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Reaction of Acetylene with Fulminic Acid. The Prototype 1,3-Dipolar Cycloaddition

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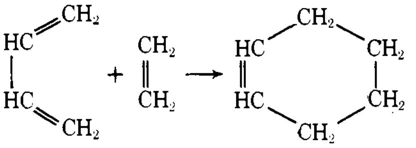
Abstract: One of the simplest 1,3-dipolar cycloaddition reactions occurs between HC≡CH and $HC{\equiv}N^+{-}O^-$ to yield the five-membered isoxazole ring. Previous theoretical studies have been divided on the key issue of whether or not the transition state is relatively symmetric. Ab initio self-consistent-field gradient methods were used in the present research. Independently employing 4-31G and (9s5p/4s2p) double ζ basis sets, the saddle-point structures and associated vibrational frequencies were predicted. The two basis sets yielded very similar and on geometrical grounds relatively symmetric transition-state geometries. However, the transition state stretching force constants for the two new bonds being formed differ by a factor of 10, suggesting a lack of symmetry in this respect. Stationary points on the C_3H_3NO potential energy surface have been further investigated using basis sets which include polarization functions or large-scale configuration interaction. Polarization functions increase the exothermicity somewhat, while correlation effects significantly reduce the barrier height and the exothermicity.

Introduction

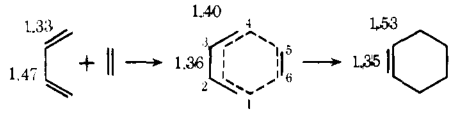
Cycloaddition reactions and especially the Diels–Alder reaction[2a] have been the subject of literally thousands of experimental studies[2b] over the past 5 decades, and several distinguished organic chemists, including Woodward,[3] have built their careers upon them. Theoretical studies of Diels–Alder and related reactions are fewer, but (considering all levels of theoretical work) exceed 100,[4,5] and have for the most part been aimed at elucidating the mechanism of this critical reaction. In recent years the goal of such mechanistic theoretical studies has increasingly[6–12] become the prediction of the precise geometrical structure of transition states. For the prototype Diels–Alder reaction of 1,3-butadiene with ethylene to give cyclohexene, two detailed theoretical studies[13,14] have appeared in the recent literature.



(1)

The first "complete" theoretical study of the prototype Diels–Alder reaction was that carried out by Dewar, Griffin, and Kirschner[13a] using the well-known MINDO/3 method. They found that the constrained symmetrical transition state yielded a force constant matrix with two negative eigenvalues, indicating that this point on the potential energy surface is *not* a true transition state. The MINDO/3 prediction of a very unsymmetrical transition state has been confirmed by a very recent and extremely detailed MNDO study by Dewar, Olivella, and Rzepa.[13b] The latter MNDO results are summarized in Figure 1, where it is seen that the lowest pathway involves two transition states separated by a biradicaloid intermediate. Considerable indirect support for the MNDO mechanism is given by the good agreement between theoretical and experimental entropies of activation and secondary isotope effects.

The most detailed ab initio study of the reaction of 1,3-butadiene with ethylene to date was that of Townshend, Ramunni, Segal, Hehre, and Salem,[14] Their general approach was to optimize the geometries of extrema (transition state, reactants, and product) using a minimum basis set in conjunction with 3 × 3 configuration interaction (CI). Finally, certain reaction pathways were recomputed using the larger 4-31G basis set[15] which is essentially equivalent to double ζ.[16] Twenty-five of the 42 independent geometrical variables were investigated, making this a genuinely monumental computational feat. However, the use of a minimal basis set and very limited CI and the assumptions made regarding certain geometrical variables suggest that these results be viewed judiciously. Salem and co-workers[14] predict that the prototype Diels–Alder reaction proceeds preferentially in a concerted manner via a symmetric transition state, schematically given by the middle sketch in the following sequence (bond distances in Å):



(2)

where $R(C_1{-}C_6) = R(C_4{-}C_5) = 2.21$ Å at the transition state. This concerted transition state lies ~43 kcal above the reactants. However, their analysis of the C_6H_{10} potential energy surface is considerably complicated by the existence of a two-step pathway with transition state only 4 kcal above the concerted transition state. Another interesting feature of the paper by Townshend et al. is their finding that the hex-2-ene-1,6-diyl system lies 11 kcal below the two-step transition state, well on the side of descent to cyclohexene. This prediction is consistent with Benson's thermochemical estimate[17] that this

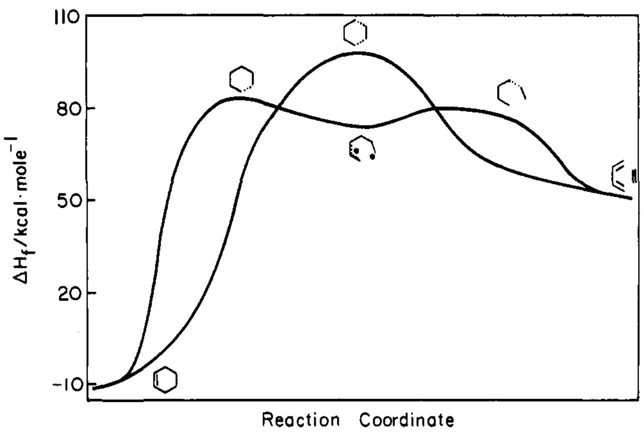


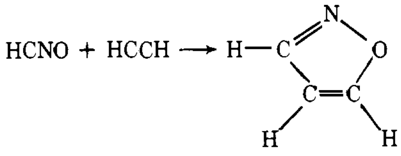
Figure 1. Summary of the MNDO predictions of Dewar, Olivella, and Rzepa for the prototype Diels-Alder reaction, 1,3-butadiene plus ethylene.

diradical lies no higher than the transition state for the cycloaddition.

1,3-Dipolar Cycloadditions. Experimental and Theoretical Background

The controversy between diradical and concerted reaction pathways, which was illustrated in the Introduction for the prototype Diels-Alder reaction, has become so central to physical organic chemistry that its challenge is irresistible. It is to be emphasized that the sort of disagreement seen between the MNDO methods and ab initio SCF (or small CI) techniques seems to occur with regularity, This fact has been noted in a recent communication by Caramella, Houk, and Domelsmith.[18] They point out that for a simpler system, the 1,3-dipolar cycloaddition of acetylene to fulminic acid, a serious discrepancy occurs between relatively symmetrical[19] (nonempirical SCF) and unsymmetrical[20] (MINDO/3) transition states. Houk[18] seems to favor the nonempirical SCF predictions, and they may turn out to be correct. However, a number of potentially quite serious approximations have been made in the ab initio study.[19] To be specific, only minimum basis sets have been carefully used, and the correlation problem has been treated at only the very simplest level. These omissions are, from an empirical point of view, most apparent (for the butadiene plus ethylene reaction) in the discrepancy between the predicted barrier (43 kcal) and the experimental activation energy (28 kcal). Perhaps more serious, however, is the fact that the two-step barrier is only 4 kcal higher, a result which could easily change by as much as 10 kcal in a more refined theoretical treatment.

The theoretical uncertainties outlined above are mirrored by experiment. In particular, two recent experimental reviews[21,22] have clearly adopted opposite positions on the question of diradical vs. concerted mechanisms for 1,3-dipolar cycloadditions. Turning attention more specifically to the acetylene-fulminic acid reaction, a number of related experimental studies should be noted. However, the experimental study of (3) is complicated by the oligomerization of HCNO.[23]



(3)

Additions of fulminic acid to alkyl-substituted acetylenes and of nitrile oxides (RCNO) to alkynes give higher product yields[24] and have been somewhat more extensively studied,

The slow generation of fulminic acid has made possible[25] in situ cycloaddition reactions to alkynes of sufficient dipolarophilic activity. For weak dipolarophiles, oligomerization of HCNO competed with the cycloadditions. Further, the additions of 17 nitrile oxides to five α,β-unsaturated carboxylic esters showed regiochemistry best explained in terms of the electronic structure of the nitrile oxide and influenced only to a minor extent by substituents.[26]

Although perturbation molecular orbital (PMO) treatments of substituent effects on 1,3-dipolar cycloadditions have appeared,[25-27] there have been no ab initio calculations on the systems RCCR + RCNO except for R = H.[19] The PMO work rationalizes much of the experimental data on regioselectivity using a concerted transition state model.[26]

To the extent that substituent effects are of relatively minor importance, it is of great interest to treat the simplest 1,3-dipolar cycloaddition at a reliable ab initio level. A PMO treatment of substituent effects might then be performed using rigorously optimized ab initio geometries for reactants, products, and transition states, and incorporating predicted heats of activation and reaction and molecular orbital characteristics.

The only previous ab initio study of the HCCH + HCNO reaction is that of Poppinger.[19] Minimum basis set (STO-3G) SCF theory was used to predict the transition-state structure and then single-point calculations were carried out on the reactants, product, and transition state using the larger 4-31G basis set.[28] Although such an approach has been qualitatively quite successful for stable hydrocarbons,[29] it may not be as realistic for transition states. For example, Poppinger, Radom, and Pople[12] found the minimum basis and 4-31G basis transition states for the carboxime-cyanic acid rearrangement

$$\mathrm{HONC} \rightarrow \mathrm{HOCN} \qquad (4)$$

to be quite different.

Dewar[20] has suggested that the ab initio transition state reported by Poppinger[19] might not be a true transition state. MNDO calculations suggest that there is a nearby stationary point on the potential surface corresponding to the structure expected for a synchronous transition state but that this structure is not a true transition geometry, having two negative eigenvalues for the force-constant matrix.[20] The obvious procedure for avoiding uncertainties of this type is to carry out a full vibrational analysis of the transition state.[30]

In the present paper theoretical studies are reported of the acetylene plus fulminic acid reaction at levels of theory substantially beyond those previously employed.[19] Thus, this research traverses a significant portion of the path from the present state of affairs to a genuinely quantitative theory of the 1,3-dipolar cycloaddition reaction.

Theoretical Methods

Both SCF and configuration interaction (CI) methods have been utilized in the present investigation. At the SCF level, all of the stationary point structures were located with the GRADSCF program system[33] which simultaneously evaluates both the energy and the gradient, and thereby allows the use of some very efficient methods of locating equilibrium as well as saddle-point structures.[30] The alternative, a point-by-point energy determination of the acetylene plus fulminic acid transition state, although achievable in principle, would have been an exceedingly laborious procedure. The optimization procedures for determining the various structures have been previously described.[30,38] The starting points for the stable species were taken as the experimental geometries, while for the acetylene-fulminic acid transition state the minimal basis set structure found by Poppinger[19] was chosen.

Although the GRADSCF program system does not explicitly allow the use of symmetry in molecular calculations, symmetry was implicitly used in locating both the equilibrium as well as

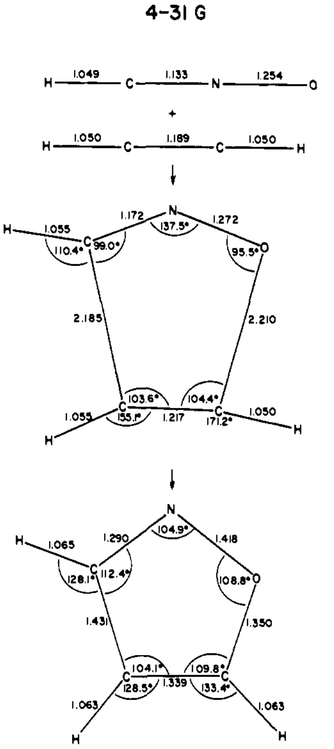


Figure 2. Predicted 4-31G SCF transition state structure for the acetylene plus fulminic acid reaction. The theoretical structures of the reactants and products are also indicated.

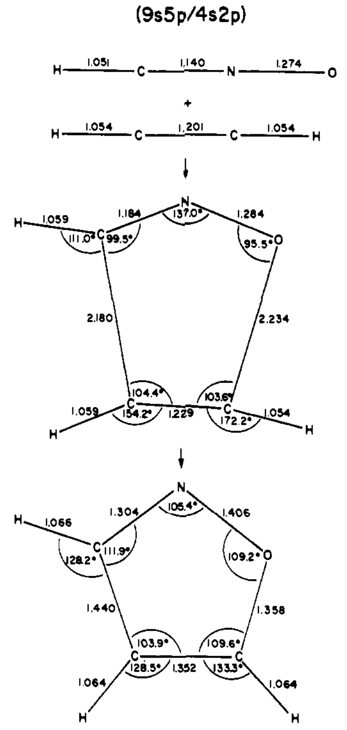


Figure 3. Predicted double ζ basis set SCF transition state structure for the HCCH + HCNO → isoxazole reaction.

the saddle-point structures. Since the gradient methods are symmetry conservative,[30] only the totally symmetric space was searched in each case. This significantly reduced the computational effort in locating the saddle-point structure.

For all of the relevant structures reported here, two basis sets were employed in the location of the stationary points. The first was the 4-31G split-valence basis of Pople and co-workers,[28] while the second employed the Huzinaga (9s5p/4s) double ζ set contracted to [4s2p/2s] as suggested by Dunning.[31] Using the predicted 4-31G stationary point geometries, individual calculations were also performed at the double ζ plus polarization level (DZP). This DZP basis can be designated as (9s5p1d/4s1p) contracted to [4s2p1d/2s1p]. The polarization function orbital exponents were chosen to be $\alpha d(\mathrm{C}) = 0.8$, $\alpha d(\mathrm{N}) = 0.85$, and $\alpha d(\mathrm{O}) = 0.9$, while the hydrogen p function exponent was chosen as 1.1. In all cases the hydrogen atom s functions were scaled by a factor of $(1.2)^2 = 1.44$.

Finally, at the SCF level, the force constants were computed by the finite difference technique described previously,[38] which established the structures as reactants, products, and transition state. The structures located at the double-ζ level were subsequently used in the configuration interaction calculations.

The CI calculations were performed using the double-ζ basis of 56 contracted functions. The transition state and product isoxazole have only a plane of symmetry (C_s point group) and the molecular orbitals thus divide into 46 a′ and 10 a″. The general CI approach adopted was to include only single and double excitations relative to the closed shell SCF reference configuration. This approach was justified since the wave functions for reactants, transition state, and product were dominated by the Hartree-Fock determinant which has a coefficient in the CI expansion of >0.93 in all cases.

The five highest virtual orbitals were deleted in all CI calculations, since these orbitals are the unoccupied "complements" (in a double-ζ basis) of the frozen C, N, and O 1s core orbitals. With this obvious restriction, several levels of CI were carried out, which are distinguished by the number of electrons correlated. In the simplest treatment, only the a″ orbitals, the three highest occupied SCF orbitals, were correlated, for a total of 3334 configurations. However, this treatment was extended to encompass correlation effects for the five highest occupied molecular orbitals (7053 configurations), six highest (10 000 configurations), and finally for the seven highest, four a′ and three a″ occupied SCF orbitals (13 672 ^{1}A′ configurations).

Results

The predicted 4-31G and double ζ SCF structures are shown in Figures 2 and 3. Although the transition states are of primary interest, some idea of their reliability may be obtained by comparison of the theoretical and experimental structures of acetylene,[34] fulminic acid,[35] and isoxazole.[36] Such a comparison with experiment is drawn in Table I.

The most obvious conclusion to be recognized from Table I is that the 4-31G and Dunning double ζ basis sets yield very similar structural predictions. This result is, of course, expected, since both basis sets allocate two functions per atomic valence shell orbital. In all but two cases (the NO distances in HCNO and isoxazole), the (9s5p/4s2p) bond distances are very slightly longer than the analogous 4-31G distances. However, the largest of these differences is only 0.014 Å, which occurs for the CN bond distance in isoxazole.

The second conclusion which may be drawn from Table I is that both the 4-31G and (9s5p/4s2p) SCF predictions are in good accord with experiment. Among the 17 independent geometrical parameters given in Table I, 4 are closer to the 4-31G predictions and 11 to the predictions from the Huzinaga-Dunning basis. For both basis sets, the single parameter in poorest agreement with experiment is the NO distance of HCNO. The 4-31G NO distance is 0.055 Å and the double ζ distance 0.075 Å larger than the experimental value, $r_e(\mathrm{NO}) = 1.199$ Å. Other discrepancies with experiment are rather small. For example, the largest (9s5p/4s2p) disagreement for the product isoxazole bond distances is 0.013 Å (the C_2–C_3 distance).

Turning to the transition-state structures, Figures 2 and 3 indicate immediately that both predicted transition states are more symmetrical than the structure found by MINDO.[20]

Table I. Theoretical and Experimental Equilibrium Geometries for Acetylene, Fulminic Acid, and Isoxazole[d]

	4-31G	(9s5p/4s2p)	expt
	Acetylene		
r_e(CH)	1.050	1.054	1.060[a]
r_e(CC)	1.189	1.201	1.203
	HCNO		
r_e(CH)	1.049	1.051	1.050[b]
r_e(CN)	1.133	1.140	1.169
r_e(NO)	1.254	1.274	1.199
	Isoxazole		
$r_e(C_1C_2)$	1.339	1.352	1.358[c]
$r_e(C_2C_3)$	1.431	1.440	1.427
$r_e(C_3N)$	1.290	1.304	1.314
r_e(NO)	1.418	1.406	1.398
$r_e(OC_1)$	1.350	1.358	1.346
$r_e(C_1H_1)$	1.063	1.064	1.075
$r_e(C_2H_2)$	1.063	1.064	1.076
$r_e(C_3H_3)$	1.065	1.066	1.077
$\theta_e(OC_1C_2)$	109.8	109.6	110.5
$\theta_c(C_1C_2C_3)$	104.1	103.9	103.1
$\theta_c(C_2C_3N)$	112.4	111.9	112.0
$\theta_e(C_3NO)$	104.9	105.4	105.5
$\theta_e(NOC_1)$	108.8	109.2	108.8
$\theta_c(H_1C_1C_2)$	133.4	133.3	133.4
$\theta_e(H_2C_2C_1)$	128.5	128.5	128.4
$\theta_c(H_3C_3C_2)$	128.1	128.2	128.8

[a] Experimental acetylene structure is from Herzberg, ref 34. [b] Experimental fulminic acid structure is from Bunker, Landsberg, and Winnewisser, ref 35. [c] Experimental isoxazole structure is from Stiefvater, Nösberger, and Sheridan, ref 36. [d] In labeling the isoxazole molecule, the carbon adjacent to oxygen is C_1 and that adjacent to nitrogen is C_3. Hydrogens are numbered according to the carbon atom they are bonded to. Bond lengths in ångstroms, angles in degrees.

Such structures are consistent with but do not demand a concerted mechanism for the 1,3-dipolar cycloaddition. More specifically, the transition state has a structure which might be anticipated from a planar least motion approach of HCNO to HCCH. Although the levels of theory employed are not reliable enough to ascribe absolute certainty to this prediction, nevertheless this research supports the earlier lower level theoretical work of Poppinger.[19] The predicted transition state is also consistent with Hammond's postulate, which states that for a strongly exothermic reaction the transition state should more closely resemble the reactants.

As was the case for reactants and product, the (9s5p/4s2p) transition state bond distances, with the exception of the C_2–C_3 separation, are somewhat longer than the comparable 4-31G predictions. However, these differences are of a minor nature, the largest being only 0.024 Å for the CO distance. Taking the reactant and product geometry predictions as a guide, both theoretical transition states should be qualitatively reliable. However, it must be noted that transition states occur in rather tortured regions of potential energy surfaces and thus some caution is in order.[37]

Finally, it may be noted again that the transition states in Figures 1 and 2 are in reasonably qualitative agreement with the minimum basis set structure of Poppinger.[19] As expected, the differences are greatest for the transition-state specification of the position of the HCNO relative to the HCCH. The most obvious difference is the minimum basis set distance C_2–C_3 (see caption to Table I for subscript nomenclature), which is 2.369 Å, significantly longer than the (9s5p/4s2p) prediction of 2.180 Å.

Force Constants and Vibrational Frequencies

To ascertain the true nature of the stationary point described above, quadratic force constants were obtained at the 4-31G level of theory. These force constants were then used in a standard normal mode analysis,[38] which yielded the vibrational frequencies for reactants, products, and transition state given in Table II. First, and most critically, the split-valence structure was shown to correspond to a genuine transition state. That is, a single imaginary vibrational frequency is found for this structure. To demonstrate unequivocally that this transition state connects reactants with products, Figure 4 illustrates the transition vector calculated with the split-valence set. It is obviously apparent that this transition state connects the reactants, acetylene plus fulminic acid, to the product, the five-membered ring, isoxazole.

Table II. Vibrational Frequencies (cm^{-1}) Associated with the Reactants, Transition State, and Product for the Acetylene plus Fulminic Acid Reaction at the 4-31G SCF Level of Theory[e]

	acetylene	transition state	isoxazole
σ_g	3738 (3373)[a]	a′ 3693	a′ 3504 (3140)[d]
	2231 (1974)	3616	3477 (3128)
σ_u	3617 (3294)	3584	3461 (3086)
π_g	889 (612)	2102	1765 (1653)
π_u	889 (729)	2035	1603 (1560)
		1143	1517 (1432)
		947	1377 (1373)
		898	1258 (1217)
		820	1151 (1128)
		640	1126 (1089)
		499	1031 (1021)
		274	999 (856)
	fulminic acid		873 (651)
σ	3715 (3335)[b]	a″ 907	a″ 1109 (1033)
	2435 (2190)[b]	835	1068 (889)
	982 (1251)[b]	712	918 (764)
π	750 (538)[b]	535	702 (632)
	516 (224)[c]	278	639 (595)
		reaction coordinate	
		684 i	

[a] Acetylene experimental frequencies from ref 34. [b] W. Beck and K. Feldl, *Angew. Chem., Int. Ed. Engl.*, **5**, 722 (1966). [c] Reference 35. [d] S. Califano, F. Piacenti, and G. Speroni, *Spectrochim. Acta, Part A*, **15**, 86 (1959). [e] Experimental vibrational frequencies are in parentheses.

Experimental vibrational frequencies are available for all three molecules and have been included in Table II. It is now generally well known that force constants and vibrational frequencies calculated at the SCF level of theory are larger than those from experiment by about 10–15%.[39] The present results confirm this trend, with the exception of the NO stretching frequency in HCNO, where our calculations predict a value of 982 cm^{-1} while the experimental value is 1251 cm^{-1}. The addition of polarization functions, with the larger (9s5p1d/4s1p) contracted to a [4s2p1d/2s1p] basis, increased the NO stretching frequency to 1294 cm^{-1}, in good agreement with experiment. This agreement is somewhat fortuitous since harmonic frequencies have been calculated and the experimental values have not been corrected for anharmonic effects.

The calculated vibrational frequencies have also been used to allow an assessment of the importance of differences in zero-point energies on both the barrier height and the exothermicity. For the species involved the respective zero-point energies follow: acetylene plus fulminic acid, 29.3; transition state, 30.3; isoxazole, 35.5 kcal. Thus it is seen that zero-point corrections increase the classical barrier height by 1.0 kcal and decrease the classical exothermicity by 6.2 kcal.

In recent years the changes which take place in the course of a chemical reaction have frequently been analyzed in terms of bond orders[40] and more recently by Morokuma in terms of an energy decomposition at the transition state.[41] In an effort to better understand this 1,3-dipolar cycloaddition the force

Table III. Comparison of Harmonic Force Constants (mdyn/Å)

	coordinate	isoxazole	transition state
F_r	(1) C-O	7.56	0.31
	(2) C-C	10.04	3.07
	(3) C-C	14.36	24.07
	(4) C-N	11.65	18.98
	(5) C-H_1	6.65	7.19
	(6) C-H_2	6.61	6.98
F_α	(1) O-C-C	6.50	13.02
	(2) C-C-C	10.59	16.72
	(3) C-C-N	5.05	2.05
	(4) C-C-H_1	0.78	0.39
	(5) C-C-H_2	0.74	0.32
	Interaction Force Constants		
r_1r_2		−2.22	−1.14
r_1r_3		1.50	1.29
r_2r_3		2.13	2.61
r_2r_4		1.44	−1.21
$r_1\alpha_1$		0.99	0.48
$r_1\alpha_2$		−1.35	−0.003
$r_1\alpha_3$		−1.59	−0.34
$r_2\alpha_1$		0.95	3.23
$r_2\alpha_2$		4.93	5.02
$r_2\alpha_3$		4.00	2.63

constants at the transition state and for the product isoxazole have also been examined in detail. These force constants are presented in Table III, where the units are mdyn/Å.

Since the force constants in internal coordinates are known to be roughly transferable from one bonding environment to another, they offer not only a measure of the progress of the reaction at the transition state, but also a measure of the strength of the new bonds. An examination of Table III reveals the extent of bonding in the transition state. As the reactants approach, the C-O (r_1) and the C-C (r_2) distances decrease and the force constants increase from their initial value of zero to 0.31 and 3.07 mdyn/Å, respectively. The remaining stretching force constants show similar though less pronounced changes. Turning attention to the bending modes, it is found that in some respects the transition state is more rigid than the product if measured by the magnitudes and the changes in the O-C-C and the C-C-C bending force constants.

The changes in the interaction force constants behave in a similar manner. The calculations have shown that the coupling between some of the stretches and bends is unusually strong. As in the case of the diagonal force constants, some of the interactions undergo dramatic changes as the reaction proceeds from transition state to product. Of particular interest are the changes observed in r_2r_4 where the coupling constant changes sign, as well as the changes in magnitude in r_1r_2 and $r_2\alpha_2$.

The major impetus for this work has been an attempt to ascertain whether this reaction proceeds in a concerted fashion, through a relatively symmetric transition state, or in a stepwise biradical manner with a highly distorted nonsymmetric transition state. A few years ago, McIver suggested an analysis of cycloaddition transition states in terms of the force constants of the bonds being formed.[42] Focusing attention on r_1 and r_2, McIver's analysis was based on the assumption that these two are the only important degrees of freedom, that they are equal in the transition state, and finally that the energy is stationary within a particular symmetry. If these conditions held, a 2 × 2 block of the force constant matrix could be considered as determining the nature of the transition state. This block would have eigenvalues of $\lambda = f_{11} \pm f_{12}$. The direction corresponding to the positive sign would be symmetric, while that of the negative sign would correspond to the antisymmetric stretch of r_1 and r_2. Since the bonds being formed are on opposite sides of the molecule, and in general could be removed by several bonds, it seemed unlikely that the interaction force constant, f_{12}, would be larger in magnitude than the diagonal ones. Thus it was concluded[42] that a symmetric structure could either be a stable intermediate or a maximum with respect to at least two directions depending on the sign of the diagonal force constants, but *not* a true transition state.

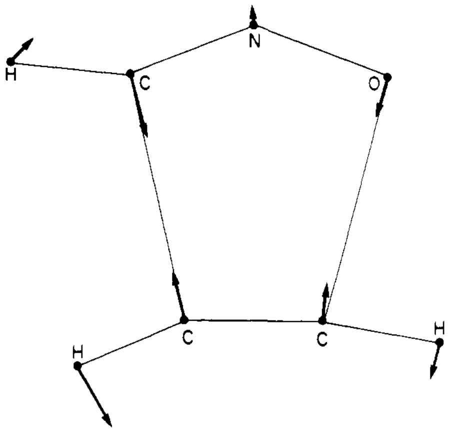


Figure 4. Reaction coordinate for the prototype 1,3-dipolar cycloaddition reaction.

Although r_1 and r_2 are roughly equal in magnitude, the magnitudes of the diagonal force constants are far from equal. Both diagonal force constants are found to be positive, while the interaction between them is both large and negative. Thus, these calculations demonstrate that, in a simple localized picture, distortion along either bond r_1 or r_2 will produce an increase in energy. Only a symmetric motion along both bonds will lead either to reactants or to products. Since both diagonal force constants are positive, the assumption of a small off-diagonal force constant would have produced a symmetric intermediate rather than the transition state which was found.

This analysis of the magnitudes of the interaction force constants offers a plausible explanation for the existence of a relatively symmetric transition state at the ab initio SCF level. Since it has now been well established that ab initio SCF theory produces interaction force constants which are in good agreement with experiment,[39] it is felt that inclusion of polarization functions and/or correlation in the transition state would probably not qualitatively alter the present findings of a relatively symmetric saddle-point structure.

The calculations have shown that it is generally incorrect to assume that only two degrees of freedom will dominate the topology of the potential-energy surface at the transition state. It is seen that a symmetric structure is possible and that a transition state may occur where the potential surface has two positive curvatures along the bonds being formed. Previously similar arguments were advanced in an investigation of the Cope rearrangement.[43]

Before we close this section, it should be noted that there is a perspective from which the present transition state may be viewed as *nonsymmetric*. This perspective is appreciated by comparing the force constants in Table III for the two new bonds being formed as the five-membered ring comes into being. The C-O force constant is in fact ten times smaller than the C-C force constant. Since bond energies are often roughly proportional to the corresponding bond stretching force constants, it might be argued that the C-C bond at the transition state is ten times stronger than the C-O bond.

Energetic Predictions

The SCF absolute and relative energies of reactants, transition state, and product are summarized in Table IV. The evaluation of these results is somewhat difficult, since both the activation energy and the exothermicity for the HCCH +

Table IV, Total and Relative SCF Energies for the Prototype 1,3-Dipolar Cycloaddition

	STO-3G[a]	4-31G	(9s5p/4s2p)	(9s5p1d/4s2p1d)[b]
		Absolute Energies (hartrees)		
HCCH + HCNO	−241.248 46	−244.081 53	−244.375 88	−244.496 44
transition state	−241.214 40	−244.036 34	−244.326 84	−244.441 10
isoxazole	−241.492 05	−244.209 21	−244.503 81	−244.635 92
		Relative Energies (kcal)		
HCCH + HCNO	0.0	0.0	0.0	0.0
transition state[c]	21.4	28.4	30.8	34.7
isoxazole	−152.9	−80.1	−80.3	−87.5

[a] Poppinger, ref 19. [b] At 4-31G stationary point geometries; structures not optimized at this level of theory. [c] As a rough comparison, experimental activation energies of 25.1, 27.5, and 34.3 kcal/mol have been found[44,45] for the somewhat analogous 1,3-butadiene and ethylene reaction.

Table V. Total and Relative CI Energies[a] for the Prototype 1,3-Dipolar Cycloaddition

	level of CI[b]			
	0a′ + 3a″ 3334	2a′ + 3a″ 7053	3a′ + 3a″ 10 000	4a′ + 3a″ 13 672
		Absolute Energies (hartrees)		
HCCH + HCNO	−244.451 14	−244.544 42	−244.584 93	−244.606 05
transition state	−244.405 09	−244.506 23	−244.548 78	−244.574 94
isoxazole	−244.587 17	−244.654 60	−244.681 76	−244.718 13
		Relative Energies (kcal)		
HCCH + HCNO	0.0	0.0	0.0	0.0
transition state	28.9	24.0	22.7	19.5
isoxazole	−85.4	−69.1	−60.8	−70.3

[a] Double ζ basis set at the double ζ SCF optimized geometries. [b] Number and symmetry of the occupied molecular orbitals correlated and total number of configurations included in the CI.

HCNO reaction are unknown experimentally. However, the activation energy might be expected to be roughly comparable to the values 25.1,[44] 27.5,[44] and 34.3 kcal[45] found from experiment for the prototype Diels-Alder reaction, that of 1,3-butadiene with ethylene. For HCCH + HCNO itself, Simonetta and co-workers[46] on the basis of standard bond energies[47] (but neglecting conjugative effects) estimate an exothermicity of 60 kcal/mol. By analogy,[46] they suggest an activation energy of ~15 kcal. Finally we note that Huisgen[48] has estimated an activation energy of 8-12 kcal for the fulminic acid plus acetylene reaction.

The predicted 4-31G and (9s5p/4s2p) SCF activation energies, 28.4 and 30.8 kcal, agree well both with each other and with the Diels-Alder activation energy for 1,3-butadiene + ethylene cited above. Perhaps surprisingly, the addition of polarization functions to the basis set at the 4-31G stationary point geometries increases the predicted barrier to 34.7 kcal. This finding is contrary to the usual observation[37] for simpler systems that polarization functions generally lower predicted barriers. However, since no other transition state for a molecular system of this size (or of this general type) has ever been treated with a basis set this large, preconceived notions should be avoided in the interpretation of the results.

The predicted exothermicities from the 4-31G and Dunning basis sets are in very close agreement, both being ~80 kcal. The addition of polarization functions increases this exothermicity to 88 kcal. A measurement of the heat of formation of isoxazole would be most desirable as it would allow an assessment of the quality of the predicted exothermicities. However, it can be tentatively concluded that polarization functions do not appear to cause great distortions in the qualitative shape of the C_3H_3NO potential energy surface.

Table V summarizes the present treatment of the energetics of this 1,3-dipolar cycloaddition using configuration interaction (CI). The CI energy differences must be viewed cautiously since, short of the practically impossible correlation of all occupied valence orbitals, it is of great importance that the reactants, transition, and product be described equally well. The CI involving only the three a″ or π molecular orbitals has relatively little effect on either the activation barrier or the exothermicity. The activation energy is decreased by 1.9 kcal relative to the SCF value of 30.8 kcal and the exothermicity increases from 80.3 to 85.4 kcal. This result implies that strictly π-electron correlation effects have relatively little influence on the topology of the C_3H_3NO potential energy surface.

However, the remaining entries in Table IV indicate clearly that the further incorporation of σ-electron correlation effects significantly reduces both the predicted barrier height and exothermicity. In other words, the Hartree-Fock approximation is best for isoxazole, less adequate for the reactants HCCH + HCNO, and relatively poor for the transition state. The most complete variational treatment (13 672 $^1A'$ configurations) suggests a barrier of 19.5 kcal and an exothermicity of 70.3 kcal.

An examination of the effect of a two-configuration SCF (TCSCF) treatment on the barrier height and exothermicity was undertaken using the double ζ basis set and geometries. The two configurations differ in having $(15a')^2$ or $(16a')^2$ as their highest occupied molecular orbitals. The TCSCF results support the above statement regarding the adequacy of the Hartree-Fock or single configuration approximation. For isoxazole, the primary configuration which involves $(15a')^2$ has a coefficient of 0.9910 in the TCSCF wave function, while for the reactants and transition state these coefficients are 0.9830 and 0.9790, respectively. However, the overall changes in the barrier height or exothermicity were rather small. The TCSCF barrier is decreased by 0.2 kcal relative to the SCF result while the exothermicity decreased by 0.6 kcal.

Further calculations were carried out to determine the effect on the barrier and exothermicity of correlating additional a′ molecular orbitals. A CI calculation was performed in which 4a′ and 0a″ MO were correlated. Combining the separate results of the CI calculations in which (4a′ and 0a″) and (0a′ and 3a″) MO were correlated gave values of 71.7 and 20.3 kcal for the exothermicity and barrier height. These results are in reasonable agreement with those given by the CI calculation in which 4a′ and 3a″ MO were explicitly correlated (i.e., 70.3 and 19.5 kcal). Although not rigorous, the agreement from this approximate procedure which assumes a sort of separability of σ and π correlation effects was sufficiently accurate to warrant carrying out a series of CI calculations in which 6a′ and 0a″ MO were correlated for a total of 13 306 configurations. The results of the 6a′ and 0a″ CI calculations were then combined with the 0a′ and 3a″ CI calculations to provide rough estimates of the barrier height and exothermicity which would result if 6a′ and 3a″ MO were correlated. A barrier of 22.5 kcal and an exothermicity of 63.1 kcal were found by this procedure. It does not appear that simply correlating additional a′ MO in the CI will markedly decrease the barrier height.

When correlation effects at the double excitation level of CI produce significant changes in a potential-energy surface, it usually means that these changes will be somewhat amplified when higher excitations are properly incorporated in the theory. Perhaps the simplest reasonable way of dealing with these unlinked cluster effects is Davidson's approximation[49]

$$\Delta E_{\mathrm{Q}} = (1 - C_0^2)\Delta E_{\mathrm{SD}} \qquad (5)$$

In (5) ΔE_{Q} is the correlation energy due to quadruple excitations, C_0 is the coefficient of the SCF configuration in the double excitation CI, and ΔE_{SD} is the correlation energy due to single and double excitations. Applying (5) to our most complete variational results (4a′ and 3a″) yields a barrier of 16.1 kcal and an exothermicity of 67.6 kcal.

Concluding Remarks

This research lends support to the view that transition states for 1,3-dipolar cycloadditions have relatively symmetric geometries. Examination of the transition force constants provides an understanding of why such a symmetric transition state is possible. The present calculations provide no indication that there is a biradical reaction path with a highly nonsymmetric transition state of comparable or lower energy but cannot definitely rule out such a possibility in the absence of further explorations in other regions of the potential-energy surface. The relatively minor energetic changes due to a two-configuration SCF treatment do suggest that there is not a very low-lying doubly excited state as is often found to stabilize biradicaloid species. Although correlation effects should have relatively little effect on the geometrical structures calculated here, the predicted barrier height is reduced by a factor of 2 (from 30.8 to 16.1 kcal) by large-scale configuration interaction. In this sense, the present research probably represents the first qualitatively reliable nonempirical theoretical study of the 1,3-dipolar cycloaddition reaction.

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