Nitrosoacetaldehyde and Its Enol and Oxime Isomers. A Theoretical Investigation of an Asymmetric 1,5-Sigmatropic Hydrogen Shift[1]

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Abstract: Ab initio molecular orbital calculations with minimal (STO-3G) and split-valence (4-31G) basis sets have been carried out for nitrosoacetaldehyde (O=NCH$_2$CH=O, **1**), nitrosovinyl alcohol (O=NCH=CHOH, **2**), and glyoxal monoxime (HON=CHCH=O, **3**). Optimized structures and relative energies of several conformations of **1**, **2**, and **3** are reported. The enol **2** is predicted to be slightly lower in energy than the keto isomer **1**, i.e., the nitroso substituent appears to reverse the ordering of stabilities from that observed in the parent keto/enol pair, acetaldehyde and vinyl alcohol. The oxime **3** is, however, still lower in energy. Two paths connecting the enol **2** and the oxime **3** are considered: firstly, that involving successive 1,3 shifts (i.e., proceeding via the aldehyde **1**); secondly, a direct 1,5-sigmatropic shift. The transition state **4** for the 1,5-hydrogen shift has been determined and this pathway provides a low-energy route for the isomerization of **2** to **3**. The structure of **4** resembles more closely the higher energy isomer **2** than the lower energy isomer **3**, which is consistent with the Hammond postulate.

Introduction

In recent papers,[2,3] we have examined theoretically the effect of substituents on the keto–enol equilibrium in the acetaldehyde–vinyl alcohol system. For the parent molecules, the keto form (acetaldehyde, $CH_3CH{=}O$) is found to lie lower in energy than the enol (vinyl alcohol, $CH_2{=}CHOH$) by about 50 kJ mol^{-1}; we were interested in designing a system with a preferred enol isomer. We found[2,3] that the preference for the keto isomer is diminished by substituents which are π-electron acceptors and σ-electron acceptors. In particular, we found[3] that for the nitroso substituent, the enol (nitrosovinyl alcohol, O=NCH=CHOH, **2**) is marginally lower in energy than its keto isomer (nitrosoacetaldehyde, O=NCH$_2$CH=O, **1**). Thus, nitrosovinyl alcohol appeared to be a possible condidate for a simple, stable enol. However, the situation in this system is complicated by the additional possibility of nitroso–oxime tautomerism, and the stability of the enol (**2**) with respect to the oxime (glyoxal monoxime, HON=CHCH=O, **3**) needs to be investigated.

In this paper, we use ab initio molecular orbital theory to examine the relationship to one another of the keto (**1**), enol (**2**), and oxime (**3**) isomers of the $C_2H_3NO_2$ system. Our main points of interest are the thermodynamic and kinetic stabilities of the enol **2** with respect to the other isomers. Fully optimized geometries are reported for **1**, **2**, and **3** and for the transition state (**4**) for the 1,5 shift from **2** to **3**. The latter represents the first ab initio determination of the transition state for an asymmetric 1,5-sigmatropic rearrangement.

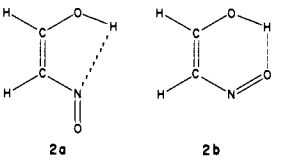
Method and Results

Standard ab initio LCAO SCF calculations were performed with a modified version [4]of the GAUSSIAN 70 system of programs[5] and the STO-3G[6] and 4-31G[7] basis sets. Likely preferred conformations of **1**, **2**, and **3** were determined on the basis of preliminary calculations with standard[8] bond lengths and angles reported previously[3] for **1** and **2** and shown in Table I for **3**. Full STO-3G optimizations of these conformations (**1**, **2a**, and **3a**) and of additional conformations **2b**, **3b**, and **3c**, relevant to the 1,5 shift were carried out using a gradient optimization procedure[9a] subject only to specified symmetry constraints. The transition state (**4**) for the 1,5-hydrogen shift was obtained by minimization of the gradient norm[9b] while ensuring that the matrix of second derivatives of the energy had one negative eigenvalue. The optimized structures obtained in this manner are displayed in Figure 1, with corresponding STO-3G (denoted STO-3G//STO-3G) and 4-31G (denoted 4-31G//STO-3G) energies listed in Table II. The latter are more reliable for energy comparisons and in several studies[7,10] have been found to yield relative energies of isomeric acyclic systems to within about 10–15 kJ mol^{-1}. The 4-31G//STO-3G energies have been used to construct the reaction profile for the 1,5-hydrogen shift, **2** → **3**, shown in Figure 2. Also included for comparison in Table II are the corresponding 4-31G energies for the standard (i.e., nonoptimized) structures (denoted 4-31G//std). Finally, in order to obtain a more reliable estimate of the relative energies of **2a** and **2b**, the more important parameters in the STO-3G optimized structures were reoptimized at the 4-31G level. The results are discussed within the text.

Discussion

Preferred Conformations of the Keto, Enol, and Oxime Isomers. In a previous study,[3] we carried out 4-31G calculations with standard bond lengths and angles on a number of conformations of nitrosoacetaldehyde (O=NCH$_2$CH=O), generated by internal rotation about the N–C and C–C bonds. The best conformation had ONCC trans and NCCO trans. This is the only conformation of **1** considered in the present work and its optimum geometry is shown in Figure 1.

For nitrosovinyl alcohol (O=NCH=CHOH), we optimized two structures, one with ONCC trans, NCCO cis, and CCOH cis (**2a**) and the other with ONCC cis, NCCO cis, and CCOH cis (**2b**). The former had emerged with lowest energy



2a **2b**

in our preliminary calculations[3] with standard bond lengths and angles. It was desirable to optimize the structure of **2b** for two reasons. In the first place, the presence of an intramolecular hydrogen bond in **2b** should make the energy particularly sensitive to geometry optimization; secondly, **2b** is the conformation of nitrosovinyl alcohol most naturally involved in the 1,5 shift. Optimization does indeed have a large effect on **2b** and, after optimization, the energies of **2a** and **2b** are close together (cf. Table II). In order to probe further the question of the relative stabilities of **2a** and **2b**, we reoptimized, at the

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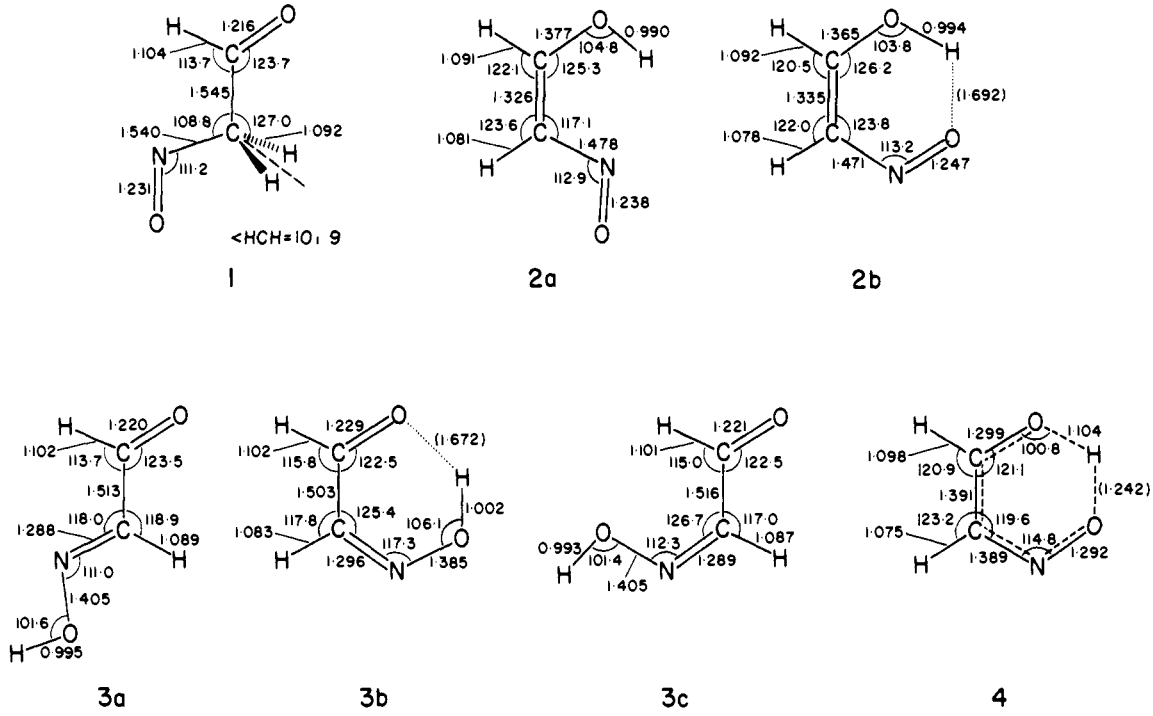


Figure 1. STO-3G optimized geometries for conformations of nitrosoacetaldehyde (**1**), nitrosovinyl alcohol (**2a**, **2b**), glyoxal monoxime (**3a**, **3b**, **3c**), and the transition state (**4**) for the rearrangement **2b** → **3b**. C_s symmetry constraint in each case. Bond lengths in ångstroms, bond angles in degrees.

Table I. Calculated Total Energies (hartrees) and Relative Energies (kJ mol^{-1}) for Conformations of HON=CHCH=O

conformation[a]			4-31G//std	
∠HONC	∠ONCC	∠NCCO	total energy	rel energy
0	0	0	−281.083 26	137.5
0	0	180	−281.083 93	135.7
0	180	0	−281.108 29	71.7
180	0	0	−281.109 77	67.8
0	180	180	−281.118 67	44.5
180	0	180	−281.130 53	13.3
180	180	0	−281.126 50	23.9
180	180	180	−281.135 61	0

[a] Dihedral angles in degrees.

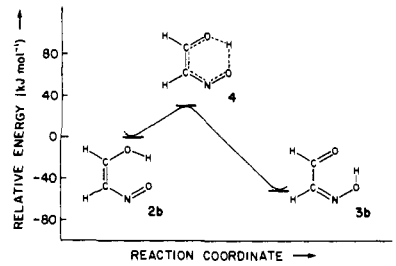
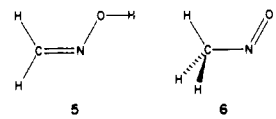


Figure 2. Reaction profile for the 1,5-sigmatropic hydrogen shift of nitrosovinyl alcohol (**2b**) to glyoxal monoxime (**3b**).

4-31G level, the two angles (ONC and COH) in the STO-3G structure which are most directly involved in the hydrogen bond. This resulted[11] in **2b** being very slightly favored (by 0.3 kJ mol^{-1}) over **2a**. We conclude that **2a** and **2b** have very similar energies.

Glyoxal monoxime (HON=CHCH=O) has not been studied previously and we therefore carried out initial calculations with the 4-31G basis set and standard bond lengths and angles on the eight isomers shown in Table I. The all-trans isomer (**3a**) emerges with lowest energy. This is consistent with the all-trans crystal structure of glyoxime[12] and with the microwave structures of formaldoxime[13] and *syn*- and *anti*-acetaldoxime,[14,15] which all have HONC trans. STO-3G optimizations were carried out both for **3a** and for the all-cis (**3b**) and HONC trans, ONCC cis, NCCO trans (**3c**) structures. These confirm (Table II) that the preferred conformation of glyoxal monoxime is **3a**.

Relative Energies of the Keto, Enol, and Oxime Isomers. Our calculations clearly show (Table II) that, although nitrosovinyl alcohol does lie slightly lower in energy (by about 6 kJ mol^{-1}) than its keto isomer nitrosoacetaldehyde, the oxime isomer, glyoxal monoxime, lies lower still by about 86 kJ mol^{-1}. This result is not unexpected: primary and secondary nitroso compounds are generally thought to exist in solution (where thermodynamic equilibration is rapid) as their oxime tautomers.[16] On the other hand, there are several instances where both the nitroso and oxime isomers have been characterized. For example, the preparation and microwave spectra for both formaldoxime (**5**)[13,17] and its nitroso isomer, nitrosomethane[18,19] (**6**), have been reported. Clearly, the possibility of observation of the enol **2** is dependent on the barrier for intramolecular rearrangement to **3**.



1,5-Sigmatropic Hydrogen Shift from Nitrosovinyl Alcohol to Glyoxal Monoxime. There are two possible pathways by which nitrosovinyl alcohol might rearrange intramolecularly to its lower energy isomer glyoxal monoxime, as shown in Scheme I. Pathway A involves successive 1,3-hydrogen shifts. The first shift is an enol → keto interconversion. We have previously shown[20,21] for the parent rearrangement, vinyl alcohol → acetaldehyde, that the barrier to such a shift is substantial, i.e., that vinyl alcohol should be stable with respect to a 1,3-intramolecular hydrogen shift. Indeed, the microwave spectrum of vinyl alcohol has recently been recorded.[22] Approximate calculations[23] indicate that this conclusion is unlikely to be modified by the presence of a nitroso substituent.

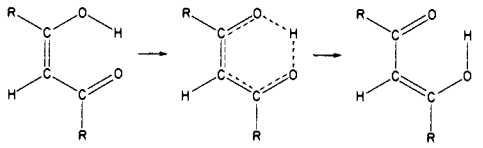
Table II. Calculated Total Energies (hartrees) and Relative Energies (kJ mol^{-1}) for the $C_2H_3NO_2$ Isomers

structure[a]	STO-3G//STO-3G		4-31G//std		4-31G//STO-3G	
	total	rel	total	rel	total	rel
1	−277.870 50	29.7	−281.103 53	84.2	−281.101 02	91.8
2a	−277.859 42	58.8	−281.105 13	80.0	−281.103 28	85.9
2b	−277.859 58	58.4	−281.077 68	152.1	−281.102 49	88.0
3a	−277.881 82	0	−281.135 61	0	−281.136 00	0
3b	−277.875 60	16.3	−281.083 26	137.5	−281.121 86	37.1
3c	−277.879 47	6.2	−281.130 53	13.3	−281.133 02	7.8
4	−277.852 05	78.2			−281.090 72	118.9

[a] See Figure 1.

The second shift in pathway A involves interconversion of nitroso and oxime isomers. A detailed study of such a rearrangement for the parent system, nitrosomethane → formaldoxime, is in progress.[24] However, regardless of the barrier found for this second step, the high barrier calculated for the first step ensures that pathway A does not present a viable means for conversion of **2** to **3**.

The alternative pathway B shown in Scheme I involves a 1,5-hydrogen shift. The corresponding degenerate 1,5 shifts (**7**) in the enols of malondialdehyde and acetylacetone have



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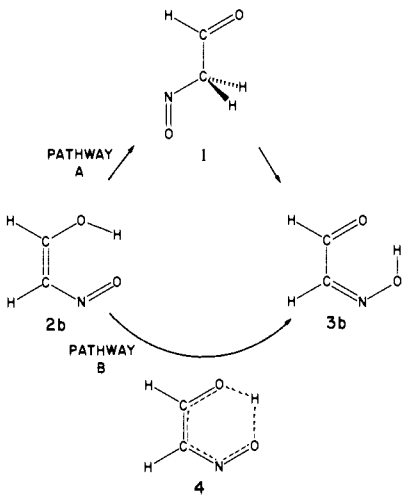
been studied extensively, both theoretically[21,25-28] and experimentally.[29-31] In agreement with orbital symmetry considerations[32] which predict that the suprafacial 1,5-hydrogen shift is an allowed process, the calculated barriers are small. The best ab initio calculations to date for malondialdehyde predict a barrier of 48 kJ mol^{-1} at the SCF level which is reduced only slightly to 42 kJ mol^{-1} in an extensive configuration interaction treatment.[26,28] This result lends confidence to the predictions of calculations within the Hartree–Fock framework for problems of this type. We therefore proceeded to study the asymmetric 1,5 shift, **2** → **3**.

The theoretical structure for the transition state for the rearrangement **2b** → **3b**, obtained under a C_s symmetry constraint, is shown as **4** in Figure 1. Displacement of the migrating hydrogen perpendicular to the plane of the molecule led to an increase in energy, thus justifying the assumption of C_s symmetry. In agreement with the Hammond postulate,[33] the transition state **4** resembles more closely the higher energy isomer **2b** than the lower energy isomer **3b**. The barrier to rearrangement is quite low at 30.9 kJ mol^{-1} (4-31G//STO-3G). It is somewhat lower than the corresponding calculated barrier[21] (43.1 kJ mol^{-1}) for the enol of malondialdehyde, which is not surprising in the light of the exothermicity of the process **2** → **3**. The cyclic transition state contains six π electrons and is therefore formally aromatic.

Whereas we have found that **2b** is likely to be the most stable isomer of **2**, **3b** is not the lowest energy form of **3**. It is of interest to examine the energy required to convert **3b** to the more stable isomers **3a** and **3c**. Transformation of the cis-cis-cis structure **3b** to the trans-cis-trans structure **3c** requires rotation about the O–N and C–C *single* bonds. Such rotations normally have small barriers and hence **3c** should be readily formed from **3b**. On the other hand, formation of the trans-trans-trans isomer **3a** requires, in addition, rotation about the N=C *double* bond or inversion at nitrogen and, by analogy with related systems, such processes should have considerably larger barriers. It may well be then that the product ultimately formed from a 1,5-hydrogen shift in nitrosovinyl alcohol will be **3c** rather than the lower energy (but less accessible from **3b**) isomer **3a**.

Scheme I



Conclusions

Ab initio molecular orbital calculations with complete geometry optimization suggest that the enol, nitrosovinyl alcohol (**2**), lies slightly lower in energy than its keto isomer nitrosoacetaldehyde (**1**). However, the oxime, glyoxal monoxime (**3**), lies still lower in energy. Rearrangement of **2** to give **3** via **1** by means of two successive 1,3-hydrogen shifts is unlikely. The alternative 1,5-hydrogen shift from **2** to **3** is found to have a low activation barrier. The transition state (**4**) for this 1,5 shift has been determined and, in accordance with the Hammond postulate, resembles **2**, the reactant higher in energy. Finally, the asymmetric 1,5-hydrogen shift from **2** to **3** bears a close relationship to the symmetrical 1,5-hydrogen shift in the enol of malondialdehyde.

References and Notes

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Protonation and Proton Affinity of Anisole. A Theoretical Study

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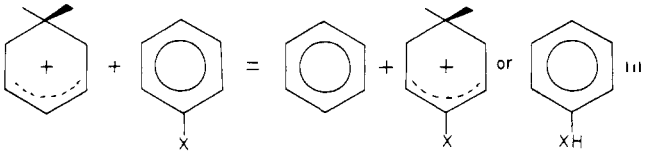
Abstract: We have performed an ab initio study of the protonation of anisole. From linear correlations between experimental proton affinities and theoretical 1s binding energies of para carbon and oxygen atoms we conclude that anisole is a stronger base than phenol, in agreement with experimental evidence. Theoretically predicted protonation sites depend on the conformation of the methoxy group relative to the aromatic ring.

I. Introduction

Considerable effort has been devoted to studying the basicity of aromatic compounds and the intrinsic substituent effects on this property.[1] This has been possible because, at present, gas-phase proton affinities can be measured with high accuracy, using different techniques.[2] Measured values are not affected by solvent effects and therefore they can be directly compared with those obtained from theoretical calculations, most of which evaluate the energy change in the "isodesmic" proton transfer reaction.[3]

In general, good agreement was attained[4] between these theoretical values and the experimental enthalpy change for reaction 1, although there are some exceptions. The experi-



mental proton affinity for anisole is 4.40 kcal/mol higher than that of phenol.[5] The theoretical energy change[5] for the "isodesmic" reaction for phenol is a little greater (16.0 kcal/mol) than that of anisole (15.7 kcal/mol). The reason of this disagreement is not clear.[5] Moreover, it is not well established if these systems protonate on the substituent or on the ring.[5-8]

We present in this paper ab initio calculations on anisole and phenol to show that the particular conformation of the methoxy group relative to the aromatic ring has a strong influence on the protonation of anisole.

II. Results and Discussion

We have recently proved[9] that there is a good linear correlation between experimental proton affinities and theoretical 1s binding energy of the para carbon atom for those monosubstituted benzenes that protonate on the ring. The relationship

$$PA = 1035.75E_{C_{1s}} + 11\,607.97 \qquad r = 0.977,\ \sigma_{PA} = 1.0 \text{ kcal/mol} \quad (2)$$

where the experimental proton affinity (PA) is in kcal/mol and the C_{1s} orbital energy ($E_{C_{1s}}$) is in atomic units, is similar to that proposed by Benoit and Harrison[10] between O_{1s} binding energies and proton affinity values of oxygen bases. We have also shown that eq 2 is applicable to all positions of the ring.[11]

We have carried out an ab initio calculation of anisole, using a STO-3G minimal basis set[12] and the experimental geometry of ref 13. Using eq 2 we have obtained the ring proton affinities that are presented in Figure 1. The PA value for protonation on the oxygen was obtained from the relationship

$$PA = 311.00E_{O_{1s}} + 6506.44 \qquad r = 0.999,\ \sigma_{PA} = 0.85 \text{ kcal/mol} \quad (3)$$

where PA is in kcal/mol and $E_{O_{1s}}$ in atomic units.

This equation was obtained from O_{1s} binding energies and experimental proton affinities for benzaldehyde,[5] acetophenone,[1] and phenolate, 3-hydroxyphenolate, and 3-fluorophenolate anions.[14]

The values obtained for σ_{PA} in eq 2 and 3 are smaller than those found by Benoit and Harrison[10] for the linear correlation between experimental O_{1s} binding energies and proton affinities for carbonyl and single-bonded oxygen compounds. However, more recent experimental proton affinity values result in a considerable decrease of their σ_{PA}. The value reported by Benoit and Harrison for single-bonded oxygen

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