

72. The Mass Spectra of Organic Compounds

8th Communication¹⁾

1-Buten-3-yn-2-ol. A New Kinetically Unstable C₄H₄O Isomer

by František Tureček

The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Máchova 7, 12138 Praha 2,
Czechoslovakia

and Zdeněk Havlas

Institute of Organic Chemistry and Biochemistry, 16610 Praha, Czechoslovakia

and Francis Maquin²⁾ and Tino Gäumann*

Institute of Physical Chemistry, Swiss Federal Institute of Technology, CH-1015 Lausanne

(9.XII.85)

The unstable neutral enol, 1-buten-3-yn-2-ol, and its deuterium-labelled analogues were generated in the gas phase by high-vacuum flash pyrolysis of the corresponding 2-*exo*-ethynylborn-5-en-2-ols, or alternatively from 1-ethynylcyclobutanol. The ionization energy of the enol was measured as 8.92 ± 0.03 eV. The cation radical $(\text{HC}\equiv\text{C}(\text{OH})=\text{CH}_2)^{+\cdot}$ was prepared by electron-impact ionization of the neutral enol, or by dissociative ionization of 1-hexyn-3-ol and 1-ethynylcyclobutanol, and its heat of formation was determined as $944 \text{ kJ}\cdot\text{mol}^{-1}$. The heat of formation of the neutral enol was assessed as $83 \pm 7 \text{ kJ}\cdot\text{mol}^{-1}$ in good agreement with MNDO calculations. Cation radicals $\text{HC}\equiv\text{C}-\text{C}(\text{OH})=\text{CH}_2^{+\cdot}$ undergo four main unimolecular fragmentations due to losses of the OH H-atom, a CH₃ group incorporating the C(1) methylene and the OH H-atom, CO, and H₂O. The structure of the neutral enol and the mechanisms of the ionic decompositions are discussed.

1. Introduction. – The family of C₄H₄O valence-bond isomers comprises six enol forms derived from four basic C-skeletons: 1-buten-3-yne, 1,2,3-butatriene, cyclobutadiene, and methylenecyclopropene. Simple enols [1] and dienols [2] are as a rule less stable than the corresponding oxo forms (aldehydes and ketones), with the difference in the heats of formation ranging between 16 and 40 kJ·mol⁻¹ [2–7]. In spite of recent theoretical investigations [8] [9], the cause for the lower stability of simple enols has not been completely clear. A conspicuous feature of simple enols, as revealed by semiempirical [8] and *ab initio* calculations [10], is their asymmetric charge distribution resulting in a net negative charge at the double bond terminus β to the O-atom.

Electron-withdrawing groups, *e.g.* carbonyl, nitrile, nitro, or sulfonyl [1] [9], as well as electron donating (*e.g.* methyl) [6] or neutral (*e.g.* vinyl) [11], tend to stabilize the enol system relative to the oxo form, if placed at C(β). By contrast, substitution by methyl or vinyl at C(α) has little effect [2] [7] [9]. In this respect, it was of interest to investigate the

¹⁾ 7th Communication: *Helv. Chim. Acta* **1984**, *67*, 425.

²⁾ Present address: *Société Roussel Uclaf*, Département des études physico-chimiques et structurales, F-93230 Romainville.

properties of 1-buten-3-yn-2-ol (**1**) in which the triple bond, a weak electron acceptor, is attached to the C(α) of the enol system. Enol **1** represents a challenging problem from two points of view. 1) Simple enols of $\text{CH}_2=\text{C}(\text{OH})-\text{R}$ type are extremely sensitive to catalyzed enol-keto isomerization [2] [7] [12], which virtually prevents them to be maintained and investigated in solution [12]. 2) The evaluation of the effect of the triple bond on the enol stability requires thermochemical data of good quality. An earlier estimate [13] reported the difference in the heats of formation between 3-butyne-2-one (**2**) and **1** to be as high as $88 \text{ kJ} \cdot \text{mol}^{-1}$, which should indicate a considerable destabilization of the enol system by the α -triple bond. Here, we report on experimental thermochemical data for **1**, which are compared with semiempirical MNDO [14] calculations. Slow and fast decompositions of cation-radicals $\mathbf{1}^+$ in the gas phase will also be discussed.

2. Experimental. – *Materials.* 3-Butyn-2-one was purchased from Aldrich and distilled *in vacuo* before use. 1-Ethynylcyclobutanol was prepared from cyclobutanone (Fluka) and lithium trimethylsilylacetylide followed by desilylation [15]. The product was distilled *in vacuo*, and its purity was checked by GC to be $> 98\%$. 1-Hexyn-3-one was prepared from butanal and lithium trimethylsilylacetylide followed by desilylation [15] and oxidation with pyridinium chlorochromate [16]. The final product **4** showed a single spot in TLC and was of ca. 98% purity (GC). 2-*exo*-Ethynylnorborn-5-en-2-ol (**3**) was described in [11]. The labelled derivatives **3b** and **3c** were prepared analogously, starting from [3-*exo*-D]norborn-5-en-2-one [**4**] (for **3b**) or using $\text{CH}_3\text{OD}/\text{NaOD}$ in the desilylation step [11].

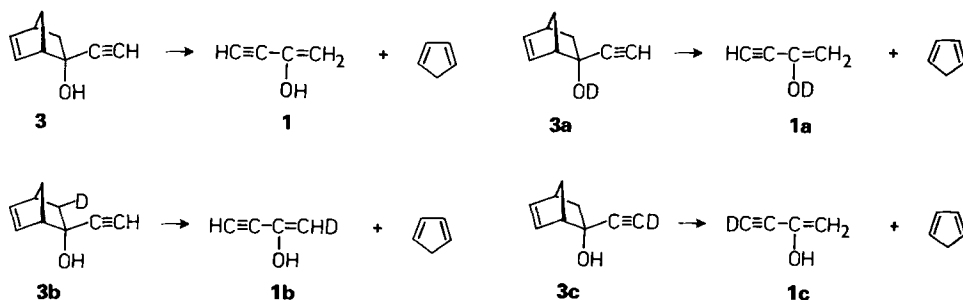
Methods. The electron-impact mass spectra were recorded on a Jeol D-100 mass spectrometer using a direct inlet or a pyrolyzer described in [4]. The ionization and appearance energies were measured with $50 \mu\text{A}$ emission current, and the repeller voltage set to $0.00 \pm 0.01 \text{ V}$. Ion intensities were measured in 50-meV steps with a data system from ca. 0.5 eV below the threshold up to 2.0–2.5 eV above it, and processed by the inverse convolution procedure [20]. MeI (IE = 9.545 eV) was used to calibrate the energy scale. The reported IE and AE values are averages of 6–8 independent measurements. The PE spectra of 1-hexyn-3-one were measured on a VG Scientific UVG 3 spectrometer using a mixture of Ar and Xe for energy-scale calibration.

The MIKE and CID spectra were measured on a ZAB 2F spectrometer furnished with a pyrolysis oven [4]. The metastable-peak half widths were measured under conditions of good energy resolution (0.15–0.2 V fwhm of the main beam). The background pressure was $1 \cdot 10^{-8}$ Torr for the MIKE spectra. The CID spectra were obtained with He as collision gas at 40% attenuation of the main beam.

3. Results and Discussion. – *Preparation.* The enol **1** and its deuterium-labelled derivatives **1a**, **1b**, and **1c** were generated by the *retro-Diels-Alder* reaction [17] of the corresponding 2-*exo*-ethynylnorborn-5-en-2-ols **3**, **3a**, **3b**, and **3c** (Scheme) in a molecular-flow microoven attached to a mass spectrometer [4].

Conversion as high as 90% can be achieved under optimized conditions (720–750° at 10^{-6} Torr), as judged by the increase of the $(\text{C}_4\text{H}_4\text{O})^+/\mathbf{3}^+$ abundance ratio in the 12-eV

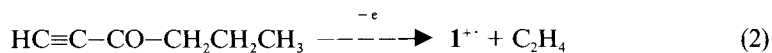
Scheme



MS of the pyrolysate. An independent check was provided by monitoring the $(C_5H_5)^+ / (C_5H_6)^+$ abundance ratio in the 75-eV MS, which closely approached that of a standard sample of cyclopentadiene introduced under the same conditions. For ionization-energy measurements (*vide infra*), **1** was prepared by [2 + 2] cycloreversion of 1-ethynylcyclobutanol [18] at $930^\circ/10^{-6}$ Torr, in order to avoid interferences at m/z 68 due to $C_3^{13}C_2H_6$ species from cyclopentadiene. Conversions of *ca.* 50% were achieved in the pyrolysis of 1-ethynylcyclobutanol.

The purity of the enol formed, especially with respect to the content of ketone **2**, was followed by examining the relative abundance of daughter ions from metastable $C_4H_4O^+$ decomposing in the field-free regions of the mass spectrometer. While metastable 2^+ [13] [18] give abundant $(M - CH_3)^+$ fragments at m/z 53, $(M - CH_3)^+ / (M - CO)^+ = 0.57$ for ions decomposing in the second field-free region of a ZAB 2F spectrometer, metastable 1^+ afford $(M - CH_3)^+$ ions of very low relative abundance [18] ($(M - CH_3)^+ / (M - CO)^+ = 0.01$). Thus, the relative abundance of $(M - CH_3)^+$ provides a convenient means for estimating the content of **2** in the C_4H_4O mixture, provided the ionization cross sections of the isomers do not differ much. The content of **2** was found to depend crucially on the temperature and surface qualities of the ion source. When working with a clean and cold ($t < 100^\circ$) ion source, we were able to keep the content of **2** below estimated 5–10%. At 200° , mixtures of **1** and **2** were obtained in which the content of the latter ranged between 40 and 50%. All spectra and energy measurements were, therefore, performed under conditions minimizing the formation of **2**.

Thermochemistry. The heat of formation of **1** can be obtained by combining thermochemical data pertinent to two processes.



4

The reaction enthalpies, *i.e.* IE in Eqn. 1 and the appearance energy (AE) in Eqn. 2 are observables, while standard heats of formation ($\Delta H_{f,298}^\circ$) of **4** and ethylene can be estimated by the group additivity scheme [19] or taken from [19] [20]. Eqn. 1 and 2 afford for a given reaction temperature T :

$$\Delta H_{f,298}^\circ(\mathbf{1}) = \Delta H_{f,298}^\circ(\mathbf{4}) + AE(\mathbf{1}^+) - E_{rev} - E_{exc} - \Delta H_{f,298}^\circ(C_2H_4) - IE(\mathbf{1}) + \int_{298} \Delta C_p dT \quad (3)$$

The first five terms in Eqn. 3 constitute the $\Delta H_{f,298}^\circ(\mathbf{1}^+)$, provided the reverse activation energy E_{rev} and the excess energy in the transition state E_{exc} are kept to a minimum [21]. The last term in Eqn. 3 is small ($2 \text{ kJ} \cdot \text{mol}^{-1}$) for $T = 400 \text{ K}$ in systems of similar size [20], and probably compensates the small contribution of E_{rev} and E_{exc} of opposite sign.

Two different values for $\Delta H_{f,298}^\circ(\mathbf{1}^+)$ have been reported by *Holmes* and coworkers [13] [18]. The first was estimated as larger than $1004 \text{ kJ} \cdot \text{mol}^{-1}$ [13], while the second was determined experimentally as $908 \text{ kJ} \cdot \text{mol}^{-1}$ on the basis of Eqn. 2 [16]. We have reproduced AE measurements using Eqn. 2 and have arrived at a yet different value which we wish to comment upon here. The AE reported in [18] ($AE = 10.08 \text{ eV}$) is very close to our

measured value of IE(4) (10.00 ± 0.04 eV by PE spectroscopy). The deconvoluted [22] ionization-efficiency curve of ions at m/z 68 in the spectrum of 4 shows indeed a tail down to *ca.* 10.1 eV. However, high-resolution measurements revealed that ions at m/z 68 are composed of a doublet of $C_4H_4O^+$ (major) and $C_5H_8^+$, in which the latter, although being a minor component, persisted down to 10.0–10.1 eV. *AE* measurements at resolving power of 2000, which was sufficient to separate the C_4H_4O – C_5H_8 doublet without loss of sensitivity, afforded ionization efficiency curves that showed clear onsets at 10.22 ± 0.04 eV after deconvolution of the electron energy [22].

The second point in question is the $\Delta H_{f,298}^\circ$ (4). *Burgers et al.* [18] used nonstandard group equivalents to estimate it as -11 kJ·mol⁻¹. Since standard [19] group equivalents has been used earlier by *Holmes and Terlouw* [13] and *Willett and Baer* [23] to estimate the $\Delta H_{f,298}^\circ$ of the lower homologue 2, we have performed MNDO calculations [14] to assess the latter value. The calculated MNDO value (50 kJ·mol⁻¹) is in perfect accord with the estimate based on the additivity scheme [19], if standard group equivalents are used. Since MNDO tends rather to overstabilize acetylenic compounds [24], we believe that the above value represents the lower limit at worst. From the $\Delta H_{f,298}^\circ$ (2) = 50 kJ·mol⁻¹, we calculate $\Delta H_{f,298}^\circ$ (4) = 10.5 kJ·mol⁻¹, using standard equivalents for C–(C_d)(C)(H₂) [19]. Hence, the $\Delta H_{f,298}^\circ$ (1⁺) can be determined as 944 kJ·mol⁻¹.

IE measurements afforded curves with well-developed linear portions near the threshold (*Figure*) from which the *IE*(1) can be determined as 8.92 ± 0.03 eV. According to *Eqn. 3* the $\Delta H_{f,298}^\circ$ of the neutral enol 1 can be calculated as 83 ± 7 kJ·mol⁻¹. Thus the difference in $\Delta H_{f,298}^\circ$ between 1 and 2 (33 kJ·mol⁻¹) does not deviate from those determined for similar enols of $CH_2=C(OH)–R$ type [2] [4] [7].

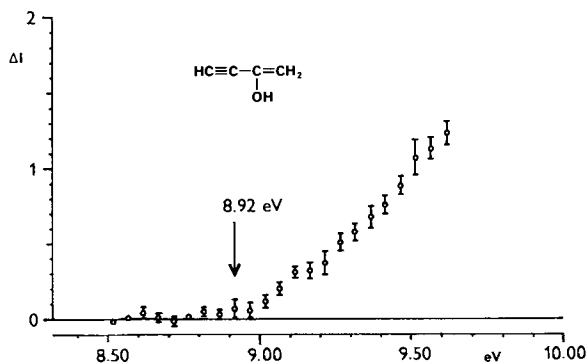


Figure. Ionization energy measurement of 1-buten-3-yn-2-ol (1)

MNDO calculations afforded $\Delta H_{f,298}^\circ$ (1) = 77.5 kJ·mol⁻¹ in a reasonable agreement with the experimental value. The optimized geometry of 1 (*Table 1*) revealed no unusual features, the lengths of the C–C and C–O bonds were very similar to those calculated by MNDO for the parent vinyl alcohol [8]. However, the calculation predicts that ground state 1 exists as a planar *anti*-isomer, in contrast to vinyl alcohol which prefers *syn*-geometry [25]. The calculated difference in energy between the *anti*- and *syn*-forms of 1 is very small (2.5 kJ·mol⁻¹), as is the height of the barrier separating both rotamers (7.5 kJ·mol⁻¹ above the *anti*-form). These results may be affected by a possible weak intramolecular

Table 1. MNDO Geometry and Net Charge Populations in **1**

$\text{H(4)-C(4)\equiv C(3)-C(2)=C(1)-H(1)}$ $\begin{array}{c} \text{H(2)} \\ \\ \text{C(2)} \\ \\ \text{H(3)-O} \end{array}$			
Bond length [Å]		Bond angle [°]	
C(1)-H(1)	1.088	C(2)-C(1)-H(2)	121.9
C(1)-H(2)	1.087	C(3)-C(2)-C(1)	123.4
C(1)-C(2)	1.360	C(4)-C(3)-C(2)	178.4
C(2)-C(3)	1.430	H(4)-C(4)-C(3)	180.2
C(3)-C(4)	1.197	H(1)-C(1)-C(2)	123.8
C(4)-H(4)	1.052	O-C(2)-C(1)	118.5
C(2)-O	1.368	C(2)-O-H(3)	112.7
OH(3)	0.947		

Net charge populations		Net charge populations	
H(1)	+0.06	C(2)	+0.14
H(2)	+0.05	C(3)	-0.17
H(3)	+0.19	C(4)	-0.08
H(4)	+0.16	O	-0.26
C(1)	-0.09		

H-bond between the OH H-atom and the π_y orbital of the triple bond for which MNDO has no adequate expression [24]. Nevertheless, the small energy difference predicted by MNDO for the rotamers is consistent with the moderate ionization cross section of **1**, as indicated by the slope of the ionization efficiency curve near the onset [6]. This means that there is a large fraction of molecules of **1** the geometry of which correlates with that of the ground state ion $\mathbf{1}^{+\bullet}$, so that the ionization can occur with a high *Franck-Condon* factor [5] [6].

In contrast to the molecular geometry, MNDO calculations of the charge distribution in **1** (Table 1) show a considerable effect of the triple bond on the net charge population at the enolic double bond. Compared to that in vinyl alcohol [8] [9], the double bond in **1** is much less polarized, the negative charge being shared mostly by the O-atom and the inner C-atom of the triple bond. The terminal C-atom of the double bond carries only a slight negative charge.

Despite the calculated electron density flow from the enol system, the difference in the ΔH_f° between **1** and **2** shows no special stabilization of the enol. It can be concluded that the charge distribution in the enol subsystem and the destabilization of the whole enol against the corresponding keto form need not be directly related. It appears to be more probable that on the difference in the ΔH_f° results from many small contributions due to the bonding and repulsive terms [8] [9].

Fragmentations of Cation Radicals $\mathbf{1}^{+\bullet}$. Following ionization, cation radical $\mathbf{1}^{+\bullet}$ decomposes unimolecularly through four main fragmentation routes: *i*) loss of hydrogen; *ii*) loss of H_nO ($n = 1, 2$); *iii*) loss of CH_3 , and *iv*) loss of CO. The decomposition of high-energy, short-lived $\mathbf{1}^{+\bullet}$ and its deuteriated analogues **1a**, **1b**, **1c** are illustrated with the 75 eV electron-impact mass spectra (Table 2).

Loss of H-atom from $\mathbf{1}^{+\bullet}$ occurs to a much greater extent than observed for the keto form $\mathbf{2}^{+\bullet}$ (Table 2). At 75 eV, the H-atom originates mainly from the OH group (66% from **1a**, Table 2), while the contributions from C(1) (17%, **1b**) and C(4) (9%, **1c**) are

Table 2. The 75-eV EI-MS Data of **1**, **1a**, **1b**, **1c**, and **2**

<i>m/z</i>	Relative abundance ^{a)} ^{b)}				
	1	1a	1b	1c	2
70	–	6.7	5.3	7.9	–
69	4.3	99	88	73	1
68	85	30	24	19	18
67	13	20	5	2.1	0.5
66	1.3	5	–	–	0.3
55	–	–	–	3.5	–
54	3.3	3.5	3.4	100	3.3
53	100	100	100	5.8	100
52	1.9	3.5	3	21	1.8
51	15	25	21	23	1.4
50	23	37	17	13	3.7
49	11	19	8	9	2.8
48	3.7	2.3	4.2	4.2	0.9
44	–	6.5	6.7	–	–
43	9.4	12	13	11	8.6
42	22	21	5.1	21	5.7
41	2.3	52	63	45	1
40	25	52	38	44	11
39	56	45	41	33	6.9
38	17	21	9	18	4.9
37	14	18	4.8	12	6.1
36	3.8	5.6	4.2	5.4	2
30	–	^{c)}	3.4	1.5	–
29	7.1	– ^{c)}	6.5	5.8	0.7
27	0.8	1.5	5.3	6.9	0.7
26	3.7	4.2	5.3	10	2
25	8.3	11	10	2.5	5.6
24	3.2	4.4	5.7	3.7	1.4
15	11	– ^{c)}	17	12	9.3
14	7.6	– ^{c)}	3.3	8.8	3.1
13	2.5	– ^{c)}	2.4	3.2	1.2
12	1.5	– ^{c)}	3.2	2.2	0.9

^{a)} Ion intensities at *m/z* 36–41, 24–27, and 12–15 were corrected for contributions from cyclopentadiene.

^{b)} The D contents in the labelled compounds were determined from the 11-eV EI spectra: **1a**: 82.5% D₁, 17.5% D₀; **1b**: 5.6% D₂, 88.9% D₁, 5.5% D₀; **1c**: 95.2% D₁, 4.8% D₀.

^{c)} Interference from isobaric ions from CH₃OD used for H/D exchange.

smaller. When the fast high-energy processes are filtered off by lowering the energy of ionizing electrons, or by selecting metastable ions that decompose in the microsecond time region, the regioselectivity of the OH H-atom loss increases to 86%.

The mass-analyzed ion kinetic energy (MIKE) spectrum of metastable **1**⁺ shows a composite peak for the loss of H, with a dish-top component of large kinetic energy release ($T_{0.5} = 626$ meV) capped with a narrower *Gaussian*-like peak of $T_{0.5} = 60$ meV. The loss of D from metastable **1a**⁺ gives only a dish-top peak ($T_{0.5} = 613$ meV), while a narrower peak of $T_{0.5} = 56$ meV appears at *m/z* 68 due to the loss of H. The narrow peak amounts in surface of *ca.* 8% of the wide one. The loss of H from metastable **1b**⁺ and **1c**⁺ also shows the dish-top peak only ($T_{0.5} = 631$ and 634 meV, respectively). The corresponding loss of D amounts to less than 2% of *M* indicating a large isotope effect. The large

kinetic-energy release associated with the loss of $H\cdot$ from $1^{+\cdot}$ indicates a profound rearrangement of the C skeleton to form the $C_4H_3O^+$ products and is also indicative of an energy barrier to the reverse process [26]. The $C_4H_3O^+$ ions originating from low-energy $1^{+\cdot}$ may be of acylium type, $C_3H_3-CO^+$, by analogy with decompositions of other enolic cation radicals [27], but at present, there are no reference data on these highly unsaturated species to allow for their identifications.

The loss of $CH_3\cdot$ from $1^{+\cdot}$ is mechanistically very clean; the methyl eliminated incorporates the OH H-atom and the C(1) CH_2 group with a specificity exceeding 95%. The regioselectivity of the H transfer onto the CH_2 terminus remains high in collision-induced decompositions (CID) of stable $1^{+\cdot}$, $1a^{+\cdot}$, $1b^{+\cdot}$, and $1c^{+\cdot}$ (Table 3). The relative abundance

Table 3. The CID Spectra of $1^{+\cdot}$, $1a^{+\cdot}$, $1b^{+\cdot}$, and $1c^{+\cdot}$

<i>m/z</i>	Relative abundance ^{a)}				Reference ^{c)}
	$1^{+\cdot}$	$1a^{+\cdot}$	$1b^{+\cdot}$	$1c^{+\cdot}$	
68	–	(6.8)	(53)	(55)	–
67	(51)	(74)	15	14	(59)
66	17	28	4.6	6.4	15
65	2.3	2.4	1	–	2
55	–	4.8	1.6	1.6	–
54	0.8	0.8	1	62	2.7
53	69	71	58	4	46
52	2.1	3.4	36	42	1.6
51	24	39	46	58	29
50	63	100	33	38	62
49	33	51	19	24	34
48	5.6	7.8	6.4	6.3	4
44	–	10	7.5	0.9	–
43	6.8	11	40	8.4	3
42	39	26	6	22	34
41	–	(66)	(46)	(46)	0.1
40	(51)	100	100	100	(47)
39	100	57	39	38	100
38	33	34	28	29	34
37	32	39	25	24	35
36	7.5	11	8.2	10	6.7
31	–	–	–	–	0.3
30	–	14	2.9	0.8	–
29	13	8.8	11	13	15
28	2.5	4.6	4.8	4.5	2.1
27	2.7	4	6	5.6	3.2
26	8.9	7	5.3	14	9.3
25	13	16	12	8.3	12
24	4.8	5.6	5	4.9	3.5
16	–	7.8	4.8	2.2	–
15	2.6	3.2	3.4	5	2.7
14	4.2	2.8	1.4	3.9	3.8
13	1.7	1.8	1.1	1.2	1.5
12	1.5	2	1.2	1.6	1.4

^{a)} Peak areas.

^{b)} The values in parentheses contain contributions from unimolecular decompositions.

^{c)} From dissociative ionization of 1-ethynylcyclobutanol.

Table 4. The CID Spectra of C_3HO^+ Ions from $[1]^{++}$, $[1a]^{++}$, $[1b]^{++}$, and $[2]^{++}$

m/z	Relative abundance ^{a)}		m/z	Relative abundance ^{a)}	
	$[1]^{++}$, $[1a]^{++}$, $[1b]^{++}$	$[2]^{++}$		$[1]^{++}$, $[1a]^{++}$, $[1b]^{++}$	$[2]$
52	77 ± 2	78	28	26 ± 0.5	26
41	0.7 ± 0.1	0.8	26.5	1.8 ± 0.4	1.4
40	15 ± 1	14	25	100	100
37	8.2 ± 0.5	8.7	24	39 ± 1	39
36	19 ± 1	20	13	2.6 ± 0.1	2.4
29	5 ± 0.2	5.2	12	5.9 ± 0.2	6

^{a)} Average values for C_3HO^+ prepared by loss of CH_3^{\cdot} from $[1]^{++}$ and by loss of CH_2D^{\cdot} from $[1a]^{++}$ and $[1b]^{++}$.

of the $(M - C(H,D)_3)^+$ ions in the CID spectra of 1^{++} and $1a^{++}-c^{++}$ prepared by electron-impact ionization of unstable enols are higher than that of $(M - CH_3)^+$ in the CID spectrum of reference 1^{++} prepared by dissociative ionization of 1-ethynylcyclobutanol [18] (Table 3). This is due to a small admixture of the keto form 2^{++} , in the CID spectrum of which the $(M - CH_3)^+$ fragment constitutes 55% of the total fragment ion current [18].

The CID spectra of C_3HO^+ ions from 1^{++} , $1a^{++}$, and $1b^{++}$ are identical with that of C_3HO^+ from 2^{++} (Table 4). This, together with the labelling data, indicates that the loss of CH_3 from 1^{++} proceeds *via* a 1,3-H shift from the OH onto C(1) to produce transiently 2^{++} which then decomposes to $HC\equiv C-CO^+$ and CH_3^{\cdot} [23]. The *AE* of $(M - CH_3)^+$ from **1** was measured as 11.20 ± 0.07 eV, which gives the energy of the transition state, $E_{TS} = 1163$ kJ·mol⁻¹, referred to $\Delta H_f^\circ(1)$ (*vide supra*). The E_{TS} value exceeds the experimental threshold for $HC\equiv C-CO^+ + CH_3^{\cdot}$ (1111 kJ·mol⁻¹) [23], which suggests that the isomerization of 1^{++} to 2^{++} is the rate-determining step for the CH_3 loss from the former ion. The kinetic energy release for the CH_3 loss from metastable 1^{++} ($T_{0.5} \approx 50$ meV) is higher than that of the same decomposition of metastable 2^{++} ($T_{0.5} = 28$ meV), which is consistent with the assumption that vibrationally excited 2^{++} is formed transiently by the isomerization of 1^{++} [28]. The high critical energy for the loss of CH_3 from 1^{++} ($E_c = E_{TS} - \Delta H_f^\circ(1^{++}) = 220$ kJ·mol⁻¹) accounts for the low abundance of $HC\equiv C-CO^+$ in the MIKE spectrum.

Decompositions of low-energy 1^{++} are dominated by loss of CO, producing $C_3H_4^{++}$ ions. The *AE* of this fragmentation was measured with **1c** in which the resulting $C_3H_3D^{++}$ ion does not coincide with C_3 -fragments from cyclopentadiene co-formed by pyrolysis. The value obtained ($AE = 10.22 \pm 0.08$ eV) affords the energy of the transition state, $E_{TS} = 1069$ kJ·mol⁻¹, which is very close to the threshold energy for the formation of (propyne)⁺⁺ ($E_{TH} = 1073$ kJ·mol⁻¹) [20] [23], and somewhat exceeds that of (allene)⁺⁺ ($E_{TH} = 1015$ kJ·mol⁻¹) [20] [23]. Therefore, according to the *AE* measurements both these stable $C_3H_4^{++}$ isomers could be energetically accessible by loss of CO from 1^{++} . The ionized keto form 2^{++} has been shown by photoelectron-photoion coincidence study to produce (propyne)⁺⁺ by loss of CO [23]. With 1^{++} decomposing to $C_3H_4^{++}$ the intermediacy of 2^{++} appears to be unlikely, since the rearrangement *via* the 1,3-H shift requires much higher energy than does the loss of CO (*vide supra*). Moreover, the reported breakdown diagram of 2^{++} [23] predicts that the formation of $C_3H_4^{++}$ would be disfavoured against that of C_3HO^+ , starting from 0.6 to 0.7 eV above the lowest fragmentation onset, so that the $(C_3H_4)^{++}/(C_2HO)^+$ abundance ratio would be greater than one only for a slight and sharply limited low-energy fraction of decomposing molecular ions [23]. In contrast to

this, the observed abundance ratios $(C_3H_3D)^+/(C_3HO)^+$ from **1a** to **1c** are greater than one up to 17 eV ionizing energy. Although ionization with non-threshold electrons produces cation radicals with broad distribution of internal energies, it can be assumed that there would have been a substantial fraction of higher energy 2^{+} formed from 1^{+} at 17 eV, were the isomerization to proceed by some feasible mechanism. It, therefore, appears to be more probable that the reaction path leading to $C_3H_4^{+}$ commences by H migration from the OH to the triple bond in 1^{+} and eventually produces (allene) $^{+}$.

Conclusions. – The presence of the triple bond in **1** does not cause any significant stabilization of the enol against the keto form **2**. At the MNDO level, the enol subsystem in **1** is calculated to be less polarized than in other simple enols [9] [10], and is predicted to prefer planar *anti*-conformation. Ion chemistry of 1^{+} shows only a single reaction, due to loss of CH_3 , which interconnects the ionized enol and keto forms. Other primary fragmentations of 1^{+} proceed without involvement of the ionized keto form.

Support of this work by the *Swiss National Science Foundation* is greatly acknowledged. The authors wish to thank Dr. *T. Vondrák* (Heyrovský Institute, Praha) for the measurement of the PE spectrum.

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