldehyde, $(CH_3)_2NN{=}CH_2$. The absence of 1,2,2-trimethyltriazanium chloride, the expected product, is explained in terms of the weaker nucleophilicity of trimethylhydrazine compared to that of 1,1-dimethylhydrazine, which reacts with chloramine to form 2,2-dimethyltriazanium chloride, $[(CH_3)_2N^+(NH_2)_2]Cl^-$. The principal product of the chloramination of trimethylhydrazine, when the reaction is carried out in acetonitrile, is 2,2-dimethyltriazanium chloride. Mechanisms are proposed for the chloraminations in both solvents. Chloraminations of the dimethylhydrazone of formaldehyde and of tetramethyl-2-tetrazene, $(CH_3)_2NN{=}NN(CH_3)_2$, carried out for purposes of comparison, also resulted in formation of some 2,2-dimethyltriazanium chloride. Attempts to synthesize 1,1,2-trialkyltriazanium chlorides by reaction of 2,2-dimethyltriazanium chloride with alkyl halides were unsuccessful, resulting either in no reaction or in the formation of 2,2-dimethyltriazanium iodide. A mechanism for the formation of 2,2-dimethyltriazanium chloride by the chloramination of trimethylhydrazine is proposed.

The chemistry of 2,2-dialkyltriazanium salts, compounds of interest because they contain the –N–N–N– chain and yet are stable at ordinary temperatures, has been discussed extensively in previous publications.[1–7] The chlorides can be most conveniently prepared by the reaction of chloramine with 1,1-dialkylhydrazines[2,3] or with secondary amines.[7] In a previous paper,[1] in which we reported the determination of the crystal structure of 2,2-dimethyltriazanium chloride, $[(CH_3)_2N(NH_2)_2]Cl$, and 1,1,1-trimethylhydrazinium chloride, $[(CH_3)_3NNH_2]Cl$, we suggested that the stability of 2,2-dialkyltriazanium salts is a result of the quaternization of the central nitrogen.

It seems reasonable to expect that 1,2,2-trialkyltriazanium salts would similarly be stable and could be prepared by the chloramination of trialkylhydrazines. However, Kren[8] isolated 2,2-dimethyltriazanium chloride instead of the expected 1,2,2-trimethyltriazanium chloride $[(CH_3)_2N(NH_2)(NHCH_3)]Cl$ from the solid portion of the trimethylhydrazine–chloramination reaction mixture.

We have continued the investigation of the chloramination of trimethylhydrazine in order to identify other products, to formulate a reaction mechanism, and to determine possible reasons for the formation of 2,2-dimethyltriazanium chloride and the absence of 1,2,2-trimethyltriazanium chloride.

Experimental Section

Spectra. Infrared spectra of solid samples in pressed KBr pellets and liquid samples placed between KBr plates were recorded on a Beckman IR-10 spectrometer. Nuclear magnetic resonance spectra of $CDCl_3$ or $Me_2SO\text{-}d_6$ solutions of samples were recorded on a Varian Model A-60A NMR spectrometer at 40 °C. Tetramethylsilane and the sodium salt of 3-trimethylsilylpropanesulfonic acid were used as internal standards in the respective solvents.

Analyses. A Perkin-Elmer Model 820 gas chromatograph equipped with twin 12-ft 15% Carbowax columns was used for gas–liquid chromatography. An internal standard was used to relate peak areas to percents of compounds of interest.[9] Melting points were determined on a Thomas-Hoover capillary tube melting point apparatus. Elemental analyses were done by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

Materials. Trimethylhydrazine, $(CH_3)_2NNH(CH_3)$,[10] tetramethyl-2-tetrazene,[11] $(CH_3)_2NN{=}NN(CH_3)_2$, and the dimethylhydrazone of formaldehyde,[10] $(CH_3)_2NN{=}CH_2$, were prepared by methods found in the literature. Prior to chloramination, these compounds were analyzed by gas–liquid chromatography and nuclear magnetic resonance spectroscopy to ascertain that they were free of contaminants, especially 1,1-dimethylhydrazine. Nuclear magnetic resonance spectral peaks for products and reactants in this study are listed in Table I. A sample of 2,2-dimethyltriazanium chloride prepared for our previous study[1] was also used in this study. Anal. Calcd for $C_2H_{10}N_3Cl$: C, 21.52; H, 8.97; N, 37.62. Found: C, 21.62; H, 8.96; N, 37.50. Chloramine was produced in a Sisler–Mattair generator[12] by the gas-phase reaction of ammonia and chlorine. The rate of formation of chloramine was ca. 0.08 mol of NH_2Cl/h. All other reagents and solvents were obtained from commercial sources and were used without further purification.

Reactions on the Chloramine Generator. The general procedure is given here. Details for specific reactions are listed in Table II. The chloramine–ammonia generator effluent was bubbled through a solution of the reactant at room temperature. After completion of chloramination, the reaction mixture was allowed to stand in a flask protected from moisture by a Drierite-filled drying tube. After 24 h, the solid which had formed was separated from the solution by filtration.

Preparation of Ammonia-Free Chloramine. The generator effluent was bubbled through 1 L of dry ether for 2 h. The mixture was then allowed to stand overnight after which the volume of solvent was reduced by passing a stream of nitrogen over the solution until the desired chloramine concentration was obtained (ca. 0.2 M). The chloramine concentration was determined by addition of an aliquot of the chloramine solution to an acidic potassium iodide solution followed by titration of the liberated iodine with a standard sodium thiosulfate solution. This chloramine solution is relatively stable; it can be stored for days without appreciable decomposition of chloramine. The last traces of ammonia were removed by pouring the chloramine solution through a column packed with anhydrous copper sulfate.[13]

Other Chloraminations of Trimethylhydrazine (See Table II for Details). Trimethylhydrazine, dissolved in ether, was placed into a nitrogen-swept three-necked flask equipped with a condenser, mechanical stirrer, and a pressure-equalized dropping funnel. Ethereal chloramine, either in ammonia-free form or in the stable solution described above, was added dropwise with stirring. After addition was complete, stirring was continued for 3 h after which time all of the chloramine had reacted. The reaction mixture was then filtered.

Reaction of Ammonia-Free Chloramine with Trimethylhydrazine in Acetonitrile. Ammonia-free chloramine (35 mmol dissolved in 130 mL of ether) was mixed with 200 mL of acetonitrile in a nitrogen-swept flask cooled in an ice bath. Trimethylhydrazine, 0.3 mL (31 mmol) in 100 mL of acetonitrile, was added dropwise with stirring. A white solid began forming immediately. Stirring was continued for 2 h after addition of trimethylhydrazine was complete; the mixture was then allowed to stand overnight. The white solid, collected by filtration, was found to consist entirely of ammonium chloride. The solvent was removed from the filtrate under reduced pressure leaving a small amount of an oily residue which could not be further characterized.

Identification of 2,2-Dimethyltriazanium Chloride. After each mixture was filtered, the solid products were washed with ether and dried under vacuum. Samples of from 50 to 200 mg were dissolved in 1 M sulfuric acid and titrated iodometrically[14] to determine the amount of triazanium salts present (1 mol of triazanium ions oxidizes 2 mol of iodide). Ammonium chloride, identified by its infrared spectrum, was the only solid product formed in reactions where ammonia-free solutions of chloramine were added dropwise to ethereal trimethylhydrazine.

Table I. Nuclear Magnetic Resonance Spectral Peaks of Reactants and Products of This Study

	Solvent	τ peak 1, ppm	τ peak 2, ppm	Ratio of peak areas: 1/2
2,2-Dimethyltriazanium chloride, $[(CH_3)_2N^+(NH_2)_2]Cl^-$	Me_2SO-d_6	3.23 (NH_2)	6.43 (CH_3)	4/6
2,2-Dimethyltriazanium iodide, $[(CH_3)_2N^+(NH_2)_2]I^-$	Me_2SO-d_6	3.62 (NH_2)	6.42 (CH_3)	4/6
Dimethylhydrazone of formaldehyde, $(CH_3)_2NN{=}CH_2$	$CDCl_3$	3.17 (CH_3)	7.20 (CH_3)	2/6
Trimethylhydrazine, $(CH_3)_2NNH(CH_3)$	$CDCl_3$	7.48 (CH_3)	7.62 (CH_3)	3/6/(1)[a]
Tetramethyl-2-tetrazene, $(CH_3)_2NN{=}NN(CH_3)_2$	$CDCl_3$	7.19 (CH_3)		

[a] NH peak appears at τ 7.78 ppm.

Table II. Reaction Conditions and Amounts of Products Formed in Chloraminations

	Amt of reactant, mmol	Amt of NH_2Cl, mmol	Solvent	Products	Amt of product
Trimethylhydrazine	9	25[a]	Ether	Dimethylhydrazone of formaldehyde 2,2-Dimethyltriazanium chloride	0.69 mol/mol of trimethylhydrazine 0.09 mol/mol of NH_2Cl
Trimethylhydrazine	7	6[b]	Ether	Dimethylhydrazone of formaldehyde	0.96 mol/mol of NH_2Cl
Trimethylhydrazine	23	16[c]	Ether	Dimethylhydrazone of formaldehyde	0.62 mol/mol of NH_2Cl
Trimethylhydrazine	9	25[a]	Acetonitrile	2,2-Dimethyltriazanium chloride	0.66 mol/mol of trimethylhydrazine
Dimethylhydrazone of formaldehyde	23	50[a]	Ether	2,2-Dimethyltriazanium chloride	0.11 mol/mol of dimethylhydrazone
Dimethylhydrazone of formaldehyde	23	50[a]	Acetonitrile	2,2-Dimethyltriazanium chloride	0.09 mol/mol of dimethylhydrazone
Tetramethyl-2-tetrazene	8	25[a]	Acetonitrile	2,2-Dimethyltriazanium chloride	0.64 mol/mol of tetramethyl-2-tetrazene

[a] Generator effluent bubbled through solution of reactant. [b] Chloramine, in stable solution not made ammonia-free, added dropwise to ethereal trimethylhydrazine. [c] Ammonia-free chloramine added dropwise to ethereal trimethylhydrazine.

The solids which contained triazanium ions were extracted into boiling 3:1 acetone:ethanol mixtures. When the solutions had cooled, ether was added to reprecipitate the extracted materials which were collected by filtration. These solids were all identified as 2,2-dimethyltriazanium chloride by their infrared and NMR spectra and melting points which were identical with those of an authentic sample of 2,2-dimethyltriazanium chloride. The nonextractable solid remaining was identified as ammonium chloride.

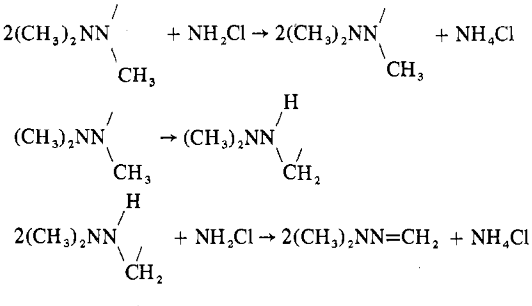
Identification of the Dimethylhydrazone of Formaldehyde. After chloramination had been completed, aliquots of the ethereal solutions from the trimethylhydrazine–chloramine reactions were analyzed by gas–liquid chromatography to determine products present. The only peak found in each chromatogram (in addition to that of unreacted trimethylhydrazine) appeared at the retention time expected for the peak of the dimethylhydrazone of formaldehyde. An authentic sample of the latter compound added to these solutions caused the area of this peak to increase. After the solids were removed by filtration, enough ether was distilled from each solution to reduce the volume to ca. 10 mL, the infrared spectrum of this solution was found to contain a peak at 1585 cm^{-1} characteristic of the C=N stretch of the dimethylhydrazone of formaldehyde[15] and the NMR spectrum of this solution contained peaks consistent with those found in the NMR spectrum of the dimethylhydrazone of formaldehyde.

Reactions of 2,2-Dimethyltriazanium Chloride with Alkylating Agents. 2,2-Dimethyltriazanium chloride, 0.45 g (4.0 mmol), was dissolved in 15 mL of absolute ethanol in a nitrogen-swept flask equipped with a magnetic stirrer and a reflux condenser. After 3 mL of methyl iodide was added, the solution was refluxed for 1 h. After the solution had cooled, ether was added to precipitate the solid product. This solid was collected by filtration and recrystallized from a 3:1 acetone:ethanol mixture. Anal. Calcd for $C_2H_{10}N_3I$: C, 11.82; H, 4.93; N, 20.69. Found: C, 11.82; H, 4.96; N, 20.69. Melting points: lit.[5] for 2,2-dimethyltriazanium iodide, 181 °C dec; found, 169–170 °C dec.

Under the same conditions 2,2-dimethyltriazanium iodide was the only triazanium salt obtained from the reaction of 2,2-dimethyltriazanium chloride with ethyl iodide. Attempts to react 2,2-dimethyltriazanium chloride with ethyl bromide under the same conditions were successful; the starting material was recovered unchanged.

Results and Discussion

The principal product of all three reactions of trimethylhydrazine with chloramine in ether was the dimethylhydrazone of formaldehyde and ammonium chloride. It is not certain whether the small amount of 2,2-dimethyltriazanium chloride, 0.09 mol/mol of trimethylhydrazine, formed in the reaction run on the generator, is a product of the chloramination of trimethylhydrazine or of the dimethylhydrazone of formaldehyde. Chloramination of the latter compound in ether also resulted in formation of small amounts of 2,2-dimethyltriazanium chloride, 0.11 mol/mol of dimethylhydrazone. The following mechanism is proposed for the formation of the dimethylhydrazone of formaldehyde from trimethylhydrazine:



$$2(CH_3)_2N\overset{H}{\underset{CH_3}{N}} + NH_2Cl \rightarrow 2(CH_3)_2N\overset{}{\underset{CH_3}{N}} + NH_4Cl \quad (1)$$

$$(CH_3)_2N\overset{}{\underset{CH_3}{N}} \rightarrow (CH_3)_2N\overset{H}{\underset{CH_2}{N}} \quad (2)$$

$$2(CH_3)_2N\overset{H}{\underset{CH_2}{N}} + NH_2Cl \rightarrow 2(CH_3)_2NN{=}CH_2 + NH_4Cl \quad (3)$$

Steps 1 and 3 are considered reasonable because abstractions of amino hydrogens by chloramine are well-known. For example, tetramethyl-2-tetrazene, also a product of the chloramination of 1,1-dimethylhydrazine, is believed[14] to be formed by the coupling of two molecules of $(CH_3)_2N{=}N$

which are formed through the abstraction of the amino hydrogens of 1,1-dimethylhydrazine by chloramine. The transfer shown in step 2 of a hydrogen atom from the carbon to the adjacent nitrogen is postulated on the ability of amino radicals to abstract hydrogen atoms from carbons. For example, it has been shown that amino radicals abstract hydrogens from olefins rather than adding to double bonds.[16]

In contrast to the chloramination of trimethyhydrazine, good yields of products of both nucleophilic substitution (2,2-dimethyltriazanium chloride) and hydrogen abstraction (tetramethyl-2-tetrazene) can be obtained by chloramination of 1,1-dimethylhydrazine[14] in ether which indicates that the two reactions occur at comparable rates. The absence of 1,2,2-trimethyltriazanium chloride, the expected substitution product, is evidence that the rate of nucleophilic substitution of trimethylhydrazine or chloramine in ether is much slower than the rate of abstraction of the amino hydrogen. We believe that the rate of substitution of chloramine is slower for trimethylhydrazine than for 1,1-dimethylhydrazine because trimethylhydrazine is a weaker nucleophile. Although nucleophilicities of these compounds have not been measured, trimethylhydrazine is a weaker base than 1,1-dimethylhydrazine (pK's are 6.79 and 7.44, respectively).[17] Relative basicity is not a reliable measure of relative nucleophilicity in cases where a less basic atom is more polarizable than a more basic one or where the more basic atom is more sterically hindered. However, it is reasonable to assume that the greater basicity of 1,1-dimethylhydrazine is evidence of greater nucleophilicity because polarizabilities of the two compounds are likely to be similar and because trimethylhydrazine, the compound with more steric crowding, is the weaker base.

Trimethylhydrazine was chloraminated in acetonitrile to determine whether there would be changes in reaction products if chloramination occurred in a more polar solvent. When trimethylhydrazine in acetonitrile was treated with the ammonia–chloramine effluent from the generator, the major product formed was 2,2-dimethyltriazanium chloride, the amount of 2,2-dimethyltriazanium chloride produced being much greater than when trimethylhydrazine is chloraminated in ether, 0.66 mol/mol of trimethylhydrazine compared with 0.09 mol/mol of trimethylhydrazine, respectively. In contrast, the yield of 2,2-dimethyltriazanium chloride obtained from the chloramination of the dimethylhydrazine of formaldehyde remains essentially unchanged regardless of whether the dimethylhydrazone of formaldehyde is chloraminated in ether or in acetontrile (0.09 mol/mol of dimethylhydrazone and 0.11 mol/mol of dimethylhydrazone, respectively).

The formation of 2,2-dimethyltriazanium chloride from trimethylhydrazine in acetontrile must proceed through formation of an intermediate product followed by reaction of this intermediate with chloramine or ammonia. The higher yield of 2,2-dimethyltriazanium chloride resulting from chloramination of trimethylhydrazine than from chloramination of the dimethylhydrazone of formaldehyde in acetontrile implies that the intermediate is mostly, if not entirely, a species other than the dimethylhydrazone of formaldehyde.

According to Utvary,[18] 2,2-dimethyltriazanium chloride is also formed by the reaction in ether of a chloramine–ammonia mixture with tetramethyl-2-tetrazene. In order to consider the possibility that tetramethyl-2-tetrazene is the intermediate in the chloramination of trimethylhydrazine in acetonitrile, tetramethyl-2-tetrazene in acetonitrile was chloraminated with the generator effluent. The amount of 2,2-dimethyltriazanium chloride found, 0.64 mol/mol of tetramethyl-2-tetrazene, is approximately half the amount found when trimethylhydrazine is chloraminated since 2 mol of trimethylhydrazine would be required to form 1 mol of tetramethyl-2-tetrazene. Therefore, it is reasonable to assume that the intermediate in the formation of 2,2-dimethyltriazanium chloride from trimethylhydrazine is not tetramethyl-2-tetrazene.

In an attempt to isolate the intermediate in this reaction, trimethylhydrazine was allowed to react with ammonia-free chloramine in acetonitrile. No 2,2-dimethyltriazanium chloride was found. The absence of 2,2-dimethyltriazanium chloride from the ammonia-free reaction is evidence that ammonia is necessary for the formation of 2,2-dimethyltriazanium chloride.

A feasible, although speculative, mechanism for the formation of 2,2-dimethyltriazanium chloride from the chloramination of trimethylhydrazine in acetonitrile in the presence of ammonia can be postulated which involves the formation of 1,2,2-trimethyltriazanium chloride followed by transamination.

$$(CH_3)_2NNH(CH_3) + NH_2Cl \rightarrow [(CH_3)_2N(NH_2)(NH(CH_3))]Cl \tag{4}$$

$$[(CH_3)_2N(NH_2)(NH(CH_3))]Cl + NH_3 \rightarrow [(CH_3)_2N(NH_2)_2]Cl + CH_3NH_2 \tag{5}$$

Nucleophilic substitution followed by transamination has been suggested as a mechanism for the formation of 2,2-dimethyltriazanium chloride from the reaction of 2-dimethylamino-1,3,2-dioxophospholane with the chloramine–ammonia generator effluent.[19]

Reaction of 2,2-Dimethyltriazanium Chloride with Alkylating Agents

We unsuccessfully attempted to prepare 1,1,2-trialkyltriazanium salts by alkylation of 2,2-dimethyltriazanium chloride using methyl and ethyl bromide both at room and at elevated temperatures. At room temperature no reaction occurred and the 2,2-dimethyltriazanium chloride was recovered unchanged. Refluxing an ethanolic solution of ethyl bromide and 2,2-dimethyltriazanium chloride also did not effect any reaction; refluxing 2,2-dimethyltriazanium chloride with methyl and ethyl iodide resulted in formation of 2,2-dimethyltriazanium iodide. This compound has been previously prepared by adding potassium iodide to 2,2-dimethyltriazanium chloride in liquid ammonia.[5]

The inertness of the terminal nitrogens of 2,2-dimethyltriazanium chloride toward alkylation by alkyl halides is also characteristic of terminal nitrogens in quaternary hydrazinium salts. For example, methyl iodide does not alkylate 1,1,1-trimethylhydrazinium iodides; no reaction occurs except under extreme conditions where the hydrazinium salt decomposes.[20]

Although the attempt to react 2,2-dimethyltriazanium chloride with alkyl halides did not result in alkylation at the terminal nitrogens, it did further point out the previously discussed[1] resemblence of 2,2-dialkyltriazanium salts to 1,1,1-trialkylhydrazinium salts.

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Registry No. $[(CH_3)_2N^+(NH_2)_2]Cl^-$, 13166-44-4; $(CH_3)_2N^+(NH_2)_2$, 44025-19-6; $(CH_3)_2NN{=}CH_2$, 2035-89-4; $(CH_3)_2NNH(CH_3)$, 1741-01-1; $(CH_3)_2NN{=}NN(CH_3)_2$, 6130-87-6; NH_2Cl, 10599-90-3; $[(CH_3)_2N^+(NH_2)_2]I^-$, 20446-73-5.

References and Notes

(1) T. J. Giordano, G. J. Palenik, and H. H. Sisler, *Inorg. Chem.*, **15**, 751 (1976).
(2) K. Utvary and H. H. Sisler, *Inorg. Chem.*, **5**, 1835 (1966).
(3) K. Utvary and H. H. Sisler, *Inorg. Chem.*, **7**, 698 (1968).
(4) K. Utvary, *Monatsh. Chem.*, **99**, 1473 (1969).
(5) K. Utvary, *Monatsh. Chem.*, **99**, 1483 (1968).
(6) K. Utvary, *Monatsh. Chem.*, **99**, 2324 (1968).
(7) K. Utvary, H. H. Sisler, and P. Kitsmantel, *Monatsh. Chem.*, **100**, 401 (1969).

(8) R. M. Kren, private communication, 1974.
(9) H. M. McNair and E. J. Bonelli, "Basic Gas Chromatography", Varian Aerograph, Walnut Creek, Calif., 1969, Chapter VII.
(10) J. B. Class, J. G. Aston, and T. S. Oakwood, *J. Am. Chem. Soc.*, **75**, 2937 (1953).
(11) W. E. Bull, J. A. Seaton, and L. F. Audrieth, *J. Am. Chem. Soc.*, **80**, 2516 (1958).
(12) R. Mattair and H. H. Sisler, *J. Am. Chem. Soc.*, **73**, 1619 (1951).
(13) I. T. Gilson and H. H. Sisler, *Inorg. Chem.*, **4**, 273 (1965).
(14) H. H. Sisler, R. M. Kren, and K. Utvary, *Inorg. Chem.*, **8**, 2007 (1969).
(15) R. H. Wiley, S. C. Slaymaker, and H. Kraus, *J. Org. Chem.*, **22**, 204 (1957).
(16) H. Prakash and H. H. Sisler, *J. Org. Chem.*, **35**, 3111 (1970), and references therein.
(17) R. I. Hinman, *J. Org. Chem.*, **23**, 1587 (1958).
(18) K. Utvary, unpublished results, 1970.
(19) S. E. Frazier and H. H. Sisler, *Inorg. Chem.*, **11**, 1223 (1972).
(20) C. Harries and T. Haga, *Ber. Dtsch. Chem. Ges.*, **31**, 56 (1898).

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Core Electron Binding Energies of Cyclotriphosphazenes and Cyclotetraphosphazenes

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The core electron binding energies of $(NPF_2)_3$, $(NPF_2)_4$, $(NPCl_2)_3$, $(NPCl_2)_4$, and $[NP(CH_3)_2]_4$ have been determined in the gas phase by x-ray photoelectron spectroscopy. The data show a reasonable correlation with the eleconegativities of the substituent groups. On going from $(NPF_2)_4$ to $(NPF_2)_3$ or from $(NPCl_2)_4$ to $(NPCl_2)_3$, the binding energies increase by only 0.22 eV or less. This near-constancy of the binding energies suggests that the degree π bonding is similar in the trimers and tetramers.

The cyclophosphazenes are often cited as examples of inorganic aromatic systems.[3] A large number of experimental data, including structural parameters,[4] ionization potentials,[5,6] and mass spectrometric fragmentation patterns,[7] have been interpreted in terms of the presence of delocalized π bonding in the rings. Any increase in the degree of this π bonding involves the transfer of negative formal charge from the ring nitrogen atoms to the phosphorus atoms or to substituent groups on the phosphorus atoms. Therefore the atomic core electron binding energies should be sensitive to the degree of π bonding.

In this study we have used x-ray photoelectron spectroscopy to determine the core electron binding energies of $(NPF_2)_3$, $(NPF_2)_4$, $(NPCl_2)_3$, $(NPCl_2)_4$, and $[NP(CH_3)_2]_4$ in the gas phase in an attempt to provide experimental information related to the bonding arrangements in these compounds.

Results and Discussion

The core binding energies of the phosphazenes and, for comparison, some phosphorus halides and oxyhalides, are listed in Table I. Most of the differences in the core binding energies of the compounds in Table I can be qualitatively interpreted in terms of differences in atomic charges. For example, the increases in the P $2p_{3/2}$ and N 1s binding energies in the series $[NP(CH_3)_2]_4 < (NPCl_2)_{3,4} < (NPF_2)_{3,4}$ probably correspond to increasing positive charge on the phosphorus atoms and decreasing negative charge on the nitrogen atoms and reflect relative electronegativities of the methyl group, chlorine, and fluorine. Similarly, the P $2p_{3/2}$ binding energy shifts between $(PNX_2)_{3,4}$ and the compounds PX_3 and POX_3 can be rationalized in terms of electronegativities. The similarity of the P $2p_{3/2}$ binding energies of the fluorophosphazenes and PF_3 shows that the two nitrogen atoms attached to a phosphorus atom in a cyclophosphazene are essentially equivalent in their combined electron-withdrawing power to one fluorine atom. Although the phosphorus atom in POF_3 has the same coordination number as that in a fluorophosphazene, the four highly electronegative ligand atoms in POF_3 make the phosphorus atom much more positively charged than a phosphorus atom in a fluorophosphazene, where two of the ligand atoms are nitrogen atoms (with relatively low electronegativities). Thus we can understand why the P $2p_{3/2}$ binding energy of POF_3 is by far the highest listed in Table I. The two nitrogen atoms bonded to a phosphorus atom in a phosphazene have slightly more combined electron-withdrawing power than one chlorine atom; hence the P $2p_{3/2}$ binding energy of PCl_3 is slightly less than that of the chlorophosphazenes. As expected, the high electronegativity of oxygen causes the P $2p_{3/2}$ binding energy of $POCl_3$ to be considerably greater than that of the chlorophosphazenes.

The shifts in the phosphorus, nitrogen, and halogen binding energies on going from a tetrameric phosphazene to the corresponding trimer are quite small (0.22 eV or less), and the significance of these shifts is not as obvious as in the cases just discussed. It has been shown that a core binding energy, E_B, can be represented as a sum of three terms[8,9]

$$E_B = (kQ + l) + V - E_R$$

The first term is a linear function of the atomic charge, Q; the second term, V, is the electrostatic potential due to the other charged atoms in the molecule, and the third term, $-E_R$, is the negative of the relaxation energy associated with the migration of electron density toward the core hole. The data in Table I show that, in the change from a tetramer to the corresponding trimer, an increase occurs in the binding energies of all the corresponding atoms. Because the charges of *all* the atoms cannot become more positive on going from a tetramer to a trimer (the sum of the charges must remain zero), we infer that the sum of the second and third terms must change in the case of at least one of the atoms. Unfortunately, our present understanding of methods of calculating V and E_R is too poor to account for chemical shifts as small as 0.1 or 0.2 eV. However, if we make the assumption that the observed shifts are entirely due to changes in the values of Q, we can, using estimated k values,[10] calculate that the changes in the atomic charges are the following: for phosphorus, 0.01; for nitrogen, 0.01; for fluorine, 0.01; for chlorine, 0.02. It is reasonable to assume that the actual changes in the charges are not much greater than these values. Therefore, we conclude that the atomic charges in the trimeric cyclophosphazenes differ very little (probably less than 0.02 unit) from those in the corresponding tetrameric compounds.

One model of the bonding in cyclophosphazenes is based on the assumption that the $2p\pi$ orbitals of the nitrogen atoms and the $3d\pi$ (and perhaps the $4p\pi$) orbitals of the phosphorus atoms are at least partly involved in ring π bonding and that the 3s and 3p orbitals of each phosphorus atom are completely