

volved. If anything the calculations show a very small destabilization of about 1 kcal/mol. When an oxygen or nitrogen molecule is put inside a cage the charge in the cage is changed in such a way that the oxygens gain electrons. The charge migration is very small and the resulting stabilization is in the range 4 to 7 kcal/mol in these ten-membered cages with 12 hydrogen bonds. Sobol, *et al.*,⁹ estimate from their experiments the effect of an oxygen or a nitrogen molecule to be 0.1 kcal/mol per hydrogen bond (stabilizing effect) in unspecified structured water. The agreement is quite good.

It is reasonable to connect the stabilization effect with charge polarization as dipole interaction is supposed to be the leading term in what we call hydrogen bonding. The question is then why oxygen or nitrogen would have this effect on a water structure while a non-hydrogen-bonded water molecule would not have it or at least to a lesser extent. That is at least a possible interpretation of the experiments by Sobol, *et al.* These experiments revealed a direct relation between the air content in the water and the surface tension. For the discussion of the possible effect of a "free" water molecule to be meaningful, one has to assume a model for water similar to those proposed by Némethy and Scheraga³ and Samoilov⁴ mentioned in the introductory section. To study this possibility we put a water molecule inside the cage described in Figure 1b. The molecule was placed in a plane bisecting the angle between the *xz* and *yz* planes. The resulting sym-

metry is C_{2v} . The position along the *z* axis and the orientation of the bond angle with respect to the positive *z* direction were varied. It was found that the water molecule had no stabilizing effect on the cage. In these cases we had a resulting dipole moment in the cage. The charge redistribution in the cage itself was smaller than the changes due to oxygen or nitrogen molecules. The main changes were in the two cage water molecules on the *z* axis. The interstitial molecule has attractive interaction with one of them and repulsive interaction with the other one. To diminish this repulsion the polarity of the latter cage molecule is weakened and thus its contribution to the stability of the cage too. In the opposite cage molecule the trend is reversed. The over-all effect seems to be a cancellation of these different contributions to the total energy of the system.

Conclusion

Our theoretical method shows that it is quite possible that an oxygen or a nitrogen molecule would have a small but measurable stabilizing effect on a local water structure. This stabilization is due to a slightly increased polarization of the water molecules. The advantage of an oxygen or a nitrogen molecule over a non-hydrogen-bonded water molecule could be that this polarization can take place without any repulsive electrostatic interaction between the interstitial molecule and the surrounding water structure.

Substituent Effects on Proton Affinities of Simple Molecules

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Abstract: Molecular orbital studies of proton affinities of amino, hydroxyl, and fluoro groups predict that the proton affinity of these groups is in the expected order $NH_2 > OH > F$. In addition, methyl and amino groups bonded to the proton acceptor group increase its proton affinity; hydroxyl and fluoro decrease the proton affinity relative to the simple hydrides NH_3 , H_2O , and HF . The agreement with experiment is good in those cases where the proton affinity has been measured; some of the proton affinities presented here are predictions. Application to organic chemical rearrangements is also made.

With the advent of techniques such as chemical ionization mass spectrometry² and ion-cyclotron resonance,³ interest in the proton affinities of various molecules has increased. In addition to interest in the values of proton affinities *per se*, the magnitude of substituent effects on the proton affinities is of interest when compared to these substituent effects on the stability

of carbonium ions⁴ and strength of hydrogen bonds.⁵ The role of adjacent lone pairs (the "α effect") on the reactivity of nucleophiles⁶ has been of some interest so that quantitation of the inherent basicities, *i.e.*, proton affinities, is of relevance. The site of protonation in substituted hydroxylamines and fluoro amines

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(2) See F. H. Field, *Accounts Chem. Res.*, **1**, 42 (1967); *J. Amer. Chem. Soc.*, **92**, 2672 (1970), and references therein.

(3) J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).

(4) P. A. Kollman, W. F. Trager, S. Rothenberg, and J. E. Williams, *J. Amer. Chem. Soc.*, **95**, 5460 (1973).

(5) J. Del Bene, *J. Chem. Phys.*, **58**, 3139 (1973); **57**, 1899 (1972); *J. Amer. Chem. Soc.*, **95**, 5460 (1973).

(6) See, for example, J. O. Edwards and R. G. Pearson, *J. Amer. Chem. Soc.*, **84**, 16 (1962); N. J. Fina and J. O. Edwards, *Int. J. Chem. Kinet.*, **5**, 1 (1973); J. F. Liebman and R. M. Pollack, *J. Org. Chem.*, **38**, 3444 (1973).

is of importance in certain reaction mechanisms and the studies reported here might provide some insight. There has been one general theoretical study of proton affinities by *ab initio* molecular orbital techniques⁷ and the studies presented here will be related to this previous work.

Computational

All calculations were carried out within the closed shell formalism first described by Roothaan.⁸ These *ab initio* studies used the MOLE quantum chemistry system⁹ and a "double ζ " Gaussian basis set, with Whitten's¹⁰ 10s set for C, N, O, and F and 5s set for H and Huzinaga's¹¹ 5p set for C, N, O, and F. The 10s set was contracted as suggested by Whitten to 4, 3, 2, 1 and the hydrogen s's and C, N, O, and F p's were contracted to 4, 1. The hydrogen atom orbitals were scaled by $2^{1/2}$ from their values for the atomic calculation.

No extensive geometry optimization was done; the geometries for the neutral molecules were taken from experimental values. The geometrical parameters for the protonated species were based on the geometries for the corresponding neutral species within the same number of protons and electrons. The bond lengths were kept the same as the unprotonated species (see Table I). These are reasonable assumptions for observing trends in proton affinities as long as exact values are not expected. For example, in H_3O^+ , accurate theory¹² predicts a bond length ~ 0.2 Å longer than in H_2O . With a reasonable choice of O-H force constant of 10^6 dyn/cm, such a bond length difference results in a difference in proton affinity of ~ 2 kcal/mol. Also the difference in energy between the $\theta(\text{HOH}) = 112^\circ$ and 120° geometries of H_3O^+ is ~ 1.5 kcal/mol. Thus we see energies are not especially sensitive to $\theta(\text{HOH})$ or to the bond length.

To get proton affinities in near-quantitative agreement with experiment one should do the following: (1) include polarization functions in the basis set, (2) optimize the geometries for neutral and protonated species, (3) carry out both SCF and CI type calculations on the neutral and protonated species, and (4) make some estimate of the vibrational corrections to the protonation energies. We do not feel it worthwhile to carry out step 2 very precisely, without the use of a better basis set (step 1) and a good CI calculation (step 3), since polarization functions can significantly affect the optimum geometries and proton affinities¹² and correlation effects can contribute significantly to the proton affinities.¹²

Let us now briefly examine our assumptions or logical steps to improved quantitative agreement between theory and experiment. The lack of polarization effects in the basis set, step 1, will cause the calculated proton affinities to be too high since "double ζ " basis

Table I

Molecule	Geometrical parameters used	Ref
HF	$r(\text{HF}) = 0.91$ Å	a
H_2F^+	$r(\text{HF}) = 0.91$ Å, $\theta(\text{HFF}) = 120^\circ$	
H_2O	$r(\text{HO}) = 0.96$ Å; $\theta(\text{HOH}) = 104^\circ$	a
H_3O^+	$r(\text{HO}) = 0.96$ Å; $\theta(\text{HOH}) = 109.5^\circ$; C_{3v} sym	
NH_3	$r(\text{HN}) = 1.01$ Å; $\theta(\text{HNN}) = 107^\circ$; C_{3v} sym	b
NH_4^+	$r(\text{HN}) = 1.01$ Å; H^+ along C_3 axis of NH_3	
F_2	$r(\text{FF}) = 1.41$ Å	c
HF_2^+	$r(\text{FH}) = 0.91$ Å; $r(\text{FF}) = 1.41$ Å; $\theta(\text{HFF}) = 120^\circ$	
FOH	$r(\text{OF}) = 1.44$ Å; $r(\text{OH}) = 0.96$ Å; $\theta(\text{HOF}) = 97.2^\circ$	d
FOH_2^+	$r(\text{OF}) = 1.44$ Å; $r(\text{OH}) = 0.96$ Å; $\theta(\text{HOH}) = 108^\circ$; $\theta(\text{FOH}_{\text{bis}}) = 120^\circ$	
HFOH'^+	$r(\text{OF}) = 1.44$ Å; $r(\text{OH}') = 0.96$ Å; $r(\text{HF}) = 0.91$ Å; $\theta(\text{HOF}) = 97.2^\circ$; $\theta(\text{OFH}) = 120^\circ$; $\phi(\text{H}'\text{OFH}) = 180^\circ$	
HOOH	$r(\text{OO}) = 1.475$ Å; $r(\text{OH}) = 0.95$ Å; $\theta(\text{HOO}) = 94.8^\circ$; $\phi(\text{HOOH}) = 180^\circ$	e
$\text{H}_2\text{OOH}'^+$	$r(\text{OO}) = 1.475$ Å; $r(\text{OH}) = 0.96$ Å; $\theta(\text{HOH}) = 108^\circ$; $\theta(\text{OOH}') = 103^\circ$; $\theta(\text{OOH}_{\text{bis}}) = 115^\circ$	
$\text{NH}_2\text{OH}'$	$r(\text{ON}) = 1.41$ Å; $r(\text{OH}) = 0.96$ Å; $r(\text{NH}) = 1.01$ Å; $\theta(\text{NOH}') = 103^\circ$; $\theta(\text{ONH}_{\text{bis}}) = 115^\circ$; $\theta(\text{HNNH}) = 107^\circ$	
$\text{NH}_3\text{OH}'^+$	$r(\text{ON}) = 1.41$ Å; $r(\text{NH}) = 1.01$ Å; $r(\text{OH}) = 0.96$ Å; $\theta(\text{NOH}') = 103^\circ$; $\theta(\text{HNNH}) = 107^\circ$; $\phi(\text{NHOH}') = 60^\circ$; C_{3v} sym around N	
$\text{NH}_2\text{OH}_2'^+$	$r(\text{ON}) = 1.41$ Å; $r(\text{NH}) = 1.01$ Å; $r(\text{OH}) = 0.96$ Å; $\theta(\text{HNNH}) = 107^\circ$; $\theta(\text{H}'\text{OH}') = 108^\circ$; $\theta(\text{NOH}'_{\text{bis}}) = 129^\circ$; $\theta(\text{ONH}_{\text{bis}}) = 129^\circ$; $\phi(\text{H}_{\text{bis}}\text{NOH}'_{\text{bis}}) = 180^\circ$	
$\text{NH}_2\text{NH}_2'$	$r(\text{NH}) = 1.47$ Å; $r(\text{NH}) = 1.01$ Å; $\theta(\text{HNNH}) = 107^\circ$; $\theta(\text{NNH}_{\text{bis}}) = 129^\circ$; $\phi(\text{H}_{\text{bis}}\text{NNH}'_{\text{bis}}) = 180^\circ$	g
$\text{NH}_2\text{NH}_3'^+$	$r(\text{NN}) = 1.47$ Å; $r(\text{NH}) = 1.01$ Å; $\phi(\text{HNNH}) = 107^\circ$; $\theta(\text{NNH}_{\text{bis}}) = 129^\circ$; $\phi(\text{HNNH}') = 60^\circ$	
NH_2F	$r(\text{NF}) = 1.40$ Å; $r(\text{NH}) = 1.01$ Å; $\theta(\text{HNNH}) = 107^\circ$; $\theta(\text{FNH}_{\text{bis}}) = 120^\circ$	h
NH_3F^+	$r(\text{NF}) = 1.40$ Å; $r(\text{NH}) = 1.01$ Å; $\theta(\text{HNNH}) = 107^\circ$; C_{3v} sym around N	
$\text{NH}_2\text{FH}'^+$	$r(\text{NF}) = 1.40$ Å; $r(\text{NH}) = 1.01$ Å; $\theta(\text{HNNH}) = 107^\circ$; $\theta(\text{FNH}_{\text{bis}}) = 120^\circ$; $\phi(\text{H}'\text{FNH}_{\text{bis}}) = 180^\circ$	
CH_3F	$r(\text{CH}) = 1.097$ Å; $r(\text{CF}) = 1.384$ Å; $\theta(\text{FCH}) = 108.5^\circ$	i
$\text{CH}_3\text{FH}'^+$	CH_3 has same geometry as in CH_3F compd; has same geometry as in CH_3OH except $r(\text{CF}) = 1.38$ Å; $r(\text{FH}) = 0.91$ Å	
$\text{CH}_2\text{OH}'$	$r(\text{CH}) = 1.096$ Å; $r(\text{CO}) = 1.427$ Å; $r(\text{OH}') = 0.956$ Å; $\theta(\text{HCC}_2) = 109.9^\circ$; $\theta(\text{COH}') = 108.9^\circ$; O is tilted off C_3 methyl axis by 3.34° ; $\phi(\text{HCOH}') = 180^\circ$	j
$\text{CH}_3\text{OH}_2'^+$	Methyl group from CH_3OH ; OH_2' geometry from CH_3NH_2 with $r(\text{CO}) = 1.427$ Å; $r(\text{OH}) = 0.96$ Å	
$\text{CH}_3\text{NH}_2'$	$r(\text{CH}) = 1.093$ Å; $r(\text{CN}) = 1.474$ Å; $r(\text{NH}) = 1.011$ Å; $\theta(\text{HCC}_2) = 109.3^\circ$; N is 3.5° off C_3 axis of methyl; $\theta(\text{CNH}'_{\text{bis}}) = 129^\circ$; $\theta(\text{H}'\text{NH}') = 106.2^\circ$; $\phi(\text{HCC}_2\text{H}') = 60^\circ$	k
$\text{CH}_3\text{NH}_3'^+$	Staggered ethane geometry with $r(\text{CN}) = 1.474$ Å; $r(\text{CH}) = 1.093$ Å; $r(\text{NH}) = 1.01$ Å; $\theta(\text{HCN}) = 109.3^\circ$; $\theta(\text{CNH}') = 109.5^\circ$	

(7) A. C. Hopkinson, N. K. Holbrook, K. Yates, and I. G. Csizmadia, *J. Chem. Phys.*, **49**, 3596 (1968).

(8) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 65 (1951).

(9) S. Rothenberg, P. Kollman, M. Schwartz, E. F. Hayes, and L. C. Allen, *Int. J. Quantum Chem., Symp.*, **3**, 715 (1970).

(10) J. W. Whitten, *J. Chem. Phys.*, **44**, 359 (1966).

(11) S. Huzinaga, *J. Chem. Phys.*, **43**, 1293 (1965).

(12) For example, when one compares the proton affinities calculated for geometry optimized H_2O and H_3O^+ , one finds a proton affinity of 180 kcal/mol with a "double ζ " basis and 173 kcal/mol with a "double ζ plus polarization basis": see P. A. Kollman and C. F. Bender, *Chem. Phys. Lett.*, **21**, 271 (1973). Correction from zero-point energy difference will lower these computed proton affinities by ~ 5 kcal/mol, and correlation corrections may increase or decrease the proton affinity.

^a See P. A. Kollman and L. C. Allen, *J. Amer. Chem. Soc.*, **93**, 4991 (1971), for experimental geometries. ^b W. S. Benedict and E. K. Plyler, *Can. J. Chem.*, **35**, 1235 (1957). ^c S. Fraga and B. J. Ransil, *J. Chem. Phys.*, **36**, 1127 (1962). ^d H. Kim, E. F. Pearson, and E. H. Appelman, *J. Chem. Phys.*, **56**, 1 (1972). ^e H. Kaldor and I. Shavitt, *J. Chem. Phys.*, **44**, 1823 (1966). ^f P. A. Giguere and I. U. Liu, *Can. J. Chem.*, **30**, 948 (1952). ^g A. Yamaguchi, I. Schiskima, T. S. Shimanouchi, and S. Mrzushima, *Spectrochim. Acta*, **16**, 1471 (1960). ^h By analogy to NH_2OH and NH_2NH_2 . ⁱ N. C. Baird and R. K. Datta, *Can. J. Chem.*, **49**, 3708 (1971). ^j W. H. Fink and L. C. Allen, *J. Chem. Phys.*, **46**, 2261 (1967). ^k W. H. Fink and L. C. Allen, *J. Chem. Phys.*, **46**, 2276 (1967).

sets tend to exaggerate the dipole moment of most molecules. Optimization of the geometry, step 2, may change the absolute proton affinities by about 3.5 kcal/mol, as shown in the earlier discussion on H_3O^+ . However, since we make consistent geometry choices throughout the series of molecules, we expect this should not greatly influence the relative proton affinities. For example, the preferred rotamer of the isoelectronic molecules CH_3NH_2 , CH_3OH_2^+ , and NH_3^+NH_2 is expected to be the same. In any case, inversion and internal rotation barriers are usually small compared to the numbers of interest. The correlation and vibration contributions to the proton affinities should be very similar and thus steps 3 and 4 should not affect the relative values. Kaufman¹³ suggests that there is slightly less correlation energy in H_3O^+ than in H_2O . She believes that protonation of a lone pair will in general slightly decrease the total correlation energy. We postulate that assumptions 1 through 4, although necessary for quantitative agreement with experiment, are unlikely to affect the relative values and substituent effects we wish to consider.

Proton Affinities

Comparison with Experimental Values. The calculated proton affinities are tabulated in Table II and

Table II. Proton Affinities Calculated for R-X (kcal/mol)

R	X		
	NH_2	OH	F
H	221	174	114
CH_3	230	185	129
NH_2	223	178	130
OH	201	168	121
F	191	131	78

comparisons with experimental values found by ion-cyclotron resonance² are of interest. The proton affinities determined experimentally for $\text{R} = \text{H}$ (NH_3 , H_2O , and HF) are 207, 164, and 116¹⁴ kcal/mol compared with the theoretical values of 221, 174, and 114 kcal/mol (see also ref 7). With the exception of the HF proton affinity, the calculated values for the proton affinity are somewhat high due mainly to deficiencies in the basis set.¹² The agreement with experiment for the calculated proton affinity of HF is due to a fortuitous cancellation of errors.¹⁵ For $\text{R} = \text{CH}_3$ (CH_3NH_2 , CH_3OH , and CH_3F) the proton affinities are 216, 180, and 151 (experimental)² and 239, 185, and 129 (calculated). The difference between the experimental and calculated proton affinity of methyl fluoride is surprisingly high, whereas that difference in the proton affinity of CH_3OH and CH_3NH_2 is small and of the same order as found for $\text{R} = \text{H}$. As one goes from the first to the second row in Table II, the trend for the proton affinity in $\text{X} = \text{OH}$ and NH_2 is similar (an increase for $\text{R} = \text{CH}_3$ of ~ 10 – 16 kcal/mol), but the difference in the experimental proton affinities of HF and CH_3F is surprisingly large (37 kcal/mol). The proton affinity of methane² is 126 kcal/mol, close to the

(13) J. J. Kaufman, personal communication.

(14) M. S. Foster and J. L. Beauchamp, unpublished results.

(15) The geometry chosen for HF may be sufficiently closer to the truth than that for H_2F^+ so that the proton affinity is not overestimated as much as in our calculation of the H_2O and NH_3 proton affinities.

value calculated for the F protonation of CH_3F . However, we may recast our result in terms of the hydrogen atom affinity, HA, of the CH_3F^+ ion and compare this H-F bond energy with that of HF. Hydrogen atom affinities of cations are easily related to proton affinities of the corresponding neutrals

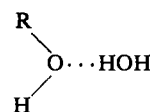
$$\text{HA}(\text{X}^+) = \text{PA}(\text{X}) + \text{IP}(\text{X}) - \text{IP}(\text{H})$$

We find $\text{HA}(\text{CH}_3\text{F}^+) = 126$ kcal/mol^{2,16a} while the F-H bond energy of HF is 120 kcal/mol.^{16b} The slightly higher H-halogen bond strength of the $\text{CH}_3\text{F}^+-\text{H}$ ion than in HF is also observed in the corresponding $\text{CH}_3-\text{ClH}^+-\text{HCl}$, $\text{CH}_3\text{BrH}^+-\text{HBr}$, and $\text{CH}_3\text{IH}^+-\text{HI}$ pairs.^{16a} As such, we doubt that CH_3FH^+ is fundamentally different from the other CH_3XH^+ ions. In view of the above, we have some confidence in the trends we find for $\text{X} = \text{NH}_2$ and OH and $\text{R} = \text{NH}_2$, OH, and F; the trends for $\text{X} = \text{F}$ are more questionable in view of the difference between the calculated and experimental proton affinity of CH_3F .

Inductive Effects

As has been noted for carbonium ions,⁴ CH_3 and NH_2 appear to be inductively stabilizing and OH and F inductively destabilizing relative to H, when $\text{X} = \text{NH}_2$ and OH. That is, the proton affinities for $\text{RNH}_2(\text{ROH})$ are greater than that of $\text{NH}_3(\text{H}_2\text{O})$ when $\text{R} = \text{CH}_3$ and NH_2 and less than that of $\text{NH}_3(\text{H}_2\text{O})$ when $\text{R} = \text{OH}$ and F. This has been previously rationalized⁴ on the basis of the inductive stabilizing effects of protons. When $\text{X} = \text{F}$, even OH appears to be inductively stabilizing.

It is worthwhile to compare the inductive effects found in carbonium ions and proton affinities with those found in hydrogen bonds



for $\text{R} = \text{CH}_3$, NH_2 , OH, and F. All of these groups inductively withdraw electrons from the oxygen and form weaker H bonds than found in the water dimer ($\text{R} = \text{H}$). Thus, it appears that there is a qualitative as well as a quantitative difference between weak hydrogen bonds (where there is only a small perturbation on the system) and proton affinities, where the perturbation is much larger. It is probably reasonable to conclude that F is inductively withdrawing in all situations but that CH_3 and NH_2 may donate electrons (proton affinities) or withdraw them (H bonds) depending on the perturbation.

Relation to Other Experimental Work

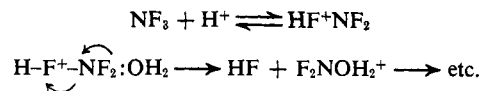
The existence of an " α effect" (adjacent lone pair interaction) has been postulated.⁶ The results we find here do not support the idea that adjacent lone pairs will always increase the rate of or facilitate a particular chemical process. For example, the adjacent lone pairs in hydrazine, NH_2-NH_2 , cause it to have a higher proton affinity than NH_3 , whereas $\text{HO}-\text{OH}$ has a lower proton affinity than H_2O . The calculated difference of

(16) (a) J. L. Beauchamp, D. Holtz, S. D. Woodgate, and S. L. Patt, *J. Amer. Chem. Soc.*, **94**, 2798 (1972). (b) J. Berkowitz, W. A. Chupka, P. M. Guyon, J. H. Holloway, and R. Spohr, *J. Chem. Phys.*, **54**, 5165 (1971).

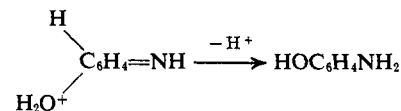
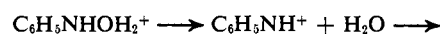
the proton affinities of N_2H_4 and NH_3 is 2 kcal/mol. The corresponding experimental difference as determined by ion-cyclotron resonance is 2.6 kcal/mol.¹⁷ No corresponding experimental data exist as to the relative proton affinities of H_2O_2 and H_2O . The near equality of the calculated and experimental differences of the proton affinities of N_2H_4 and NH_3 increases our confidence in the remaining numbers and comparisons.

In NH_2OH , NH_2F , and HOF , the site of protonation has not been answered definitively, and our results would support N protonation in NH_2OH and NH_2F and O protonation in HOF . The difference in energy between N and F protonation in NH_2F (61 kcal/mol) makes it quite clear that N protonation will take place. Salts of NH_2F have been indirectly synthesized and shown to be N protonated by proton nmr.¹⁸ The trifluoromethylsulfonate salt¹⁹ deprotonates to the acid and fluoramine on vaporization^{18,20} by analogy to ammonium salts. Salts of neither NH_2Cl nor substituted derivatives are known, although the latter invoking N protonation are customarily cited as intermediates in the Hoffmann-Löffler reaction.²¹ The reaction of HNF_2 and CH_3NF_2 with protic²²⁻²⁴ and Lewis acids²³⁻²⁵ has been investigated and some evidence of nitrogen basicity presented. Reaction of alkyldifluoramines with BF_3/H_3PO_4 yields fluoroimmonium ions.^{26,27} N protonation is essentially reversible²⁸ and energetically preferred. However, F protonation is not reversible owing to sequential F-H bond formation²⁹ and/or N-F bond polarization³⁰ and concerted loss of HF and rearrangement. Intuitively, we would expect the salt forming ability of NF_3 to be less than HNF_2 or its alkyl derivatives. No salts of NF_3 are known, in accord with this logic. The proton affinity of NF_3 has been measured to be 151 kcal/mol.³¹ Our calculated results support the interpretation³¹ that one has N protonation in NF_3 since the proton affinity for F protonation in NF_2F is certainly lower than that in NH_2F (<130 kcal/mol). This assertion is justified by both intuition on the inductive effects of fluorine and by noting that $PA(CF_3F)$ is 120 ± 6 kcal/mol³² while $PA(CH_3F) = 151$ kcal/mol.² However, as with HNF_2

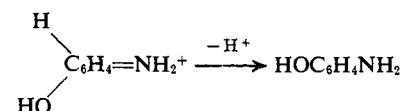
and its derivatives, fluorine protonation is a necessary reaction in understanding the reaction chemistry; the hydrolysis of NF_3 is accelerated by acid,²⁹ *i.e.*



We now turn to protonation of NH_2OH and note that the difference in energy between N and O protonation (23 kcal/mol greater for N protonation) is modest. We doubt, but cannot prove, that more precise calculations would alter this order of protonation. Rearrangement of *N*-arylhydroxylamines in acid to form amino arenols has been shown to proceed through O-protonated intermediates.³³ O protonation is consistent with qualitative basicity trends and *pK* values: arylamines are in general less basic than ammonia and alkylamines.^{34,35} Accordingly, we would anticipate the oxygen of arylhydroxylamines to be of more commensurate basicity to the nitrogen thereof. However, gas phase basicity studies have shown that aniline is more basic than ammonia.^{36,37} Without invoking solvation effects, we may simply explain the apparent disparity of the preference of O protonation and yet the higher basicity of the N atom. As with alkyldifluoramines, we argue that N protonation is reversible while O protonation is not owing to rapid rearrangement. This would appear to violate organic chemical intuition noting that



and



appear almost equally acceptable. However, the ionization potential of C_6H_5NH is much lower than that of OH (8.3 eV *vs.* 13.2 eV),³⁸ and N-H bond strengths are nearly commensurate with O-H.³⁹ We may thus conclude $C_6H_5NH^+ + H_2O$ is indeed energetically preferred over $C_6H_5NH_2 + OH^+$. Accordingly, the former fragmentation is more likely as noted above.

Analogous logic may be useful in understanding acid catalyzed rearrangements of *N,N'*-diarylhydrazines

(33) (a) E. D. Hughes and C. K. Ingold, *Quart. Rev., Chem. Soc.*, **6**, 34 (1952); (b) T. B. Patrick and J. A. Schield, *Tetrahedron Lett.*, 445 (1973).

(34) See, for example, J. March, "Advanced Organic Chemistry," Vol. 8, McGraw-Hill, New York, N. Y., 1968, p 219.

(35) However, R. W. Alder, P. S. Bowman, W. R. S. Steele, and D. R. Winterman, *Chem. Commun.*, 723 (1968), report that 1,8-bis(dimethylamino)naphthalene has a *pK_b* of 12.3, 2 units higher than NH_3 .

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(i.e., the benzidine rearrangement^{33,40,41}), *N,O*-diarylhydroxylamines,⁴² substituted triphenylmethylhydroxylamines,⁴³ hydroxyimines (i.e., oximes, cf. Beckmann rearrangement⁴⁴), oxaziridines,⁴⁵ and alkyl and α -hydroxylalkyl hydroperoxides (cf. the Baeyer-Villiger reaction⁴⁶). One can also consider syn-anti isomerization⁴⁴ and even hydrolysis of oximes.⁴⁷

Let us now briefly consider reactions of HOF and F₂ and their protonated species. For HOF we calculated a 12-kcal/mol difference between O and F protonation favoring the former. HOF is one of the most thoroughly investigated triatomic molecules with regard to physical properties.⁴⁸ However, few chemical reactions have been performed most probably due in large part to the inherent instability of aqueous HOF solutions. In base, HOF decomposition yields O₂ while in acid it yields H₂O₂.⁴⁸ The latter may be explained in terms of either F protonation or O-F bond polarization³⁰ and a subsequent SN2 attack on the oxygen by a water molecule to form H₂OOH⁺, i.e., protonated H₂O₂. Analogous O-F bond polarization has been invoked³⁰ in a discussion of the reaction of OF₂ with primary amines to form the corresponding

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nitroso compound.⁴⁹ To the best of the authors' knowledge, protonated F₂ has not been proposed in the literature. We note, however, that protonated Cl₂ and Br₂ have recently been invoked in aromatic halogenations⁵⁰ and proton-polarized F₂ in low-temperature olefin-fluorine reactions (ref 30 discussing the results in ref 51).

Conclusion

In general, the theoretically calculated proton affinities here are in reasonable agreement with experimental values and give us some confidence in the predictions of proton affinities for NH₂OH, NH₂F, HOOH, HOF, and F₂. CH₃F is a molecule where a more precise calculation of the proton affinity would be of interest. When a plus charge is placed on a molecule (as in substituted carbonium ions RCH₂⁺ or in protonated species such as RNH₃⁺), R = CH₃ and NH₂ appear to be inductively stabilizing and R = OH and F destabilizing relative to R = H.

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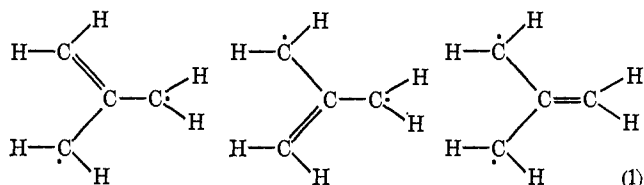
Triplet Electronic Ground State of Trimethylenemethane^{1a}

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Abstract: A nonempirical quantum mechanical study of the electronic structure of C(CH₂)₃ has been carried out. A double ζ basis set of contracted Gaussian functions was employed, and self-consistent-field wave functions were obtained for the triplet ground state. The planar (*D_{3h}*) configuration is predicted to lie 17 kcal/mol below the orthogonal (*C_{2v}*) form. The electronic structure is discussed in terms of Mulliken populations and orbital perspective plots. Some preliminary results for the lowest singlet states are reported.

There is a long history of interest among theoretical organic chemists in the trimethylenemethane radical, traditionally represented by the three structures



(1) (a) Work performed under the auspices of the U. S. Atomic Energy Commission; (b) Charles Fish Fellow; (c) Alfred P. Sloan Fellow.

Interest in C(CH₂)₃ began in 1948 with the work of Moffitt, who was cited in a paper by Coulson² as having shown the central atom in trimethylenemethane to have the greatest π bond order attainable by a carbon atom. In a related paper appearing 4 years later, Greenwood³ discussed the critical role of C(CH₂)₃ in the notion of "free valence," defined by Coulson²

$$FV = N_{\max} - N \quad (2)$$

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