Experimental and ab Initio Molecular Orbital Studies on CH₃O²⁺· Dications

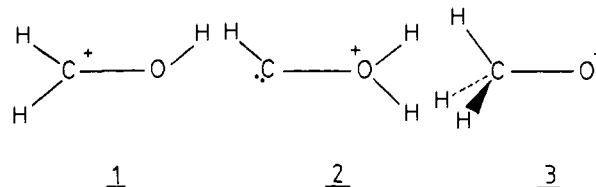**Wolfram Koch,**[1a] **Francis Maquin,**[1b] **Helmut Schwarz,**[*1a] **and Daniel Stahl**[*1b]

Contribution from the Institut für Organische Chemie der Technischen Universität Berlin, D-1000 Berlin 12, West Germany, and the Institut de Chimie Physique, Ecole Polytechnique Fédérale, CH-1015 Lausanne, Switzerland. Received July 20, 1984

Abstract: The CH₃O²⁺· ground-state potential energy surface was examined by ab initio molecular orbital theory corrected for the effects of zero-point energies and for electron correlations by means of Møller–Plesset perturbation theory terminated to second order (MP2/6-31G**) by using 6-31G optimized geometries for equilibrium structures and 4-31G optimized geometries for transition states. The global minimum corresponds to the oxoniomethylene dication HCOH₂²⁺· (**5**, *Cₛ*), which is more stable by 22.7 kcal/mol (MP2/6-31G**//6-31G + ZPE) than the second minimum found, i.e., the hydroxymethyl dication H₂COH²⁺· (**4**, *C₂ᵥ*). The heats of formation of **4** and **5**, which are prevented by a barrier of 24 kcal/mol (relative to **4**) from facile interconversion, were determined to 668 kcal/mol (**4**) and 645 kcal/mol (**5**) in satisfying agreement with the experimentally reported value of 659 kcal/mol for **4**. The thermochemical and kinetic stabilities of **4** and **5** are evaluated in detail. Although these dications are thermochemically highly unstable, dissociation to various monocations is prevented by substantial barriers, thus making observation in the gas phase feasible. In fact, **4** can be generated in a charge-stripping experiment from the hydroxymethyl cation **1**, and the experimentally determined energy for removing an electron is Q_{min} = 22.45 eV in good agreement with the calculated (MP2/6-31G**//6-31G) vertical ionization energy of IE$_v$ = 22.18 eV. The vertical ionization energy to generate **5** from (the experimentally inaccessible) oxoniomethylene cation **2** was calculated to IE$_v$ = 17.77 eV. Consideration of hypothetical hydride-transfer reactions to **4** and **5** by using isodesmic reactions indicates that it seems quite impossible to ever generate CH₃O²⁺· dications as viable chemical intermediates in solution for the reason that the dications will strip an electron or an atom from an adjacent neutral (or negatively charged) molecule with avidity.

Charge-stripping (CS) mass spectrometry[2] and other methods have led recently to the observation of a great number of stable dications in the gas phase,[3,4] including even small molecules whose Coulomb repulsion is expected to be quite substantial. High-level ab initio molecular orbital (MO) calculations in conjunction with experimental studies provided a detailed description of many features of these emerging class of remarkable species.[3,5] Although small dications have a tendency to fragment into two monocations because of Coulomb repulsion, many experiments have indicated that such doubly charged species may persist for several microseconds. This is mainly due to the fact that although fragmentation is often exothermic, these processes may be hindered by a significant barrier. In this context, theory should be able to provide answers to a number of important questions about these molecules and some of their unusual features. These questions concern, among others, the following: (i) In the first place, it is desirable to known whether or not there are several minima on the potential energy surface, and if so, what are the geometries (equilibrium structures) and relative energies of these species, and by what barriers are they prevented from facile interconversion. (ii) If the species are metastable, i.e., thermochemically unstable

toward dissociation but kinetically hindered to do so, what kind of barriers do exist? (iii) Which of the theoretically predicted species are accessible experimentally, for example, via charge stripping from the corresponding monocations, and what is the energetic of removing a further electron from a monocation?

We report here our theoretical and experimental studies on the ground-state potential energy surface of radical dications of the elemental composition CH₃O. Whereas many studies—both experimental and theoretical—have been performed on mono-charged CH₃O⁺ systems, there is brief mentioning only in the literature on some properties of CH₃O²⁺· in the context of discussing the 2E mass spectra of low molecular weight oxygen-containing hydrocarbons.[6] From the study of the CH₃O⁺ species, it is now firmly established[7] that the most stable form is that of hydroxymethyl cation **1**. The oxoniamethylene cation **2**, for which

1   **2**   **3**

no experimental observation has yet been reported, is predicted by "state of the art" ab initio calculations[7b] to be 78 kcal/mol less

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Table I. Total Energies (in hartrees), Relative Energies (in kcal/mol), and Zero-Point Energies (ZPE, in kcal/mol) for Dications **4–6**

	species		
	H_2COH^{2+}·, **4** (C_{2v})	$HCOH_2^{2+}$·, **5** (C_s)	H_3CO^{2+}·, **6** (C_s)
6-31G//6-31G	−113.3773	−113.4057	−113.2567
6-31G*//6-31G	−113.4195	−113.4442	−113.3104
MP2/6-31G*//6-31G	−113.6568	−113.6953	−113.5278
6-31G**//6-31G	−113.4308	−113.4589	−113.2897
MP2/6-31G**//6-31G	−113.6784	−113.7194	−113.5332
ZPE(4-31G)	18.7	21.7	*a*
E_{rel}(MP2/6-31G**// 6-31G+ZPE)	22.7	0.0	116.8[b]

a Not calculated because of convergence problems (see text). *b* Without ZPE.

stable than **1**. However, it is noteworthy to mention that **2** is prevented from spontaneous isomerization to **1** by a barrier as high as 30 kcal/mol; thus, if a means of generating this isomer is devised, it should be experimentally observable. The methoxy cation **3** is not found to exist as a stable species on the singlet potential energy surface of CH₃O⁺ but to rearrange spontaneously to **1**. However, **3** may exist as a high-energy triplet[7]

Methods

Standard ab initio molecular orbital calculations have been carried out by using a modified version of the GAUSSIAN 76 series of programs.[8] Stationary points on the ground-state potential energy surface have been located by using gradient optimization techniques[9] with the split-valence 6-31G basis set.[10] More reliable energy comparisons have been obtained by performing single-point calculations at the 6-31G geometries with the dp-polarized 6-31G** basis set[11] and by incorporating valence electron correlation via second-order Møller–Plesset perturbation (MP2) theory.[12] The GRADSCF series of programs[13a] were used to locate the transition-state structures and the vibrational frequencies, determined at the 4-31G level,[14] in order to characterize the various points of minima (equilibrium structures) or saddle points (transition states, TS)[13] and also to allow the inclusion of the effects of zero-point energies (ZPE) in estimating relative energies. A scaling factor of 0.9 was used for calculating ZPE in order to account for the fact that the normal frequencies are overestimated at the Hartree–Fock level by 10%.[15]

6-31G optimized geometries of the minima and 4-31G optimized studies of transition states are displayed within the text. Bond lengths are given in angstroms (Å) and bond angles in degrees; charge distribution calculated at the 6-31G (minima) and 4-31G level (transition states) are given in parentheses at the structures.

Charge-stripping experiments have been used to determine the Q_{min} value for generating CH₃O²⁺· from the corresponding CH₃O⁺ monocations; the latter were generated from various precursors (see below) by using a VG analytical ZAB-2F mass spectrometer in which the magnetic sector preceeds the electrostatic sector. Mass separated CH₃O⁺ ions of 8-keV energy were collided with O₂ at a pressure of ca. 10⁻⁴ torr. The products of the collision-induced reactions were studied by scanning the electrostatic analyzer. For an accurate measurement of Q_{min}, the energy

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scale was calibrated by admitting toluene as a reference compound for which Q_{min} is known to be 15.7 eV for the process $C_7H_8^+$· → $C_7H_8^{2+}$·.[16] The Q_{min} value was obtained by extrapolating to the base line of the high-energy side of both the main beam (CH₃O⁺· ions, m/z 31) and the charge-stripping peak, as recommended by Beynon and co-workers.[2d]

Results and Discussion

(1) Equilibrium Structures of CH₃O²⁺·. At the 6-31G level, we have located three minima (structures **4–6**) (Table I) on the CH₃O²⁺· potential energy surface. These minima correspond to the C_{2v} isomer of the hydroxymethyl dication **4**, the oxonio-methylene dication **5**, and the methoxy dication **6**. Isomers of
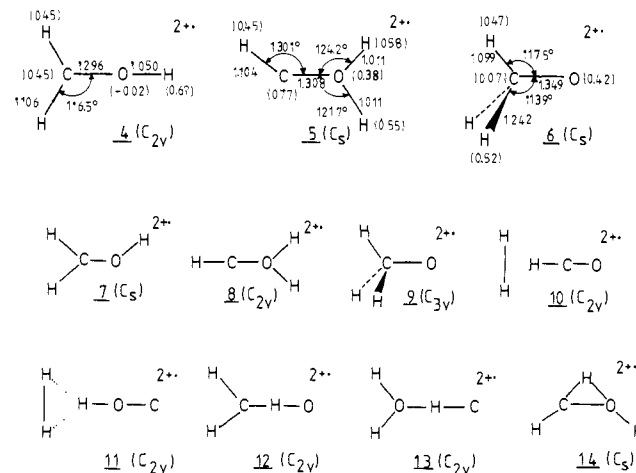
4, 5, and **6** having C_s, C_{2v}, or C_{3v} symmetries, respectively, i.e., the species **7–9**, were not found to exist in potential minima. Similarly, neither the hydrogen–bound complexes **10** and **11** nor the dications **12–14** could be located as stable species.

At all levels of theory used the global minimum among the CH₃O²⁺· isomers is that of **5**, which at the highest level (MP2/6-31G**//6-31G + ZPE) is 22.7 kcal/mol *more* stable than the hydroxymethyl dication **4**. Note the reversal of stability when comparing **4/5** with the corresponding monocations **1/2**.[17] The methoxy dication **6** is 116.8 kcal/mol less stable than **5**; this result together with the fact that we were not able to calculate the zero-point energy of **6** (because of convergence problems) and also the computational finding that the transition state for rearranging **6 → 4** is *lower* in energy than **6** (see below) makes it questionable that **6** is a stable, viable entity on the CH₃O²⁺· potential energy surface. We suggest that only **4** and **5**, which are isoelectronic with the vinyl radical H₂C=ĊH, are species potentially accessible in an appropriate experiment.

4 and **5** are prevented from facile isomerization via 1,2 hydrogen migration (involving TS₁) by a substantial barrier. At the highest level of theory (MP2/6-31G**//4-31G + ZPE) TS₁ is 46.8 kcal/mol higher in energy than **5**. TS₂, which connects **4** and
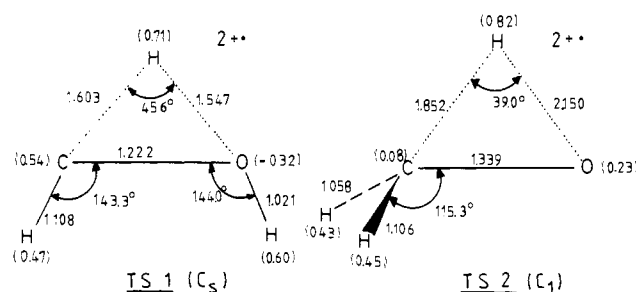
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Scheme I. Some Dissociation Reactions of **4** and **5** as Calculated by MP2/6-31G**//6-31G + ZPE

$$\Delta H_r^{\circ},$$ kcal/mol

$$CH_2OH^{2+}\cdot \xrightarrow{TS_3} CH_2O^{+}\cdot + H^{+} \ (1) \qquad -68.5$$
$$\quad \mathbf{4} \qquad\qquad \mathbf{15} \quad\ \mathbf{16}$$

$$CH_2OH^{2+}\cdot \xrightarrow{TS_4} HCOH^{+}\cdot + H^{+} \ (2) \qquad -70.0$$
$$\quad \mathbf{4} \qquad\qquad trans\text{-}17$$

$$CH_2OH^{2+}\cdot \xrightarrow{TS_5} CH_2^{+}\cdot + OH^{+} \ (3) \qquad -33.0$$
$$\quad \mathbf{4} \qquad\qquad \mathbf{18} \quad\ \mathbf{19}$$

$$CHOH_2^{2+}\cdot \xrightarrow{TS_6} CH^{+} + H_2O^{+}\cdot \ (4) \qquad -19.8$$
$$\quad \mathbf{5} \qquad\qquad \mathbf{20} \quad\ \mathbf{21}$$

$$CHOH_2^{2+}\cdot \xrightarrow{TS_7} COH_2^{+}\cdot + H^{+} \ (5) \qquad +5.9$$
$$\quad \mathbf{5} \qquad\qquad \mathbf{22}$$

$$CHOH_2^{2+}\cdot \xrightarrow{TS_8} HCOH^{+}\cdot + H^{+} \ (6) \qquad -47.3$$
$$\qquad\qquad\qquad trans\text{-}17$$

Table II. Heats of Formation, ΔH_f° (in kcal/mol), for **4** and **5** Derived from the Dissociation Reactions 1–6 (Scheme II)

species	reaction	ΔH_f°	ΔH_f° av	ΔH_f° exptl
$H_2COH^{2+}\cdot$ (**4**)	1	658		
	2	673	668	659
	3	675		
$HCOH_2^{2+}\cdot$ (**5**)	4	641		
			645	
	6	650		

6, lies much higher in energy (i.e., 102.3 kcal/mol relative to **5** and 109.0 kcal/mol without ZPE). The fact that TS$_2$, whose force constant matrix has one and only one negative eigenvalue, thus demonstrating that TS$_2$ is indeed a transition state, is *lower* in energy than **6** supports our above mentioned conclusion that **6** is unlikely to play a role in the chemistry of CH$_3$O$^{2+}\cdot$. Therefore, **6** will not be discussed any longer in this paper. The geometries and charge distribution of **4**, **5**, and TS$_1$ deserve a brief mentioning. In all three species, the positive charges are dispersed substantially to the hydrogen periphery which is favored both electrostatically and by the electropositive nature of hydrogen. The quite short C–O bonds of **4**, **5**, and TS$_1$ are certainly due to the electrostatic attraction between the positively charged carbon and the negatively charged oxygen atom. In the isoelectronic vinyl radical, the C–C bond is with 1.339 Å (6-31G) substantially larger.

(2) Thermodynamic Stabilities of H$_2$COH$^{2+}\cdot$ (4) and HCOH$_2^{2+}\cdot$ (5) and Some Dissociation Pathways. Approximate values for the heats of formation, ΔH_f°, of the dications **4** and **5** are available by calculating the heats of reaction, ΔH_r°, for the processes outlined in Scheme I, which are chemically the most likely ones. When the so-obtained ΔH_r° values are combined with experimentally determined values for the heats of formation of the products of reactions 1–4 and 6,[18] i.e., H^{+} (365 kcal/mol),[19] H$_2$CO$^{+}\cdot$ (224),[19] HCOH$^{+}\cdot$ (238),[20] CH$_2^{+}\cdot$ (334),[19] OH^{+} (308),[19] HC^{+} (387),[19] and H$_2$O$^{+}\cdot$ (234),[19] respectively, the approximate heats of formation of **4** and **5** can be obtained. The data for **4** and **5** are displayed in Table II; **4** has an averaged ΔH_f° of 668 kcal/mol and **5** of 645 kcal/mol. From appearance energy measurements for generating CH$_3$O$^{2+}\cdot$ from methanol, Teleshefsky et al.[6] arrived at ΔH_f° = 659 kcal/mol for **4**, in satisfying agreement with our estimate. No independent value has yet been reported in the literature for **5** because of the lack of suitable precursor molecules. Table III contains the computationally determined values for the various species displayed in Schemes I and II.

Scheme II. Disproportionation Reactions of **4** and **5**[a]

	ΔH_r°, kcal/mol	
	calcd	exptl
$CH_2OH^{2+}\cdot + CH_4 \rightarrow CH_3OH^{+}\cdot + CH_3^{+}$ (7)	-176	-179
$\ \ \mathbf{4} \qquad\quad \mathbf{23} \qquad\quad \mathbf{24} \qquad\ \mathbf{25}$		
$CH_2OH^{2+}\cdot + C_2H_4 \rightarrow CH_3OH^{+}\cdot + C_2H_3^{+}$ (8)	-194	-203
$\ \ \mathbf{4} \qquad\quad \mathbf{26} \qquad\qquad\qquad\quad \mathbf{27}$		
$HCOH_2^{2+}\cdot + CH_4 \rightarrow CH_2OH_2^{+}\cdot + CH_3^{+}$ (9)	-172	-172
$\ \ \mathbf{5} \qquad\qquad\qquad\qquad\quad \mathbf{28}$		
$HCOH_2^{2+}\cdot + C_2H_4 \rightarrow CH_2OH_2^{+}\cdot + C_2H_3^{+}$ (10)	-189	-196
$\ \ \mathbf{5}$		

[a] The calculated heats of reaction, ΔH_r° calcd, were obtained by MP2/6-31G**//6-31G + ZPE; for ΔH_r° exptl, see text.

The extreme thermodynamic instability of the dications **4** and **5** is emphasized by the disproportionation reactions 7–10 (Scheme II), for which we find quite good agreement between the calculated (MP2/6-31G**//6-31G + ZPE) and experimental ΔH_r° values. For calculating the latter, the following ΔH_f° were used: CH$_4$ (-16 kcal/mol),[19] CH$_3$OH$^{+}\cdot$ (202),[19] CH$_3^{+}$ (292),[19] CH$_2$OH$^{2+}\cdot$ (659),[6] C$_2$H$_4$ (15),[19] C$_2$H$_3^{+}$ (269),[19] and CH$_2$OH$_2^{+}\cdot$ (195).[22] As there is no experimental value for **5** available, we have taken from this work the calculated ΔH_f° = 645 kcal/mol. All isodesmic[23] processes are strongly exothermic, and the driving force of the reactions is undoubtedly charge separation. Since CH$_3^{+}$ and C$_2$H$_3^{+}$ have not been observed directly in super acidic media, it seems quite impossible that H$_2$COH$^{2+}\cdot$ and HCOH$_2^{2+}\cdot$ (like other dications[3h]) could be viable chemical intermediates under such conditions. They will strip an electron or an atom from an adjacent neutral (or negatively charged) molecule with avidity.

While H$_2$COH$^{2+}\cdot$ and HCOH$_2^{2+}\cdot$ are calculated to be minima on the potential energy surface prevented by a substantial barrier (TS$_1$) from facile interconversion, these species are not likely to be more than transients unless reasonably large barriers to the various possible fragmentation processes (Scheme I, reactions 1–6) are present. As revealed by the data displayed in Table IV, all reactions—except eq 3; for reasons see below—are associated with substantial barriers. Thus, in spite of their high thermochemical instabilities, **4** and **5** are not expected to dissociate spontaneously; the dications can be viewed as prototypes of persistent species. We did not try to calculate the barrier for reaction 3 (Scheme II), because Hartree–Fock theory is inappropriate for describing this dissociation which is associated with a multiplicity change. An appropriate procedure is not available by using the GAUSSIAN 76 or GRADSCF programs, which we had to employ in our study. The total energies of the respective transition states are given in Table IV, and the geometries and charge distributions are available upon request from us.

In conclusion, the ab initio MO calculations on the CH$_3$O$^{2+}\cdot$ potential energy surface predict that the hydroxymethyl dication **4** and the oxoniomethylene dication **5** do exist in potential minima. High barriers for the interconversion **4** $\rightleftarrows$ **5** as well as significant barriers toward dissociation to thermochemically more stable monocations clearly indicate that **4** and **5** should be observable experimentally. The potential energy diagram is given in Scheme III.

(3) Charge-Stripping Experiments. Charge stripping from **1**, which was conveniently generated via electron impact ionization of CH$_3$OH, CH$_3$CH$_2$OH, and CH$_3$OCH$_3$, respectively, gives rise to the formation of **4**. The energy of the process **1** $\rightarrow$ **4** + e^{-} was determined to Q_{min} = 22.45 ± 0.2 eV; this value corresponds very well with the calculated vertical ionization energy, IE$_v$ = 22.18 eV, obtained at the MP2/6-31G**//6-31G level by using a

(18) The heat of formation of **2i** from reaction **5** (Scheme II) is not known experimentally.

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Table III. Total Energies (in hartrees) and Zero-Point Energies (in kcal/mol) for the Dissociation products of **4** and **5**, Reactions 1–6 (Scheme II), and Their Disproportionation Reactions 7–10 (Scheme III)

species	6-31G//6-31G	6-31G*//6-31G	MP2/6-31G*// 6-31G	6-31G**//6-31G	MP2/6-31G**// 6-31G	ZPE//4-31G
$H_2C\!=\!O^+$· (**15**)	−113.4628	−113.5206	−113.7687	−113.5245	−113.7827	15.6
HCOH$^+$· (**17**)^a	−113.4445	−113.5011	−113.7671	−113.5105	−113.7851	15.6
H_2C^+· (**18**)	−38.5539	−38.5661	−38.6352	−38.5705	−38.6492	9.8
OH$^+$ (**19**)^b	−74.9485	−74.9687	−75.0656	−74.9746	−75.0747	4.1
HC$^+$ (**20**)	−37.8816	−37.8955	−37.9617	−37.8975	−37.9690	4.0
H_2O^+· (**21**)	−75.5882	−75.3138	−75.7520	−75.6270	−75.7722	10.9
CH$_4$ (**23**)	−40.1806	−40.1952	−40.3324	−40.2017	−40.3646	29.0
CH$_3$OH$^+$· (**24**)	−114.6431	−114.6846	−114.9451	−114.6961	−114.9779	28.8
CH$_3$$^+$ (**25**)	−39.2162	−39.2306	−39.3251	−39.2363	−39.3465	18.9
C_2H_4 (**26**)	−78.0045	−78.0317	−78.2844	−78.0388	−78.3169	31.0
$C_2H_3$$^+$ (**27**)^c	−77.0606	−77.0866	−77.3066	−77.0929	−77.3276	21.8
CH$_2$OH$_2$$^+$· (**28**)	−114.6615	−114.6914	−114.9696	−114.7095	−115.0069	29.2

^{a}Trans geometry assumed for **17**; at a very high level of theory, the cis form of **17** was found to be 4.1 kcal/mol less stable than the trans conformer, and the barrier to rotation between the two isomers was calculated to be ∼18 kcal/mol.[21] ^{b}For the less stable singlet form of OH$^+$, the following data were obtained: −74.8124, −74.8302, −74.9397, −74.8368, −74.9533, and 4.2, respectively. ^{c}C_{2v} symmetry assumed for **27**; the bridged $C_2H_3$$^+$ vinyl cation has comparable energies.

Tabel IV. Total Energies (in hartrees), Zero-point Energies (in kcal/mol), and Relative Energies^a (in kcal/mol) for TS$_1$–TS$_8$ (Except TS$_5$; See Text)

transition state	6-31G// 4-31G	6-31G*// 4-31G	MP2/6-31G*// 4-31G	6-31G**// 4-31G	MP2/6-31G**// 4-31G	ZPE// 4-31G	E_{rel}MP2/6-31G**// 4-31G + ZPE
TS$_1$	−113.2822	−113.3357	−113.6134	−113.3500	−113.6354	15.8	46.8
TS$_2$	−113.2477	−113.2713	−113.5236	−113.2769	−113.5455	15.0	102.3
TS$_3$	−113.3324	−113.3808	−113.6251	−113.3852	−113.6389	15.8	44.6
TS$_4$	−113.2915	−113.3462	−113.6273	−113.3563	−113.6442	15.0	40.5
TS$_6$	−113.3044	−113.3375	−113.5555	−113.3525	−113.5814	b	86.5^c
TS$_7$	−113.2790	−113.3110	−113.5667	−113.3257	−113.5876	16.1	77.0
TS$_8$	−113.3135	−113.3631	−113.6255	−113.3724	−113.6431	16.6	42.7

^{a}Relative energies are referred to E_5 = 0 kcal/mol. ^{b}Not calculated because of nonconvergence. ^{c}Does not include ZPE.

Scheme III. Potential Energy Diagram for Isomerization and Dissociation Reactions of **4** and **5**^{a}

^{a} For relevant data see Tables I–IV and text.

MP2/6-31G**//6-31G value of −114.4671 hartress for **1** and of −113.6519 hartress for **4**, having the geometry of **1**. For the dication **5**, we predict a vertical ionization energy of IE$_v$ = 17.77 eV (using the MP2/6-31G**//6-31G value of −114.3346 hartress for **2** and of −113.6815 hartress for **5** with the geometry of **2**). However, this value remains unmatched with an experimental number because of the lack of a suitable precursor to unequivocally make the oxoniomethylene cation **2**.

We should also mention that the dication **4** is directly accessible in the ion source by electron impact ionization of methanol.[6] By using CD$_3$OH, we generated specifically CD$_2$OH^{2+}·, whose unimolecular decomposition was monitored in a "2E" spectrum,[24] showing that CD$_2$OH^{2+}· undergoes specific loss of H$^+$, whereas

elimination of D$^+$ is completely absent.[25] This result is in conflict with our ab initio study which predicts that, starting from **4**, the dissociation process 2 (Schemes I and III) is slightly favored over reaction 1. In other words, CD$_2$OH^{2+}· is expected to dissociate preferentially to D$^+$ + DCOH$^+$· and *not* to H$^+$ + CD$_2$O$^+$·, in contrast with the experiment. This discrepancy might be due to the operation of a primary kinetic isotope effect favoring the elimination of H$^+$ over D$^+$.[26] To this end we have studied the unimolecular dissociation of CH$_2$OD^{2+}· (generated from CH$_3$OD) and observed that from this dication, the ratio of D$^+$/H$^+$ losses is approximately 100:1, thus clearly ruling out any isotope effect as the origin of the discrepancy. We are therefore left with the conclusion that MP2/6-31G** does not predict properly the dissociation of CH$_2$OH^{2+}·. It should be mentioned that the energies of TS$_{3,4}$ are extremely sensitive to the level of theory used. Without inclusion of correlation energies, TS$_3$ is *lower* than TS$_4$, whereas at the MP2-level the opposite is found. As MP2 is known to over-estimate[27] the effects of correlation energies, it may well be that at MP3 or MP4, a reversal of stability is again observed. It is also important to recall that the relative stabilities of CH$_2$O$^+$· vs. HCOH$^+$· (and consequently the respective transition-state energies for making this ions) are extremely dependent on the level of theory used. Only at a sophisticated level of theory, involving a double-ζ-plus polarization basis set and taking into account configuration interaction of a total of 16290 configurations, Schaefer et al.[21] showed that H$_2$CO$^+$· is by 5.5 kcal/mol *more* stable than *trans*-HCOH$^+$·, in qualitative agreement with the experimental results,[19,20] which predicts a difference of 14 kcal/mol favoring H$_2$CO$^+$·. Nevertheless, the central conclusion that the oxoniomethylene dication **5** and the hydroxymethyl dication **4** are

(24) Kemp, D. L.; Cooks, R. G. In "Collision Spectroscopy"; Cooks, R. G., Ed., Plenum Press: New York, 1978; Chapter 5.

(25) Exclusive loss of the *Hydroxylic* proton was also observed for both the unimolecular and the collision-induced dissociation of the hydroxymethylene dication HCOH^{2+}: Stahl, D. Maquin, F. *Chem. Phys. Lett.* **1984**, *106*, 533.

(26) For an exhaustive compilation of kinetic isotope effects, see: Derrick, P. J., Douchi, K. F. In "Comprehensive Chemical Kinetics"; Bamford, C. H., Tipper, Elsevier: Amsterdam, 1983; Vol. 24, Chapter 2. See also: Eckart, K.; Zummack, W.; Schwarz, H., *Org. Mass Spectrom.*, in press.

(27) For many references to this problem see ref 17b.

stable species on the potential energy surface of $CH_3O^{2+} \cdot$ dications is not questioned by the result. It should also be mentioned that in line with the theoretical results, neither spontaneous nor collision-induced dissociation of $CH_3O^{2+} \cdot$ dications to either $CH_2^+ \cdot / OH^+$ and $HC^+ / H_2O^+ \cdot$ (eq 3 and 4, Scheme I) has been observed.

An MC–SCF Study of the Thermal Cycloaddition of Two Ethylenes

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Abstract: The transition structure region of the reaction of two ethylenes to form cyclobutane has been investigated in detail by ab initio molecular orbital methods. The calculations have been performed at the MC–SCF level with minimal (STO-3G) and extended (4-31G) basis sets. The various critical points have been fully optimized with MC–SCF gradients and characterized by computing the corresponding hessian matrices. On examination of the "forbidden" concerted supra–supra reaction path, it was found that no true transition structure exists: the critical points involved are, in fact, second-order saddle points. The concerted supra–antara approach was found to proceed via a very high energy transition state. The favored pathway is thus found to involve a stepwise approach proceeding via a gauche or trans tetramethylene diradical intermediate and involving corresponding fragmentation transition states.

I. Introduction

The thermal cycloaddition of two ethylenes is one of the "textbook" examples used in the illustration of the Woodward–Hoffmann rules[2] of orbital symmetry control in concerted reactions and is an example of a concerted thermally forbidden reaction. Thus the topology (i.e., the number and nature of the stationary points) of this surface is of considerable interest. Because orbital symmetry is not conserved for the $[2_s + 2_s]$ concerted reaction, one expects a sharply avoided crossing in the region of the transition state which cannot be described at the SCF level. For the nonconcerted process the transition states and intermediate minima will correspond to diradicaloid species which also require computational methods which transcend the SCF method.

The objective of the present work is to characterize the structure and nature of the critical points on the potential energy surfaces for the $[2_s + 2_s]$, the $[2_s + 2_a]$, and the nonconcerted approaches at the same level of computational accuracy. The use of MC–SCF gradient methods developed previously[3,4] should permit a reliable determination of the features of the full energy surface because diradicaloid structures and closed-shell species can be described with a similar degree of accuracy. On the other hand, this computational approach is not expected to provide an accurate treatment of the energetics of the reaction, which will probably

Scheme I
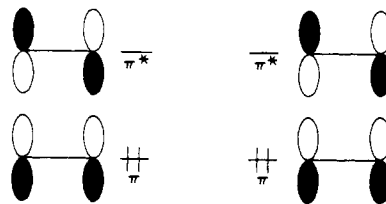
require dynamic correlation and large basis sets.

Previous calculations on the topology of this reaction have not been conclusive. Wright and Salem[5] have located a transition state for the $[2_s + 2_s]$ process using an STO-3G[6] basis with 2 × 2 CI (HOMO-LUMO); however, only partial geometry optimization was performed, and a detailed study of the nature of Hessian matrix was not performed. Segal[7] has investigated the nonconcerted approaches using an SCF treatment at the STO-3G level followed by a 15-dimensional CI and has found that the tetramethylene diradical is a thermodinamicaly stable species existing in two stable conformations, a gauche and a trans.

Doubleday et al.[8] have questioned this finding on the basis of results obtained with a 2-configuration MC–SCF wave function at the extended 3-21G[9] level and have suggested that only the trans

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