corded on a Cary 17 spectrophotometer and fluorescence spectra on a Perkin-Elmer MPF-44B spectrofluorimeter.

The photochemical quantum yields (ϕ_r^S and ϕ_r^T) were determined by means of an optical bench, equipped with a Hanovia 1000-W xenon-mercury high-pressure lamp, a Schöffler-Kratos monochromator, and a 1-cm UV sample cell. The photon flux was calibrated by means of 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH)[9] and ferrioxalate as actinometers.[8]

The chemical yield of benzotricycloheptene (BTH) was measured on a Carlo Erba Fractovap 2900, employing a 50-m capillary column packed with OV-101 and operated at a split ratio of 1:50, injector, column, and detector temperatures of 175, 130, and 200 °C, respectively, and a nitrogen carrier gas flow of 1.1 mL/min. 2-Methylnaphthalene was used as internal standard.

The chemical yield of the aziridine BDTN was determined by HPLC on a Waters liquid chromatograph equipped with a model 6000-A pump and a 440 detector, employing a Waters μ-Bondapak C_{18} column, operated at an eluant flow rate of 1.7 mL/min and a pressure of 2500 psi. As eluant 40:60 methanol/0.01 M phosphate buffer (pH 7.7) was used with UV detection at 254 nm. *p*-Aminoacetophenone served as internal standard.

The dioxetane kinetics were carried out on a Mitchell-Hastings photometer,[24] equipped with a RCA PF1006 photomultiplier and a Lauda Thermostat NB-D8/17 for temperature control of the cell compartment. The Hastings-Weber scintillation cocktail[25] served as calibration standard of the light flux. Packard scintillation vials were used as reaction vessel. A Servogor 210 recorder registered the output signal of the kinetic run. The data were processed on a Tektronix 4051 desk computer.

The results and experimental conditions are collected in Tables I–IV.

Chemicals. All solvents were purified according to standard literature methods to reproduce the reported physical constants.

The 1,2-dioxetanes **1a–e** were prepared and purified according to the published procedures.[2] In all cases materials of better than 95% purity were used for the quantitative studies.

7,8-Benzo-2,3-diazatricyclo[4.3.0.$0^{4,9}$]nona-2,7-diene, the azoalkane BDT, mp 74–75 °C from petroleum ether (lit.[7] mp 74–75 °C), was prepared via cycloaddition of 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) and benzonorbornadiene and subsequent hydrolysis of the resulting urazole. The material is sensitive even to diffused daylight resulting in denitrogenation, so that all purifications and handling were performed in the dark. Purity checks by CGC and HPLC confirmed the absence of benzotricycloheptene (BTH) and aziridine (BDTN), respectively.

Authentic 2,3-benzotricyclo[3.2.0.$0^{4,6}$]hept-2-ene (BTH) was prepared from the azoalkane BDT via photodenitrogenation[7] and purified by GC collection on a Varian 920 instrument. BTH is stable at elevated temperatures up to 160 °C.

Authentic 7,8-benzo-2,3-diazatricyclo[4.3.0.$0^{2,9}$]nona-3,7-diene (BDTN) was prepared from azoalkane BDT via benzophenone-sensitized photorearrangement.[7] Repeated recrystallizations from 1:1 acetone/pentane afforded HPLC pure product, mp 143 °C dec (lit.[7] mp 140 °C dec). Control experiments confirmed that aziridine BDTN is easily hydrolyzed and decomposes readily above 80 °C.

General Procedure for the Chemical Titrations. Separate stock solutions of ca. 0.3 M dioxetane and of ca. 0.06 M BDT in benzene were prepared. By means of a calibrated microsyringe, 50-μL aliquots of the dioxetane and 10–100-μL aliquots of the BDT stock solution were transferred into a set of eight constricted test tubes and diluted with benzene to a total volume of 150 μL. After sealing, the ampules were heated in an oil bath, which was kept within 1 °C of the desired temperature, until complete consumption of the dioxetane. Details of the specific conditions for the individual dioxetanes are given in Table IV.

For the chemical titrations, 50-μL aliquots of the decomposed dioxetane solutions were taken, combined with 20 μL of internal standard solution in benzene (2-methylnaphthalene for the capillary GC analysis in the singlet titration and *p*-aminoacetophenone for the HPLC analysis in the triplet titration), and submitted to quantitative analysis. The conditions and results are summarized in Table IV.

Acknowledgment. We are grateful for the generous financial support of the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Professor K. Sandros (University of Gotheborg, Sweden) and Professor K. Schaffner (Max-Planck-Institute Mülheim, FRG) for measuring the fluorescence quantum yields.

Registry No. 1a, 35856-82-7; **1b**, 22668-10-6; **1c**, 84065-56-5; **1d**, 35544-39-9; **1e**, 82817-35-4; BDT, 70332-88-6; BTH, 7213-64-1; BDTN, 73834-11-4; nitrogen, 7727-37-9.

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Theoretical ab Initio Study of 1,3-Dipolar Cycloaddition of Fulminic Acid to Acetylene. Support for Firestone's Mechanism

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Abstract: A two-step pathway passing through a highly unsymmetrical transition state and an extended diradical intermediate has been investigated by ab initio computations with the 4-31G basis set and including various levels of electron correlation. Unrestricted Hartree–Fock and restricted Hartree–Fock plus 3 × 3 configuration interaction calculations are inadequate for the description of the energy surface around the diradical transition structure and for comparison of the concerted and diradical paths. A minimum of 4a′ and 3a″ occupied orbitals must be included in the CI treatment. With a multireference iterative perturbation technique using 17 reference determinants and ca. 2.4 million configurations, the extended diradical transition state was found to be 3.6 kcal mol^{-1} below the concerted, synchronous structure. While this energy difference is too small to favor one route unambiguously, the present calculations indicate that Firestone's diradical mechanism merits serious consideration, at least for the fulminic acid cycloaddition to acetylene and probably for other propargyl–allenyl type 1,3 dipoles.

The cycloadditions of 1,3 dipoles to olefins have been the object of a long controversy between Huisgen[2,3] and Firestone,[4-6] and among theoreticians. Huisgen classified the 1,3-dipoles into two catagories: the allyl type and the proparagyl–allenyl type, the latter having an additional π bond in the plane perpendicular to the allylic π system. In what follows we will refer to these as type I and type II, respectively.

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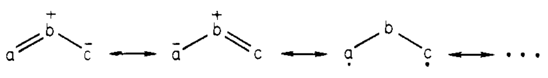
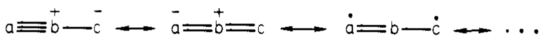
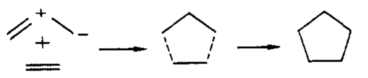


type I



type II

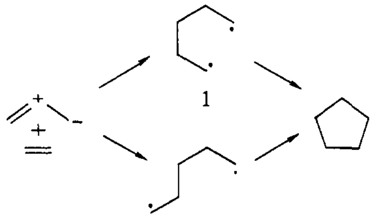
For both types of 1,3 dipoles, Huisgen proposed a unified synchronous or concerted, cycloaddition mechanism (eq 1), in



(1)

which the two new σ bonds are formed simultaneously. His arguments are based on experimental data and are supported by theoretical considerations. The 1,3 dipoles have four electrons distributed among three parallel p orbitals, which can interact with an olefin in a six-electron transition state, energetically favored according to the Woodward–Hoffman rules.[7] If one prefers the frontier-orbital language,[8] the highest occupied MO (HOMO) of the 1,3 dipole may have a stabilizing overlap with the lowest unoccupied MO (LUMO) of the olefin. Type II 1,3 dipoles are linear and must bend in the transition state. However, Huisgen points out that the allylic resonance of the four-electron π system is unaffected by this bending and predicts that both types of 1,3 dipoles and dipolarophiles should approach each other in two parallel planes, forming an envelope-like transition structure.

Firestone, on the contrary, proposed a diradical mechanism (eq 2), also based on experimental data and supported by theoretical



(2)

2

considerations. Only one σ bond is formed in the first step, leading to a diradical in either a cyclo or an extended conformation (**1** or **2**, respectively). Then in a second step, this diradical would close to the final five-membered ring after passing over a small energy barrier. The electronic structure of diradicals is readily discussed in terms of Linnett theory[9] and both types of 1,3 dipoles can be treated with this mechanism.

Harcourt[10] has argued that Huisgen's mechanism and Firestone's might not be very different if the two incipient σ bonds are very unequal in the "synchronous" transition state, or if the radical centers are very close together in the transition state lead to **1**. However, if the diradical mechanism passes through **2**, Huisgen's and Firestone's proposals are unreconcilable. This possibility seems to have been somewhat overlooked by theoreticians, who devote their efforts mainly to the investigation of transition states in a more or less cyclo conformation (note, however, some exceptions[11-13]). The degree of synchronism of the reaction is then estimated by assuming that a relatively symmetrical structure supports Huisgen while a significantly unsymmetrical structure supports Firestone.

A number of theoretical investigations of cycloadditions have appeared in the literature during the past decade and display a clear dichotomy between ab initio and semiempirical calculations. A systematic ab initio study of a wide variety of 1,3-dipolar cycloaddition and Diels–Alder reactions has been undertaken by Leroy and Sana.[14-17] Transition structures were determined by partial geometry optimization at the minimal basis set level. Final energetics were calculated with extended basis sets and in some instances included limited configuration interaction (CI). Full geometry optimization using a minimal basis set was carried out by Poppinger[18] for the addition of fulminic acid to ethylene and acetylene. Since these were closed-shell calculations without configuration interaction, the discovery of any diradical intermediates was precluded and only quite symmetrical transition states were found. The most accurate study to date on the fulminic acid plus acetylene reaction is the work by Komornicki, Goddard, and Schaefer.[19] A rather symmetrical transition structure[20] was the result of full optimization at the double-ζ basis set level. Energetic features of the reaction were investigated by using a double ζ plus polarization basis set and CI involving up to 13672 configurations. Thus, all the ab initio calculations predict the existence of a synchronous transition state for both types of 1,3 dipoles, although they do not rule out the possibility of a two-step pathway since highly unsymmetrical regions of the potential energy surface have not been explored adequately. Furthermore, transition states for type II 1,3 dipoles are found to be planar, contrary to Huisgen's prediction.[3]

Semiempirical calculations, on the other hand, consistently support a two-step mechanism going through a very unsymmetrical transition structure in a cyclo conformation, then forming a diradical which closes to the products after passing over a second, lower energy transition state. MINDO/3 has been applied to the additions of carbonyl ylide and azomethine ylide to ethylene,[21] and fulminic acid to acetylene.[22] The latter reaction has also been investigated by MNDO/2, which is better adapted to molecules such as HCNO.[23] Diels–Alder reactions show similar discrepancies between semiempirical and ab initio calculations.[11,22,24]

The diagreement between ab initio and semiempirical results has been analyzed by Lluch and Bertran,[21] Caramella et al.,[25] and Basilevsky et al.[26] Two factors seem to contribute to this difference: (i) semiempirical methods underestimate the "closed-shell" or "exchange" repulsion, and (ii) ab initio calculations did

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(20) While the geometry for the concerted transition structure was found to be symmetrical, rather unsymmetrical force constants are reported for the two bonds, being formed, 3.07 and 0.31 mdyn/Å for the C–C and C–O, respectively. This is an artifact of the coordinate system used by Komornicki, Goddard, and Schaefer. Lengthening the C–C bond partially stretches the NO bond. The C–O stretch is coupled to the CNO bend. If the C–C and the C–O stretching force constants are determined by keeping all of the bond lengths constant and fixing the CNO angle, values more charactistic of a symmetrical transition state are obtained, 0.32 and 0.46 mdyn/Å, respectively.

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Table I. Total and Relative Energies for the Reaction of Fulminic Acid with Acetylene[a]

	3×3 CI[b]	two reference determinant second-order Møller–Plesset[c] 2a' + 3a"	3a' + 3a'	4a' + 3a"	full[d]	CIPSI[e]
		Absolute Energies, au				
synchronous transition state	−244.045 40	−244.212 33	−244.267 67	−244.306 53	−244.593 21	−244.597 31
asynchronous transition state	−244.035 21	−244.209 98	−244.263 22	−244.316 47	−244.606 19	−244.603 08[f]
diradical **2**	−244.079 90				−244.608 07	
isoxazole	−244.209 23	−244.348 84	−244.384 42	−244.435 05	−244.716 04	−244.719 15
		Relative Energies, kcal/mol				
synchronous transition state	102.8	87.7	73.3	80.6	77.1	76.4
asynchronous transition state	109.2	87.1	76.1	74.4	68.9	72.8[f]
diradical **2**	81.2				67.8	
isoxazole	0.0	0.0	0.0	0.0	0.0	0.0

[a] RHF optimized geometry used for isoxazole and the synchronous transition state, and the geometries in Figures 1b and 2a for the diradical species, unless indicated otherwise. [b] Involving the HOMO and LUMO only. [c] Excitations from the indicated occupied orbitals. [d] Excitations from all occupied valence orbitals. [e] A large multireference second-order Møller–Plesset and CI method; see text. [f] Using the geometry in Figure 2b.

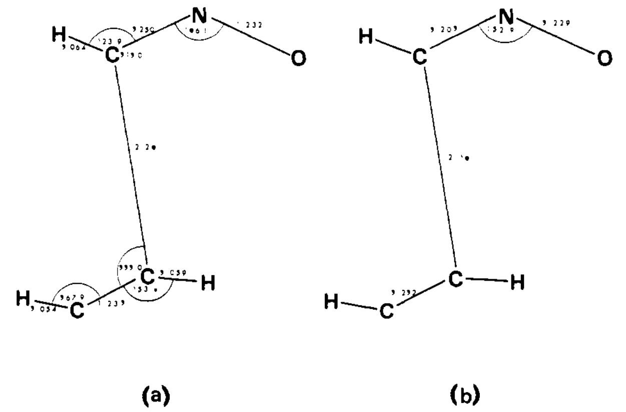
not, as yet, include correlation in the transition structure search while semiempirical methods include it by virtue of the parameterization. These factors have opposing effects, so that it is impossible to decide a priori which theoretical prediction more closely resembles experiment, without undertaking more accurate calculations.

The aim of the present study is to carry out a comparison of the synchronous and the asynchronous transition states at a reliable level of theory, by carefully exploring the unsymmetrical region of the energy surface, using highly correlated ab initio calculations. The addition of fulminic acid to acetylene was chosen for several reasons: (i) the symmetrical region and the synchronous transition state have already been investigated to a high degree of accuracy by Komornicki, Goddard, and Schaefer;[19] (ii) the smallness of the system and its C_s symmetry allow both transition states to be compared by means of rather sophisticated calculations; and (iii) since the extended diradical is planar due to resonance stabilization in the π system, the extended asynchronous transition state *must* exist even if the calculational method artificially disfavors it. In order to make a valid comparison, we have tried to investigate the unsymmetrical region of the potential energy surface in a manner consistant with Schaefer's exploration of the symmetrical region, i.e., similar quality geometry optimization with the same basis set using a corresponding SCF method to locate the diradical structures.

Methods

Ab initio molecular orbital calculations were performed with HONDO,[27] GAUSSIAN 76,[28] and GAUSSIAN 80,[29] using the 4-31G basis set. Schaefer's study[19] indicates that the 4-31G geometries are very similar to calculations with larger basis sets. The diradical transition structure was optimized at the unrestricted Hartree-Fock (UHF) level, using an analytical gradient procedure[31] (final rms gradient less than 0.0005 au).

After the geometry optimization at the SCF level, the relative energies of the synchronous and the asynchronous transition structure were calculated with the inclusion of electron correlation using the restricted Hartree-Fock formalism. For a proper description of diradicals on the basis of an RHF reference function, a minimum of two determinants are required: the RHF determinant and the lowest doubly excited configuration. The simplest level of configuration interaction used in the present work is a 3×3 CI involving only the frontier orbitals. The main purpose of this CI is to check the reliability of the single determinantal calculations. In order to compare with Schaefer's results, we carried out a series of medium-size correlation calculations based on two reference determinants, in which excitations from all of the a″ orbitals and two, three, or four of the a′ orbitals were treated with second-order Møller–Plesset perturbation theory.[32]



(a) (b)

Figure 1. (a) UHF/4-31G optimized structure of the asynchronous transition state. (b) RHF/4-31G + 3×3 CI reoptimized parameters for the asynchronous transition state (parameters not indicated were fixed at their UHF/4-31G optimized values).

The final energy estimates were obtained with the CIPSI algorithm,[33] a multireference iterative perturbational technique. In this method, a variational zeroth-order wave function is built from an iterative selection of the most important determinants. All single and double substitutions derived from each of the determinants in the zero-order wave function are generated and taken into account through second-order Møller–Plesset perturbation theory.[32] Determinants having a coefficient (according to Epstein–Nesbet perturbation theory[34]) larger than a given threshold in the first-order wave function are then included in the zeroth-order wave function and the perturbation calculation is repeated. In a refinement of this algorithm, a middle class of determinants is defined and treated variationally rather than perturbationally, but from which no substitutions are generated.

Results and Discussion

Figure 1a displays the planar, extended diradical transition state found at the UHF/4-31G level ($E = -244.06171$). As anticipated from the resonance stabilization of the π system, this highly unsymmetrical transition state does not spontaneously collapse to the synchronous one. The transition vector is dominated by the C–C stretch with small contributions coming from all of the CH bends.

The reliability of the structure in Figure 1a is somewhat uncertain, because of the rather large value for S^2 obtained from the UHF wave function. In fact, $S^2 = 1.53$ is closer to the value for a triplet than a singlet. Therefore, the main parameters of the transition state were reoptimized with the restricted SCF plus a 3×3 CI. Since only those configurations are included that are

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essential for the proper description of the diradical in a singlet spin state, this wave function and transition-structure geometry should be more directly comparable with Schaefer's single determinantal calculation on the synchronous transition state.[35] The reoptimized structure is given in Figure 1b, and shows somewhat shorter heavy atom bond lengths than the UHF structure. This may be a reflection of the large S^2 value and near triplet character of the UHF wave function. The RHF + 3 × 3 CI structure, Figure 1b, has been used for all of the calculations of the asynchronous transition state listed in Table I. At the 3 × 3 CI level, the asynchronous transition state is still 6.4 kcal mol^{-1} higher in energy than the synchronous structure, despite a 4.6 kcal mol^{-1} stabilization obtained in the reoptimization.

Before proceeding to the more extensive correlation energy calculations comparing the transition states, we tested Huisgen's proposal that the synchronous transition structure should have an envelope-like geometry.[3] Both Poppinger's minimal basis set optimizations[18] and Schaefer's extended basis set frequency computations[19] indicate that the planar structure is favored in single determinantal calculations. The present calculations at the RHF/4-31G + 3 × 3 CI level yield the same conclusion. The dihedral angle between the HCNO and the CCCO planes was changed from 180° to 120° without reoptimizing the remainder of the transition structure. The envelope conformation is gradually destabilized, up to a value of 28 kcal mol^{-1} above the planar structure, and does not show any sign of a secondary minimum. It is highly unlikely that further geometry optimization or the inclusion of additional configuration interaction would make a strongly puckered structure more stable than the planar one.

In order to obtain more reliable relative energies for the transition states and the product,[35-37] we carried out a series of second-order Møller–Plesset perturbation calculations based on a two determinant reference wave function. The results are summarized in Table I and reveal an interesting trend. As more σ orbitals are included in the treatment, the energy gap between the concerted and the diradical transition states decreases and then changes sign. When four a′ orbitals are included, the asynchronous transition state lies 6.2 kcal mol^{-1} below the synchronous structure. The energy difference between the transition states and the product also decreases as more orbitals are included. These changes are within 1 kcal mol^{-1} of those found by Schaefer in a series of CI calculations using the same sets of orbitals, but including all single and double excitations relative to the SCF configuration. Calculations involving all valence orbitals ("full" in Table I) affirm these trends and yield an asynchronous transition state 8.2 kcal mol^{-1} lower than the synchronous one.

To verify the relative ordering of the transition structures, we recomputed the energies with the CIPSI method, applied to the full set of valence molecular orbitals. Determinants with coefficients larger than 0.06 were included in the zero-order wave function; determinants with coefficients between 0.03 and 0.06 were placed in the middle class and treated variationally; the remainder were hanlded by perturbation theory. With these thresholds, the final calculations for the asynchronous and synchronous transition states used reference spaces built from 17 and 18 determinants, respectively, from which about 2.4 × 10^6 determinants were generated. The absolute energies of the asynchronous and synchronous transition state, −244.61202 and −244.59731 au, respectively, are slightly lower than the best values in Table I. However, the energy gap is practically unchanged, with a final value of 9.2 kcal mol^{-1}.

The optimized geometry of the extended diradical **2** is given in Figure 2a. The parameters indicated were optimized at the RHF/4-31G + 3 × 3 CI level. Other parameters were assigned reasonable values: both the CCC and the CCN angles were fixed at 120° with the corresponding CH bonds bisecting them. The CH bond lengths were kept equal to the values optimized in the transition state (Figure 1b). With the 3 × 3 CI, the diradical **2** is found to be 28.0 kcal mol^{-1} more stable than the transition state. However, when electron correlation is introduced at our highest level (CIPSI), the energy gap is dramatically reduced to 1.5 kcal mol^{-1}. This discrepancy is not really surprising if one notes that the 3 × 3 CI describes the energy of the diradical relative to the product reasonably well but considerably overestimates the energy difference between the transition states and the product (Table I). Apparently, more highly correlated wave functions are needed to describe the transition structures equally well.

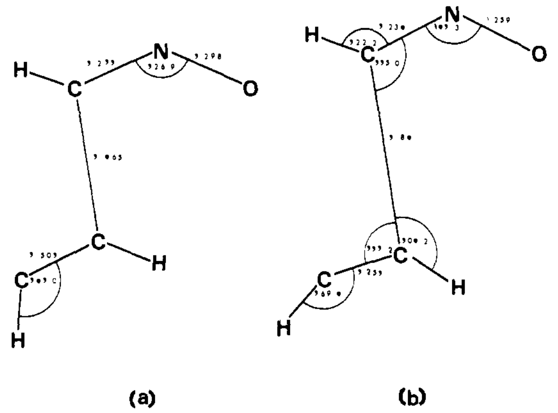

Figure 2. (a) RHF/4-31G + 3 × 3 CI optimized structure of the extended diradical. (b) Geometry of the asynchronous transition state obtained with the CIPSI method. This structure represents the highest energy point on a linear path interpolating the geometries of the asynchronous transition state and the diradical optimized at the RHF/4-31G + 3 × 3 CI level.

The above results indicate that rather important changes can occur in the diradical region of the potential energy surface when correlation is included. As a consequence, we calculated the energies of several points along the reaction pathway connecting the asynchronous transition state and the diradical, using our highest level of accuracy. The HCC–CHNO bond length was varied in steps of 0.15 Å, and the other parameters were assumed to change linearly from the transition structure to the diradical. At a HCC–CHNO bond length of 1.84 Å, the energy curve displays a maximum (−244.60308 au), lying 7.1 kcal mol^{-1} above the diradical **2** and only 3.6 kcal mol^{-1} below the concerted transition state. This structure, shown in Figure 2b, represents our best estimate of the transition structure geometry. Electron correlation has made the transition state more product-like, i.e., a shorter C–C bond. This effect can be interpreted readily: the calculations without correlation overestimate the exothermicity of the reaction and, in accord with Hammond's postulate, predict a transition structure that is too reactant-like.

Before closing to isoxazole, the extended diradical **2** must pass over a barrier to rotation, estimated to be ca. 5 kcal mol^{-1} by analogy with the rotation barrier of butadiene, which has the same central CC bond length.[38] Thus, the second transition state should be lower than the first and would not be rate determining.

To estimate the activation energy of the reaction, we also calculated the energies of the reactants at our highest level, using the SCF optimized geometries published by Schaefer.[19] The reactants (−244.61805 au) lie 9.4 kcal mol^{-1} below the true transition state of the asynchronous path, i.e., the maximum of the energy curve calculated above. This value of the activation energy is in good aggreement with Huisgen's estimate[39] of 8–12 kcal mol^{-1}. The calculated exothermicity, 63.4 kcal mol^{-1}, is also in good agreement with the 60 kcal mol^{-1} value estimated by Simonetta.[40]

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(35) For some conjugated diradicals, even RHF + 3 × 3 CI and two configuration SCF calculations may not be qualitatively correct,[36] necessitating larger CI or MCSCF computations.

(36) Borden, W. T.; Davidson, E. R.; Feller, D. *Tetrahedron* **1982**, *38*, 737.

(37) Feller, D.; Tanaka, K.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1982**, *104*, 967.

(38) Daudey, J. P.; Trinquier, G.; Barthelat, J. C.; Malrieu, J. P. *Tetrahedron* **1980**, *36*, 3399; for an experimental value, see: Aston, J. C.; Szasz, C.; Wooley, H. W. Brickwedde, F. G. *J. Chem. Phys.* **1946**, *14*, 67.

(39) Quoted in ref 18 as Huisgen, R., personnal communication.

Conclusions

It is apparent from this study that calculations at the RHF/4-31G + 3 × 3 CI and UHF/4-31G levels are insufficient to provide energetic predictions for the asynchronous portion of the energy surface. Limited configuration interaction is also inadequate. A minimum of seven occupied orbitals must be included in the CI in order to obtain reliable energies for this reaction. This and recent work by Davidson et al.[36,37] suggests that electron correlation may be more important than previously beleived for diradical-like structures.

In addition, it is evident that a low-lying two-step pathway exists for the addition of fulminic acid to acetylene via the extended diradical **2** and that it is energetically comparable with the one-step, concerted path. A second asynchronous pathway passing through the cyclo diradical transition state cannot be excluded, despite previous ab initio investigations of the symmetrical region of the potential energy surface. The present study suggests that a cyclo diradical transition state, if it exists, is destabilized by the lack of CI and would probably be missed in any search at the SCF level. As suggested by Harcourt[9] and Schaefer,[19] it is quite possible that no distinction exists between the cyclo diradical transition structure and the synchronous one.

For the particular case of the 1,3-dipolar cycloaddition of fulminic acid to acetylene, Huisgen's and Firestone's mechanisms (at least via the extended diradical) require comparable activation energies at our highest level of calculation, with the latter slightly favored by 3.6 kcal mol^{-1}. This energy difference is too small to rule out one mechanism or the other. Quite probably both mechanisms compete, depending on substituents and solvent effects, although the latter are known to be relatively unimportant. This conclusion cannot be extended to type I dipoles or Diels-Alder reactions, without similar quality calculations on specific examples of these reaction. Although any generalizations would be venturesome in the absence of other accurate calculations, our results suggest that Firestone's mechanism now merits serious attention for type II 1,3 dipoles.

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Registry No. Fulminic acid, 506-85-4; acetylene, 74-86-2.

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[40] Beltrame, P.; Cattania, M. G.; Simonetta, M. *Z. Phys. Chem. (Frankfurt am Main)* **1974**, *91*, 225. Note that conjugative effects have been neglected in this estimate.

A van der Waals Model of Chiral Mixtures Using a Chiral Lennard-Jones Potential. Applications to the Pasteur Experiment and Phenomena in Chiral Solvents

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Abstract: Much of the understanding of the behavior of simple fluids stems from the combination of a simple Lennard-Jones potential and a subsequent van der Waals approach to the statistical thermodynamics of such fluids. In this paper, both are generalized to incorporate the effects of chirality as a basis for the discussion of the properties of chiral mixtures at the simplest level. In this way, the role of chirality in leading to characteristic thermodynamic effects may be rigorously defined. Although the model may be too simple to apply quantitatively in that chiral mixtures are frequently relatively complex in structure, it serves as a natural starting point for understanding and defining the role of chirality in thermodynamic phenomena in the solution phase. The model is applied to a number of solution phenomena, such as the possible role of solution configurations in spontaneous resolutions (the Pasteur experiment), and equilibrium shifts of labile racemates or differential enantiomeric solubilities in chiral solvents.

Introduction

In spite of the importance of chirality in many areas of chemistry, statistical-thermodynamic theories are generally concerned with achiral systems. The reason is, of course, a simple one. It is only natural to develop theories for simpler systems, gradually incorporating greater degrees of theoretical complexity in application to more complicated systems once the general behavior of the simpler systems has been understood. Thus an understanding of the interactions between, for example, inert gas atoms in terms of a Lennard-Jones potential leads to quantities such as excluded volume and well depths which may be used quantitatively for inert atom interactions and parametrically for more complex systems. The Lennard-Jones potential then serves as a basis for a range of statistical-mechanical approaches of different degrees of sophistication in linking the microscopic potential parameters to thermodynamic variables. The insensitivity of the usual Lennard-Jones potential to chirality means, however, that it cannot serve as a basis for discussing chiral phenomena.

In the case of chiral fluids, we are immediately confronted with seemingly insurmountable complications in an attempt to discuss the statistical-thermodynamic properties in a simple way. Firstly, a chiral molecule has, in general, a complex molecular structure which cannot be modeled in terms of a chiral atomic system (a contradiction in itself!). Secondly, the effects of chirality will only manifest through an interaction of two chiral systems, so that a statistical-thermodynamic treatment must be based at least on a binary mixture. (For example, the thermodynamics of a single component chiral system is identical with that of the reflected or inverted system if spatial parity is conserved, which seems to be the case at least on a chemical plane.) Thirdly, the interactions between chiral systems must be modeled in some way by a potential which is sensitive to chirality, but which will collapse into the usual forms in the achiral limit.

In this paper, therefore, we shall attempt the modest goal of understanding the effect of chirality at the simplest level by establishing an effectively chiral Lennard-Jones potential which

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