

[2 + 2] Cycloadditions. A Concerted Pathway for Acetylene Plus Ethylene

B. ANDES HESS, JR. AND L. J. SCHAAD

Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235 U.S.A.

D. N. REINHOUDT

Laboratory of Organic Chemistry, Twente University of Technology, 7500 AE Enschede, The Netherlands

Abstract

The $[2_s + 2_a]$ cycloaddition of ethylene and acetylene has been studied. A transition structure of C_2 symmetry was located on the potential surface. Activation energies for the process are also reported.

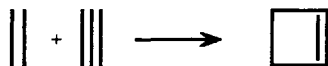
1. Introduction

Woodward and Hoffmann rules [1] predict that $[2 + 2]$ cycloadditions will not occur in a concerted fashion by the $[2_s + 2_s]$ pathway. This has recently been given support by an MC-SCF study of the cycloaddition of two ethylenes by Bernardi, Bottoni, Robb, Schlegel, and Tonachini. They were unable to locate a $[2_s + 2_s]$ transition structure but did find a diradical intermediate. This lends strong support to the step-wise formation of cyclobutane from two ethylenes:



They were also able to locate a transition structure of C_2 symmetry for the concerted $[2_s + 2_a]$ cycloaddition. However, they found it to lie considerably higher in energy on the potential surface than any point on the diradical pathway, and they suggested that the $[2_s + 2_a]$ cycloaddition is unlikely to be a viable pathway.

A related reaction is the cycloaddition of acetylene and ethylene to give cyclobutene.

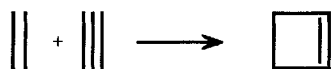


Our interest in this reaction stems from experimental results obtained in Enschede where it was found that thermal $[2 + 2]$ -cycloaddition reactions of alkenes and acetylenes to give cyclobutenes take place under relatively mild conditions when the reactants are strongly polarized and have opposite electron densities [3]. Previously it was reported that reactions of enamines (electron-rich alkenes) react with electron-deficient acetylenes, e.g., dimethyl acetylenedicarboxylate, in two different ways [4]. In apolar solvents 3-(*N,N*-dialkylamino) cyclobutenes are formed, but in polar

solvents pyrrolizines are the reaction products. These observations led to the conclusion that in the first step of the thermal reaction of the acetylene with the alkene, a 1,4-dipolar intermediate is unlikely, and that the reaction may well be concerted.

This is in contrast with the reactions of electron-deficient alkenes with electron-rich alkenes for which Huisgen has shown that the [2 + 2]-cycloaddition to form cyclobutane proceeds via a 1,4-dipolar intermediate [5]. Recently, it has been found that the reaction of electron-deficient alkenes (*viz.* 1-nitroalkenes) with electron-rich acetylenes (*viz.* ynamines) also takes place under mild conditions to give a 3-nitrocyclobutene when the reactions are carried out in apolar solvents [6]. In more polar solvents these reactions give different products. Based on these experimental results it was postulated [4] that a concerted [2 + 2]-cycloaddition reaction between acetylenes and alkenes cannot be excluded.

For this reason we have undertaken an *ab initio* study of the potential surface of the reaction of ethylene with acetylene to form cyclobutene as follows:



Since the [2_s + 2_s] pathway is likely not to exist we have limited ourselves to the [2_s + 2_a]-reaction pathway. We report here our results for unsubstituted ethylene and acetylene.

2. Calculations and Results

All minima and saddle points were located with People's GAUSSIAN 80 program [7]. The basis sets used were those stored internally in GAUSSIAN 80. MP2

TABLE I. Geometry of the ethylene plus acetylene transition structure.^a

Coordinate	sto-3G	3-21G	6-31G*
C ₁ -C ₂	1.221	1.237	1.233
C ₁ -H ₃	1.080	1.056	1.061
C ₅ -C ₆	1.420	1.421	1.418
C ₅ -H ₇	1.086	1.065	1.065
C ₅ -H ₈	1.103	1.089	1.092
C ₁ -C ₅	2.124	2.140	2.136
<H ₃ C ₁ C ₂	158.8	155.1	155.0
<H ₇ C ₅ C ₈	124.6	122.6	123.3
<H ₈ C ₅ C ₆	115.7	116.6	116.6
<C ₁ C ₂ C ₆ C ₅	33.2	32.7	33.3
<H ₇ C ₅ C ₆ H ₁₀	106.2	109.1	108.5
<H ₇ C ₅ C ₆ H ₉	116.7	109.5	109.9
<H ₃ C ₁ C ₅ H ₇	76.7	78.2	77.2
<H ₃ C ₁ C ₅ H ₈	14.2	20.1	20.7

^aBond lengths in angstroms, and angles in degrees. Atoms are numbered as in Fig. 1.

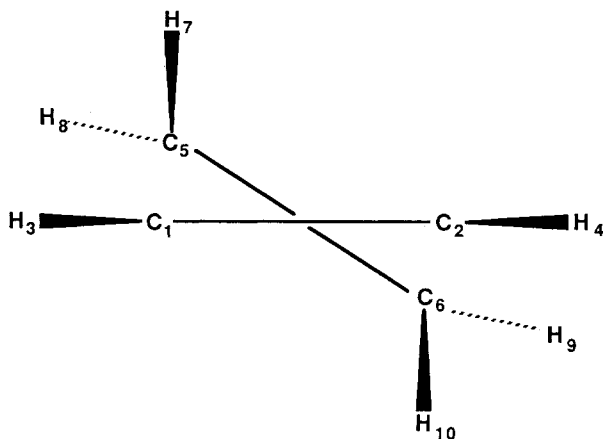


Figure 1. Ethylene plus acetylene transition structure.

computations were done with an MP2 program [8] written to take advantage of molecular symmetry. Force constant calculations were carried out analytically with GAUSSIAN 82 [9].

The search for the $[2_s + 2_a]$ -transition structure was first made with the STO-2G basis set. For the initial guess of the starting geometry a value of each internal coordinate was chosen intermediate between that of reactants (ethylene and acetylene) and product (cyclobutene). The distance between the two reacting C—C bonds was 2.0 Å, and the twist angle between these two bonds was 60°. C_2 symmetry was maintained throughout the search. A stationary point was located after fourteen cycles (the maximum Cartesian force was 0.0002 hartrees/bohr). The final structure was very similar to the initial guess with the exception of the twist angle mentioned above, which was found to be 33.7°. The geometry obtained was used as the starting geometry for the STO-3G search. Similarly the STO-3G geometry was used with the 3-21G basis set, and the 3-21G geometry in turn used for the 6-31G* search. Second derivatives were computed for stationary points found with the STO-3G and 3-21G basis sets, and in both cases diagonalization of the force-constant matrix led to one negative eigenvalue as required for a transition structure. In Table I are given the

TABLE II. Energy of ethylene, acetylene, cyclobutene, and transition structure.^a

	STO-3G	3-21G	6-31G*	6-31G*/MP2 ^b
ethylene	-77.0740 ^c	-77.6010	-78.0317	-78.2844 ^d
acetylene	-75.8562 ^c	-76.3960	-76.8178 ^c	-77.0642
cyclobutene	-153.0403 ^c	-154.0307	-154.8996 ^c	-155.4091 ^d
trans. struc.	-152.7464	-153.8378	-154.6886	-155.2285

^aIn hartrees.

^bComputed at the optimized 6-31G* geometry.

^cReference 11.

^dReference 12.

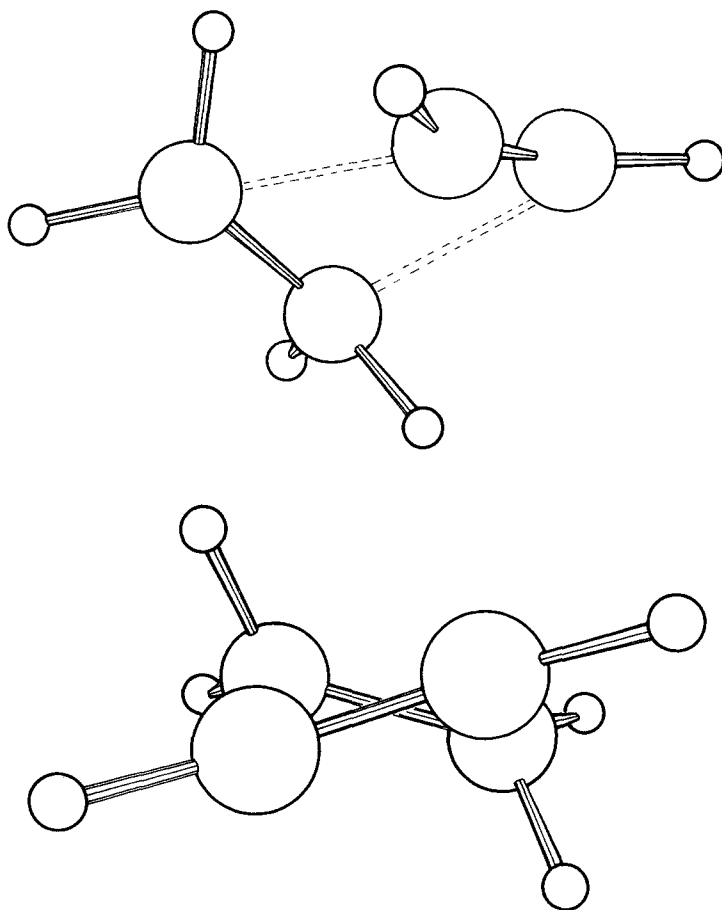


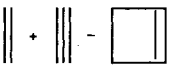
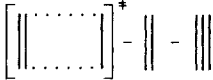
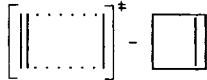
Figure 2. ORTEP drawings of the transition structure found for the [2 + 2] cycloaddition of ethylene and acetylene.

geometries of the transition structure for the various basis sets. Energies are in Table II. ORTEP plots [10] for the 6-31G* transition structure are shown in Figure 2.

In order to compute activation energies of both the forward and reverse reactions, energies were obtained for the optimized geometries of ethylene, acetylene, and cyclobutene with the STO-3G, 3-21G, and 6-31G* basis sets [11, 12]. These energies are tabulated in Table II. Finally, single-point 6-31G*/MP2 energies were obtained at the 6-31G* geometries, and these are also given in Table II.

With the data in Table II, the difference in energy between reactants and products, the activation energy for the [$2_s + 2_a$] cycloaddition of ethylene and acetylene, and the activation energy for the decomposition of cyclobutene (reverse cycloaddition) to give ethylene and acetylene were computed. These are given in Table III for the vari-

TABLE III. Relative energies.^a

Basis Set			
STO-3G	69	115	184
3-21	21	101	121
6-31G*	31	101	132
6-31G*/MP2 ^b	38	75	113

^akcal/mol.^bComputed at the optimized 6-31G* geometry.

ous levels of computation employed. In all cases cyclobutene was found to be more stable than isolated ethylene and acetylene. The value of 38 kcal/mole obtained with 6-31G*/MP2 compares very favorably with 39.5 kcal/mole computed from experimental heats of formation [13] of ethylene, acetylene, and cyclobutene even though zero-point energy and temperature corrections were not made [12].

Even with inclusion of correlation the activation energy for the [$2_s + 2_a$] cycloaddition is very high (75 kcal/mole), and it is unlikely that such a reaction can be observed for the unsubstituted acetylene and ethylene. Nevertheless, we have shown that a transition structure for this pathway does exist and it is hoped that introduction of substituents will significantly lower this activation energy [14]. Comparison of this computed activation energy (75 kcal/mole) with that found for the [$2_s + 2_a$] cycloaddition of two ethylenes with an STO-3G MC-SCF wave function [2] (88 kcal/mole) indicates that the two reactions are likely to be reasonably similar in their activation energies. This is particularly true if one considers that Bernardi [2] with the better 4-31G MC-SCF wave function (and perhaps more comparable to our 6-31G*/MP2 wave function) obtained lower activation energies for other transition structures on the C_4H_8 potential surface than those computed with an STO-3G MC-SCF wavefunction.

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