26. Molecular Ions of Transient Species: Vinyl-Alcohol Cation

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Summary

Vinyl alcohol **1** was prepared by thermolysis of cyclobutanol and its photoelectron spectrum was determined. $I_a^1 = 9.18$ eV and $I_v^1 = 9.52$ eV were found, the vibrational progression ($\tilde{\nu} = 1400$ cm^{-1}) for this lowest energy transition $\mathbf{1}(X) \rightarrow \mathbf{1}^+(\tilde{X})$ indicating significant skeletal changes in the ion. The question of the relative stability of the *syn* ($\mathbf{1}_s^+$)- *vs.* *anti*-ions ($\mathbf{1}_a^+$) is discussed in the light of theoretical calculations. The energy of the second π-state of $\mathbf{1}^+$ is estimated at 13.6–14.1 eV above the ground state of **1**.

Introduction. – Vinyl alcohol **1**, the unstable tautomer of acetyldehyde **2**, has been suggested for a century [1] as an intermediate in various chemical reactions. Only ten years ago, it was identified for the first time in solution [2], and subsequently in the gas phase [3] where its molecular structure could be derived from its microwave spectrum. The existence of related species in interstellar space (*e.g.* **2**, CH_3OH, C_2H_5OH, CH_2CHCN) suggests, however, that **1** may also be detected there provided sufficient knowledge about its molecular constants is available [3]. Detection of its radical cation $\mathbf{1}^+$ may even be more likely given that its heat of formation is 62.7 kJmol^{-1} lower than the one of isomeric $\mathbf{2}^+$ [4], contrary to the situation prevailing for the neutrals. In this paper the electronic states of $\mathbf{1}^+$ are investigated using photoelectron (PE) spectroscopy.

Experimental. – The details of the PE setup have been described in [5]. **1** was prepared by pyrolysis of cyclobutanol **3** [4] in a Pt/Rh-tube (∅ = 0.9 mm) containing a silica capillary insert and attached directly to the target chamber. This silica insert proved to be crucial since pyrolysis in the hot metal tube alone led exclusively to **2** and ethylene. Heating was achieved by applying a controlled voltage at the tube (used as a resistor); 550–600° were found to be optimal for decomposition of **3**. The temperature of the fragments (cooled down through collisions with the walls) in the ionization chamber was estimated to be 100°–150° from the intensity of the hot vibrational band in the third PE transition of naphthalene (= 'internal molecular thermometer'), investigated under the same conditions and compared to the results given in [5]. Calibration of the energy scale was done with MeI, Xe and Ar. From the halfwidth of the $^2E_{3/2}$-peak of MeI a resolution of ≈ 30 meV was determined.

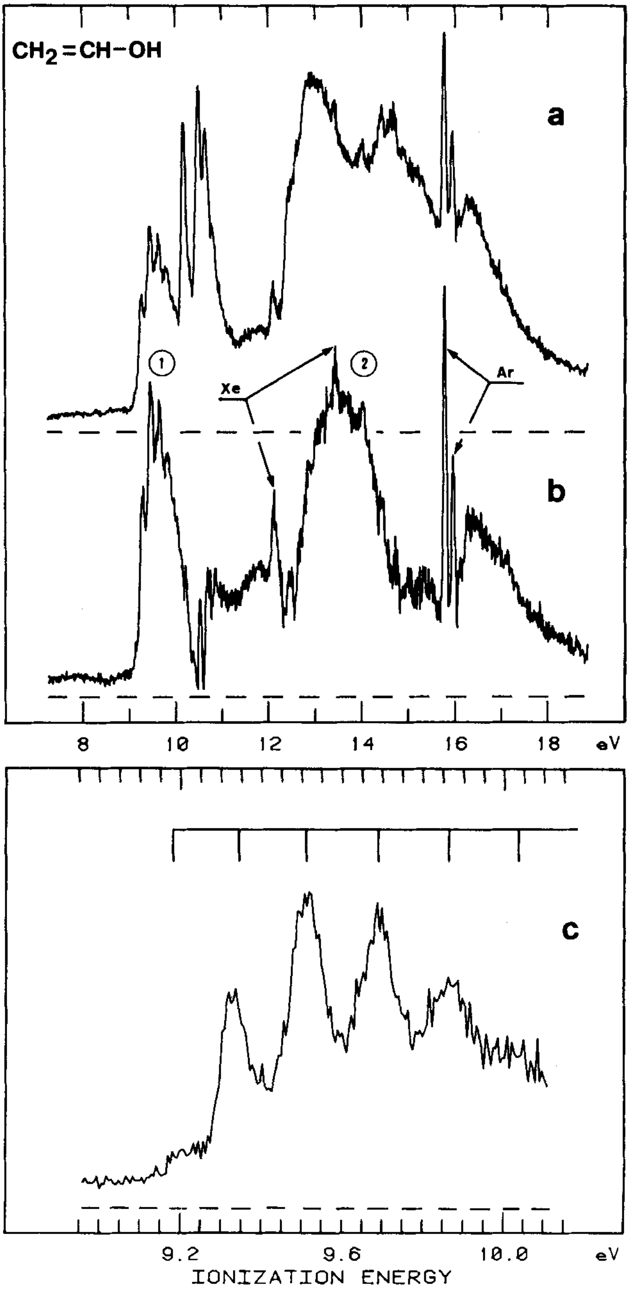

Figure. a) *PE spectrum of pyrolysed cyclobutanol* (see *Experimental*). b) *Spectrum* a *from which the PE spectra of ethylene and acetaldehyde were digitally subtracted, employing weight factors calibrated from the intensity of the first PE peaks of these by-products from* a. The spectrum corresponds essentially to that of vinyl alcohol, apart from spurious peaks due to a non-perfect subtraction. c) *Band system* ① *of vinyl alcohol, expanded scale.*

Results and Discussion. – The *Figure* shows the PE spectrum of **1** together with that of ethylene and isomeric **2,** the latter being apparently formed through catalytic action of the oven surface. **1** possesses two filled π-orbitals; the subsequent discussion is restricted to the two ionic $^2A''(\pi)$-states of $\mathbf{1}^+$ derived from ejection of an electron out of these two orbitals.

Band System ①. $I_v^1 = 9.52$ eV can be deduced from band system ①. This value is significantly higher than those determined for alkylvinylethers CH_2CHOR ($I_v^1 = 9.14$ eV (R = Me); = 9.15 eV (R = Et); = 9.10 eV (R = Bu) [6]). This finding is in line with the fact that from perturbation theory based on iso-π-electronic allyl anion as well as from MNDO calculations, the HOMO of **1** is strongly localized in the C = C-fragment. Various alkyl substituents at the O-atom thus provide a rather constant inductive destabilization to this orbital (≈ 0.4 eV) since they do not significantly engage in ionic hyperconjugation. The MNDO-prediction $I_v^1 = 9.4$ eV (applying *Koopmans'* theorem) is in good agreement with experiment. This value was calculated for the minimum energy structure of **1** which – in line with experiment [3] – turned out to be the *syn*-form ($\mathbf{1}_s$).

Band ① displays a long vibrational progression of 1400 cm^{-1} indicating that considderable nuclear rearrangement takes place upon $\mathbf{1} \rightarrow \mathbf{1}^+ + e^-$. Qualitative arguments as well as numerical calculations [7] predict for this process a lengthening of the C=C and a shortening of the C–O bonds (from [7]: $\Delta R_{C=C} = +10$ pm, $\Delta R_{C-O} = -10$ pm). The observed frequency is not unexpected for a corresponding fundamental excited in the ion, also in view of the C=C stretching frequency in iso-π-electronic allyl radical (1477 cm^{-1} [8]).

A recent investigation of the appearence potential of $\mathbf{1}^+$ using mass-spectrometric techniques has shown a low cross section for ionization over the initial portion of the ion production efficiency curve [4]. Small *Franck-Condon* (FC) factors for an adiabatic process $\mathbf{1} \rightarrow \mathbf{1}^+$ were made responsible for this observation, and rationalized through the theoretical prediction [7] that – contrary to the most stable conformation for **1** (*i.e.* $\mathbf{1}_s$) – the ion $\mathbf{1}^+$ prefers the *anti*-conformation (*i.e.* $\mathbf{1}_a^+$). Indeed MNDO yields 10.9 $kJmol^{-1}$ for the difference $\Delta H_f^\circ(\mathbf{1}_s^+) - \Delta H_f^\circ(\mathbf{1}_a^+)$. However, MNDO also yields a significant barrier for $\mathbf{1}_s^+ \rightarrow \mathbf{1}_a^+$ of 96.5 $kJmol^{-1}$, in contrast to the corresponding value for the neutrals of 10.5 $kJmol^{-1}$. Hence, the ion potential wells are well-developed with respect to this torsional coordinate. In fact one might ask if $\mathbf{1}_s^+$ and $\mathbf{1}_a^+$ can be addressed as 'rotamers' in the usual sense (*i.e.* low barriers to interconversion), or if the notion 'isomers' would not better apply. We note in this context that the resonance energy of iso-π-electronic vinylamine cations is estimated experimentally to be ≈ 1 eV [9]. The PE transition ① therefore most likely corresponds to $\mathbf{1}_s \rightarrow \mathbf{1}_s^+$. Its vibrational activity due to the already discussed in-plane skeletal change indicates a considerable non-adiabaticity which might be the reason for the low ion production efficiency noted in [4].

In our view neither of the two techniques (guided by the FC principle) has yielded information about the energy of the most stable form $\mathbf{1}_a^+$, *i.e.* about I_a^1 ($\mathbf{1}_s \rightarrow \mathbf{1}_a^+$). A value for I_a^1 ($\mathbf{1}_s \rightarrow \mathbf{1}_s^+$), can, however, be derived from the shoulder at 9.18 eV, in good agreement with [4]. This shoulder has been reproduced several times and its intensity did not vary with decomposition temperature. Furthermore it appears as a member of the 1400 cm^{-1} progression. These arguments exclude it from being a hot band, given also the effective temperature of **1** (see *Experimental*). Finally, a signal due to a small thermal equilibrium population of $\mathbf{1}_a$ can be excluded as the microwave spectrum obtained under similar conditions [3] did not reveal the presence of this rotamer.

Band System ②. MNDO predicts two $^2A'(\sigma)$-states ($\tilde{A}$ and $\tilde{B}$) of $\mathbf{1}^+$ at 13.42 and 13.57 eV, and a second $^2A''(\pi)$-state ($\tilde{C}$) at 14.12 eV. Another crude estimate is obtained through the PE-LCBO model [10], using $H_{C=C} = -10.5$ eV (from ethylene) and $H_{\ddot{O}} = -12.6$ eV (from water). With the experimental value ε_{HOMO} $(\mathbf{1}) = -9.52$ eV, $\varepsilon = -13.58$ eV for the subjacent π–MO is derived.

There are ionic states present in the energy region 13.6–14.1 eV, but a clear-cut assignment of the second $^2A''(\pi)$-state of $\mathbf{1}^+$ is not possible due to overlapping bands from the σ-states, as well as non-perfect subtraction of the bands from the pyrolysis by-products. Nevertheless, as a rough estimate for the strongly allowed $\tilde{C} \rightarrow \tilde{X}$ emission of the ion $\mathbf{1}^+$ the UV region 250–300 nm looks acceptable. However, from the lower lying excited σ-states $\tilde{A}$ and $\tilde{B}$ emission is also weakly allowed for this C_s-species.

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