Photoelectron Spectra of Allene and Keten; Jahn–Teller Distortion in the Ionisation of Allene

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Summary The photoelectron spectrum of allene shows the effect of Jahn–Teller instability in the ion, and the symmetry of the molecule gives rise to an electronic structure differing greatly from that of the isoelectronic molecule, keten.

DESPITE the formal similarity between keten and allene (they are isoelectronic), their photoelectron spectra, and hence their electronic structures, differ greatly. In the keten spectrum, the first band (numbering from lowest ionisation potential) probably relates to ejection of an electron from an orbital centred on oxygen but partly delocalised over the $C{=}C$ region, since both in-phase and out-of-phase CCO stretching vibrations occur (ν_2, ν_4). Also the resemblance to the first band in the spectrum of formaldehyde[1] is stronger than to that of ethylene.[1] This assignment differs from that given by Price,[2] who related the first ionisation (measured from Rydberg series convergence) to that of a $C{=}C$ π-electron. In allene, however, the first I.P. is probably due to π-electron loss (*cf.* ethylene, I.P. 10·51 ev). The first band in the allene spectrum is moreover much more complex than that of the keten spectrum, although only two more atoms are present in the molecule.

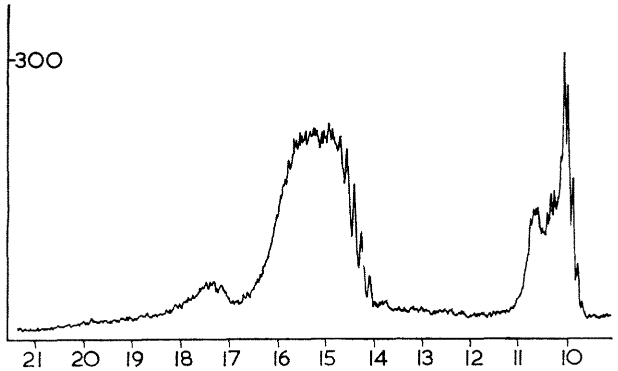

FIGURE 1. *Photoelectron spectrum of allene vapour, obtained using the* He 584 Å *resonance line.* [*Ordinate, counts per second; abscissa, ionisation potential* (ev)].

It has been noticed[1] that in the ionisation of tetrahedral molecules, in which an electron is lost from the (pt_2) orbital (in methane) or from the corresponding degenerate (π_e) orbital in monohalogeno-methanes, the ion shows evidence of Jahn–Teller distortion. In the photoelectron spectrum,[1] this takes the form of a double maximum,[3] indicating two electronic states, separated by 0·6—0·8 ev.

A similar situation arises in allene in that the ground ionic state, if this results from π-electron loss, should be subject to Jahn–Teller distortion to a configuration with unequal $C{=}C$ bond lengths and possibly unequal C–H bond lengths and bond angles. There is one $C{=}C$ vibrational mode (ν_6) and two C–H modes (ν_5, ν_7) which have the property of removing the electronic degeneracy which would follow this ionisation.

In the photoelectron spectrum (Figure 1), we see a marked double maximum (at 10·0 and 10·6 ev), together with vibrational fine structure which is complex (as expected in cases where Jahn–Teller distortions occur). A regular series of peaks can be seen below 10 ev, the mean spacing indicating a vibration of frequency 720 cm.$^{-1}$. This seems only interpretable in terms of the *symmetric* C=C stretching mode, which has a molecular frequency of 1073 cm.$^{-1}$. The large change in intensity between the peaks at 10·04 and 10·10 ev, and the variation in the intensities of the peaks between 10·1 and 10·4 ev, may be a result of the superimposition of peaks associated with vibration in higher frequency antisymmetric modes, which would not in this case form regular progressions.† This interpretation assumes that the only ionisation occurring in this region of the spectrum is π. (*Cf.* ethylene,[1] where the highest σ-level has an I.P. greater than 12 ev).

Ionisation energies of allene and keten, and the vibrational frequencies in some of their ionic states.

Ionic state	Ionisation energy (ev)	Results by other workers	Vibrational frequencies observed and assignments (cm.$^{-1}$)	Molecular frequencies[4] (cm.$^{-1}$)
Allene $\tilde{X}$	9·69(a), 10·0(v)	10·19(S)[5] 10·16(EI)[6] 9·62(PI)[7]	720 ν_3(Symm. C=C stretch)	1073
$\tilde{A}$	10·6(v)			
$\tilde{B}$	14·10(a), 14·9(v)		1090 ν_2(Symm. CH_2 def.)	1443
$\tilde{C}$	15·4(v) ?			
$\tilde{D}$	17·4(v)			
$\tilde{E}$	19·5(v) ?			
Keten $\tilde{X}$	9·64(a)	9·605(S)[2]	2140 ν_2(CCO out-of-phase stretch) 1020 ν_4(CCO in-phase stretch)	2153 1118
$\tilde{A}$	13·84(a)		1130 ?	
$\tilde{B}$	14·62*		940 νf(CCO in-phase stretch)	1118
$\tilde{C}$	16·08(a)		1020 ν_3(CH_2 def.)	1388

* First measurable peak. The true adiabatic I.P. may be obscured by the second band.
(a) = adiabatic. (v) = vertical. (S) = spectroscopic. (EI) = electron impact. (PI) = photoionisation.

The second spectral band has regular fine structure corresponding to a vibrational frequency of 1090 cm.$^{-1}$, which probably relates to the excitation of a CH_2 deformation.

In the spectrum of keten the third band (Figure 2) is very similar to the second in the formaldehyde spectrum,[1] and occurs at approximately the same energy. Comparison with the molecular orbitals of formaldehyde suggests that the second excited state of CH_2CO^+ should come from an orbital which is CCO π-bonding, and hence the vibration excited, with a frequency of 940 cm.$^{-1}$, may be ν_4.

The fourth band contains a vibrational series corresponding to a frequency of 1020 cm.$^{-1}$. The strongly bonding nature indicated for this orbital precludes the mode excited from being ν_4, for a large change in ω must be expected, and it is more likely to be the CH_2 deformation ν_3. This assignment might be tested by a study of [$^2H_2$]keten. The fine structure disappears at about 16·7 ev. This may be the result of two overlapping bands in the 16—18 ev region, or the dissociation of the CH_2CO^+ ion at this energy.

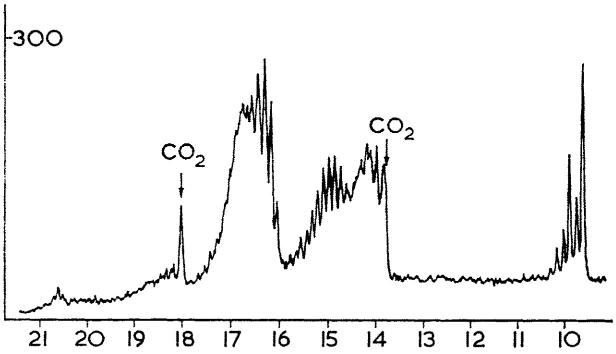

FIGURE 2. *Photoelectron spectrum of keten vapour, obtained using the* He 584 Å *resonance line.* [*Ordinate, counts per second; abscissa, ionisation potential* (ev)].

The ionisation energies of allene and keten, and the vibrational frequencies in the various ionic states, are tabulated.

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† *Note added in proof.* We should not exclude the possibility that a perturbation of the ionisation continuum at 584 Å by an autoionising process is responsible for this irregularity.

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