1974

Photoelectron Spectroscopy of Carbonyls.

James L. Meeks
Louisiana State University and Agricultural & Mechanical College

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Chemistry, physical

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PHOTOELECTRON SPECTROSCOPY OF CARBONYLS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy in

Department of Chemistry

by

James L. Meeks

B.S., Cumberland College, 1962

May, 1974
DEDICATION

To Suzanne and Peggy who worried about the "big book."

and

William Bowling and Charles Ball
ACKNOWLEDGEMENT

I wish to express my sincere appreciation to Dr. Seán P. McGlynn under whose direction this work was performed, for his guidance, continuous encouragement, inspiration and advice which made the completion of this work possible.

I would also like to thank present and past members of Dr. McGlynn's Research Group: Dr. Petr Hochmann, Dr. H. J. Maria, Dr. O. S. Khalil, Dr. D. B. Larson and Anne Wahlborg for their discussions and suggestions. I wish to acknowledge Dr. R. V. Nauman and Dr. K. N. Houk for their interest and suggestions in this work, and Ms. Suzann W. Finley for the typing. Thanks are expressed to the rest of the faculty, staff and graduate students at Louisiana State University for their collaboration.

I would like to thank Dr. J. M. Boswell, Board of Trustees and Faculty of Cumberland College for the Sabbatical leave granted in the pursuit of this work.

This work was supported by the United States Atomic Energy Commission-Biology Branch via contract with the Louisiana State University. Financial assistance in preparation of this dissertation was provided by the Charles E. Coates Memorial Fund of Louisiana State University Foundation donated by George H. Coates. This support and assistance is gratefully acknowledged.

Finally, I express my gratitude to Mr. and Mrs. John E. Taylor and especially to my wife, Peggy, for her patience, understanding and encouragement during the years of my graduate work.
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ABSTRACT

The photoelectron spectroscopy (pes) of carbonyl-containing molecules was investigated. Pes spectra were obtained and are reported for monocarbonyls (urea, dimethyl carbonate, and acetaldehyde), of $\alpha$-dicarbonyls (oxamide, N,N'-dimethyloxamide, N,N'-di-$n$-propyloxamide, N,N,N',N'-tetramethyloxamide, oxamic acid, ethyl oxamate, N,N-dimethyl ethyl oxamate, oxalic acid, dimethyl oxalate, diethyl oxalate, biacetyl, pyruvic acid, methyl pyruvate, pyruvamide, oxalyl chloride and ethyl oxalyl chloride), and tricarbonyls (parabanic acid, methylparabanic acid, dimethylparabanic acid and di-$n$-propylparabanic acid). These spectra are interpreted in terms of (1) Additivity effects: The introduction of a given substituent into any molecule of a class of closely-related molecules is found to produce a change in the ionization potential which is sensibly constant and, for multiple substitution, roughly additive; (2) Correlative studies: Monocarbonyls, such as formaldehyde or formamide, constitute a basis for a composite-molecule model applicable to the $\alpha$-dicarbonyls; (3) N-methylation (N-alkylation) shifts: The $\pi_\text{C}$ MO's are more sensitive to alkyl substitution than the $\sigma$-nonbonding (n) MO's; (4) O-alkylation (esterification): The formation of an ester will cause a decrease in the n/$\pi_\text{C}$ separation relative to the acid; (5) CNDO/s computations: Low-energy ionization events exhibit excellent agreement with computed values when Koopmans' Theorem is invoked.
CHAPTER I

INTRODUCTION
Molecules containing one or more carbonyl (i.e., \( \geq C = O \)) groups occur widely and are of enormous importance in preparative organic chemistry.\(^1\) They are also widely dispersed in biological systems\(^2\) and have reputed chemotherapeutic value as anti-carcinogens.\(^3\) As a result, the electronic structure of these systems has been of considerable interest and has involved much investigative effort. Unfortunately, these efforts have not been very successful.

The interest of these Laboratories, being directed toward excited electronic states, was primarily vested in visible, ultraviolet and vacuum ultraviolet absorption spectroscopy and in emission spectroscopy. These studies,\(^4,5,6,7\) while certainly successful in their own right, emphasized the importance associated with a detailed knowledge of ground state electronic configurations. The most direct experimental ingress to those ground state properties which are pertinent to excited state electronic considerations is provided by photoelectron spectroscopy (pes); hence, the origins of the present study.

The photoelectron spectroscopic technique, as developed by Turner,\(^8\) provides ground state ionization energies. The advantage of the photoelectron spectroscopic technique lies in the ease of measurement and not in its accuracy;
for example, the precision of pes data is considerably below that obtainable by series limiting techniques in Rydberg spectroscopy. However, the series limiting technique is very time consuming and is probably restricted to a few low-energy ionizations in any one molecule.

The importance of the ionization data lies in the fact that, via Koopmans' theorem, the ionization energies may be equated to molecular orbital energies. As such, pes data provide direct measurement of the energies of the populated molecular orbitals.

Methods which have proven helpful for assigning pes ionization events are:

(1) Vibronic structure;¹¹
(2) Photoionization cross-sections;¹² and
(3) Perfluoro effects.¹³

These diagnostic methods have proven useful in the assignments of the pes bands of carbonyl compounds such as formaldehyde.

In addition, assignments may often be made, or at least substantiated, by making direct correspondence to the results of semi-empirical or ab initio molecular orbital calculations. A one-to-one correspondence between the computed MO energies, as multiplied by some empirical factor¹⁴ which supposedly compensates for the electron reorganization which occurs during ionization, and the pes band energies is usually invoked. This procedure, while admittedly dangerous, has had much success.
The purpose of this work was to investigate previous assignments of the pes data of mono-carbonyl molecules, where available, and to develop methods which would be useful in the interpretation of the pes data for \( \alpha \)-dicarboxyls. A list of those methods which were found to be helpful is given below:

(1) Additivity effects: It was found that the chemical substitution of slightly perturbing groups produced variations in the ionization energies which were additive and whose magnitudes were relatively constant and characteristic of both the substituent and the nature of the ionization event.

(2) Correlative studies: A certain relatedness of the pes data for groups of similar molecules could be inferred and served to characterize the nature of the ionization events.

(3) N-Methylation (N-Alkylation) shifts: The substitution of methyl or alkyl groups on the amide group, \(-\text{CON} -\), was expected to be most perturbative of ionization events which involved removal of electrons which were heavily localized on the amidic group.

(4) O-Alkylation (esterification) shifts: The formation of an ester from an acid was expected to be most perturbative of ionization events which involve removal of \(-\text{OH} \) or \(-\text{COOH} \) electrons.

(5) CNDO/s computations: Semi-empirical computations (CNDO/2, INDO, MINDO and CNDO/s) have been found to be very useful in assigning pes bands. A similar utility, particularly for CNDO/s results, was established in this work.
The material discussed in Chapter II deals with the first point, additivity effects. In Chapter III, the second point correlation studies, is developed and discussed. The third point, N-methylation (or N-alkylation), is covered in Chapter IV. O-alkylation (esterification) is developed in Chapter V. The fifth point, CNDO/s computations, is used in Chapters II-VI to establish the validity of such computations and to serve as a guide for the correlative studies. Chapters VI and VII deal with all of the five points and Chapter VIII is a summary of the ionization energies and assignments which constitute this work.
REFERENCES


CHAPTER II.

BAND ASSIGNMENTS IN MONOCARBONYLS AND τ-DICARBONYLS
INTRODUCTION

Various experimental criteria have been used to relate photoelectron spectra (pes) to the ionization of electrons from specific types of molecular orbitals. Among these are Franck-Condon band shapes and vibronic considerations, the "perfluoro" effect, pes intensity dependence on photon excitation energy, the association of large or small substituent effects with the anti-nodal/nodal characteristics of an MO wavefunction, etc.

All of these criteria, however, are useful in limited experimental ranges, and, thus, the development of other criteria for ranges not readily tractable by any presently-known means is important.

One of the purposes of this work is to discuss the existence of a simple, additive, substituent effect on ionization potentials. Specifically, the ionization potential $I(i, NX)$, where $i$ is an MO index, $X$ is a substituent index and $N$ is the number of substituents, is found to be

$$I(i, NX) - I(i) = N \Delta I(i, X)$$

where $I(i)$ is the ionization potential of type $i$ of some specified parent, unsubstituted molecule and $\Delta I(i, X)$ is a constant for a given substituent $X$ within a class of closely-related parent molecules. The catch in our phraseology resides in the phrase "closely-related parent molecules." The limits associated with this phrase
are yet to be defined. Indeed, we have merely selected a series of molecules in which we have significant interest, the monocarbonyls and \( \alpha \)-dicarbonyls, and have found that Eq. 1 exhibits a broad range of validity and is useful in making pes band assignments.

As an example, consider the tentative assignment, by Brundle et al., of the 13.4eV pes band of acetone to \( I(\pi) \), where \( \pi \) is the \( \pi \) MO localized on the \( \geq C = O \) group. This assignment may be validated by considerations of the series formaldehyde (\( H_2CO \)), acetaldehyde (\( CH_3CHO \)), and acetone (\( CH_3COCH_3 \)). The \( I(\pi) \) band of formaldehyde has \( I(\pi) \) at 14.5eV (vertical) or 14.09eV (adiabatic). The \( I(\pi) \) band of formaldehyde may be corrected with either the 2nd or 3rd pes bands of acetaldehyde which occur at \( I(2nd) = 13.2eV \) (vertical) or 12.61eV (adiabatic) and \( I(3rd) \) at 14.19eV (vertical) and 13.54eV (adiabatic), respectively. The \( I(\pi) \) band of formaldehyde may also be correlated with the 2nd or 3rd bands of acetone which occur at \( I(2nd) \) = 12.6eV (vertical) or 11.99eV (adiabatic) and \( I(3rd) \) = 13.4eV (vertical) or 12.79eV (adiabatic), respectively. If the three sets of data are evaluated simultaneously, the adiabatic ionization potential differences for correlation of \( I(\pi) \) of \( H_2CO \) with \( I(2nd) \) of \( CH_3CHO \) and \( (CH_3)_2CO \) are

\[
H_2CO \rightarrow H_2CO \rightarrow H_2CO \rightarrow H_2CO \rightarrow H_2CO \rightarrow H_2CO
\]

whereas an assumed correlation of \( I(\pi) \) of \( H_2CO \) with \( I(3rd) \) yields
The latter scheme exemplifies the view expressed in Eq. 1 and, to the extent that Eq. 1 is meaningful, it supports the acetone assignment $I(\pi) = 13.4 \text{eV}$. Other evidences supportive of this same assignment are:

(i) The $I(\pi)$ values for methylated ethylenes\textsuperscript{12} are:

CH$_2$ = CH$_2$(10.50\text{eV}); CH$_2$ = CHCH$_3$(9.73\text{eV}); CH$_2$ = C(CH$_3$)$_2$(9.23\text{eV});

HCH$_3$C = C(CH$_3$)$_2$(8.67\text{eV}); (CH$_3$)$_2$C = C(CH$_3$)$_2$(8.30\text{eV}). The CH$_2$ = C and $> C = C(CH_3)_2$ groups are "isoelectronic" with the $> C = 0$ group and the average values of $\Delta I(\pi, CH_3)$ for the ethylenic groups, -0.64 and -0.47\text{eV} respectively, are comparable to the values of -0.59 and -0.71\text{eV} found for the carbonyl group in Eq. 3.

(ii) The adiabatic ionization potentials of Eq. 2, 12.61 (13.2, vertical) and 11.99\text{eV}(12.6, vertical) for CH$_3$CHO and (CH$_3$)$_2$CO respectively, correspond to the 1st pes band of CH$_4$ at 12.5(13.5, vertical) and undoubtedly represent ionization of an electron which has significant amplitude on the -CH$_3$ group.

As a result, the assignment of Brundle et al.\textsuperscript{2} may be considered to be well established. Additionally, the attitude of Eq. 1 has been found to be useful. The remainder of this text is concerned with development of the perturbative approach of Eq. 1 and its use in making pes band assignments for monocarbonyls and $\alpha$-dicarbonyls. Prior to doing so, however, a consistent notation is needed.
ORBITAL NOTATION

The orbital notation used for the π-system of mono-carbonyls HCOX, where X is a substituent such as -OH or -NH₂ which introduces a readily-ionizable π-electron pair into the original π-system, is shown in Figure 1 for the specific example of formamide. The n MO is not shown; this MO is largely of 2p type, is largely localized on the oxygen center and, in the case of H₂CO, is both in-plane and perpendicular to the ≈ C = O bond. The π MO, being largely localized on the substituent X, is akin to the "π MO" in molecules like aniline or phenol; it is also an MO type introduced by substituents such as CH₃ where formal π/σ distinctions break down. The π MO is largely an ≈ C = O localized orbital which has been modified by conjugative interactions with the substituent.

The α-dicarbonyls studied in this work have the general structure X - C ≈ C - Y where X, Y : H, R, OH, OR, NH₂, NHR, NR₂, C₂H₅ and R = CH₃, C₂H₅. The α-dicarbonyls subdivide into two basic classes: Symmetric when X = Y and non-symmetric when X ≠ Y. However, for purposes of MO designation, it is convenient to introduce a secondary classification based on the degree of substitution. Thus, if we define "substitution" as the introduction of a group, X or Y, which yields an easily-ionizable MO of type π, we can sub-divide the α-dicarbonyls into "unsubstituted," "monosubstituted," and "disubstituted" types. The utility of this sub-division is embodied in Table I where the MO's of these
Figure 1: Molecular orbitals of π-type for formamide, as generated in a CNDO/s calculation. Numbers above the π lobes refer to MO coefficients at the center in question.
-11.23 eV; $2a''(C_s)$; $\pi_0$

-15.25 eV; $1a''(C_s)$; $\pi$
**Table I.**

\( \pi \) and \( \pi \) MO's of Monocarbonyls and \( \sigma \)-Dicarbonyls\(^a\)

<table>
<thead>
<tr>
<th>MONOCARBONYLS</th>
<th>( \sigma )-DICARBONYLS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsubstituted</td>
<td>Substituted</td>
</tr>
<tr>
<td>( \psi ) (1) 2 3</td>
<td>( \psi ) (1) 2 3 4 5 (6)</td>
</tr>
<tr>
<td>( \pi ) (( \cdot )) + +</td>
<td>( \pi ) (( \cdot )) + +</td>
</tr>
<tr>
<td>( \pi ) (( \cdot )) + + +</td>
<td>( \pi ) (( \cdot )) + + +</td>
</tr>
</tbody>
</table>

\(^a\)This table, modified to some degree, is taken from D. B. Larson.\(^7\) Some discussion of it is available in Larson and McGlynn.\(^8\) The + and - signs refer to the phasing of the wavefunctions on the various atomic centers. The dot indicates zero or near-zero wavefunction amplitude. The numbering system for the atomic centers is

![Numbering System Diagram](image)

The \( \pi \) and \( \pi \) nomenclature used is strictly valid for wholly planar \( \sigma \)-dicarbonyls but retains qualitative significance even when \( X = CH_3, C_2H_5 \) or when the \( \sigma \)-dicarbonyl is non-planar.\(^7,8\)
three sub-types are related to each other and to those of the monocarbonyls by means of a consistent, self-evident MO notation.

The ionizations of interest in this work are those which involve \( n, \pi_0 \) and \( \pi \) electrons in the monocarbonyls and \( n_+, n_- \), \( \pi_+ \) and \( \pi_- \) electrons in the \( \alpha \)-dicarbonyls. The ionizations which involve \( \pi_0 \) electrons in the \( \alpha \)-dicarbonyls will not be discussed here but will be deferred to a following paper. Further detail on the notational system for the \( \alpha \)-dicarbonyl MO's is available in Larson where an extension to an excited state notation is also provided.

**EXPERIMENTAL CONSIDERATIONS**

Photoelectron spectra were obtained on a Perkin-Elmer PS-18 instrument. Experimental details and representative spectra will be discussed elsewhere. Many of these spectra are diffuse and exhibit only a remnant vibrational structure. Consequently, the \( I(i) \) values quoted here refer to Franck-Condon band maxima, regardless of whether a given band exhibits structure or not.

Diffuse spectra are the most difficult to unravel and assign because most of the normal assignment criteria are inapplicable. It is our opinion that the perturbation tactics to be discussed here are most useful in cases of diffuse spectra and that they will play only supportive roles where rich vibronic details are available.
MONOCARBONYLS

n-IONIZATION

The effects of -CH$_3$ and -OH substitution on I(n) of formaldehyde are

\[
\begin{align*}
\text{CH}_2=O & \quad \Delta I(n, \text{CH}_3) = -0.68 \text{ eV} \\
\text{CH}_3\text{CH}=O & \quad \Delta I(n, \text{OH}) = -0.54 \text{ eV} \\
\text{CH}_3\text{CH}=\text{CH}_2 & \quad \Delta I(n, \text{OH}) = -0.69 \text{ eV}
\end{align*}
\]

where $\Delta I(n, \text{CH}_3)$, in eV, is indicated on the horizontal arrows, $\Delta I(n, \text{OH})$ on the vertical arrows, and I(n) is in brackets below the molecular representation. Methylation of either formaldehyde or formic acid yields similar $\Delta I(n, \text{CH}_3)$ values. Substitution of an -OH group in either formaldehyde or acetaldehyde yields identical $\Delta I(n, \text{OH})$ values. It also appears that multiple substitution is only slightly saturative, as witness the small change from -0.68 to -0.54 eV caused by the series methylation which yields acetone. These additivity effects are also found in an acrolein/acrylic acid cycle$^{15}$ and are
Finally, the effects of -CH₃ and -NR₂ (R = H, CH₃) substitution on $\Delta I(n)$ of formamide are illustrated for the formamide/N,N-dimethylacetamide series in the cycle.

It appears that N-methylation decreases $\Delta I(n)$ by 0.27 eV whereas C-methylation produces a decrease of 0.36 eV.

The effects of methylation on the simplest homologs are

$$
\begin{align*}
\text{H}_2\text{CO} & \rightarrow \text{CH}_3\text{CHO} \quad \Delta I(n) = -0.68 \\
\text{HCOOH} & \rightarrow \text{CH}_3\text{COOH} \quad \Delta I(n) = -0.69
\end{align*}
$$
The small magnitude of the last value relative to the first two entries immediately demands explanation. In formaldehyde/acetaldehyde, the adiabatic and vertical ionization energies are coincident. The vertical ionization energies of formic/acetic acids are coincident with the 2nd vibronic peaks of the coupled vibrational progression in the $> C = 0$ stretching mode. Hence, the $\Delta I(n)$ values are identical for those two couples whether we use vertical or adiabatic ionization values. In formamide/acetamide, the vertical energies occur at the 2nd and 3rd vibronic peaks, respectively, of the coupled vibrational progression in the $> C = 0$ stretching mode. Hence, the adiabatic $\Delta I(n)$ for this couple differs from the vertical $\Delta I(n)$ by one quantum of a $> C = 0$ stretching vibration. In this fashion, we find for formamide/acetamide that $\Delta I(n)$ is $-0.55eV$ (adiabatic) and $-0.36eV$ (vertical). Hence, the apparent discrepancy in the above tabulation is resolved to within the error of experiment. At the same time, this example points up a limitation intrinsic to the use of vertical $\Delta I(n)$ quantities.

$\Pi$-IONIZATION

The effects of methylation on $I(\pi o)$ in the formamide/$N,N$-dimethylacetamide cycle$^{16,17}$ are
The decrements for N-methylation are surprisingly constant at ~0.6eV and for C-methylation at ~0.2eV. A comparable cycle for C-methylation and O-methylation in the formic acid/methyl acetate series$^{16,17}$ is
π-IONIZATION

Similar cycles may be formulated for I(π). Several such cycles, all pertinent to the formaldehyde/N,N-dimethylacetamide series, are

\[
\begin{align*}
\text{H} & \quad \text{C} = 0 \quad +0.25 \quad \text{H} & \quad \text{C} = 0 \quad -0.45 \quad \text{H} & \quad \text{C} = 0 \quad -0.60 \\
\text{H} & \quad \text{C} = 0 \quad -0.31 \quad \text{H} & \quad \text{C} = 0 \quad -0.55 \\
\text{CH}_3 & \quad \text{C} = 0 \quad +0.01 \\
\end{align*}
\]

Some comment on the left-most cycle, where obvious discrepancies occur, is required. These discrepancies are associated with the fact that the vertical ionization potentials differ from the adiabatic ionization energies by varying numbers of vibrational quanta. To be specific, in the formaldehyde/acetaldehyde couple, the vertical ionization energy of formaldehyde occurs on the third vibronic peak, whereas in acetaldehyde it must, in order to bring the value -0.31 into accord with the other values for C-methylation, fall on the fifth vibronic peak. If 1210 cm\(^{-1}\) is used for the coupled vibrational quantum, this correction yields
\[ \Delta I(\pi) = -0.61\text{eV} \] for the formaldehyde/acetaldehyde couple. In addition, this same assertion yields \[ \Delta I(\pi) = 0.31\text{eV} \] for the acetaldehyde/acetamide couple and removes the discrepancy which existed with respect to the formaldehyde/formamide couple.

Finally, this same supposition leads to an adiabatic ionization energy of 14.59eV for \( I(\pi) \) of acetaldehyde, a value that is in excellent agreement with the value 14.5eV found by Gaussian analysis of the photoelectron spectrum.

In terms of the cited cycle and the analysis just given, we find that \( \Delta I(\pi, \text{CH}_3) \) for C-methylation is remarkably constant at -0.55eV, \( \Delta I(\pi, \text{NH}_2) \) at +0.25eV, \( \Delta I(\pi, \text{NHCH}_3) \) at -0.25eV, \( \Delta I(\pi, \text{N(CH}_3)_2) \) at -0.85eV, and \( \Delta I(\pi, \text{CH}_3) \) for N-methylation at approximately -0.55eV.

**SUBSTITUENT EFFECTS**

The totality of \( \Delta I(\pi) \)'s, referred to formaldehyde as a parent molecule, are listed for \( I(\pi) \) and \( I(\pi) \) in Table II. No \( \Delta I(\pi) \) values are listed since these may not be referred to a formaldehyde "parent." The \( I(\pi) \) ionizations are, in fact, introduced by the substituent groups themselves, in the sense that these ionizations involve removal of an electron which is heavily group localized. Thus, in an effort to refer the \( I(\pi) \) ionizations to the appropriate substituent group, Table II includes a listing of \( I(\pi_0) \). The quantity \( \delta I(\pi_0) \) is defined as \( I(\pi_0) \) for an RCOX.
TABLE II.

EFFECTS OF SUBSTITUTION ON IONIZATION POTENTIALS (in eV)
OF FORMALDEHYDE

<table>
<thead>
<tr>
<th>Substituent, X</th>
<th>( \Delta \Omega(n) )</th>
<th>( \Delta \Omega(\pi) )</th>
<th>( \delta \Omega(\pi_0) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>-H</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>-OH</td>
<td>+0.63</td>
<td></td>
<td>-0.10</td>
</tr>
<tr>
<td>-OCH(_3)</td>
<td>+0.14</td>
<td>-</td>
<td>-0.28</td>
</tr>
<tr>
<td>-NH(_2)</td>
<td>-0.36(^a)</td>
<td>+0.25</td>
<td>-0.33</td>
</tr>
<tr>
<td>-CH(_3)</td>
<td>-0.68</td>
<td>-0.55(^b)</td>
<td>-0.30</td>
</tr>
<tr>
<td>-CH = CH(_2)</td>
<td>-0.75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-NHCH(_3)</td>
<td>-0.85</td>
<td>-0.20</td>
<td>+0.17</td>
</tr>
<tr>
<td>-N(CH(_3))(_2)</td>
<td>-1.12</td>
<td>-0.80</td>
<td>+0.35</td>
</tr>
</tbody>
</table>

\(^a\)See text.

\(^b\)Vertical ionization energy of acetaldehyde has been adjusted by 2 quanta to obtain this value (see text).
molecule \textit{minus} the lowest ionization energy of an HX molecule, both energies being vertical. Thus, the number listed under \(-\text{NHCH}_3\) for \(\delta I(\pi_0)\) is \(I(\pi_0)\) for HCONHCH\(_3\) minus the vertical energy of the first pes band of \(\text{NH}_2\text{CH}_3\). In view of the small values of \(\delta I(\pi_0)\) found in this way, the \(\pi_0\) identifications given appear to be relatively secure. That is, all \(\pi_0\) pes bands assigned in HCOX molecules are energetically very similar to the lowest-energy pes bands of related HX molecules. All pes band identifications for HCOX molecules are summarized in Figure 2.
Figure 2: MO energy levels for HCOX and HX molecules as obtained from pes data. The numbering system for X is as follows: (1), (CH₃)₂N⁻; (2) CH₃NH⁻; (3) NH₂⁻; (4) CH₃O⁻; (5) OH⁻; and (6) CH₃⁻. Data for the lowest-energy pes bands of HX were obtained from the following sources: (CH₃)₂NH and (CH₃)NH₂ (reference 18); HOH, CH₃OH and CH₄ (reference 19); and NH₃ (reference 10). All energies plotted are vertical energies.
**α-DICARBONYLS**

The ionization potentials $I(n_+), I(n_-), I(n_+)$ and $I(n_-)$ of the symmetric α-dicarbonyls are listed in Table III. The substituent effects, $\Delta I(i,X)$ were evaluated using

$$\Delta I(i,X) = \frac{1}{2}[I(i), (\text{HCO})_2 - I(i), (\text{XCO})_2]$$

Thus, $\Delta I(n_+, \text{OH}) = \frac{1}{2}(10.52 - 11.20) = +0.34\text{eV}$. The list of substituent effects is given in Table IV. Ionization potentials of non-symmetric α-dicarbonyls may be computed from Table IV using

$$I(i), \text{XCO}Y = I(i), (\text{HCO})_2 + \Delta I(i,X) + \Delta I(i,Y)$$

or, equivalently, from Table III, using

$$I(i), \text{XCO}Y = \frac{1}{2}[I(i), (\text{XCO})_2 + I(i), (\text{YCO})_2]$$

Equation 4 makes possible the extraction of the $\Delta I(i,X)$ values of Table IV and serves no other purpose.

Ionization potentials for the non-symmetric α-dicarbonyls, as obtained from Table IV, are listed in Table V where they are compared with the experimental values. The agreement of calculated and experimental quantities in Table V is well within experimental
### TABLE III.

VERTICAL IONIZATION POTENTIALS (in eV) OF "SYMMETRIC"

$\alpha$-DICARBONYLS.

<table>
<thead>
<tr>
<th>MOLECULE</th>
<th>$I(n_+)$</th>
<th>$I(n_-)$</th>
<th>$I(\pi_-)$</th>
<th>$I(\pi_+)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCOCOH$^a$</td>
<td>10.52</td>
<td>12.19</td>
<td>13.85</td>
<td>15.88</td>
</tr>
<tr>
<td>CH$_3$COCOCH$_3$</td>
<td>9.55</td>
<td>11.46</td>
<td>13.20</td>
<td>14.73</td>
</tr>
<tr>
<td>H$_2$NCOCONH$_2$</td>
<td>9.80</td>
<td>11.72</td>
<td>13.39</td>
<td>16.15</td>
</tr>
<tr>
<td>HOCOCOOH</td>
<td>11.20</td>
<td>13.25</td>
<td>14.40</td>
<td>16.62</td>
</tr>
<tr>
<td>CH$_3$OCOCOOCH$_3$</td>
<td>10.36</td>
<td>11.74</td>
<td>13.48</td>
<td>16.38</td>
</tr>
<tr>
<td>C$_2$H$_5$OCOCOOCH$_2$H$_5$</td>
<td>10.19</td>
<td>11.41</td>
<td>13.19</td>
<td>16.30</td>
</tr>
<tr>
<td>CH$_3$NHCOCONHCH$_3$</td>
<td>9.33</td>
<td>11.20</td>
<td>12.42</td>
<td>---</td>
</tr>
<tr>
<td>(CH$_3$)$_2$NCOCON(CH$_3$)$_2$</td>
<td>9.02</td>
<td>10.49</td>
<td>12.32</td>
<td>---</td>
</tr>
<tr>
<td>ClCOCOCl</td>
<td>11.26</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

$^a$The assignments quoted for glyoxal are from Turner et al.\textsuperscript{10} All other assignments in this table will be discussed elsewhere.\textsuperscript{14}
TABLE IV.

EFFECTS OF SUBSTITUTION ON IONIZATION POTENTIALS (in eV) OF GLYOXAL.

<table>
<thead>
<tr>
<th>Substituent X</th>
<th>ΔI(n_+,X)</th>
<th>ΔI(n_-,X)</th>
<th>ΔI(π_-,X)</th>
<th>ΔI(π_+,X)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Cl</td>
<td>+0.37</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>OH</td>
<td>+0.34</td>
<td>+0.53</td>
<td>+0.28</td>
<td>+0.37</td>
</tr>
<tr>
<td>OCH$_3$</td>
<td>-0.08</td>
<td>-0.22</td>
<td>-0.34</td>
<td>+0.25</td>
</tr>
<tr>
<td>OC$_2$H$_5$</td>
<td>-0.16</td>
<td>-0.39</td>
<td>-0.61</td>
<td>+0.21</td>
</tr>
<tr>
<td>NH$_2$</td>
<td>-0.36</td>
<td>-0.24</td>
<td>-0.23</td>
<td>+0.14</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>-0.48</td>
<td>-0.36</td>
<td>-0.32</td>
<td>-0.58</td>
</tr>
<tr>
<td>NHCH$_3$</td>
<td>-0.60</td>
<td>-0.50</td>
<td>-0.71</td>
<td>---</td>
</tr>
<tr>
<td>N(CH$_3$)$_2$</td>
<td>-1.50</td>
<td>-0.85</td>
<td>-0.76</td>
<td>---</td>
</tr>
</tbody>
</table>
TABLE V.

EXPERIMENTAL AND CALCULATED IONIZATION POTENTIALS (in eV) OF NON-SYMMETRIC \(\alpha\)-DICARBONYLS

<table>
<thead>
<tr>
<th>MOLECULE</th>
<th>ORIGIN</th>
<th>(I(n_+^*))</th>
<th>(I(n_-))</th>
<th>(I(n_-^*))</th>
<th>(I(n_+))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CH}_3\text{COCOOH})</td>
<td>Calc.</td>
<td>10.38</td>
<td>12.36</td>
<td>13.81</td>
<td>15.67</td>
</tr>
<tr>
<td></td>
<td>Expt.</td>
<td>10.42</td>
<td>12.31</td>
<td>13.79</td>
<td>15.64</td>
</tr>
<tr>
<td>(\text{CH}_3\text{COCOOCH}_3)</td>
<td>Calc.</td>
<td>9.96</td>
<td>11.61</td>
<td>13.19</td>
<td>15.55</td>
</tr>
<tr>
<td></td>
<td>Expt.</td>
<td>9.88</td>
<td>11.56</td>
<td>13.04</td>
<td>15.42</td>
</tr>
<tr>
<td>(\text{CH}_3\text{COCONH}_2)</td>
<td>Calc.</td>
<td>9.68</td>
<td>11.59</td>
<td>13.30</td>
<td>15.44</td>
</tr>
<tr>
<td></td>
<td>Expt.</td>
<td>9.71</td>
<td>11.48</td>
<td>13.01</td>
<td>15.54</td>
</tr>
<tr>
<td>(\text{HOCONCONH}_2)</td>
<td>Calc.</td>
<td>10.50</td>
<td>12.48</td>
<td>13.90</td>
<td>16.39</td>
</tr>
<tr>
<td></td>
<td>Expt.</td>
<td>10.51</td>
<td>12.40</td>
<td>14.21</td>
<td>16.40</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_3\text{COCONH}_2)</td>
<td>Calc.</td>
<td>10.00</td>
<td>11.56</td>
<td>13.00</td>
<td>16.22</td>
</tr>
<tr>
<td></td>
<td>Expt.</td>
<td>9.85</td>
<td>11.73</td>
<td>13.15</td>
<td>---</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_3\text{OCOCOCl})</td>
<td>Calc.</td>
<td>10.73</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>Expt.</td>
<td>10.77</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_3\text{OCOCON(CH}_3)_2)</td>
<td>Calc.(^a)</td>
<td>8.86</td>
<td>10.95</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>Expt.</td>
<td>9.31</td>
<td>11.09</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

\(^a\)This molecule is twisted (i.e., \(\theta \approx 90^\circ\)) as is the symmetric \((\text{CH}_3)_2\text{NCOCON(CH}_3)_2\) entity of Table III from which the \(-\text{N(CH}_3)_2\) substituent effect of Table IV is obtained. Since these are the only two molecules of Table III and V which are severely twisted, it is not improbable that the discrepancy between \(I(n_+^*)\), calculated and experimental, for \(\text{C}_2\text{H}_3\text{OCOCON(CH}_3)_2\) in Table V is a result of these non-planarities. In turn, this discrepancy may imply that conjugative effects on \(I(n_+^*)\), while small, are not negligible.
error in all instances except one. The sole exception is \( I(n_{+}) \) of 
\( \text{C}_2\text{H}_5\text{OCOCON(CH}_3\text{)}_2 \), this exception is noteworthy because 
this is the only compound in Table V for which the dicarbonyl 
dihedral angle is \( 0 \ll \theta \ll 180^\circ \) and for which our additive approach 
is clearly invalid anyway. Table V confirms both the 
additive \( \Delta I(i) \) approach and the correlation of levels listed under 
a given \( I(i) \). It must be emphasized, however, that the assignments which have been made require specific identifications 
(i.e., \( i = n_{+}, n_{-}, \pi_{+} \) or \( \pi_{-} \)) for one compound, preferably 
the parent molecule glyoxal. Such identifications, fortunately, 
are available.

Table IV, and Table II, points up the largely inductive nature of the effects being studied: The better donors 
produce large negative \( \Delta I \)'s; the better acceptors produce small 
positive \( \Delta I \)'s; and the over-all order of \( \Delta I \) agrees with ordinary 
chemical notions of donor-acceptor character. The order of 
substituent effects is identical in both Tables IV and II, implying 
that identifications in the monocarbonyls may, in many cases, 
be used to classify \( n/n \) types in the \( \gamma \)-dicarbonyls. The \( \Delta I \) 
values also tend to be larger for \( n \) MO's than for \( \pi \) MO's. Thus, 
the enumerated \( \Delta I \) effects appear to be largely inductive. As a 
result, and in view of the fact that the ratio \( \Delta I(i,X) \) is, in 
most instances, not larger than 5% of \( I(i) \), the approximate 
validity of a perturbation theory approach is assured. This, 
we believe, provides the rationale for the additivity regularities
which have been observed.

To suppose that conjugative interactions are entirely negligible would be wrong; conjugative effects must be held responsible for the opposite values of $\Delta I(\pi^\perp)$ found in many instances. Such effects are undoubtedly related to overlap densities in the $-X-C=\equiv$ regions, densities which are assuredly determined by the nodal differences of the $\perp$ MO's of $\pi$-type.
COMPUTATIONAL RESULTS

The results of CNDO/s computations for various amides are given in Figure 3.

COMPUTED ΔI's

As seen in Figure 3, the n and \( \pi_0 \) energies behave quite differently with respect to the two types of methylation, N- and C-. In fact, for the monocarbonyls, the values of \( \overline{\Delta I}(i,X) \), where

\[
\overline{\Delta I}(i,X) = \frac{\Delta I(i,X) + \Delta I(i,NX)}{(N + 1)}
\]

are

<table>
<thead>
<tr>
<th>Structure</th>
<th>CNDO/s</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \overline{\Delta I}(n, \text{CH}_3 \text{ on N}) )</td>
<td>-0.12</td>
<td>-0.27</td>
</tr>
<tr>
<td>( \overline{\Delta I}(n, \text{CH}_3 \text{ on C}) )</td>
<td>-0.29</td>
<td>-0.35</td>
</tr>
<tr>
<td>( \overline{\Delta I}(\pi_0, \text{CH}_3 \text{ on N}) )</td>
<td>-0.52</td>
<td>-0.63</td>
</tr>
<tr>
<td>( \overline{\Delta I}(\pi_0, \text{CH}_3 \text{ on C}) )</td>
<td>-0.03</td>
<td>-0.18</td>
</tr>
</tbody>
</table>

The agreement with the experimental values, not only with regard to order but even with respect to magnitudes, is excellent. The results support the additivity attitudes.
Figure 3: MO energies, as obtained by a CNDO/s computational scheme, for various amides. The upper $\pi_O$ MO (or, in urea, MO's) refers to a $\pi$-MO heavily localized on the amidal nitrogen. The bottom set of MO's refer to $\pi$-MO's which are largely "methyl group" in character; the type of methyl group (i.e., N-methyl or O-methyl) can be decided by inspection of the figure. The geometric parameters chosen were those for the gaseous molecules, except for urea for which X-ray crystallographic data was used. Computations followed the Del Bene-Jaffé routine. The amides ($C_s$ symmetry) are correlated with formaldehyde and urea ($C_{2v}$ symmetry).
MOLECULAR ORBITAL ENERGIES

Figure 3 indicates that the n and π MO's of formamide reverse order in N-methylformamide and that this latter order is retained in N,N-dimethylformamide, in N,N-dimethylacetamide, and in urea. A second reversal to the original formamide order is shown to occur in acetamide and in N-methylacetamide. Whether or not we believe the results of Figure 3, it is clear that the n/π order in N-methylformamide (which, incidentally, is also the order found by Brundle et al., 17) can not be used to infer a similar order in N-methylacetamide. Such an inference has been made. 16

The predicted n/π orderings of Figure 3 agree with all previously available assignments except for the one instance of N-methylacetamide which will be discussed later.

METHYLATION EFFECTS ON I(π) and I(n)

A plot of I(π) - I(n) for various formyl and acetyl derivatives is given in Figure 4. The two correlation lines are roughly parallel and exhibit a vertical separation of ~0.18eV. Since this vertical separation also equals

\[ [I(\pi, CH_3) - I(\pi, H)] - [I(n, CH_3) - I(n, H)] \]

where substitution is on the formyl carbon, this vertical
separation can be computed from the $\Delta I(n, \text{CH}_3)$ and $\Delta I(\pi, \text{CH}_3)$ values of Table II. The result is 0.18 eV.

Figure 4 is essentially identical to Figure 7 of Sweigart-Turner\textsuperscript{16} except in two regards: The HCONHCH\textsubscript{3} point is taken from Brundle et al.,\textsuperscript{17} and corresponds to their B band/A band energy separation; and the CH\textsubscript{3}CONHCH\textsubscript{3} point is obtained by assuming that the 9.68 eV pes maximum represents the vertical process for both the $n$ and $\pi_0$ ionizations. In any event, simple parallelism of the two curves of Figure 4 supports the assumption of near-coincidence of the vertical values of $I(\pi_0)$ and $I(n)$ in N-methylacetamide.

**N-METHYLACETAMIDE**

The additivity attitudes used here are a remarkable vindication of the Sweigart-Turner assignments. In only one instance, N-methylacetamide, do we find any disagreement. The assignments made here for N-methylacetamide, $I(n) = I(\pi_0) = 9.68$ eV, differ from those of Sweigart-Turner, $I(n) = 9.85$ and $I(\pi_0) = 9.68$ eV, by only 0.17 eV and that only for $I(n)$. Nonetheless, it is important to decide which set of assignments is the more reasonable. Such a determination should provide a critical test of additivity attitudes.

The Sweigart-Turner assignment was made for two reasons:

(i) It seemed\textsuperscript{16} logical on the basis of inductive considerations. Since the considerations indulged here are inductive also, the differences lie not in the attitudes but in the
Figure 4: A plot of $I(\pi) - I(n)$ for various $HCOX$ and $\text{CH}_3\text{COX}$ molecules.
manner of their use. Hence, further discussions along inductive line will not resolve the dilemma.

(ii) It was thought\textsuperscript{16} that the $I(n)/I(\pi)$ order in N-methylacetamide should be the same as in N-methylformamide where quite secure identifications did exist and where $I(\pi) < I(n)$. This sort of argument, as shown above, is not in agreement with computational CNDO/s results.

We now return to the experimental basis for the Sweigart-Turner assignment. The lowest-energy pes band of N-methylacetamide has a maximum at 9.68eV and an inflection at 9.85eV. It is clear, on the basis of both intensity and correlative arguments, that this pes band encompasses two ionization events. However, it is not obvious that these events correspond, respectively, to the 9.68(max) and 9.85(infl.)eV features. In fact, since the separation of the two features is 1452cm\textsuperscript{-1}, it is equally logical to suppose that the inflection is of vibronic nature (i.e., a C\textsubscript{=O} stretching quantum). Indeed, since the half-width of this band, \~0.7eV, is fully as small as that for molecules in which the $I(n)$ band is totally resolved (\~0.6eV in CH\textsubscript{3}COOH, \~0.5eV in HCOOH), it is equally sensible to assume that the $\pi$ and $\pi\_0$ vertical ionizations both lie at the maximum (i.e., at 9.68eV).

In sum, we feel free to reassign the $I(n)$ and $I(\pi\_0)$ energies in N-methylacetamide. We do not claim that our reassignment is correct; our only contention is that our reversal
of the Sweigart-Turner order in this compound is entirely consistent with the available experimental and computational data, and, additionally, that it is required by the accuracy we impute to additivity arguments.
CONCLUSION

Substituent additivity arguments which are somewhat similar to those produced here have been discussed by a few other authors; these are: Sustmann and Schubert, Hashmall and Heilbronner, and Johnstone and Mellon. However, the molecules of interest to these authors were quite different from those considered here and, additionally, the additivity algorithm was not used for assignment purposes. Since we will validate many of our assignments, by independent means, in the forthcoming chapters, we conclude that the additivity approach introduced here is a valid and viable correlative tool for pes assignments. However, as with all correlative algorithms, it must be used carefully.

This latter caution should be obvious from the textual discussion. In order to be specific, however, it is clear that only the use of adiabatic ionization energies has any theoretical meaning. The vertical ionization energies differ from the adiabatic values by varying numbers of vibrational quanta and unless these are known, the $\Delta I(i)$ results may be wholly misleading. Unfortunately, the adiabatic values are rarely known experimentally and must be obtained by Gaussian resolution or other inferential techniques. Thus, since the direct experimental results are usually of vertical nature, one is forced to make use of these
quantities. It is thought that this work demonstrates the logical use of these quantities and, on the basis of them, makes useful correlative arguments relating to cationic state identifications.
REFERENCES


The Program used here was QCPE: CNDO 174.


The CH$_4^+$ ionization potential entered in Figure 2 is 13.5eV and is the value associated with lowest-energy Jahn-Teller component of the $^2T_2$ ionic state by Rabalais et al. [J. W. Rabalais, T. Bergmark, L. O. Werme, L. Karlsson and K. Siegbahn, Physica Scripta, 3, 13(1971)].


CHAPTER III.

CORRELATION STUDIES
INTRODUCTION

The $\text{C}=\text{O}$, or carbonyl group, is one of the more important functional entities in both organic chemistry$^1$ and biochemistry.$^2$ This importance extends to $\alpha$-dicarbonyl systems. These systems are useful in preparative chemistry; they occur commonly in biological systems; and they have recently been advanced$^3$ as chemotherapeutic agents for cancer.

As a result, the electronic structure of $\alpha$-dicarbonyl systems is of considerable interest and much work, both theoretical and experimental, has been devoted to them. Unfortunately, almost all of this work has been of a standard electronic photon-emission and absorption type,$^4,5$ and it has not led to any final resolution of a number of important questions. These questions relate to:

(i) Circular dichroism of and chirality in the $\alpha$-diketones$^6$

(ii) The nature of the low-energy excited states of the $\alpha$-dicarboxyls$^7$

(iii) The unique emission properties of the $\gamma$-dicarboxyls$^8$

(iv) The molecular orbital energy-level diagram pertinent to the various electronic states.$^9$

Photoelectron spectroscopy (pes) can provide information on question (iv), at least for the ground state. While pes provides no direct answers to questions (i) - (iii), it should generate information which
might eliminate various speculative possibilities concerning all of
them. Hence, the purpose of this work is to provide pes data for
some key α-dicarbonyl compounds.

The focus of this work is on the molecules oxamide and
oxamic acid. The pes of the monocarbonyl analogues, formic acid\(^{10}\)
and formamide\(^{10}\) are available but no data are available on 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 \(\text{HCONH}_2 \rightarrow \text{H}_2\text{NCONH}_2 \rightarrow \text{H}_2\text{NCOCONH}_2\). Hence, this work is
also concerned with the pes of urea and its interpretation.

The discussion of oxalic acid given here is brief and rep­
resents no more than the presentation of an energy level diagram de­
duced from more detailed studies; these studies will be presented
in a following paper. Indeed, the discussion of oxalic acid given
here is pertinent only to the correlative effort by which we seek
to identify the one-electron levels of oxamic acid in terms of those
for oxamide and oxalic acid.
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\(^\circ\) (21.22eV) 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\(^\circ\) to 119\(^\circ\)C. 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 20-25meV.

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

Semi-empirical CNDO/s-CI calculations\(^\text{11}\) were carried out for formaldehyde, formamide, urea, oxamide, oxalic acid and oxamic acid in geometries appropriate to their ground states.\(^\text{12}\) The MO notation used has been discussed previously\(^\text{13}\) and is quite straightforward. The MO's of a monocarbonyl such as HCONH\(_2\) are labeled \(n\), \(\pi\) and \(\pi^*\). They have the following significance: \(n\) is a non-bonding \(\sigma\) MO with dominant amplitude on the carbonyl oxygen; \(\pi\) is the \(\pi\)-MO of the carbonyl group in \(H_2CO\), appropriately delocalized to...
embrace the nitrogen center in formamide; and \( \pi_0 \) is a \( \pi \)-MO with large amplitude on the amine group. In a symmetric dicarbonyl such as oxamide, the MO notation is expanded, in a quite obvious way, to \( \pi_+ \), \( \pi_- \), \( \pi_+^\text{t} \), \( \pi_-^\text{t} \), and \( \pi_\Theta \), where the extra +/- subscripts denote bonding/antibonding combinations of the constituent formamide MO's. This latter notation is inexact in the case of unsymmetrical dicarboxyls such as oxamic acid but, for want of a better, 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 \( \pi, \pi, \pi_\Theta \) and \( \pi_\Theta \) 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, 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 pes 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 10.8eV. The second of these features, the 10.5eV region, appears to exhibit a substructure with an ~1400cm\(^{-1}\) interval. If this inference be correct, we may suppose this 1400cm\(^{-1}\) 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 18eV, 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 \(\text{H}_2\text{CO}\), \(\text{HCONH}_2\) and \(\text{H}_2\text{NCONH}_2\) are given in Figure 2, where they are correlated on the basis of MO wavefunction analogies and are compared with the 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.
TABLE I.

IONIZATION POTENTIALS OF UREA AND \( \gamma \)-DICARBONYLS (in eV)\(^2\).

<table>
<thead>
<tr>
<th></th>
<th>IP(1)</th>
<th>IP(2)</th>
<th>IP(3)</th>
<th>IP(4)</th>
<th>IP(5)</th>
<th>IP(6)</th>
<th>IP(7)</th>
<th>IP(8)</th>
<th>IP(9)</th>
<th>IP(10)</th>
<th>IP(11)</th>
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</thead>
<tbody>
<tr>
<td>UREA</td>
<td>10.15</td>
<td>10.5</td>
<td>10.8</td>
<td>14.5</td>
<td>15.9</td>
<td>17.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(H(_2)NCO(_4)H(_2))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MO TYPE</td>
<td>(\pi)</td>
<td>(\sigma)</td>
<td>(\pi)</td>
<td>(\sigma)</td>
<td>(\pi)</td>
<td>(\sigma)</td>
<td>(\pi)</td>
<td>(\sigma)</td>
<td>(\pi)</td>
<td>(\sigma)</td>
<td>(\pi)</td>
</tr>
<tr>
<td>OXAMIDE</td>
<td>9.41(A)</td>
<td>10.50(A,V)</td>
<td>11.04(A,V)</td>
<td>11.52(A)</td>
<td>13.26(A)</td>
<td>14.33(A)</td>
<td>14.90(A,V)</td>
<td>15.70</td>
<td>16.15</td>
<td>17.80</td>
<td>18.70</td>
</tr>
<tr>
<td>(H(_2)NCOCONH(_2))</td>
<td>9.80(V)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\nu)(_{vib})</td>
<td>440cm(^{-1})</td>
<td>1321cm(^{-1})</td>
<td>1291cm(^{-1})</td>
<td>1559cm(^{-1})</td>
<td>1570cm(^{-1})</td>
<td>1371cm(^{-1})</td>
<td>1412cm(^{-1})</td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>MO TYPE</td>
<td>(n^+)</td>
<td>(\pi)</td>
<td>(\pi)</td>
<td>(\sigma)</td>
<td>(\pi)</td>
<td>(\sigma)</td>
<td>(\pi)</td>
<td>(\sigma)</td>
<td>(\pi^+)</td>
<td>(\sigma)</td>
<td>(\pi)</td>
</tr>
<tr>
<td>(H(_2)NCOOH)</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
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</tr>
<tr>
<td>MO TYPE</td>
<td>(n^+)</td>
<td>(\pi)</td>
<td>(\pi)</td>
<td>(\sigma)</td>
<td>(\pi)</td>
<td>(\sigma)</td>
<td>(\pi^+)</td>
<td>(\sigma)</td>
<td>(\sigma)</td>
<td>(\pi)</td>
<td>(\sigma)</td>
</tr>
<tr>
<td>(HOOCOOH)</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MO TYPE</td>
<td>(n^+)</td>
<td>(\pi)</td>
<td>(\pi)</td>
<td>(\sigma)</td>
<td>(\pi)</td>
<td>(\sigma)</td>
<td>(\pi^+)</td>
<td>(\sigma)</td>
<td>(\sigma)</td>
<td>(\pi)</td>
<td>(\sigma)</td>
</tr>
</tbody>
</table>

\(^2\)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 \(\nu\)\(_{vib}\) denote coupled vibrational energies of the ion.
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. All orbitals not labelled are $\sigma$ MO's.
The experimental data used in construction of Figure 2 are taken, for \( \text{H}_2\text{CO} \), from Turner et al.\(^{14}\) and, for \( \text{HCONH}_2 \), 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 14.2eV (\( \pi \)) and 14.75eV (\( \sigma \)) assignments of formamide might well be inverted [i.e., 14.2eV (\( \sigma \)) and 14.75eV (\( \pi \)) ] since such an inversion would in no way counter the experimental facts. The salient predictions concerning urea are that the \( \pi^* \) ionization of \( \text{HCONH}_2 \) should split into two, \( \pi^* \) and \( \pi_0^* \); that the \( \pi/\pi^* \) ionization order in \( \text{HCONH}_2 \) should invert in urea [i.e., \( I(\pi_0^*) < I(\pi) \)]; and that a similar inversion should occur for the \( \sigma/\pi \) ionizations in the 15-16eV 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 3(a) and exhibits at least eleven 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 computational
Figure 3: Photoelectron spectra of oxamide, oxamic acid and oxalic acid.
Figure 4: Detail of high-resolution pes of oxamide. Band assignments and vibrational analyses are also indicated. The coupled vibrational frequencies are Band $n_d$ [Figure 4(a)], 440 and 1620cm$^{-1}$; Band $\eta_\Theta$ [Figure 4(b)], 1320cm$^{-1}$; Band $\eta_r$ [Figure 4(b)], 1290cm$^{-1}$; Band $n_\pi$ [Figure 4(c)], 1560cm$^{-1}$; Band $n_\pi$ [Figure 4(d)], 1570cm$^{-1}$; Band $\sigma$, 14.5eV [Figure 4(e)], 1370cm$^{-1}$; Band $\sigma$, 14.90eV [Figure 4(e)], 1410cm$^{-1}$.
Figure 5: Correlation diagram for urea, oxamide and formamide on the basis of both computational and experimental results. All levels not labelled are of σ type.
with respect to number (2 for HCONH₂, 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 14.5eV band could well be π whereas any one of the two bands, 15.7 and 16.15eV, could be assigned as π⁺.

The large n⁺/n⁻ splitting of 1.92eV which occurs in oxamide is in accord with computation which predicts 2.25eV. This splitting is attributable to "through-bond mixing" of the n⁺ and -C-C- σ MO's of oxamide and has already been discussed by Swenson et al. and Cowan et al. for various other α-dicarboxyls. 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 440cm⁻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 non-ionic ground states. The structure in the n⁺ band is, as expected, dominated by two progressions in an ~1600cm⁻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
Figure 6: Correlation of experimental pes data and computational CNDO/s MO data for oxalic acid, oxamic acid and oxamide. All levels not labelled are of $\sigma$ type.
*E N E R G Y  (eV)*

\[ \begin{array}{c}
0 \\
HCC0H \\
\_0 \\
HOCCHOH \\
0 \\
HOCCHNH_2 \\
0 \\
H_2NCCHNH_2 \\
0
\end{array} \]

\[ \begin{array}{c}
n_+ \\
\pi_+ \\
\pi_0 \\
n_- \\
\pi_0 \\
\pi_-
\end{array} \]

**ENERGY (eV)**

---

\[ \begin{array}{c}
10 \\
12 \\
14 \\
16 \\
18 \\
20 \\
22
\end{array} \]

**a. PES**

**b. CNDO/s**
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 acid are given in Figure 4(c) and (b), 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; this analysis will be discussed in a following paper.18

The experimental data for the three di-keto 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 12.42eV band of oxamic acid appears to consist of two ionization events. The evidence for this consists of its 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 \( \pi^* \) ionization events and the \( n^- \) ionization event.

(ii) The order of the \( \pi^* \) events in oxamic acid is inverted relative to the order in either oxamide or oxalic acid. The subscripting is not rigorous in oxamic acid because of the unsymmetrical nature of this acid. Nonetheless, the notation has a basis, though admittedly a weak one, in the computational data for the MO wavefunctions. In any event, it is well to stress that the 11.24eV band of oxamic acid is, on the basis of energy, heavily involved with the amic group of oxamide and that this conclusion concurs with
computation, where the $\pi^*$ MO of oxamic acid is found to have dominant amplitude on the $-\text{CONH}_2$ side of the molecule. The opposite conclusion applies to the 12.40eV region (i.e., the $\pi^*$ band) where computation and experiment suggest dominant amplitude on the $-\text{COOH}$ 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 $\pi^+_+$ ionization events in oxamic acid is not very secure. These identifications are largely based on barycenter considerations [i.e., $\pi^-_+$ (oxamic acid) = $\frac{1}{2} \pi^-_-$ (oxamide) + $\frac{1}{2} \pi^-_-$ (oxalic acid)]; this attitude, while computationally consistent for $\pi^-$, is not borne out by the computational data for $\pi^+_+$.

(v) All bands not assigned are, by default, attributed to $\sigma$ 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 massively impressive and substantiates the assignments.

A few other comments also appear to be in order:

(vii) The oxalic acid ionization region 12.8-13.3eV appears to contain three ionization events. Firstly, 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. Secondly, the computations do predict the occurrence of three separate events in this region. They are assigned as \( n_\Theta \), \( n_\Theta^\perp \) and \( n_- \) ionization events.

(viii) The \( n_\Theta /n_\Theta^\perp \) 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 \( n_\Theta \) and \( n_\Theta^\perp \) bands are largely localized on individual sides of the molecule, -CONH\(_2\) and -COOH sides respectively, and is not a consequence of larger \( \pi \)-interactions along the skeletal framework.
REFERENCES


6. E. Charney and L. Tsai, J. Amer. Chem. Soc., 93, 7123(1971);


11. The program used here was QCPE:CNDO 174.


CHAPTER IV.

N-METHYLATION SHIFTS
INTRODUCTION

Previous discussion in this work\textsuperscript{1,2} has been concerned with photoelectron spectra of various carbonyl-containing molecules and their interpretation in terms of composite models.\textsuperscript{1,2} The present work represents an attempt to carry the composite molecule approach to a higher degree of complexity: it essays an interpretation of the pes of parabanic acid (imidazolidinetrione).

\[
\begin{array}{c}
\text{O} \\
\text{H} \\
\text{N} \\
\text{C} \\
\text{N-H} \\
\text{1} \\
\text{O=C} \\
\text{C=S} \\
\end{array}
\]

Parabanic acid may be viewed as a composite of (i) urea and cis-glyoxal; (ii) a single carbonyl group and cis-oxamide; (iii) three carbonyl groups and two sp\textsuperscript{2} hybridized nitrogens; (iv) two formamides and one carbonyl group; and (v) one imide and one amide. It will be shown that the composite molecule approach remains valid and that the partitioning of most utility is (i).

The effect of N-methylation on the ultraviolet absorption spectra of amides\textsuperscript{3} and oxamides\textsuperscript{4} has been a useful diagnostic tool in making distinction between $1\pi\pi^* \leftarrow 1\sigma_1$ and $1\pi^* \leftarrow 1\sigma_1$ transitions. It is expected that similar diagnostic utility should reside in N-methylation effects on pes ionization energies. Thus, an $\pi$-MO largely localized on the $\geq C=O$ groups should be much less sensitive to N-methylation than a $\pi_{\text{C-MO}}$ which has large amplitude
on the amine nitrogens. Indeed, it has been asserted\textsuperscript{5} that such
differential effects of N-methylation are responsible for a reversal
of the two lowest energy pes bands of formamide, where $I(n) < I(\pi_\sigma)$,
on going to N-methylformamide, where $I(\pi_\sigma) < I_n$. It is a purpose of
the present work to investigate the diagnostic utility of N-methylation
(or N-alkylation) in corroborating prior assignments\textsuperscript{2} of the pes of
oxamide and in making assignments of the pes of parabanic acid.

The MO notation used in the discussion of oxamides has
been elaborated previously\textsuperscript{2} and consists of the set $\{n_+, n_-, \pi_\sigma^n, \pi_\sigma^e, \pi_\sigma^o, \pi_\sigma^t\}$, the $\sigma$-MO's remaining undifferentiated. The MO notation
used in the discussion of urea consists of the set $\{n, \pi_\sigma^n, \pi_\sigma^e, \pi_\sigma^t\}$. The MO notation which has been found useful in discussing parabanic
acid consists of two subsets: $\{n_+, n_-, \pi_\sigma^n, \pi_\sigma^e, \pi_\sigma^o, \pi_\sigma^t\}$ of oxamide
and $\{n, n\}$ of urea. It should not be inferred that these two sub­
sets do not overlap; it may be inferred, however, that the overlap
is small.
EXPERIMENTAL AND COMPUTATIONAL

Instrumentation and techniques have been described previously. All chemicals were prepared and purified in these Laboratories and are described elsewhere. Semi-empirical CNDO/s-CI calculations were carried out for cis-glyoxal, urea, parabanic acid, N-methylparabanic acid and N,N'-dimethylparabanic acid at geometries appropriate to their ground states.
RESULTS

The experimental pes data consist of ionization band energies, band intensities, vibronic structure associated with a given band, and N-methylation effects on specific band energies. The number of specific identifications of band type which can be made on the basis of such data is not very large. Nonetheless, in the discussion of this section we will append identifications to the majority of the observed bands. The justification for such identifications resides in correlative schemes and in comparison with CNDO/s computational results which will be discussed later, and in the consistency of application of additivity rules which have been discussed previously.¹

The photoelectron spectra of the oxamides are shown in Figure 1 and those of the parabanic acids are shown in Figure 2. The experimental pes data, with assignments, are shown in Table I.

The n-band of these systems is the only one which consistently exhibits vibronic structure. These bands, where resolvable, are shown in Figures 3 and 4, and are detailed in Table II. The coupled vibration, in all instances, is the simple carbonyl stretching mode. The n⁺ band is vibronically resolvable only in oxamide² where it exhibits skeletal modes as well as a carbonyl stretching mode. We take the presence of low-frequency modes in the n⁺ band of oxamide as a vindication of the "through-bond" coupling⁹ of the n⁺-MO and the σ-bonding MO of the C-C bond of oxamide. The multiple
Figure 1: Photoelectron spectra of (a) \( N,N,N',N' \)-tetramethyloxamide, (b) \( N,N' \)-dimethyloxamide; (c) oxamide; (d) \( N,N' \)-di-\( n \)-propyloxamide.
Figure 2: Photoelectron spectra of (a) dipropylparabanic acid; (b) dimethylparabanic acid; (c) methylparabanic acid; and (d) parabanic acid.
Figure 3: Photoelectron spectra of the n_ band of (a) OX; (b) DMOX; (c) TMOX.
RELATIVE COUNT RATE

ELECTRON VOLTS

a  OX  
b  DMOX  
c  TMOX  

11.4  11.8  12.2  12.6  13.0  10.8  11.2  11.6  12.0  10.0  10.4  10.8  11.2
Figure 4: Photoelectron spectra of the $n_\sigma$ band of (a) PBA;

(b) MPBA; and (c) DMPA.
<table>
<thead>
<tr>
<th>MOLECULE</th>
<th>I(1)</th>
<th>I(2)</th>
<th>I(3)</th>
<th>I(4)</th>
<th>I(5)</th>
<th>I(6)</th>
<th>I(7)</th>
<th>I(8)</th>
<th>I(9)</th>
<th>I(10)</th>
<th>I(11)</th>
<th>I(12)</th>
<th>I(13)</th>
</tr>
</thead>
<tbody>
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<td>OX</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td>DMOX</td>
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<td></td>
<td></td>
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<td></td>
</tr>
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<td>9.08</td>
<td>9.34</td>
<td>10.49</td>
<td>12.0</td>
<td>13.90</td>
<td>14.46</td>
<td>15.12</td>
<td>16.20</td>
<td>17.9</td>
<td></td>
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<td>TMOX</td>
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<tr>
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<td></td>
<td></td>
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<tr>
<td>PARABANIC ACID</td>
<td>10.67</td>
<td>11.34</td>
<td>11.57</td>
<td>11.79</td>
<td>12.58</td>
<td>14.10</td>
<td>14.57</td>
<td>15.55</td>
<td>16.3</td>
<td>16.8</td>
<td>17.55</td>
<td>18.8</td>
<td></td>
</tr>
<tr>
<td>PBA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>N-METHYLPARABANIC ACID</td>
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<td>10.68</td>
<td>11.2</td>
<td>11.39</td>
<td>12.29</td>
<td>13.73</td>
<td>14.43</td>
<td>15.60</td>
<td>16.10</td>
<td>16.7</td>
<td>17.6</td>
<td>18.1</td>
<td>19.6</td>
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<td></td>
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<tr>
<td>DMPBA</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
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<tr>
<td>N,N'-DIPROPYL PARABANIC ACID</td>
<td>9.90</td>
<td>10.10</td>
<td>10.65</td>
<td>11.90</td>
<td>12.15</td>
<td>12.63</td>
<td>13.90</td>
<td>15.15</td>
<td>16.3</td>
<td>17.0</td>
<td>19.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DPPBA</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
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</tr>
</tbody>
</table>

*Vertical ionization energies are denoted by V; bands so denoted exhibit vibrational structure.*

*bThe vertical and adiabatic ionization energies are identical for these bands.*
vibronic coupling evident in the $n_+$ band of oxamide, as well as the indistinct resolution found in oxamide, provide a good rationale for our inability to resolve any vibrational structure in this band in any of the more complex molecules.

The lowest-energy pes band of the alkyl oxamides is highly intense and, on the basis of relative cross-section, must be supposed to contain three distinct ionization events. This conclusion also follows from direct comparison with the oxamide spectrum: N-alkylation moves the $n_\pi$ and $n_\sigma$ bands towards lower ionization energies faster than it does the $n_+$ band; as a result, all three bands tend toward coincidence, and almost achieve coincidence in TMOX.

The 14eV region of oxamide undergoes massive increase as a result of N-methylation. This region represents the location of new $n$ and $\sigma$ ionization events introduced by N-methylation. A similar statement applies to the 11-14eV region of DPPBA.

The intense, 11-12eV, band of PBA contains three ionization events: $n_\pi$, $n$ and $n_\sigma$ which correspond to the 11.34, 11.57 and 11.79eV pes peaks. However, the precise order of correspondence is not known. The energy of the $n_-$ band is quite insensitive to N-alkylation, as is also the $n_+$ band. The effects of N-alkylation are to move the $n_\sigma$ and $n_\pi$ bands toward the $n_+$ band, in such a way that in DPPBA, the lowest-energy ionization event is $n_\pi$. The energy of the $n_\pi$ band is somewhat more sensitive than that of $n_\sigma$, with the result that these bands become more distinct as a result of methylation. The effects of methylation on the $n$-ionization are somewhat more
difficult to follow; however, it does appear that the $n$ and $\pi^*$ events also invert on proceeding from PBA to DMPBA.

The 14.73eV band of PBA remains distinct in all four compounds and encroaches, as a result of increasing N-alkylation, on the $n_\pi$ band. This 14.73eV band of PBA is identified, as a result, as the $n_\pi$ band. This band lies at 13.11eV in DMPBA and exhibits a weakly defined vibrational progression in an 800cm$^{-1}$ interval.
A consideration of ionization potentials devolves, via Koopmans' theorem, to a consideration of molecular orbitals. Hence, a brief resumé of the types of orbitals which CNDO/s calculations provide for parabanic acids is given and these orbitals are related to those of the two entities, cis-oxamide and urea, into which parabanic acid is most aptly partitioned.

The effects of N-methylation are discussed from both computational and experimental points of view, and the two views are shown to be concordant. The viability of N-methylation as a diagnostic tool is validated.

Finally, CNDO/s results are correlated with the experimental ionization data and the assignments given in Table I are, to some extent, validated.

**MOLECULAR ORBITALS OF PARABANIC ACIDS**

The highest-energy filled MO of all \( \sigma \)-dicarboxyls discussed here, DMPBA and DPPBA being possible exceptions, is of \( \sigma \)-type, is largely localized on the oxygens of the \( \sigma \)-dicarboxyl group, but also possesses considerable \( \sigma \)-bonding character of carbonyl-carbonyl nature, and, following Swenson and Cowan et al., is classified as \( n^+ \). All other \( n \) orbitals lack the intercarbonyl bonding characteristic. The \( n \)-MO is essentially identical to that of urea, and is almost entirely situated on the oxygen of the isolated
carbonyl group. The $n_\text{-MO}$ is the most delocalized of all $n$-MO's, possesses amplitude on all three oxygen centers, but retains a dominant cis-glyoxal identity.

The $\pi_\text{O}$-MO's are heavily localized on the amine residues and are essentially non-bonding. The highest energy $\pi_\text{O}$-MO is $\pi_{\text{cis}}$; the $\pi_{\text{cis}}$-MO embraces both the N-centers and all three carbonyl-centers, and is N- (C = O) antibonding in all instances. The $\pi_{\text{cis}}$-MO is similarly antibonding but possesses a node at the isolated carbonyl group. The $\pi_{\text{cis}}$-MO's are very similar to the corresponding $\pi_{\text{cis}}$ pair of urea but also possess one-to-one correspondences with the $\pi_{\text{cis}}$ pair of cis-oxamide. The $\pi_{\text{cis}}$-MO's possess large amplitudes on the nitrogen centers, ~50%; consequently, they are expected to be very sensitive to N-methylation. In contrast, N-amplitudes for the $\{n_+, n_-, n\}$-MO set is usually less than 8%; hence, their insensitivity to N-methylation.

The $\pi_-$-MO is entirely cis-oxamide localized and is highly N - C - O $\pi$-bonding. It contains ~40% amplitude on the N-centers and this, coupled with its highly conjugative N - C - O nature, should make it exceedingly sensitive to N-methylation.

The $\pi_\text{+}$-MO of cis-glyoxal splits into two in parabanic acid. The one of higher energy has a node between the glyoxal and urea residues and is ~60% urea-localized. This MO is termed $\pi$ and is very similar to the corresponding MO of urea. The other component, which we term $\pi_\text{+}$, is ~80% localized on the cis-oxamide fragment; hence, our retention of the $\pi_\text{+}$ designation. The $\pi$-MO
has less than 5% density on the N-centers, whereas that of the
$\pi^+\text{-MO}$ is $\sim 40\%$. As a result, the sensitivity of these MO's to
N-methylation effects is expected to be quite variant.

The introduction of methyl groups introduces another
sub-set of MO's, some of which are highly conjugative. The effects
of this conjugation are most obvious in the $\pi^+\text{-MO}$, which happens
to be quasi-degenerate with the pseudo $\pi\text{-MO}$ of the $-\text{CH}_3$ group.
The effects of $\pi$-conjugation with the $-\text{CH}_3$ group(s) is shown,
in self-evident notation, in Figure 5 and 6.

**N-ALKYLATION**

The effects of N-methylation on the lower-energy set of
ionizations of oxamide is shown in Figure 7. All four ionizations
move to lower energies, those designated as $I(\pi^+)$ and $I(\pi^-)$
are much less sensitive than $I(\pi^\phi)$ and $I(\pi^\varphi)$. The effects
of various N-alkylations on oxamide ionization energies are
tabulated in Table III. It seems clear that this technique is a useful
means of distinguishing between n and $\pi$ ionization events.

The effects of N-alkylation on the ionization energies of
parabanic acid (PBA) are illustrated in Figure 8 and are tabulated
in Table IV, where they are compared with predictions based on
CNDO/s computations. It seems clear from both computational and experimental evidence, that the diagnostic value of N-methylation in
n/$\pi$ discrimination is considerable.

It will be noted that the two $\pi^\phi$ bands diverge, as a
Figure 5: Computational CNDO/s correlation diagram for cis-glyoxal, PBA, MPBA, DMPBA and urea molecules. The comparison of the two correlation diagrams of Figures 5 and 6, as also the textual language, implies the use of Koopmans' theorem. The computations of Figure 5 are for cis-glyoxal; the experimental pes data of Figure 6 are for trans-glyoxal.
Figure 6: Experimental pes correlation diagram for trans-glyoxal,\textsuperscript{12} PBA, MPBA, DMPBA and urea molecules.
The diagram shows the energy levels of different electronic orbitals in the molecules PBA, MPBA, and DMPBA. The energy is measured in electron volts (eV) on the vertical axis, and the horizontal axis represents the energy levels of various orbitals, including n, π, π⁺, π⁻, and n⁺. The molecules are depicted with their respective chemical structures.
Figure 7: High-resolution photoelectron spectra of the low-energy ionization region of (a) OX; (b) DMOX; and (c) TMOX.
### TABLE II.

VIBRONIC CHARACTERISTICS OF THE n- BAND

<table>
<thead>
<tr>
<th>MOLECULE</th>
<th>NUMBER OF VIBRONIC PEAKS</th>
<th>( \nu_{\text{Av}} (\text{cm}^{-1}) )</th>
<th>( \nu (\text{cm}^{-1}) ) in ( \Gamma_1 )</th>
<th>( \nu^a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>OX</td>
<td>6</td>
<td>1560</td>
<td>1656&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1</td>
</tr>
<tr>
<td>DMOX</td>
<td>5</td>
<td>1530</td>
<td>1650&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1</td>
</tr>
<tr>
<td>TMOX</td>
<td>5</td>
<td>1540</td>
<td>1660&lt;sup&gt;d&lt;/sup&gt;</td>
<td>1</td>
</tr>
<tr>
<td>DPOX</td>
<td>Band Occluded</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>PBA</td>
<td>4</td>
<td>1550</td>
<td>1760&lt;sup&gt;e&lt;/sup&gt;</td>
<td>0</td>
</tr>
<tr>
<td>MPBA</td>
<td>4</td>
<td>1700</td>
<td>---</td>
<td>0</td>
</tr>
<tr>
<td>DMPBA</td>
<td>4</td>
<td>1620</td>
<td>---</td>
<td>0</td>
</tr>
<tr>
<td>DPPBA</td>
<td>Band Partially Occluded</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

<sup>a</sup>The number of quanta of the carbonyl stretching mode which, superposed on \( \Gamma_1 \) (vertical), yields \( \Gamma_1 \) (adiabatic).


<sup>d</sup> D. B. Larson, Ph.D. Dissertation; Louisiana State University, Baton Rouge, Louisiana, August 1972.

### TABLE III.

**N-ALKYLATION SHIFTS (in eV) IN THE PES OF OXAMIDES**

<table>
<thead>
<tr>
<th>MOLECULE</th>
<th>( I(n_+^-) )</th>
<th>( I(\pi^-) )</th>
<th>( I(\pi^-) )</th>
<th>( I(n_-^-) )</th>
<th>( I(\pi_-^-) )</th>
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<tbody>
<tr>
<td>OXAMIDE</td>
<td>0.0</td>
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<td></td>
</tr>
<tr>
<td>DMOX</td>
<td>Expt -0.47</td>
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<td>-0.97</td>
<td>-0.52</td>
<td>-0.97</td>
</tr>
<tr>
<td></td>
<td>Calc -0.25</td>
<td>-0.62</td>
<td>-0.51</td>
<td>-0.28</td>
<td>-1.22</td>
</tr>
<tr>
<td>TMOX</td>
<td>Expt -0.78</td>
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<td>-1.70</td>
<td>-1.23</td>
<td>-1.39</td>
</tr>
<tr>
<td>DFOX</td>
<td>Expt -0.68</td>
<td>-1.25</td>
<td>-1.25</td>
<td>-0.55</td>
<td>-1.55(?)</td>
</tr>
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</table>
Table IV.
N-ALKYLATION SHIFTS (in eV) IN THE PES OF PARABANIC ACIDS

<table>
<thead>
<tr>
<th>MOLECULE</th>
<th>Expt</th>
<th>Calc</th>
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<tbody>
<tr>
<td>PBA</td>
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<td>0.0</td>
</tr>
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<td>MPBA</td>
<td>-0.15</td>
<td>-0.16</td>
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<tr>
<td></td>
<td>-0.66</td>
<td>-0.39</td>
</tr>
<tr>
<td></td>
<td>-0.37</td>
<td>-0.13</td>
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<td></td>
<td>-0.40</td>
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<td>-0.37</td>
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<td>DMPBA</td>
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<td>0.47</td>
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<td>-0.92</td>
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<td>-0.27</td>
</tr>
<tr>
<td></td>
<td>---</td>
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</tr>
</tbody>
</table>
Figure 8: High-resolution photoelectron spectra of the 10-13eV region of (a) PBA; (b) MPBA; and (c) DMPBA.
RELATIVE COUNT RATE
result of N-alkylation, in the parabanic acids, whereas they converge in the oxamides. It will also be noted that the $\pi_e/\pi_o$ order is inverted in these two sets of molecules. This inversion, as a computational result, is vested in the cis/trans "isomerism" which may be supposed to differentiate between the two sets of compounds. Whether or not this cis/trans "isomerism" and the resultant $\pi_e/\pi_o$ inversion has anything to do with the divergency/convergency characteristics is difficult to determine.

**CORRELATION DIAGRAMS**

The results of CNDO/s computations are summarized in Figure 5 and may be compared with the experimental correlation diagram of Figure 6. This comparison is massively impressive, particularly in the lower ionization energy regime. Any assignments which might be made in the higher ionization energy regime (apart from direct comparison with the computational results -- a procedure which is more than suspect) would have little foundation; hence, this region is left largely unassigned.
REFERENCES


7. The program used here was QCPE:CNDO 174.

8. Geometrical parameters used in CNDO/s-CI are:

   Bond lengths and bond angles for PBA were those of D. R. Davis and J. J. Blum, Acta Crystallog., 8, 129(1955).

   Standard structural parameters were used for the -CH₃ groups of the PBA derivatives. Urea: A. Caron and
   J. Donohue, Acta Cryst., 17, 544(1964); cis-glyoxal:


CHAPTER V.

O-ALKYLATION (ESTERIFICATION)
INTRODUCTION

Carbonates and oxalates play key biological roles.\(^1\) Since a composite molecule approach has proven useful in the interpretation of the pes spectra\(^2,3\) of various other mono-, di-, and tricarboxyls, the purpose of the present work is to extend such considerations to the carbonates and oxalates.

Oxalic acid may be viewed as two interacting carboxyl groups. Since the lower-energy ionization events of formic acid\(^4\) are relatively well established, oxalic acid is a prime candidate for a very simple composite molecule approach. Dimethyl carbonate occupies an important niche in the hierarchy HCOOCH\(_3\) \(\rightarrow\) CH\(_3\)OCOOCH\(_3\) \(\rightarrow\) CH\(_3\)OCOCOOCH\(_3\) and should aid in the correlative assignment of the pes of dimethyl oxalate. Unfortunately, the dimethyl carbonate spectrum was rather poorly resolved; hence, a comparative study of dimethyl carbonate and ethylene carbonate was initiated in the hope that the greater rigidity of the latter would lead to higher pes resolution and aid in the interpretation of the poorly speciated spectrum of the former.

Finally, given independent correlative assignments of the pes of oxalic acid and dimethyl oxalate, it was thought that the differential shifts of ionization energies caused by O-alkylation (i.e., esterification) should prove useful in cross-checking the two sets of assignments. Hence, this chapter also exhibits some concern for O-alkylation effects.
EXPERIMENTAL AND COMPUTATIONAL

Oxalic acid dihydrate (Allied Chemical, 99.5%) was recrystallized three times from water. Dimethyl oxalate (MCB), was vacuum sublimed twice. Dimethyl carbonate (Eastman), diethyl oxalate (MCB) and ethylene carbonate (Aldrich) were used without further purification.

Instrumentation and techniques used in studying solid samples have been discussed previously. Liquid samples were degassed three times by a freeze-thaw cycle; the vapor was then bled from a one-liter reservoir through a needle valve into the spectrometer. This latter technique eliminated fluctuations of sample pressure in the sample chamber. An "electron multiplier" detector was used for dimethyl carbonate and ethylene carbonate; a "channeltron" detection system was used for all other compounds.

Semi-empirical CNDO/s calculations were carried out for formic acid, methyl formate, oxalic acid, dimethyl oxalate, ethylene carbonate and dimethyl carbonate at geometries appropriate to their ground state. The MO notation used has been discussed previously: the MO's of a monocarbonyl such as HCOOH are labelled $n$, $\pi_c$ and $\pi$. In the case of esters such as HCOOCH$_3$ a new type of $\pi$ MO, one which has large amplitude on the carbon center of the methyl group and which is $\pi$-C-O-antibonding, occurs. This $\pi$ MO is designated $\pi_{OCH_3}$. The MO notation used for the symmetric $\gamma$-dicarboxyls,
oxalic acid and dimethyl oxalate, is the same one used previously for oxamide. The MO's of the $\alpha$-dicarbonyls are designated $n_+, n_-, \pi^\sigma$, $\pi^\rho$, $\pi^\gamma$, $\pi^\delta$, and $\pi^\alpha$, where the extra +/- subscripting denotes bonding/anti-bonding combinations of the monocarbonyl MO's.

The pes spectra are interpreted in terms of simple one-electron ionization events. Several of the compounds have many bands which exhibit little or no structure and which must, on the basis of relative photon cross-sections, be adjudged to embrace two or more electron ionization events.

**MONOCARBONYLS**

The pes of dimethyl carbonate is shown in Figure 1. The pes of ethylene carbonate obtained here is identical to that of Sweigart et al., with the exception of the lowest-energy band. This lowest-energy band is shown in Figure 2; apart from the extra resolution, it is identical, shape-wise, to the corresponding band of dimethyl carbonate found here or the same band of ethylene carbonate given by Sweigart et al. 8

A vibronic analysis of ethylene carbonate is schematized in Figure 2 and is detailed in Table I. Three origins are clearly observable. Strong progressions in the carbonyl stretching mode are built on the first two origins. We associate the first origin with the 0,0 band of the $n$ ionization and the second with a series of side bands in a $1160\text{cm}^{-1}$ frequency. The weak origin at 11.145eV is attributed to a $\pi^\sigma$ ionization. However, since the two $\pi^\sigma$ ionizations are expected to
Figure 1: Photoelectron spectrum of dimethyl carbonate.
Figure 2: Photoelectron spectrum of the lowest energy ionization band of ethylene carbonate.
TABLE I.

VIBRONIC ANALYSIS OF LOWEST-ENERGY PES BAND
OF ETHYLENE CARBONATE\textsuperscript{a}

<table>
<thead>
<tr>
<th>$\nu$(eV)</th>
<th>$\Delta\nu$(eV)/$\nu$</th>
<th>$\Delta\nu$(eV)$^a$/v</th>
<th>$\Delta\nu$(eV)$^b$/v</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.40</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>10.54$^c$</td>
<td>0.14$^c$</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>10.63</td>
<td>0.23/1</td>
<td>0.25/1</td>
<td>---</td>
</tr>
<tr>
<td>10.79</td>
<td>0.23/1</td>
<td>0.48/2</td>
<td>0.69/3</td>
</tr>
<tr>
<td>10.87</td>
<td>0.47/2</td>
<td>0.67/3</td>
<td>---</td>
</tr>
<tr>
<td>11.03</td>
<td>0.69/3</td>
<td>0.80/4</td>
<td>---</td>
</tr>
<tr>
<td>11.09$^c$</td>
<td>0.69/3</td>
<td>0.80/4</td>
<td>---</td>
</tr>
<tr>
<td>11.14$^c$</td>
<td>---</td>
<td>0.80/4</td>
<td>---</td>
</tr>
<tr>
<td>11.21$^c$</td>
<td>---</td>
<td>0.80/4</td>
<td>---</td>
</tr>
<tr>
<td>11.33</td>
<td>0.93/4</td>
<td>0.80/4</td>
<td>---</td>
</tr>
<tr>
<td>11.42$^c$</td>
<td>0.28/2</td>
<td>0.80/4</td>
<td>---</td>
</tr>
<tr>
<td>11.56</td>
<td>0.41/3</td>
<td>0.80/4</td>
<td>0.61/4</td>
</tr>
<tr>
<td>11.76</td>
<td>0.61/4</td>
<td>0.80/4</td>
<td>1.16/5</td>
</tr>
</tbody>
</table>

\[\Delta\nu$(cm$^{-1}$) \quad 1840$^c$ 1880$^c$ 1160$^b$]

\textsuperscript{a}The observed band-head energies are denoted $\nu$; the frequency differences relative to the specified origin are denoted $\Delta\nu$; the number of coupled vibrational quanta is denoted $v$. 
TABLE I.  
(Continued)

\[ \text{This frequency probably corresponds to } \nu_{16}(b_1), \text{ which is skeletal stretch and occurs}^{10} \text{ at 1125-1180cm}^{-1} \text{ in the ground state. It might also correspond to } \nu_{10}(a_2, \text{ CH}_2 \text{ twist, 1225 in } ^1\Gamma_1) \text{ or to } \nu_{17}(b_2, \text{ skeletal stretch, 1220 in } ^1\Gamma_1). \text{ In any event, the non-totally symmetric nature of this mode indicates} \]

\[ \text{either that the molecule does not have } C_{2v} \text{ symmetry in the gas phase or that the } \nu_5 \text{ mode (a}_1, \text{ skeletal stretch, 1076cm}^{-1} \text{ in } ^1\Gamma_1) \text{ has undergone an increase of frequency in the ionic states. It is also possible that the 10.54 eV origin is vibronic; however, this is not feasible for the 11.14 eV origin where an actual progression in the 1160cm}^{-1} \text{ interval is observable.} \]

\[ \text{This is the } > \text{ C = O stretching vibration, } \nu_8(a_1), \text{ which occurs}^{10} \text{ at 1810-1870cm}^{-1} \text{ in the ground state.} \]
be similar energetically, since the integrated intensity of the band indicates the presence of three ionization events, and since the general band shape leads to a similar inference, a third origin, also attributed to the π↓ ionization, is presumed to lie somewhere in the 11.5 - 11.8eV region. The near identity of the corresponding band of dimethyl carbonate leads to similar conclusions.

Band energies are tabulated in Table II.

**OXALIC ACID**

The pes of oxalic acid is shown in Figure 3(a). Band energies are cited in Table II.

A correlative diagram based on CNDO/s computations is given in Figure 4(b) and is to be compared with that based on experiment, Figure 4(a). Ionization energies are in good accord with computation with regard to number, energy, and the order of occurrence.

The source of the identifications on Figure 4(a) and, hence, the correlation lines is as follows: (i) The data and identifications for H₂CO and HCOOH are taken, without change, from Turner et al.⁹ and Brundle et al.,⁴ respectively. (ii) The second band of oxalic acid (12.5 -13.5eV) consists of three ionization events: π↓ at 12.81eV; π↑ at 12.35eV; and n- somewhere in the 13.0 - 13.4eV region. The reason for this inference lies in the intensity of the band; in the expected ~2eV separation of n+ and n- events, the n↓ being supposed to lie at 11.20eV; in the expected near degeneracy of
Figure 3: Photoelectron spectra of: (a) oxalic acid; (b) dimethyl oxalate; and (c) diethyl oxalate.
the $\pi_e$ and $\pi_o$ events; and in the great sensitivity of the $\pi_o$ events to methylation of the acid oxygens. (iii) The $\pi_-$ event is identified as such on the basis of prior additivity arguments\(^7\) and because of its great sensitivity to esterification. (iv) The $\pi_+$ assignment is largely conjectural.

Apart from specific assignments and conjectures, the comparison of Figure 4(a and b) is impressive and constitutes a potent argument for the assignments given.

**ESTERS**

The pes of dimethyl oxalate is given in Figure 3(b) and the results are tabulated in Table II. The band in the 11-13eV region is supposed to contain three ionization events; the reasons for this supposition are identical to those given for oxalic acid.

The correlative MO diagram of Figure 5(a and b) compares CNDO/s and experimental results. The band identifications in the 10 - 12eV region are quite secure and are impressively validated by the computational considerations. Identifications in the higher energy region are tentative. The data and assignments for $\text{HCOOCH}_3$ used in constructing Figure 5 are taken from Sweigart et al.\(^8\)

The pes of diethyl oxalate is shown in Figure 3(c) and the data are tabulated in Table II. The sharp peaks in the 15 - 17eV region are due to $\text{N}_2$ but do not obscure any detail in this broad spectrum. This spectrum is remarkable only for the evidence it provides for alkyl related ionizations in the 12.5 - 14.5eV regions.
<table>
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<tr>
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<th>I(1)</th>
<th>I(2)</th>
<th>I(3)</th>
<th>I(4)</th>
<th>I(5)</th>
<th>I(6)</th>
<th>I(7)</th>
<th>I(8)</th>
<th>I(9)</th>
<th>I(10)</th>
<th>I(11)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIMETHYL CARBONATE</td>
<td>11.00</td>
<td>11.15</td>
<td>11.6</td>
<td>12.9</td>
<td>13.4</td>
<td>14.2</td>
<td>15.1</td>
<td>15.7</td>
<td>17.0</td>
<td>18.1</td>
<td>19.3</td>
</tr>
<tr>
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<td>n</td>
<td>π⁺</td>
<td>π⁻</td>
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</tr>
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<td>ETHYLENE CARBONATE</td>
<td>10.40(A)</td>
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<td>11.76</td>
<td>13.40</td>
<td>13.55</td>
<td>15.12</td>
<td>15.51</td>
<td>17.1</td>
<td>17.5</td>
<td>18.2</td>
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</tr>
<tr>
<td>MO TYPE</td>
<td>n</td>
<td>π⁺</td>
<td>π⁻</td>
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<td>π⁺</td>
<td>π⁻</td>
<td>n⁻</td>
<td>σ</td>
<td>π⁻</td>
<td>π⁺</td>
<td></td>
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<tr>
<td>DIMETHYL OXALATE</td>
<td>10.30</td>
<td>11.42</td>
<td>11.74</td>
<td>~11.74</td>
<td>13.17</td>
<td>13.48</td>
<td>14.56</td>
<td>14.89</td>
<td>16.4</td>
<td>16.8</td>
<td>18.7(?)</td>
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<td>π⁻</td>
<td>n⁻</td>
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<td>π⁺</td>
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</tbody>
</table>

The notation (A) following an ionization energy denotes an adiabatic event; the notation (V) denotes a vertical event.
Figure 4: Experimental (pes) and computational (CNDO/s) correlation diagrams for formaldehyde, formic acid and oxalic acid. Levels not labelled are of σ type.
Figure 5: Experimental (pes) and computational (CNDO/s) correlation diagram for dimethyl carbonate, dimethyl oxalate, ethylene carbonate and methyl formate.
As found\textsuperscript{3} for N-alkylation, the effects of O-alkylation constitute a valid means of distinguishing between n and $\pi_0$ ionization events. The results are given in Table\textsc{iii} where they are compared with the available computational data. The $\pi_0$ events are seen to be considerably more sensitive to O-alkylation, this conclusion is also in accord, in a qualitative way, with computational results. These differential alkylation effects are also manifest in a decrease of the energy difference $I(\pi_0) - I(n_+)$, which is in remarkable accord with the computational results.
### TABLE III.

**DIFFERENTIAL EFFECTS OF ESTERIFICATION ON THE IONIZATION POTENTIALS OF OXALIC ACID.**

<table>
<thead>
<tr>
<th>IONIZATION EVENT(S)</th>
<th>OXALIC ACID</th>
<th>DIMETHYL OXALATE</th>
<th>DIETHYL OXALATE</th>
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<tr>
<td></td>
<td>expt</td>
<td>calc</td>
<td>expt</td>
</tr>
<tr>
<td>ΔΙ(n⁺)</td>
<td>--</td>
<td>--</td>
<td>-0.90</td>
</tr>
<tr>
<td>ΔΙ(πΟ)</td>
<td>--</td>
<td>--</td>
<td>-1.39</td>
</tr>
<tr>
<td>ΔΙ(πΟ)</td>
<td>--</td>
<td>--</td>
<td>-1.51</td>
</tr>
<tr>
<td>Ι(πΟ) - Ι(n⁺)</td>
<td>1.61</td>
<td>1.37</td>
<td>1.12</td>
</tr>
</tbody>
</table>
REFERENCES

1. The major buffer system of the blood is the bicarbonate/carbonic acid systems and the anticoagulant effect of oxalate has been demonstrated by M. Arthus and C. Page's: I. Davidsohn and B. B. Wells, "Clinical Diagnosis by Laboratory Methods," Chapter 6, W. B. Saunders Company, 1962.


5. The program used here was QCPE:CNDO 174.


CHAPTER VI.

INTERPRETATION OF PHOTOELECTRON SPECTRA

OF CARBONYLS
INTRODUCTION

This chapter continues a previous interest in the use of a composite molecule approach\textsuperscript{1,2} and of $N$-methylation effects\textsuperscript{3} in assigning photoelectron spectra of carbonyl-containing molecules. The molecules of concern here are related to pyruvic acid\textsuperscript{4} and are of type $\text{CH}_3\text{COX}$ where $X = \text{COCH}_3$, $\text{COOH}$, $\text{COOCH}_3$ and $\text{CONH}_2$. These may be viewed as composites of acetaldehyde and $\text{HX}$ where $X$ is defined above.

Previous assignments for formaldehyde,\textsuperscript{5} acetone\textsuperscript{6} and acetic acid\textsuperscript{7} are confirmed by the CNDO/s computations of the present work and are accepted and used as a basis for our correlative efforts. The MO notation used here has been discussed previously\textsuperscript{1,2} and will not be elaborated further. The photoelectron spectra of the $\alpha$-dicarboxyls tend to be crowded and rather uninformative at higher energies. Hence, the only pes assignments in these molecules in which we have faith are those pertaining to $n_+$, $\pi_\sigma^*$, $\pi_\pi^*$ and $n_-$ ionizations, all of which occur in the lower ionization energy regime. Higher ionization energy assignments are provided in the various correlation diagrams but these must be viewed as highly tentative.
**EXPERIMENTAL AND COMPUTATIONAL**

Instrumentation and techniques for the study of both solid and liquid samples have been described previously.$^{2,4,8}$

Acetaldehyde (Mallinckrodt) and acetamide (MCB) were used without further purification. Biacetyl (MCB), 2,3-butanedione, was vacuum distilled twice. Pyruvic acid (Aldrich) was vacuum distilled twice but water remained as an impurity. Pyruvamide and methylpyruvate purifications and/or preparations are described elsewhere.$^9$

Semi-empirical CNDO/s-CI calculations were carried out for acetaldehyde, acetone, acetic acid, biacetyl, pyruvic acid, methylpyruvate and pyruvamide at geometries appropriate to their ground states.$^{10}$
RESULTS

Previous assignments of pes ionization events have been based upon ionization band energies, band intensities and the vibronic structure associated with a given band. Other methods have also proven successful in the assignment of pes bands: N-methylation (N-alkylation) in the oxamides and parabanic acids, and O-alkylation (esterification) in the carbonates and oxalates. In this work, the assignment of specific bands of the unsymmetric $\alpha$-dicarbonyls are made with the aid of correlative schemes and by comparison with CNDO/s computations which will be discussed later.

The pes of acetaldehyde and biacetyl are shown in Figure 1 and those of acetamide, pyruvamide, methyl pyruvate and pyruvic acid are shown in Figure 2. Ionization events and their assignments are tabulated in Table I.

The monocarbonyls, acetaldehyde and acetamide, and their $\alpha$-dicarbonyl counterparts, biacetyl and pyruvamide, exhibit resolvable vibronic structure in their $n$ and $n_-$ bands, respectively. These high-resolution vibronic spectra are shown in Figure 3 and the observed vibrational progressions are tabulated in Table II. The $n_-$ MO's of the $\alpha$-dicarbonyls are antibonding between the carbon-carbon centers and appear to behave much as would two isolated monocarbonyls (i.e., as an $n$ orbital); hence, the presence
Figure 1: Pes of (a) acetaldehyde and (b) biacetyl below 2leV.
Figure 2: Pes spectra of (a) acetamide, (b) pyruvamide, (c) methyl pyruvate and (d) pyruvic acid.
RELATIVE COUNT RATE

ELECTRON VOLTS

H₂O

CH₃=O

CH₃COCH₃

CH₃CNH₂

10 12 14 16 18 20
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<td>$\pi_C$</td>
<td>$\pi$</td>
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<td>17.96</td>
<td>19.46</td>
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<td>15.54</td>
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</tr>
<tr>
<td>MO TYPE</td>
<td>n</td>
<td>$\pi_C$</td>
<td>$\pi$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

*The notation (A) following an ionization energy denotes an adiabatic event; the notation (V) denotes a vertical event.*
Figure 3: High resolution pes of (a,b) acetaldehyde, (c) acetamide, (d) biacetyl and (e) pyruvamide.
TABLE II.

VIBRONIC CHARACTERISTICS OF VARIOUS PES BANDS OF MONO- AND \( \rightleftharpoons \) DICARBOXYLS

<table>
<thead>
<tr>
<th>MOLECULE</th>
<th>( \text{CH}_3\text{CHO} )</th>
<th>( \text{CH}_3\text{COCOCH}_3 )</th>
<th>( \text{CH}_3\text{CONH}_2 )</th>
<th>( \text{CH}_3\text{COCONH}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MO Type</td>
<td>( n ) ( \pi^\circ ) ( n_\text{e} ) ( n ) ( n_\text{e} )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number of Vibronic Peaks</td>
<td>7</td>
<td>7</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>( \tilde{\nu}_{AV} (\text{cm}^{-1}) )</td>
<td>1303</td>
<td>1230</td>
<td>1506</td>
<td>1400</td>
</tr>
<tr>
<td>( \tilde{\nu} (\text{cm}^{-1}) )</td>
<td>1743&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1441&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1725&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1728&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>in ( 1\Gamma_1 )</td>
<td>( \nu^d )</td>
<td>0</td>
<td>5</td>
<td>0</td>
</tr>
</tbody>
</table>


<sup>d</sup>The number of quanta of the carbonyl stretching mode which, superposed on \( I(\text{vertical}) \), yields \( I(\text{adiabatic}) \).
of vibronic structure. The \( \pi^+ \) bands of the \( \sigma \)-dicarbonyls usually do not exhibit vibronic structure for reasons discussed previously. The only other pes band to exhibit vibronic structure was the \( \pi^0 \) band of acetaldehyde.

The second lowest-energy pes bands of methyl pyruvate and pyruvic acid exhibit no structure and must, on the basis of relative photon cross-sections, be adjudged to embrace two distinct ionization events.
DISCUSSION

The insertion of another carbonyl group into acetamide is demonstrated in the photoelectron spectrum of pyruvamide in Figure 2. The n and π ionizations of acetamide are contained in the first pes band whereas in pyruvamide a clear splitting occurs into three bands: the π ionization bracketed on both sides by the n+ and n events which arise from interaction of the two carbonyl n events.

Esterification of the carboxyl group of the acids decreases I(n+), as expected, but decreases I(π) more, so that the I(π) - I(n+) split decreases. The results for pyruvic acid, methyl pyruvate and other α-dicarbonyls are shown in Table III, where they are compared with computational results. Some I(n) - I(n+) splittings are also shown in Table III. The agreement with the computational results is generally good.

The I(π+), and I(π-) identifications, where given, are not very secure. These identifications are based largely on barycenter considerations which infer, for example, that I(π-) for an unsymmetric α-dicarbonyl is one half the sum of the I(π-) ionization events in the two corresponding symmetric α-dicarbonyls. Since the various π ionization energies are significantly dependent on the π "bond path" and this path
### TABLE III.

**SEPARATION OF LOW ENERGY PES BANDS OF α-DICARBONYLS (in eV)**

<table>
<thead>
<tr>
<th>MOLECULE</th>
<th>$n_- - n_+$</th>
<th>$\pi_0 - n_+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BIACETYL</td>
<td>1.91</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>2.01</td>
<td></td>
</tr>
<tr>
<td>PYRUVAMIDE</td>
<td>1.71</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>2.18</td>
<td>1.16</td>
</tr>
<tr>
<td>METHYL PYRUVATE</td>
<td>1.78</td>
<td>1.65</td>
</tr>
<tr>
<td></td>
<td>2.14</td>
<td>1.69</td>
</tr>
<tr>
<td>PYRUVIC ACID</td>
<td>2.00</td>
<td>1.89</td>
</tr>
<tr>
<td></td>
<td>2.16</td>
<td>1.99</td>
</tr>
</tbody>
</table>
is very dependent on the attached substituents, it is clear that this barycenter attitude is not a very good approach to such ionization energies.

**BIACETYL**

A correlation diagram for biacetyl constructed using CNDO/s computations is shown in Figure 4, where it is compared with one based upon experiment. There are two points of note concerning the computational diagram. Firstly, the π_0 MO's of the methyl derivatives are heavily admixed with the π MO of formaldehyde and, as a result, the π_0 subscripting merely indicates that these MO's possess some amplitude on the methyl groups; additionally, since σ/π separability is not rigorous in these compounds, even the π notation has an ambiguous meaning. Secondly, the π_0/π inverted inversions between acetone and biacetyl are notational artifacts associated with the *cisoid* nature of acetone and the *transoid* nature of biacetyl.

The experimental part of Figure 4 was constructed as follows: The n-assignment for acetaldehyde follows, by virtue of intermediacy, from those of formaldehyde and biacetyl. The n_+ assignment in biacetyl follows directly from the presence of the >C=O stretching activity exhibited in this band. Given this, as well as the usual ~2eV separation of n_+ and n_- bands in the o-dicarboxyls, the n_+ being of lower ionization energy, the n_+ assignment follows immediately.
Figure 4: Correlation of experimental and computational results for formaldehyde, acetaldehyde, acetone and biacetyl.
a. PES

b. CNDO/s
The lowest-energy $\pi_0$ ionizations are identified relatively securely in all compounds. However, all others, including $\pi_e$ of biacetyl, are tentative and justified only by comparison with the results of the CNDO/s correlations. The increase of $I(\pi_0)$ in biacetyl relative to $I(\pi_0)$ of acetone is expected on a qualitative basis because the methyl groups of biacetyl are "nearly as isolated" as the single methyl group of acetaldehyde.

**Methyl Pyruvate**

The CNDO/s correlation diagram for methyl pyruvate, taken as intermediate to acetaldehyde and methyl formate, is shown in Figure 5. The experimental correlation curve uses previous assignments for acetaldehyde and methyl formate which are relatively secure. The lowest-energy pes band of methyl pyruvate is clearly $n_+$ on the basis of comparisons with both biacetyl and pyruvic acid. The second pes band of methyl pyruvate must, on the basis of relative intensity, contain two ionization events; these, no doubt, are the $\pi_0$ event associated with the $-\text{OCH}_3$ grouping and the $n_-$ event. Correlation with the $\pi_0$ event associated with the $-\text{CH}_3$ group of acetaldehyde establishes the 13.1eV band of methyl pyruvate as a related event. The single $\pi$ identification in methyl pyruvate is based solely on additivity attitudes; it should be considered tentative.
Figure 5: Correlation of experimental and computational results for acetaldehyde, methyl pyruvate and methyl formate.
PYRUVAMIDE

Pyruvamide, viewed as an intermediate between oxamide and biacetyl, is correlated with these molecules in Figure 6. In view of the non-planarity of two of these molecules the \( \pi/\sigma \) and +/- differentiations are not strictly valid. The \( n^+_\pi \), \( n^-\pi \), \( n^\sigma \pi \), and \( n^\sigma \pi \) designations are quite secure. The \( n^-\pi \) and \( n^+_\pi \) identifications have little experimental justification apart from the facts that bands do occur at the specified locations and that similarities to the CNDO/s correlation diagrams do exist.

A second correlation diagram for pyruvamide, now viewed as a composite of acetaldehyde and acetamide, is given in Figure 7. Those assignments made in Figure 7 are vindicated by the correlations of Figure 6.

PYRUVIC ACID

Pyruvic acid, viewed as a composite of acetic acid and acetaldehyde, is correlated, from CNDO/s computational and experimental points of view, in Figure 8. Only the \( n^+_\pi \), \( n^-\pi \), \( n^\sigma \pi \), and \( n^\sigma \pi \) assignments of pyruvic acid are justified in an experimental sense. The \( \pi \) assignment for pyruvamic acid is correlative only and quite conjectural.

\( \alpha \)-DICARBONYLS

A correlative diagram for a few \( \alpha \)-dicarbonyls studied in this work is shown in Figure 9.
Figure 6: Correlation of experimental and computational result for biacetyl, pyruvamide and oxamide.
Figure 7: Correlation of experimental and computational results for acetaldehyde, pyruvamide, acetamide and formamide.
Figure 8: Correlation of experimental and computational results for acetaldehyde, pyruvic acid, acetic acid and formic acid.
a. PES

b. CNDO/s
Figure 9: Correlation of experimental and computational results for oxalic acid, pyruvic acid, biacetyl, methyl pyruvate and dimethyl oxalate.
REFERENCES


CHAPTER VII.

INTERPRETATION OF PHOTOELECTRON SPECTRA

OF CARBONYL CHLORIDES AND OXAMATES
INTRODUCTION

Previous discussion in this work has attempted the assignment of pes spectra of carbonyl-containing molecules using a composite molecule approach\textsuperscript{1} as well as N-methylation\textsuperscript{2} and O-alkylation\textsuperscript{3} (esterification) effects. The molecules of concern here are oxalyl chloride (OXCL), ethyl oxalyl chloride (EOCL), ethyl oxamate (EONH\textsubscript{2}) and N,N'-dimethyl ethyl oxamate (DMEOX). The photoelectron spectra of these molecules will be discussed within the context of the above approach\textsuperscript{1,2,3} and an assignment of the ionization events in their complicated spectra will be essayed.

Previous assignments for ionization events in oxalic acid,\textsuperscript{4} ethyl oxalate,\textsuperscript{3} oxamide,\textsuperscript{4} oxamic acid,\textsuperscript{4} N,N,N',N'-tetramethylxamide\textsuperscript{2} and phosgene\textsuperscript{5} are accepted and constitute the basis for the present correlative efforts. An MO notation appropriate to a disubstituted \(\nu\)-dicarbonyl (e.g., the oxamide system) is used here. This notation has been discussed previously.\textsuperscript{1,4}
Instrumentation and techniques for the study of both solid and liquid samples have been described previously.\textsuperscript{2,4} Ethyl oxalyl chloride (MCB), oxalyl chloride (MCB), ethyl oxamate (Aldrich) and N,N-dimethyl ethyl oxamate (Baker) were used as received.
**RESULTS**

The pes of oxalyl chloride is shown in Figure 1. The spectra of oxamic acid, ethyl oxamate, ethyl oxalyl chloride and N,N-dimethyl ethyl oxamate are shown in Figure 2. Ionization events and their assignments are tabulated in Table I.

Oxalyl chloride, ethyl oxamate and N,N-dimethyl ethyl oxamate exhibit vibronic structure in the $n_1$ ionization band; the observed vibrational spacings are cited in Table I. The $n_2$ MO's of the $\alpha$-dicarbonyls usually exhibit vibronic structure, an observation which has been discussed previously.\(^2\) The $n_1$ bands of the $\alpha$-dicarbonyl usually do not exhibit vibronic structure.\(^2\)

The second lowest-energy pes band of oxalyl chloride exhibits vibronic structure on the high-energy side; however, on the basis of relative photon cross-sections, this band must be adjudged to contain five distinct ionization events. The lowest-energy band of N,N-dimethyl ethyl oxamate must, on the basis of photon cross-sections and vibronic structure, contain two ionization events. The third band of ethyl oxamate is supposed, for similar reasons, to contain two ionization events.
Figure 1: Fes spectrum of oxalyl chloride.
Figure 2: Pos spectra of (a) oxamic acid; (b) ethyl oxamate; (c) ethyl oxalyl chloride and (d) N,N-dimethyl ethyl oxamate.
## TABLE I.

IONIZATION POTENTIALS OF UNSYMMETRIC α-DICARBOXYLS (in eV)\(^a\)

<table>
<thead>
<tr>
<th></th>
<th>I(1)</th>
<th>I(2)</th>
<th>I(3)</th>
<th>I(4)</th>
<th>I(5)</th>
<th>I(6)</th>
<th>I(7)</th>
<th>I(8)</th>
<th>I(9)</th>
<th>I(10)</th>
<th>I(11)</th>
<th>I(12)</th>
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<td>OXALYL CHLORIDE</td>
<td>11.26(V)</td>
<td>12.36</td>
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<td>12.89</td>
<td>13.42</td>
<td>13.66</td>
<td>14.86</td>
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<td>15.28</td>
<td>16.1</td>
<td>17.2</td>
<td>18.4</td>
</tr>
<tr>
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<td></td>
<td>n</td>
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<td></td>
<td></td>
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<tr>
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<td>(\pi^*)</td>
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<tr>
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<td>12.76</td>
<td>12.83</td>
<td>13.77</td>
<td>14.72</td>
<td>15.85</td>
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<td>19.0</td>
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<tr>
<td>MO TYPE</td>
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<td>(\pi^*)</td>
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<tr>
<td>C(_2)H(_5)OCOCOHN(_2)</td>
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<tr>
<td>MO TYPE</td>
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<td>(\pi)</td>
<td>(\pi^*)</td>
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</tr>
<tr>
<td>N(_2),N-DIMETHYL ETHYL OXAMATE</td>
<td>9.31</td>
<td>11.09</td>
<td>12.4</td>
<td></td>
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<td></td>
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<tr>
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<td>(\nabla_{vib})</td>
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</tr>
<tr>
<td>MO TYPE</td>
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<td>(\pi^*)</td>
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</tr>
</tbody>
</table>

\(^a\)The notation (A) following an ionization energy denotes an \textit{adiabatic} event; the notation (V) denotes a \textit{vertical} event. The energies quoted in cm\(^{-1}\) under \(\nabla_{vib}\) denotes coupled vibrational energies of the ion.
DISCUSSION

The α-dicarbonyl counterpart of phosgene is oxalyl chloride and the assignments of Chadwick\textsuperscript{5} for the former are used, without change, in drafting the experimental correlation diagram of Figure 3.

The ionization event in the 13.4eV region of oxalyl chloride has been assigned to removal of an electron from the n\textsubscript{\textit{MO}}. Two criteria have been used for this assignment:

(i) The observation of vibrational structure, mean spacing 1900cm\textsuperscript{-1}, is typical of n\textsubscript{\textit{pes}} bands; additionally, this spacing corresponds to that of a > C = O stretching mode.

(ii) A separation of ~2eV for the n\textsubscript{\textit{+}}/n\textsubscript{\textit{−}} events is consistent with that found in other α-dicarboxyls.

The ionization event at ~14.4 has been assigned to the π-MO, simply because, in structure and in shape, it is similar to other π-ionization events observed for a variety of other α-dicarboxyls.\textsuperscript{2}

The intense band of ethyl oxalyl chloride when correlated with the pes spectra of diethyl oxalate and oxalyl chloride, exhibits a π\textsubscript{o} ionization event associable with the ethoxy group.

Esterification of a carboxyl group, as previously,\textsuperscript{3} causes a shift of ionization energies, those of π\textsubscript{π} type being most sensitive. This effect is present in the ethyl ester of oxamic acid, the I(π\textsubscript{π}) and I(n\textsubscript{\textit{−}}) events are no longer degenerate as in oxamic acid, Figure 4.
Figure 3: Experimental correlation diagram for phosgene, oxalylic chloride, ethyl oxalyl chloride and ethyl oxalate.
Figure 4: Experimental correlation diagram for oxamide, oxamic acid, ethyl oxamate, N,N-dimethyl ethyl oxamate and ethyl oxalate.
N-methylation has proven to be an effective means of confirming the presence of $\pi_\pi^*$ ionization events associable with the amine group. The use of this technique is illustrated by $\text{C}_2\text{H}_5\text{OCOCON(CH}_3)_2$ in Figure 4. The $\pi_\pi^*$ MO associated with the $-\text{N(CH}_3)_2$ group and the $\pi_+^*$ MO become coincident upon N-methylation.

The second lowest-energy band of N,N-dimethyl ethyl oxamate is somewhat puzzling. It appears to contain, in terms of relative cross-sections, only one ionization event. This ionization event can be supposed to represent removal of an electron from the $\pi_\pi^*$ MO of the $-\text{OC}_2\text{H}_5$ group if, correspondingly, the 12.4 band is assigned to a $n_-$ ionization event. However, this assignment places the $n+/n_-$ separation at $\sim3\text{eV}$, which violates the $\sim2\text{eV}$ rule engendered by experience. If, on the other hand, the 2eV rule is invoked, the 11.2eV band must be assigned to the $n_-$ event. As a consequence, the 9.31eV band may be supposed to contain three ionization events (i.e., $n_-, \pi_\pi^*$ and $\pi_\eta^*$) or the 12.4eV band may be attributed to the $\pi_\pi^*$ ($-\text{OC}_2\text{H}_5$) ionization event. It is difficult to make any reasonable decision on this point. However, the general run of our experience$^{2,3}$ would indicate the correlation given in Figure 4, it being emphasized that, for this one system, we have chosen to neglect the pes intensity data.

The totality of assignments made in this work are contained in Figures 3 and 4 and Table 1. The only compound in which any ambiguity occurs is N,N-dimethyl ethyl oxamate and,
in this case, the reader should refer to the text.
REFERENCES


CHAPTER VIII.

SUMMARY
This work summarizes the photoelectron spectroscopic results for a large number of mono-, \(\alpha\)-di- and tricarbonyl compounds. The assignments which are given for the various pes bands are based largely on a composite molecule approach. For example, urea may be viewed as a composite of ammonia and formamide; parabanic acid as a composite, with appropriate elisions or weightings, of urea and \textit{cis}-glyoxal; etc. The composite molecule approach was itself formalized on the basis of CNDO/s MO computations for the molecule of interest and its component bits. As a result, the business of assignment becomes a correlative effort which attains credibility only as its ability to rationalize the pes bands of a large and diverse set of molecules is established.

The utility of CNDO/s computations, combined with correlative efforts, is reported elsewhere.\(^1,2,3,4\) The purpose of the present work is to summarize the lower-energy pes data and assignments for a variety of carbonyl-containing molecules and to itemize those effects of an experimental nature which were helpful in vindicating the theoretical assignments.

\textbf{MONOCARBONYLS}

The ionization events and assignments for five monocarbonyl molecules are tabulated in Table I. The ionization events in two of these molecules, urea and dimethyl carbonate, have not been reported previously. The pes spectra of acetamide
<table>
<thead>
<tr>
<th>MOLECULE</th>
<th>I(1)</th>
<th>I(2)</th>
<th>I(3)</th>
<th>I(4)</th>
<th>I(5)</th>
<th>I(6)</th>
<th>I(7)</th>
<th>I(8)</th>
<th>I(9)</th>
<th>I(10)</th>
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</tr>
</thead>
<tbody>
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<td>10.5</td>
<td>10.8</td>
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<td>17.7</td>
<td></td>
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</tr>
<tr>
<td>H₂NCONH₂</td>
<td>πο</td>
<td>πο</td>
<td>nπ</td>
<td>πο</td>
<td>πο</td>
<td>πο</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>DIMETHYL CARBONATE</td>
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<td>11.15</td>
<td>11.6</td>
<td>12.9</td>
<td>13.4</td>
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<td>nπ</td>
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<td>πο</td>
<td>πο</td>
<td>πο</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>ETHYLENE CARBONATE</td>
<td>10.40(A)</td>
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<td>11.76</td>
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<td>13.55</td>
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<tr>
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<td>nπ</td>
<td>πο</td>
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<td>πο</td>
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</tr>
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<tr>
<td>ν_vib(cm⁻¹)</td>
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<tr>
<td>MO TYPE</td>
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<td>πο</td>
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<tr>
<td>ACETAMIDE</td>
<td>9.62(A)</td>
<td>10.34</td>
<td>12.98</td>
<td>14.12</td>
<td>15.4</td>
<td>16.0</td>
<td>18.0</td>
<td>19.5</td>
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<tr>
<td>CH₃CONH₂</td>
<td>9.95(V)</td>
<td></td>
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<tr>
<td>ν_vib(cm⁻¹)</td>
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</table>

*The notation (A) following an ionization energy denotes an adiabatic event; the notation (V) denotes a vertical event.*
and ethylene carbonate are identical with those already available.\textsuperscript{5}
However, the lowest-energy ionization band of ethylene carbonate deserves some comments:

(i) The adiabatic ionization energy lies at 10.40eV and not at 10.70eV as previously reported.\textsuperscript{5}

(ii) Three vibrational progressions, with mean spacings of 1840, 1880 and 1160cm\textsuperscript{-1}, have been identified in this pes band.

(iii) In accord with Sweigart et al.,\textsuperscript{5} it is concluded that this band contains three distinct ionization events.

The pes spectrum of acetaldehyde has not been reported. Dewar et al.\textsuperscript{6} have provided a set of ionization energies obtained using a retardation analyser; however, the results obtained here are quite different.

\textbf{α-DICARBONYLS}

The photoelectron spectroscopy of α-dicarbonyls of type X-COCO-Y, where X,Y = NH\textsubscript{2}, NHCH\textsubscript{3}, N(CH\textsubscript{3})\textsubscript{2}, NHC\textsubscript{6}H\textsubscript{5}, OCH\textsubscript{3}, OC\textsubscript{2}H\textsubscript{5}, CH\textsubscript{3} and Cl were studied. Symmetric and unsymmetric α-dicarbonyls are characterized by X = Y and X ≠ Y, respectively. The energy levels and assignments which proceed from this work are shown in Figure 1. Figure 1, at least insofar as assignments are concerned, represents consideration of a number of different effects, all of them invested with considerable assignment capability. These are:

(i) Additivity effects: The energy of an ionization event, I(i), in unsymmetrical α-dicarbonyls is given by
Figure 1: Experimental correlation diagram for $\alpha$-dicarbonyls; trans-glyoxal, $^7$ biacetyl, pyruvic acid, methyl pyruvate, pyruvamide, diethyl oxalate, dimethyl oxalate, oxalic acid, oxamic acid, oxamide, $N,N'$-dimethyloxamide, $N,N'$-di-$n$-propyloxamide, $N,N,N',N'$-tetramethyloxamide, oxalyl chloride, ethyl oxalyl chloride, ethyl oxamate and $N,N$-dimethyl ethyl oxamate.
\[ I(i), XCOCY = \frac{1}{2}[I(i), (XCO)_2 + I(i), (YCO)_2] \]

for \( i = n_+, n_-, \pi_\text{CO}_\text{Y} \) and, possibly, \( \pi_+ \).

(ii) N-methylation (N-alkylation): The \( \pi \)-nonbonding, ionization events, \( \pi_\Theta \) and \( \pi_\Theta^\text{CO}_\text{Y} \) of the amine substituents of oxamide are more sensitive to N-alkylation than are the \( \sigma \)-nonbonding MO's, \( n_+ \) and \( n_- \). Furthermore, the separation between the \( \pi_\Theta \) and \( \pi_\Theta^\text{CO}_\text{Y} \) ionizations generally decreases upon N-methylation.

(iii) O-alkylation (esterification): The ionization potentials of pyruvic, oxalic and oxamic acid are decreased upon esterification, ionization events of \( \pi \)-type, particularly those on the -OH group, being more sensitive than those of \( \sigma \)-nonbonding type.

(iv) Specific ionization events associative with the removal of an electron which is heavily localized on some one group within the molecule (e.g., the \( \pi_\Theta \) electrons of the amine group in oxamic acid) can be discriminated by varying the site of alkyl substitution.

**TRICARBONYLS**

The only tricarboxyls studied were parabanic acid (imidazolidinetrione) and its N-alkyl derivatives. The ionization events observed are tabulated in Table II. The primary interest in these systems was concerned with the ability of composite molecule approaches to provide a description of the pes of a quite complex molecule.
### Table II

**Ionization Energies and Band Assignments of Parabanic Acids**

<table>
<thead>
<tr>
<th>MOLECULE</th>
<th>I(1)</th>
<th>I(2)</th>
<th>I(3)</th>
<th>I(4)</th>
<th>I(5)</th>
<th>I(6)</th>
<th>I(7)</th>
<th>I(8)</th>
<th>I(9)</th>
<th>I(10)</th>
<th>I(11)</th>
<th>I(12)</th>
<th>I(13)</th>
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</thead>
<tbody>
<tr>
<td>PARABANIC ACID</td>
<td>10.67</td>
<td>11.34</td>
<td>11.57</td>
<td>11.79</td>
<td>12.58&lt;sup&gt;b&lt;/sup&gt;</td>
<td>14.10</td>
<td>14.57</td>
<td>15.55</td>
<td>16.27</td>
<td>16.76</td>
<td>17.55</td>
<td>18.81</td>
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<td>FPA</td>
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<tr>
<td>N-METHYLPARABANIC ACID</td>
<td>10.52</td>
<td>10.68</td>
<td>11.2</td>
<td>11.39</td>
<td>12.29&lt;sup&gt;b&lt;/sup&gt;</td>
<td>13.73</td>
<td>14.43</td>
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<td>16.7</td>
<td>17.6</td>
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<td>1700</td>
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<tr>
<td>N,N'-DIMETHYLPARABANIC ACID</td>
<td>10.19</td>
<td>10.33</td>
<td>10.97</td>
<td>11.1</td>
<td>12.19&lt;sup&gt;b&lt;/sup&gt;</td>
<td>13.3(V)</td>
<td>14.19</td>
<td>14.87</td>
<td>15.24</td>
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<td>DMPBA</td>
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<td>1620</td>
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<tr>
<td>N,N'-DIPROPYLPARABANIC ACID</td>
<td>9.90</td>
<td>10.10</td>
<td>10.65</td>
<td>11.90</td>
<td>12.15</td>
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<td>16.3</td>
<td>17.0</td>
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</table>

<sup>a</sup>Vertical ionization energies are denoted by V; bands so denoted exhibit vibrational structure.

<sup>b</sup>The vertical and adiabatic ionization energies are identical for these bands.
RESERVATIONS

In view of the large number of ionization events and assignments that have been made here, it is expected that certain ones will and should be questioned. In specific, the $\pi_+$ assignments are most tentative. Indeed, the only evidence for these assignments is based on additivity effects and on concordance with CNDO/s MO results.
REFERENCES


SELECTED BIBLIOGRAPHY


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VITA

James L. Meeks was born in Harlan, Kentucky on October 4, 1939. He was graduated from Evarts High School, Evarts, Kentucky in 1958.

He entered Cumberland College in Williamsburg, Kentucky in September, 1958 and graduated from that Institution with a B.S. degree in Chemistry in May, 1962. He attended Purdue University from September, 1962 to October, 1964 and joined the faculty of Cumberland College in October, 1964.

In June 1966, he entered Louisiana State University as a participant of the National Science Foundation Summer Program for College Teachers. He was granted sabbatical leave from Cumberland College to attend Louisiana State University where he is presently a candidate for the degree of Doctor of Philosophy.

On August 10, 1963, he married the former Peggy Lavone Taylor and they became the parents of a daughter, Suzanne Vibete, on August 14, 1967.
EXAMINATION AND THESIS REPORT

Candidate: James L. Meeks

Major Field: (Physical) Chemistry

Title of Thesis: Photoelectron Spectroscopy of Carbonyls

Approved:

Sean P. McGlynn
Major Professor and Chairman

James E. Traughnam
Dean of the Graduate School

EXAMINING COMMITTEE:

Robert V. Narum

Philip W. West

Steven F. Watkins

K. N. Hark

Date of Examination:

April 24, 1974