Photoelectron Spectroscopy of Carbonyls. Ureas, Uracils, and Thymine[1,2]

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Abstract: The photoelectron spectra of the six possible methyl ureas, two acyl ureas, and four uracils have been obtained. Many of the low-energy set of ionization events in these molecules have been assigned empirically on the basis of methylation and other substitution effects. The data are then correlated with CNDO/s MO energies and are compared with other semiempirical and ab initio computational results which are available in the literature.

The electronic structures of uracil and thymine, because of their RNA/DNA associations, have been the subjects of numerous experimental[3] and theoretical[4-7] investigations. A urea subunit is common to all of these molecules; thus, aside from its own important biological niche, an understanding of the electronic structure of urea is a necessary preliminary step in the elaboration of those of the biological bases.

The purpose of this paper is to present and interpret the photoelectron spectra of the complete set of methyl ureas, two acyl ureas, some uracils, and thymine. The assignments are empirical and are based on the correlation of experimental ionization energies rather than comparisons with values computed by some semiempirical MO recipe. Thus, heavy use is made of methylation effects,[8] which are tested first for the simple urea system where some reasonably secure assignments already exist.[9-11] CNDO/s[12] calculations are used merely as an a posteriori means of testing the empirical assignments and to provide some general ideas concerning the types of molecular orbital which occur in complex unsymmetrical molecules such as uracil and formylurea.

Photoelectron ionization energies are equated, within the limits of Koopmans' theorem, to absolute values of the orbital energies.[13] Hence, we may, and do, speak interchangeably of the $I(\mu)$ ionization event and the μth MO.

The subset of highest energy filled MO's is usually supposed to be determinative of dative character in donor–acceptor complexes and in charge-transfer interactions. This same subset is also thought to gauge the strength of hydrogen bonding in base pairs and to be rate determining for the intercalation of foreign molecules between base pairs. Indeed, the "frontier MO" approach[14] to intermolecular interactions often limits the subset of interest to either the topmost filled MO or, if the molecule exhibits degeneracies, to the two topmost filled MO's. It is clear that photoelectron spectroscopy can provide the types of information which are essential to the viability of such approaches to intermolecular interactions and chemical reactivities.

Experience with the ureas[9-11] and with the general run of carbonyls[15] has generated a considerable amount of information on low-energy ionization events in these systems. In ureas, these events correspond to removal of electrons from molecular orbitals of the types depicted in Figure 1: The lone pair orbital on oxygen, n, and two π orbitals, π_1 and π_2, where the latter, by symmetry, is confined solely to the nitrogen centers. The totally bonding orbital of urea, π_+, cannot be assigned with any certainty but its binding energy is surely larger than 14 eV.[9-11] Acylation of urea yields formylurea and introduces another oxygen lone pair orbital into the low-energy set of MO's pertinent to urea. The main effect of acylation should consist of a general increase of ionization energies in formylurea and the appearance of an additional low-energy band associable with the introduction of the second oxygen. This second $I(\mathrm{n})$ event, $I(\mathrm{n}_2)$, should occur close to the first $I(\mathrm{n})$ event, $I(\mathrm{n}_1)$, because the splitting of the two n orbitals in β-dicarbonyls[15] is generally approximately equal to 0.8 eV.

Ring closure and the introduction of an ethylenic double bond, which yields a primitive uracil, should give rise to an additional π ionization in the low-energy region and produce some additional spread of the $I(\pi)$ events because of heavy π delocalization within the planar ring system.

Figure 1 depicts the MO coefficients of urea, formylurea, and uracil, as furnished by CNDO/s calculations. The MO's of Figure 1 are useful for qualitative discussions of substituent effects.

Experiment and Calculation

The He(I) photoelectron spectra were obtained on a Perkin-Elmer PS-18 photoelectron spectrometer equipped with a heated probe for vaporizing solids. Resolution prior to each run was 20 to 25 meV, as estimated from the half-width of the Ar $^2P_{3/2}$ line. Calibration of spectra was accomplished using the ^2P lines of Xe and Ar. Sample temperatures ranged from 50 to 177 °C, depending on sample volatility, and were maintained constant within ±2 °C for each spectroscopic run.

Trimethylurea[16] and 1,1-dimethylurea[17] were prepared and purified by published methods. Urea (MCB), uracil (MCB), formylurea (K&K), acetylurea (K&K), dihydrouracil (K&K), 1,3-dimethylurea (Eastman), thymine (Mann Research Labs), and 1,3-dimethyluracil (Pfaltz & Bauer) were repurified by sublimation. Tetramethylurea (MCB) was repurified by distillation.

Published crystal geometries (symmetries) were used in the CNDO/s calculations (QCPE 174) for urea (C_{2v}),[18] uracil (C_s),[19] and dihydrouracil (C_1).[20] The thymine (C_s) geometry was taken from the ab initio calculation of Clementi et al.[7] For molecules for which no published geometry exists, a minimization of total energy with respect to molecule geometry was investigated using CNDO/s calculations, standard bond lengths being retained invariant throughout. It was established by this means that the nitrogen centers of the methylated ureas remain planar as opposed to tetrahedral (cf. ammonia). The minimum energy for both monomethylated and dimethylated nitrogens was found to occur at a CO/NC dihedral angle of 45°. The investigated geometries for formylurea, acetylurea, and 1,3-dimethyluracil were restricted to those in which the skeletal structure remained totally planar. The MO energies reported for these latter three molecules refer, then, to the planar conformation of minimum energy. The point group symmetries which were used are: methylurea, C_1; 1,3-dimethylurea, C_2; 1,1-dimethylurea, C_1; trimethylurea, C_1; tetramethylurea, C_2; formylurea, C_s; acetylurea, C_s; and 1,3-dimethyluracil, C_1.

Results and Discussion

The photoelectron spectra of urea,[9-11] tetramethylurea,[10] and uracil[3a] have been reported. The spectra of these same molecules reported here are essentially identical with those obtained previously; however, there is some variation in the cited ionization energies (IP's). Even considering the broadness

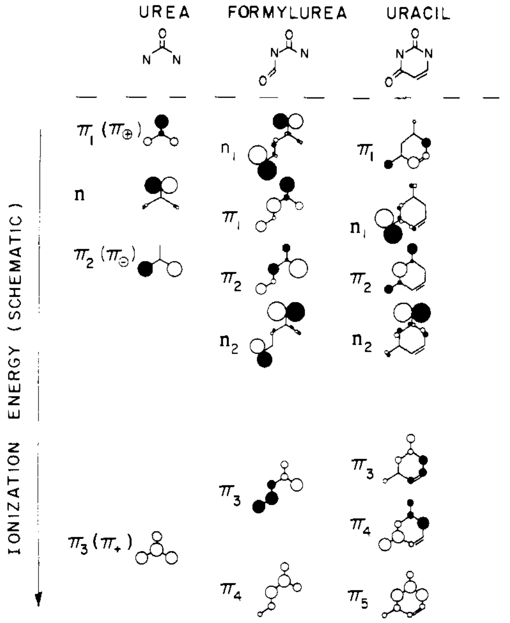

Figure 1. Schematic MO diagrams for urea, formylurea, and uracil as obtained by the CNDO/s algorithm. These diagrams illustrate the notation used in the text. The MO's for any one molecule are arranged in order of increasing binding energy. The connotations of the $\pi_\oplus/\pi_\ominus$symbols[8] are obvious in symmetric molecules but the π_1/π_2 notations, while less specific, are more generally useful.

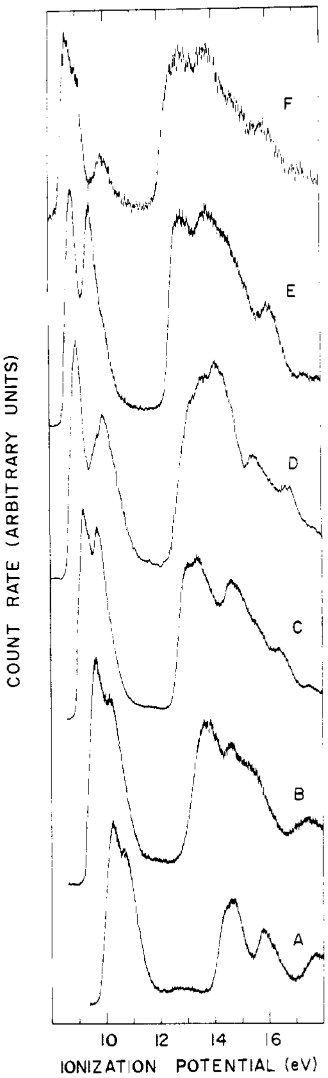

Figure 2. He(I) photoelectron spectra of (A) urea; (B) methylurea; (C) 1,3-dimethylurea; (D) 1,1-dimethylurea; (E) trimethylurea; and (F) tetramethylurea.

of the first ionization band of urea, the agreement among the reported values, including that of Table I, is surprisingly poor. For uracil, for example, the vertical IP's reported by Padva et al.[3a] and those given in Table II are in good agreement except for the fourth and fifth IP's, which differ by 0.16 and 0.10 eV, respectively. The assignments given in Tables I and II for these three molecules agree with those given previously with the exception that the fifth IP of uracil may now be assigned as π solely on the basis of experimental evidence.

Mass-spectrometric appearance potentials (in eV) have also been reported for the complete set of methylureas,[21] uracil [9.82 ± 0.1],[3b] and thymine [9.43 ± 0.1].[3b] The appearance potential for an ion, $V(X^+)$, is

$$V(X^+) = I(X) + KE + EE$$

where $I(X)$ is the adiabatic IP of the molecule, KE is the excess kinetic energy, and EE is the excitation energy imparted to the molecular ion. Although KE is usually negligible, EE may be significant. In view of this, it is not surprising that the reported appearance potentials are higher than even the vertical IP's obtained by PES.

The lowest energy photoelectron spectroscopic ionization energies, IP(1), of uracil and thymine have been reported by Hush and Cheung[22] and, on the basis of INDO computations, assigned as $I(\pi_1)$. The numbers which they cite and their assignment are in accord with the present work.

Methylureas. The photoelectron spectra of urea and its methyl derivatives are shown in Figure 2 for the 9–18 eV range. Ionization energies are listed in Table I. The distinct, poorly resolved feature between 10 and 12 eV in the urea PE spectrum is typical for the whole series. The spectra of the trimethyl and the tetramethyl derivatives demonstrate clearly that this low-energy feature contains three ionization events, two of them fairly sharp and intense, the other being weak and broad or discernible only as a shoulder. This weak shoulder is assigned to the oxygen lone pair orbital, n.[9-11] The two sharp bands are assigned as π_1 and π_2; these are located mainly on the two nitrogen centers and they possess similar shapes in all the ureas. Hence, with some justification, they may also be labeled $\pi_\oplus$ and $\pi_\ominus$, respectively.[11] Methylation produces a decrease of ionization energies, but has a greater effect on $I(\pi)$ than on $I(n)$ ionization events.

The PES data for the ureas can be summarized as follows:

(i) Methylation invariably shifts the $I(\pi_1)$ and $I(\pi_2)$ events to lower energy.

(ii) The low-energy PES features of urea, methylurea, and 1,3-dimethylurea are very similar in shape. The entire feature appears to shift to lower IP by about 0.5 eV per added methyl group.

(iii) In the series 1,1-dimethylurea, trimethylurea, and tetramethylurea, $I(\pi_1)$ shifts but slightly to lower energy, whereas $I(\pi_2)$ continues to destabilize by ~0.5 eV per added methyl group.

(iv) The $I(n)$ event is approximately constant in 1,1-dimethylurea, trimethylurea, and tetramethylurea.

In sum, destabilization of the π_1 and π_2 MO's and insensitivity of the n MO seems to be general.

The shifts of ionization potentials caused by continuing methylation are collected in Figure 3. The different effects of methylation on $I(\pi_1)$ and $I(\pi_2)$ suggest the existence of a saturation effect in the former, while little or no such effect is evident in the latter. The more heavily methylated nitrogen, where present, is expected to be the primary locus of electron density in the π_1 MO. Thus, the continuing methylation of 1,1-dimethylurea to trimethylurea and tetramethylurea should

Table I. Ionization Potentials of Urea and Methylureas (eV)[a]

	IP(1)	IP(2)	IP(3)
Urea[b]	10.28	10.78	
	9.8 (i)		
MO type	(π_1 and n)	π_2	
Methylurea[b]	9.66	10.23	
	9.25 (i)		
MO type	(π_1 and n)	π_2	
1,3-Dimethylurea[b]	9.23	9.73	
	8.9 (i)		
MO type	π_1	(n and π_2)	
1,1-Dimethylurea	8.96	9.93	9.9 ± 0.1
	8.6 (i)		
MO type	π_1	π_2	n
Trimethylurea	8.80	9.45	9.82
	8.5 (i)		
MO type	π_1	π_2	n
Tetramethylurea	8.64	9.98	9.92
	8.35 (i)		
MO type	π_1	π_2	n

[a] The notation (i) following an ionization energy denotes the low-energy initiation point of the band; all others denote vertical ionization energies. The term "initiation point" is used here in order to emphasize the fact that no distinct feature (i.e., one which is clearly identifiable as an adiabatic event) is observed. [b] One of the PES bands of this molecule contains two separate ionization events. These are identified underneath the energy of the band in question.

have only a small effect on $I(\pi_1)$ since the methylation is occurring at a center for which the electron density in the π_1 MO is small. This supposition accords with experiment. The regularity of changes in $I(\pi_2)$, by contrast, is quite striking. The behavior evidenced in Figure 3 suggests that methylation of a less-methylated nitrogen decreases $I(\pi_2)$ by ~0.5 eV, whereas methylation of an already methylated nitrogen decreases $I(\pi_2)$ by ~0.3 eV. The methylation of trimethylurea to yield tetramethylurea is interesting in that the attached methyl adds on a center which is, at once, both "less methylated" and "already methylated". Experiment resolves the dichotomy in favor of the "less methylated" status (see Figure 3). The concentration of MO electron density on the less substituted nitrogen center thus appears to be more controlling of ΔIP(2) than any prior methylation.

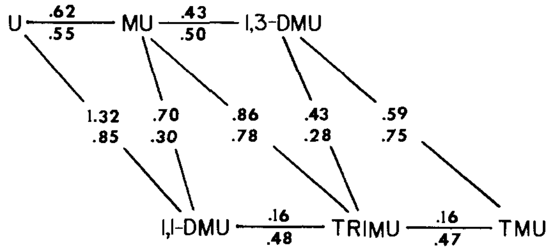

Figure 3. Vertical ionization potential shifts produced by continuing methylation of urea. ΔIP(1) values are above the connecting lines; ΔIP(2) shifts are below the connecting lings. Symbols are: (U) urea; (MU) methylurea; (1,3-DMU) 1,3-dimethylurea; (1,1-DMU) 1,1-dimethylurea; (TRIMU) trimethylurea; and (TMU) tetramethylurea.

The possibility of geometry changes which accompany dimethylation of the same nitrogen center must also be considered. The changes in spectral appearances which occur in the pairs methylurea → 1,3-dimethylurea and methylurea → 1,1-dimethylurea, respectively, are probably due to a sterically enforced rotation of the dimethylated nitrogen group, thus disrupting its conjugation with the carbonyl group. Such a possibility is substantiated by the available crystal geometries: urea[18] is known to be planar and C_{2v} whereas the tetramethylthiourea[23] skeleton is nonplanar and C_2.

Acylureas and Dihydrouracil. The evolution of urea to formylurea or acetylurea and, thence, to the uracils forms a stepwise path along which the effects of substitution on the photoelectron spectra may be followed. The photoelectron spectra, and the ionization energy correlations which they dictate, are shown in Figures 4 and 5, respectively. The IP's are listed in Table II. The low energy PES feature of formylurea, acetylurea, and dihydrouracil is expected to contain four ionization events: two I(n) events associated with the two oxygens and two $I(\pi)$ events which are largely associated with

Table II. Ionization Potentials of Acylureas and Uracils (eV)[a]

	IP(1)	IP(2)	IP(3)	IP(4)	IP(5)
Formylurea[b]	10.58	11.08	11.35	13.9	
	10.2 (i)			13.65 (a)	
MO type	(n_1 and π_1)	π_2	n_2	π_3	
Acetylurea[b]	10.3	10.8	11.1	13.1	
	9.95 (i)			12.75 (i)	
MO type	(n_1 and π_1)	π_2	n_2	π_3	
Dihydrouracil[c]	10.00	10.15	10.3	11.0	12.75
	9.8 (i)				12.45 (i)
$\bar{\nu}_{vib}$, cm^{-1}				1450 (±50)	
MO type	(n_1 and π_1)		π_2	n_2	π_3
Uracil	9.60	10.13	10.55	11.00	12.7
	9.34 (i)				12.5 (a)
$\bar{\nu}_{vib}$, cm^{-1}		1250 (±50)		1500 (±50)	
MO type	π_1	n_1	π_2	n_2	π_3
Thymine	9.20	10.05	10.44	10.88	12.30
	8.95 (i)				12.15 (a)
$\bar{\nu}_{vib}$, cm^{-1}		1300 (±50)		1500 (±50)	
MO type	π_1	n_1	π_2	n_2	π_3
1,3-Dimethyluracil	9.00	9.70	9.85	10.55	11.85
	8.73 (i)				11.70 (a)
$\bar{\nu}_{vib}$, cm^{-1}				1500 (±50)	
MO type	π_1	n_1	π_2	n_2	π_3

[a] The notations (i) or (a) following an ionization energy denote respectively the initiation point of the band or the adiabatic ionization energy when a definite origin band is observed. All others denote vertical ionization energies. [b] IP(1) contains two nearly degenerate ionization events. [c] This molecule is nonplanar and the MO's π_2 and n_2 are actually of heavily mixed σ/π character (see text).

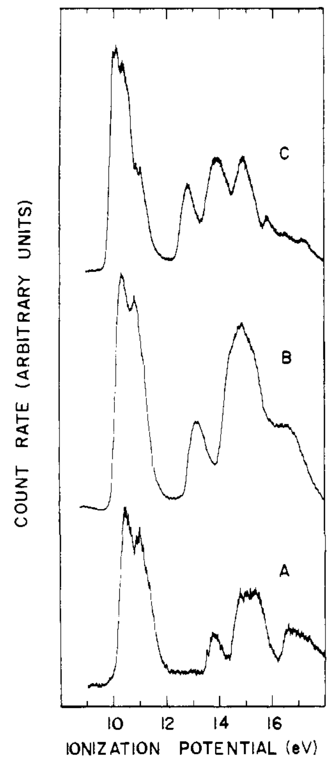

Figure 4. He(I) photoelectron spectra of (A) formylurea; (B) acetylurea; and (C) dihydrouracil.

the two nitrogens. The two $I(n)$ events, since they occur in a β-dicarbonyl, should be separated by ~0.8 eV.[15]

The ionization events at 13.9 eV in formylurea, at 13.1 eV in acetylurea, and at 12.75 eV in dihydrouracil are probably associated with removal of an electron from a π MO of carbonyl nature. This assignment is based on the fact that the corresponding band is absent in the urea spectrum and that the σ orbitals of urea, which are expected to be stabilized by formylation, cannot give rise to any ionization event at these energies. The carbonyl group orbitals of π type are expected to mix in the dicarbonyl, stabilizing the in-phase combination and destabilizing the out-of-phase combination. Hence, the 13.9, 13.1, and 12.75 eV ionizations probably correspond to the out-of-phase $I(\pi)$ event. The large decrease of this ionization energy which occurs upon methylation (i.e., on going from formylurea to acetylurea) is also suggestive of a π nature.

The shoulders at 11.35 eV in the formylurea and at 11.1 eV in acetylurea and the peak at ~11.0 eV in dihydrouracil appear to be associable with the $I(n_2)$ event. These assignments are based on the small relative shifts produced by methylation and on the vibrational structure of 1450 ± 50 cm^{-1} which occurs on the 11.0-eV peak of dihydrouracil and which may be identified as a carbonyl stretch. If the β-dicarbonyl decrement of ~0.8 eV applies to the $I(n_2) - I(n_1)$ separation in these molecules, then $I(n_1)$ may be placed at or near the 10.58-eV peak in formylurea, the 10.3-eV peak in acetylurea, and in the 10.00–10.14-eV region in dihydrouracil.

By elimination, all remaining low-energy ionization events must be associated with $I(\pi_1)$ and $I(\pi_2)$ which connote removal of electrons with heavy densities on the amine nitrogens.

Dihydrouracil is not planar in the crystalline state[20] and questions concerning the validity of retaining $n(\sigma)$ and π differentiations arise. The results of CNDO/s calculations for the nonplanar geometry indicate that the π_2 and n_2 orbitals undergo heavy mixing whereas the π_1 and n_1 orbitals do not and retain, to a large degree, the proper π/σ characteristics.

All feasible assignments are collected in Figure 5.

Uracil, Thymine, and 1,3-Dimethyluracil. The photoelectron spectra of uracil, thymine, and 1,3-dimethyluracil are presented in Figure 6. Ionization energies are collected in Table II.

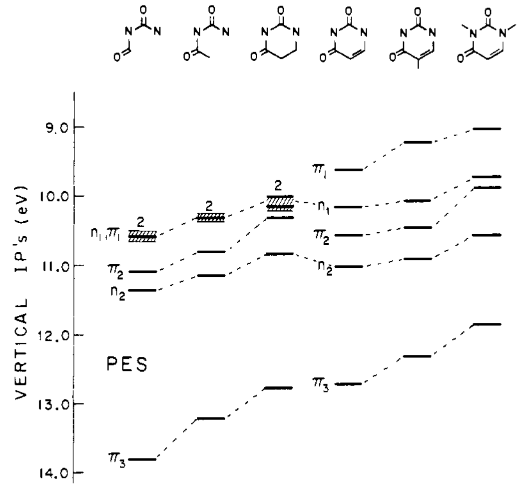

Figure 5. Correlation of the experimental photoelectron spectroscopic data for the five lowest energy ionization potentials of formylurea, acetylurea, dihydrouracil, uracil, thymine, and 1,3-dimethyluracil.

The introduction of the ethylenic double bond produces a fairly rigid molecule and the planar geometry favors π interaction. The low-energy ionization potential of ethylene[24] is $I(\pi) = 10.5$ eV. Consequently, the π_1 and π_2 orbitals of formylurea (Figure 1) are expected to mix heavily with the ethylenic π MO and, as a result, the π_1 MO of uracil should shift to lower ionization energy and all three π ionizations move apart. The larger spread of π-orbital ionization energies which occurs in uracil provides more resolution and permits an unambiguous determination of the first five ionization potentials of this molecule. In particular, some ionizations which had been hidden or which appeared as shoulders in the spectra of Figure 4 become very evident in the uracil spectrum. The fifth ionization potential of uracil is assigned to a π orbital on similar grounds as those outlined for the corresponding band in dihydrouracil. In corroboration of this assignment, the introduction of methyl groups generates σ ionization events at greater than 13.5 eV, but does not affect the integrity of IP(5).

The vibrational structuring of the IP(2) and IP(4) bands serves as a further means of assignment. In the case of uracil and thymine, both β-dicarbonyls, the IP(4) band exhibits an ~1500-cm^{-1} interval and a coincidence of the vertical and adiabatic events. The IP(2) band, on the other hand, exhibits noncoincidence of the vertical and adiabatic events and a lower vibrational interval of 1200–1300 cm^{-1}. These characteristics typify $I(n)$ events in other rigid β-dicarbonyls;[15] that is, a carbonyl stretching mode dominates $I(n_2)$ whereas $I(n_1)$ is dominated by vibronic activity which is peripheral to both the ring and carbonyl groups. Consequently, the $I(n_1)$ and $I(n_2)$ assignments of IP(2) and IP(4) are analogically sound.

The final justification for the assignment of the uracil spectrum is provided by methylation effects. Methylation is not expected to affect the $I(n)$ energies because of the heavy localization of the corresponding MO's on the oxygen centers. Methylation is expected to affect the $I(\pi)$ events because the π MO's possess large electron densities on those centers which can be methylated. Thus, methylation in the 5 position (i.e., on the C=C bond) should shift $I(\pi_1)$ and $I(\pi_3)$ considerably, whereas $I(\pi_2)$ should remain essentially constant (cf. Figure 1). On the other hand, methylation in the 1 and 3 positions should decrease all of the first three $I(\pi)$ events, $I(\pi_2)$ somewhat more than the others. Thus, in 1,3-dimethyluracil, the $I(\pi_2)$ event is shifted so much that it almost coincides with $I(n_2)$ and effectively obliterates the vibrational fine structure which

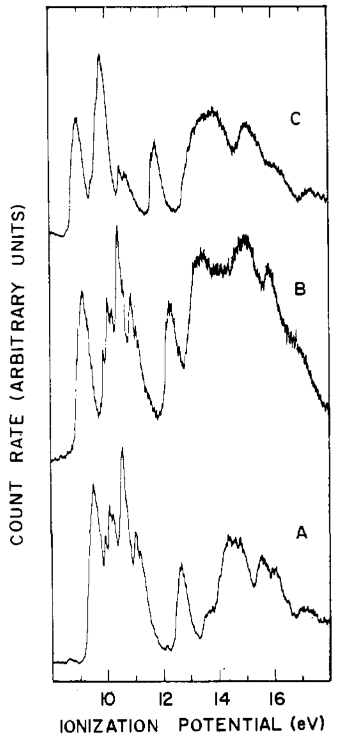

Figure 6. He(I) photoelectron spectra of (A) uracil; (B), thymine; and (C) 1,3-dimethyluracil.

characterizes the $I(n_2)$ process. This simple outline of methylation effects agrees exactly with the experimental behavior, at least as the data are correlated in Figure 5.

Given some measure of confidence in CNDO/s eigenfunctions, one may use these, in conjunction with perturbation theory, to discuss methylation effects. The total shift of $I(\mu)$ due to first-order inductive and second-order conjugative contributions is found to be proportional to the sum of squares of the AO coefficients at the substituted centers in the μth MO and is given by[25]

$$\Delta I(\mu) = k \sum_j c_{j\mu}{}^2$$

where the index j denotes substituent positions. The application of this equation to the molecules of interest here was attempted. Unfortunately, the agreement of experiment and theory was not satisfactory.

Conclusion

The major point of this work is the demonstration that photoelectron spectroscopic assignments for molecules as complex as uracil may be made solely on the basis of empirical data. All that is needed is an appropriate sequence of substitutions which lead smoothly from a simple molecule, in which the assignments have been established, to the complex one, in which they have not. By this means, coupled with some symmetry ideas concerning the shapes of MO's, the present work has managed to extrapolate the assignments for uracil from those which have been substantiated for urea.

The significance of the work is threefold. First, it is clear that similar empirical PES assignments are perfectly feasible for many other complex biological molecules and, in particular, for all of the DNA/RNA bases. Indeed, we have already obtained photoelectron spectra for a number of more complex biological species and work is continuing in an effort to generate empirical assignments. Second, the type of experimental data which is generated (i.e., ionization energies) and the empirical information deduced from that data (i.e., MO energies, types, and sequences) is both very scarce and very important. For example, these sorts of data lie at the heart of frontier orbital theory, donor-acceptor interactions, the association of biological molecules (e.g., uracil with riboflavin), etc. Third, the existence of a set of empirical assignments provides a test case for all sorts of empirical MO computations and may be used to distinguish those algorithms which are useful from those which are not.

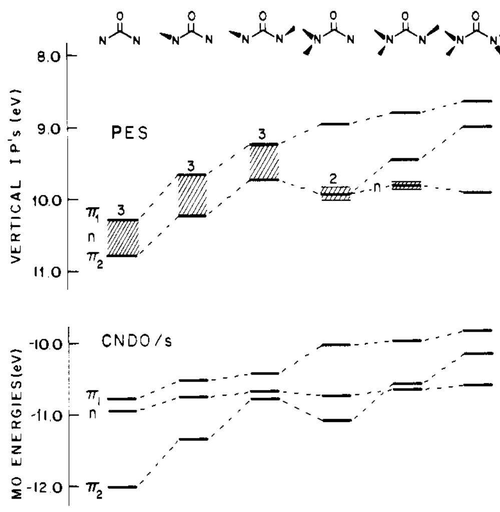

Figure 7. Correlation diagrams for the methylureas based on experimental data (top) and on CNDO/s computational results (bottom).

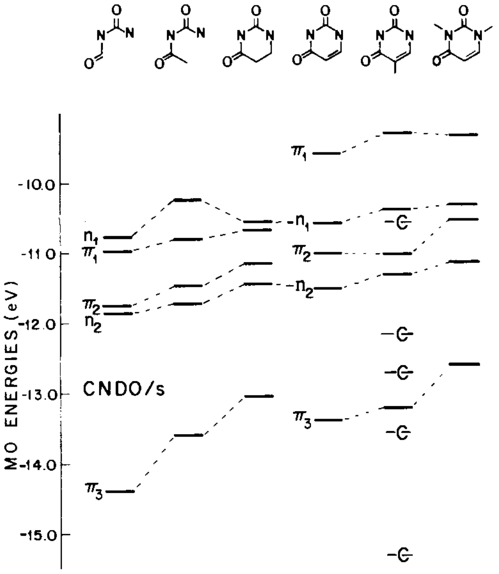

Figure 8. Correlation of CNDO/s computational results for the five highest energy filled MO's of formylurea, acetylurea, dihydrouracil, uracil, thymine, and 1,3-dimethyluracil. The computational data of Clementi[7] for the MO levels of thymine are also shown and are denoted by an insert "C".

We have presented the results of CNDO/s calculations at various points in the text. We now summarize the extent to which these results reproduce the empirical data. Figure 7 displays the comparative correlations of experimental and calculated data for the methylated ureas. The agreement is considered to be quite good since all of the major experimental trends are reproduced reasonably well by the computations. Figure 8 displays the calculated correlation diagram for the acylureas and uracils. This diagram also is in excellent correspondence with the experimental correlation diagram of Figure 5. It should be noted that the CNDO/s absolute MO energies appear to be too large by approximately 1 eV. Nonetheless, these calculations provide a faithful representation of the facts and, as a result, they solidify further the empirical assignments.

The results of Clementi's ab initio calculation for thymine,[7] specifically the MO order, are also in excellent accord with experiment but provide absolute MO energies which are ~2 eV too large.

The photoelectron spectrum of uracil has been reported by Padva et al.[3a] The assignments of these authors were based on a direct correspondence with the results of a semiempirical INDO calculation. The lowest energy ionization potentials, IP(1), of uracil and thymine have been reported by Hush and Cheung.[22] The assignments of these authors were based on direct comparison with the results of ab initio SCF-MO and semiempirical INDO calculations. It is a testament to the value of these calculations that all of them, including our own, provide the same set of assignments for IP(1) through IP(4) and that this set agrees with the empirical one. The one disagreement occurs in IP(5) which is assigned[3a] as $I(\sigma)$ on the basis of INDO calculations and as $I(\pi_3)$ on the basis of CNDO/s calculations; the empirical assignment agrees with the CNDO/s results.

An additive methylation effect on the ionization potentials of simple amides has been shown to occur.[8] We now consider the extent to which such additivity relations are valid for the methylated urea series. As may be verified in Figure 3, additivity of ΔIP(1) obtains within the triads {urea, methylurea, 1,1-dimethylurea} and {1,1-dimethylurea, trimethylurea, tetramethylurea}, but not between triads. Additivity of ΔIP(2) obtains within the triads {urea, methylurea, 1,3-dimethylurea} and {1,1-dimethylurea, trimethylurea, tetramethylurea} as well as between corresponding members of each triad. Thus, additivity behavior does exist, but its existence depends on the choice of sets and is by no means as general as that found in simple monoamides.

References and Notes

(1) This work was supported by the U.S. Energy Research and Development Administration, Division of Biomedical and Environmental Research, Physics and Technological Program and by The Deutsche Forschungsgemeinschaft via an Ausbildungsstipendium.
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Reaction of Atomic Carbon with Ethylene Oxide. A MINDO/3 Study of Possible Pathways

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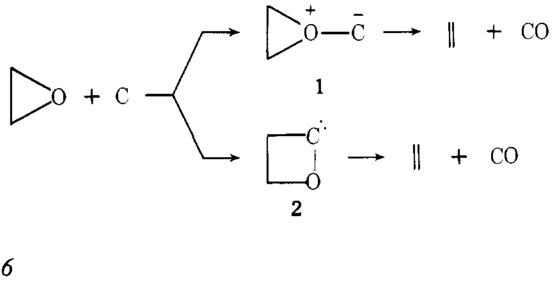
Received November 14, 1975

Abstract: A MINDO/3 semiempirical molecular orbital calculation of the energetics of the deoxygenation of ethylene oxide by atomic carbon has been carried out. The results indicate that the most favorable pathway is one in which the carbon strips the oxygen along a reaction coordinate leading directly to carbon monoxide and ethylene without local energy minima. The energetics of insertion of carbon into the C–O bond of ethylene oxide to produce 2-oxacyclobutylidene (**2**) have also been investigated. Carbene **2** is at an energy minimum and has a calculated ΔH_f of 6.7 kcal/mol. The two most likely reactions of **2** appear to be rearrangement to oxetene ($\Delta H^{\ddagger} = 36$ kcal/mol) and ring contraction to cyclopropanone ($\Delta H^{\ddagger} = 39$ kcal/mol). The activation enthalpy for the extrusion of CO from cyclopropanone via a nonlinear cheleotropic pathway is calculated to be 41 kcal/mol.

The deoxygenation of epoxides to produce carbon monoxide and an alkene is an extremely facile reaction of atomic carbon (eq 1). This reaction has been observed to occur with arc-generated carbon,[2] with carbon produced by the thermolysis of 5-tetrazoyldiazonium chloride[3] and with nucleogenic carbon-11 atoms.[4] We have recently reported that the deoxygenation of the 2-butene oxides by chemically generated carbon atoms is stereospecific.[5]



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