

## Experimental and Theoretical Evidence for the Existence of a Stable Ketene Dication in the Gas Phase

Wolfram Koch,<sup>a</sup> Francis Maquin,<sup>b</sup> Daniel Stahl,<sup>\*b</sup> and Helmut Schwarz<sup>\*a</sup>

<sup>a</sup> Institut für Organische Chemie der Technischen Universität Berlin, 1000 Berlin 12, West Germany

<sup>b</sup> Institut de Chimie Physique, Ecole Polytechnique Fédérale, CH-1015 Lausanne, Switzerland

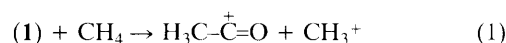
The ketene dication,  $\text{CH}_2=\text{C}=\text{O}^{2+}$  (**1**), is accessible by charge stripping from  $\text{C}_2\text{H}_2\text{O}^{+}$  with  $Q_{\text{min}} = 18.6 \pm 0.1$  eV for  $\text{C}_2\text{H}_2\text{O}^{+} \rightarrow \text{C}_2\text{H}_2\text{O}^{2+}$  which is in excellent agreement with the vertical ionization energy of 18.56 eV predicted by *ab initio* molecular orbital calculations (MP2/6-31G\*\*//4-31G); from isodesmic substitution a heat of formation of 651 kcal mol<sup>-1</sup> is estimated for (**1**) which is also predicted by the *ab initio* calculations to correspond to the global minimum on the  $\text{C}_2\text{H}_2\text{O}^{2+}$  potential energy surface followed by the oxirene dication (**2**) having  $\Delta H_f^\circ = 678$  kcal mol<sup>-1</sup> (1 kcal = 4.184 kJ).

As Schleyer has pointed out<sup>1</sup> carbocations are an emerging class of unusual molecules. Many stable carbocations are already known in solution,<sup>2</sup> and in the gas phase charge-stripping (C.S.) mass spectrometry<sup>3</sup> has led recently to the generation of a great number of stable dications, including small molecules whose coulombic repulsion is expected to be quite substantial.<sup>4</sup> High level *ab initio* calculations in conjunction with C.S. studies have provided a detailed insight into many features of these unusual species.<sup>4,5</sup>

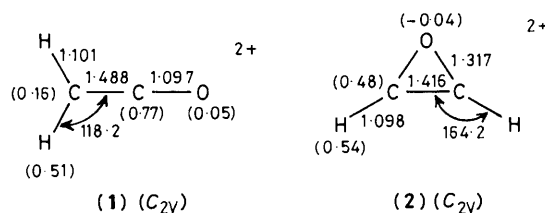
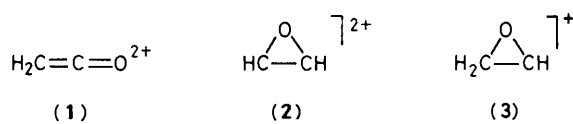
We report here our experimental and theoretical studies on the  $\text{C}_2\text{H}_2\text{O}^{2+}$  system, which in contrast to the well-understood<sup>6</sup> potential energy surface of neutral  $\text{C}_2\text{H}_2\text{O}$  has not been explored so far. The  $Q_{\text{min}}$  value, *i.e.* the energy to remove one electron from ionized ketene, which itself has been generated by electron impact ionization (70 eV) of either ketene (obtained by thermolysis of diketene in the inlet system) or *via* unimolecular  $\text{H}_2\text{O}$  loss from the molecular ion of acetic acid, has been determined in a C.S. experiment by employing a VG Analytical ZAB-2F mass spectrometer and using the technique described previously.<sup>4,5</sup> A value  $Q_{\text{min}} 18.6 \pm 0.1$  eV has been obtained which is in excellent agreement with the vertical ionization energy (I.E.<sub>v</sub>) of 18.56 eV predicted by high level *ab initio* molecular orbital calculations performed at the MP2/6-31G\*\*//4-31G level.

A thorough analysis of the ground state potential energy surface of  $\text{C}_2\text{H}_2\text{O}^{2+}$  ions revealed that among the ten minima located,<sup>†</sup> species (**1**) and (**2**) are the most stable ones, with the dication of ketene representing the global minimum. Doubly ionized oxirene (**2**) is predicted to be 26.8 kcal mol<sup>-1</sup> less stable than (**1**) at the highest level used (Table 1). For the neutral system<sup>6</sup> at the best level of theory an energy difference between (**2**) and (**1**) of *ca.* 80 kcal mol<sup>-1</sup> was obtained, which emphasized the relative destabilizing effect of the 4π electron

configurations of oxirene.<sup>7</sup> The removal of two electrons from the oxirene dication increases the stability of this unfavoured configuration. Removal of two electrons from the neutral analogue of either (**1**) or (**2**) is also associated with remarkable structural changes; the most notable ones are the lengthening of the C-C bond in ketene (1.297 → 1.488 Å) and the slight shortening of the C-O bond (1.164 → 1.097 Å); these structural alterations are even more pronounced for the oxirene system; C-C 1.248 → 1.416 Å; C-O 1.548 → 1.317 Å (Figure 1). The positive charges are, as in most other dications,<sup>1,2,4,5</sup> dispersed substantially to the hydrogen periphery which is favoured both electrostatically and by the electropositive nature of hydrogen.



An approximate value for the heat of formation,  $\Delta H_f^\circ$ , of (**1**) is available by calculating the heat of reaction,  $\Delta H_r^\circ$ , for equation (1). By combining the so-obtained  $\Delta H_r^\circ$  value [ $\Delta H_r^\circ = -213.6$  kcal mol<sup>-1</sup> at MP2/6-31G\*\*//4-31G; total energies of -40.32234 (CH<sub>4</sub>), -152.47525 (CH<sub>3</sub>CO<sup>+</sup>), -39.32503 Hartrees (CH<sub>3</sub><sup>+</sup>)] with the experimental  $\Delta H_f^\circ$  for CH<sub>4</sub> (-18 kcal mol<sup>-1</sup>),<sup>15</sup> CH<sub>3</sub>CO<sup>+</sup> (157 kcal mol<sup>-1</sup>),<sup>16</sup> and CH<sub>3</sub><sup>+</sup> (262 kcal mol<sup>-1</sup>)<sup>15</sup> a heat of formation of 651 kcal mol<sup>-1</sup> is obtained for  $\text{CH}_2=\text{C}=\text{O}^{2+}$ . This high value, together with the strongly exothermic  $\Delta H_r^\circ$  for the disproportionation reaction in equation (1), for which the driving force is undoubtedly charge separation, indicates the high thermodynamic instability of (**1**). It is highly unlikely that (**1**) (and also the other  $\text{C}_2\text{H}_2\text{O}^{2+}$  isomers) will ever be a viable chemical intermediate



**Figure 1.** Geometries (bond lengths in Å, bond angles in degrees) and charge distributions (given in parentheses) were calculated by using the 4-31G\* and 6-31G\* basis sets,<sup>9</sup> employing a modified version of the Gaussian 76 series of programmes.<sup>10</sup> Gradient optimization techniques<sup>11</sup> were used to locate stationary points. Single-point energy calculations of 4-31G geometries were performed with the 6-31G\* basis set incorporating valence electron correlation *via* second order Møller-Plesset perturbation (MP2) theory.<sup>12</sup> The GRADSF series of programmes<sup>13</sup> was used to calculate vibrational frequencies at the 4-31G level thus allowing the inclusion of the effects of zero-point energies. A scaling factor of 0.9 was used for calculating Z.P.E. in order to account for the fact that the normal frequencies are overestimated at the Hartree-Fock level by 10%.<sup>14</sup>

<sup>†</sup> Structural details as well as *ab initio* energies of all stable isomers studied are available upon request from the authors and in addition to (**1**) and (**2**) the following species were found to be minima (numbers given in parentheses are the energies [in kcal mol<sup>-1</sup> (1 kcal = 4.184 kJ), relative to  $E_1 = 0$  kcal mol<sup>-1</sup>]: C-O-CH<sub>2</sub><sup>2+</sup> (42.6), CH-C-OH<sup>2+</sup> (58.5), C-C(H)-OH<sup>2+</sup> (88.4), CH-O-CH<sub>2</sub><sup>2+</sup> (91.0), CH-C(H)-O<sup>2+</sup> (116.7), C-C-OH<sub>2</sub><sup>2+</sup> (171.9), C-C-OH<sub>2</sub><sup>2+</sup> (188.5), and CH-O(H)-C<sup>2+</sup> (234.4). The dication of oxiranylidene was, in contrast to its neutral counterpart, not found to exist in a minimum; upon geometry optimization it 'rearranges' to (**1**).

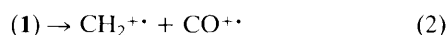
<sup>‡</sup> 1 kcal = 4.184 kJ.

**Table 1.** Total energies (Hartree), relative energies ( $E_{\text{rel}}$ , kcal mol<sup>-1</sup>), and zero-point energies (Z.P.E., kcal mol<sup>-1</sup>) for the singlet<sup>a</sup> dications of ketene (**1**) and oxirene (**2**).<sup>b</sup>

	4-31G//4-31G	$E_{\text{rel}}$	6-31G**//4-31G	$E_{\text{rel}}$	MP2/6-31G**//4-31G	$E_{\text{rel}}$	Z.P.E.//4-31G	$E_{\text{rel}}^c$
(1)	-150.5115	0	-150.75342	0	-151.13734	0	18.8	0
(2)	-150.4153	60.3	-150.70693	29.2	-151.09394	27.2	18.4	26.8

<sup>a</sup> Triplet states were also calculated for all C<sub>2</sub>H<sub>2</sub>O<sup>2+</sup> species mentioned but found to be as much as >95 kcal mol<sup>-1</sup> higher in energy than the singlet ground state of (**1**). This does not hold for the species HC-CO<sup>2+</sup>, whose triplet/singlet energies are comparable. For determining I.E., for CH<sub>2</sub>=C=O<sup>2+</sup> the following total energies (MP2/6-31G\*\*//4-31G) were used: CH<sub>2</sub>=C=O<sup>2+</sup> -151.81229; CH<sub>2</sub>=C=O<sup>2+</sup> (with the geometry of the cation radical of ketene) -151.13027. <sup>b</sup> 1 Hartree = 627.07 kcal mol<sup>-1</sup> = 2.6255 × 10<sup>3</sup> kJ mol<sup>-1</sup>. <sup>c</sup> Refers to MP2/6-31G\*\*//4-31G + Z.P.E.

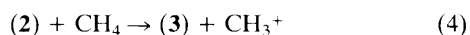
in solution, because the dications will immediately strip an electron or an atom from an adjacent neutral (or negatively charged) molecule. In the gas phase, however, dissociation according to equation (2) does not take place spontaneously, as evidenced by mass analysed ion kinetic energy analysis of possible fragmentation products in the above-mentioned charge stripping experiment. As  $\Delta H_r^\circ$  for reaction (2) is also exothermic [ $\Delta H_r^\circ = -3.3$  kcal mol<sup>-1</sup> at the MP2/6-31G\*\*//4-31G level using total energies of -38.63512 (CH<sub>2</sub><sup>2+</sup>) and -112.50749 Hartrees (CO<sup>2+</sup>)], spontaneous dissociation is prevented by a barrier, thus making the inherently thermodynamically unstable dications kinetically accessible. This is a property typical of many doubly charged species studied.<sup>1,4,5</sup>



The dication of oxirene (**2**) cannot be studied experimentally because of the lack of a stable gas phase precursor. Nevertheless, the calculations indicate that this species should be stable towards spontaneous dissociations as in equation (3); for equation (3)  $\Delta H_r^\circ$  is as high as 124.4 kcal mol<sup>-1</sup> [based on MP2/6-31G\*\*//4-31G values for O<sup>2+</sup> (-74.23307) and C<sub>2</sub>H<sub>2</sub><sup>2+</sup> (-76.66253 Hartrees)].



In analogy with (**1**), the oxirene dication (**2**) is also found to be thermodynamically extremely unstable. This is emphasized by the strongly exothermic heat of reaction for the disproportionation process, equation (4) [ $\Delta H_r^\circ = -182.4$  kcal mol<sup>-1</sup>; the MP2/6-31G\*\*//4-31G energy for the oxiranyl cation (**3**) is -152.38210 Hartrees]. This heat of reaction, in combination with the experimental value for the oxiranyl cation (216 kcal mol<sup>-1</sup>)<sup>16</sup> and of the remaining species, provides an estimate for the heat of formation for doubly-charged oxirene of 678 kcal mol<sup>-1</sup>.



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