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Nucleophilic Addition to Nitrile Oxides: Concerted or Stepwise?

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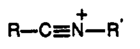
The potential energy hypersurfaces corresponding to the addition reactions of fulminic acid (HCNO) to water, ammonia, and methanol have been explored using ab initio molecular orbital calculations. Geometries of stationary points were optimized at the HF/3-21G, HF/6-31G*, and MP2/6-31G* levels of theory while relative energies were estimated at the MP4-SDQ/6-31G* and MP2/6-31G** levels. Each addition is predicted to be concerted with a single transition structure connecting the reactants and the oxime adduct. This confirms the result of an earlier ab initio study (*J. Am. Chem. Soc.* **1980**, *102*, 573) and points out a difference with recent MNDO results (*J. Mol. Struct. Theochem* **1988**, *181*, 389), which predict that the addition proceeds in two steps with the formation of a zwitterionic intermediate.

Introduction

Nitrile oxides 1, initially identified by Werner in 1894,[1] are versatile starting materials in organic synthesis.[2] These reagents readily undergo 1,3-dipolar cycloadditions with several types of unsaturated substrates (containing double and triple bonds) to form five-membered heterocyclic products. Nitrile oxides can also be regarded as stabilized nitrilium ions 2. As a consequence, they undergo a series of reactions with nucleophilic agents at carbon as shown in Scheme I. Kinetic studies[3] have found that all of these reactions are stereospecific, leading to a single *Z* oxime, even when this kinetic adduct was thermodynamically less stable than the corresponding *E* isomer. For instance, in each of the examples shown in Scheme I, the entering nucleophile and the lone pair of nitrogen are disposed in a trans relationship across the C=N bond, thus forcing the hydroxyl group into a position cis to the nucleophilic moiety.

$R-C\equiv\overset{+}{N}-\overset{-}{O}$

1

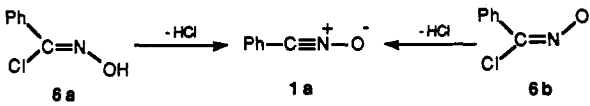


$R-C\equiv\overset{+}{N}-R'$

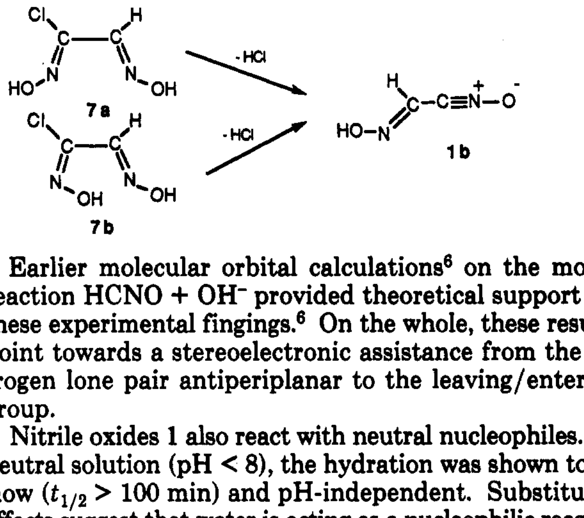
2

The acetate adduct 3 and the phenylacetylene 4 undergo further reactions involving the oxygen of the oxime functional group because of their *Z* conformation. For the same reason, the azido-oxime 5 is not converted to the tetrazoles as is generally the case,[3] again because of its *Z* configuration.

As the addition of anionic nucleophiles to nitrile oxides 1 is stereospecific, the reverse reactions should also exhibit stereospecificity. As a matter of fact, the *Z* hydroximoyl chloride **6a** has been shown to lose HCl, to give benzonitrile oxide **1a**, (6×10^7)-fold faster than its *E* isomer **6b** (eq 1).[4] Similarly, the (1*Z*,2*E*)-chloroglyoxime **7a** loses HCl 10^9 times faster than the 1*E*,2*E* isomer **7b** to form the same dipole **1b** (eq 2).[5]



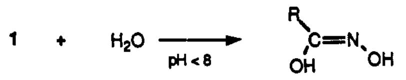
(1)



(2)

Earlier molecular orbital calculations[6] on the model reaction HCNO + OH^- provided theoretical support for these experimental fingings.[6] On the whole, these results point towards a stereoelectronic assistance from the nitrogen lone pair antiperiplanar to the leaving/entering group.

Nitrile oxides 1 also react with neutral nucleophiles. In neutral solution (pH < 8), the hydration was shown to be slow ($t_{1/2} > 100$ min) and pH-independent. Substituent effects suggest that water is acting as a nucleophilic reagent (eq 3).[3]



(3)

Similarly, primary and secondary amines add stereospecifically to nitrile oxides yielding only the *Z* amidoxime in the kinetic step (eq 4).[7] In an attempt to rationalize

(4)

the stereospecificity of addition of neutral nucleophiles to nitrile oxides, molecular orbital calculations at the minimal-basis HF/STO-3G level were carried out[8] for the

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[1] Werner, A.; Buss, H. *Chem. Ber.* **1974**, *27*, 2193.

[2] For a recent review, see: *Nitrile Oxides, Nitrones and Nitronates in Organic Synthesis*; Torssell, K. B. G., Ed.; VCH: Verlagsgesellschaft, Weinheim, 1989.

[3] Dignam, K. J.; Hegarty, A. F.; Quain, P. L. *J. Org. Chem.* **1978**, *43*, 388; *J. Chem. Soc., Perkin Trans. 2*, **1977**, 1457.

[4] Hegarty, A. F.; Mullane, M. *J. Chem. Soc., Perkin Trans 2* **1986**, 995.

[5] Fox, E. T. Ph.D. Thesis, The National University of Ireland, **1986**.

[6] Leroy, G.; Nguyen, M. T.; Sana, M.; Dignam, K. J.; Hegarty, A. F. *J. Am. Chem. Soc.* **1979**, *101*, 1988.

[7] Dignam, K. J.; Hegarty, A. F. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1437.

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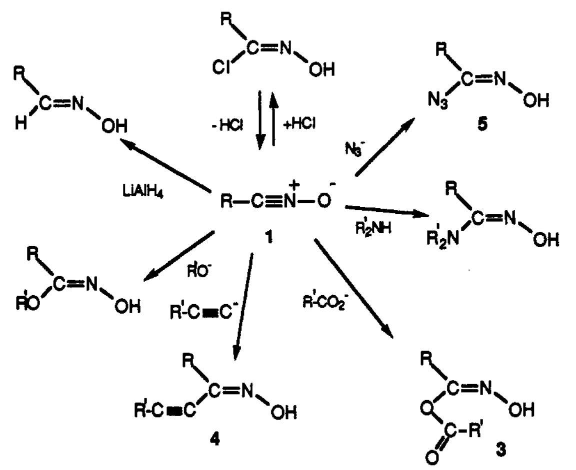
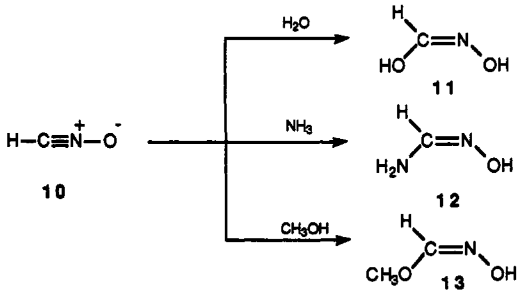
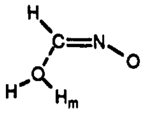
Scheme I

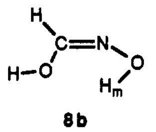


Scheme II



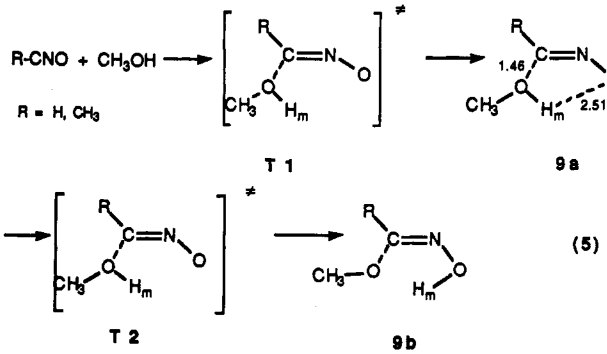
simple model reactions of water with the formonitrile oxide (HCNO) and with acetonitrile oxide (CH_3CNO). Extensive exploration of the potential energy surface for H_2O + HCNO predicted the addition to be a *concerted* but highly asynchronous process. Although only a single saddle point—corresponding to the transition structure **8a**—was found on the surface connecting the reactants with the adduct **8b**, the geometrical changes occur in two phases.


8a


8b

Firstly, as the water approaches the nitrile oxide the latter undergoes deformation in a trans mode, thereby determining the *Z* configuration of the oxime adduct; this phase may be termed heavy-atom reorganization. Secondly, as the transition structure is reached, a corridor on the energy hypersurface is entered, along which the hydrogen H_m moves unimpeded by any further barrier; this phase is proton transfer. Similar results were also obtained for the addition of water to acetonitrile oxide. The methyl group on the 1,3-dipole exerts a deactivating effect on the addition due to its electron-donating nature.[8]

Sharma and Aggarwal recently reported molecular-orbital calculations, for additions of methanol to formonitrile oxide and to acetonitrile oxide, performed with the semiempirical MNDO method.[9a] Contrary to the earlier ab initio results,[8] these authors found the additions to proceed by a *stepwise* mechanism (eq 5). In the first step, which was predicted to be rate determining, a high-energy intermediate **9a** was formed via a reactant-like transition structure **T1** (similar to **8a**). The adduct **9b** was formed in the second step via a second transition structure **T2**, which closely resembled the intermediate **9a**. Similar results were also reported by the same authors[9b] for MNDO calculations on additions of methylamine to both HCNO and CH_3CNO. Intermediates were located on all these reaction pathways and were shown to be true energy minima by virtue of having all real vibrational frequencies. It was stated[9] that the intermediates were stabilized by hydrogen bonding between the migrating hydrogen of methanol or methylamine (cf. H_m in **9a**) and the oxygen of the nitrile oxide.



(5)

These conflicting theoretical studies raise several questions. Are the earlier ab initio calculations in error, owing to the neglect of electron-correlation effects and the use of a minimal basis? Do the semiempirical calculations, by virtue of the parameterization of the MNDO method, somehow manage to correct for these deficiencies and thus provide a truer picture of the addition mechanism? Can theory be trusted at all? In order to resolve these issues, and to determine whether the mechanism of neutral nucleophilic addition to nitrile oxides is concerted or stepwise, the results of more extensive ab initio calculations are now presented. Larger basis sets are employed, and electron correlation is included. Scheme II summarizes the reactions studied in this work.

Computational Methods

The geometries of all reactants, transition structures, and products for the three reactions (Scheme II) were completely optimized at the split-valence basis HF/3-21G[10] level of Hartree–Fock theory. Harmonic vibrational frequencies were calculated at the same level of theory in order to characterize each stationary point (as either a local minimum or a saddle point) and to evaluate zero-point vibrational energies. Stationary points on the energy hypersurfaces for addition of H_2O and of NH_3 to HCNO were reoptimized at the HF/6-31G* level[11] (d polarization functions on non-hydrogen atoms), and single-point energies were then calculated by use of fourth-order Møller–Plesset perturbation theory[12] (neglecting triple substitutions) with this basis (MP4SDQ/6-31G*) and also using the larger 6-31G** basis[11] (added p polarization functions on hydrogen atoms) at the second-order MP level (MP2/6-31G**). Finally, to investigate the structural effects of electron correlation, stationary points on the NH_3 + HCNO hypersurface were further reoptimized at the MP2/6-31G* level. These calculations were performed

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(8) Nguyen, M. T.; Sana, M.; Leroy, G.; Dignam, K. J.; Hegarty, A. F. *J. Am. Chem. Soc.* **1980**, *102*, 573.

(9) (a) Sharma, K. K.; Aggarwal, A. K. *Int. J. Quantum Chem.* **1986**, *30*, 213. (b) Sharma, K. K.; Aggarwal, A. K. *J. Mol. Struct.* (*Theochem*) **1988**, *181*, 389.

(10) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(11) Hariharan, P. C.; Pople, J. A.; *Theor. Chim. Acta* **1973**, *28*, 213.

(12) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1.

Table I. Total, Relative (in Parentheses),[a] and Zero-Point Energies of Stationary Points on the HCNO + H_2O Reaction Pathway

level[b]	HCNO 10	H_2O	TS 14	oxime 11
HF/3-21G	−166.67877	−75.58596	−242.24520	−242.33406
	(0.0)		(12.3)	(−43.5)
HF/6-31G*	−167.63004	−76.01075	−243.58803	−243.69613
	(0.0)		(33.1)	(−34.7)
HF/6-31G**	−167.63260	−76.02357	−243.60271	−243.71113
	(0.0)		(33.5)	(−34.5)
MP2/6-31G*	−168.10836	−76.19597	−244.25183	−244.33918
	(0.0)		(32.9)	(−21.9)
MP3/6-31G*	−168.09678	−76.20197	−244.25216	−244.35022
	(0.0)		(29.2)	(−32.3)
MP4SDQ/ 6-31G*	−168.11125	−76.20459	−244.26958	−244.36060
	(0.0)		(29.0)	(−28.1)
MP2/ 6-31G**	−168.11553	−76.21936	−244.28171	−244.37049
	(0.0)		(33.4)	(−22.3)
MP4SDQ/ 6-31G**[c]	(0.0)		(29.5)	(−28.5)
ZPE[d]	12.5	12.3	26.8	29.4
estimated[e]	(0.0)		(31.5)	(−23.9)

[a] Relative energies with respect to the separated HCNO + H_2O system. [b] Based on HF/6-31G* optimized geometries given in Figure 1. [c] Estimated values using the additivity approximation.[16] ΔE(MP4/6-31G**) ≃ ΔE(MP4/6-31G*) + ΔE(MP2/6-31G**) − ΔE(MP2/6-31G*). [d] At HF/3-21G and scaled by 0.9. [e] Including ΔE(MP4/6-31G**) and ZPE's.

Table II. Total, Relative (in Parentheses),[a] and Zero-Point Energies of Stationary Point on the HCNO + NH_3 Reaction Pathway

level[b]	HCNO + NH_3	TS 15	oxime 12
HF/3-21G	−222.55097	−222.53512	−222.63888
	(0.0)	(9.9)	(−55.2)
HF/6-31G*	−223.81440	−223.77561	−223.88177
	(0.0)	(24.3)	(−42.3)
HF/6-31G**	−223.82813	−223.78837	−223.89796
	(0.0)	(24.9)	(−43.8)
MP2/6-31G*	−224.46207	−224.42682	−224.50977
	(0.0)	(22.1)	(−29.9)
MP3/6-31G*	−224.46222	−224.43059	−224.52627
	(0.0)	(19.8)	(−40.2)
MP4SDQ/6-31G**	−224.47953	−224.44890	−224.53574
	(0.0)	(19.2)	(−35.3)
MP2/6-31G*	−224.49849	−224.46204	−224.54855
	(0.0)	(22.9)	(−31.4)
MP4SDQ/6-31G**[c]	(0.0)	(20.0)	(−36.8)
ZPE[d]	32.8	34.8	37.6
estimated[e]	(0.0)	(22.0)	(−32.0)

[a] Relative energies with respect to the separated HCNO + H_2O system. [b] Based on HF/6-31G* geometries given in Figure 2. [c] Estimated values, see footnote *c* of Table I. [d] At HF/3-21G and scaled by 0.9. [e] Including ΔE(MP4/6-31G**) and ZPE's.

with the use of the MONSTERGAUSS,[13] GAUSSIAN 82,[14] and CADPAC[15] programs.

Throughout this paper, bond lengths are given in angstroms, bond angles in degrees, total energies in hartrees (1 Ha = 627.5 kcal mol^{-1}), relative and zero-point vibrational energies (ZPE) in kilocalories per mole. In this work, we have not considered hydrogen-bonded complexes of the type $H_2O\cdots HCNO$ and $H_3N\cdots HCNO$, since when the proton-donor H is replaced by alkyl groups in homologous nitrile oxides, these particular complexes no longer exist as minima on the potential energy hypersurfaces. Other electrostatic complexes are possible but were not systematically searched for as part of this study. The relative energies quoted in Tables I and II refer to the isolated molecules.

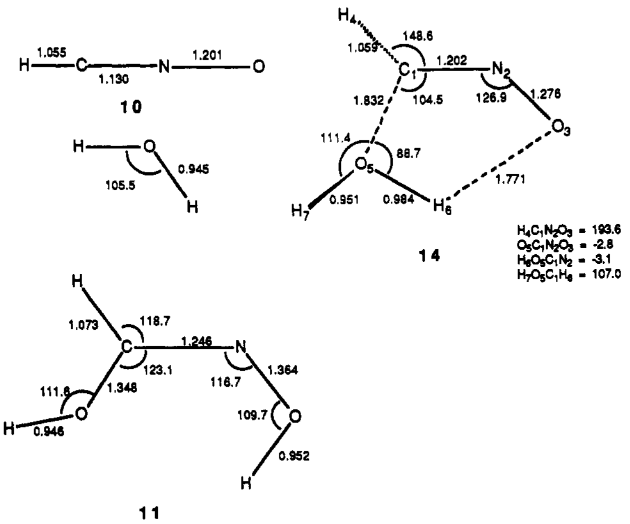

Figure 1. HF/6-31G* optimized geometries of the stationary points for the addition of water to fulminic acid.

Results and Discussion

Addition of Water to Formonitrile Acid (eq 6). The HF/6-31G* optimized geometries of the reactants HCNO and H_2O, the (*Z*)-hydroxyformaldoxime product 11 and the transition structure 14 are displayed in Figure 1. The total and relative energies of these structures are recorded in Table I.

HCNO is calculated to have a linear structure at the HF/6-31G* level. The transition structure 14 differs from that reported previously,[8] which had been constrained to be planar. The nonmigrating hydrogen atom H_7 of water in 14 lies 73° out of the plane of the heavy atoms. The intermolecular distances C_1O_5 (1.832 Å) and O_3H_6 (1.771 Å) are comparable with the previous values (1.85 and 1.88 Å, respectively) obtained at the HF/STO-3G level. The fact that H_6 is only 0.984 Å from the oxygen atom of water and 1.771 Å from the oxygen atom of the HCNO moiety in the transition structure 14 indicates that it is still part of the water molecule and very little transfer has taken place. Structure 14 possesses only one imaginary frequency (ν = 517*i* cm^{-1} at HF/3-21G) which corresponds to vibration mainly along the forming C_1O_5 bond with a small movement in the direction of the forming H_6O_3 bond. In order to find out whether or not an intermediate exists on the reaction pathway, a search was carried out on either side of the saddle point 14. This was done by optimizing structures with C_1O_5 bond distances initially at 1.7 and 2.3 Å, but with all other parameters the same as in 14. The starting structure with C_1O_5 = 1.27 Å optimized to the adduct 11, whereas the structure with C_1O_5 = 2.3 Å optimized slowly to a complex $H_2O\cdots H{-}C{\equiv}N{-}O$ having a linear HCNO fragment. Thus no intermediates were found on the reaction pathway linking the reactants HCNO + H_2O with the oxime adduct 11. Our best estimate (see Table I) indicates that the addition is exothermic to the extent of −23.9 kcal mol^{-1} but has to surmount an energy barrier of 31.5 kcal mol^{-1}. On the whole, the present study confirms the previous prediction,[8] obtained at a lower level of theory, that the addition is concerted but asynchronous, with proton transfer taking place at, or just after, the transition state without any further energy barrier.

Addition of Ammonia to Formonitrile Acid (eq 7). Figure 2 displays the HF/6-31G* optimized geometries of

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[13] Poirier, R. A.; Peterson, M. R. *Program* MONSTERGAUSS, University of Toronto, Canada, 1983.

[14] Binkley, J. S.; Frisch, M. J.; Whiteside, R. A.; Raghavachari, K.; Seeger, R.; Defrees, D.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. GAUSSIAN 82, Carnegie-Mellon University: Pittsburgh, PA, 1983.

[15] Amos, R. D.; Rice, J. E. CADPAC version 4.0, University of Cambridge, 1987.

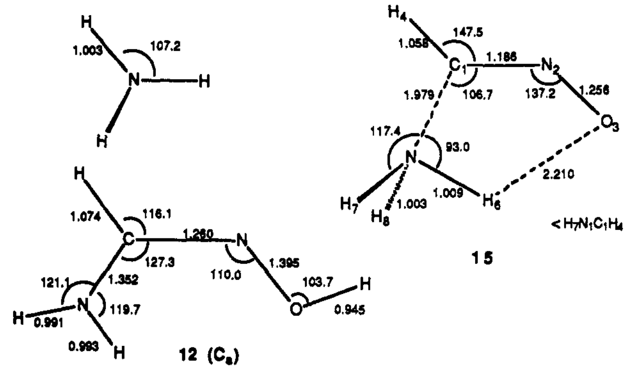
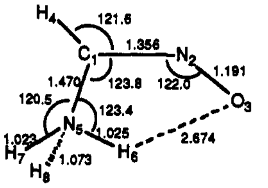


Figure 2. HF/6-31G* optimized geometries of the structures relevant to the addition of ammonia to fulminic acid.

ammonia, transition structure **15**, and the oxime adduct **12**. Table II shows the total and relative energies of the stationary points. The present structure obtained for the *Z* aminoformaldoxime **12** is broadly similar to those reported previously[16,17] using ab initio methods, but the semiempirical MNDO method gives a rather short N–O bond length (1.307 Å compared with 1.395 Å at HF/6-31G*) and a largely open CNO bond angle (118.5° compared with 110.0° at HF/6-31G*) in the oxime adduct. Again, transition structure **15** was found to be the only saddle point **15** on the addition pathway between the reactants and the adduct **12**. The addition is exothermic by −32.0 kcal mol^{-1} at the HF/6-31G* level, whereas the MNDO calculations gave a heat of reaction of −55.7 kcal mol^{-1}.[9b] In contrast to the present ab initio results, Sharma and Aggarwal[9b] predicted the existence of an intermediate **16** on the energy hypersurface, 16.9 kcal mol^{-1} less stable than the reactants. The MNDO activation energy required to form **16** is 28.9 kcal mol^{-1}, while that for conversion of the intermediate **16** to the oxime product **12** is only 2 kcal mol^{-1}. We note that in **16**, only one of the hydrogens (H_8) is out-of-the plane.



16

We now compare the additions of formonitrile oxide to water and to ammonia. Both transition structures **14** and **15** are similar. The main intermolecular distance N_5C_1 in **15** is slightly longer (1.979 Å) than the O_5C_1 in **14** (1.832 Å). The H_6O_3 distance (2.210 Å) in **15** is appreciably longer than the H_6O_3 distance (1.771 Å) in **14**. The CNO bond angle in **14** is more bent (126.9°) than that in **15** (137.2°). Overall, the energy barrier for the addition of ammonia to HCNO is calculated to be 22 kcal mol^{-1} (Table II), much smaller than that of 31.5 kcal mol^{-1} found for the addition of water (Table I). This result is in agreement with experimental observations. Kinetic studies[3] of the reactions of primary and secondary amines to benzonitrile oxides in water showed that the pseudo-first-order rate constant, k_{obs}, at a given pH is directly proportional to the total amine concentration. In addition, there is no evidence for catalysis of a second mole of amine and the rate of hydrolysis of the nitrile oxide is negligible.

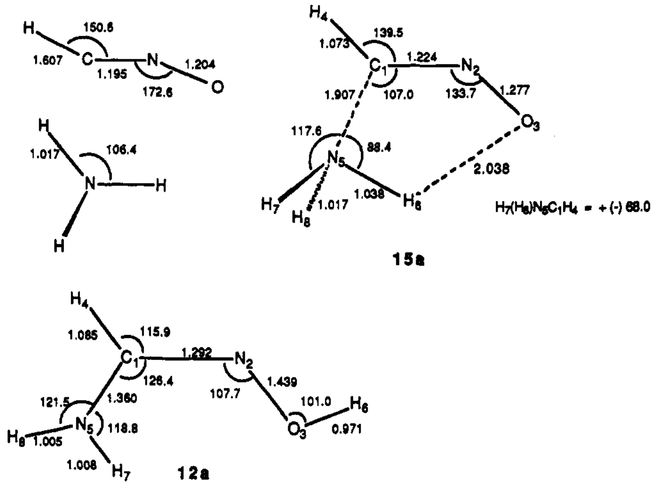


Figure 3. MP2/6-31G* optimized geometries of the structures relevant to the addition of ammonia to fulminic acid. The MP2/6-31G* energies using all MO's are as follows: HCNO, −168.12773; NH_3, −56.35738; **15a**, −224.44292; and **12a**, −224.52780 (in hartrees).

In order to study the effect of electron correlation on the shape of the potential energy surface, the geometries of the stationary points for the (HCNO + NH_3) system were reoptimized at the MP2/6-13G* level, as shown in Figure 3. It is known that at the MP2 level HCNO has a bent structure.[18] Although the linearity of this 1,3-dipole is in fact a matter of controversy,[19] recent high-level MO calculations[20] show that its shape is strongly sensitive to electron correlation. Moreover, the energy difference between linear and bent forms is small (<1 kcal mol^{-1}). The MP2/6-31G* geometries of the transition structure **15a** and the product **12a** are similar to those of the corresponding HF/6-31G* structures **15** and **12**. The MP2/6-31G* model results in a longer C_1N_2 bond length and a shorter C_1N_5 intermolecular distance in the structure **15a**. The MP2/6-31G* energy barrier and heat of reaction are respectively 25.9 and −27.4 kcal mol^{-1}, using MP2/6-31G* optimized geometries are only slightly different from the values of 22.1 and −29.9 kcal mol^{-1} obtained at the MP2/6-31G* level using the HF/6-31G* optimized geometries (see Table II).

To search for the possible existence of an intermediate at the MP2/6-31G* level, the transition structure **15a** was also distorted along the transition vector in both directions. With C_1N_5 > 1.907 Å, the supermolecule goes down hill energetically to a hydrogen-bonded complex $H_3N\cdots HCNO$, whereas with C_1N_5 < 1.907 Å, the supermolecule proceeds directly to the adduct **12a**. Although these searches are not true intrinsic reaction coordinate (IRC) gradient paths, they do nonetheless establish that no zwitterionic intermediate exists on the reaction pathway, contrary to the MNDO result of Sharma and Aggarwal.[9b] Thus, the concerted nature of the addition of ammonia to formonitrile oxide is again confirmed.

Addition of Methanol to Formonitrile Oxide (eq 8). Figure 4 displays the HF/3-21G optimized geometries of the transition structure **17** and the adduct **13** of the HCNO + CH_3OH addition. This reaction has an energy barrier of 12:1 kcal mol^{-1} and a heat of reaction of −46.2 kcal mol^{-1},

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[16] (a) Nobes, R. H.; Bouma, W. J.; Radom, L. *Chem. Phys. Lett.* **1982**, *89*, 492. (b) McKee, M. L.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1981**, *103*, 4673.

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[19] Farnell, L.; Nobes, R. H.; Radom, L. *J. Mol. Struct.* **1982**, *93*, 271.

[20] Nguyen, M. T.; Vanquickenborne, L. G., to be published.

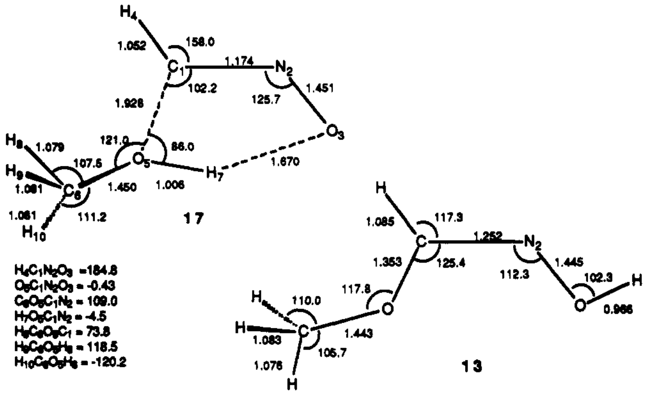

Figure 4. HF/3-21G optimized geometries of the transition structure **17** and adduct **13** in the addition of methanol to fulminic acid. The HF/3-21G energies are as follows: **17**, −281.05749; and **13**, −281.15035.

which are quite similar to the respective values of 12.3 and −43.5 kcal mol^{-1}, for the HCNO + H_2O addition at the HF/3-21G level (see Table I).

Again, in contrast with MNDO results,[9a] no intermediate can be located for this transformation. As seen in structure **17**, the O_5H_7 distance of methanol is very little lengthened (from 0.966 to 1.006 Å), and therefore proton transfer should take place after the transition state is reached.

Concluding Remarks. It has been shown using extensive calculations that the additions of water and of ammonia to formonitrile oxide are concerted reactions but are highly asynchronous. No intermediates are predicted to occur on the reaction pathways, in contrast to the findings of Sharma and Aggarwal[9] from MNDO calculations. Our results show that in each case the proton transfer to the oxygen of HNCO begins at the transition state and proceeds without any further energy barrier. This parallels the experimental results,[3] which show high stereospecificity both for protic nucleophiles (e.g. MeOH) and also for nonprotic nucleophiles (e.g. N_3^-).

Thus in each of the transition structures, heavy-atom reorganization is more advanced than proton transfer. The same result was found from HF/STO-3G calculations for concerted additions of the same three nucleophiles to formaldehyde.[21] The transition structures for additions to formonitrile oxide are, however, predicted to be considerably more reactant-like than those for additions to formaldehyde.

Sharma and Aggarwal[9b] used the intermolecular distance between the oxygen of methanol and the carbon of acetonitrile (cf. C_1O_5 in our Figure 1) as the single distinguished coordinate to generate their reaction energy profile (Figure 1 of their paper[9b]) which appears to be discontinuous. The apparent maximum at such a discontinuity does not correspond to a true saddle point.[22] We have repeated Sharma and Aggarwal's MNDO calculations, using the AMPAC program,[23] and find that their species **T1** is actually a second-order saddle point owing to the constraint of planarity for the heavy atoms. With this constraint imposed the pathway for the second, proton transfer step of the addition is indeed discontinuous and the species **T2** is not a stationary point. However, full optimization without any imposed constraints does reveal the intermediate **9a** to be a local minimum and **T1** and **T2** to be true first-order saddle points. This finding does therefore suggest that the qualitative difference between the shapes of the semiempirical and ab initio energy surfaces is due to a deficiency of the MNDO method.

A recent theoretical study[24] on the hydrogen exchange between methanol and formaldehyde showed that both MNDO and ab initio calculations provide qualitatively similar results although the MNDO method overestimates the energy barrier by about 50 kcal mol^{-1} and it was recommended that this method should not be relied on for the energetics of proton transfer between oxygens and/or between nitrogens.

It is known that semi-empirical and ab initio methods differ in the degree of "concertedness" in the Diels–Alder and 1,3-dipolar cycloadditions.[25] Ab initio methods favor more symmetrical transition structures, while semiempirical methods favor nonsymmetrical transition structures with one of the two new bonds being formed to a much greater extent than the other. In many respects, these observations are similar to the present case. Each of the transition structures located resembles what might be expected for the cycloaddition of formonitrile oxide to O–H or N–H bonds. In this regard, the intermediates located by Sharma and Aggarwal[9] are similar to the transition structures provided by semiempirical methods for ($4\pi + 2\pi$) cycloadditions.[25] It has been shown that semiempirical methods that neglect diatomic overlap inherently favor nonsymmetrical transition structures or stepwise mechanisms[25] by an overstabilization of the bonding combination.

In conclusion, the ab initio calculations at different levels of theory reported in the present work confirm the result of the previous study[8] showing that the addition of neutral protic nucleophiles to nitrile oxides are concerted processes with a single transition structure interconnecting reactants and adducts.

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