Photoelectron Band Assignments in Monocarbonyls and α-Dicarbonyls[†]

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Received August 8, 1974 (Revised Manuscript Received October 11, 1974)

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I. 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 vibrational considerations,[1] the "perfluoro" effect,[2] PES intensity dependence on photon excitation energy,[3] the association of large or small substituent effects with the antinodal–nodal characteristics of an MO wave function,[4] 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

$$I(i,NX) = I(i) + N\Delta I(i, X) \qquad (1)$$

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[5,6] and α-dicarbonyls,[7-9] 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.,[2] of the 13.4-eV PES band of acetone to $I(\pi)$, where π is the π MO localized on the $>C{=}O$ 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[10] $I(\pi)$ at 14.5 (vertical) or 14.09 eV (adiabatic). The $I(\pi)$ band of formaldehyde may be correlated with either the second or third PES bands of acetaldehyde which occur at $I(2nd)$ = 13.2 (vertical)[11] or 12.61 eV (adiabatic) and $I(3rd)$ at 14.19 (vertical)[11] and 13.54 eV (adiabatic), respectively. The $I(\pi)$ band of formaldehyde may also be correlated with the second or third bands of acetone which occur at $I(2nd)$ = 12.6 (vertical) or 11.99 eV (adiabatic) and $I(3rd)$ = 13.4 (vertical) or 12.79 eV (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

$$H_2CO \xrightarrow{-1.48} CH_3CHO \xrightarrow{-0.62} (CH_3)_2CO \qquad (2)$$

whereas an assumed correlation of $I(\pi)$ of H_2CO with $I(3rd)$ yields

$$H_2CO \xrightarrow{-0.59} CH_3CHO \xrightarrow{-0.71} (CH_3)_2CO \qquad (3)$$

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 eV. Other evidences supportive of this same assignment are as follows.

(1) The $I(\pi)$ values (eV) for methylated ethylenes[12] are 10.50, $CH_2{=}CH_2$; 9.73, $CH_2{=}CHCH_3$; 9.23, $CH_2{=}C(CH_3)_2$; 8.67, $HCH_3C{=}C(CH_3)_2$; and 8.30, $(CH_3)_2C{=}C(CH_3)_2$. The $CH_2{=}C<$ and $>C{=}C(CH_3)_2$ groups are "isoelectronic" with the $>C{=}O$ group and the average values of $\Delta I(\pi,CH_3)$ for the ethylenic groups, -0.64 and -0.47 eV, respectively, are comparable to the values of -0.59 and -0.71 eV found for the carbonyl group in eq 3.

(2) The adiabatic ionization potentials of eq 2, 12.61 (13.2, vertical) and 11.99 eV (12.6, vertical) for CH_3CHO and $(CH_3)_2CO$, respectively, correspond to the first 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.[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 α-dicarbonyls. Prior to doing so, however, a consistent notation is needed.

II. Orbital Notation

The orbital notation used for the π system of monocarbonyls HCOX is shown in Figure 1 for the specific example of

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[†] This work was supported by contract between the U/S. Atomic Energy Commission—Biomedical and Environmental Research Physics Program and The Louisiana State University.

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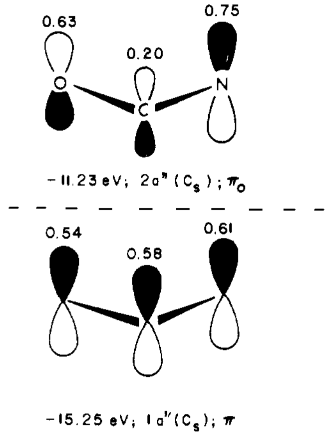


Figure 1. Molecular orbitals of π type for formamide, as generated in a CNDO/s calculation.[13] Numbers above the π lobes refer to MO coefficients at the center in question.

formamide. The substituent X is a group such as -OH or $-NH_2$ which introduces a readily ionizable π-electron pair into the original π system of formaldehyde. The π_O MO is largely localized on the substituent X and is similar to the "ℓ MO" in molecules such as aniline and phenol; it is also an MO type introduced by substituents such as CH_3 where formal π/σ distinctions break down. The π MO is the original >C=O localized π MO of formaldehyde as modified by conjugative interactions with the substituent X. The primary distinction between the π and π_O MO's of HCOX molecules resides in their nodal characteristics in the >C–X bond.

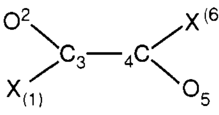
The α-dicarbonyls studied in this work have the general structure XC(=O)C(=O)Y where X, Y = H, R, OH, OR, NH_2, NHR, NR_2, Cl and R = CH_3, C_2H_5. The α-dicarbonyls subdivide into two basic classes: symmetric when X = Y and nonsymmetric when X ≠ Y. However, for purposes of MO designation, it is convenient 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_O, we can subdivide the α-dicarbonyls into "unsubstituted", "monosubstituted", and "disubstituted" types. The utility of this subdivision is embodied in Table I, where the various types of MO's are related to each other and to those of the monocarbonyls by means of a consistent notation which we now elaborate.

The ± subscripting in the case of the π MO's (i.e., $\pi_\oplus$, $\pi_\ominus$, π_+, and π_-) refers to the phasing in the -C-C- bond region of α-dicarbonyl; that is, each member of a pair is bonding (i.e., plus subscript) or antibonding (i.e., minus subscript) in the carbon–carbon bond region.

The n MO of a monocarbonyl is not shown. This MO is largely of 2p AO type; is largely localized on the oxygen center of the carbonyl group; is perpendicular to the >C=O bond axis; and, in a planar molecule such as formaldehyde, lies in the molecular plane. The nomenclature used for the n MO's of a dicarbonyl should infer physical meaning and should be general enough to cover a wide variety of dicarbonyls (i.e., α, β, γ, . . . , saturated or unsaturated, X group or H).

The group orbitals formed from the two n AO's may be distinguished with respect to the phasing of the individual n components or with respect to their transformation properties under some pertinent symmetry element of the molecular point group of the dicarbonyl. The term "phasing" is defined with respect to a line joining the two atomic centers of interest (i.e., the carbon centers in the case of the π orbitals discussed previously; the oxygen centers in the case of n orbitals). The resulting molecular orbitals of type n are defined as being negatively phased, designated n^-, if atomic orbitals on these centers are effectively orthogonal with respect to this "bond line", and positively phased, designated n^+, if they are nonorthogonal (i.e., exhibit bonding character) with respect to this same "bond line". The term "transformation properties" refers to symmetry or antisymmetry (designated n^S and n^A, respectively) with respect to a defined symmetry element of the molecular point group. Unfortunately, since the correlation between the two appropriate nomenclatures, $n^{+/-}$ and $n^{S/A}$, varies with the symmetry of the dicarbonyl, the physical content of both cannot be identical. Hence, we must evolve a physically more consistent notation.

TABLE I. n and π MO's of Monocarbonyls and α-Dicarbonyls[a]



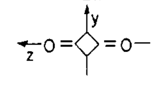
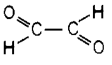
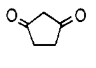
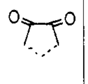
MONOCARBONYLS		α-DICARBONYLS		
Unsubstituted	Substituted	Unsubstituted	Monosubstituted	Symmettic Disubstituted
MO (1) 2 3	MO (1) 2 3	MO (1) 2 3 4 5 (6)	(1) 2 3 4 5 (6)	MO (1) 2 3 4 5 (6)
n (·) + ·	n (·) − ·	n_+ (·) + · · − (·)	n_+ (·) + · · + (·)	n_+ (·) − · · − (·)
		n_- (·) − · · − (·)	n_- (·) + · · − (·)	n_- (·) + · · − (·)
				$\pi_\ominus$ (+) − − + + (−)
	π_O (−) + +		π_O {(·) − − + + (−) or (·) + − + + (−)}	
				$\pi_\oplus$ (−) + + + + (−)
n (·) − +	— + + −	π_- (·) + + − − (·)	n$_-$ (·) − − + + (+)	π_- (−) − − + + (−)
		π_- (·) + − − − (·)	π_+ (·) + + + + (+)	π_+ (+) + + + + (−)

[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 wave functions on the various atomic centers. The dot indicates zero or near-zero wave function amplitude. The numbering system for the atomic centers is shown above. The n and π nomenclature used is strictly valid for wholly planar α-dicarbonyls but retains qualitative significance even when X = CH_3, C_2H_5 or when the α-dicarbonyl is nonplanar.[7,8]

The zero-order degeneracy of the two n group orbitals is removed by interactions with the carbon skeleton. If we restrict our initial considerations to a centrosymmetric point group, we find that inversion symmetry permits definite statements to be made about these interactions. One must first, however, discard the possibility of large interactions of the n group orbitals with virtual orbitals of skeletal nature—a supposition which, based on energy denominator criteria, seems quite safe. Thus, one of $n^{S/A}$ may interact with either σ bonding or other σ nonbonding but symmetric orbitals. Since the former constitute the majority of ground-state orbitals, interactions with these are the most likely and calculation supports this conclusion. The other one of $n^{S/A}$ may interact only with nonbonding, antisymmetric, skeletal orbitals and, again, calculation supports this conclusion. Thus, the two MO's resulting from n^A and n^S interactions with the molecular skeleton may now be relabeled n^σ and n^0, respectively. The physicochemical connotations of this nomenclature are obvious. Unfortunately, this notation does not correlate with that based on phasing of the n orbitals, nor does it correlate with the one based on symmetry in noncentrosymmetric point groups.

The highest symmetry of dicarbonyl compounds is D_{2h} (i.e., cyclobutanedione or quinone); virtually all other dicarbonyl compounds with symmetry greater than C_1 belong to one of the three point groups C_{2h}, C_{2v}, or C_s, all of which are subgroups of D_{2h}. The point group, C_{2v}, however, is not a subgroup of C_{2h} but, with careful definition of molecular symmetry axes, a symmetry correlation which maintains the uniqueness of the n^σ and n^0 notations (and renders them distinguishable with respect to at least one symmetry element) can be obtained. Such a correlation is detailed in Table II. Thus, the statements made for the centrosymmetric point group are

TABLE II. Notations

GROUP[a]	D_{2h}			$C_{2h}(C_{2x})$			$C_{2v}(C_{2y})$			$C_s(\sigma_{xy})$		
EXAMPLE												
CORRELATION CRITERIA	Γ	σ_{xy}	P	Γ	i	P	Γ	σ_{xz}	P	Γ	σ_{xz}	P
n^σ	b_{3g}	n^A	n^-	a_g	n^S	n^-	b_2	n^A	n^-	a'	n^S	n^+
n^0	b_{2u}	n^S	n^+	b_u	n^A	n^+	a_1	n^S	n^+	a''	n^A	n^-

[a] The symmetry element listed in brackets after the group symbol is the element of D_{2h} which is taken to be the principal element of the group in question. Axes for all groups are defined in the specific case of D_{2h}. The notations which are correlated are Γ, the group representation for which $n^{\sigma/0}$ forms a basis; *i* or σ, the manner in which $n^{\sigma/0}$ transforms under the symmetry operation in question; and p, the phasing of $n^{\sigma/0}$ as defined in the text.

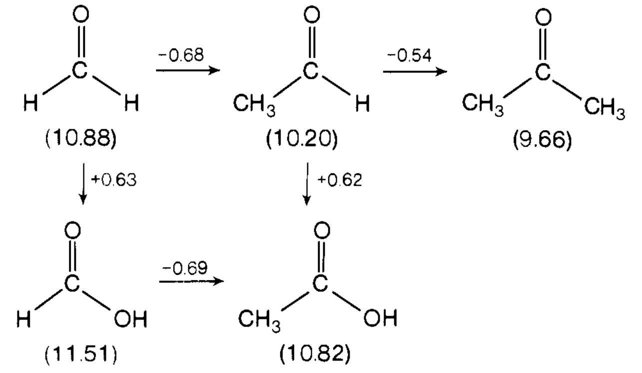
valid for all these groups, and the nomenclature retains its physical significance.

In sum, the simple symmetry designations, $n^{S/A}$, are not generally satisfactory; for example, n^σ is symmetric in C_s and C_{2h} but antisymmetric in C_{2v} and D_{2h}. Thus, the notation $n^{\sigma/0}$ provides the only unique designations, unique in the sense that their physical meaning remains invariant. This meaning is straightforward: n^σ, having interacted with bonding skeletal orbitals, has considerable amplitude on the -C-C- part of the molecule whereas n^0 has none or very little.

On the basis of a simple one-electron approximation, one expects the energy of the resultant orbitals to be $n^\sigma > n^0$ (i.e., n^σ to be the highest energy ground state MO in all cases), and, in fact, experimental evidence supports this conclusion. Ionization of the n^σ orbital should be accompanied by a distinct change in molecular geometry in the cationic state (because of the coupling with a skeletal bonding orbital). As a result, one may expect the photoelectron spectrum to exhibit a band in which the adiabatic and vertical ionizations are not coincident and in which both the carbonyl and the skeletal vibrations are approximately equally excited. On the other hand, ionization of the n^0 orbital should not cause a significant change in geometry; as a result, one may expect the photoelectron spectrum to exhibit a band in which the adiabatic and vertical ionizations are coincident (or, at most, separated by one quantum of vibration) and in which the vibrational activity is predominantly carbonyl. The above conclusions are borne out by all the available PES data for α- and β-dicarbonyls, with one exception: in tetramethylcyclobutanedione, for reasons we do not understand, the n^0 orbital is more readily ionized than n^σ.

For the sake of consistency with previous authors, we now define $n^\sigma \equiv n_+$ and $n^0 \equiv n_-$ and we will use this latter nomenclature throughout this paper. The notations $n_{+/-}$ are used in this sense in Table I.

SCHEME I



The ionization events of interest in this work are those which involve n, π_O, and π electrons in the monocarbonyls and n_+, n_-, π_+, and π_- electrons in the α-dicarbonyls. The ionizations which involve $\pi_\oplus$ and $\pi_\ominus$ electrons in the α-dicarbonyls will not be discussed here in any detail but, because of their great susceptibility to methyl perturbations (i.e., N-alkylation, O-alkylations, etc.), will be deferred to a following work.[14]

III. Experimental Considerations

Photoelectron spectra were obtained on a Perkin-Elmer PS-18 instrument. Experimental details and representative spectra will be discussed elsewhere.[14] 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 vibrational details are available.

IV. Monocarbonyls

A. n-Ionization

The effects of $-CH_3$ and -OH substitution on I(n) of formaldehyde are shown in Scheme I, where $\Delta I(n,CH_3)$, in eV, is indicated on the horizontal arrows, ΔI(n,OH) on the vertical arrows, and I(n) in parentheses below the molecular representation. Methylation of either formaldehyde or formic acid yields similar $\Delta I(n,CH_3)$ values. Substitution of an -OH group in either formaldehyde or acetaldehyde yields identical ΔI(n,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 given in Scheme II.

Finally, the effects of $-CH_3$ and $-NR_2$ (R = H, CH_3) substitution on I(n) of formamide are illustrated for the formamide-*N,N*-dimethylacetamide series[16,17] in the cycle of Scheme III. It appears that N-methylation decreases I(n) by 0.27 eV whereas C-methylation produces a decrease of 0.36 eV.

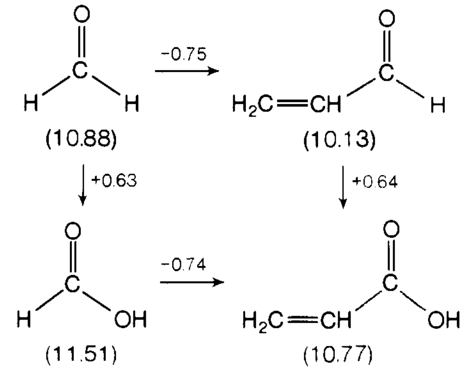
The effects of methylation on the simplest homologs are

$$H_2CO \longrightarrow CH_3CHO \quad \Delta I(n) = -0\ 68$$

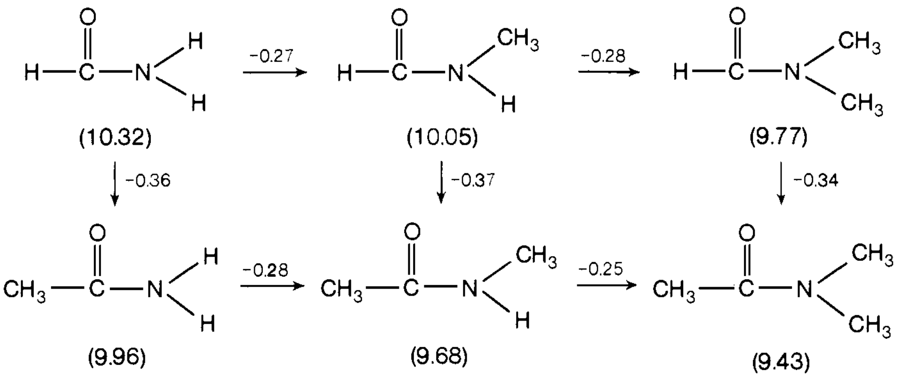
$$HCOOH \longrightarrow CH_3COOH \quad \Delta I(n) = -0.69$$

$$HCONH_2 \longrightarrow CH_3CONH_2 \quad \Delta I(n) = -0.36$$

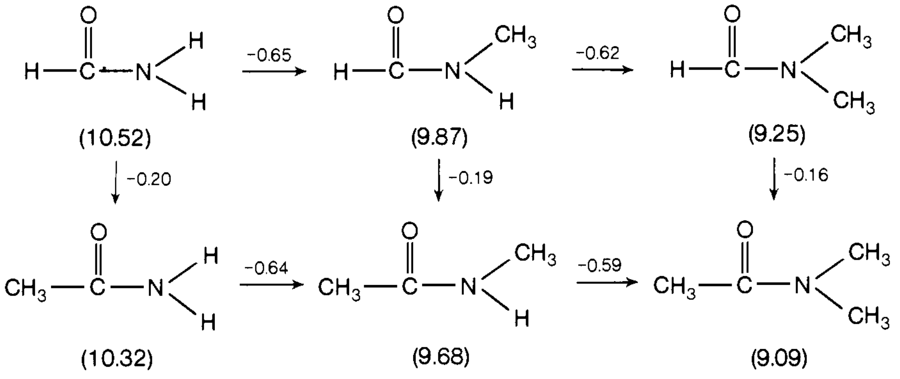
SCHEME II



SCHEME III



SCHEME IV

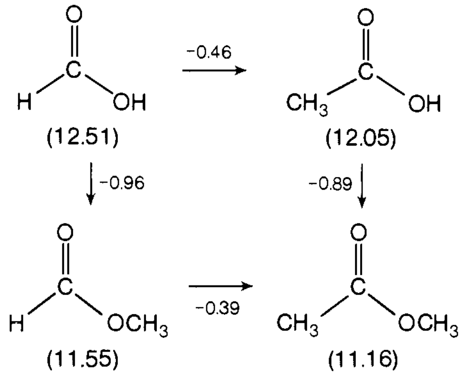


The small magnitude of the last value relative to the first two entries immediately demands explanation. In formaldehyde-acetaldehyde, the adiabatic and vertical ionization energies are coincident. The vertical ionization energies of formic-acetic acids are coincident with the second vibrational peaks of the coupled vibrational progression in the >C=O 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 second and third vibrational peaks, respectively, of the coupled vibrational progression in the >C=O stretching mode. Hence, the adiabatic $\Delta I(n)$ for this couple differs from the vertical $\Delta I(n)$ by one quantum of a >C=O stretching vibration. In this fashion, we find for formamide-acetamide that $\Delta I(n)$ is -0.55 (adiabatic) and -0.36 eV (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.

B. π_O-Ionization

The effects of methylation on $I(\pi_O)$ in the formamide-*N,N*-dimethylacetamide cycle[16,17] are shown in Scheme IV. The decrements for N-methylation are surprisingly constant at ~0.6 eV and for C-methylation at ~0.2 eV. A comparable cycle for C-methylation and O-methylation in the formic acid-methyl acetate series[16,17] is given in Scheme V.

SCHEME V



C. π-Ionization

Similar cycles may be formulated for $I(\pi)$. Several such cycles, all pertinent to the formaldehyde-*N,N*-dimethylacetamide series,[11,16,17] are shown in Scheme VI. 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 vibrational 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 vibrational peak. If 1210 cm^{-1} is used for the coupled vibrational quantum,[10] this correction yields $\Delta I(\pi) = -0.61$ eV for the formaldehyde-acetaldehyde couple. In addition, this same assertion yields $\Delta I(\pi) = 0.31$ 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 14.59 eV for $I(\pi)$ of acetaldehyde, a value that is in excellent agreement with the value 14.5 eV 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 -0.55 eV, $\Delta I(\pi,\text{NH}_2)$ at $+0.25$ eV, $\Delta I(\pi,\text{NHCH}_3)$ at -0.25 eV, $\Delta I(\pi,\text{N(CH}_3)_2)$ at -0.85 eV, and $\Delta I(\pi,\text{CH}_3)$ for N-methylation at approximately -0.55 eV.

SCHEME VI

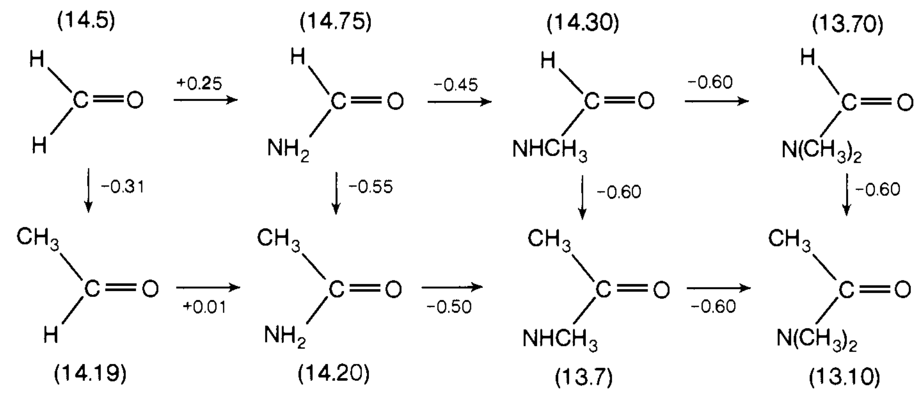


TABLE III. Effects of Substitution on Ionization Potentials (in eV) of Formaldehyde

Substituent, X	$\Delta I(\text{n})$	$\Delta I(\pi)$	$\delta I(\pi_\text{O})$
H			
OH	+0.63		−0.10
OCH_3	+0.14		−0.28
NH_2	−0.36[a]	+0.25	−0.33
CH_3	−0.68	−0.55[b]	−0.30
$CH{=}CH_2$	−0.75		
$NHCH_3$	−0.85	−0.20	+0.17
$N(CH_3)_2$	−1.12	−0.80	+0.35

[a] See text. [b] Vertical ionization energy of acetaldehyde has been adjusted by 2 quanta to obtain this value (see text).

D. Substituent Effects

The totality of ΔI's, referred to formaldehyde as a parent molecule, are listed for $I(\text{n})$ and $I(\pi)$ in Table III. No $\Delta I(\pi_\text{O})$ values are listed since these may not be referred to a formaldehyde "parent." The $I(\pi_\text{O})$ 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 $I(\pi_\text{O})$ ionizations to the appropriate substituent group, Table III includes a listing $\delta I(\pi_\text{O})$. The quantity $\delta I(\pi_\text{O})$ is defined as $I(\pi_\text{O})$ for an HCOX molecule *minus* the lowest ionization energy of an HX molecule, both energies being vertical. Thus, the number listed under $NHCH_3$ for $\delta I(\pi_\text{O})$ is $I(\pi_\text{O})$ for $HCONHCH_3$ minus the vertical energy of the first PES band of NH_2CH_3. In view of the small values of $\delta I(\pi_\text{O})$ found in this way, the π_O identifications given appear to be relatively secure. That is, all π_O 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.

V. *α-Dicarbonyls*

The ionization potentials $I(\text{n}_+)$, $I(\text{n}_-)$, $I(\pi_+)$, and $I(\pi_-)$ of the symmetric α-dicarbonyls are listed in Table IV. The substituent effects, $\Delta I(\text{i},\text{X})$, were evaluated using

$$\Delta I(\text{i},\text{X}) = -{}^1/_2[I(\text{i},\text{HCO})_2 - I(\text{i},\text{XCO})_2] \quad (4)$$

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

$$I(\text{i},\text{XCOCOY}) = I(\text{i},\text{HCO})_2 + \Delta I(\text{i},\text{X}) + \Delta I(\text{i},\text{Y}) \quad (5)$$

or, equivalently, from Table IV using

$$I(\text{i},\text{XCOCOY}) = {}^1/_2[I(\text{i},\text{XCO})_2 + I(\text{i},\text{YCO})_2] \quad (6)$$

TABLE IV. Vertical Ionization Potentials (in eV) of "Symmetric" α-Dicarbonyls

Molecule	$I(\text{n}_+)$	$I(\text{n}_-)$	$I(\pi_-)$	$I(\pi_+)$
HCOCOH[a]	10.52	12.19	13.85	15.88
$CH_3COCOCH_3$	9.55	11.46	13.20	14.73
$H_2NCOCONH_2$	9.80	11.72	13.39	16.15
HOCOCOOH	11.20	13.25	14.40	16.62
$CH_3OCOCOOCH_3$	10.36	11.74	13.48	16.38
$C_2H_5OCOCOOC_2H_5$	10.19	11.41	13.19	16.30
$CH_3NHCOCONHCH_3$	9.33	11.20	12.42	
$(CH_3)_2NCOCON(CH_3)_2$	9.02	10.49	12.32	
ClCOCOCl	11.26			

[a] The assignments quoted for glyoxal are from Turner et al.[10] All other assignments in this table will be discussed elsewhere.[14]

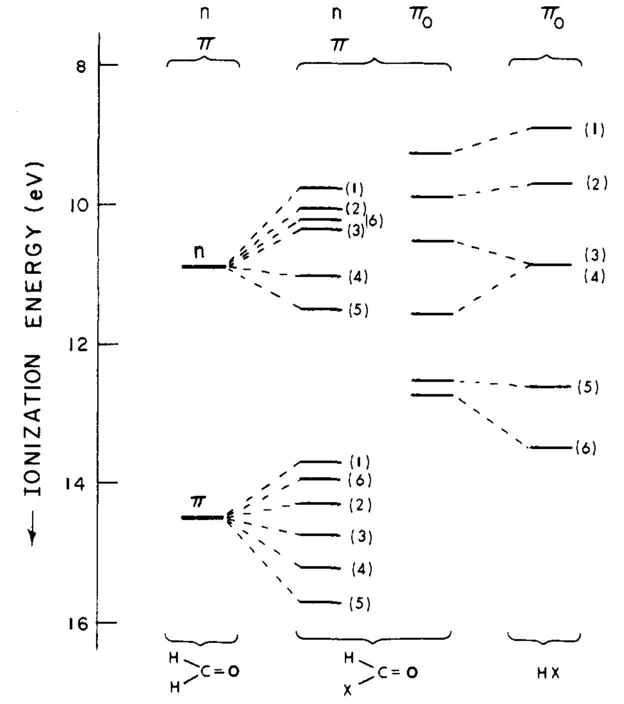


Figure 2. MO energy levels for HCOX and HX molecules as obtained from PES data. The numbering system for X is as follows: (1) $(CH_3)_2N$–; (2) CH_3NH–; (3) NH_2–; (4) CH_3O; (5) OH–; and (6) CH_3–. Data for the lowest energy PES bands of HX were obtained from the following sources: $(CH_3)_2NH$ and $(CH_3)NH_2$ (ref 18); HOH, CH_3OH, and CH_4 (ref 19); and NH_3 (ref 10). All energies plotted are vertical energies.

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

Ionization potentials for the nonsymmetric α-dicarbonyls, as obtained from Table V, are listed in Table VI where they are compared with the experimental values. The agreement

TABLE V. Effects of Substitution on Ionization Potentials (in eV) of Glyoxal

Substituent	$\Delta I(n_+)$	$\Delta I(n_-)$	$\Delta I(\pi_-)$	$\Delta I(\pi_+)$
H				
Cl	+0.37			
OH	+0.34	+0.53	+0.28	+0.37
OCH_3	−0.08	−0.22	−0.34	+0.25
OC_2H_5	−0.16	−0.39	−0.61	+0.21
NH_2	−0.36	−0.24	−0.23	+0.14
CH_3	−0.48	−0.36	−0.32	−0.58
$NHCH_3$	−0.60	−0.50	−0.71	
$N(CH_3)_2$	−1.50	−0.85	−0.76	

of calculated and experimental quantities in Table VI is well within experimental error in all instances except one. The sole exception is $I(n_+)$ of $C_2H_5OCOCON(CH_3)_2$; this exception is noteworthy because this is the only compound in Table VI for which the dicarbonyl dihedral angle[7] is $0 \ll \theta \ll 180°$ and for which our additive approach is clearly invalid anyway. Table VI confirms both the additive ΔI(i) approach and the correlation of levels listed under a given I(i). It must be emphasized, however, that the i assignments which have been made require specific identifications (i.e., i = n_+, n_-, π_+, or π_-) for one compound, preferably the parent molecule glyoxal. Such identifications, fortunately, are available.[10]

Table V and Table III point up the largely inductive nature of the effects being studied: the better donors produce large negative ΔI's; the better acceptors produce small positive ΔI's; and the overall order of ΔI agrees with ordinary chemical notions of donor–acceptor character. The order of substituent effects is identical in both Tables V and III, implying that identifications in the monocarbonyls may, in many cases, be used to classify n/π types in the α-dicarbonyls. The ΔI values also tend to be larger for n MO's than for π MO's. Thus, the enumerated ΔI effects appear to be largely inductive. As a result, and in view of the fact that the ratio ΔI(i,X) is, in most instances, not larger than 5% of I(i), the approximate validity of a perturbation theory approach is assured.[20] 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 $\Delta I(\pi_\pm)$ found in many instances. Such effects are undoubtedly related to overlap densities in the –X–C≡ regions, densities which are assuredly determined by the nodal differences of the ± MO's of π type.

VI. Computational Results

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

A. Computed ΔI's

As seen in Figure 3, the n and π_O energies behave quite differently with respect to the two types of methylation, N- and C-. In fact, for the monocarbonyls, the values of ΔI(i,X), where

$$\overline{\Delta I}(\mathrm{i,X}) \equiv [\Delta I(\mathrm{i,X}) + \Delta I(\mathrm{i},N\mathrm{X})]/(N+1) \qquad (7)$$

are

	CNDO/s	Expt
$\overline{\Delta I}(n,CH_3$ on N)	−0.12	−0.27
$\overline{\Delta I}(n,CH_3$ on C)	−0.29	−0.35
$\overline{\Delta I}(\pi_O,CH_3$ on N)	−0.52	−0.63
$\overline{\Delta I}(\pi_O,CH_3$ on C)	−0.03	−0.18

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.

B. Molecular Orbital Energies

Figure 3 indicates that the n and π_O 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_O order in *N*-methylformamide (which, incidentally, is also the order found by Brundle et al.[17]) cannot be used to infer a similar order in *N*-methylacetamide. Such an inference has been made.[16]

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

C. Methylation Effects on $I(\pi_O)$ and I(n)

A plot of $I(\pi_O) - I$(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 ~0.18 eV. Since this vertical separation also equals

$$[I(\pi_O,CH_3) - I(\pi_O,H)] - [I(n,CH_3) - I(n,H)] \qquad (8)$$

TABLE VI. Experimental and Calculated Ionization Potentials (in eV) of Nonsymmetric α-Dicarbonyls

Molecule	Origin	$I(n_+)$	$I(n_-)$	$I(\pi_-)$	$I(\pi_+)$
$CH_3COCOOH$	Calcd	10.38	12.36	13.81	15.67
	Expt	10.42	12.31	13.79	15.64
$CH_3COCOOCH_3$	Calcd	9.96	11.61	13.19	15.55
	Expt	9.88	11.56	13.04	15.42
$CH_3COCONH_2$	Calcd	9.68	11.59	13.30	15.44
	Expt	9.71	11.48	13.01	15.54
$HOCOCONH_2$	Calcd	10.50	12.48	13.90	16.39
	Expt	10.51	12.40	14.21	16.40
$C_2H_3OCOCONH_2$	Calcd	10.00	11.56	13.00	16.22
	Expt	9.85	11.73	13.15	
$C_2H_3OCOCOCl$	Calcd	10.73			
	Expt	10.77			
$C_2H_3OCOCON(CH_3)_2$	Calcd[a]	8.86	10.95		
	Expt	9.31	11.09		

[a] This molecule is twisted (i.e., $\theta \simeq 90°$) as is the symmetric $(CH_3)_2NCOCON(CH_3)_2$ entity of Table IV from which the $-N(CH_3)_2$ substituent effect of Table V is obtained. Since these are the only two molecules of Table IV and VI which are severely twisted, it is not improbable that the discrepancy between $I(n_+)$, calculated and experimental, for $C_2H_5OCOCON(CH_3)_2$ in Table VI is a result of these nonplanarities. In turn, this discrepancy may imply that conjugative effects on $I(n_+)$, while small, are not negligible.

where substitution is on the formyl carbon, this vertical separation can be computed from the $\Delta I(\pi,CH_3)$ and $\Delta I(n,CH_3)$ values of Table II. The result is 0.18 eV.

Figure 4 is essentially identical with Figure 7 of Sweigart-Turner[16] except in two regards: the $HCONHCH_3$ point is taken from Brundle et al.,[17] and corresponds to their B band/A band energy separation; and the $CH_3CONHCH_3$ point is obtained by assuming that the 9.68 eV PES maximum represents the vertical process for *both* the n and π_O ionizations. In any event, simple parallelism of the two curves of Figure 4 supports the assumption of near-coincidence of the vertical values of $I(\pi_O)$ and $I(n)$ in *N*-methylacetamide.

D. *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, $I(n) = I(\pi_O) = 9.68$ eV, differ from those of Sweigart-Turner, $I(n) = 9.85$ and $I(\pi_O) = 9.68$ 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.

(1) It seemed[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 manner of their use. Hence, further discussions along inductive lines will not resolve the dilemma.

(2) It was thought[16] that the $I(n)/I(\pi_O)$ order in *N*-methylacetamide should be the same as in *N*-methylformamide where quite secure identifications did exist and where $I(\pi_O) < I(n)$. 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 9.68 eV and an inflection at 9.85 eV. 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 1452 cm^{-1}, it is equally logical to suppose that the inflection is of vibrational nature (i.e., a C=O stretching quantum). Indeed, since the half-width of this band, ~0.7 eV, is fully as small as that for molecules in which the $I(n)$ band is totally resolved (~0.6 eV in CH_3COOH, ~0.5 eV in HCOOH), it is equally sensible to assume that the n and π_O vertical ionizations both lie at the maximum (i.e., at 9.68 eV).

In sum, we feel free to reassign the $I(n)$ and $I(\pi_O)$ 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.

VII. 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,[24] Hashmall and Heilbronner,[25] and Johnstone and Mellon.[26] However, the molecules of interest to these authors[24-26] 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 other places,[14] 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.

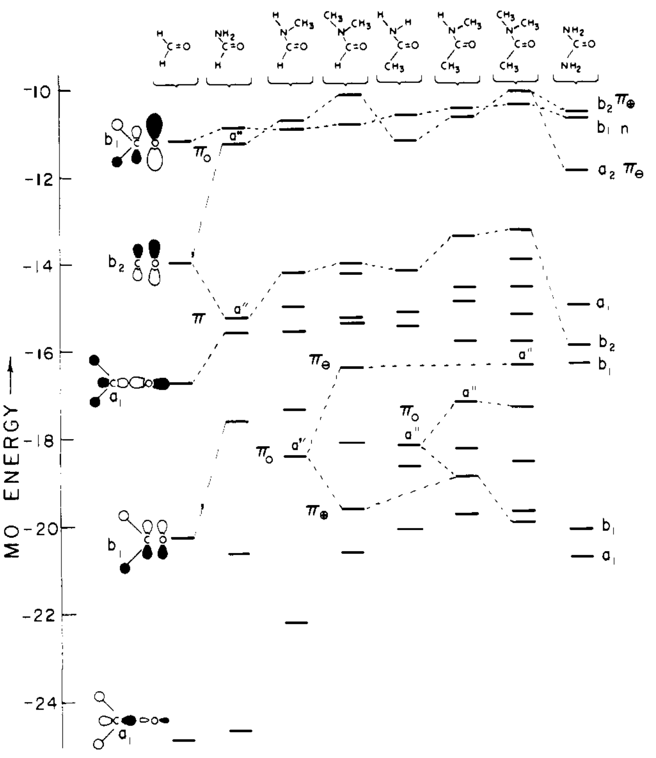


Figure 3. MO energies, as obtained by a CNDO/s computational scheme, for various amides. The upper π_O MO (or, in urea, MO's) refers to a π MO heavily localized on the amidic nitrogen. The bottom set of MO's refer to π MO's which are largely "methyl group" in character; the type of methyl group (i.e., *N*-methyl or *O*-methyl) can be decided by inspection of the figure. The geometric parameters chosen were those for the gaseous molecules,[21] except for urea, for which X-ray crystallographic data[22] were used. Computations followed the Del Bene-Jaffé routine.[23] The amides (C_s symmetry) are correlated with formaldehyde and urea (C_{2v} symmetry).

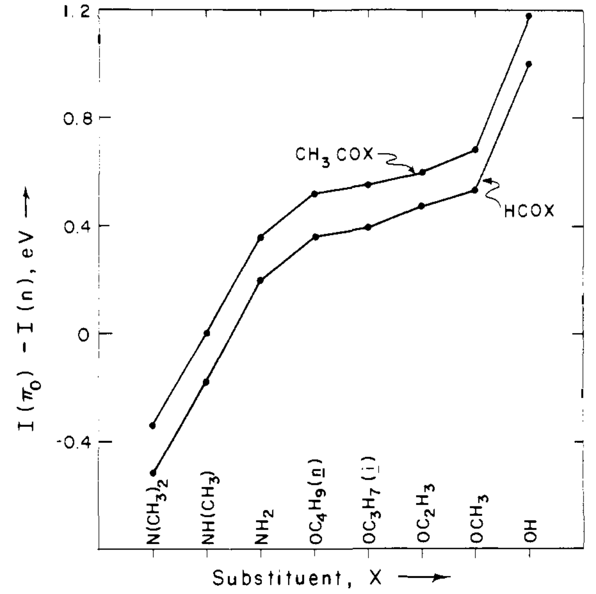


Figure 4. A plot of $I(\pi_O) - I(n)$ for various HCOX and CH_3COX molecules.

This latter caution should be obvious from the textual discussion. In order to be specific, however, it is clear that the additivity algorithm is restricted to the use of adiabatic ionization energies. The vertical ionization energies differ from the adiabatic values by varying numbers of vibrational quanta, and, unless these are known, the ΔI(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 proper use of these quantities and, on the basis of them, makes useful correlative arguments relating to cationic state identifications.

Vertical ionization potentials are commonly used in photoelectron spectroscopy for two reasons: (i) they are the only type which are readily measurable (in other words, it is difficult to extract an adiabatic potential from a vibronically unstructured PES band but rather easy to read off the band maximum); (ii) if the Franck–Condon principle is valid, the vertical ionization event refers to the production of a cationic state which is geometrically identical with the ground state; as such, by invoking Koopmans' theorem, we can equate the vertical ionization energy to a ground-state canonical SCF MO energy—a result which is both fortunate and convenient.

Consequently, the effects of substituents on individual *vertical* ionization energies correspond, in a theoretical sense, to a study of substituent effects on individual MO energies. It is in this specific context that the interpretation of PES spectra becomes "easy". The effects of substituents on individual *adiabatic* ionization energies correspond, in a theoretical sense, to a study of substituent effects on the energy difference between "vibrationless" cationic and ground states, each in its minimum energy geometric configuration. In this latter context, the interpretation of PES spectra could become exceedingly difficult. As long as the difference I(vertical) − I(adiabatic) is not altered by substitution [or, more specifically, if $\Delta I = h\Sigma_i v_i'\nu_i'$, where v_i' is the number of quanta of the normal mode i of frequency ν_i' excited in the cationic state, is invariant to substitution], the interpretation of adiabatic ionization energy differences reverts to that pertinent to the vertical differences and also becomes "easy". When, however, ΔI is altered by substitution, as is the case in some instances reported here, the meaning of adiabatic energy differences grows complex.

Thus, the finding that the substituent additivity algorithm applies to adiabatic processes but not to vertical processes is a bit unfortunate: Additivity applies in a realm which is interpretively difficult (i.e., adiabatic events) and not in one which is interpretively "easy" (i.e., vertical events). In any event, the results obtained do not necessarily contravene Koopmans' theorem; they merely note that MO's do not, in general, exhibit additivity effects. Whether or not the observation that the adiabatic ionization energies do exhibit additivity effects implies that the molecular orbitals of the cation are not simply or smoothly related to those of the neutral molecule (and, hence, that Koopmans' theorem does not apply) is a matter for conjecture.[27]

VIII. References and Notes

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