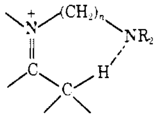
(17) Intramolecular proton abstraction by carboxylate ion in a protonated imine has been postulated (see Table V of ref 15), and carboxylate ion has been proposed as the proton-abstracting moiety in aldolases (H. P. Meloche and J. P. Glusker, *Science*, 181, 350 (1973).

(18) Numerous studies on the ionization of carbonyl compounds[19] have shown that the preferred conformation for proton removal places the departing proton in a plane perpendicular to the plane of the O═C—C system, i.e., in the plane of the π-bond system of the C═O group. Almost certainly the same preference holds for α-proton removal from imines and iminium compounds, and in testing the geometric requirements for intramolecular proton abstraction in imines, Hine and coworkers[20] have shown that a pseudo-eight-membered relationship provides the most suitable arrangement in the compounds that they studied; i.e.



where $n = 3$

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Photoelectron Spectroscopy of Carbonyls. Urea, Oxamide, Oxalic Acid, and Oxamic Acid[1]

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Abstract: Photoelectron spectra are reported for urea, oxamide, oxalic acid, and oxamic acid. These spectra are interpreted in terms of a composite molecule model in which formaldehyde and formamide PES spectra play key roles. The correlative interpretation of the PES spectra of the larger molecules devolves on the manner of evolution of MO sets: n and π for H_2CO; n, π, and π_O for $HCONH_2$ and HCOOH; n, π, $\pi_\oplus$, and $\pi_\ominus$ for H_2NCONH_2; and n_+, n_-, $\pi_\oplus$, $\pi_\ominus$, π_+, and π_- for the three dicarbonyls. CNDO/s calculations are of considerable help in developing the composite molecule model and provide a remarkably good representation of experiment.

α-Dicarbonyl systems are of common occurrence[3] and they possess chemotherapeutic advantage[4] in cancer. Despite considerable work on the electronic structure of α-dicarbonyls,[5] no resolution of a number of important questions has been achieved. These questions relate to: (i) circular dichroism and chirality;[6] (ii) the nature of their low-energy electronically excited states;[7] (iii) their unique emission properties;[8] and (iv) their orbital energy level structure.[9] Photoelectron spectroscopy (PES) can provide some information on question iv and may be of indirect help in resolving questions i–iii.

The intent of this work is the analysis of the photoelectron spectra of oxamide and oxamic acid. The PES of the monocarbonyl analogs, formic acid and formamide, are available[10] but no data exist for their α-dicarbonyl counterparts. Additionally, in the correlative efforts which we undertook in order to relate the one-electron levels of these molecules, it seemed that urea occupied an important slot in the hierarchy $HCONH_2 \rightarrow H_2NCONH_2 \rightarrow H_2NCOCONH_2$. Hence, this work is also concerned with the PES of urea and its interpretation.

The discussion of oxalic acid given here consists of the presentation of an energy level diagram deduced from more detailed studies.[11] A general discussion ot PES data and assignments for monocarbonyls and α-dicarbonyls is available[12] and should be consulted for nomenclature. A summary of ionization data for monocarbonyls, α-dicarbonyls, and tricarbonyls is also available.[13]

Experimental and Computational

PES spectra were recorded on a Perkin-Elmer Model PS-18 photoelectron spectrometer with a 10-cm radius cylindrical electrostatic field deflection analyzer. A Bendix "Channeltron" Electronic Multiplier (Model CEM-4028) was used as a detector. The ionization energy was provided by the 584 Å (21.22 eV) HeI resonance line. Solid samples were sublimed in a heated probe, the temperature of which was adjusted for maximum count rate. The range of temperatures used for solid samples was 72 to 119°. Spectra were calibrated with regard to both energy and resolution using the $^2P_{1/2}$ and $^2P_{3/2}$ lines of xenon; the resolution was in the range 20–25 meV.

Oxamide (MCB), oxamic acid (MCB), and oxalic acid (Baker) were purified by recrystallization from water. Urea (Baker Reagent Grade) was used without further purification.

Semiempirical CNDO/s calculations were carried out for formaldehyde, formamide, urea, oxamide, oxalic acid, and oxamic acid in geometries appropriate to their ground states.[14] The MO notation used has been discussed previously[12] and is quite straightforward. The MO's of a monocarbonyl such as $HCONH_2$ are labeled n, π, and π_O. They have the following significance: n is a nonbonding σ MO with dominant amplitude on the carbonyl oxygen; π is the π MO of the carbonyl group in H_2CO, appropriately delocalized to embrace the nitrogen center in formamide; and π_O is a π MO with large amplitude on the amine group. In the case of formic acid, the n and π notations retain the same meaning as in formamide but π_O now refers to a π MO with large amplitude on the hydroxyl group. In a symmetric dicarbonyl such as oxamide, the MO notation is expanded, in a quite obvious way, to n_+, n_-, π_+, π_-, $\pi_\oplus$, and $\pi_\ominus$, where the extra +/− subscripts denote bonding/antibonding combinations of the constituent formamide MO's. This latter notation is inexact in the case of unsymmetrical dicarbonyls such as oxamic acid but, for want of a better notation, is used here. In the case of urea which may be supposed to consist of two amide groups, the single carbonyl entity doing double duty, the appropriate notation becomes n, π, $\pi_\oplus$, and $\pi_\ominus$ and should cause no confusion.

All PES spectra are supposed to consist of simple one-electron ionization events and are so interpreted. In the case of oxamide,

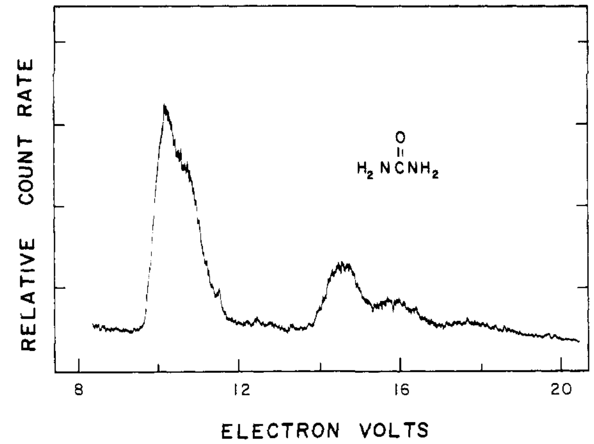

Figure 1. The photoelectron spectrum of urea.

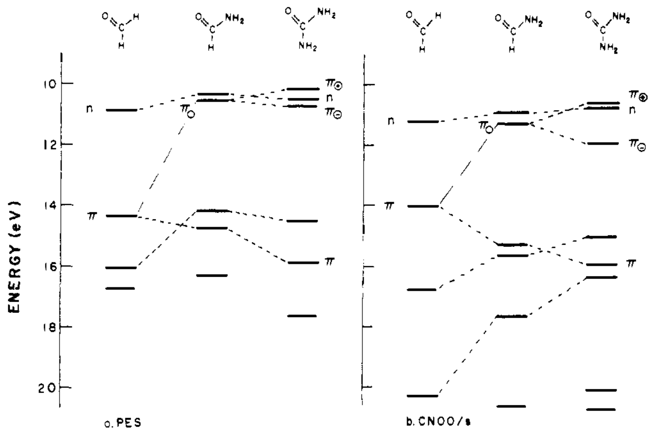

Figure 2. Computational CNDO/s and experimental MO correlation diagrams for the formaldehyde, formamide, and urea molecules. The comparison of these two correlation diagrams, as also the textual language, implies the use of Koopmans' theorem.[15] All orbitals not labeled are σ MO's.

several of the PES bands exhibit resolvable fine structure which is attributed to vibrational excitation of the ion. On the other hand, many of the bands exhibit no structure and must, on the basis of relative photon cross sections, be adjudged to embrace two or more electron ionization events.

Results

Monocarbonyls. The photoelectron spectrum of urea is shown in Figure 1. It exhibits four diffuse bands, the lowest energy of which, on the basis of relative intensity, must contain three separate electron ionization events. We suppose that these three events produce the features at 10.15, 10.5, and 10.8 eV. The second of these features, the 10.5 eV region, appears to exhibit a substructure with an ~1400 cm^{-1} interval. If this inference is correct, we may suppose this 1400 cm^{-1} interval to correspond to a C=O stretching frequency of the ion and, thus, may identify the corresponding ionization as that from an n MO. The total information intrinsic to the spectrum of Figure 1 is that the urea molecule exhibits six ionization events below 18 eV, that these are clumped into two groups of three, and that the second lowest energy band may be the n ionization. The experimental data for urea are tabulated in Table I.

The results of CNDO/s computations for H_2CO, $HCONH_2$, and H_2NCONH_2 are given in Figure 2, where they are correlated on the basis of MO wave function analogies and are compared with tne experimental correlation diagram. It seems clear that the CNDO/s results reproduce the experimental data remarkably well for urea and that the CNDO/s correlation diagram is a satisfactory mimic of the experimental one, particularly at lower binding energies.

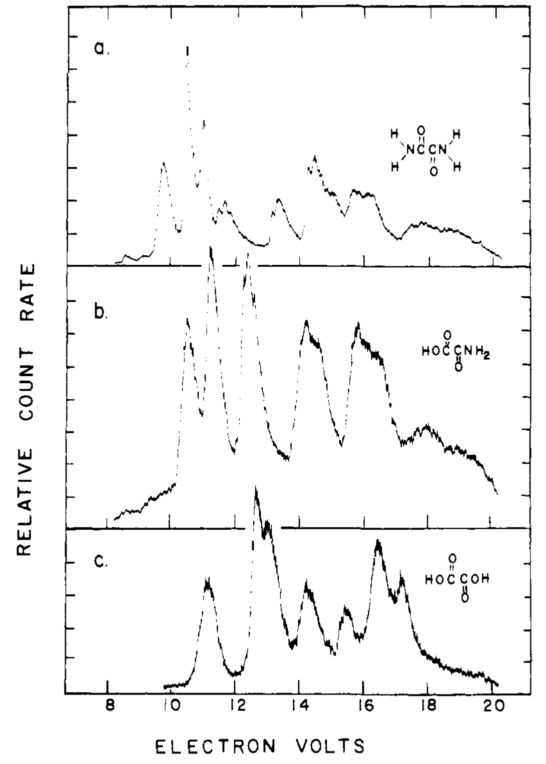

Figure 3. Photoelectron spectra of oxamide, oxamic acid, and oxalic acid.

The experimental data used in construction of Figure 2 are taken, for H_2CO, from Turner et al.[16] and, for $HCONH_2$, from Brundle et al.[10] The assignments made by these authors are used without change and are, in our opinion, suspect in only one regard: The 14.2 eV (π) and 14.75 eV (σ) assignments of formamide might well be inverted [i.e., 14.2 eV (σ) and 14.75 eV (π)] since such an inversion would in no way counter the experimental facts. The salient predictions concerning urea are that the π_O ionization of $HCONH_2$ should split into two, $\pi_\oplus$ and $\pi_\oplus$; that the n/π_O ionization order in $HCONH_2$ should invert in urea [i.e., $I(\pi_\oplus) < I(n)$]; and that a similar inversion should occur for the σ/π ionizations in the 15-16 eV region. The experimental correlation diagram suggests that all of these predictions are in accord with experiment.

Oxamide. The photoelectron spectrum of oxamide is shown in Figure 3a and exhibits at least 11 distinct ionization events. These are tabulated in Table I where they are identified with respect to MO origins using CNDO/s and correlative arguments. The details of some of the PES bands are shown enlarged in Figure 4 where an attempt at vibrational analysis is also indicated.

A correlation diagram based on CNDO/s results is shown in Figure 5 where it is compared with one based upon experiment. The lower energy ionizations are in remarkable agreement with computation with respect to number (2 for $HCONH_2$, 3 for urea and 4 for oxamide), with respect to energy, and with respect to the order of occurrence of assigned types. Agreement is also good for the set of deeper π ionizations, but this latter "goodness" is largely unsubstantiable. We have already mentioned the possibility of a π/σ assignment reversal in formamide and we now note that the 14.5 eV band could well be π_- whereas any one of the two bands, 15.7 and 16.15 eV, could be assigned as π_+.

The large n_+/n_- splitting of 1.92 eV which occurs in oxamide is in accord with computation which predicts 2.25 eV. This splitting is attributable to "through-bond mixing"

Table I. Ionization Potentials of Urea and α-Dicarbonyls (in eV)[a]

	IP(1)	IP(2)	IP(3)	IP(4)	IP(5)	IP(6)	IP(7)	IP(8)	IP(9)	IP(10)	IP(11)
UREA	10.15	10.5	10.8	14.5	15.9	17.7					
(H_2NCONH_2)											
MO TYPE	$\pi_{\oplus}$	n	$\pi_{\ominus}$	σ	π	σ					
OXAMIDE	9.41(A)	10.50(A,V)	11.04(A,V)	11.52(A)	13.26(A)	14.33(A)	14.90(A,V)	15.70	16.15	17.80	18.70
($H_2NCOCONH_2$)	9.80(V)			11.72(V)	13.39(V)	14.50(V)					
$\bar{\nu}_{vib}$	440cm^{-1} 1620cm^{-1}	1321cm^{-1}	1291cm^{-1}	1559cm^{-1}	1570cm^{-1}	1371cm^{-1}	1412cm^{-1}				
MO TYPE	n_+	$\pi_{\ominus}$	$\pi_{\oplus}$	n_-	π_-	σ	σ	σ	π_+	σ	σ
OXAMIC ACID	10.51	11.24	12.40	12.40	14.21	14.54	15.85	16.46	17.85	19.29	
($H_2NCOCOOH$)											
MO TYPE	n_+	$\pi_{\oplus}$	$\pi_{\ominus}$	n_-	π_-	σ	σ	π_+	σ	σ	
OXALIC ACID	11.20	12.81	13.25	13.25	14.40	15.59	16.62	17.34	18.41(?)		
(HOCOCOOH)											
MO TYPE	n_+	$\pi_{\ominus}$	$\pi_{\oplus}$	n_-	π_-	σ	π_+	σ	σ		

[a] The notation (A) following an ionization energy denotes an adiabatic event; the notation (V) denotes a vertical event. The energies quoted in cm^{-1} under $\bar{\nu}_{vib}$ denote coupled vibrational energies of the ion.

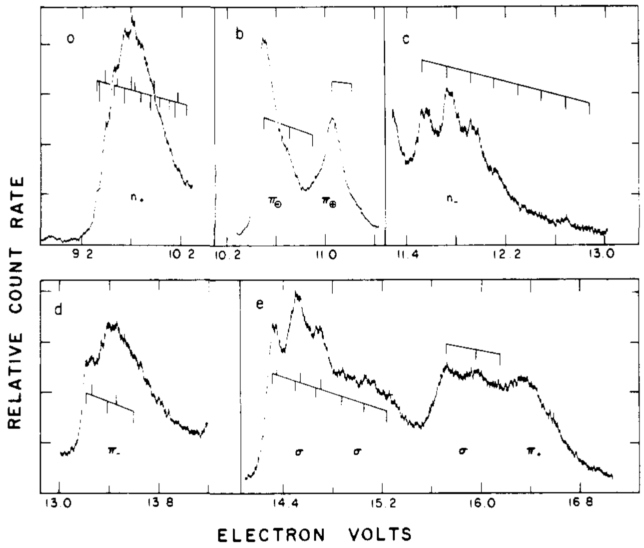

Figure 4. Detail of high-resolution PES of oxamide. Band assignments and vibrational analyses are also indicated. The coupled vibrational frequencies are: band n_+ (Figure 4a), 440 and 1620 cm^{-1}; band $\pi_{\ominus}$ (Figure 4b), 1320 cm^{-1}; band $\pi_{\oplus}$ (Figure 4b), 1290 cm^{-1}; band n_- (Figure 4c), 1560 cm^{-1}; band π_- (Figure 4d), 1570 cm^{-1}; band σ, 14.5 eV (Figure 4e), 1370 cm^{-1}; band σ, 14.90 eV (Figure 4e), 1410 cm^{-1}.

of the n_+ and -C-C- σ MO's of oxamide and has already been discussed by Swenson et al.[17] and Cowan et al.[18] for various other α-dicarbonyls. It is this mixing which is responsible for the extensive -C-C- σ character of the n_+ MO; for the fact that the vibrations coupled to the n_+ ionization involve, at least in part, skeletal movement of parts of the molecule other than the >C=O group (i.e., the 440 cm^{-1} mode); and for the Franck-Condon shape of the n_+ ionization band which is indicative of a considerable geometry change between the ionic state and nonionic ground states.[3b] The structure in the n_+ band is, as expected, dominated by two progressions in an ~1600 cm^{-1} frequency, which no doubt corresponds to a >C=O stretching mode.

Oxamic Acid. Correlation diagrams of both experimental and computational nature are shown in Figure 6. The view adopted in these diagrams is that oxamic acid is a composite of oxalic acid and oxamide. The experimental and computational data used for oxamide are taken from the previous analysis. The PES spectra of oxalic acid and oxamic

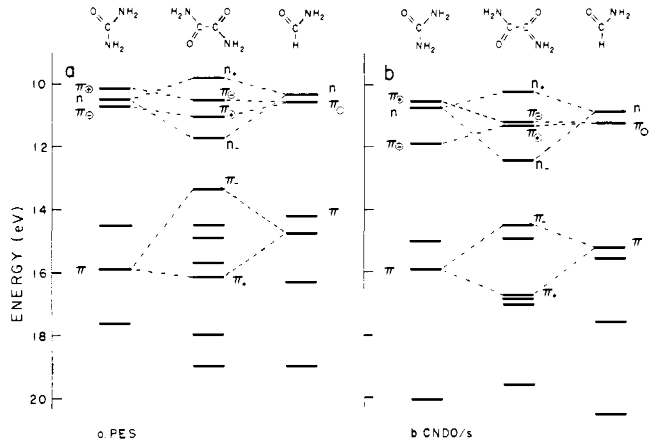

Figure 5. Correlation diagram for urea, oxamide, and formamide on the basis of both computational and experimental results. All orbitals not labeled are σ MO's.

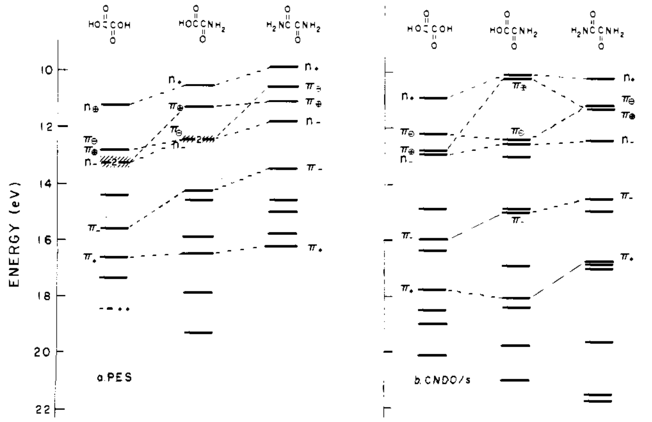

Figure 6. Correlation of experimental PES data and computational CNDO/s MO data for oxalic acid, oxamic acid, and oxamide. All orbitals not labeled are σ MO's.

acid are given in Figures 4c and 4b, respectively, and constitute the data used in constructing the experimental portion of Figure 6. The analysis of oxalic acid implicit in the experimental portion of Figure 6 follows from an analysis of the oxalic acid spectrum in terms of PES data for formic and carbonic acids.[11]

The experimental data for the three diketo acids are tabulated in Table I where identifications with respect to MO origins are taken from the correlations of Figure 6. A few comments concerning these identifications and correlations are in order.

(i) The 12.42 eV band of oxamic acid appears to contain two ionization events. The evidence for this consists of the band area, which is ~2 times that of the n_+ ionization event, and its "skewedness" to higher energies. Consequently, we suppose this band to consist of *one* of the $\pi_\oplus$ ionization events and the n_- ionization event.

(ii) The order of the $\pi_\oplus$ events in oxamic acid is shown to be inverted relative to the order in either oxamide or oxalic acid. The $\oplus$ subscripting is not rigorous in oxamic acid because of the unsymmetrical nature of this acid. Nonetheless, the notation used has a basis, though admittedly a weak one, in the computational data for the MO wave functions. In any event, it is well to stress that the 11.24 eV band of oxamic acid is, on the basis of energy, heavily involved with the amidic group of oxamide and that this conclusion concurs with computation, where the $\pi_\oplus$ MO of oxamic acid is found to have dominant amplitude on the -$CONH_2$ side of the molecule. The opposite conclusion applies to the 12.40 eV region (i.e., the $\pi_\ominus$ band) where computation and experiment suggest dominant amplitude on the -COOH side of oxamic acid.

(iii) The n_+ and n_- PES bands of oxamic acid lie at the barycenters of the corresponding n_+ pair and n_- pair respectively of oxalic acid and oxamide. This attitude is vindicated computationally in Figure 6 for the n_- bands, but not for the n_+ bands.

(iv) The identification of the $\pi_\pm$ ionization events in oxamic acid is not very secure. These identifications are largely based on barycenter considerations [i.e., π_-(oxamic acid) = $\frac{1}{2}\pi_-$(oxamide) + $\frac{1}{2}\pi_-$(oxalic acid)]; this attitude, while computationally consistent for π_-, is not borne out by the computational data for π_+.

(v) All bands not assigned are, by default, attributed to σ ionization events of "whole-molecule" nature.

(vi) Despite the reservations implicit in comments i–v, the comparison of the two sides of Figure 6 is substantiative of the assignments made.

A few other comments also appear to be in order.

(vii) The oxalic acid ionization region 12.8–13.3 eV appears to contain three ionization events. First, despite the fact that two distinct peaks are contained in this region, the integrated intensity of this region is ~3 times that of the n_+ event. Second, the computations do predict the occurrence of three separate events in this region. They are assigned as $\pi_\oplus$, $\pi_\ominus$, and n_- ionization events.

(viii) The $\pi_\oplus/\pi_\ominus$ splitting decreases in the order oxamic acid > oxamide > oxalic acid. That the splitting in oxamide is larger than that in oxalic acid is simply a result of the higher electronegativity of the OH group than the NH_2 group and the consequent lesser delocalization that is predicted to occur in oxalic acid. The large splitting observed in oxamic acid is related to the fact that the individual $\pi_\oplus$ and $\pi_\ominus$ bands are largely localized on individual sides of the molecule, -$CONH_2$, and -COOH sides respectively, and is not a consequence of larger π interactions along the skeletal framework.

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