Predictive Value of Proton Affinity. Ionization Energy Correlations Involving Oxygenated Molecules

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Abstract: Linear relationships between proton affinities and O (1s) core electron binding energies are established for oxygen-containing compounds. From these correlations we deduce that the most stable form of protonated carbon monoxide involves protonation at the carbon, while for anisole the most stable form involves protonation of the aromatic ring, in contrast to benzaldehyde, where protonation at the carbonyl oxygen is favored energetically. Proton affinities are estimated for a number of molecules and for a number of secondary basic (oxygen) sites in molecules where equilibrium measurements provide information only on the most basic site. Linear correlations between proton affinities and valence shell ionization potentials and core binding energies also are observed. The predictive value of these correlations is explored.

The fundamental concept of basicity, defined by Brønsted[2] as the tendency of a molecule B to accept a proton in the reaction

$$B + H^+ \rightarrow BH^+ \qquad (1)$$

has long been of concern to chemists. By definition $-\Delta H_1$ is the proton affinity (PA) of the base B. Although relative basicities in solution have been established for some time, it is only relatively recently that gas-phase basicity measurements have been made by mass spectrometric techniques. Such measurements are essential in evaluating the role of solvation effects on solution basicities and, additionally, are of importance in understanding gas-phase ion-molecule chemistry and its applications in such areas as chemical ionization mass spectrometry.

Early gas-phase measurements[3] used reaction bracketing techniques which provided only approximate relative basicities or proton affinities. More recently, quantitative measurements of equilibrium constants for reactions of the type

$$B_1H^+ + B_2 \rightleftarrows B_2H^+ + B_1 \qquad (2)$$

by ion cyclotron resonance techniques,[4] by high pressure mass spectrometry,[5] and by flowing-afterglow experiments[6] have permitted the determination of relative proton affinities to a precision of ±0.2 kcal mol^{-1}. By the use of suitable reference compounds these can be put on an absolute scale.

The measurement of such equilibrium constants in many cases is not easy and, if the molecule contains more than one basic site, the interpretation of the results is not devoid of ambiguity. Consequently, it is of interest to attempt to correlate proton affinities with some molecular property which can be determined unambiguously. Recently, Martin and Shirley[7] and, independently, Davis and Rabelais,[8] have proposed a linear relationship between relative PAs and inner shell ionization energies for oxygen-containing and nitrogen-containing molecules given by

$$PA = -IE(X_{1s}) + \text{constant} \qquad (3)$$

where IE (X_{1s}) is the ionization energy for the 1s electron (X = O or N). This relation is based on a theoretical model of the ionization process (either addition of a proton or removal of a core electron), where the energy involved is composed of two terms, one related to the electron density in the orbital where ionization occurs (initial state) and the other related to the stabilization of the charge following ionization (final state). Substituents may alter either the first term (inductive effects) or the second term (polarization effects) and the linear relation implies that the latter effect dominates for both modes of ionization. The early work[7,8] showed that the PA values available at that time were not inconsistent with the linear relationship proposed. Carroll, Smith, and Thomas[9] studied more singly and doubly bonded oxygen compounds, which provided further support for the correlation and, also, led to the conclusion that for carboxylic acids and esters the most stable protonated species involved protonation at the carbonyl oxygen. Very recently, Mills, Martin, and Shirley[10] have reported further studies of core binding energy-PA correlations for oxygen- and nitrogen-containing compounds and have shown that similar correlations are observed for sulfur- and phosphorus-containing compounds. They suggested that core binding energies could be used to predict proton affinities.

A major difficulty associated with the previous correlation studies, particularly with respect to the possible predictive value, is that the PA data were taken from numerous sources and, thus, contain inconsistencies related to the reference proton affinity used. Recently, Yamdagni and Kebarle[5b] have reported a consistent set of proton affinity data for a relatively large number of oxygen-containing molecules which have been confirmed by independent measurements.[11,12] It appeared that a further examination of PA-IE correlations using this consistent set of data could provide a more rigorous test of the model proposed and could evaluate the usefulness of such correlations in predicting proton affinities and/or the site of protonation. As will be shown below good linear correlations are obtained, from which it is possible to determine the site of protonation, provide an estimate of the PAs of molecules not amenable to direct experimental study, or, alternatively, evaluate PAs for secondary basic sites in molecules where the experimental measurements pertain only to the most basic site.

In addition, Davis and Rabelais[8] observed a linear correlation between PAs and valence shell ionization potentials (IPs) for oxygen-containing molecules, although such a correlation is not predicted by theoretical models. We have also examined this type of correlation, as well as valence shell IP-inner shell IE correlations, and show that such correlations also have predictive uses.

Experimental Section

Valence shell ionization potentials were obtained from UV photoelectron spectra (He I) obtained using a MacPherson Model 36 photoelectron spectrometer operating with an electron energy resolution of 0.02 eV. The energy scale was calibrated by admitting argon along with the sample of interest and all ionization potentials are relative to the Ar($^2P^3/2$) ionization potential of 15.76 eV.[13]

Oxygen 1s binding energies were determined on the same instrument operating in the x-ray mode and were measured relative to CO_2 ($IE(O_{1s})$ = 541.3 eV[9]), which was introduced simultaneously.

All samples used were commercially available and showed no detectable impurities in their mass spectra.

Table I. Proton Affinities, Ionization Potentials, and O (1s) Ionization Energies of Oxygen-Containing Compounds[a]

Compd	Proton affinity, eV	IP, eV	O (1s) IE, eV
O_2	4.54[b]		543.1[h]
CO	6.12[c]		542.3_0
CO_2	5.58[d]	13.78	541.3_0
H_2O	7.32	12.61	539.6_5
CH_3OH	7.91	10.86	539.1
C_2H_5OH	8.10	10.61	538.8
$(CH_3)_2O$	8.24	9.98	538.5
$(C_2H_5)_2O$	8.59	9.59	538.1
1,4-Dioxane	8.21[e]		538.5
Tetrahydrofuran	8.45[e]		538.1_5
H_2CO	7.28[f]	10.90[g]	539.4_2[i]
CH_3CHO	8.04	10.23	538.6
C_2H_5CHO	8.15	9.96	538.6
n-C_3H_7CHO	8.16[e]	9.85	538.5
n-C_4H_9CHO	8.20[e]	9.82	538.3
$(CH_3)_2CO$	8.44	9.68	537.9
$C_2H_5COCH_3$	8.53[e]	9.49	537.6
HCOOH	7.73	11.34	539.1, 540.6
CH_3COOH	8.12	10.63	538.4, 540.1
C_2H_5COOH	8.20	10.51	538.3, 540.1
$HCOOCH_3$	8.14	10.85	538.5, 539.8
$HCOOC_2H_5$	8.29	10.61	538.4, 539.7
HCOO-n-C_3H_7	8.31	10.50	538.3, 539.5
HCOO-n-C_4H_9	8.28[e]	10.52	538.2, 539.2
CH_3COOCH_3	8.47	10.25	537.9, 539.0
$CH_3COOC_2H_5$	8.59	9.90	537.8, 539.0
CH_3COO-n-C_3H_7	8.61	9.92	537.8, 538.6

[a] Unless otherwise indicated proton affinities from ref 5b and ionization potentials and O (1s) binding energies from this work. For acids and esters lowest O (1s) binding energy is for carbonyl oxygen, higher value for singly bonded oxygen (see ref 9). [b] Reference 20. [c] Reference 18. [d] Reference 19. [e] Reference 12. [f] See text. [g] Reference 13. [h] A. D. Baker and D. Betteridge, "Photoelectron Spectroscopy", Pergamon Press, New York, N.Y., 1972. [i] Reference 9.

Results and Discussion

The O (1s) ionization energies, valence shell ionization potentials, and proton affinities used in establishing the correlations are presented in Table I. The O (1s) ionization energies determined in the present work are in satisfactory agreement with the values reported by Carroll et al.[9] and by Mills et al.,[10] where comparisons can be made. Similarly, the valence shell ionization potentials are, in general, in agreement with the photoionization or photoelectron values reported in ref 13.

Some comment is necessary concerning the proton affinity data. The majority of the values are taken from the work of Yamdagni and Kebarle[5b] where the absolute values were assigned relative to PA (isobutene) = 193.0 kcal mol^{-1} (8.37 eV) as determined from the heat of formation of the *tert*-butyl cation established by monoenergetic electron impact studies.[14] A further tie-point for these values derives from the agreement of PA(CH_3CHO) = 8.04 eV with the value of 8.03 eV derived from $\Delta H_f(CH_3\dot{C}H{=}OH)$ = 141 kcal mol^{-1} established by photon impact measurements.[15] The PA(CH_2O) value listed is obtained from $\Delta H_f(\dot{C}H_2{=}OH)$ = 170 kcal mol^{-1} derived from the average of three independent measurements of AP-($CH_2{=}^+OH$) = 11.67,[15] 11.76,[16] and 11.72 eV[17] from CH_3OH. Similarly, PA(CO) is derived from measurements of $\Delta H_f(HCO^+)$ by photoionization mass spectrometry,[18] while PA(CO_2) is derived with reference to PA(CO) from equilibrium measurements made by the flowing-afterglow technique.[19] The proton affinity of O_2 was derived[20] with reference to PA(H_2) and has not been tied directly to the scale linking

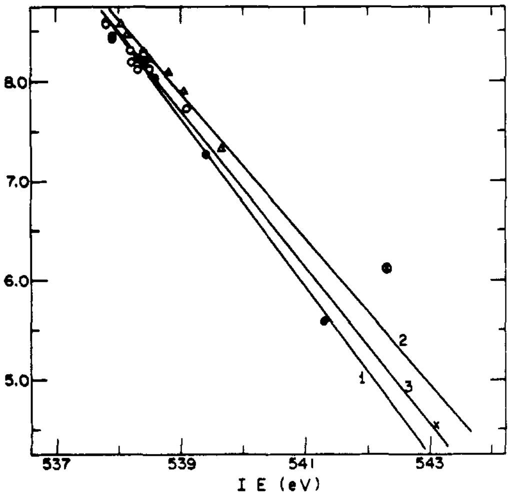


Figure 1. Correlation of proton affinities with O (1s) ionization energies: ○ acids and esters; ● aldehydes, ketones, CO_2; △ alcohols, ethers, H_2O; × O_2; ⊗ CO. Lines 1, 2, and 3 are least-squares lines from eq 4, 5, and 6, respectively.

the other PA data. A number of the proton affinity values are taken from the work of McIver et al.,[12] who have established a scale proton affinities in good agreement with the results reported by Yamdagni and Kebarle.

Proton Affinity–Core Binding Energy Correlations. Figure 1 shows a plot of the measured PA values vs. the O (1s) binding energies (IE). Three separate straight lines have been drawn through these data, one involving carbonyl compounds only (but including acids, esters, and CO_2), one involving singly bonded oxygen compounds (alcohols and ethers), and a third involving all compounds, including O_2. Carbon monoxide has been excluded from all correlations; the significance of this will be discussed below. From least-squares analyses the following relationships were obtained with the correlation coefficients, r, and standard deviations shown (all data in electron volts). Carbonyl compounds (17 data points)

$$\mathrm{PA} = -0.843\mathrm{IE} + 462.0,\ r = 0.99,$$
$$\times\ \sigma_{\mathrm{PA}} = 0.11,\ \sigma_{\mathrm{slope}} = 0.03_5,\ \sigma_{\mathrm{Int}} = 19 \quad (4)$$

Single-bonded oxygen (7 data points)

$$\mathrm{PA} = -0.746\mathrm{IE} + 410.0,\ r = 0.99,$$
$$\times\ \sigma_{\mathrm{PA}} = 0.07,\ \sigma_{\mathrm{slope}} = 0.05,\ \sigma_{\mathrm{Int}} = 29 \quad (5)$$

All data, including O_2 (25 data points)

$$\mathrm{PA} = -0.792\mathrm{IE} + 434.6,\ r = 0.99,$$
$$\times\ \sigma_{\mathrm{PA}} = 0.13,\ \sigma_{\mathrm{slope}} = 0.02,\ \sigma_{\mathrm{Int}} = 13 \quad (6)$$

The excellent correlation coefficients and low error limits provide strong confirmation of the linear correlations observed previously[7-10] using less extensive data. The σ_{PA} values of 0.07–0.13 eV are particularly good considering that the proton affinities and binding energies each have an uncertainty of approximately 0.1 eV.[21] It should be noted that the slopes are in no case equal to −1 as predicted by the simple theoretical model,[7,8] indicating that the stabilization of the positive charge by the polarization effects of the substituents is greater for inner shell ionization than for ionization by proton addition. Although three different correlations are presented, they cannot be distinguished from each other by statistical analysis, although from the σ_{PA} values it appears that the separate correlations can provide better estimates of the proton affinities of doubly bonded and singly bonded oxygens. It should be noted that, in agreement with previous studies,[9,10] a satisfactory fit for the PA data for carboxylic acids and esters is ob-

Table II. Proton Affinities of Singly Bonded Oxygen[a]

Compd	IE, eV	PA[b]	PA[c]	PA[d]
n-C_3H_7OH	538.5_5	8.07	8.24	8.12
i-C_3H_7OH	538.4	8.19	8.35	8.15
n-C_4H_9OH	538.6_5	7.99	8.17	8.15
s-C_4H_9OH	538.6	8.03	8.20	8.23
t-C_4H_9OH	538.3_5	8.23	8.39	8.22
$(n$-$C_3H_7)_2O$	538.0	8.50	8.65	8.52
$(n$-$C_4H_9)_2O$	538.1	8.42	8.58	8.56
t-$C_4H_9OCH_3$	537.8	8.66	8.80	8.55
$HCOOH$	540.6	6.44	6.71	
CH_3COOH	540.1	6.84	7.09	
C_2H_5COOH	540.1	6.84	7.09	
$HCOOCH_3$	539.8	7.08	7.31	
$HCOOC_2H_5$	539.7	7.16	7.38	
$HCOO$-n-C_3H_7	539.5	7.32	7.53	
CH_3COOCH_3	539.0	7.71	7.91	
$CH_3COOC_2H_5$	539.0	7.71	7.91	
CH_3COO-n-C_3H_7	538.6	8.03	8.20	

[a] For acids and esters refers to singly bonded oxygen (RC(=O)-*O*R). [b] From overall correlation, eq 6. [c] From singly bonded oxygen correlation, eq 5. [d] Proton affinity derived from Pa-IP correlation, eq 10.

Table III. Measured and Estimated Proton Affinities of Benzene Derivatives

		Proton affinity, eV	
Compd	$IE(O_{1s})$, eV	Measd[a]	Calcd
$C_6H_5OCH_3$	538.9	8.60	7.98,[b] 7.79[d]
C_6H_5CHO	537.7_5	8.59	8.69,[c] 8.70[d]

[a] Reference 23. [b] Estimated from eq 5. [c] Estimated from eq 4. [d] Estimated from eq 6.

tained only if protonation at the carbonyl oxygen is assumed. This will be discussed further below.

As shown in Figure 1 the datum point for CO (PA = 6.12 eV) lies significantly above any of the correlation lines. This is in agreement with theoretical calculations,[22] which show that structure a is more stable than structure b by approximately 0.8 eV; i.e., the most stable protonated form involves protonation at carbon and not oxygen. From the overall correlation we estimate a PA for protonation at oxygen of 5.10 eV, indicating that a is more stable than b by ~1 eV in agreement with the theoretical calculations.

$$H{-}^{+}C{=}O \qquad C{\equiv}^{+}O{-}H$$

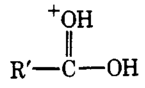
a b

From either the correlation developed for singly bonded oxygen or from the overall correlation it also is possible to estimate proton affinities for singly bonded oxygens in molecules where such values are not known or cannot be measured experimentally. A collection of such values is assembled in Table II. Although the singly bonded oxygen correlation is likely to lead to more accurate PAs, the values estimated from the two correlations do not differ greatly (0.18 eV (4 kcal mol^{-1}) maximum). The proton affinities of the higher alcohols are difficult to determine from equilibrium measurements because of their tendency to form more highly solvated protons, $(ROH)_xH^+$, while at temperatures sufficiently high to preclude this clustering the protonated alcohol is unstable with respect to dissociation to the alkyl ion plus water. The data in Table II indicate that the proton affinities of the higher alcohols are in the range 8.2-8.4 eV (189-194 kcal mol^{-1}) depending on the extent of branching at the carbon adjacent to the oxygen.

Of particular interest are the calculated PAs given in Table II for the proton affinities of the singly bonded oxygen in carboxylic acids and esters. These proton affinities are 0.8-1.1 eV lower than the proton affinity of the carbonyl oxygen in the same compound. The use of these data to conclude that the ion formed in the dissociative ionization

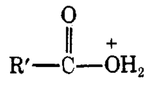
$$R'C\text{-}OR^{+\cdot} \rightarrow R'CO_2H_2^{+} + (R - 2H) \qquad (7)$$

has the carbonyl protonated structure c rather than the hydroxyl protonated structure d is discussed elsewhere.[23] It is



$$R'{-}C({=}{}^{+}OH){-}OH$$

c



$$R'{-}C({=}O){-}{}^{+}OH_2$$

d

interesting to note from a comparison of PA(HC(=O)*O*R) (Table II) with PA(HOR) (Table I) for various R groups that the formyl group decreases the proton affinity of the singly bonded oxygen by approximately 0.75 eV. A similar comparison shows that the acetyl group decreases the proton affinity of the singly bonded oxygen by approximately 0.25 eV. These effects are in line with the known electron attracting power of the two groups.

A further interesting application of the correlation concerns the site of protonation in aromatic compounds containing oxygen. From a study of substituent effects on the proton affinities of benzene derivatives Lau and Kebarle[24] concluded that for anisole protonation occurred on the ring, since anisole fitted the observed PA vs. substituent σ^+ correlation. By contrast, Martinson and Butrill[25] concluded from chemical ionization studies using H_2O as reagent gas that clustering (i.e., formation of $MH^+{\cdot}H_2O^+{\cdot}2H_2O$, etc.) and lack of H/D interchange of the aromatic hydrogens in the D_2O CI spectrum was indicative of protonation on the substituent rather than the ring. From their results they concluded that for both benzaldehyde and anisole protonation occurred at the substituent. In Table III we compare the proton affinities reported by Lau and Kebarle[24] for benzaldehyde and anisole with the proton affinities calculated from the appropriate PA-IE correlation. For benzaldehyde there is quite good agreement between measured and calculated values, confirming that the most stable protonated form of benzaldehyde involves proton addition to the carbonyl oxygen. On the other hand, the estimated PA for oxygen protonation of anisole is ~0.6 eV (14 kcal mol^{-1}) lower than the measured proton affinity, indicating, in agreement with Kebarle, that the ring-protonated species is the more stable. The conclusion that the most stable protonated form of anisole involves ring protonation does not invalidate Butrill's conclusion that protonation occurred at the oxygen in his system. The oxygen proton affinity of anisole (8 eV) is considerably higher than PA(H_2O) = 7.3 eV, with the result that in the nonequilibrium H_2O chemical ionization studies of Butrill protonation at the ether oxygen might well occur preferentially, since the system is presumably under kinetic control rather than thermodynamic control. The present results indicate that, under equilibrium conditions, the ring-protonated form will be favored over the oxygen-protonated form by a factor of $>10^{10}$ at room temperature.

Proton Affinity-Valence Shell Ionization Potential Correlations. As mentioned previously Davis and Rabelais[8] observed a linear correlation between PAs and valence shell ionization potentials (IPs) for oxygen-containing molecules. Figure 2 shows the PA-IP correlations obtained using the data from Table I. Three separate correlations are obtained as follows: Acids and esters (10 points)

$$PA = -0.591IP + 14.49,\ r = 0.97, \qquad \sigma_{PA} = 0.06,\ \sigma_{slope} = 0.05,\ \sigma_{Int} = 0.5 \qquad (8)$$

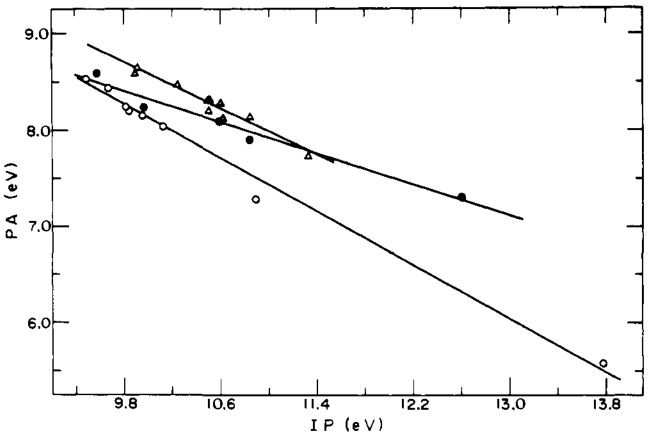


Figure 2. Correlation of proton affinities with valence shell ionization potentials: ○ aldehydes, ketones, CO_2; △ esters and acids; ● alcohols, ethers, and H_2O. Lines are least-squares lines through data; see text.

Ketones, aldehydes, and CO_2 (8 points)

$$PA = -0.690IP + 15.03, r = 0.97,$$
$$\sigma_{PA} = 0.11, \sigma_{slope} = 0.03, \sigma_{Int} = 0.3 \quad (9)$$

Alcohols and ethers (5 points)

$$PA = -0.397IP + 12.29, r = 0.99,$$
$$\sigma_{PA} = 0.09, \sigma_{slope} = 0.04\ \sigma_{Int} = 0.4 \quad (10)$$

The correlation coefficients in each case are quite good and the errors in the estimated PAs are satisfactorily small. There appears to be little doubt that each class of compound requires a separate correlation, in contrast to the PA-IE correlation where all the data fitted a single correlation satisfactorily (including O_2, which does not fit any of the PA-IP correlations). Attempts to fit all the PA-IP data to a single correlation led to a correlation coefficient, r, of 0.87, much poorer than that obtained for the separate fits given by eq 8-10. It appears that, as for proton addition and core electron ionization, the major effect of substituents in the case of valence shell ionization is due to polarization effects on the final state; however, this effect differs for each class of compounds, probably reflecting the nature of the molecular orbital from which the electron is removed. The slopes of the three correlations 8-10 differ substantially from -1, indicating that the substituents are better able to stabilize the positive charge following valence shell ionization than following proton addition.

In the final column of Table II we list the proton affinities of a number of alcohols and ethers estimated from the PA-IP correlation (eq 10). The values obtained from this correlation are in satisfactory agreement with the values estimated from the PA-IE correlations.

As discussed below the lowest ionization potential of benzaldehyde involves removal of a nonbonding oxygen electron. Consequently it should be possible to estimate the (oxygen) proton affinity of benzaldehyde from eq 9. From this equation we obtain a PA of 8.49 eV in reasonable agreement with the experimental value of 8.58 eV and with the value of 8.70 eV estimated from the PA-IE correlation.

Valence Shell Ionization Potential-Core Ionization Energy Correlations. It follows that if there are linear relationships between proton affinities (PAs) and both core ionization energies (IEs) and valence shell ionization energies (IPs), there should be linear correlations between IPs and IEs. The three correlations established were:
Acids and esters (16 points)

$$IP = 0.927IE - 488.5, r = 0.95,$$
$$\sigma_{IP} = 0.13, \sigma_{slope} = 0.09, \sigma_{Int} = 46 \quad (11)$$

Table IV. Ionization Potentials and O (1s) Ionization Energies of Oxygen-Containing Compounds[a]

Compd	IP, eV	O (1s) IE, eV
n-C_3H_7OH	10.51	538.5_5
s-C_3H_7OH	10.44	538.4
n-C_4H_9OH	10.43	538.6_5
s-C_4H_9OH	10.23	538.6
t-C_4H_9OH	10.26	538.3_5
$(n\text{-}C_3H_7)_2O$	9.49	538.0
$(n\text{-}C_4H_9)_2O$	9.40	538.1
t-$C_4H_9OCH_3$	9.41	537.8
n-C_3H_7CHO	9.85	538.3_5
n-C_4H_9CHO	9.82	538.3
n-$C_3H_7COCH_3$	9.44	537.7
n-$C_4H_9COCH_3$	9.38	537.8
n-$C_5H_{11}COCH_3$	9.36	537.7
n-$C_6H_{13}COCH_3$	9.38	537.6_5
n-$C_7H_{15}COCH_3$	9.38	537.9_5
n-C_3H_7COOH	10.38	538.1
$HCOO$-i-C_3H_7	10.44	538.1
$C_2H_5COOCH_3$	10.30	537.7
C_2H_5COO-n-C_3H_7	9.96	537.7_5
C_2H_5COO-i-C_4H_9	9.94	537.6
n-$C_3H_7COOCH_3$	10.15	537.8_5

[a] O (1s) ionization energies of acids and esters refer to carbonyl oxygen.

Table V. Measured and Calculated Ionization Potentials of Substituted Benzenes

	Ionization potential, eV		
		Valence shell	
Compd	O (1s)	Measured	Estimated
$C_6H_5C(=O)OCH_3$	537.7_5[a]	9.34	10.03[b]
$C_6H_5OCH_3$	538.9	8.25	10.77[c]
$C_6H_5CH_2OH$	539.9_5	9.11	12.27[c]
$C_6H_5C(=O)H$	537.7_5	9.54	9.60[d]
$C_6H_5C(=O)CH_3$	537.1_5	9.35	9.17[d]

[a] For carbonyl oxygen; 539.55 for singly bonded oxygen. [b] From eq 11. [c] From eq 13. [d] From eq 12.

Aldehydes and ketones (6 points)

$$IP = 0.715IE - 374.9, r = 0.91,$$
$$\sigma_{IP} = 0.13, \sigma_{slope} = 0.11, \sigma_{Int} = 58 \quad (12)$$

Singly bonded oxygen (13 points)

$$IP = 1.497IE - 796.0, r = 0.97,$$
$$\sigma_{IP} = 0.18, \sigma_{slope} = 0.13, \sigma_{Int} = 68 \quad (13)$$

For the acids and esters and for the singly bonded oxygen compounds these correlations are based, in part, on additional IP and IE data which are not given in Table I, but are summarized in Table IV. The correlation for acids and esters is for the lowest IP, which is known[26] to correspond to removal of nonbonding electrons from the carbonyl oxygen, and IE (O_{1s}) for the carbonyl oxygen.

Although the IP-IE correlations exhibit substantially greater scatter than the PA-IE or PA-IP correlations, they should be useful in establishing the origin of bands in photoelectron spectra and, particularly, in establishing the functional group with which the lowest IP should be associated. As an example, Table V compares the measured ionization potentials of a number of oxygen-containing benzene derivatives with the ionization potentials calculated from the appropriate IP-IE correlation using the experimentally measured IE (O_{1s}) values given in Table V. The calculated IPs therefore refer to ionization involving removal of an oxygen nonbonding electron. For methyl benzoate, anisole, and benzyl alcohol the calculated (oxygen) IPs are higher than the measured IP, indicating that the lowest IP must involve removal of an electron from the π system of the aromatic ring. However, for benzaldehyde and acetophenone the calculated IPs for ionization at the carbonyl oxygen are in agreement with the measured ionization potentials, indicating that for these two compounds the lowest energy ionization process involves removal of an oxygen nonbonding electron.

Conclusions

The correlations developed between the energies associated with the three modes of ionization, proton addition, core electron ionization, and valence electron ionization have several areas of usefulness as has been illustrated in this paper. Such correlations enable one to estimate the proton affinities of molecules (or functional sites) whose proton affinities cannot be determined experimentally. As an extension of this use, the correlations permit one to deduce the site of protonation to which the established PA refers. The correlations also permit the estimate of molecular ionization potentials involving specific sites in polyfunctional molecules. Although the equations developed here apply only to oxygen-containing compounds, similar relationships undoubtedly are applicable to other heteroatom systems, as has been illustrated elsewhere.[10]

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Synthesis of Platinum Derivatives of Polymeric and Cyclic Phosphazenes[1,2]

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Abstract: Polymeric and oligomeric, water-soluble anticancer derivatives have been synthesized by the reaction of $[NP(NHCH_3)_2]_n$ or $[NP(NHCH_3)_2]_4$ with K_2PtCl_4. Two types of compounds were isolated. The first was formed in organic media in the presence of 18-crown-6 ether. The products contained a square planar platinum atom bonded to the nitrogen atoms of the phosphazene skeleton, as verified by the x-ray structure of $Pt^{II}Cl_2[N_4P_4(NHCH_3)_8]$. The second type of derivative was formed in aqueous acid as the salt, $[H_2N_4P_4(NHCH_3)_8]^{2+}[PtCl_4]^{2-}$. The compounds showed tumor inhibitory activity in initial anticancer screening tests. Related derivatives of formula $Pt^{II}Cl_2[N_4P_4(CH_3)_8]$ and $[H_2N_4P_4(CH_3)_8]^{2+}[PtCl_4]^{2-}$ were formed when $[NP(CH_3)_2]_4$ reacted respectively with $PtCl_2$ in organic media or with K_2PtCl_4 in aqueous media.

The anticancer properties of square planar platinum compounds, first reported by Rosenberg,[3] have generated considerable interest. However, clinical studies[4] of platinum complexes, such as *cis*-$Pt^{II}(NH_3)_2Cl_2$ showed that the marked chemotherapeutic effects are accompanied by serious toxic side effects, including bone marrow depletion, damage to the intestinal mucosa, and kidney damage.

We have reasoned that many of these side effects (particularly, kidney damage) may result from the fact that all the platinum derivatives examined to date have been small-molecule complexes that can be excreted rapidly through the semipermeable membranes of the kidney system. Because high polymers cannot pass through semipermeable membranes, the binding of a platinum complex to a polymer should retard the