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Theoretical Study on the Reactions of 1,3-Dipoles with Nucleophiles. The Fulminic Acid–Hydroxide Ion System[1]

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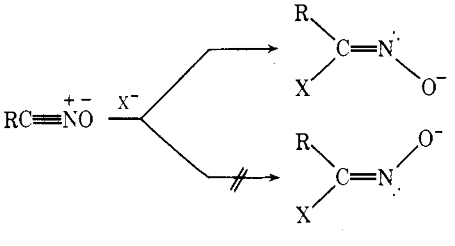
Abstract: The potential energy hypersurface for the reaction of HO^- with $HC{\equiv}N^+O^-$ to give $HC(OH){=}NO^-$ has been studied by ab initio methods using a 4-31G basis set. The energy along the reaction pathway was minimized by varying seven parameters (bond angles and bond lengths). The transition state is reached when R (the distance between the approaching oxygen and carbon) is 2.20 Å, and in the transition state the oxygen on the starting nitrile oxide bends over *toward* the incoming nucleophile (CNO = 37° in the transition state); other arrangements, including that in which the nucleophile and oxygen of the nitrile oxide are trans, are of higher energy. The reaction is therefore predicted to be stereospecific and literature data which support this conclusion are discussed. It is also shown that $HC{\equiv}N^+O^-$ is an easily deformed molecule but that it is easier to bend the H and O in opposite directions (trans deformation), similar to the preferred configuration of the transition state. A second minimum (at higher energy) appears when R is $\leqslant 2.0$ Å, showing that, although the oxime product is formed stereospecifically, the two oximes (E, Z) may not differ greatly in energy. In addition, a H-bonded complex ($HO^- \cdots HC{\equiv}N^+O^-$) is formed when $R = 2.60$ Å; however, such a complex can only be formed with fulminic acid and is not expected to be general for other nitrile oxides.

Introduction

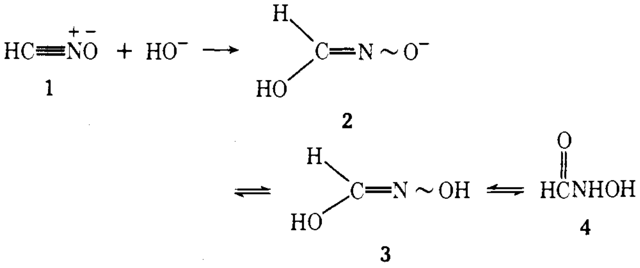
Recently, several groups have been concerned with quantum mechanical calculations which would clarify the mechanism of allowed cycloadditions such as the Diels–Alder reaction[3-5] or the reaction of 1,3 dipoles with dipolarophiles such as ethylene or acetylene.[6,8,9] Although all of the methods used (ab initio, MINDO/3) predict a single energy maximum on the reaction pathway (i.e., the absence of intermediates), there are significant discrepancies between the degree of "concertedness" (which in this context is the extent to which the two bonds are formed for a given value of the reaction coordinate) calculated for the transition state using the various methods. This problem has been critically examined by Houk and co-workers,[7] who ascribe this difference to the importance (or lack of it) which is attached to overlap in the computation method used.

In this work we are interested in studying the stereochemistry of the reaction of nitrile oxides with nucleophiles. Reaction occurs exclusively at carbon in this case and recent experimental work has shown[10,11] a striking stereospecificity in that only one of the two possible oxime isomers is formed as product. The most unequivocal example of this is the formation of Z amidoximes on reaction with secondary amines (see Table I); their formation is undoubtedly kinetically controlled since the E isomer is rapidly formed in a subsequent reaction. Table I summarizes other literature data supporting stereospecific reaction.



In some cases the initially formed oxime can undergo cyclization with an electrophilic center on the original nucleophile; in Table II are summarized several examples. The oxime is an ambident nucleophile (reaction can occur via nitrogen or oxygen attack); however, cyclization only via oxygen has been observed (see Table II) when the initial oxime isomer formed is allowed to react further, again supporting stereospecific reaction of the nucleophile with the nitrile oxide in the first step.

We have chosen the reaction of the nitrile oxide, fulminic acid (**1**), with hydroxide ion to give the hydroximate **2** as a model system. Because of rapid protonation and tautomerization to the hydroxamic acid **4**, the stereochemistry of **2** has not been determined directly by experiment. However, the closely related reaction of alkoxide ions with benzonitrile oxides has been examined and shown to be stereospecific.[11] Protonation of the anion **2** to **3** is a thermodynamically favored (diffusion controlled) process in aqueous solution and occurs in a rapid subsequent step; it could therefore be ignored in the initial reaction of HO^- with **1**.



Method of Calculation

The calculations were carried out by the ab initio method of Roothaan.[26] In each case the basis set 4-31G of Pople has been used and the calculations have been carried out using the GAUSSIAN-70 program.[27] We have recalculated some points along the reaction pathway with a limited configuration interaction (CI) employing the mono- and biexcitations between the following groups of orbitals: the two highest occupied molecular orbitals (HOMO) and the two lowest unoccupied orbitals (LUMO) of the supermolecule (CI 15 × 15); the three HOMOs and three LUMOs (CI 55 × 55). For that purpose the CI program of Segal[29] has been used. In the study of the reaction of HO^- and HCNO we have adopted the method of the supermolecule. Charge centroids were obtained using the localization method of Foster-Boys.[28]

Results and Discussion

Reactants and Product. A. Geometry. The optimal geometries of the nitrile oxide and the product hydroximate calcu-

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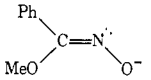
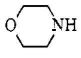
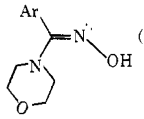
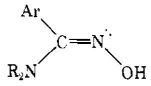
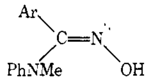
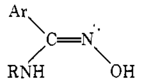
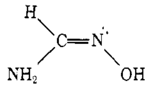
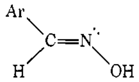
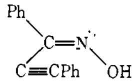
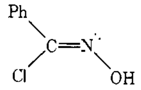
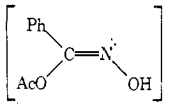
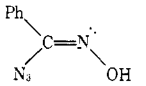
Table I. Stereospecific Reactions of Nitrile Oxides

nucleophile (X^-)	nitrile oxide (RCNO), R =	product	most stable isomer	ref
MeO^- or MeOH	Ph	 (*Z*)	$Z \rightleftarrows E$	11
	p-$NO_2C_6H_4$	 (*Z*)	*E*	10
R_2NH, $R_2 = Me_2$ or $(CH_2)_4$-	Ar	 (*Z*)	*E*	10, 12-14
PhNHMe	p-$NO_2C_6H_4$	 (*Z*)	$E \rightleftarrows Z$	10
RNH_2	2,4,6-$Cl_3C_6H_2$	 (*Z*)	*Z*	15
NH_3	H	 (*Z*)	*Z*	16
BH_4^- or AlH_4^-	p-$NO_2C_6H_4$	 (*E*)	*Z*	17
PhC≡CH or PhC≡C^-	Ph		?	18
Cl^-	Ph	 (*Z*)	*Z*	19
AcO^-	Ph		?	20
N_3^-	Ph	 (*Z*)	?	21

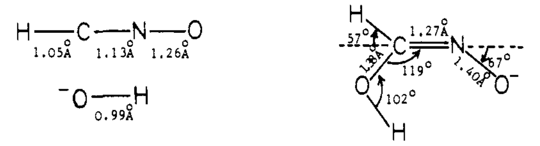
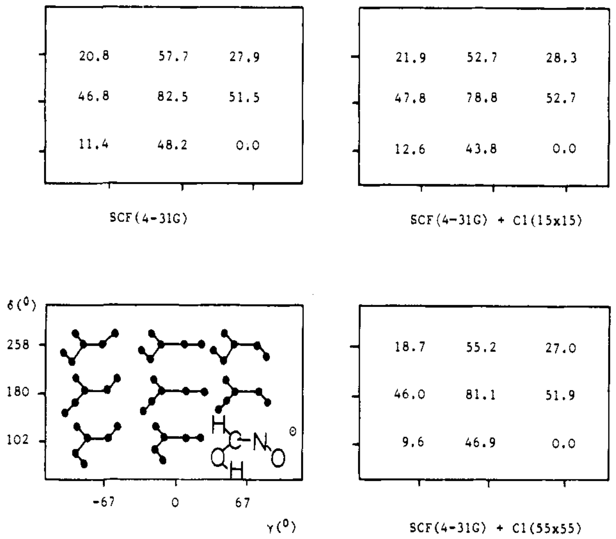


Figure 1. Optimized geometry of reactants and product.



SCF(4-31G)

	-67	0	67
258	20.8	57.7	27.9
180	46.8	82.5	51.5
102	11.4	48.2	0.0

SCF(4-31G) + CI(15x15)

	-67	0	67
258	21.9	52.7	28.3
180	47.8	78.8	52.7
102	12.6	43.8	0.0

SCF(4-31G) + CI(55x55)

	-67	0	67
258	18.7	55.2	27.0
180	46.0	81.1	51.9
102	9.6	46.9	0.0

Figure 2. Calculated energy functions, $E(\gamma, \delta)$, for the anion HC(OH)=NO^- (kcal mol^{-1}) using the basis set 4-31G; γ is the complement of the CNO angle, and δ is the COH angle.

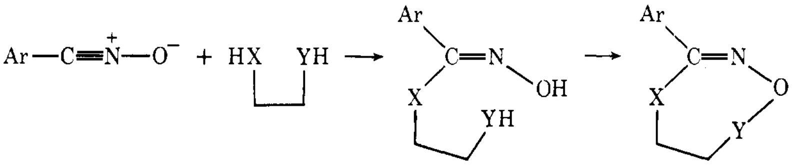
lated using the basis set 4-31G are summarized in Figure 1. For the nitrile oxide our results agree quite well with those of Poppinger.[8]

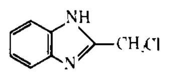
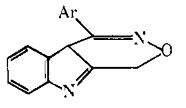
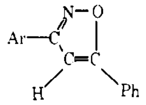
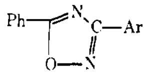
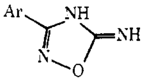
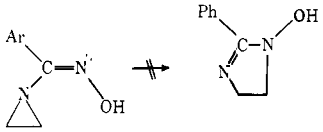
The corresponding total energies are as follows: −167.370 012 au for HCNO, −75.229 789 au for HO^-, −242.745 492 au for HC(OH)NO^-. The hydroximate (**2**) is thus 91.4 kcal mol^{-1} more stable than the reactants (HCNO + HO^-). For the reactants and product, all of the occupied orbitals have a negative energy when the basis set 4-31G is used (which, however, is not the case for the STO-3G basis set).

The energies of the hydroximate anion for the possible nuclear configurations obtained by variation of the CNO (180° − γ) and COH (δ) angles are listed in Figure 2. For each structure the parameters α, r_{CN}, r_{NO}, and r_{CO} have been optimized. Clearly the structure given in Figure 1 is favored, independent of the method used in the calculation.

B. Electronic Structure. In Figure 3 are summarized the principal electronic characteristics of the molecules studied.

Table II. Cyclic Products Obtained on Reaction of Nitrile Oxides with Nucleophiles[a]



nucleophile HX YH	product	ref
		22
PhC≡CH		18
$PhCONH_2$		23
NH_2—C≡N		24
		25

[a] In each case the intermediate material was isolated and characterized and shown to cyclize to the product indicated.

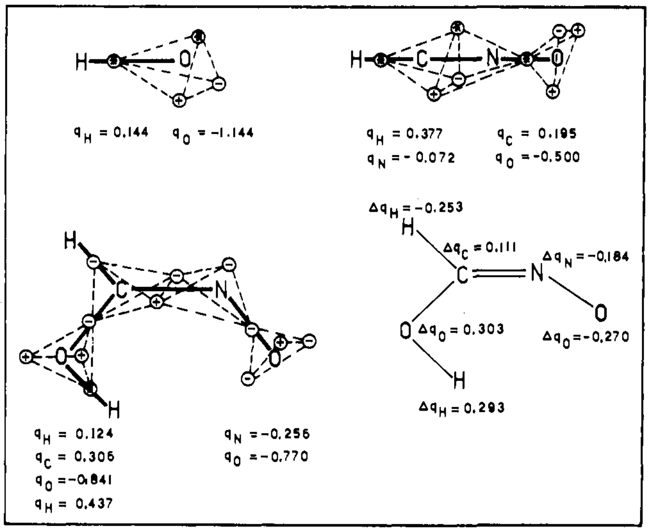


Figure 3. Electronic structures of reactants and products: net charges on the atoms and the position of charge centroids are calculated using basis set 4-31G (⊕, ⊖, and ⊛ indicate whether the centroid is found above, below, or in the plane of the paper, respectively). The variation in charge between the reactants and product ($\Delta q = q_P - q_R$) is also noted.

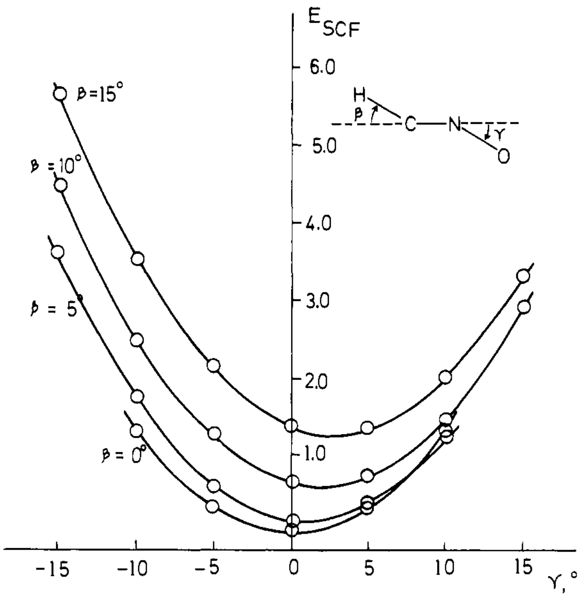


Figure 4. Energies required (kcal mol^{-1}) to deform fulminic acid (basis set 4-31G).

In particular it should be noted that the carbon of fulminic acid bears a net positive charge (q_C) consistent with its being the center for attack by HO^-. The charge centroids obtained by the Foster-Boys localization procedure are also given in Figure 3. The distribution of these centroids shows that during the course of the approach of the reactants, the only reorganization required is the transformation of the CN triple bond into a double bond and the formation of a lone pair on nitrogen.

Also noted in Figure 3 are the variations in the net charges (Δq_X) on passing from the reactants to products. The nucleophile HO^-, in the course of its approach, thus looses 60% of its negative charge (comprising 0.6 e^-) to the hydrogen, oxygen, and nitrogen atoms of the fulminic acid.

C. Deformation of HCNO. Although the ground-state structure of fulminic acid is linear, it is relatively easy to cause deformations of this structure by bending the HCN and CNO

Table III. Geometric Parameters and Total Energies along the Reaction Pathway

R, Å	α, deg	δ, deg	β, deg	γ, deg	r_{CN}, Å	r_{NO}, Å	E_{SCF}, au
			0	0	1.13	1.26	−242.599 801
5.00	180	105	0	0	1.13	1.26	−242.616 858
3.00	180	105	0	0	1.13	1.26	−242.674 737
2.60[a]	180	105	0	0	1.13	1.26	−242.692 009
2.50	180	105	0	0	1.13	1.26	−242.688 322
2.25	180	105	0	0	1.13	1.26	−242.674 823
2.20[b]	125	100	30	30	1.14	1.27	−242.640 434
2.15	125	100	30	30	1.15	1.28	−242.644 714
2.10	125	100	30	30	1.16	1.29	−242.649 123
2.07	125	100	30	30	1.17	1.29	−242.651 819
2.05	125	100	30	30	1.17	1.30	−242.653 632
2.00	122	100	35	37	1.19	1.31	−242.658 206
1.70	122	100	45	52	1.24	1.36	−242.701 801
1.38[c]	119	102	57	67	1.27	1.40	−242.745 493

[a] Complex: OH⁻ . . . HCHO. [b] Transition state. [c] Product: HC(OH)CNO⁻.

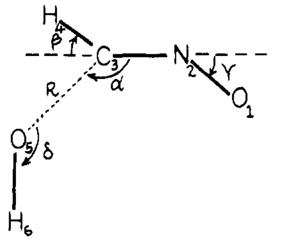


Figure 5. Geometric parameters which are varied in the calculations.

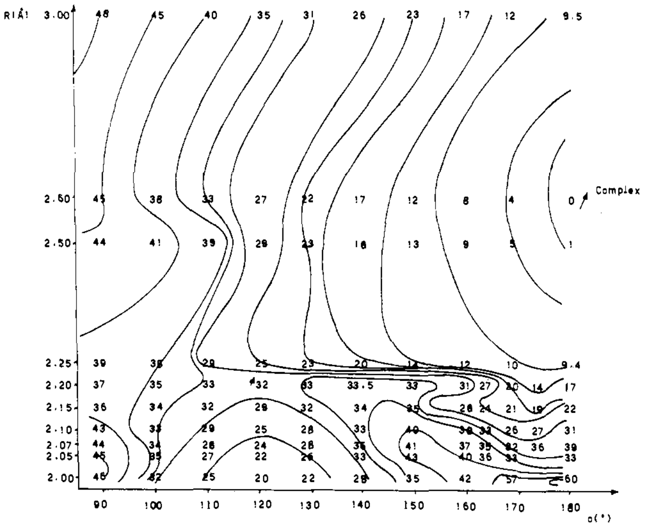


Figure 6. Relative energies along the reaction pathway (kcal mol⁻¹) with respect to the energy of the complex; the complex is at the upper right of the figure.

angles. For example, a deformation of these angles by 10° requires only 0.63 and 1.34 kcal mol⁻¹, respectively.

However, it requires less energy to deform the oxygen and hydrogen away from rather than toward one another. This is shown in Figure 4, where the plots of energy vs. angles (β, γ) of deformation are plotted. It should be noted that, for β different from zero, these curves have a unique minimum in which the H and O atoms are trans. This important observation will have a bearing on the direction of deformation of fulminic acid during reaction (see below).

Reaction of HO⁻ with HCNO. In Figure 5 are listed the geometrical parameters considered in the calculation of the hypersurface of the reaction. As reaction coordinate the distance O_5-C_3 (denoted by R) was chosen.

The variables used were the angles α, β, γ, and δ and the bond lengths C_3-O_5, C_3-N_2, and N_2-O_1. The bond lengths C_3-H_4 and O_5-H_6 were maintained constant with values of 1.07 and 1.00 Å, respectively.

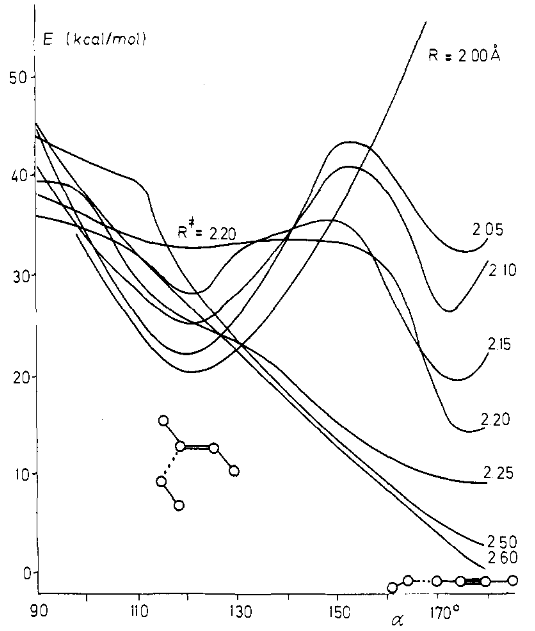


Figure 7. Relative energies along the reaction coordinate as a function of the distance of approach R and angle α.

When the reactants are brought together from a distance ($R \geqslant 2.25$ Å), they approach so that the atoms O_5, H_4, C_3, N_2, and O_1 form a single line; only the hydrogen H_6 lies off this line (the angle, δ, is 105°). Clearly an intermediate "complex" is being formed which is stabilized by the formation of a hydrogen bond between H_4 and O_5.

In Figure 6 are listed the relative energies with respect to this complex for various values of R and of α. For each point, the parameters β, γ, δ, r_{CN}, r_{NO}, and r_{CO} have been optimized. One finds that around the transition state ($2.25 > R > 2.05$ Å) the structural modifications are small (see Table III). It is noted from this that on going from reactants (HO⁻, HCNO) to product (HC(OH)=NO⁻), the minimum energy route passes through the point $R = 2.20$ Å, $\alpha = 120°$. This point is denoted by ≠ in the figure. Figure 6 is unusually complex owing to the presence of two simultaneous reaction pathways: formation of the complex, E (R, $\alpha = 180°$) and formation of the hydroximate, E (R, $\alpha = 120°$).

Figure 7 also illustrates this; in particular it is noted that the energy curve corresponding to the transition state E (R = 2.20

Table IV. Net Atomic Charges and Charge Transferred along the Reaction Pathway (4-31G)

R	N_2	O_1	C_3	H_4	O_5	H_6	t_{HCNO}
∞	−0.072	−0.500	0.195	0.377	−1.144	0.144	0.000
5	−0.049	−0.562	0.181	0.427	−1.096	0.099	0.003
3	−0.139	−0.619	0.161	0.441	−1.007	0.162	0.155
2.60[a]	−0.145	−0.641	0.141	0.462	−1.000	0.183	0.182
2.50	−0.139	−0.648	0.134	0.470	−1.009	0.193	0.184
2.25	−0.120	−0.669	0.106	0.461	−0.988	0.209	0.221
2.20[b]	−0.163	−0.638	0.263	0.221	−0.940	0.258	0.318
2.15	−0.166	−0.644	0.260	0.216	−0.931	0.265	0.334
2.10	−0.170	−0.651	0.257	0.212	−0.922	0.273	0.352
2.07	−0.172	−0.655	0.256	0.209	−0.916	0.278	0.362
2.05	−0.174	−0.658	0.255	0.207	−0.913	0.282	0.369
2.00	−0.177	−0.665	0.253	0.203	−0.903	0.290	0.386
1.70	−0.215	−0.811	0.227	0.156	−0.829	0.376	0.547
1.38[c]	−0.256	−0.770	0.306	0.124	−0.841	0.437	(0.595)

[a-c] See Table III.

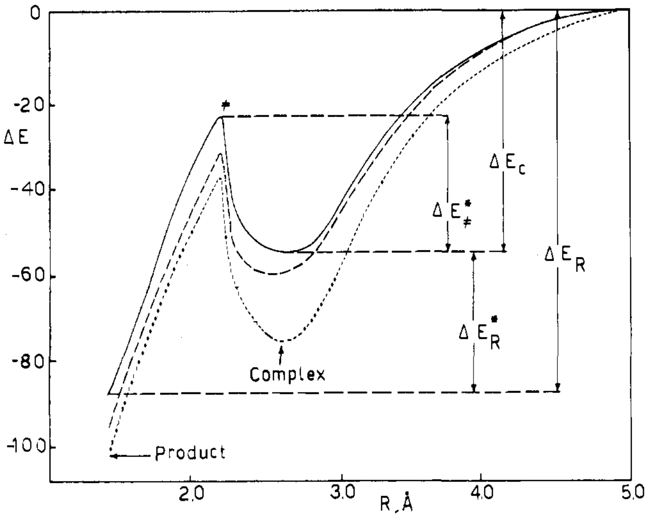


Figure 8. Relative energies (kcal mol^{-1}) and activation parameters calculated (using the basis set 4-31G) as a function of the reaction coordinate R. The calculated values are as follows: for SCF (solid line, —) $\Delta E_c = -58.84$ kcal mol^{-1}: $\Delta E^*_{\neq} = 32.35$, $\Delta E^*_R = -33.55$; for CI (15 × 15) (broken line - - -) $\Delta E_c = -62.65$, $\Delta E^*_{\neq} = 29.06$, $\Delta E^*_R = -32.62$; for CI (55 × 55) (dotted line . . .) $\Delta E_c = -78.54$, $\Delta E^*_{\neq} = 38.58$, $\Delta E^*_R = -25.22$.

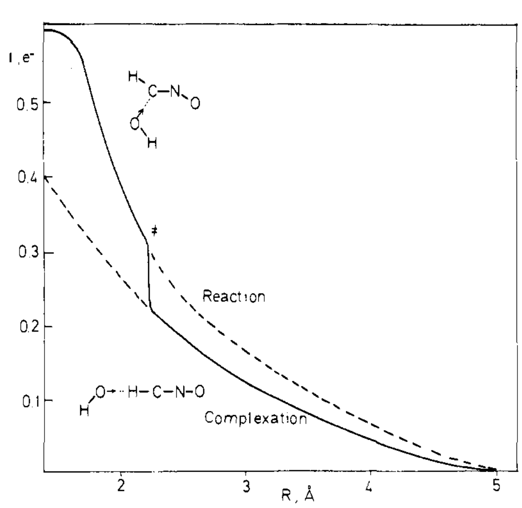


Figure 9. Charge transfer along the reaction pathway.

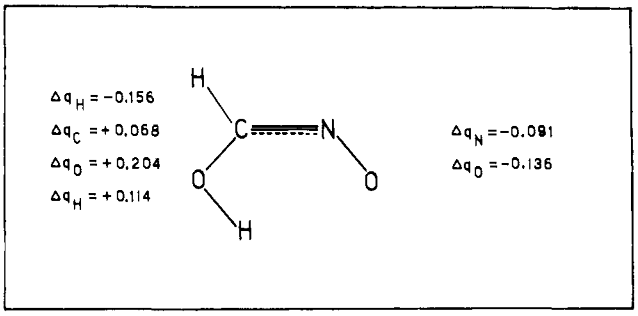


Figure 10. Variation in the net charges on passing from reactants to the transition state.

Å, α) is almost a perfect plateau for all values of α between 110 and 150°. It is to be noted that the Mc Iver criterion in the 7-parameter subspace has not been used. However, we employ carefully enough the steepest descent procedure to obtain a good representation of the transition state in this reaction.

In Table III are given the values of the structural parameters and the total energies calculated along the reaction pathway. We may also dissect the activation barrier for going from the complex to the transition state into two parts, each dependent on structural parameters: (1) R changes from 2.6 to 2.2 Å, ±17 kcal mol^{-1}, (2) α changes from 180 to 120°, ±15 kcal mol^{-1}, making in all the total of 32 kcal mol^{-1} corresponding to $\Delta E^*_{\neq}$ with respect to the energy of the complex. Such a separation is probably realistic since 15 kcal mol^{-1} actually corresponds to the energy required to deform fulminic acid by angles of 30° (for β and γ, see Figure 4).

Table III shows that the Z configuration is favored in the transition state. For $R = 2.20$ Å there is just a single minimum in the curve of $E(\gamma)$ which occurs when $\gamma = 30°$. The distance R must be compressed to 2.00 Å before the second minimum appears. For $R = 2.00$ Å the two minima have the following energies (relative to the reactants): $\gamma = -37°$, 24.1 kcal mol^{-1}; $\gamma = +37°$, -36.6 kcal mol^{-1}. For $\gamma = 0$, the relative energy would be 24.5 kcal mol^{-1}. It is thus apparent that the second minimum (corresponding to the E configuration) occurs at a positive energy region and thus the formation of the Z product alone is assured.

The relative energies along the reaction pathway are summarized in Figure 8. We have also indicated the energy parameters and the curves calculated with the configuration interactions limited to the two highest occupied and lowest unoccupied orbitals CI (15 × 15) or the three highest occupied and three lowest unoccupied CI (55 × 55). These curves are qualitatively comparable.

In Table IV we have summarized the results of the population analysis along the reaction coordinate and Figure 9 shows the progress of charge transfer.

Figure 10 shows the variation in net charge on the atoms on going from reactants to the transition state. If we compare Figures 10 and 3 then it is obvious that there is a proportionality between the charges on the atoms in the transition state and those in the reaction product. In fact charge evolution has proceeded to 50-60% (of the values in the product) in the transition state. Figure 11 gives the principal electronic characteristics of the complex and of the transition state. Note that in the complex a lone pair of the anion HO^- is oriented toward the hydrogen of fulminic acid; the angle formed by the lines joining respectively this centroid and atoms O_5 and H_4 is 2.5°. In the isolated hydroxide ion the distance between the center of gravity of the lone pair and the oxygen atom is 0.32 Å, and 0.39 Å in the case where hydrogen bonding is involved. In the transition state (R = 2.20 Å), the oxygen of the HO^- group presents a lone pair toward the carbon of fulminic acid; this lone pair is found 0.5 Å from the oxygen atom O_5 showing that this pair will form the new C_3-O_5 σ bond.

The calculations thus clearly show (in line with the experimental results, see Table I) that the formation of one oxime isomer is predetermined by the preferential bending of the 1,3-dipole in the transition state. The energy barrier leading to the other isomer is so high as to be unattainable. For example, as indicated above, for R = 2.00 Å, the barrier is approximately equal to 24.5 kcal/mol ($\gamma = -0°$) minus −36.6 kcal/mol ($\gamma = -37°$), i.e. 61 kcal/mol. However, the energy difference between the E and Z isomers of the possible products is predicted to be much less (see Figure 2 for an example), so that the kinetically formed and thermodynamically most stable isomers may be different. Some examples of this are in fact known (see Table I); the oxime system is particularly favored for the experimental study of this phenomenon because of the relatively high energy barrier to interconversion between E and Z isomers.[30] The observed stereoelectronic control of the addition of nucleophiles to 1,3-dipoles is therefore expected to be of wide application in synthesis.

A key factor which determines the bending of the 1,3-dipole in the transition state is the forming lone pair on the central nitrogen trans to the attacking nucleophile (see Figure 11). The 1,3-dipole fulminic acid (1) bears a structural similarity to nitrilium ions 5, diazonium 6, and iminium ions 7 and it would be of interest to determine if similar factors are operative in these cases also. There is experimental evidence that the addition of nucleophiles to 5 and to 6 is stereoelectronically controlled[31,32] but clearly further data are required before a general theoretical picture can emerge.


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

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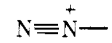
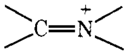
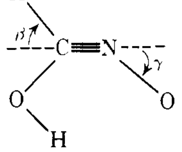

$N\equiv\overset{+}{N}-$

6


$>C=\overset{+}{N}<$

7

The similarity between the timing and geometric relationships of the transition state predicted here for the reaction of 1 with HO^- at carbon (8) and the transition state described[8] for the cycloaddition of 1 with acetylene or ethylene (9) is most striking. Not only are the angles β and γ almost the same (30 and 37° for 8, 32 and 44° for 9) but the transition states are reached with about the same distance of approach (R = 2.20 Å for 8 and 9).



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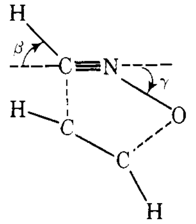

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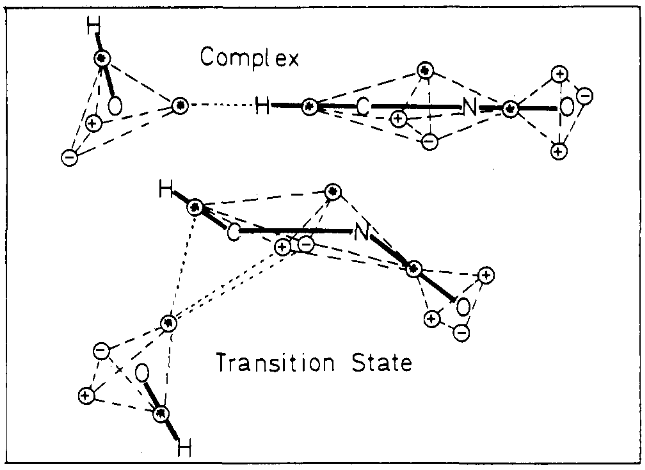

Figure 11. Summary of the electronic characteristics of the complex (R = 2.20 Å) and of the transition state (R = 2.60 Å).

In conclusion, therefore, the ab initio calculations show that the 1,3-dipole fulminic acid 1 is preferentially deformed in a trans manner. When approached by a nucleophile this type of deformation also takes place so that the configuration of the product is determined early in the reaction coordinate and is independent of product stability. The bending of the 1,3-dipole induced by the approach of the nucleophile at carbon is the major factor required to bring the reactants to the transition state. This is similar to the conclusion reached for the transition state of the cycloaddition 9 (also using the ab initio method),[8] but most importantly the configuration of 8 arises without assuming any bonding between the oxygen terminus of the 1,3-dipole and the incoming nucleophile.

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Theoretical Studies of the Oxy Anionic Substituent Effect[1]

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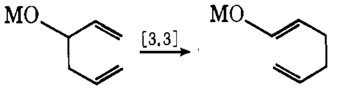
Abstract: Employing ab initio generalized valence bond and configuration interaction theoretical methods, we calculated C-H bond energies for H_3COH, H_3CONa, H_3COK, and H_3CO^- leading to bond energies (at 0 K) of 90.7 (the experimental value is 91.8 ± 1.2), 80.6, 79.0, and 74.2 kcal/mol, respectively. This dramatic decrease in the adjacent bond strength due to an oxy substituent helps explain the oxy anionic substituent effect in which very marked rate enhancements have been obtained.

Introduction

One of the fundamental pursuits in chemistry is the acquisition of greater insight into the processes of bond making and bond breaking. Questions dealing with mechanism and the interrelationship of structure and reactivity have been probed by both theory and experiment for a great body of chemical reactions. It is now well established that reaction rates may be strongly affected by structure; nonetheless, in many cases the effect of substituents on bond making and breaking is still poorly understood.

One of the most striking examples of a substituent-promoted rate acceleration for a sigmatropic rearrangement has recently been documented in these laboratories (eq 1).[3-5] For the general [3,3] sigmatropic rearrangement (1), numerous cases document the trend that a powerful rate acceleration (ca. 10^{12}-10^{17}) is attendant with a substituent change of M = H to M = K. Recent stereochemical studies indicate that there is *no* change in mechanism[5] so that a direct comparison of the two oxy substituents -OH and -OK is meaningful. In addition, recent related observations have been made on the acceleration of [1,3] sigmatropic rearrangements (cf. eq 2).[6]



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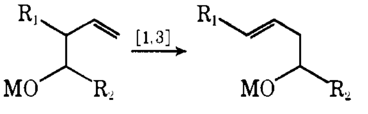

(2)

Two questions immediately arise: (1) What are the detailed electronic mechanisms of these particular sigmatropic rearrangements? (2) What is the general effect of various oxy substituents (-OH, -ONa, -OK, $-O^-$) on neighboring center chemistry? In reaction 1 a carbon-carbon bond adjacent to the carbon-oxygen bond is (formally) broken. Thus, to answer the second question, one might determine the effects of oxy substituents (OM) on the strengths of adjacent bonds as in (3).

$$MOCH_2\text{-}R \rightarrow MO\text{-}\dot{C}H_2 + R\cdot \qquad (3)$$

Herein we report ab initio theoretical calculations of the carbon-hydrogen bond strengths for methanol, sodium methoxide, potassium methoxide, and the methoxide anion. The comparison among these bond energies provides part of the explanation of the substituent effect noticed, for example, in the oxy-Cope rearrangement (1).

Details of the Calculations

Basis Set. For all calculations we employed the Dunning[7] valence double ζ Gaussian basis set. This was supplemented with polarization functions on the carbon and oxygen atoms (d functions: $\alpha_{\text{carbon}} = 0.75$, $\alpha_{\text{oxygen}} = 0.85$) and on the hydrogen atom whose bond to carbon was to be broken (p functions: $\alpha = 1.00$). In order to describe the anionic oxygen center, sets of diffuse[8] s and p functions were added to the oxygen basis (except for methanol). Ab initio effective potentials[9] were used for the metal atoms.

SCF Calculations. To calculate the bond energies, we carried out generalized valence bond (GVB) calculations[10] on the closed-shell species, correlating each of the seven valence electron pairs. Two natural orbitals were included for each electron pair, except for the C-H bond being broken, for which additional correlation effects were included by allowing five natural orbitals to describe this electron pair. The resulting calculation is referred to as GVB (7/17), indicating that seven electronic pairs are described by 17 natural orbitals. For the radical, the corresponding level of calculation is GVB (6/12) in which the six valence pairs are described by 12 orbitals.

CI Calculations. The prime consideration in the configuration interaction (CI) calculations was to provide sufficiently balanced descriptions of both H_3COM and H_2COM as to yield a reliable C-H bond energy. Harding and Goddard[11] have shown that the minimal level of calculation leading to reliable bond energies for cases such as $D(H_3C\text{-}CH_3)$ can be obtained by first partitioning the electrons into an *active set* and an *inactive set* where the active set (the C-C pair in the ethane case) includes electrons that are affected directly by bond scission and where the inactive set (the C-H pairs in the ethane case) includes the electrons not directly affected by the scission (but which may be involved in correlations that do affect the bonding electrons). The electrons having been thus partitioned, a high level of correlation s allowed among the active electrons while a lower level of correlation is allowed within the inactive set.

As discussed below, breaking the C-H bond leads to a strong

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