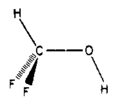
XVIII

structure has two FCOH gauche arrangements which are found to be strongly favored in fluoromethanol itself.[1,19-21]

Conclusions

Several conclusions may be drawn from this work. (1) The predicted stable conformations for the trisubstituted methanes are in agreement with the small amount of experimental information available. (2) The conformational preferences in the trisubstituted methanes are well represented as a superposition of results for disubstituted methanes. (3) Calculated bond separation energies are in reasonable agreement with experimental values. (4) The bond separation energies estimated by adding appropriate values for disubstituted methanes are found to be less than those given by the full calculation, *i.e.*, there is a "saturation" of the stabilizing interactions. (5) Isopropyl derivatives (i-C_3H_7X) are predicted to be more stable than corresponding n-propyl isomers (n-C_3H_7X) and the calculated and experimental energy differences are in quite good agreement.

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Ab Initio Gaussian Lobe Self-Consistent Field Computations on the Interconversion of Ammonium Oxide with Hydroxylamine, and Implications for the Rearrangements of Substituted Hydroxylamines

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Abstract: *Ab initio* restricted SCF calculations in a minimal basis of Slater-type orbitals mimicked by two or four Gaussian lobe functions on the system H_3NO interconverting with H_2NOH (Figure 1) elucidate a non-least-motion rearrangement path, bearing some resemblance to the allowed motion for 1,3-sigmatropic shifts. We discuss the observed stability of F_3NO relative to F_2NOF, and the course of a rearrangement of a tris(trialkylsilyl)hydroxylamine with reference to these model calculations.

The chemistry of substituted hydroxylamines includes O to N migration[2] and insertion of O substituents into the O–N bond.[3] In an effort to rationalize the stereochemical course of these rearrangements, and with the hope of tracing the cause of stability of F_3NO (known[4]) relative to F_2NOF (unknown), we have undertaken an exploration of portions of the potential surface of the H_3NO–H_2NOH system. Our method is conventional restricted Hartree–Fock computation in the LCAO–MO–SCF formalism of Roothaan,[5] with a very small basis of Gaussian lobe mimics of Slater-type basis functions. After establishing the degree of reliability of this mode of calculation, we show by numerical result and qualitative argument that the rearrangement is of the "non-least-motion" type. The effect of p and d orbitals of the migrating fragment on the path of reaction is considered, with reference to the experimentally established rearrangement of tris(trialkylsilyl)hydroxylamine.[6]

Computational Details

The program which performs the SCF computation is a collection of familiar methods and has been described elsewhere.[7] A minimal basis of Slater-type orbitals mimicked by Gaussian lobe functions was employed. In surface explorations only two Gaussian lobes were used to represent each STO; for a few significant geometries, a four-Gaussian mimic was employed. Neither of these computational modes yields highly accurate results; we are led to emphasize qualitative features of the results.

To ease the geometry variation in the surface exploration, the programs PROXYZ and STEPIT,[8] which compute geometries and vary chosen parameters, respectively, were adapted to drive the SCF program.

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[1] (a) Alfred P. Sloan Fellow, 1971–1973; University of Virginia; (b) Virginia Commonwealth University.

[2] R. West, P. R. Boudjouk, and T. A. Matuszko, *J. Amer. Chem. Soc.*, **91**, 5184 (1969).

[3] F. A. Carey and L. Hayes, *ibid.*, **92**, 7613 (1970).

[4] N. Bartlett, J. Passmore, and E. J. Wells, *Chem. Commun.*, 213 (1966); W. B. Fox, J. S. MacKenzie, N. Vanderkooi, B. Sukornick, C. A. Wamser, J. R. Holmes, R. E. Eibeck, and B. B. Stewart, *J. Amer. Chem. Soc.*, **88**, 2604 (1966).

[5] C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

[6] P. Boudjouk and R. West, *J. Amer. Chem. Soc.*, **93**, 5901 (1971).

[7] C. Trindle and D. D. Shillady, *Int. J. Quantum Chem.*, in press.

[8] Quantum Chemistry Program Exchange, Indiana University, Department of Chemistry, Bloomington, Ind. 47001.

Table I. Energy Computations on Hydroxylamine and Ammonium Oxide

	2G	4G	PM[12b]	FPA[12a]
		Hydroxylamine		
$-E_{\text{total}}$ (cis) (au)	125.016	129.7318	129.69440	130.88024
$-E_{\text{total}}$ (trans)	125.019	129.7470	129.70614	130.89742
Barrier (kcal/mol)	5.6	11.0	9.9	11.95
Angle (θ, deg)	60[a]	60[a]	60	53.5
Isomerization energy (kcal/mol)	2.1	9.5	7.37	10.95
		Ammonium Oxide		
$-E_{\text{total}}$ (au)	124.767	129.5658		
Isomerization energy (kcal/mol)	158	114		
Isomerization activation energy (kcal/mol)	62			

[a] Assumed.

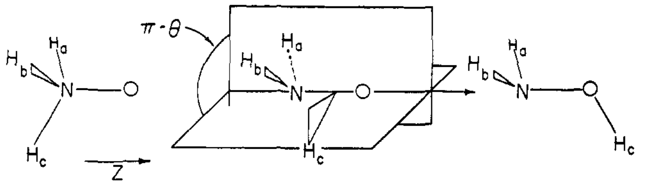

Figure 1. The interconversion pathway connecting ammonium oxide (left) with *trans*-hydroxylamine (right) is specified by two variables: Z, which is the coordinate followed by H_c, and θ, which is the dihedral angle between the H_cNO plane and the plane of symmetry common to ammonium oxide and hydroxylamine.

The nine geometric parameters were not all rigorously optimized, for economic reasons. The following simplifying assumptions were made: the z coordinates of oxygen and the three hydrogens were varied linearly between the reference values for hydroxylamine[9] and a H_3NO geometry derived from the F_3NO structure,[10] with an NH distance assigned the value 1.0 Å. Referring to the hydrogens remaining bound to nitrogen as H_a and H_b, the H_aNO and H_bNO angles were set equal to one another and varied linearly between reference values for H_2NOH and H_3NO. The geometric parameters which were varied were the x and y coordinates of the migrating hydrogen, H_c.

Energy Difference between Stable Species and the Rotational Barrier of Hydroxylamine

A number of computations of hydroxylamine geometry and internal-rotation barrier have appeared, ranging in quality from CNDO[11] to near-Hartree–Fock.[12] These results are reproduced in part in Table I. Our 4G results are in acceptable agreement with the most accurate prior results for cis–trans energy difference and rotational barrier, but the 2G results are distinctly poorer.

There is a considerable discrepancy between 4G and 2G predictions of the energy difference between hydroxylamine and ammonium oxide. The much smaller energy difference computed in the 4G mode suggests that 2G computations may be biased generally against crowded systems, in contrast to ZDO-based computations which favor compact systems.[13] It is quite likely that the 4G computation is biased in the same direction as the 2G computation, though not so seriously. Even though ammonium oxide is computed to be exceedingly unstable relative to hydroxylamine, the C_{3v} species occupies a relative minimum in the energy surface and may enjoy considerable kinetic stability. The computed energy barrier to rearrangement of ammonium oxide to hydroxylamine, on the order of 60 kcal/mol, is sufficient to make the oxide long lived, even if our estimate is in error by a factor of 3 or 4.

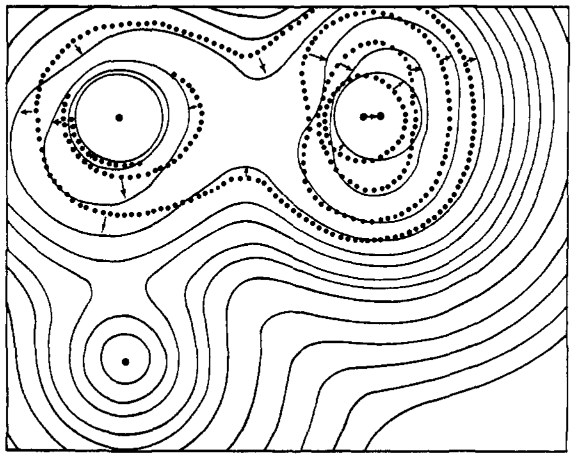

Figure 2. Charge-density contours for the transition state of the ammonium oxide–hydroxylamine interconversion are shown, for the H_cNO plane. Dots represent the nuclei; innermost contours correspond to 0.5 electron/(bohr)^3, and other contours correspond to members of the geometric series $(0.5)^n$, $n = 2, 3, \ldots$. Dotted contours represent the density of the ammonium oxide system. Dotted and solid contours linked by arrows refer to identical densities. For a discussion of the significance of contour shifts, see text.

A qualitative idea of the source of this rearrangement barrier can be gained from inspection of a contour diagram of the charge density[14] in the H_c–N–O plane for the computed transition-state geometry (Figure 2). Dotted lines, representing density contours for ammonium oxide, are linked with corresponding contours for the transition state by arrows. Although there is a marked similarity between the transi-

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[9] E. A. Myers and W. N. Lipscomb, *Acta Crystallogr.*, **8**, 583 (1955); P. A. Giguere and I. D. Liu, *Can. J. Chem.*, **30**, 948 (1952).

[10] V. Plato, W. D. Hartford, and K. Hedberg, *J. Chem. Phys.*, **53**, 3488 (1970).

[11] M. S. Gordon, *J. Amer. Chem. Soc.*, **91**, 3122 (1969).

[12] (a) W. H. Fink, D. C. Pan, and L. C. Allen, *J. Chem. Phys.*, **47**, 985 (1967); (b) L. Pederson and K. Morokuma, *ibid.*, **46**, 3941 (1967).

[13] L. Radom and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 1813 (1971).

[14] J. L. J. Rosenfeld, "Electron Distribution and Chemical Binding," Technical Report 13, Institute of Theoretical Physics, University of Stockholm, Sweden.

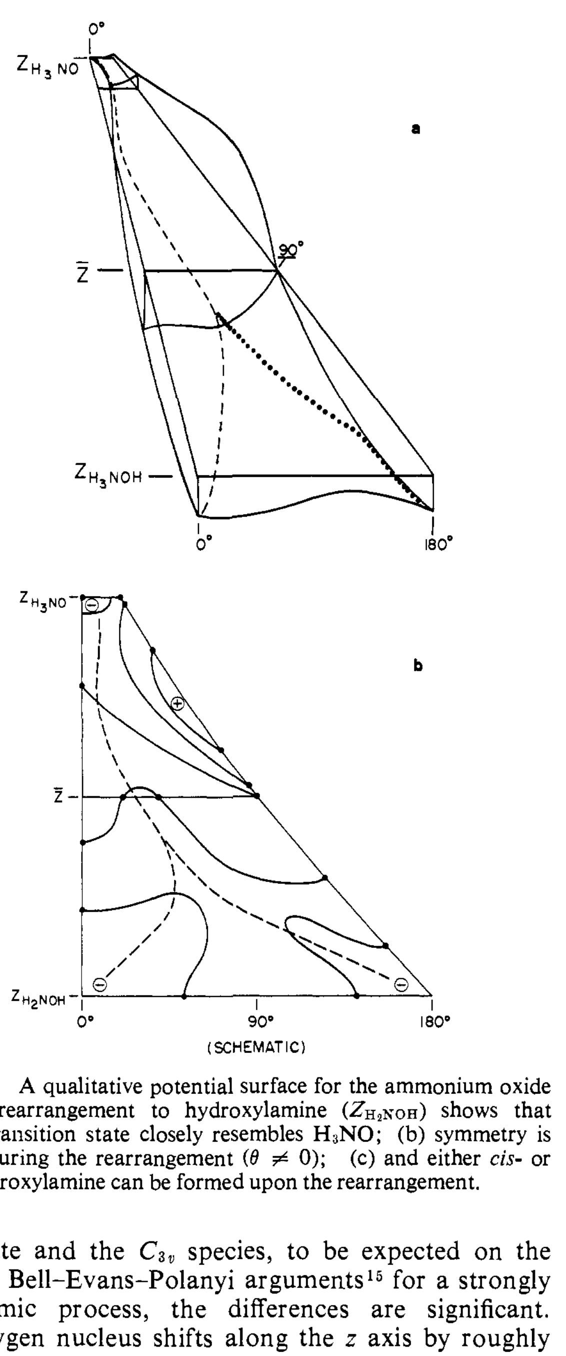

Figure 3. A qualitative potential surface for the ammonium oxide (Z_{H_3NO}) rearrangement to hydroxylamine (Z_{H_2NOH}) shows that (a) the transition state closely resembles H_3NO; (b) symmetry is broken during the rearrangement ($\theta \neq 0$); (c) and either *cis*- or *trans*-hydroxylamine can be formed upon the rearrangement.

tion state and the C_{3v} species, to be expected on the basis of Bell–Evans–Polanyi arguments[15] for a strongly exothermic process, the differences are significant. The oxygen nucleus shifts along the z axis by roughly 0.12 Å, carrying the highest density contour with it. The remaining contours associated with oxygen only are reoriented toward the migrating hydrogen, but no oxygen–H_c bond has been formed. No particular stabilization or destabilization would be expected from this portion of the charge reorganization.

Contours associated with nitrogen are shifted so that the incipient nitrogen lone pair begins to develop. This shift occurs without substantial effect on the density associated with N–H_c bonding, but at the expense of N–O bonding. Not only is the lowest density N contour swung away from the N–O direction, but the highest density contour linking N and O is appreciably indented. These observations imply that the major contribution to the rearrangement barrier arises from a weakening of the N–O bond as migration begins.

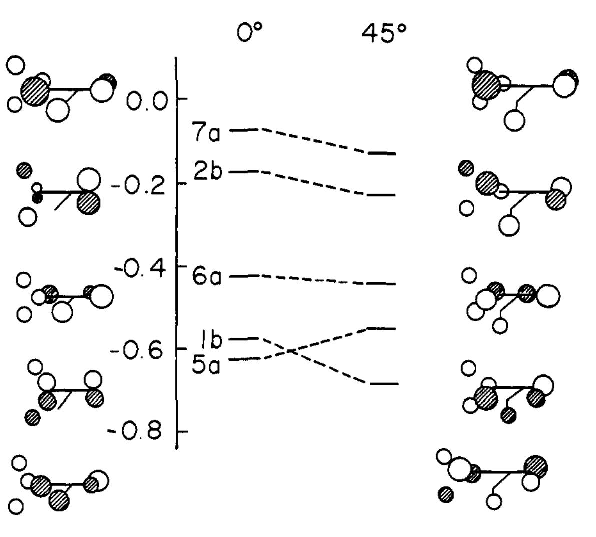

Figure 4. A MO lobe diagram shows the source of the stabilization associated with symmetry breaking. Antibonding interactions are relieved as in MO 7a, or new bonding interactions are made possible as in MO's 1b, 2b.

Non-Least Motion in the Ammonium Oxide–Hydroxylamine Rearrangement. The migration path followed by H_c as ammonium oxide converts to hydroxylamine is governed by a potential surface, sketched in Figure 3. We intend to stress qualitative features of the surface and deliberately leave the energy axis unscaled so that quantitative meaning is not imputed. The z axis (a measure of the linear motion referred to above) and the angle θ between the H_cNO plane and the plane formed by the NO bond and the bisector of the H_aNH_b angle are plotted; the C_{3v} species and *trans*-hydroxylamine share a zero value for this angle θ. Heavy lines in the diagram are supported by detailed computation. Occasional points elsewhere on the surface were determined and are consistent with the diagram. This surface is constructed from a collection of 2G computations.

The notable feature of the potential surface is the indication that the motion of H_c after the transition state is not such that a plane of symmetry is maintained. One asks: how is the system stabilized by symmetry breaking, and is the least-motion path forbidden in the sense of Woodward and Hoffmann? Both questions can be answered by reference to lobe diagrams of the molecular orbitals (Figure 4).

H_c motion will be easy if the migrating fragment maintains bonding overlap with the site it leaves at the same time that it develops bonding overlap with the site it approaches. The lobe diagram shows that this situation is not achieved if the migrant is constrained to a plane of symmetry. In the highest occupied MO's, degenerate in the C_{3v} species, the migrant either has no interaction with the remainder of the molecule for symmetry reasons, or must change phase upon passage to oxygen. In lower orbitals the phase change is not essential, and the motion is tolerated. The net result is that the motion maintaining a plane of symmetry is discouraged. By symmetry breaking the phase change is made easier, either because antibonding interactions are made less severe (as in MO 7a) or because bonding interactions are established which were formerly symmetry prohibited (as in MO 2b).

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(15) A clear account from a modern view is given by M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1970.

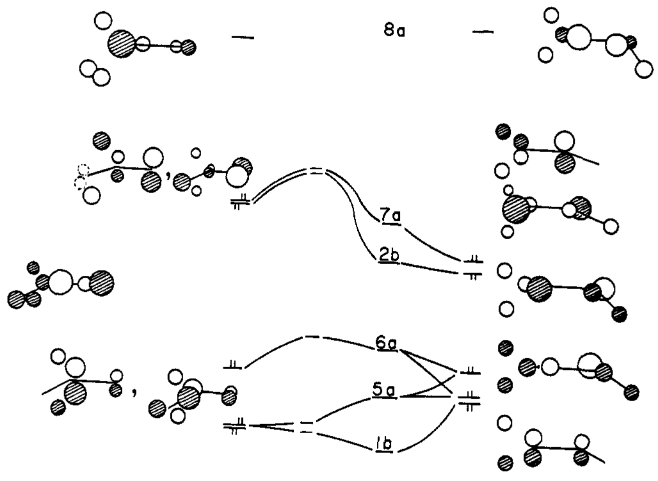

Figure 5. A qualitative MO correlation diagram for the ammonium oxide–hydroxylamine interconversion, where H_c motion is limited so to maintain a plane of symmetry, shows no level crossing between occupied and virtual MO's. However, appeal to the principle of phase conservation indicates that a substantial barrier to the interconversion exists.

Although a phase change in the highest occupied MO is required in order to accomplish the ammonium oxide–hydroxylamine rearrangement, construction of an orbital correlation diagram does not immediately suggest that the motion is symmetry forbidden (Figure 5). In this case the operative symmetry element contains the moving bond and is not relevant according to Woodward and Hoffmann.[16] Although the simplest orbital symmetry analysis is not informative in this case, use of the "phase conservation" hypothesis of Goddard[17] or the "state overlap" which enters the mapping analysis of concerted reactions[18] makes the forbidden character clear.

The analogy between the H_c migration to form hydroxylamine from ammonium oxide and sigmatropic shifts in alkenes[16] rests on the analogous nodal structure of the highest occupied orbital in the two systems. The highest occupied orbital in H_2NO^- is essentially antibonding in a π fashion between the N and O termini; the highest occupied MO in $(CH_2CHCH_2)^-$ is π antibonding between the terminal carbons, and the 1,3-sigmatropic shift can be shown to be non-least motion in CH_3CHCH_2 as it is in H_3NO. The main distinctions between the systems are that ammonium oxide is far less stable than hydroxylamine, whereas the propylenes are naturally comparable in energy, and also that the nonleast motion in the hydrocarbon has discernible stereochemical consequences.[16]

Thus far we have presumed that a single determinant provides an adequate description of the qualitative features of the potentialfor the ammonium oxide–hydroxylamine interconversion. It is necessary to anticipate whether configuration mixing would modify any of our conclusions, particularly the prediction of a nonleast motion interconversion. The rotational barrier of hydroxylamine is well described by single-determinant wave functions,[12] so our attention should be directed to the ammonium oxide and the nearby transition state.

Configuration mixing is likely to be significant when (a) the lower unoccupied orbitals are close to the higher occupied orbitals in energy, and (b) the lower unoccupied orbitals occupy roughly the same region as the higher occupied orbitals.

In this particular case, configuration mixing can affect our qualitative conclusions if the mixing tends to minimize the N–O π antibonding which governs the nonleast motion. Inspection of our computations shows that (a) the minimum HOMO–LUMO gap is 0.42 au (in the transition state) and (b) the HOMO's, essentially oxygen lone pairs, are large in regions of the molecule where the LUMO's, essentially N–H antibonding functions, are small. Further the N–O π antibonding is *common* to both HOMO's and LUMO's. Therefore, configuration mixing is probably not large, and, whatever its extent, the essential nodal structure of the system will not be radically altered.

Implications on the Stability of Trifluoramine Oxide

The motion linking X_3NO with X_2NOX which maintains a plane of symmetry has the effect, at least in the initial stages of the motion, of mixing the highest occupied and lowest occupied orbitals of like symmetry.[19] We can rationalize the NO bond weakening accompanying H_c motion by considering the nodal structure of the lowest unoccupied orbital of ammonium oxide. In this orbital N–H antibonding accompanies a weakening in the NO bond. The stronger the NO bond in X_3NO, and the stronger the NX bond, the more difficult this motion will be. One expects the NO bond to have more double-bond character with the powerful electron-attracting F than the electropositive H. We expect F_3NO to be less prone to rearrangement than H_3NO.

The kinetic stability of X_3NO is enhanced if X bears p orbitals. In the high-lying two-election MO's of X_3NO, the wave function for X is out of phase with the wave function near 0 in one case, and vanishes by symmetry in the other case. If p orbitals, are added, the wave functions are out of phase in both cases, increasing the difficulty of migration.

These arguments rationalize a kinetic stability for trifluoramine oxide, but in view of the fact that this molecule is prepared in a fluorine flame,[20] the molecule must be thermodynamically stable as well. The only experimental indication of an easy rearrangement in this system is an anomalously low FNF bending frequency. Whereas the lowest frequency modes in PF_3 and F_3PO are virtually identical, the lowest frequency mode in F_3NO is 100 cm^{-1} lower in frequency than the lowest mode in NF_3[21] (Table II).

Rearrangement of a Substituted Hydroxylamine

A number of rearrangements of hydroxylamines have been reported,[2,3] but we limit our attention to the tris(trialkylsilyl)hydroxylamine system, which seems particularly bewildering at first glance. Boudjouk and West[6] describe the following reaction.

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[16] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie—Academic Press, Weinheim, 1970.

[17] W. A. Goddard, III, *J. Amer. Chem. Soc.*, **92**, 7520 (1970).

[18] C. Trindle, *ibid.*, **92**, 3251, 3255 (1970).

[19] L. Salem and J. S. Wright, *ibid.*, **91**, 5947 (1969).

[20] W. B. Fox, B. Sukornick, J. S. Mackenzie, R. L. Sturtevant, A. F. Maxwell, and J. R. Holmes, *ibid.*, **92**, 5240 (1970).

[21] (a) ONF_3: ref 4; (b) PF_3 and OPF_3: H. S. Gutowsky and A. D. Liehr, *J. Chem. Phys.*, **20**, 1652 (1952); M. K. Wilson and S. R. Polo, *ibid.*, **20**, 1716 (1952); **21**, 1426 (1953); (c) NF_3: Wilson and Polo, *op. cit.*; L. Pace and L. Pierce, *ibid.*, **23**, 1248 (1955).

Table II. Vibrational Frequencies for PF_3, F_3PO, NF_3, and F_3NO[a]

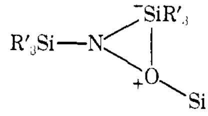
	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
Fe_3PO	1415	873	473	990	485	345
F_3P		892	487	860		344
F_3NO	1691	743	528	883	558	398
F_3N		1032	647	905		493

[a] Mode 2 is the a_1 XF stretch, 3 is the a_1 XF bend, 4 is the e XF stretch, and 6 is the e XF bend, where X is the central atom.

$$(R'_3Si)_2NOSiR_3 \longrightarrow (R'_3Si)RN(SiR_2)OSiR'_3$$

We presume that the initial motion is such that a three-membered ring is formed (Figure 6). The ring is stabilized by admixture of the formally vacant 3d orbital of the silicon atom into the NO π-antibonding orbital. The effect of this admixture would seem to be an accentuated weakening of the NO bond and the establishment of a Si–N bonding interaction. At this point in the reaction the best single valence-bond representation of the system placed a formal positive charge on nitrogen and a formal negative charge on silicon. This charge separation can be alleviated by a migration of one silicon substituent toward nitrogen, breaking of the weakened NO bond, and a nonleast motion migration of a R'_3Si fragment from N to O. In this motion, all orbital phase directives are obeyed. The motion seems exceedingly complex, and in fact the reaction is not facile.

The arguments above apply to systems where migration of the N substituents is precluded, either by the *absence* of an atom which can accept another bond as Si can, or for steric reasons. Professor West[22] has observed products of the tris(trialkylsilyl)hydroxylamine system which can best be rationalized by proposing that the three-membered ring pictured below be formed.



Inspection of Figure 6A shows that this structure may be formed while enjoying the stabilization arising from the interaction of the N–O π-antibonding function and a Si (largely vacant) d orbital. All that needs to be altered in Figure 6 to account for the product which West observes when R_3 = $Me_2(t\text{-}Bu)$ is to replace $>N(SiR'_3)_2^+$ by $>N(SiR'_3)$ and $>O$ by $^+{>}O{-}SiR_3$. The motions indicated in B and C of Figure 6 lead to $Me_3Si(NMe)(SiMe_2)OSiMe_2(t\text{-}Bu)$, as reported.[22] These remarks do not constitute a complete rationale of West's data but are intended to show how phase conservation can be employed to discuss the course of reactions for which symmetry arguments are not very helpful.

Summary

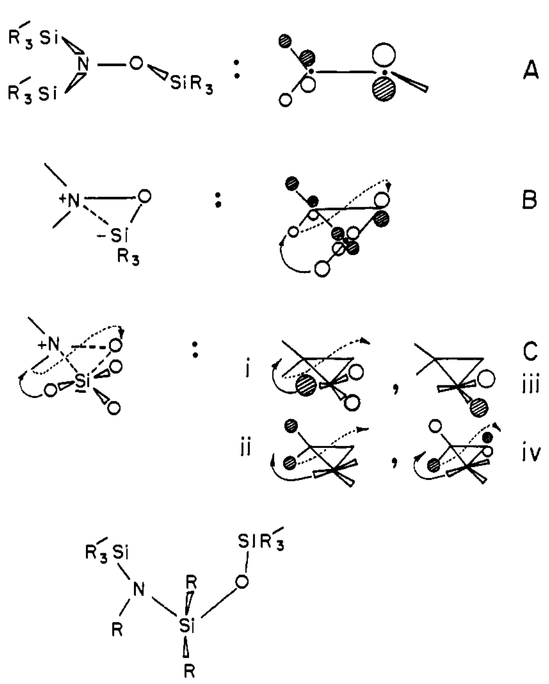


Figure 6. Lobe diagrams of certain high-lying MO's illustrate the interconversion of a tris(trialkylsilyl)hydroxylamine (upper left) to the species at lower left. Diagram A shows the highest filled MO in the substituted hydroxylamine which is analogous in nodal structure to the highest filled MO in the model hydroxylamine. The SiR_3 fragment attached to the oxygen takes a short step along the rearrangement pathway elucidated for the ammonium oxide-hydroxylamine system, producing the arrangement B. The mainly vacant Si d orbitals on the migrating fragment can stabilize a ring arrangement. The nodal structure of the original highest MO is maintained, however. In arrangement B, one of the alkyl groups connected to the migrating silicon is indicated, with arrows linking regions of the highest MO sharing the same phase indicating the course of the eventual rearrangement. In arrangement C, some of the high-energy (localized) MO's associated with the migrating SiR_3 and the $(R'_3Si)_2N$ fragments are shown. Lobe diagrams C(i) and C(iii) show a pair of local MO's which would be nearly degenerate if the local symmetry were nearly C_{3v}. Diagrams C(ii) and C(iv) show the symmetric and antisymmetric combinations of N–(SiR'_3) bonds. The latter participates in the MO shown in diagrams A and B. The set of diagrams C show that the indicated least motion transfer of R′ from Si to N and the nonleast motion transfer of SiR_3 from N to O is consistent with the phases of the high-lying MO's. While inspecting the figures, consider that C(i) and C(ii) are likely to be mixed, as are C(iii) and C(iv).

Model *ab initio* Gaussian lobe SCF computations on the hydroxylamine–ammonium oxide systems provide a reference for the discussion of experimentally interesting hydroxylamines and related species. The H_3NO–H_2NOH interconversion occurs by a non-least-motion path reminiscent of 1,3-sigmatropic rearrangements, but is opposed by a considerable activation energy apparently derived from the weakening of the NO bond in the transition state.

Qualitative arguments suggest that trifluoramine oxide is less likely than ammonium oxide to rearrange to a hydroxylamine, and that hydroxylamines with a substituent which may assume a hypervalent form can undergo insertion of that substituent into the weak NO bond.

Acknowledgments. This research was made possible by a grant from the U. S. National Science Foundation (GP-30817) and support from the A. P. Sloan Foundation.

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[22] Thanks to Professor West for so kindly making available to us results of his researches presented at the 3rd International Symposium on Organosilicon Chemistry, Madison, Wis., 1972.