27. Molecular Ions of Transient Species: Vinylamine-Cation

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Summary

Vinylamine **1** was prepared by thermolysis of cyclobutylamine and its photoelectron spectrum was measured. $I_a^1 = 8.20$ eV and $I_v^1 = 8.65$ eV were found, the dominant vibrational progression ($\tilde{\nu} = 725$ cm^{-1}) indicating that in the course of $\mathbf{1}(X) \rightarrow \mathbf{1}^+(\tilde{X})$ flattening around the N-atom occurs. The *Franck-Condon* profile of this band, however, suggests that a skeletal mode of $\tilde{\nu} \approx 1400$ cm^{-1} (observed also in the iso-π-electronic systems vinyl-alcohol-cation and allyl radical) may also be excited. Comparison with the data for the isomer acetaldehyde-imine **2** and its cation $\mathbf{2}^+$ shows that the isomer couple **1**/**2** constitutes a further notable example for a relative thermochemical stability inversion on going from the neutrals to the cations.

Introduction. – Enamines are important species in many chemical processes [1], their characteristic behaviour being due to the N-lone pair/C=C-π interaction which is greatly enhanced upon electrophilic attack. Although various physico-chemical data are available for this class of substances, the parent compound vinylamine **1** has been rather elusive due to its high kinetic instability. It was first prepared in 1975 [2] and its microwave spectrum determined, whose finer details were subsequently analysed in [3]. As a mode of preparation, pyrolysis of ethylamine was chosen. This led to a variety of by-products some of which were detected in interstellar space [2], among them the more stable tautomer of **1**, acetaldehyde-imine **2** [4]. It is therefore quite probable that **1** exists also under these conditions. Since from simple theoretical arguments the relative stability conditions of the $\mathbf{1}^+/\mathbf{2}^+$ isomer couple may be similar to those of the couple vinyl alcohol$^+$/acetaldehyde$^+$ [5], a study of the states of $\mathbf{1}^+$ via PE spectroscopy was desirable.

Experimental. – The experimental setup has been described in [5]. **1** was prepared from thermal decomposition of cyclobutylamine, which promised, based on the experience of [5], fewer products than the procedure followed in [2]. Optimal decomposition temperatures were found around 600° yielding only **1** and ethylene; around 700° acetylene and HCN-fragments appeared in the PE spectrum. However, **2** whose PE spectrum was reported in [6], was not detected at either temperature. Note, that contrary to the case of vinyl alcohol [5] a silica capillary insert in the metal thermolysis tube was not necessary here.

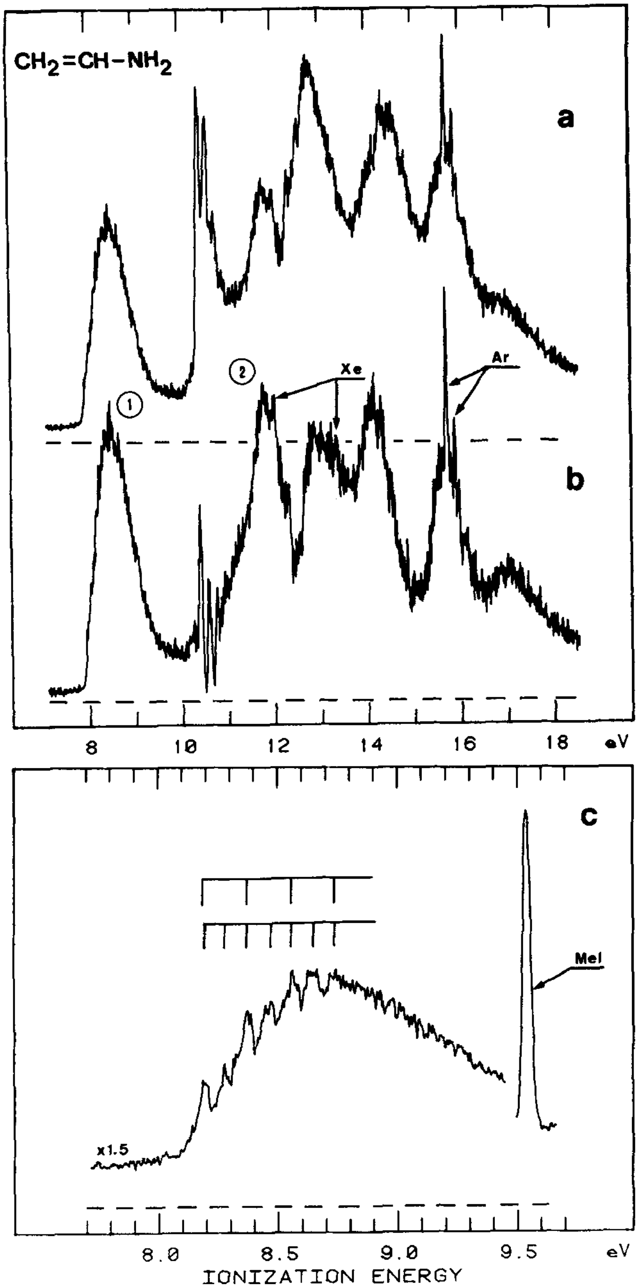

Figure. a) *PE spectrum of pyrolysed cyclobutylamine* (see *Experimental*). b) *Spectrum* a *from which the PE spectrum of ethylene was digitally subtracted, employing a weight-factor calibrated from the intensity of the first PE peak of this by-product from* a. The spectrum corresponds essentially to that of vinylamine, apart from spurious peaks due to non-perfect subtraction. c) *Band system* ① *of vinylamine, expanded scale.*

Results and Discussion. – The *Figure* shows the PE spectrum of **1** and the by-product ethylene. **1** possesses two π-orbitals, yielding two $^2A''(\pi)$-states for the molecular ion $\mathbf{1}^+$ on which the subsequent discussion shall concentrate.

Band System ①. $I_v^1 = 8.65$ eV, derived from this band-system, is only in fair agreement with the MNDO prediction of 9.13 eV, for reasons presently not understood. On the other hand, our experimental value finds good support through high quality *Hartree-Fock* calculations including polarization functions on all atoms, *i.e.* $I_v^1(\text{theor.}) = 8.70$ eV [4]. The more stable isomer **2** has an experimental $I_v^1 = 10.18$ eV [6]. From the onsets of these bands in the two spectra, we deduce $I_a^1(\mathbf{2}\text{–}\mathbf{1}) \approx 1.7$ eV, being aware that the corresponding energies may not truly reflect the 0–0 transitions. On the other hand, this estimate finds support through $I_v^1(\mathbf{2}\text{–}\mathbf{1}) = 1.52$ eV: both bands are likely to have about the same halfwidth since both transitions $\mathbf{1} \rightarrow \mathbf{1}^+$ and $\mathbf{2} \rightarrow \mathbf{2}^+$ occur in a strongly non-adiabatic fashion. Given further $\Delta\Delta H_f^0(\mathbf{1}\text{–}\mathbf{2}) = 27.6$ [7] or 21.9 [4] kJmol^{-1} (this relative energy sequence being in line with experimental indications [8]) *we are* entitled to predict for the ions: $\Delta H_f^0(\mathbf{2}^+) > \Delta H_f^0(\mathbf{1}^+)$ whereas for the neutrals $\Delta H_f^0(\mathbf{2}) < \Delta H_f^0(\mathbf{1})$. Hence, similar conditions prevail for the isomer couple **1**/**2** as found for CH_3CHO/CH_2CHOH [9], $CH_3OH/\dot{C}H_2O\dot{C}H_2$ [10], HCN/HNC [11], CH_2CCH_2/CH_3CCH [12], HNNH/NNH_2 [13]: *the relative stability of the isomeric neutral partners changes sign on passing to their radical ions!* Practical chemical consequences of these circumstances still await proper probing.

The vibrational progression of 725 cm^{-1} observed in band ① may correspond to excitation of the out-of-plane motion around a trigonal N-atom in $\mathbf{1}^+$. The microwave spectrum of **1** suggests a pyramidal conformation at this center, in line with theoretical predictions [4] [14]. Arguments carried over from pyrrole [15] suggest that also for **1** the lone-pair promotion energy to be spent for N-trigonalisation would not be offset by the associated increase in enamine resonance. For $\mathbf{1}^+$ this resonance energy was, however, experimentally estimated to be ≈ 1 eV [16], hence the driving force for N-trigonalisation is much larger. We take the vibrational structure of band ① as strong indication that $\mathbf{1}^+$ is essentially planar around the N-atom.

The corresponding band for vinyl alcohol displayed a 1400 cm^{-1} progression, associated with C=C- and C–O-bond length changes upon ionization [5]. The same will happen upon $\mathbf{1} \rightarrow \mathbf{1}^+$ for its C=C and C–N bonds. Since the corresponding frequency will also lie around the above value, its progression members may not be observable as distinct peaks since they would match roughly with the even members of the 725 cm^{-1} bending mode discussed above. The somewhat peculiar intensity ratios for the first few peaks might indeed indicate that the asymetric skeletal stretch in $\mathbf{1}^+$ is also excited.

MNDO predicts a value of 113 kJmol^{-1} for the torsional barrier of $\mathbf{1}^+$ in agreement with the earlier experimental estimate for its resonance energy (≈ 1 eV [16]). The potential well with respect to this non-totally symmetric mode is therefore well-developed and may be regarded as harmonic up to a considerable energy height. Excitation of this mode above this energy region may, however, start blurring out the fine structure; this may occur above ≈ 8.7 eV. We do not believe that this disappearence of fine structure indicates a thermodynamic threshold for decomposition of $\mathbf{1}^+$ as we do not recognize any energetically favorable reaction path ≈ 0.5 eV above the first observable vibrational peak at 8.2 eV which we assign to $I_a^1(\mathbf{1})$.

Band System ②. MNDO predicts for the second $^2A''(\pi)$-state ($\tilde{A}$) of $\mathbf{1}^+$ an energy of 12.13 eV above **1**. From a simple PE-LCBO argument, taking $\mathbf{H}_{C=C} = -10.5$ eV (from ethylene) and $\mathbf{H}_{\ddot{N}} = -10.8$ eV (from NH_3) and matching the ε(HOMO) to -8.65 eV ($= -I_v^1(\mathbf{1})$) yields for the subjacent π-MO $\varepsilon = -12.65$ eV. It is therefore clear that the band with $I_v^2 = 11.90$ eV must correspond to that second π-state. MNDO predicts the first $^2A'(\sigma)$-state ($\tilde{B}$) of $\mathbf{1}^+$ to lie higher, at 13.3 eV. For the allowed $\tilde{A} \rightarrow \tilde{X}$ emission of $\mathbf{1}^+$ the region around 400 nm can be expected.

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