

An MO Theoretical Study on the Stability of Tetrahedrane

Herbert Kollmar

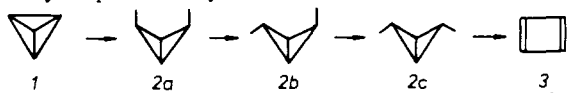
Contribution from the Lehrstuhl für Theoretische Chemie der Ruhr-Universität, 463 Bochum, West Germany. Received August 8, 1979

Abstract: From ab initio calculations which include electron correlation the heats of formation of tetrahedrane and of cyclobutadiene are estimated to be 134 and 105 kcal/mol, respectively. The rearrangement of tetrahedrane to cyclobutadiene passes through three conformers of the bicyclobutyl diradical. From PMCSCF calculations which include the total correlation energy of one optimized electron pair, an activation energy for this process of approximately 30 kcal/mol is deduced. The decay of tetrahedrane leading to two acetylene molecules and the rearrangement of tetrahedrane to methylenecyclopropene are hindered by even larger barriers. Breaking of one CC bond in tetrahedrane needs only about 10 kcal/mol and leads to a singlet diradicaloid species which might be a reactive intermediate in bimolecular reactions.

I. Introduction

While unsubstituted cyclobutadiene has been known for some time,¹ attempts to prepare a derivative of the isomeric tetrahedrane succeeded only very recently, when Maier et al.² reported the synthesis of tetra-*tert*-butyltetrahedrane as a surprisingly stable compound. The stability of tetrahedrane was also the subject of several semiempirical^{3,4} and ab initio MO studies.⁵⁻⁷

An extensive study of the potential surface of the C₄H₄ system was performed by Dewar et al.⁴ using the MINDO/3 method.⁸ This study showed that the lowest energy path of the rearrangement of tetrahedrane leads to cyclobutadiene and needs an activation energy of about 11 kcal/mol. The calculated reaction coordinate passes through the three different conformers of the bicyclobutyl diradical (**2a**, **2b**, and **2c**). The rearrangement of tetrahedrane to cyclobutadiene is symmetry forbidden.⁹ If C_{2v} symmetry would be imposed on the reaction path, the orbital crossing would occur on the path connecting the diradicals **2a** and **2c**. The orbital crossing is avoided in the optimum reaction coordinate by passing through the conformer **2b** which has lower symmetry. The role of the conformer **2a** as a potential precursor for the synthesis of tetrahedrane was recently emphasized by Böhm and Gleiter.³



Schulman and Venanzi⁶ found in their ab initio study that 18 kcal/mol is required for a moderate stretching of a CC bond in tetrahedrane to 1.81 Å. However, these authors considered a diradicaloid structure corresponding to the conformer **2c** only. Thus, their point on the potential surface with a bond length of 1.81 Å does not belong to the optimum reaction path. The best SCF calculations performed so far for tetrahedrane were reported by Hehre and Pople,⁷ who, however, did not study any reaction paths.

We have investigated the structures and energies of tetrahedrane and of cyclobutadiene within the ab initio MO formalism and with inclusion of electron correlation in order to assess the thermochemical as well as the kinetic stability of tetrahedrane.

II. Computational Methods

The ab initio SCF program used is based on the integral program developed by Ahlrichs.¹⁰ Triplet states were computed with a restricted open-shell SCF program written by Staemmler.¹¹ Three different basis sets were used in the calculations: (1) minimal basis (MB) contracted from a 5.2/2 Gaussian lobe basis (the optimum exponents and contraction coefficients were obtained from molecular calculations);¹² (2) double ζ basis (DZ) denotes a 7.3/3 basis of Huzinaga¹³

contracted to (4,1,1,1, 2,1/3). The lobes at the hydrogen atoms were contracted to one basis function with the contraction coefficients taken from a SCF calculation of H₂. (3) DZ + D denotes the DZ basis augmented by one set of d functions at the carbon atoms with an exponent of 1.0 (cf. ref 36).

Only a limited number of points on the potential surface could be calculated with the DZ + D basis. Many of the structural optimizations were performed within the DZ basis, while the MB was used for exploratory calculations of larger areas of the potential surface.

As a method which allows the computation of the full valence electron correlation energy (within the given basis) the CEPA^{14,15} scheme has been applied to points on those parts of the potential surface where the wave function can be reasonably well represented by one determinant. The CEPA approach is equivalent to a configuration interaction treatment which includes all double excitations (those involving the carbon 1s core orbitals were neglected) with respect to a ground-state determinant plus an implicit estimate of the contributions of quadruple and higher excitations. The CEPA method fails if the most important double excitation has a large weight in the wave function (CI coefficient $< \approx -0.3$). Thus, the contribution of electron correlation along the reaction path 1 \rightarrow 3 involving the diradicals **2** had to be calculated by a different way. We used the PMCSCF¹⁶ approach in which the (within the given basis) complete electron correlation of one optimized electron pair is included. Dissociation energies of CH and CC single bonds can be reproduced with this method with an error of about 5 kcal/mol.¹⁶ The method requires only modest computational effort. It basically consists of subsequent calculations of natural orbitals for an electron pair and for a hole pair using the method of Ahlrichs and Driessler.¹⁷ These types of natural orbital expansions are depicted graphically in Figure 1. The transformation mixing the remaining SCF orbitals with virtual orbitals is accomplished by an SCF-like formalism. The convergence of the method is fast and the results do not depend on the choice of the starting MOs (closed-shell SCF as well as open-shell triplet SCF MOs have been used). The method leads to a multiconfigurational SCF function¹⁸ for one electron pair (PMCSCF). In comparison to a 3 \times 3 or other small limited CI calculations¹⁹ our method has two advantages: (1) Not only the left-right but the (within the basis) full correlation of the electron pair corresponding to the bond considered is included. (This is also an advantage over the DCSCF²⁰ approach.) (2) The occupied MOs which are held fixed in classical CI calculations are optimized in order to give the lowest total energy for a wave function with one correlated electron pair.

The PMCSCF scheme includes the correlation of one electron pair. The most important part of electron correlation contributing to the breaking of a single bond is thus included.

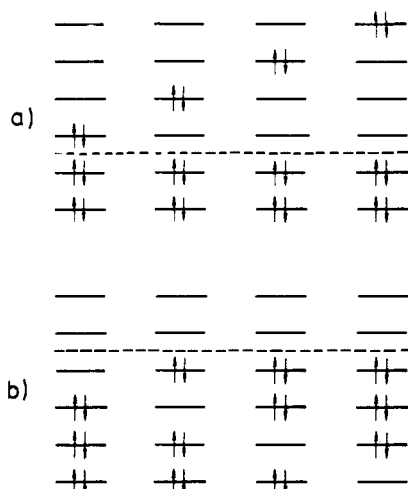


Figure 1. Diagonal pair natural orbital expansions (a) for an electron pair and (b) for a hole pair.

Table I. Optimized Structure of Cyclobutadiene^a

basis set method	MB		DZ		DZ + D	
	SCF	CEPA	SCF	CEPA	SCF	CEPA
C=C	1.343	1.390	1.321	1.357	1.313	1.336
C—C	1.593	1.619	1.605	1.627	1.572	1.571
C—H	1.087		1.082		1.073	
*C—C—H	133.0		134.8		134.6	
C=C (ethene)	1.335	1.374	1.313	1.342	1.309	1.328
C—C (ethane)	1.554	1.575	1.545	1.558	1.532	1.530
C—H (methane)	1.101		1.095		1.095	

^a Bond lengths in angstroms; valence angles in degrees.

However, in processes where bonds are broken which involve atoms bearing lone pairs, some of the contributions of correlation involving other electron pairs can no longer be neglected. The PMCSCF dissociation energies are too low in such cases by up to 18 kcal/mol (F₂).

III. Structures and Thermochemistry of Cyclobutadiene and of Tetrahedrane

In agreement with previous investigations^{7,21-23} we find in SCF a rectangular structure of cyclobutadiene with long CC single bonds. We have been able to determine the optimum structure of the carbon skeleton with electron correlation included in the calculations. The results (Table I) show that the effects of electron correlation on bond lengths can correctly be obtained only if a basis set is used which included polarization functions. Within smaller basis sets which describe only the left-right correlation (MB) and the in-out correlation (DZ) considerably too long bonds result. In this connection we note the known overestimation of bond lengths within the DCSCF method.²⁰ While double bonds come out too short within SCF, the influence of correlation on CC single bond lengths is negligible.

In tetrahedrane (Table II) we find very short CC single bonds;^{6,7} with CEPA and the DZ + D basis a value of 1.47 Å is obtained. The short CH bonds are a consequence of the high character of these bonds.²⁴

The thermochemical stability of cyclobutadiene and of tetrahedrane can be estimated from calculated heats of reactions involving molecules whose heats of formation are known experimentally. In Table III such reactions are listed. Hydrogenation energies were calculated within SCF, the other heats

Table II. Optimized Structure of Tetrahedrane^a

	MB, SCF	DZ, SCF	DZ + D, SCF	DZ + D, CEPA
C—C	1.523	1.492	1.460	1.470
C—H	1.072	1.069	1.064	

^a Bond lengths in angstroms.

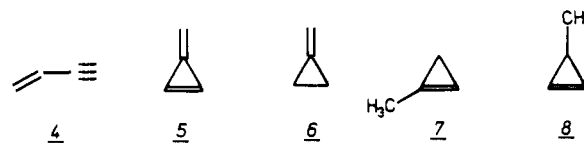
Table III. Heats of Formation of Cyclobutadiene and of Tetrahedrane Estimated from Calculated Heats of Reactions (DZ + D Basis, kcal/mol)

reaction	SCF	CEPA	correction	estimated ΔH_f
+ H ₂ →	-76.5		5.4	108.5
→ 2	-0.6	+3.3		105
→	-45.7	-38.7		107 ^a
→	-19.0	-11.2		105 ^b
→	-26.7	-28.8		134
+ H ₂ →	-84.8		1.8	135

^a Heat of formation of butenyne estimated to be 68 kcal/mol.

^b Heat of formation of methylenecyclopropene estimated to be 94 kcal/mol (cf. text).

of reactions with CEPA. The calculated hydrogenation energies of ethylene (to ethane) and of ethane (to 2CH₄) are 5.4 and 1.8 kcal/mol respectively larger than the corresponding experimental heats of hydrogenation (at 298 K). The main source of these differences is the contribution of zero-point vibrations.²⁵ The deviations from experiment were applied as corrections to the calculated heats of formation of cyclobutadiene and of tetrahedrane. The isomerization energies of cyclobutadiene to butenyne (**4**) and to methylenecyclopropene (**5**) are also given in the table. As the experimental heat of formation of **4** we use a value of 68 kcal/mol, which can be derived from measured hydrogenation energies²⁶ of alkyl-substituted derivatives of **4** (cf. ref 27 and 28). The value of 94 kcal/mol as an estimated heat of formation of **5** was obtained using the following data. According to SCF calculations of Hehre and Pople⁷ the hydrogenation energy of the exocyclic double bond in **5** is 10.5 kcal/mol smaller than in **6**, whose hydrogenation energy is known from experiment²⁹ (cf. the resonance energy of **5** of 9 kcal/mol³⁰). Experimentally known also is the heat of formation of **7**,²⁷ which is according to calculations⁷ 4.9 kcal/mol less stable than the isomer **8**.



From the data collected in Table III the heats of formation of cyclobutadiene and of tetrahedrane are estimated to be 105 and 134 kcal/mol, respectively. (The value of 108.5 kcal/mol for cyclobutadiene obtained from the SCF hydrogenation energy is probably too high, since SCF is expected to overestimate the unfavorable repulsion of the double-bond orbitals in cyclobutadiene.) Our heat of formation of tetrahedrane is in agreement with a value given by Schulman and Venanzi⁶ which was derived from SCF calculations with a double ζ basis considering heats of reactions where different contributions of ring strain canceled surprisingly well. The good agreement of the MINDO/3 energies⁴ of tetrahedrane and of methylenecyclopropene relative to cyclobutadiene (32 and -13 kcal/mol, respectively) with our corresponding CEPA values (29 and -11 kcal/mol, respectively) may be considered as

Table IV. Total Energy of Cyclobutadiene (au) and Energies of Two Acetylenes and of Tetrahedrane Relative to Cyclobutadiene (kcal/mol)

	-total energy		2 acetylenes		tetrahedrane	
	SCF	CEPA	SCF	CEPA	SCF	CEPA
MB	152.0146	152.2990	-4.2	-5.0	41.2	54.6
DZ	153.4253	153.8061	-12.7	-12.2	51.2	62.1
DZ + D	153.4963	153.9994	-0.6	+3.3	26.7	28.8

supporting evidence for the reliability of the calculated MINDO/3 surface.

The energies of two molecules of acetylene and of tetrahedrane relative to cyclobutadiene obtained with various basis sets within SCF and with CEPA are collected in Table IV. Since ring strain is present in **1** and **3** to a different extent, the relative SCF energies change considerably when d functions are included in the basis. (Further enlargement of the basis is not expected to change relative energies by more than 1 or 2 kcal/mol, since hydrocarbon basis sets containing one set of d functions are almost saturated in SCF with respect to the addition of further d or of f functions to the basis.³⁷) The contributions of electron correlation depend also very much on the basis sets. The results demonstrate again the very disappointing situation that one needs fairly large basis sets for the calculation of correlation energies. Not even trends of the contributions of electron correlation to relative energies of isomers are reproduced correctly within smaller basis sets. In π bonds, the left-right correlation represents a larger fraction of the total correlation energy than in σ bond orbitals. Hence, CEPA calculations with smaller basis sets favor π systems over corresponding σ -bonded systems (e.g., cyclobutadiene vs. tetrahedrane).

From the results of this section we conclude:

(1) Cyclobutadiene is about as stable as two acetylene molecules. The antiaromaticity of the π system³¹ is best demonstrated by the hydrogenation energy of one double bond in cyclobutadiene,³² which is about 40 kcal/mol larger than the hydrogenation energy of cyclobutane.

(2) Tetrahedrane is calculated to be 29 kcal/mol less stable than cyclobutadiene (cf. ref 4, 5, and 7). The molecule is extremely strained. The hydrogenation of one single bond in **1** is according to the calculations by 67 kcal/mol more exothermic than in ethane. Considering the dissociation energy of the CC bond in ethane of 88 kcal/mol,³³ one would expect that only about 20 kcal/mol will be required for breaking one bond in tetrahedrane.

IV. Stability of the Bicyclobutyl Diradicals

According to the MINDO/3 potential surface the minimum-energy path connecting tetrahedrane with cyclobutadiene passes through the diradicals **2a-c**. Therefore, the relative energies of these conformers of the bicyclobutyl diradical were computed. As a first step, the singlet and triplet energies for **2a-c** were calculated with the PMSCF method and with the DZ + D basis assuming structures which are derived from the experimental structure of bicyclobutane³⁴ by removal of two hydrogen atoms. The results are listed in Table V. The triplet energies for the three conformers are not very different with the sterically least hindered **2c** having the lowest energy. In **2b**, the two singly occupied MOs of the triplet are nearly degenerate and the singlet is slightly above the triplet. In **2a** and in **2c**, the singly occupied triplet MOs are no longer degenerate. Hence, both conformers have a singlet ground state.

In **2a**, the lower of the singly occupied triplet MOs is symmetric with respect to the C_2 axis. Relaxation of the carbon skeleton of the singlet with its wave function of the type $c_1\sigma_g^2 + c_2\sigma_u^2 + \dots$ leads to a partial ring closure until a distance

Table V. Relative Energies^a of the Singlet and of the Triplet States of the Conformers of the Bicyclobutyl Diradical (DZ + D Basis, PMCSCF)

	2a	2b	2c
triplet ^b	+6.7	0.0	-0.6
singlet ^b	-7.8	+2.3	-11.9
triplet ^c		-2.4 ^d	
singlet ^c	-19.8		-31.4

^a Energies in kcal/mol relative to the triplet energy of **2b**. ^b The structural parameters of the carbon skeleton were taken from bicyclobutane; the angles between the CH bonds at the radical centers and the planes of the three-membered rings were optimized. ^c Optimized structure (the CH bond lengths were assumed as 1.085 Å). ^d 24.7 kcal/mol above the PMCSCF energy of tetrahedrane.

between the nonbonded C atoms of about 2.05 Å is reached. Within PMCSCF, the optimized singlet **2a** is separated from **1** by a small barrier (~2 kcal/mol). In a full CI calculation of the CEPA type a monotonic increase for the energy along the path **1** → **2a** is obtained. When we relate the energy of **2a** with that of tetrahedrane we have to deal with the problem of comparing energies of a closed- and of an open-shell state. The relative PMCSCF energy of **2a** is 5.5 kcal/mol above that of tetrahedrane. The corresponding CEPA value is 13.6 kcal/mol. In Table VII the energies are compared which are needed for stretching a CC bond to a length of 2.05 Å in tetrahedrane, in cyclopropane, and in ethane. The results show clearly that the CC bond in tetrahedrane is much weaker than in cyclopropane. According to the CI coefficient of the σ_u^2 configuration (c_2), **2a** with a CC distance of 2.05 Å has a considerably larger diradicaloid character than cyclopropane and ethane with stretched CC bonds of the same lengths. The relative CEPA energies are larger than the PMCSCF energies, mainly because of the neglect of interpair correlation contributions in the PMCSCF scheme. The CEPA formalism, on the other hand, which takes into account the correlation of all electron pairs, fails for large coefficients c_2 . With PMCSCF the full dissociation energies of the CC bonds in ethane and in cyclopropane are calculated to be 90.5 and 58.9 kcal/mol, respectively, with the DZ + D basis. The experimental values are 93 (88³³ + 5 kcal/mol as an estimated correction for zero-point vibration) and 64³⁵ kcal/mol, respectively. From these numbers and the values of Table VII we conclude that PMCSCF underestimates dissociation energies, though the error is somewhat smaller than the CEPA calculations of **2a** indicate. In the region of the diradicals **2a-c** the PMCSCF energies relative to tetrahedrane are low by probably 5–10 kcal/mol.

In the singlet of **2c** the highest occupied MO is antisymmetric with respect to the C_2 axis. Relaxation of its structure within the restriction of C_{2v} symmetry leads to a local minimum, in which the dihedral angle between the three-membered rings is widened to 146°, while the perimeter bonds are shortened to 1.43 Å and the CC bond at the basis is lengthened to 1.70 Å. Even though no Kekulé structure without unpaired electrons can be written for **2c**, it represents—according to the size of the CI coefficient c_2 (Table VI)—an almost normal closed shell singlet state. Without symmetry constraint, **2c** rearranges to cyclobutadiene. The PMCSCF energy of **2c** is about 18 kcal/mol above the energy of the rectangular cyclobutadiene. The CEPA energy difference is 30 kcal/mol. In the reaction **2c** → **3** a considerable rearrangement of bond orbitals takes place, such that the PMCSCF method in which the correlation of only one electron pair is included is not the best approach for the study of this process.

For **2b**, not CEPA but only PMCSCF can be applied. Its triplet is calculated to be 24.7 kcal/mol above tetrahedrane. The real energy difference is probably 5–10 kcal/mol larger (see above). Thus, this estimation yields a higher energy for

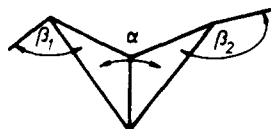


Figure 2. The geometrical parameters α , β_1 , and β_2 .

Table VI. SCF, PMCSCF, and CEPA Energies for Some Points along the Reaction Path Connecting Tetrahedrane with Cyclobutadiene^d

compd	dihedral angle ^a	SCF	CEPA	PMCSCF	$-c_2^b$	Δ CEPA/PMCSCF ^c
1	72	0.0	0.0	0.0	0.11	
2a	90	19.7	11.9	6.6	0.24	5.3
2a	106	34.6	13.6	5.5	0.36	8.1
2a	112	41.1		6.9	0.40	
2a	122	63.0		17.6	0.46	
2c	122	38.8		11.9	0.41	
2c	146	1.0	1.5	-7.6	0.26	9.1
3	180	-26.7	-28.8	-25.3	0.17	-3.5

^a Dihedral angle between the planes of the three-membered rings in degrees. ^b Coefficient of the most important doubly excited configuration. ^c Difference in the relative energies obtained with CEPA and with PMCSCF. ^d Energies in kcal/mol relative to tetrahedrane; DZ + D basis.

Table VII. Energy Required for the Stretching of a CC Single Bond to a Length of 2.05 Å (kcal/mol, DZ + D Basis)

molecule	SCF	DCSCF	PMCSCF	CEPA	$-c_2$	Δ CEPA/PMCSCF
ethane	45.6	34.9	38.2	41.4	0.19	3.2
cyclopropane	45.9	29.7	32.3	37.1	0.28	5.2
tetrahedrane	34.2	2.1	5.5	13.6	0.36	8.5

2b than had to be expected from thermochemical considerations. From the heat of hydrogenation we have estimated the dissociation energy of one CC bond in tetrahedrane to be only 20 kcal/mol. Furthermore, using the value of 101 ± 3 kcal/mol for the dissociation energy of a CH bond in a three-membered ring³³ and the heat of formation of bicyclobutane²⁹ the heat of formation of **2b** can be estimated to be 150 ± 6 kcal/mol, which is about 15 kcal/mol above tetrahedrane.

V. Reaction Paths for the Decomposition of Tetrahedrane

The results listed in Table V show that on the singlet potential surface **2b** corresponds to a much higher energy than **2a** and **2c**. If the minimum-energy path for the interconversion of **2a** and of **2c** has to pass through a **2b**-like structure as predicted by MINDO/3, then this process would need a considerable activation energy. This problem has been studied in some detail within the PMCSCF approach and with MB. For different dihedral angles α (Figure 2) the potential-energy surface was calculated as a function of the two parameters β_1 and β_2 , which are the angles between the CH bonds at the radical centers and the planes of the three-membered rings. For $\alpha = 106^\circ$ and for $\alpha = 144^\circ$ only one minimum is found on the potential surfaces which corresponds to **2a** and to **2c**, respectively. For $\alpha = 122^\circ$, which corresponds to the carbon skeleton of bicyclobutane, we obtain two minima belong to **2a** and **2c**. The vertical singlet of the optimum triplet of **2b** ($\beta_1 = 140^\circ$, $\beta_2 = 230^\circ$) is not far from the saddle point of the singlet surface (Figure 3). The triplet surface for $\alpha = 122^\circ$ exhibits three minima which represent the three conformers **2a-c**. The inversions at the radical centers require only about 3 kcal/mol in the triplets. The actual saddle point for the singlet conversion **2a** \rightarrow **2c** can only be obtained when α also is varied. The results of such calculations showed that the transition state has the structure of **2b** ($\alpha \approx 122^\circ$, $\beta_1 \approx 140^\circ$, and $\beta_2 \approx 230^\circ$). Since

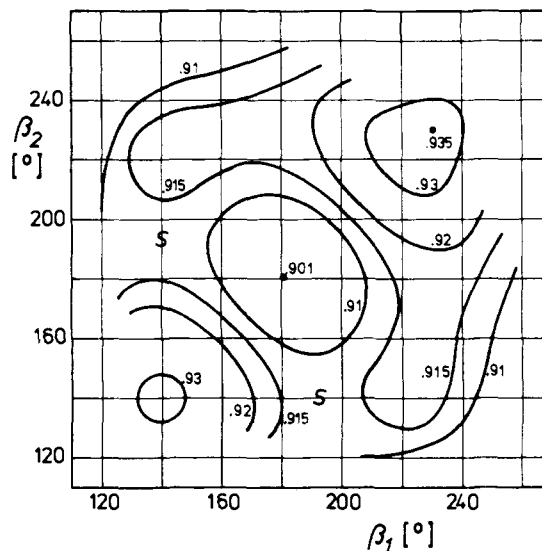


Figure 3. Contour line diagram for the interconversion of the bicyclobutyl diradicals. Energies ($-E - 151.0$) in au for the PMCSCF method with the minimal basis (S denote the saddle points).

the singlet of **2b** is only about 2.3 kcal/mol above the triplet (Table V) and since we did not optimize the structure of the transition state completely, we expect the energy of the transition state to be very close to the energy of the optimized triplet **2b**. Thus, using the values with the DZ + D basis which were discussed in the previous section, we estimate the PMCSCF activation energy for the rearrangement of tetrahedrane to cyclobutadiene to be 25 kcal/mol, to which an amount of 5–10 kcal/mol must be added because of errors inherent in the PMCSCF approach.

Are there other modes of rearrangements of tetrahedrane which need less activation energy? According to the MINDO/3 potential surface, both the decay into two acetylenes and the rearrangement into methylenecyclopropane (**4**) need higher activation energies and pass through the carbene **9** as an intermediate. According to our calculations **9** is 34.7



kcal/mol (CEPA, DZ + D) less stable than tetrahedrane. This result indicates that those channels for unimolecular reactions of tetrahedrane are hindered by even larger barriers than its decomposition to cyclobutadiene.

More difficult to answer is the question whether tetrahedrane can undergo bimolecular reactions more readily. We have found that little energy (about 10 kcal/mol) is required for breaking one CC bond in tetrahedrane and generating the diradicaloid **2a**. Our present knowledge allows no prediction of the reactivity of such a singlet biradicaloid which is neither a good closed-shell nor a real open-shell state.

VI. Conclusions

In spite of the extremely high amount of strain incorporated in the tetrahedrane molecule the lowest energy path for its unimolecular decomposition needs an activation energy in the order of 30 kcal/mol and leads to cyclobutadiene. Bimolecular reactions may proceed with much smaller barriers though no estimate can be given, since little is known about the reactivity of biradicaloids like **2a**.

The present investigation demonstrated how helpful it can be for an ab initio study to use the information provided by a semiempirical study which allows the computation of large areas of potential surfaces of fairly large systems with the

optimization of all geometrical parameters (within any restrictions desired).

Acknowledgment. The author is grateful to Dr. Kutzelnigg for stimulating discussions. The calculations were performed on a minicomputer (Interdata 8/32) which was granted to our group by the Deutsche Forschungsgemeinschaft.

References and Notes

- (1) Lin, C. Y.; Krantz, A. *J. Chem. Soc., Chem. Commun.* **1972**, 1111. Chapman, O. L.; McIntosh, C. L.; Pacansky, J. *J. Am. Chem. Soc.* **1973**, *95*, 614.
- (2) Maier, G.; Pfriem, S.; Schäfer, U.; Matusch, R. *Angew. Chem.* **1978**, *90*, 552.
- (3) Böhm, M. C.; Gleiter, R. *Tetrahedron Lett.* **1978**, 1179.
- (4) Bingham, R. C.; Carrion, F.; Dewar, M. J. S.; Kollmar, H., to be published.
- (5) Buenker, R. J.; Peyerimhoff, S. D. *J. Am. Chem. Soc.* **1969**, *91*, 4342.
- (6) Schulman, J. M.; Venanzi, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 4739.
- (7) Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 6941.
- (8) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285.
- (9) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.
- (10) Ahlrichs, R. *Theor. Chim. Acta* **1974**, *33*, 157.
- (11) Staemmler, V. *Theor. Chim. Acta* **1977**, *45*, 89.
- (12) Kollmar, H., unpublished.
- (13) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.
- (14) Meyer, W. *J. Chem. Phys.* **1973**, *58*, 1017.
- (15) Ahlrichs, R.; Lischka, H.; Staemmler, V.; Kutzelnigg, W. *J. Chem. Phys.* **1975**, *62*, 1225.
- (16) Kollmar, H. *Habilitationschrift*, Bochum, 1978.
- (17) Ahlrichs, R.; Driessler, F. *Theor. Chim. Acta* **1975**, *36*, 275.
- (18) Hinze, J.; Roothaan, C. C. J. *Prog. Theor. Phys., Suppl.* **1967**, *40*, 37. Veillard, A.; Clementi, E. *Theor. Chim. Acta* **1967**, *7*, 133.
- (19) Salem, L. *Pure Appl. Chem.* **1973**, *33*, 317.
- (20) Das, G.; Wahl, A. C. *J. Chem. Phys.* **1966**, *44*, 87.
- (21) Kollmar, H.; Staemmler, V. *J. Am. Chem. Soc.* **1977**, *99*, 3583; **1978**, *100*, 4304.
- (22) Borden, W. T.; Davidson, E. R.; Hart, P. *J. Am. Chem. Soc.* **1978**, *100*, 388.
- (23) Jafri, J. A.; Newton, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 5012.
- (24) Kollmar, H. *Theor. Chim. Acta* **1978**, *50*, 235.
- (25) Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 289.
- (26) Skinner, H. A.; Snelson, A. *Trans. Faraday Soc.* **1959**, *55*, 404. Flitcroft, T. L.; Skinner, H. A. *Ibid.* **1958**, *54*, 47.
- (27) Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. "The Chemical Thermodynamics of Organic Compounds"; Wiley: New York, 1969.
- (28) Duff, R. E.; Bauer, S. H. *J. Chem. Phys.* **1962**, *36*, 1754. Cowperthwaite, M.; Bauer, S. H. *Ibid.* **1962**, *36*, 1745.
- (29) Wiberg, K. B.; Fenoglio, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 3395.
- (30) Kollmar, H. *J. Am. Chem. Soc.*, in press.
- (31) Bauld, N. L.; Welscher, T. L.; Cessac, J.; Holloway, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 6920.
- (32) Dewar, M. J. S. *Pure Appl. Chem.* **1975**, *44*, 767.
- (33) Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465.
- (34) Cox, K. W.; Harmony, M. D.; Nelson, G.; Wiberg, K. B. *J. Chem. Phys.* **1969**, *50*, 1976; **1970**, *53*, 858.
- (35) Horsley, J. A.; Lean, Y.; Moser, C.; Salem, L.; Stevens, T. M.; Wright, J. S. *J. Am. Chem. Soc.* **1972**, *94*, 279.
- (36) Ahlrichs, R.; Lischka, H.; Zurawski, B.; Kutzelnigg, W. *J. Chem. Phys.* **1975**, *63*, 4685.
- (37) Ahlrichs, R.; Driessler, F.; Lischka, H.; Staemmler, V.; Kutzelnigg, W. *J. Chem. Phys.* **1975**, *62*, 1235.

Ab Initio Study of $(\text{NO}_2)_2^+$ and $(\text{CO}_2)_2^-$

Y. Yoshioka and K. D. Jordan*

Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260. Received October 1, 1979

Abstract: Ab initio calculations are employed to investigate the structure and stability of the $(\text{NO}_2)_2^+$ ion and these results are compared with those obtained earlier for the isoelectronic $(\text{CO}_2)_2^-$ ion. For both species, the lowest energy structure is well described as a monomeric ion "solvated" by a neutral molecule. The $\text{NO}_2^+\cdot\text{NO}_2$ structure, with the electron essentially localized on one of the monomers, is 1.56 eV more stable than the D_{2h} structure with the odd electron equally shared between the two NO_2 monomers. The ion-molecule complex form of $(\text{CO}_2)_2^-$ is only 0.31 eV more stable than the lowest energy symmetric structure. The bonding in the $\text{CO}_2^-\cdot\text{CO}_2$ and $\text{NO}_2^+\cdot\text{NO}_2$ ions is interpreted in terms of electrostatic interactions between the ionic and neutral monomers.

I. Introduction

During the past few years a wide variety of techniques have been applied to the study of molecular clusters. The ion cyclotron resonance (ICR), flowing-afterglow, and nozzle expansion methods have yielded much information on ion clustering in the gas phase. ESR and Raman spectroscopy of cluster ions formed in matrices have also provided new information on the ions of dimers and larger aggregates.

One of the most interesting questions concerning clusters containing unpaired electrons is whether these electrons are delocalized over the cluster or localized on one of the monomer units. Even for the ions of most molecular dimers, it is not known whether the odd electron is localized. For this reason we have undertaken a study of the structure of the $(\text{NO}_2)_2^+$ and $(\text{CO}_2)_2^-$ ions and the energetics of the $\text{NO}_2 + \text{NO}_2^+ \rightarrow (\text{NO}_2)_2^+$ and $\text{CO}_2 + \text{CO}_2^- \rightarrow (\text{CO}_2)_2^-$ reactions.

Results of ab initio calculations on the properties of $(\text{CO}_2)_2^-$ were reported in a recent communication¹ by Rossi and Jordan. In this study it was found that the structure consisting of a bent

CO_2^- "solvated" by a nearly linear CO_2 was the most stable form of the complex. The stability of this structure was attributed to charge-induced dipole and charge-quadrupole interactions. In the present paper we carry out similar calculations on the isoelectronic $(\text{NO}_2)_2^+$ ion and then compare the bonding in these two ions.

Neutral $(\text{NO}_2)_2$, which has a planar symmetric (D_{2h}) equilibrium structure, has been the subject of several theoretical and experimental studies.²⁻¹³ Much of this interest is due to the fact that the N-N bond in this molecule is unusually long and weak. Ab initio self-consistent-field (SCF) calculations³ suggest that the stability of the D_{2h} structure is due to a σ -type 1,4 interaction^{14,15} between the oxygen atoms. Recent calculations of Cederbaum et al.¹² and Harcourt¹³ have apparently resolved the controversy concerning the assignments of the vertical ionization potentials (IP) of $(\text{NO}_2)_2$ as measured by the He(I) photoelectron spectrum.⁷⁻¹⁰ However, we are not aware of any theoretical studies addressing the adiabatic ionization processes of $(\text{NO}_2)_2$.

In the present article, we employ ab initio SCF calculations to investigate the D_{2h} and D_{2d} forms of $(\text{NO}_2)_2^+$ as well as the planar nonsymmetric $\text{NO}_2^+\cdot\text{NO}_2$ complex. The bonding in

* Alfred P. Sloan Foundation Fellow, Camille and Henry Dreyfus Teacher-Scholar.