

hydrochloric acid) in pentane, and the solvent was removed. The residue was fractionally sublimed at 100 °C (0.05 torr), and a portion of the sublimate was found to contain $[\text{N}_3\text{P}_3(\text{OH})(\text{OCH}_2\text{CF}_3)_3]$,¹⁸ identified by ³¹P NMR methods and by mass spectrometry. A parent ion was found at 647 au (calcd. for $[\text{N}_3\text{P}_3(\text{O}_6\text{C}_{10}\text{H}_{11}\text{F}_3)]$, 647).

Reactions of $[\text{N}_3\text{P}_3(\text{ONa})\text{Cl}_3]$ (16) with Amines. Under nitrogen, a stirred solution of the intermediate $[\text{N}_3\text{P}_3(\text{ONa})\text{Cl}_3]$ (prepared as described above) at 0 °C was treated with an excess of methylamine (>100 mL), added by means of a dry ice condenser. After 48 h, the solvent was removed with the use of a rotary evaporator. Water was added to the residue, and the mixture was centrifuged. The oil layer was removed. A ³¹P NMR spectrum of the aqueous layer was compatible with an A₃ spin system plus an AB₂ spin system. These were consistent with the structures $[\text{NP}(\text{NHCH}_2)_3]$ and $[\text{N}_3\text{P}_3(\text{ONa})(\text{NHCH}_2)_3]$, respectively.

Similarly, ammonia (>100 mL) or a filtered solution of ethyl glycinate at 0 °C (prepared from a boiling mixture of glycine ethyl ester hydrochloride (12 equiv, 4.81 g, 0.0138 mol) in triethylamine (30 g, 0.297 mol) after 4 h at reflux followed by cooling by means of an ice bath) was added to a stirred solution of the intermediate 16 under nitrogen at 0 °C. After a 48-h reaction, the solvent was removed. Water was added, and, after centrifugation, the oil was removed from the mixture. Part of the ³¹P NMR spectrum of the aqueous layer was interpreted as an AB₂ spin system assigned to the structures $[\text{N}_3\text{P}_3(\text{ONa})(\text{NH}_2)_3]$ or $[\text{N}_3\text{P}_3(\text{ONa})(\text{NHCH}_2\text{COOC}-\text{H}_2\text{CH}_3)_3]$, respectively. When treated with methylamine at 0 °C, the latter compound in tetrahydrofuran (50 mL) was converted to $[\text{N}_3\text{P}_3(\text{ONa})(\text{NHCH}_2\text{CONHCH}_3)_3]$, as identified by ³¹P NMR spectroscopy (see Table I). The preparation of the hydrolysis intermediate $[\text{N}_3\text{P}_3(\text{OH})(\text{N}_2\text{C}_3\text{H}_3)_3]$ (imidazolyl), from the reaction between 16 and imidazole, is described elsewhere.¹⁹

Preparation of Poly[bis(methylglycinamido)phosphazene], $[\text{NP}(\text{NHCH}_2\text{CONHCH}_3)_2]_n$. The polymer $[\text{NP}(\text{NHCH}_2\text{COOCH}_2\text{CH}_3)_2]_n$ ¹⁰ (2.50 g, 0.001 mol) was dissolved in tetrahydrofuran (150 mL) and was cooled to 0 °C by means of an ice bath.

To this solution was added methylamine (150 mL) by means of a dry ice condenser. The methylamine was retained in the reaction vessel for 4 h. It was then allowed to volatilize and escape in a stream of nitrogen over a period of 16 h. The solvent was removed with the use of a rotary evaporator. The solid residue was washed with petroleum ether and was reprecipitated twice from 2-propanol into petroleum ether. The resultant white polymer (>30% yield) had a glass transition temperature (by thermomechanical analysis) of 36 °C. A ³¹P NMR spectrum and the microanalytical data were compatible with the structure $[\text{NP}(\text{NHCH}_2\text{CONHCH}_3)_2]_n$. A ¹³C NMR spectrum of the material was similar to that of $[\text{NP}(\text{NHCH}_2\text{CONHCH}_3)_2]_3$ (5). Anal.²⁴ Calcd for $[\text{NP}(\text{NHCH}_2\text{CONHCH}_3)_2]_n$: C, 32.88; H, 6.39; N, 31.96; P, 14.16; Cl, 0.0. Found: C, 32.90; H, 6.43; N, 31.86; P, 14.09; Cl, 0.15.

Hydrolysis of Poly[(amino)phosphazenes]. An aqueous solution of polymers $[\text{NP}(\text{NHR})_2]_n$ (where $n \approx 10000$) (0.03 M) was treated as described previously. The resultant polymers were then characterized by ³¹P NMR spectrometry.

Acknowledgment. This work was supported by the National Institutes of Health through Grant No. HL 11418.

Registry No. 2, 13597-92-7; 3, 1635-63-8; 4, 79839-15-9; 5, 79839-16-0; 6, 74868-58-9; 7, 58419-88-8; 8, 79839-17-1; 9, 13264-13-6; 10, 79839-18-2; 11, 4864-72-6; 12, 2277-98-7; 13, 53521-33-8; 14, 940-71-6; 16, 75283-92-0; 18, 24524-93-4; 20, 79839-19-3; 21, 79839-20-6; $\text{N}_3\text{P}_3(\text{NH}_2)_3\text{OH}$, 79839-21-7; $\text{N}_3\text{P}_3(\text{NHCH}_3)_3\text{ONa}$, 75267-53-7; $\text{N}_3\text{P}_3(\text{NHCH}_3)_3\text{OH}$, 75267-52-6; $\text{N}_3\text{P}_3(\text{OCH}_2\text{CF}_3)_3$, 1065-05-0; $\text{N}_3\text{P}_3(\text{OCH}_2\text{CF}_3)_3\text{OH}$, 35825-49-1; $\text{N}_3\text{P}_3(\text{NHCH}_2\text{CONHCH}_3)_3(\text{ONa})$, 79839-22-8; $[\text{NP}(\text{NHCH}_2)_2]_n$, 40101-94-8; $[\text{NP}(\text{NHCH}_2\text{COOCH}_2\text{CH}_3)_2]_n$, 79839-05-7; $[\text{NP}(\text{NHCH}_2\text{CONHCH}_3)_2]_n$, 79839-06-8; $(\text{NPCl}_2)_n$, 26085-02-9; imidazole, 288-32-4; glycine ethyl ester HCl, 623-33-6; methylamine, 74-89-5; trifluoroethylamine HCl, 373-88-6; benzylamine, 100-46-9; pyrrole, 109-97-7; pyrrolidine, 123-75-1; morpholine, 110-91-8; triphenylsilanol, 791-31-1; sodium trifluoroethoxide, 420-87-1.

Contribution from the Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794

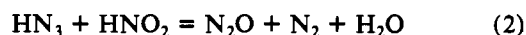
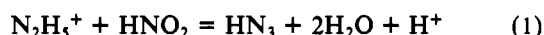
Cyclic Azide as an Aqueous Solution Intermediate: Evidence Pro and Con¹

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Received July 13, 1981

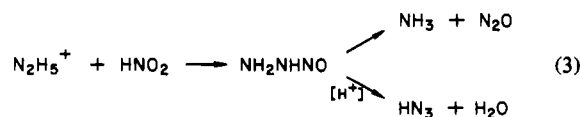
Isotope tracer experiments on the reaction between H^{15}NO_2 and N_2H_5^+ corroborate the existence of separate high- and low-acidity pathways. Experiments at 0.60 M H^+ , with $([\text{HNO}_2]/[\text{N}_2\text{H}_5^+])_0 = 2.0$, yield N_2O and N_2 of the isotopic composition predicted for N-atom scrambling caused by a cyclic azide intermediate, but these data and others at different stoichiometric ratios can also be interpreted as mixtures of reaction products resulting from double nitrosation and linear azide pathways. No evidence of photochemical cyclization of linear azide in solution was found in irradiation experiments, although it has been reported to occur in alkali-metal azide crystals.

The products of the hydrazine-nitrous acid reaction have long been known to include NH_3 , HN_3 , N_2 , and N_2O . In acid solution, it has been established that HN_3 is the virtually exclusive product, with N_2 and N_2O resulting from a rapidly sequential HN_3 - HNO_2 reaction:^{2,3}



Perrott, Stedman, and Uysal³ established that reactions 1 and

2 constitute a limiting (high-acidity) pathway and postulated that NH_3 and directly formed N_2O arise from a competing pathway whose importance increases with decreasing acidity:



An isotopic tracer study of the reaction between ^{15}N -labeled hydrazine ($^{15}\text{N}_2\text{H}_5^+$) and excess nitrous acid, presenting evidence for a cyclic azide intermediate species, has recently been reported from the University College of Swansea.⁴ An in-

(1) Research supported by the National Science Foundation, Grant No. 78-24176.

(2) Biddle, P.; Miles, J. H. *J. Inorg. Nucl. Chem.* 1968, 30, 1291.

(3) Perrott, J. R.; Stedman, G.; Uysal, N. *J. Chem. Soc., Dalton Trans.* 1976, 2058.

(4) Phelan, K. G.; Stedman, G. *J. Chem. Soc., Chem. Commun.* 1981, 299.

dependent investigation of the same reaction, using H^{15}NO_2 , was under way in this laboratory when the Swansea work came to our attention. We report here the results of this study, which was extended to conditions which make it complementary to the labeled hydrazine study. We also report unsuccessful efforts to achieve cyclization of aqueous linear azide by photochemical means. K.G.P. has participated in these studies in both laboratories.

Experimental Section

Reactions were carried out in Y-shaped vessels, employing vacuum-line techniques. Degassed solutions of reactants (5.0 mL each) were mixed by rotation of the vessel. In general, the reactant present in excess was added to the other reactant; however, experiment showed that the results were unaffected by the order of mixing. After the reaction had been allowed to go essentially to completion, the solution medium was frozen at dry-ice temperature; and the gas products were transferred to sample bulbs for analysis. For gas chromatography, the entire gas mixture was collected by Toepfer pump. For mass spectrometry, gas products were separated by condensing N_2O at 77 K, followed by Toepfer pump collection of N_2 and distillation of N_2O . In excess N_2H_5^+ , however, the gas phase was found to include HN_3 , and so that interference with the mass spectrometry could be prevented, an ethyl acetate slush bath (189.6 K) was used to hold it back.

Gas chromatographic analyses were performed with a vacuum-line-GC interface and, in one instance, CF_4 as internal reference gas.⁵ Mass spectrometry was carried out on an AEI MS-30 mass spectrometer.⁶

All results reported for the $\text{N}_2\text{H}_5^+ - \text{HNO}_2$ reaction were carried out with a fixed starting concentration $[\text{NaNO}_2] = 5.00 \times 10^{-3}$ M. The concentration of hydrazine was varied between the limits 5.00×10^{-4} and 5.00×10^{-2} M. The acidity was established by inclusion of H_2SO_4 , whose concentration was varied from 5.0×10^{-4} to 0.300 M. During the freeze-pump-thaw procedure, the acid was always contained with the hydrazine, to avoid losses due to HNO_2 disproportionation. For tracer experiments, $\text{Na}^{15}\text{NO}_2$ at 32.35% ^{15}N (Stohler) was employed (assay based on $\text{HNO}_2 - \text{HN}_3$ reaction).

Irradiation experiments were carried out with end-labeled KNN^{15}N , labeled position at 99.4% ^{15}N (Prochem). Solutions of KN_3 and HClO_4 (as needed, depending upon the desired acidity of the final mixture) were separately deaerated. The photochemical reaction cell (cylindrical, 29 mm, silica) was flushed with He and sealed with a septum cap; reactant solutions were then introduced into the cell with He-flushed syringes. Irradiation was carried out with a 450-W xenon lamp at a distance of 65 cm, the beam being filtered only with H_2O to remove IR wavelengths. Following irradiation, reaction between irradiated azide solutions and equimolar quantities of isotopically normal nitrite in 0.6 M H^+ (eq 2) was carried out, using vacuum-line techniques. The product gases N_2O and N_2 were then separated and isotopically analyzed.

Azide solutions are known to undergo photolysis;⁷ the products include N_2H_4 and NH_2OH , either or both of which could interfere with our use of reaction 2 for isotopic analysis of azide. After each irradiation the reaction product mixture was therefore allowed to stand in 1 M NaOH solution for 24 h, effecting complete oxidative decomposition of N_2H_4 ⁸ and at least partial decomposition of NH_2OH .⁹ In any event NH_2OH could not interfere seriously, since the reactivity of HNO_2 is known to be very much less toward NH_3OH^+ than toward HN_3 .¹⁰ Furthermore, control experiments indicated that no more than 5% of total azide present underwent photolysis under the conditions of our experiments, so that the possibility of error from this source was small.

Results and Discussion

$\text{N}_2\text{O}-\text{N}_2$ Product Ratios. Results of gas chromatographic analyses of reaction products at high acidity and changing

Table I. $\text{N}_2\text{O}/\text{N}_2$ Product Ratios for the Hydrazine-Nitrous Acid Reaction under Varying Conditions

(1) High-Acidity, Varying Reactant Ratio						
$(n_{\text{N}_2\text{H}_4}/n_{\text{HNO}_2})^0$	10	10	1.0	0.50	0.50	0.10
$[\text{H}_2\text{SO}_4]$ (M)	0.30	0.30	0.30	0.50	0.25	0.30
$n_{\text{N}_2\text{O}}/n_{\text{N}_2}$	1.08	1.06	1.06	0.965	1.04	1.05
(2) High Reactant Ratio, Varying Acidity $(n_{\text{N}_2\text{H}_4}/n_{\text{HNO}_2})^0 = 10.0$						
$[\text{H}_2\text{SO}_4]$ (M)	0.30	0.30	0.20	0.13	0.025	0.005
$n_{\text{N}_2\text{O}}/n_{\text{N}_2}$	1.08	1.06	1.21	1.60	2.24	4.19
(3) Low Reactant Ratio, Varying Acidity $(n_{\text{N}_2\text{H}_4}/n_{\text{HNO}_2})^0 = 0.50$						
$[\text{H}_2\text{SO}_4]$ (M)	0.50	0.25	0.050	0.025	0.0050	0.0005
$n_{\text{N}_2\text{O}}/n_{\text{N}_2}$	0.965	1.04	1.23	1.42	1.88	3.18

Table II. Calculated Mass Spectra

	low acidity	linear azide	cyclic azide
N_2O {			
46	0.0025	0.0539	0.0368
45	0.3242	0.3805	0.3617
44	0.6726	0.5647	0.6006
% ^{15}N (N_2O)	16.47	24.44	21.78
% ^{15}N (N_2)	a	8.40	11.10

^a No N_2 expected.

Table III. Mass Spectrometry, Low-Acidity Product

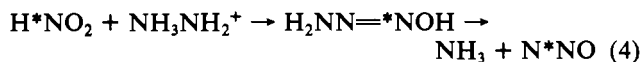
	$n_{\text{N}_2\text{H}_4}/n_{\text{HNO}_2} = 10$ $[\text{H}_2\text{SO}_4] = 0.0025$ M	$n_{\text{N}_2\text{H}_4}/n_{\text{HNO}_2} = 10$ $[\text{H}_2\text{SO}_4] = 0.0025$ M	$n_{\text{N}_2\text{H}_4}/n_{\text{HNO}_2} = 0.50$ $[\text{H}_2\text{SO}_4] = 0.0020$ M
N_2O {			
46	0.0024	0.0057	0.0179
45	0.3261	0.3339	0.3400
44	0.6716	0.6604	0.6420
% ^{15}N (N_2O)	16.55	17.27	18.79
% ^{15}N (N_2)	a	a	9.21

^a N_2 yield insufficient for isotopic analysis.

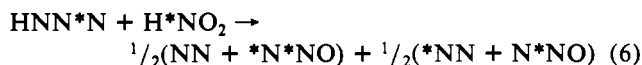
reactant ratio, and at two different reactant stoichiometric ratios and varying acidity, are shown in Table I. These observations refute an earlier report of a single gas product ratio¹¹ and support the acidity-dependent mixture of pathways represented by eq 3.³ Since our method of mixing is slow in relation to a reaction that is very fast ($R = 668 - 831[\text{H}^+][\text{HNO}_2][\text{N}_2\text{H}_5^+]$),³ we cannot claim that the mixtures of pathways reflected in these ratios are the "true" ones for the conditions explored, but the trends and the existence of extremes are unmistakable.

Calculated Mass Spectra. The isotopic tracer data will be examined against the predicted mass spectra for gases produced along three possible pathway extremes, as follows:

(1) Low-acidity pathway leading to direct N_2O formation



(2) High-acidity pathway leading to linear azide, followed by its reaction with HNO_2



- (5) Pearsall, K. A.; Bonner, F. T. *J. Chromatogr.* **1980**, *200*, 224.
 (6) Stony Brook Mass Spectrometry Facility.
 (7) Shinohara, K.; Shida, T.; Saito, N. *J. Chem. Phys.* **1962**, *37*, 2791.
 (8) Gilbert, E. C. *J. Am. Chem. Soc.* **1929**, *51*, 2744.
 (9) Hughes, M. N.; Nicklin, H. G. *J. Chem. Soc. A* **1971**, 164.
 (10) (a) Morgan, T. D. B.; Stedman, G.; Hughes, M. N. *J. Chem. Soc. B* **1968**, 334. (b) Perrott, J. R.; Stedman, G. *J. Inorg. Nucl. Chem.* **1977**, *39*, 325.

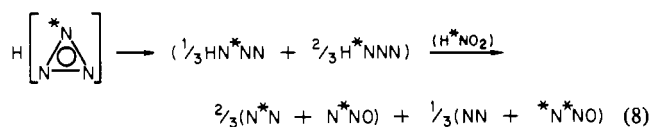
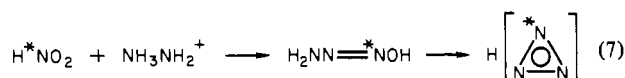
- (11) Koltunov, V. S.; Nikol'shii; Agureev, Yu. P. *Kinet. Catal. (Engl. Transl.)* **1962**, *3*, 764.

Table IV. Mass Spectrometry, High Acidity Products ($[\text{H}_2\text{SO}_4] = 0.30 \text{ M}$)

Expt. No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
$(^{15}\text{N}_2\text{H}_4/^{15}\text{HNO}_2)^0$	10	10	10	10	1.0	0.50	0.50	0.50	0.10	0.10	0.10	0.10	0.10	0.10
N_2O	0.0037	0.0118	0.0070	0.0149	0.0276	0.0369	0.0309	0.0315	0.0363	0.0424	0.0430	0.0407	0.0434	0.0345
	0.3341	0.3357	0.3312	0.3392	0.3535	0.3628	0.3594	0.3550	0.3613	0.3715	0.3768	0.3674	0.3687	0.3631
	0.6622	0.6524	0.6612	0.6459	0.6189	0.6002	0.6098	0.6135	0.6024	0.5860	0.5801	0.5919	0.5880	0.6024
$\% \text{ } ^{15}\text{N}_2\text{O}$	17.08	17.97	17.26	18.45	20.43	21.83	21.06	20.91	21.70	22.82	23.15	22.43	22.77	21.60
$\% \text{ } ^{15}\text{N}_2$	12.4	12.9	a	12.06	10.87	10.48	a	10.33	a	a	a	a	9.36	a

^a Not measured or not reported due to incomplete separation of NO.

(3) Formation of cyclic azide with resultant scrambling of N atoms prior to $\text{HN}_3\text{-HNO}_2$ reaction



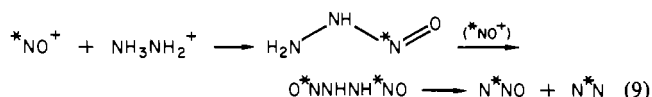
Calculated mass spectra for these three cases, on the basis of the experimental value $^*\text{N} = 0.3235^{15}\text{N}$, 0.6765^{14}N , and with natural abundance ^{15}N , ^{17}O , and ^{18}O taken into account, are shown in Table II.

Tracer Experiments. (A) Low Acidity. Mass spectrometry results for three experiments carried out at low acidity are shown in Table III. The results of the excess hydrazine experiments provide an extremely close match to the mass spectrum predicted for N_2O from the pure low-acidity pathway. Perrott et al.³ report that this pathway is never more than 70% dominant, and the low yield of N_2 in this case indicates that very little reaction between nitrite and HN_3 occurs when hydrazine is in excess. We consider these results to be corroborative of the low-acidity pathway as proposed by Perrott et al.³ The result of the experiment at excess HNO_2 can be interpreted as resulting from addition of $\text{HN}_3\text{-HNO}_2$ reaction product to N_2O that has been produced directly (see eq 3).

(B) High Acidity. These results are reported in Table IV show that under conditions of excess HNO_2 (experiments 6–14) the isotopic composition of N_2O is generally much closer to that predicted for an N-scrambling (i.e., cyclic) intermediate than for linear azide. The experiments carried out at 2:1 excess nitrite, in fact, exhibit an extremely close match to the predicted cyclic azide spectrum (experiments 6–8). The ^{15}N content of product N_2 in these experiments is higher than predicted for linear azide but somewhat less than predicted for the cyclic case. Since 28 is the only peak requiring background correction in these mass spectra, and since the most minor atmospheric contamination of sample would tend to lower the apparent ^{15}N content, the observed and predicted values may be considered to be in reasonable agreement.

The results of experiments 6–8 are complementary to the observations reported for doubly labeled hydrazine,⁴ and taken by themselves they are clearly supportive of the hypothesis of a cyclic azide intermediate. When viewed as part of a continuum in the reaction products between 10-fold excess of hydrazine and 10-fold excess of nitrous acid, however, the situation is not so clear. The N_2O in experiments 1–4 resembles that predicted for the low-acidity pathway (Table II),

but it is clear that it arises from an HN_3 reaction since N_2O and N_2 are in 1:1 ratio (Table I). The ^{15}N content of the N_2 is higher than can be accounted for on any of the postulated routes. These observations could be explained by postulation of a double nitrosation:⁴



The N_2O in this pathway would have very nearly the isotopic content observed in experiments 1–4,¹² identical with the low-acidity pathway. The N_2 ^{15}N content would be 16.2%, i.e., substantially greater than observed, but reasonable if both gases are viewed as resulting from a minor contribution of linear azide pathway to a predominant double nitrosation pathway (eq 9). The results of experiments 5–14 can then be interpreted as indicating an increasing proportion of linear azide pathway in a series of two-pathway mixtures, with increasing excess of HNO_2 . The shift at mass 46 to values >4% and decline of ^{15}N content of N_2 are highly suggestive of such a continuum, and the results at $\text{N}_2\text{H}_4/\text{HNO}_2 = 0.5$, which are apparently in close agreement with a cyclic azide pathway, can be equally well accounted for as such a mixture. (The possibility of such an interpretation was recognized in ref 4.) Thus it is not certain that our results sustain the cyclic intermediate hypothesis, although we are unable to offer a rational explanation for an increase in the double nitrosation pathway with decreasing relative HNO_2 concentration.

Irradiation Experiments. There have been two independent reports of the onset of new sets of IR bands and color centers when alkali-metal azides are irradiated with UV light at low temperatures, phenomena that have been interpreted convincingly as arising from a species with D_{3h} symmetry, i.e., cyclic N_3^- .^{13,14} It therefore seemed reasonable to attempt photochemical promotion of linear azide (K^{15}NNN) into such an excited state in solution, an event whose consequence should be the scrambling of N atoms. Calculated mass spectra for the N_2O product of reaction 2 showed that without scrambling the ^{15}N content should be 25.23% and with complete scrambling it should be 17.02%, with very little mass 46 in either case. The ^{15}N content of N_2 should be 25.13% without and 33.38% with scrambling. A control experiment (without irradiation) gave N_2O and N_2 of a composition in close agreement with the calculated values (unscrambled). Eight irradiation experiments were carried out, with $[\text{N}_3^-]^0 \approx 0.010$

(12) Both here and in the results of Table III, the 31/30 ratio in N_2O is supportive of the N^*NO rather than $^*\text{NNO}$ isotopomer, although there is evidence of substantial electron-impact rearrangement.

(13) Bryant, J. I. *Spectrochim. Acta* 1966, 22, 1475.

(14) Papazian, H. A. *J. Phys. Chem. Solids* 1965, 27, 906; 1968, 30, 462.

M, acidity in the range 3 M to pH 9, and with irradiation times of 2 h in seven experiments and 24 h in one.

The N₂ gas derived from irradiated azide in all these experiments showed no significant increase over the 25% ¹⁵N level, indicating no scrambling of N atoms. The only significant departure from the unscrambled composition observed in N₂O product occurred at high acidity and consisted of an increase at mass 46, giving N₂O of ¹⁵N content greater than 25%, opposite to the trend predicted for N scrambling. (The probable reason for this is the presence of a small residual of photolysis product.)

The irradiation experiments lend no support to the cyclic azide hypothesis but do not rule out the possibility of formation

of such an intermediate species in the reaction sequence eq 1 and 2. While we have observed isotopic evidence in apparently close support of the hypothesis (experiments 6-8; Table IV), these data can be interpreted in an alternative way that seems to provide a more satisfactory view of the entire range of stoichiometries represented in Table IV. In summary, the evidence presented here must be taken as more con than pro cyclic azide.

Acknowledgment. We are grateful to Dr. M. J. Akhtar for assistance with mass spectrometry and Dr. G. Stedman for helpful discussions.

Registry No. HNO₂, 7782-77-6; N₂H₅⁺, 18500-32-8.

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Direct Fluorination of Hexamethyldigermane and Hexamethyldisilane

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The low-temperature direct fluorination of hexamethyldigermane and hexamethyldisilane resulted in cleavage of the metal-metal bond in both compounds. From hexamethyldisilane, partially fluorinated derivatives of trimethylsilyl fluoride were obtained. The reaction of fluorine with hexamethyldigermane gave tris(trifluoromethyl)germanium fluoride in 66% yield.

Introduction

Controlled direct fluorination at low temperatures with careful manipulation of temperature and fluorine dilution is capable of preserving molecular structures that would normally be destroyed. As a result, a wide variety of organic, inorganic, and organometallic compounds have been synthesized.¹⁻⁶ The preservation of germanium and silicon carbon bonds during fluorination⁷ earlier suggested the possibility that this technique might be capable of effecting fluorination while preserving metal-metal bonds in compounds such as hexamethyldigermane and hexamethyldisilane.

The reaction scheme followed is illustrated in Figure 1.

Experimental Section

The fluorine apparatus was described previously.¹ Specific reaction conditions were chosen to minimize breakage of metal-carbon bonds while at the same time replacing the maximum amount of hydrogen with fluorine. Procedures found most suitable for the silane and germane are presented in Tables I and II.

Mass spectra were measured on a CEC 491 spectrometer at 70 eV. Proton NMR spectra were measured on Varian HA-100 and N-T 200 spectrometers. The fluorine NMR spectra were taken on Varian Em-390 and Bruker WH-90 spectrometers. Infrared spectra

Table I. Fluorination of Hexamethyldigermane^a

temp, °C	time, h	temp, °C	time, h
-100	48	-50	23
-90	25	-40	24
-80	24	-30	11
-70	21	-20	15
-60	24	amb	24

^a Helium flow rate 60 cm³/min throughout; fluorine flow rate 1.0 cm³/min, except at ambient temperature when it was stopped.

Table II. Fluorination of Hexamethyldisilane^a

temp, °C	time, h	temp, °C	time, h
-150	20	-120	10
-140	5.5	-110	9
-130	15	-100	15

^a Helium flow rate 60 cm³/min throughout; fluorine flow rate 1 cm³/min throughout.

Table III. Gas Chromatographic Separation Program for Partially Fluorinated Tris(trimethylsilyl) Fluorides

temp, °C	time, min
0	30
40	increase at 1.5 °C/min to 40 °C
60	increase at 1.0 °C/min to 60 °C
	increase at 5 °C/min to 185 °C

were obtained in the gas phase on a Beckman IR 20A spectrophotometer. Gas chromatographic separation of the products was done on a Bendix gas chromatograph equipped with a cryogenic controller and a thermal conductivity detector. A 25 ft × 3/8 in. column with

- (1) N. J. Maraschin, B. D. Catsikis, L. H. Davis, G. Jarvinen, and R. J. Lagow, *J. Am. Chem. Soc.*, **97**, 513 (1975).
- (2) J. L. Adcock and R. J. Lagow, *J. Am. Chem. Soc.*, **96**, 7588 (1974).
- (3) N. J. Maraschin and R. J. Lagow, *Inorg. Chem.*, **14**, 1855 (1975).
- (4) J. L. Adcock and R. J. Lagow, *J. Org. Chem.*, **38**, 3617 (1973).
- (5) J. L. Margrave and Richard J. Lagow, *Prog. Inorg. Chem.*, **26**, 161 (1979).
- (6) J. A. Morrison and Richard J. Lagow, *Adv. Inorg. Chem. Radiochem.*, **23**, 199 (1979).
- (7) E. Liu and R. J. Lagow, *J. Am. Chem. Soc.*, **98**, 8270 (1976).