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Mark S. Gordon

J. A. Boatz

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Marie G. Friederichs



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Insertion of Methylene into Ethane and Cyclopropane

Mark S. Gordon,*† J. A. Boatz,† David R. Gano,† and Marie G. Friederichs†

Contribution from the Department of Chemistry, North Dakota State University, Fargo, North Dakota 58105, and the Department of Chemistry, Minot State College, Minot, North Dakota 58701.. Received August 15, 1986

Abstract: The insertions of methylene into the CH and CC bonds of ethane and into a CC bond of cyclopropane are calculated by using third-order perturbation theory with the 6-31G(d) basis set. At this level of theory, the barriers for these reactions are predicted to be 0.2, 46.0, and 2.2 kcal/mol, respectively. Thus, the introduction of strain has a dramatic effect on the barrier to insertion into a heavy atom-heavy atom bond.

In their closed shell singlet states, the dominant reaction of CH₂ and SiH₂ is believed to be insertion into available bonds. There is experimental¹ and theoretical² evidence that methylene inserts into H-H and C-H bonds with no energy barrier. Likewise, the most recent experimental³ and theoretical⁴ evidence suggests that the insertion of silylene into H-H to form silane occurs with little or no barrier. The most recent estimates^{5,6} place the barriers to insertion of methylene into both the C-H bond of methane and the Si-H bond of silane and of silylene into the Si-H bond of silane at close to zero. The barrier for insertion of silylene into the methane C-H bond is believed to be about 20 kcal/mol.^{6,7}

The rates of insertions of CH₂ and SiH₂ into single bonds between heavy atoms X,Y are apparently much slower than those for X-H insertions. The reason for this could be statistical or a higher barrier for the X-Y insertions. X-Y insertions might be facilitated by introducing strain into the system, thereby weakening the X-Y bond. In this paper, we present the results of preliminary ab initio calculations on the insertions of methylene into the C-H and C-C bonds of ethane and into a CC bond of cyclopropane.

Optimized geometries for RHF stationary points were obtained by using the 6-31G(d)⁸ basis set and the Schlegel optimization method⁹ in GAUSSIAN82.¹⁰ Minima and transition states were verified by establishing that the matrices of energy second derivatives have zero and one negative eigenvalue, respectively. For the prediction of reaction energetics second- and third-order Møller-Plesset perturbation theory corrections¹¹ (MP2 and MP3) were added.

The 6-31G(d) structures for methylene, ethane, propane, cyclopropane, and cyclobutane are available elsewhere.¹² The 6-31G(d) transition states for the three reactions of interest are shown in Figure 1, and the energetics for the reactions are summarized in Table I. All transition-state optimizations were carried out in C₁ symmetry; however, the saddle-point structures for the insertions into the CC bonds have essentially C_s symmetry.

For all three reactions, the approach of methylene to the substrate is skewed, with the methylene hydrogens avoiding steric interactions with substrate atoms. This is easiest for the attack at the ethane CH bond (Figure 1a) and most difficult for attack at the ethane CC bond (Figure 1b). This has a dramatic effect on the internuclear distances at these two saddle points. The newly forming bonds (CC and CH for the CH insertion; CC and CC for the CC insertion) are stretched by roughly 25% relative to their final equilibrium values for the CH insertion and 31 and 42% for the CC insertion. In contrast, while the breaking CH bond has only stretched 11% by the CH insertion transition state, the analogous CC bond in the CC insertion has stretched by 28%,

Table I. Energetics (kcal/mol) for Insertion Reactions^a

	CH ₂ + C ₂ H ₆ → C ₃ H ₈				
	CH insertion		CC insertion		ΔE
	E _f	E _r	E _f	E _r	
SCF	16.5	118.5	65.1	167.2	-102.0
MP2	-4.1	118.6	41.1	163.8	-122.7
MP3	0.2	117.7	46.1	163.6	-116.5

	CH ₂ + c-C ₃ H ₆ → c-C ₄ H ₈		
	E _f	E _r	ΔE
	SCF	19.4	123.5
MP2	-4.1	120.9	-125.0
MP3	2.2	128.9	-126.3

^a E_f, E_r, and ΔE refer to the forward and reverse barriers and the net energy difference for the reaction, respectively.

in order to minimize steric interactions. This extra loss of bonding should result in a larger barrier for the CC insertion, since both reactions have the same reactants and product.

For the ring insertion, CH₂ can approach a "bent"¹³ CC bond, allowing greater electronic interactions at longer internuclear distances. Indeed, the forming CC bonds are stretched by 37 and 25%, relative to their values in cyclobutane, while the cyclopropane

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*North Dakota State University.

†Minot State College.

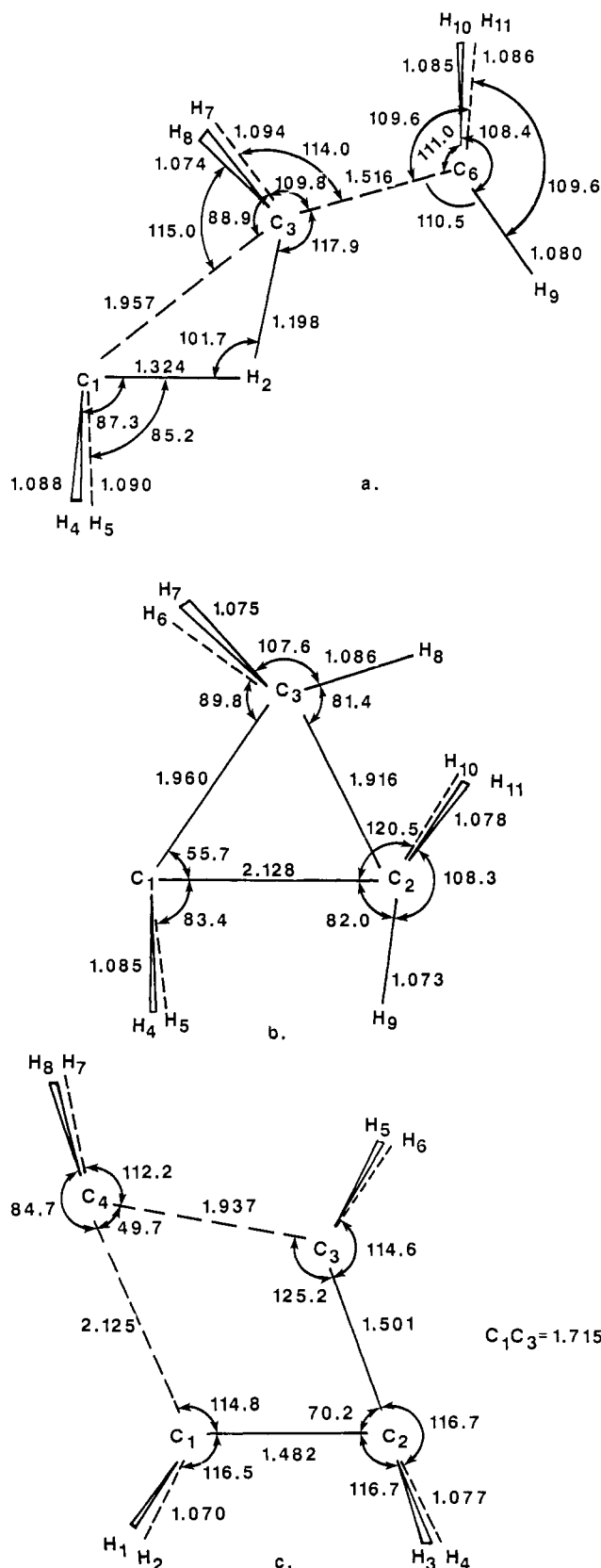


Figure 1. RHF/6-31G(d) transition-state structures. Bond lengths in Å, angles in deg. (a) CH₂ insertion into the ethane CH bond. Angles H₄-C₁-C₃ and H₅-C₁-C₃ = 106.6 and 107.1°, respectively. Dihedral angles C₆-C₃-H₂-C₁ and H₉-C₆-C₃-H₁ = -75.9 and 47.4°, respectively. C₁ is the attacking methylene carbon. (b) CH₂ insertion into the ethane CC bond. Dihedral angles H₄-C₁-C₂-C₃, H₈-C₃-C₂-C₁, and H₉-C₂-C₁-C₃ = 124.6, 180.0, and 180.0°, respectively. C₁ is the attacking methylene carbon. (c) CH₂ insertion into the cyclopropane CC bond. Dihedral angle C₄-C₃-C₂-C₁ = 0.0°. C₄ is the attacking methylene carbon.

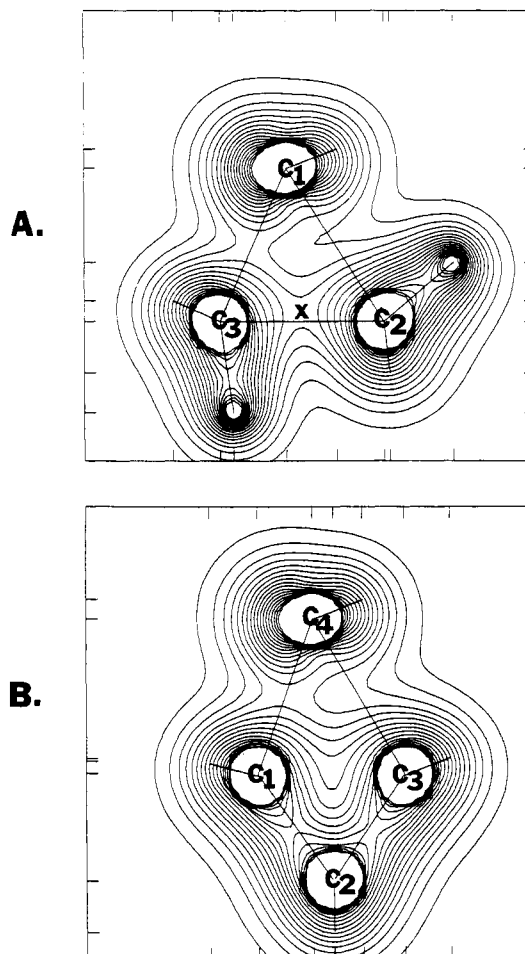


Figure 2. Total density plots for (A) CH₂ + ethane (attacking methylene carbon = C₁) and (B) CH₂ + cyclopropane (C₄ is the attacking methylene carbon). The plotting plane contains the carbon atoms, with the atoms numbered as in Figure 1. The increment between contours is 0.02 bohr^{-3/2}. Contours above 0.35 bohr^{-3/2} are not shown.

CC bond being broken is only stretched by 14% at the saddle point. Thus, this transition state is somewhat earlier than that for the insertion into the ethane CC bond, and one anticipates a smaller barrier for the cyclopropane insertion.

The foregoing is verified by the energies in Table I. At the highest level of theory, MP3/6-31G(d), the barriers to insertion into the CH and CC bonds of ethane are calculated to be 0.2 and 46.1 kcal/mol, respectively. In contrast, the insertion into the strained CC bond of cyclopropane proceeds with a barrier of only 2.2 kcal/mol. Since one expects such predicted barriers to decrease by several kcal/mol with the use of larger basis sets and higher levels of theory,⁴ it is likely that the CH and strained CC insertions will ultimately be predicted to occur with no barrier, whereas the insertion into the unstrained CC bond must overcome a large barrier.

Total electron density plots at the transition states of the C-C insertions are shown in Figure 2. For the ethane insertion (Figure 2A) there is a saddle point (X) in the C₂-C₃ internuclear region, indicating ample bond character.¹⁴ For the cyclopropane insertion (Figure 2B) there is no saddle point in the C₁-C₃ region. So, this bond is essentially broken¹⁴ at the transition state, even though the C₁-C₃ distance in Figure 2B is shorter than the C₂-C₃ distance in Figure 2A. This supports the notion of "bent" bonds allowing greater electronic interactions at longer distances.

The overall energy differences of the two reactions considered here may be compared with experiment in a manner described

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in a recent paper:¹⁵ With use of known heats of formation at 298 K and ($H_{298}^{\circ} - H_0^{\circ}$)¹⁷ and the 6-31G(d) frequencies¹⁶ scaled by a factor of 0.89,¹⁷ "experimental" energy changes are estimated to be -112.0 and -113.6 kcal/mol for propane and cyclobutane, respectively. The theoretical values in Table I overestimate the exothermicity of both reactions.

Higher level calculations on these reactions, as well as the

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analogous silylene insertions and CH₂ and SiH₂ insertions into strained and unstrained C-Si and Si-Si bonds, are currently under way in this laboratory.

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Registry No. Methylene, 2465-56-7; ethane, 74-84-0; cyclopropane, 75-19-4.

Gas-Phase Hydrolysis of Protonated Oxirane. Ab Initio and Semiempirical Molecular Orbital Calculations

George P. Ford* and Christopher T. Smith

Contribution from the Department of Chemistry, Southern Methodist University, Dallas, Texas 75275. Received June 30, 1986

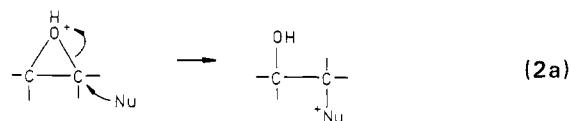
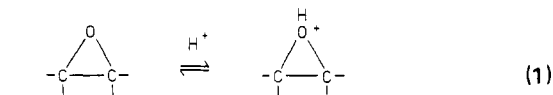
Abstract: MP2/6-31G**//HF/6-31G* ab initio molecular orbital theory predicts the gas-phase unimolecular ring opening of protonated oxirane **2** to lead to protonated acetaldehyde via an activation barrier of 24.6 kcal mol⁻¹ with no intervening minima. The gas-phase bimolecular hydrolysis of **2** is predicted to occur via a transition state 9.1 kcal mol⁻¹ below the isolated reactants but 4.1 kcal above an intermediate ion-dipole complex. The transition structure is predicted to be "early", but probably less so than for the analogous aqueous phase reactions. Reaction profiles calculated with use of the semiempirical MNDO and smaller basis set ab initio procedures are qualitatively different from those at this level.

Derivatives of the highly reactive three membered heterocycle, oxirane **1**, are intermediates in the metabolic activation of many known or suspected carcinogens. These include the intensively

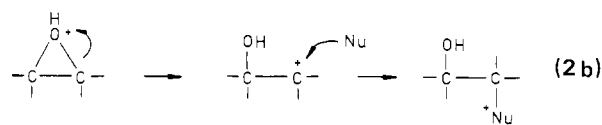


studied polycyclic aromatic hydrocarbons,^{1a,2a,3} the aflatoxins,^{1b,2b,4} and many vinylic compounds.^{5,6} The carcinogenic properties⁷ of these epoxides appear to be associated with their ability to alkylate, or aralkylate, nucleic acid base sites.^{1-3,8} However, where

they have been studied, the kinds and amounts of such adducts formed depend markedly on the structure of the epoxide.^{5,9}



(A2 mechanism)



(A1 mechanism)

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In neutral aqueous media it is now generally accepted,^{10,11} that epoxides undergo initial protonation in a fast reversible step (eq 1) followed by rate determining opening of the conjugate acid. This is usually discussed in terms of two limiting processes.¹¹ In

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