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PHOTOELECTRON SPECTRUM OF VINYLCYCLOPROPANE

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The photoelectron spectrum of vinylcyclopropane has been measured by using the 21.22 eV helium resonance lines. Eleven ionization potentials have been observed. The values of the first two ionization potentials have been explained by the conjugative interaction between the σ-orbitals of the cyclopropane ring and the bonding π-orbital of the vinyl group.

It is known that the cyclopropane ring shows conjugative properties when joined directly to an unsaturated grouping. For example, the π-π^* band of ethylene experiences a bathochromic shift of about 300 nm upon being substituted by cyclopropyl$^{1)}$. Also Nishida et al.$^{2)}$ observed that the ionization potentials of ethylenes substituted by cyclopropyl group(s) are lower by 1 – 1.5 eV than those of methyl substituted analogue.

In order to study the conjugative effect of the cyclopropane ring we have measured the photoelectron spectrum of vinylcyclopropane by using the 21.22 eV helium resonance lines.

The source of radiation is a differentially pumped dc discharge in helium. Energy spectra of electrons have been measured by a photoelectron spectrometer with a 10 cm radius cylindrical electrostatic field deflection analyzer. The detail of the spectrometer will be described elsewhere.

The photoelectron spectrum of vinylcyclopropane is shown in Fig. 1. As will

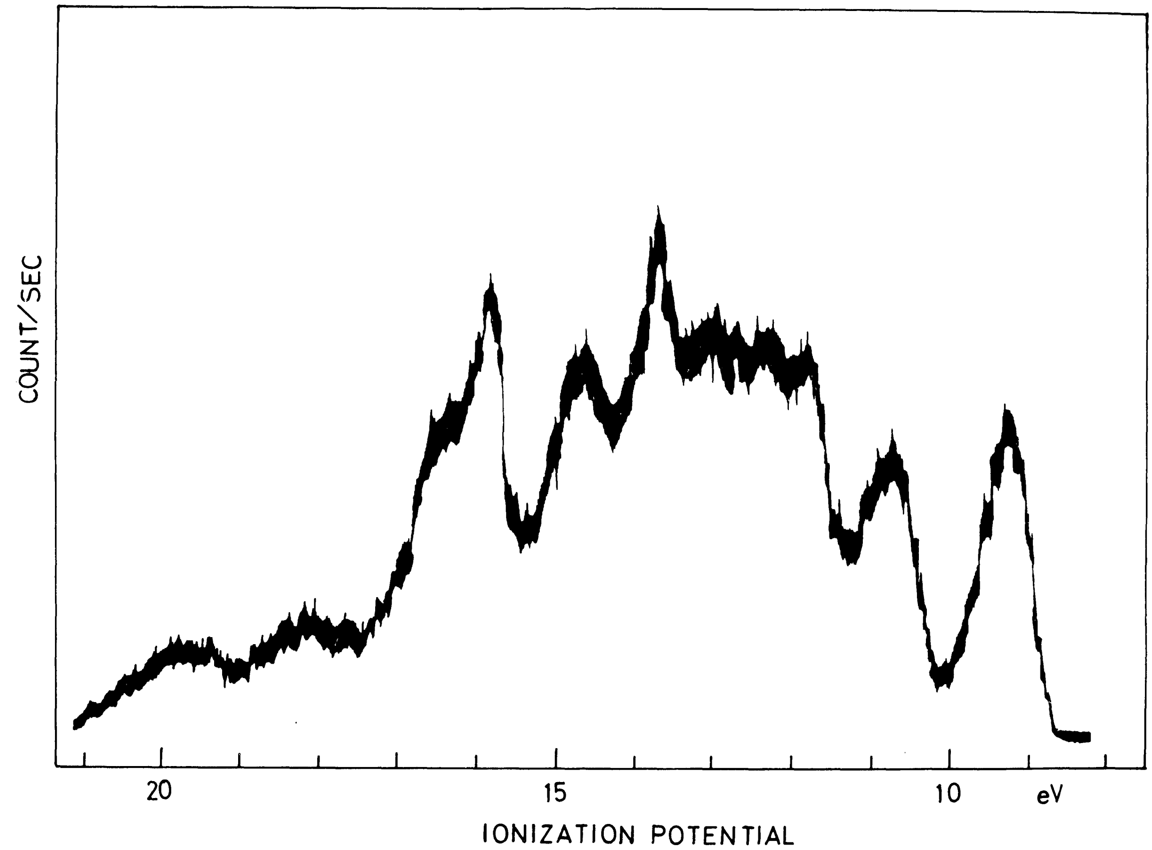
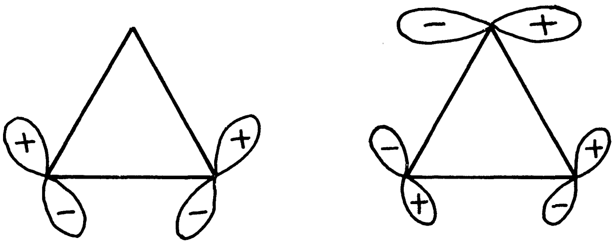


Fig. 1. The Photoelectron Spectrum of Vinylcyclopropane
(pressure, 0.02 Torr)

be seen from the figure, the adiabatic ionization potential of the first band is 8.7 eV, which is lower than both of the corresponding values of ethylene (10.51 eV)$^{3)}$ and cyclopropane (9.8 eV)$^{4)}$. Also from the figure we see that there appear to be 11 bands due to different molecular orbitals. The vertical ionization potentials of these bands are 9.2_5, 10.7_6, 11.7_9, 12.3, 12.9, 13.7_0, 14.6_8, 15.8_5, 16.4, 18.1 and 19.6 eV, respectively. Gleiter et al.$^{5)}$ have reported preliminary results concerning the photoelectron spectrum of vinylcyclopropane and observed the first three vertical ionization potentials to be 9.2, 10.7 and 11.7 eV, respectively, which are in good agreement with our results.

The values of the first two ionization potentials can be explained by the conjugative interaction between the σ-orbitals of the cyclopropane ring and the bonding π-orbital of the vinyl group$^{5)}$. The first band in the photoelectron spectrum of cyclopropane corresponds to ionization of the highest occupied e' orbitals (Fig. 2) and shows two maxima (10.5 eV, 11.3 eV) due to Jahn-Teller splitting$^{4)}$. The center of the band lies at 10.9 eV. In Fig. 2 the shapes of the e'-orbitals are shown. The orbital e'_s is symmetric, e'_a antisymmetric with



e'_s, symmetric orbital e'_a, anti-symmetric orbital

Fig. 2. The Highest occupied e' Orbitals of Cyclopropane

respect to the plane of symmetry.

Evidence from electron diffraction study of vinylcyclopropane[6] shows that the trans conformation is stable at room temperature (Fig. 3). For trans conformation, the orbital e'_a can conjugate with the bonding π-orbital of the vinyl group, while the conjugative interaction between the e_s and the π-orbital is not expected owing to the difference of symmetry. Hence, the first band of vinylcyclopropane (vertical I. P. 9.2_5 eV) which is shifted by 1.6 eV from the center of the e' band of cyclopropane may be correlated to the e'_a orbital of the compound. On the other hand, the second band (vertical I. P. 10.7_6 eV) may be related to the e'_s orbital, because the shift is negligible. This assignment has been confirmed by a modified CNDO calculation which yields 10.1 and 10.9 eV for the first two ionization potentials of vinylcyclopropane[7].

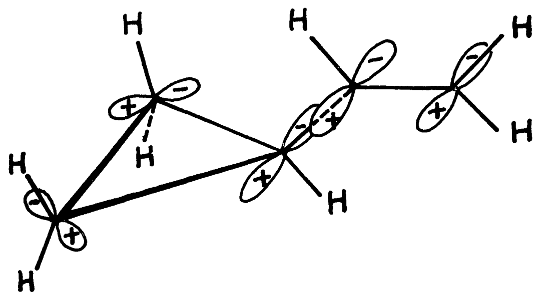


Fig. 3. Conformation of Vinylcyclopropane

The assignment of the other bands are not so obvious as that of the first two and will be discussed in a forthcoming paper.

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