however, NO should surely be produced in increasing proportion as pH is decreased and the fraction of $H_2N_2O_3$ increases. Instead, however, NO is not observed as product at pH 3 although this fraction should be 24% if $pK_1 = 2.51$. (This value may be open to some question, since it is based upon potentiometric titrations which were not extended below pH 4.6.[4b]) Also, although a mixture of N_2O and NO is found at pH 2 and the NO contains N atoms from both sides of the $H_2N_2O_3$ molecule, the N_2O appears to include some atoms from both sides also, in contrast to the observations at higher pH. This does not appear to be consistent with a simple competition between N=N breakage-controlled and dehydration-controlled processes. It is known that NO does not exchange oxygen atoms with H_2O under a broad range of conditions,[23] and again it seems reasonable to discount the dehydration mechanism. (It is also known that no oxygen atoms from solvent H_2O appear in the N_2O product of $HN_2O_3^-$ decomposition.[22])

We postulate that cleavage of the N=N bond in oxyhyponitrite to form asymmetric products remains the primary process in its decomposition in strongly acidic as well as basic solutions. That the rate of this cleavage is faster for the doubly protonated form than for $HN_2O_3^-$ is illustrated by the observed increase in rate at pH 3, an increase that is not accompanied by production of NO. Thus, we believe that the decomposition rate is controlled by the production of HNO (or NOH) and NO_2^- at all conditions. Over the vast pH range ~3–8, N_2O is produced in a rapid-follow process involving only nitroxyl. Below pH 3, we postulate the inception of a competing rapid-follow process, which quickly becomes dominant, in which a species derived from HNO attacks NO_2^- (or HNO_2), producing NO in a redox reaction. In view of the sharp pH dependence, we speculate that this species could be H_2NO^+, for example, in which case the final NO producing reaction would be the process

$$H_2NO^+ + NO_2^- \rightarrow 2NO + H_2O$$

or

$$H_2NO^+ + HNO_2 \rightarrow 2NO + H_3O^+$$

That it cannot be the increasing concentration of HNO_2 with decreasing pH that is the critical factor in NO production is demonstrated by the fact that there is no direct NO product at pH 3, although a large proportion of nitrite produced at that pH would be rapidly protonated. This factor may well play an important role in the rapid rise in decomposition rate at low pH values, however. Finally, in order to account for the apparent scrambling of nitrogen atoms in the N_2O that constitutes a portion of the product gas at pH 2, we speculate that the transition-state species ($H_2N_2O_3$ or $H_3N_2O_3^+$) must have some tendency to re-form HNO, a tendency that rapidly gives way to direct NO production with decreasing pH.

Registry No. $Na_2N_2O_3$, 13826-64-7; $Na_2(O^{15}NNO_2)$, 53716-33-9.

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Self-Consistent Field Calculation of Nitrosyl Hydride and Nitrogen Hydroxide

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SCF calculations of nearly double-ζ quality have been done on the nitrosyl hydride molecule and its isomer, HON. The system is found to have a low-lying triplet state, which is expected to aid in the dimerization to $H_2O_2N_2$, hyponitrous acid.

Some interest has been centered upon nitrosyl hydride, HNO, as a system which is produced in an excited state by the reaction of H and NO. There is subsequent chemiluminescence, presumably from the transition $^1A''$ to $^1A'$. Thrush and his coworkers have studied this reaction extensively.[1] The spectrum of HNO has been obtained both in the gas phase[2] and in the solid.[3] In the gas phase HNO is known to undergo further reaction, the first step of which is apparently dimerization to $H_2N_2O_2$.[4]

On the theoretical side Peslak, Klett, and David[5] and Ditchfield, Del Bene, and Pople[6] have given SCF calculations of the geometry of HNO, and Salotto and Burnelle[7] have given calculations using the unrestricted Hartree–Fock method. Peslak, Klett, and David have also examined the geometry of the isomer HON, nitrogen hydroxide. Krauss[8] has examined this system to test mechanisms for the H–NO afterglow.

The various properties of HNO which lead to these observations have been attributed to the effect of the perturbation of the hydrogen atom on the diatomic molecule orbitals of NO by Orgel.[9] Heretofore, such considerations have apparently been qualitative only, and it is of considerable interest to examine the perturbation of these orbitals with *ab initio* techniques. Therefore, a series of calculations was undertaken to examine both the orbital energies and the total energy as

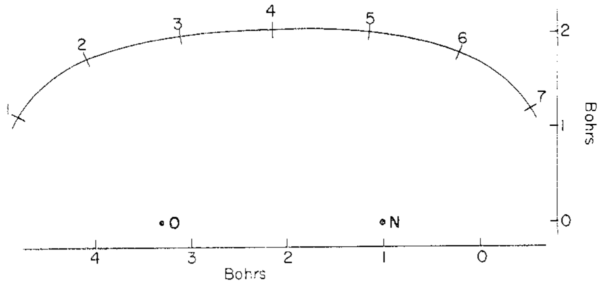


Figure 1. Hydrogen trajectory for calculations of the energy of HNO.

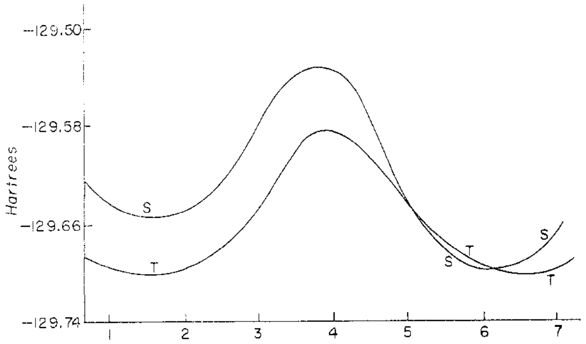


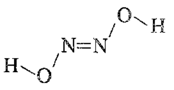
Figure 2. Total energies in the lowest singlet and triplet states as a function of the position along the trajectory of Figure 1. The numbers on the abscissa refer to the trajectory of Figure 1.

a function of a restricted set of positions of the H atom, with the view to interpreting the experimental facts in the light of the calculated results.

The calculations were done with the gaussian lobe basis similar to that of Whitten[10] with the s-type orbitals grouped 3-4-2-1 and the p-type orbitals grouped 4-1 on each O and N. The gaussians on H were grouped 4-1 also. In each case the gaussian with the longest range was separated out from the others of the group, and thus the effect of a double-ζ type calculation is produced.[11] There are 21 orbitals in all in the calculation. The lowest singlet and triplet energy was obtained along a trajectory as shown in Figure 1. The HNO end of the trajectory is arranged at the experimental H–N distance, the HON end was determined at the Peslak, Klett, and David H–O distance, and the central part was determined by optimizing the distance between the H atom and the remainder of the molecule. Although other distances were not relaxed completely along the trajectory, it is felt that the present results are qualitatively correct and give a very useful picture of the effects operating in this molecule.

The energies obtained are given in Figure 2, where the abscissa points are the marked positions shown in Figure 1. The singlet and triplet energies are very close at the HNO end of the trajectory and are separated by about 31 kcal (0.049 au) at the other end. For the singlet state the calculated equilibrium angles are HNO = 109° and HON = 115°. For the triplet state the angles are 124 and 122°, respectively. Since SCF calculations are known to underestimate lowest singlet–triplet separation energies, it is felt that the singlet curve should be lowered about 6–10 kcal with respect to the triplet so that the predicted stable geometry is HNO. This added energy is due to the correlation between the two electrons in the highest filled orbital, 7a, for the singlet state. This correlation is largely missing in the triplet state, of course; such reasoning also assumes that the correlation energy from all other pairs of electrons approximately cancels in taking differences.

Thus this calculation predicts that HNO has a singlet ground state with a low-lying triplet state only a few kilocalories above it, and hence this substance would be expected to be quite reactive. The prediction of a triplet state for HON is in good agreement with the experimental evidence, which strongly suggests that the dimer, hyponitrous acid, is the stable form. The predicted triplet state is expected to dimerize readily, and the geometry of $H_2O_2N_2$ is expected to be



This is predicted from the geometry of the hyponitrile ion.

The calculated barrier between the two isomers of 70 kcal is probably too high because of the unrelaxed N–O distances, and the value given should be looked upon as no more than an upper limit to the correct one.

The difference in behavior of the singlet–triplet separation at the two ends of the molecule has a very interesting origin, which can be uncovered by an examination of the orbital energies along the trajectory. Figures 3 and 4 show the graphs of these quantities *vs.* the same abscissa points as those used in Figure 2, omitting the 1a' and 2a' orbitals which involve the inner shells only. If attention is centered upon the energies of the two singly occupied orbitals of the triplet state, it is seen that the 2a'' orbital energy is nearly independent of the H atom position and the 7a' orbital energy depends strongly upon this position. Geneologically, these derive from the π^* orbitals of the NO molecule, and it is evident that the interaction between the H and the NO is greater at the nitrogen end of the

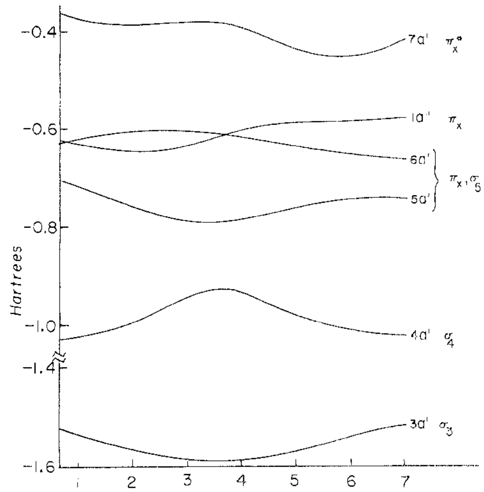


Figure 3. Orbital energies in the singlet state. The abscissa refers to the trajectory of Figure 1.

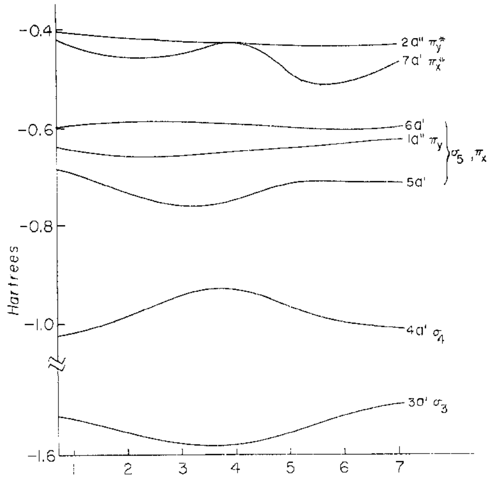


Figure 4. Orbital energies in the triplet state. The abscissa refers to the trajectory of Figure 1.

molecule. If both of these electrons are forced to occupy the 7a' orbital, we obtain the singlet state, and the energy parallels the triplet 7a' about 31 kcal higher. Thus on the HNO side of the molecule the separation between 7a' and 2a'' is sufficiently large virtually to overcome the added repulsion energy from a doubly occupied 7a' orbital and the singlet and triplet have the same energy. On the HON side of the molecule the separation is only half that on the other and the electrons prefer to be in different orbitals. The difference between the two ends of the NO is largely due to the greater size of the N AO's and the consequent greater interaction with the H.

We may look at the effects operating in these molecules in another way that is very useful. HNO is isoelectronic with O_2 and also with H_2CO, formaldehyde. We can envisage a partially united atom approach in which we start with O_2, move one proton out to get HNO, and then move a second to get H_2CO. Figure 5 shows qualitatively the changes in the energies of the important states. For O_2 the $^3\Sigma_g{}^-$ is lowest and the $^1\Delta_g$ is considerably higher. When one proton is moved out at an angle the degeneracy of the Δ state is split and the resulting $^3A''$ and $^1A'$ have about the same energy. By the time that two protons are placed off-center, the splitting of the original $^1\Delta_g$ is so large that the first excited triplet state of formaldehyde is much higher in energy than the singlet. It is also quite evident from the calculations reported here that the proton in HON cannot split the $^1\Delta_g$ state far enough to bring the $^1A'$ energy below the $^3A''$. These calculations have allowed us to put the graph originally given by Orgel[8] on a somewhat more quantitative level.

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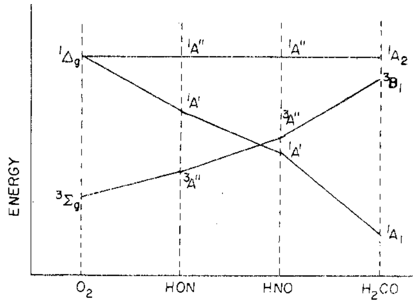

Figure 5. Qualitative representation of the energies in passing from O_2 to H_2CO.

Registry No. HNO, 14332-28-6; HON, 35337-59-8.

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Photoreactions of Tetrafluorodiphosphine with Nonsubstituted Olefins and Perfluoroolefins[1]

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The photoreactions of P_2F_4 with C_2H_4, C_3H_6, 2-C_4H_8, C_6H_{10}, C_2F_4, and C_3F_6 have resulted in the formation of $F_2PCH_2CH_2PF_2$, $CH_3CHPF_2CH_2PF_2$, $CH_3CHPF_2CHPF_2CH_3$, $C_6H_{10}(PF_2)_2$, $F_2PCF_2CF_2PF_2$, and $CF_3CFPF_2CF_2PF_2$. No recoverable amount of comparable products was obtained in similar mixtures of P_2F_4 and 2-C_4F_8 or of P_2F_4 and C_6F_{10}. The new compounds were characterized by ir, nmr, and mass spectrometry. $C_6H_{10}(PF_2)_2$ displays temperature-dependent nmr spectra consistent with the trans isomer.

Introduction

The ability of P_2F_4 to generate PF_2 radicals has been established by physical means.[2,3] Although it has been suggested that the PF_2 radical might be involved in syntheses of certain compounds,[4-6] the chemical behavior of the PF_2 radical remains unexplored. In a recent communication[7] we reported the reaction of P_2F_4 with ethene in the presence of ultraviolet light, a reaction which did not proceed in the absence of uv light. We wish to report in this paper the reaction of P_2F_4 with olefins and perfluoroolefins which resulted in the preparation and characterization of 1,2-bis(difluorophosphino)propane ($C_3H_6P_2F_4$), 2,3-bis(difluorophosphino)butane ($C_4H_8P_2F_4$), *trans*-1,2-bis(difluorophosphino)cyclohexane ($C_6H_{10}P_2F_4$), 1,2-bis(difluorophosphino)perfluoroethane ($C_2F_4P_2F_4$), and 1,2-bis(difluorophosphino)perfluoropropane ($C_3F_6P_2F_4$) and the attempted syntheses of 2,3-bis(difluorophosphino)perfluorobutane ($C_4F_8P_2F_4$) and 1,2-bis(difluorophosphino)perfluorocyclohexane. Data for $C_2H_4P_2F_4$, reported earlier,[7] are included for comparison.

Experimental Section

General Techniques. Standard high-vacuum techniques were used throughout.[8] Apiezon N grease was used for joints in general, although Kel-F No. 90 was found to give cleaner products in experiments with fluorocarbons. Infrared spectra were obtained using a low-temperature infrared cell[8] and a 75-mm path length gas cell with KBr windows on a Beckman IR-20-A spectrometer. ^{31}P, ^{19}F, and ^1H nmr spectra of the neat liquids were obtained at 40.4, 94.1, and 100.1 MHz, respectively, with a Varian Associates XL-100-12 instrument. External standards were used for chemical shift measurements unless noted otherwise. Chemical shift values are given in ppm from 85% orthophosphoric acid, CCl_3F, and TMS. Mass spectra were obtained with an Hitachi Perkin-Elmer RMU-6E spectrometer. A Rayonet photochemical reactor (Southern N.E. Ultraviolet Co., Middleton,