The Electronic Structure of Cyclopropenone

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Summary Non-empirical LCAO–MO–SCF calculations with Gaussian-type functions have been performed on cyclopropenone and some of its transformation products.

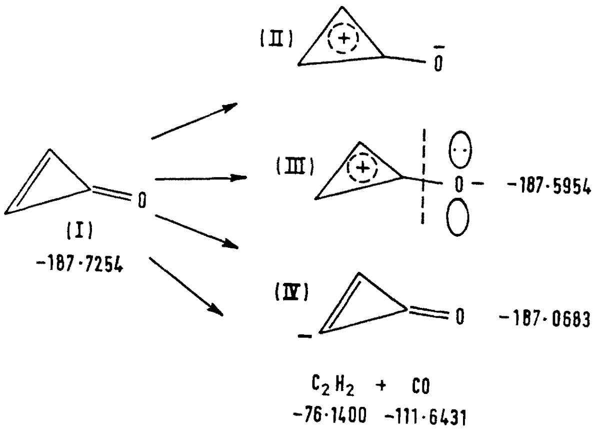
THE reactions of cyclopropenone (I),[1,2] suggest that the molecule possesses considerable conjugative stabilization. We now report the results of a non-empirical LCAO–MO–SCF investigation of the electronic structure of cyclopropenone and some of its transformation products which support this view. The calculations described in this work have been carried out as previously described,[3] using a basis set of 5*s* and 6*p* Gaussian-type functions (G.T.F.) for each carbon and oxygen, and 2*s* for each hydrogen, a total of 48 G.T.F. for cyclopropenone. The geometry of the cyclopropenone ring system was taken to be that of cyclopropene[4] with a C–O bond length of 1·21 Å as in formaldehyde.[4]

On the basis of the substantial delocalization energy of cyclopropenyl cation, it has been suggested[1] that in valence bond formalism (II) makes a considerable contribution to the ground state wavefunction of cyclopropenone. It is therefore of interest to calculate the energy involved in localizing a lone pair of electrons in a $2p_z$ orbital on the oxygen atom (I) → (III). This amounts to an energy loss of no less than 81·6 kcals/mole, which indicates the large delocalization energy of the π-system of cyclopropenone.

Gross atomic populations for cyclopropenone

Atom	σ	π	Total
O	7·019	1·363	8·382
C(1)	4·710	0·815	5·525
C(2), C(3)	5·451	0·911	6·362
H(1), H(2)	0·684	—	0·684

The gross atomic populations are shown in Table 1. A striking feature is the small σ-electron drift to oxygen. There is a substantial migration of electrons from C(1) and the hydrogens to C(2) and C(3) and an overall π-electron drift from the carbons to oxygen. The total dipole moment is calculated to be 3·58 D. The electron population on the vinylic hydrogens (0·684e) may be compared with that in cyclopropene (0·766e) computed with a comparable basis set.[3] This substantial difference is reflected in the large shift[1,2] of 2 p.p.m. to low field in the ^{1}H n.m.r. spectra in going from cyclopropene to cyclopropenone.



Energies in a.u.

A further point of interest is the acidity of these vinylic hydrogens in the two molecules. The calculated energy change (I) → (IV), 412·32 kcals/mole, may be compared with that previously reported for the corresponding process in cyclopropene 425·25 kcals/mole,[3] and indicates the much higher acidity of the hydrogens in the carbonyl compound.

As we have previously indicated[5] the basis set employed in these calculations can provide good estimates of enthalpy changes in organic reactions. The calculations indicate that the decarbonylation of cyclopropenone (I) → C_2H_2 + CO is exothermic to the extent of 36·21 kcals/mole and this coupled with the favourable entropy change would indicate that the transformation is thermodynamically very favourable. However a concerted mechanism in which C_{2v} symmetry is retained is readily shown to be symmetry-forbidden in the ground state, and the relatively high temperatures required for the decarbonylations, provide confirmation for this.[1]

Applying Koopman's theorem the first two ionization potentials of cyclopropenone are calculated to be 9·54 ev and 11·26 ev, for the removal of a σ and π electron respectively. This is in striking contrast to cyclopropene where the ionization potentials are almost the same 9·73 ev and 11·42 ev, but the assignment is *reversed* and the first ionization corresponds to removal of a π-electron.

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