The Electronic Structure of Cyclopropanone

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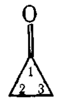
Abstract: The ultraviolet photoelectron spectrum of cyclopropanone has been investigated. Theoretical computations (ab initio, MINDO/3, and CNDO/S) together with the photoelectron spectra of other simple ketones have been used to interpret the spectrum of cyclopropanone and to probe the electronic structure of the molecule. The nonbonding molecular orbital for cyclopropanone is substantially delocalized throughout the molecule. The mode of delocalization is an interaction between the in-plane p atomic orbital on oxygen and the antibonding Walsh molecular orbital on the ring as suggested earlier by Jorgensen and Salem. It has been concluded that photoelectron spectroscopy used in conjunction with molecular orbital calculations provides an excellent means of estimating the amount of delocalization of nonbonding molecular orbitals.

The simplest cyclic ketone cyclopropanone has generated considerable interest among organic and physical chemists for many years.[1] The parent molecule was first synthesized by Turro and Hammond[2] and by DeBoer and co-workers.[3] Its geometric structure has since been studied by microwave spectroscopy[4] and by electron diffraction.[5] Thomas and coworkers[6,7] have made an extensive study of the gas-phase photochemistry of cyclopropanone and have measured its heat of formation from the appearance potential of the $C_2H_4^+$ ion.[7] Several theoretical studies of cyclopropanone at various levels of approximation have been reported.[8-13] Of primary concern in most of the theoretical studies was whether the most stable isomer of C_3H_4O is the classical closed ring ketone **1** or one of the tautomers, oxyallyl **2** or allene oxide **3**. The extended Hückel method[8] predicts that **2** is more stable than **1** by 23 kcal/mol and that **2** is more stable than **3** by 21 kcal/mol. However, all of the other methods predict **1** to be more stable than **2** by varying amounts (MINDO/2, 78 kcal/mol;[9] INDO, 220[11] and 232 kcal/mol;[12] ab initio, 83 kcal/mol;[12] and MINDO/3, 66 kcal/mol[13]). The microwave spectral study[4] also strongly indicates that the most stable isomer is **1**, although the C_2–C_3 bond is quite long (1.575 Å).



1

2

3

Another interesting aspect of cyclopropanone chemistry is the interaction of the nonbonding electrons on oxygen with the strained σ bonds of the cyclopropane ring. Jorgensen and Salem[14] have pointed out that the in-plane p atomic orbital on oxygen has the proper symmetry to interact with the lowest antibonding Walsh orbital of the cyclopropane ring. The magnitude of this interaction, which lowers the energy of the nonbonding orbital while raising that of the unoccupied σ_{cc}^* orbital, should become apparent from the photoelectron spectrum of **1**.

In view of the considerable interest in cyclopropanone among experimentalists and theoreticians, a study of its photoelectron spectrum would seem desirable. This paper reports the UV photoelectron spectrum of cyclopropanone. Theoretical computations (ab initio, MINDO/3, and CNDO/S), qualitative considerations of orbital interactions, and the photoelectron spectra of several other simple ketones have been employed in our interpretation of the spectrum of **1**. It should be noted that Schweig and co-workers[15] have reported recently the photoelectron spectra of cyclopropenone, 2,3-di-*tert*-butylcyclopropenone, and *trans*-2,3-di-*tert*-butylcyclopropanone, and Wiberg and co-workers[16] have studied the photoelectron spectra of some molecules related to those in this study (methylenecyclopropane, methylenecyclobutane, methylenecyclopentane). To our knowledge, the photoelectron spectrum of the labile cyclopropanone has not yet been studied.

Experimental Section

Compounds. Cyclopropanone was prepared by a procedure similar to that developed by Turro and Hammond[2] and purified by the method of Rodriguez, Chang, and Thomas.[7] Samples of **1** were distilled from −63 to −196 °C under vacuum prior to use. Mass spectral analysis indicated that **1**, obtained in this manner, contained less than 2% cyclobutanone. All other ketones employed in this work were purchased commercially and used without further purification except for extensive degassing in the volatile inlet system of the photoelectron spectrometer.

Photoelectron Spectra. The photoelectron spectra were obtained on a Perkin-Elmer PS 18 photoelectron spectrometer. For all of the spectra reported, the He I resonance line at 21.22 eV was used for excitation. Xenon and argon were employed as internal calibrants. The resolution, as determined by the width at half maximum of the Xe^+ $^2P_{3/2}$ peak was approximately 30 meV in these studies. The cyclopropanone sample was maintained in the volatile inlet probe of the spectrometer at a temperature of −55 °C to minimize decomposition and polymerization.

Theoretical Computations. Two SCF molecular orbital procedures were employed primarily in this work. One was the MINDO/3 SCF MO method recently developed by Dewar and co-workers.[17] The other was the ab initio SCF MO method of Pople and co-workers (the Gaussian 70 program).[18] For the MINDO/3 calculations complete geometry optimizations were performed, the only constraints being that the symmetries of the molecules be maintained. The geometries employed for the ab initio calculations were in general the optimum geometries predicted by MINDO/3, although an ab initio calculation was also performed for the experimental geometry[4] of cyclopropanone. The ab initio SCF energy was slightly lower for the experimental geometry than for the MINDO/3 geometry (by ca. 0.09 eV), but the change in electronic distribution, which is the parameter most critical to our spectral interpretation, was negligible. Most of the ab initio calculations reported here utilized an STO-3G basis set, but calculations on cyclopropanone and acetone were also performed with an extended 4-31G basis set. The CNDO/S MO method developed by Jaffé and co-workers[19] has also been employed for cyclopropanone. Koopmans' approximation has been assumed for all vertical ionization potentials calculated in this work.

Results

The photoelectron spectrum of cyclopropanone is shown in Figure 1. The first bands of the photoelectron spectra of cyclopropanone, cyclobutanone, cyclopentanone, and acetone are presented in Figure 2. The experimental and theoretical vertical ionization potentials for cyclopropanone are given in Table I along with possible assignments. Table II contains the vertical ionization potentials measured and calculated for the n_O and π bands for each ketone. Figure 3 shows the orbital electron densities at the various centers as calculated by the

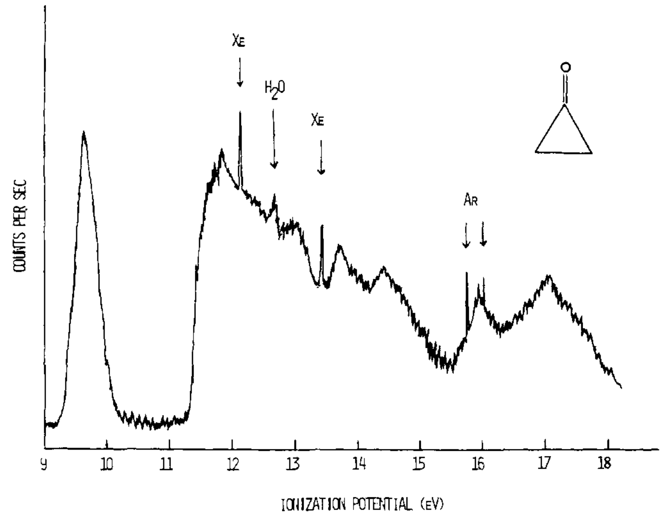


Figure 1. The photoelectron spectrum of cyclopropanone. The excitation source was the 584-Å resonance line of helium.

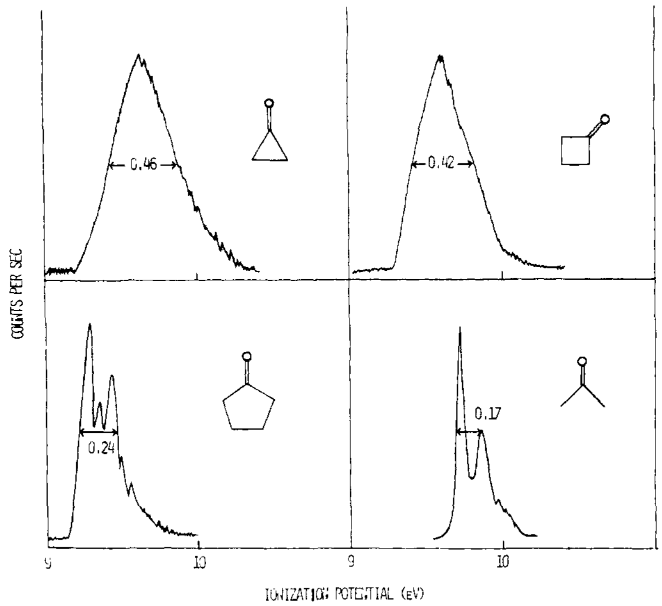


Figure 2. The 9-11-eV region of the photoelectron spectra of cyclopropanone, cyclobutanone, cyclopentanone, and acetone. The excitation source was the 584-Å resonance line of helium.

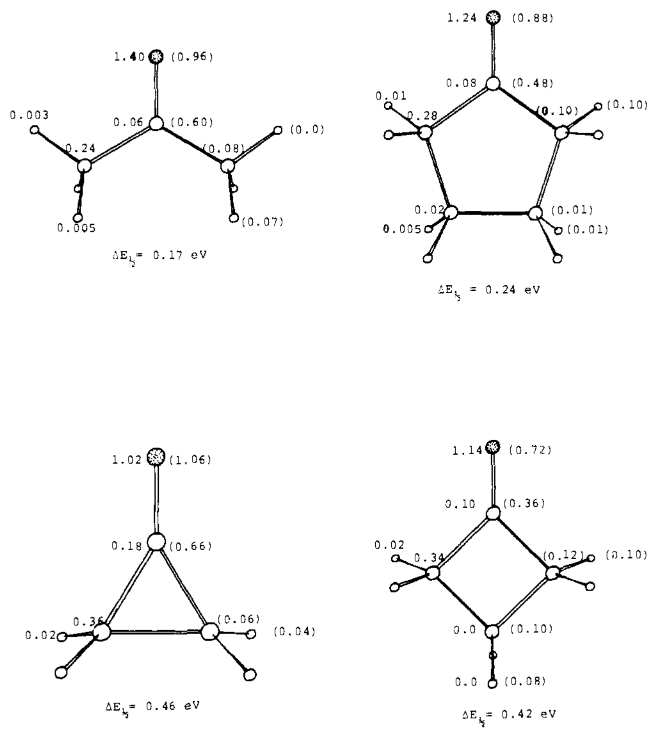


Figure 3. The calculated orbital electron densities at the various centers for the n_0 molecular orbital and the π molecular orbital (the latter in parentheses) for the four ketones. The width at half maximum ($\Delta E_{1/2}$) for the n_0 ionization band for each ketone is also given.

ab initio method for the so-called "lone-pair" molecular orbital (n_0) and the carbonyl π molecular orbital for the four ketones. The orbital electron density on atomic center i is defined to be $q_i^{\mu} = \Sigma 2a_{ij}^2$, where a_{ij} is the coefficient in molecular orbital μ of atomic basis function j on center i. The width at half maximum ($\Delta E_{1/2}$) of the first band in the photoelectron spectrum of each ketone is given also in Figure 3.

Discussion

The photoelectron spectra of cyclobutanone,[20] cyclopentanone,[20,21] and acetone[22] have all been previously reported. They were repeated only to obtain an accurate measure of the widths at half maximum of the n_0 band on our instrument and the $\pi - n_0$ difference. Our ionization potentials, and vibrational spacings where measureable, were in good agreement with the previously reported values.

Because of the extreme lability of cyclopropanone and the difficulty of preparing the material in quantity, it was necessary to scan its photoelectron spectrum quickly in order to obtain a complete spectrum before the sample was exhausted. Thus, although several samples were employed in accumulating spectra, the signal/noise (S/N) ratio was lower than is the case when more "stable" molecules are studied. As a result, errors attributed to the measured vertical ionization potentials are rather large (±0.1 eV) for all bands other than the first two (±0.02 eV). The S/N ratio was also too low to identify any band positions in the 18-21-eV region. Nevertheless, we did resolve seven ionization bands in the 9-18-eV region, which is precisely the number expected in this region as predicted by both the ab initio and MINDO/3 calculations. There is no doubt that the lowest energy band (I_1) in the spectrum at 9.63 eV corresponds to removal of an electron from the predominantly nonbonding molecular orbital n_0. This value may be compared to a reported adiabatic first ionization potential of 9.34 ± 0.05 eV obtained by mass spectrometry.[23] If appropriate scaling factors are employed, both theoretical methods predict that the second ionization band at 11.88 eV should correspond to ionization of a σ molecular orbital transforming under irreducible representation a_1 in point group C_{2v}.

The assignment of the ionization potential corresponding to the carbonyl π MO is less certain. The ab initio method predicts that the third band in the spectrum at 12.9 eV should refer to the $\pi_{C=O}$ orbital. However, the ab initio difference in energy between n_0 and π ($\pi - n_0$) predicted is 3.57 eV, which might imply that our I_4 band at 13.7 eV would better correspond to the π MO. In addition, MINDO/3 predicts that I_4 at 13.7 eV should be the π band with a calculated $\pi - n_0$ difference of 4.08 eV, in remarkable accord with the experimental $I_4 - I_1$ of 4.07 eV. It is well known that all semiempirical SCF MO methods including MINDO/3 are notorious for predicting some σ molecular orbitals to be too unstable (low ionization energy) when π electrons are present in the molecule.[24]

Table I. Vertical Ionization Potentials for Cyclopropanone[a,b,c]

Exptl	Ab initio	MINDO/3
9.63 ± 0.02 b_2 (n_O)	8.25 $4b_2$ (n_O)	9.05 $3b_2$ (n_O)
11.88 ± 0.02 a_1	11.11 $8a_1$	11.00 $5a_1$
12.9 ± 0.1 b_1 or a_2 (π)[d]	11.82 $2b_1$ (π)	12.38 $1a_2$
13.7 ± 0.1 a_2 or b_1 (π)[d]	13.70 $1a_2$	13.13 $2b_1$ (π)
14.4 ± 0.1 b_2 or a_1	15.12 $3b_2$	14.24 $4a_1$
15.9 ± 0.1 a_1 or b_2	15.85 $7a_1$	14.63 $2b_2$
17.0 ± 0.1 b_1	17.18 $1b_1$	16.43 $1b_1$
	19.01 $6a_1$	19.21 $3a_1$

[a] All values are in eV. [b] Only experimental values up to 18 eV have been tabulated because the sensitivity of our instrument was poor in the range 18–21.22 eV. [c] Symmetries of irreducible representations under which the eigenvectors transform refer to the C_{2v} point group with the molecular plane being σ_{xy} and the plane normal to the molecular plane being σ_{xz}; MINDO/3 contains no 1s basis orbitals for C or O, hence the apparent discrepancy in numbering the orbitals. [d] See text.

Nevertheless, it can be seen in Table II that MINDO/3 does a very good job of predicting the $\pi - n_O$ difference for the other three ketones. It also should be noted that the π ionization energy for formaldehyde is 14.4 eV,[25] so 13.7 eV is reasonable since the π MO on cyclopropanone, like that in formaldehyde, is quite localized (Figure 3). However, the lower π ionization energy for acetone (12.46 eV) tends to support the 12.9 eV value for cyclopropanone. Schweig et al.[15] do not discuss the π ionization process in their work which mentions di-*tert*-butylcyclopropanone. The predicted assignments for bands I_5 and I_6 at 14.4 and 15.9 eV, respectively, are inverted by the two theoretical methods, but both methods agree that I_7 at 17.0 eV should be assigned to ionization corresponding to a b_1 (σ) molecular orbital.

Turning our attention now to the data in Table II, it is evident that the experimental first ionization potential of cyclopropanone (9.63 eV) which must correspond to the b_2 nonbonding MO is slightly higher than that for cyclobutanone (9.60 eV) and substantially higher than that for cyclopentanone (9.28 eV). It is interesting that neither the MINDO/3 nor the ab initio calculations correctly predict the actual trend in the ionization potentials for the nonbonding electrons. However, the qualitative orbital interaction arguments of Jorgensen and Salem[14] nicely rationalize the fact that the n_O orbital in **1** is lower in energy than that in either cyclobutanone or cyclopentanone. The stability of the n_O orbital in **1** results from the interaction of the in-plane p orbital with an antibonding Walsh orbital as shown in Figure 4. Simply, the σ^* orbital of cyclopropanone is lower in energy than in the less strained cyclobutanone and cyclopentanone, and consequently is better able to interact with the n_O orbital.

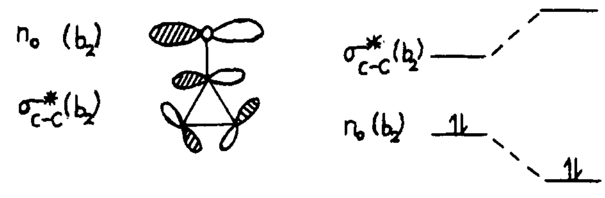


Figure 4.

Since both the ab initio and the MINDO/3 methods did not include configuration interaction (CI), it is not surprising that they underestimate the effect of mixing an excited orbital with n_O. When the CNDO/S method, which includes some CI, is used to calculate the ionization potential corresponding to n_O in **1**, a value of 9.96 eV is obtained. Thus the CNDO/S value is closer to the experimental value than either MINDO/3 or STO-3G, presumably as a result of inclusion of CI. The $\pi - n_O$ difference calculated by CNDO/S is 3.33 eV, providing further support for the experimental 12.9 eV ionization potential being due to ionization of b_1 (π) as the experimental $I_3 - I_1$ is 3.27 eV. It should be pointed out that a 4-31G ab initio calculation without CI also increases I_1 for cyclopropanone to 10.44 eV, a_1 (σ) to 12.76 eV, and b_1 (π) to 14.04 eV, which is a reasonable fit of the experimental results. However, the extended basis set calculation underestimates the $\pi - n_O$ difference by over 1 eV for acetone.

An examination of the spectra in Figure 2 reveals that the widths of the n_O band for the four ketones decreases in the order cyclopropanone > cyclobutanone > cyclopentanone > acetone, with the latter two ketones exhibiting well-resolved vibrational structure. The half-widths of these bands are tabulated in Figure 3. The width at half maximum of a photoelectron spectral band is indicative of the amount of geometry reorganization upon ionization, and so reflects the bonding character of the molecular orbital being ionized.[26] It has long been recognized that a pure nonbonding molecular orbital should give rise to a sharp spike in the photoelectron spectrum corresponding to the adiabatic $0 \leftarrow 0$ transition from the ground vibrational state of the molecule to the ground vibrational state of the ion. Such pure nonbonding molecular orbitals are rarely encountered. Theoretical calculations have always predicted that nonbonding molecular orbitals are delocalized, and it was a great triumph in quantum chemistry when photoelectron spectroscopy verified this. Thus, our trend of decreasing widths at half maximum of the n_O band should provide at least a qualitative measure of the bonding character (or delocalization) of n_O, and it is clear that cyclopropanone indeed contains the most delocalized n_O. This is the basis for our conclusion that substantial interaction of the oxygen in-plane p orbital with an antibonding Walsh orbital of the cyclopropane ring occurs. Cyclobutanone also has a substantially delocalized n_O, and consequently no vibrational structure was resolved in the n_O band. Cyclopentanone and acetone have much more localized "lone pairs" as is evidenced by their narrow n_O band and the fact that the lowest energy vibrational peak for each is the most intense, i.e., their adiabatic and vertical ionization potentials are equal. The ab initio (Figure 3) and MINDO/3 calculations reproduce this trend of delocalization for the four ketones. In all cases MINDO/3 predicts greater delocalization of the n_O orbital than does ab initio (for MINDO/3, the orbital electron density on oxygen is predicted to be as follows: cyclopropanone, 0.63; cyclobutanone, 0.71; cyclopentanone, 0.84; acetone, 0.98), while CNDO/S predicts the n_O orbital of cyclopropa-

Table II. Vertical Ionization Potentials Corresponding to the n_O and π Molecular Orbitals for Several Ketones[a]

Ketone	Exptl		Ab initio		MINDO/3	
	n_O	π	n_O	π	n_O	π
Cyclopropanone	9.63	12.9 or 13.7[b]	8.25	11.82	9.05	13.13
Cyclobutanone	9.60	11.97	8.60	10.84	9.52	11.72[c]
Cyclopentanone	9.28	11.89	8.57	10.63	9.63	12.04[c]
Acetone	9.72	12.46	8.97	10.77	9.93	12.41

[a] All values are in eV. [b] See text for discussion. [c] The first MO with b_1 (π) character; for cyclobutanone and cyclopentanone a more stable b_1 MO with appreciable π character also was predicted.

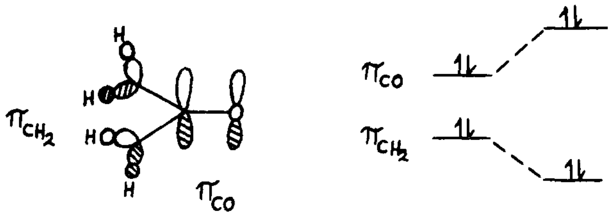


Figure 5.

none to be 84% delocalized. Schweig and co-workers[15] have noted that substitution of two *tert*-butyl groups on cyclopropenone lowers the ionization potential corresponding to the n_O MO and have thus concluded that this orbital is also substantially delocalized in cyclopropenone.

An additional point of interest in the photoelectron spectra of **1** is the existence of an $a_1(\sigma)$ orbital between the n_O and π orbitals. The STO-3G calculations predict this band to be at 11.11 eV, in good agreement with our experimental value of 11.88 eV. This band was not observed in the photoelectron spectra of the other carbonyl compounds investigated, nor is it predicted by the ab initio calculations. Since this $a_1(\sigma)$ orbital is calculated to consist mainly of a bonding Walsh orbital, it is not surprising that its energy lies between the n_O and π orbitals. The observed ionization potential corresponding to the degenerate Walsh orbitals in cyclopropane is 10.9 eV,[25] a value between that reported here for the n_O and π orbitals of 1.

The data in Table I show that the ionization potentials corresponding to the π orbitals decrease as the ring size of the cyclic ketone increases. A simple consideration of π orbital energies based on ring strain would lead to an ordering of ionization potentials opposite to that observed. Hence, if ring strain is important, it must manifest itself in the ionic state rather than the ground state. This would seem unlikely since a change in hybridization of the carbonyl carbon upon ionization is expected to relieve ring strain rather than introduce additional strain.

The orbital electron densities tabulated for the π orbital in Figure 3 demonstrate that this orbital is most localized for cyclopropanone, less so for cyclobutanone, and least for cyclopentanone. An examination of the calculated eigenvectors reveals that this delocalization is the result of the interaction between the π_{CO} orbital and the π_{CH_2} orbitals shown in Figure 5.

This interaction raises the energy of the π_{CO} orbital while lowering that of the π_{CH_2}. Since the energy of the C-H bonds is expected to increase in the order cyclopropanone < cyclobutanone < cyclopentanone, this interaction should be least in cyclopropanone and greatest in cyclopentanone. Hence, the π orbital in **1** lies at lowest energy, as it is destabilized least by interaction with adjacent C-H bonds. Although the ordering of the π ionization potentials is also that expected to result from inductive stabilization of the ionic states, we feel that interaction with adjacent C-H bonds must also play a significant role.

Conclusions

The photoelectron spectrum and ab initio, MINDO/3, and CNDO/S calculations indicate that the b_2 (n_O) molecular orbital of cyclopropanone is highly delocalized. This delocalization is the result of an interaction between the in-plane p orbital on oxygen and an antibonding Walsh orbital of the ring, which undoubtedly accounts for the long C_2-C_3 bond for cyclopropanone in its closed form **1**. Furthermore, the photoelectron spectra and the calculations prove that an a_1 (σ) orbital lies between the nonbonding and π orbitals for cyclopropanone, but not the other ketones studied in this work. The ionization potential corresponding to the π orbital in **1** is higher than that of the other cyclic ketones primarily due to minimal destabilizing interaction with adjacent C-H bonds. It is apparent also that photoelectron spectroscopy, employed together with appropriate theoretical computations, can be used to qualitatively determine the amount of delocalization of nonbonding molecular orbitals.

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