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THE PHOTOELECTRON SPECTRA OF CYCLIC KETONES

David Chadwick, D.C. Frost, and Larry Weiler[1]

Department of Chemistry, University of British Columbia,
Vancouver 8, British Columbia, Canada

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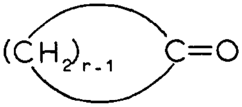
Recently we have utilized photoelectron spectroscopy (PES) to study the ionization potentials of some organic ketones.[2] Now we have extended this study to the simple cycloalkanones 1 (r = 4-8). The results of the high resolution He I PE spectra of these compounds are summarized in the table. In each spectra the first IP is assigned to ionization from one of the oxygen n levels. The strong 0-0 component of the first band for r = 5-8 demonstrates



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Photoelectron Spectra of Cyclic Ketones 1.

r	n IP (eV)[a]	σ Onset (eV)
4	9.61 (very complex)	11.4
5	9.25 (710 and 1220 cm^{-1})	11.3
6	9.14 (627 and 1229 cm^{-1})	10.9
7	9.17 (665 and 1233 cm^{-1})	10.6
8	9.09 (740 and 1267 cm^{-1})	10.3

[a] Vertical IP, ±0.02 eV (st. dev.).

[b] Vibrational spacings in parentheses, ±40 cm^{-1}.

the essentially non-bonding character of the orbital concerned. In contrast, the first IP of cyclobutanone appears as a broad PE band. Cocksey, et al., have recently reported the first IP's for 1 (r = 5-7);[3] their values for cyclopentanone (9.28 eV) and cyclohexanone (9.16 eV) agree very well with the above vertical IP's. But there is a significant difference in their first IP of cycloheptanone (9.49 eV) and our vertical IP. In our results there is a definite trend to lower IP as the ring size increases. This trend may be attributed to the ability of an alkyl group to lower the IP of a similar type level in a homologous series. This alkyl effect has been found in the PES of a series of aliphatic aldehydes, ketones, iodides, and ethers.[3] However, the effect of an alkyl substituent γ and δ to the site of the "lone pair" is not clear cut.

Several years ago, Cook[4] obtained a correlation of oxygen n IP with the carbonyl stretching frequency (ν_{CO}) for a large number of carbonyl compounds. In the figure is shown

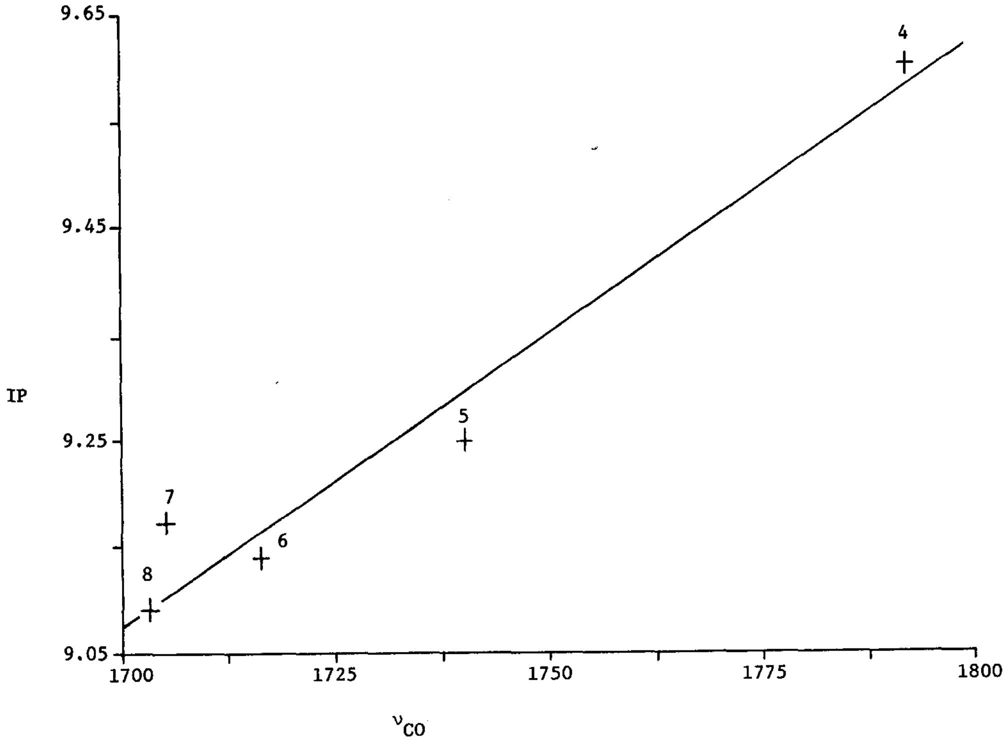

Figure I. Plot of first photoelectron IP (eV) versus ν_{CO} (cm^{-1}) for 1 (r = 4-8).

a similar plot of ν_{CO} versus our PES n IP's for the cyclic ketones. There is a good least squares fit between ν_{CO} and IP. Since these first IP's correspond to ionization from an orbital in the σ network of the molecule, this correlation indicates that the ring effect is transmitted mainly *via* the σ network rather than the π network. Furthermore, it offers experimental support to the postulate that the ν_{CO} shifts in cyclic ketones are due to hybridization effects in the σ frame of the ring.

The first IP of cyclobutanone is significantly greater than all the other cyclic ketones we have measured. We cannot explain this large stabilization of the n level in cyclobutanone in terms of interactions of the n orbital with the Walsh orbitals of the cyclobutyl ring.[5-7] The stabilization of the n level in cyclobutanone is probably due to the hybridization changes in the four-membered ring (*vide supra*). The broadness (*cf*. Table) of the cyclobutyl n IP may be due to weak interactions between the n orbital and the lowest unoccupied σ^* orbital and/or one of the highest occupied σ orbitals. It has been suggested [8] that the shift of the uv maximum of cyclobutanone (4.405 eV) compared to cyclopentanone (4.132 eV), $\Delta E = 0.373$ eV, is due to a destabilization of the π^* orbital in cyclobutanone as a result of hybridization changes. In contrast, however, the PE results would indicate that the changes in the ground state, due to hybridization effects, may also be important, Δ(n IP) = 0.36 eV.[9]

(1) Address correspondence to this author.

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