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Acidities and Basicities of Carboxylic Acids. Correlations between Core-Ionization Energies, Proton Affinities, and Gas-Phase Acidities

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Abstract: Core-ionization energies for a number of carboxylic acids and esters have been measured with the view of establishing the relative importance of initial-state charge distribution and final-state charge rearrangement in determining core-ionization energies, proton affinities, and gas-phase acidities. Results are reported for RCOOH (R = H, CH₃, CF₃, CF₂H), for RCOOCH₃ (R = H, CH₃, CF₃), for RCOOC₂H₅ (R = H, CH₃, CF₃, CF₂H, CFH₂, CClH₂, CBrH₂), and for acetone and methyl carbonate. A linear correlation with slope -1.6 is found between core-ionization energies and proton affinities for double-bonded oxygen. Compounds in which initial-state effects are important and those in which final-state effects are important fit the correlation line equally well. Although there is no simple correlation between anion proton affinity (the negative of acidity) and core-ionization energies, the data are consistent with an expected negative correlation when inductive effects are important and a positive correlation when relaxation is important. A quantitative analysis of these results is in good agreement with theoretical results obtained by Davis and Shirley. Correlations among the various core-ionization energies indicate that positive charge on a carboxyl group, whether produced by core ionization or by protonation, is extensively delocalized by valence-electron rearrangement.

One of the fundamental concepts in chemistry is that of acidity and basicity. In the most general terms acidity is the ability of a substance to accept negative charge and basicity is the ability to accept positive charge. In the Lewis definition,

the charge is transferred by gain or loss of an electron pair. In the Lowry–Brønsted definition, the charge is transferred by gain or loss of a proton.

Martin and Shirley,¹ noting the formal similarity between

gain of a proton and loss of a core electron, have extended the ideas of basicity to include the ease with which core electrons are removed. From their initial work, and from similar observations by Davis and Rabalais,² has developed a series of correlations between gas-phase proton affinities (basicities) and core-ionization energies for a wide range of compounds containing oxygen,³⁻⁵ nitrogen^{4,6} sulfur,⁴ phosphorus,⁴ and arsenic.⁷

In general, the proton affinity and core-ionization energy depend on two terms: the electrostatic potential at the site in the neutral molecule to which the positive charge is to be added and the ease with which the positive charge can be delocalized over the entire molecule by rearrangement of the valence electrons.^{1,2,8,9} The first of these is known as the inductive or ground-state effect and depends on the charge distribution in the initial molecule. The second, known as a relaxation, polarization, or final-state effect, depends on the polarizability of the surrounding molecule.

Almost without exception,¹⁰ the studies of correlations between proton affinities and core-ionization energies have involved substances in which the variation in these quantities is dominated by relaxation effects. Most work has been concerned with replacing H with CH₃ and CH₃ with larger alkyl groups. Some work has been done with aromatic compounds.⁶ Very few results have been reported in which the inductive character of substituent groups has been varied. We have therefore investigated the correlation between proton affinity and core-ionization energy for the series of compounds RCOOH (R = CH₃, CHF₂, CF₃), RCOOCH₃ (R = CH₃, CF₃), and RCOOC₂H₅ (R = CH₃, CH₂F, CHF₂, CF₃, CH₂Cl, CH₂Br). For these, the core-ionization energy shifts are expected to be dominated by inductive effects. For the chloro and bromo compounds, both inductive and relaxation effects should be important. We find that the data for all of these compounds fall on the same correlation line as that for similar compounds in which the shifts are completely dominated by relaxation effects.

Gas-phase acidities (proton affinity of the anion) depend, as do proton affinities and core-ionization energies, on inductive and relaxation effects, but in a somewhat different way.⁹ An initial-state charge distribution that favors electron removal will hinder proton removal. The relaxation, which depends only on the magnitude of the charge and not on the sign, assists in the removal of charge of either sign. Comparison of gas-phase acidities with gas-phase proton affinities can, in principle, be used to determine the relative importance of inductive and relaxation effects in determining acidity and basicity.⁹ In practice, however, such comparisons are not very extensive because of the difficulty of obtaining both the proton affinity and the acidity for the same site in a given molecule. This problem is relieved if we consider the relationship between core-ionization energies and gas-phase acidities, since (1) the core-ionization energy for any atom (other than hydrogen) in a molecule is easily measured and (2) there are well-established linear relationships between core-ionization energies and proton affinities. To investigate the relative importance of inductive and relaxation effects, we have also measured core-ionization energies in HCOOR (R = H, CH₃, C₂H₅). These compounds, taken with those already mentioned, provide a series in which either the inductive or the relaxation effects are varied. The results of our analysis of these data into inductive and relaxation contributions are in excellent agreement with recent theoretical calculations of Davis and Shirley.⁹

In addition to the above results, we report core-ionization energies for acetone and dimethyl carbonate, which are included in our correlations.

During the course of this work we became aware of other correlations among core-ionization energies. These have led us to the conclusion that a positive charge deposited on a car-

boxyl group, either by addition of a proton or by core ionization, is completely delocalized over the entire carboxyl group. This conclusion, which is based on an interpretation of the experimental results, can be rationalized in terms of resonance structures. It is supported by the results of theoretical calculations. This result illustrates an important feature of X-ray photoelectron spectroscopy as a probe of molecular properties, namely, its ability to investigate any atom in the molecule.

Experimental Section

Materials. All of the compounds used in this study were obtained commercially and, except for formic acid, were used without further purification. An NMR spectrum of the formic acid indicated the presence of a significant amount of water. It was dried by refluxing for 6 h with an excess of phthalic anhydride and recovered by distillation. An NMR spectrum of the dried formic acid indicated that the water had been effectively removed.

Photoelectron Spectra. Carbon 1s and oxygen 1s spectra were obtained in the Oregon State University cylindrical mirror electrostatic analyzer¹¹ using Al and Mg K α radiation. All measurements were made in the gas phase. In almost every case, the reported ionization energy is based on more than one measurement. Each sample gas was mixed either with neon, carbon dioxide, or carbon monoxide as calibrants. When neon was used for calibration, alternate scans were taken over the neon 1s, neon 2s, carbon 1s, and oxygen 1s regions. Each series of such scans took 1 or 2 min and was repeated several hundred times during the course of a measurement. When carbon monoxide or carbon dioxide was used for calibration, scans were taken only over the carbon 1s and oxygen 1s region. The known ionization energies given by Thomas and Shaw¹² for neon and carbon dioxide and by Smith and Thomas¹³ for carbon monoxide were used for the calibration. The voltages applied to the spectrometer were measured with a Julie TD-1000 differential voltmeter.

Least-Squares Fitting. The positions of the photoelectron peaks were determined by least-squares fitting of Gaussian peaks with a linear background. The fitting was originally done without any constraints. This approach proved to be unsatisfactory for fitting closely spaced peaks. To illustrate the problem, we consider the oxygen 1s spectrum of ethyl chloroacetate, which should have two peaks of equal area, corresponding to the two chemically inequivalent oxygen atoms. For three separate measurements, fit without constraints, the area ratios were found to be 0.58, 1.67, and 0.98. The corresponding ionization energies for the peak with the higher ionization energy were 539.67, 539.33, and 539.53 eV; there is a range of 0.34 eV in these results. When the same data were fit under the constraint that the areas should be equal, the corresponding energies were 539.54, 539.49, and 539.52; in this case, the range is only 0.05 eV.

The procedure finally adapted was to fit the data first without constraints. If the calculated area ratios differed by more than 5% from the stoichiometric values, then the data were refit with the areas constrained to the stoichiometric value.

Recoil and Relativistic Correction. In calculating ionization energies from measured electron kinetic energies it is necessary to include the kinetic energy of the recoiling ion. This correction, which ranges from 0.003 eV for oxygen 1s in ethyl bromoacetate up to 0.023 eV for carbon 1s in carbon monoxide, is included in our reported ionization energies. A small relativistic correction¹² (less than 0.02 eV) has also been included in the determination of kinetic energies from measured voltages.

Uncertainties. The ionization energies reported in this study were each based on a small number of spectra (two, three, or four in most cases). As a consequence, the distribution of the individual measurements was considered to be of little statistical significance and not necessarily indicative of the actual uncertainty of the resulting mean value. We have estimated our uncertainties by determining the contributions from the calibration techniques and from the statistical uncertainties given by the least-squares fitting procedures. The resulting uncertainties range from 0.02 to 0.04 eV.

Results and Discussion

The core-ionization energies measured by us are summarized in Table I. We include here also results for acetone, for which we have reported a preliminary value elsewhere,³ and for dimethyl carbonate, for which no values have been reported.

Table I. Experimental Core Ionization Energies (eV)^a

compd	α -C	>C=	>CH ₂	-CH ₃	>O	=O
acids						
HCOOH		295.80 (6)			540.65 (3)	539.00 (3)
CH ₃ COOH	291.55 (4)	295.38 (4)			540.09 (3)	538.29 (3)
CF ₃ COOH	299.28 (4)	296.55 (4)			541.28 (3)	539.56 (3)
CF ₂ HCOOH	296.39 (4) ^b	296.39 (4) ^b			540.99 (3)	539.25 (3)
methyl esters						
HCOOCH ₃		295.14 (3)		292.78 (3)	539.88 (3)	538.45 (3)
CH ₃ COOCH ₃	291.30 (5)	294.85 (5)		292.55 (5)	539.46 (3)	537.92 (3)
CF ₃ COOCH ₃	299.03 (5)	295.93 (5)		293.34 (5)	540.48 (3)	539.03 (3)
ethyl esters						
HCOOC ₂ H ₅		294.99 (7)	292.57 (7)	291.04 (8)	539.58 (3)	538.26(3)
CH ₃ COOC ₂ H ₅	291.07 (4) ^b	294.76 (4)	292.45 (4)	291.07 (4) ^b	539.20 (3)	537.78 (3)
CF ₃ COOC ₂ H ₅	298.86 (3)	295.72 (3)	293.07 (3)	291.37 (3)	540.15 (4)	538.83 (4)
CF ₂ HCOOC ₂ H ₅	295.79 (5) ^b	295.79 (5) ^b	292.85 (6)	291.18 (6)	539.91 (3)	538.57 (3)
CFH ₂ COOC ₂ H ₅	293.70 (5)	295.05 (4)	292.58 (5)	291.06 (5)	539.57 (3)	538.17 (3)
CClH ₂ COOC ₂ H ₅	292.64 (3) ^b	295.01 (4)	292.64 (3) ^b	291.07 (4)	539.52 (3)	538.10 (3)
CBrH ₂ COOC ₂ H ₅	292.38 (4) ^b	294.96 (4)	292.38 (4) ^b	290.90 (4)	539.45 (3)	538.01 (3)
others						
CH ₃ OCOOCH ₃		296.14 (4)		292.75 (4)	539.75 (3)	538.06 (3)
CH ₃ COCH ₃		293.71 (4)		291.15 (3)		537.96 (3)

^a Figures in parentheses give the uncertainty in the last decimal place. ^b The average ionization energy for two chemically inequivalent but unresolvable carbons.

Table II. Core-Ionization Energies and Proton Affinities of Double-Bonded Oxygen

compd	ionization potential (eV)			PA (eV) ^d
	<i>a</i>	<i>b</i>	<i>c</i>	
(1) HCOOH	539.00	538.98	539.1	7.80
(2) CH ₃ COOH	538.29	538.34	538.4	8.14
C ₂ H ₅ COOH		538.26	538.3	8.24
CClH ₂ COOH	538.68 ^e			7.93
CFH ₂ COOH	538.76 ^e			7.96
(3) CF ₃ COOH	539.56	539.58		7.51
(4) HCOOCH ₃	538.45	538.47	538.5	8.13
(5) CH ₃ COOCH ₃	537.92	537.94	537.9	8.46
(6) CF ₃ COOCH ₃	539.03			7.81
(7) HCOOC ₂ H ₅	538.26	538.32	538.4	8.28
(8) CH ₃ COOC ₂ H ₅	537.78	537.84	537.8	8.58
(9) CF ₃ COOC ₂ H ₅	538.83			7.93
HCOOC ₃ H ₇		538.25	538.3	8.33
CH ₃ COOC ₃ H ₇		537.78	537.8	8.60
(10) CH ₃ OCOOCH ₃	538.06			8.54
H ₂ CO	539.44 ^f	539.56		7.56
CH ₃ CHO	538.62 ^g	538.62	538.6	8.01
C ₂ H ₅ CHO		538.48		8.14
C ₃ H ₇ CHO			538.5	8.21
C ₄ H ₉ CHO			538.3	8.25
(11) CH ₃ COCH ₃	537.96		537.9	8.40
C ₂ H ₅ COCH ₃			537.6	8.49 ^h

^a This work, unless otherwise labeled. ^b Determined using shifts reported in ref 4 and the acetone value listed above. ^c Reference 5. ^d Based on data from ref 14 and 15, assuming that the proton affinity of NH₃ is 202 kcal/mol (ref 16). Data for 300 K were used when available, 600 K otherwise. ^e Approximate values determined from shifts of corresponding esters. See text. ^f T. X. Carroll and T. D. Thomas, *J. Electron Spectrosc. Relat. Phenom.*, **10**, 215 (1977). ^g Reference 3. ^h Reference 5, adjusted by 0.4 eV to correspond to a proton affinity of 202 kcal/mol for NH₃.

A portion of these data is given again in Table II, where they are compared with results given by Mills, Martin, and Shirley⁴ and by Benoit and Harrison.⁵ Mills, Martin, and Shirley have reported shifts relative to oxygen; we have converted their values to an absolute scale by normalizing their data to ours at acetone. Except for formaldehyde, the agreement between our values and theirs is well within the combined errors of a few

hundredths of an electron volt. So far as the data in Table II show, the agreement between our results and those of Benoit and Harrison is within their uncertainties of about 0.1 eV. There are, however, two striking discrepancies between their data and ours or those of Mills, Martin, and Shirley. For methyl acetate, Benoit and Harrison give a splitting between the two inequivalent oxygens of 1.1 eV compared to 1.54 eV

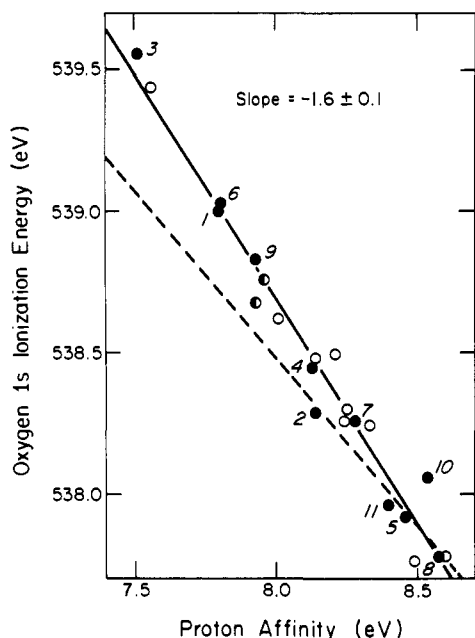


Figure 1. Correlation between carbonyl oxygen ionization energy and proton affinity. Filled and half-filled points represent measurements reported here. Numbers refer to entries in Table II. Open circles represent other data listed in Table II. The solid line is a least-squares fit to the filled points. The dashed line is the fit given by Benoit and Harrison (ref 5).

from our results and 1.53 eV from Mills, Martin, and Shirley. Similarly, Benoit and Harrison give 0.8 eV for *n*-propyl acetate compared to 1.42 from Mills, Martin, and Shirley. These discrepancies may result from the difficulties discussed above of determining accurate energies of closely spaced peaks.

Correlation between Proton Affinities and Core-Ionization Energies. Also given in Table II are the gas-phase proton affinities for the various species studied. These are taken from the work of Yamdagni and Kebarle¹⁴ and of Wolf et al.¹⁵ The absolute values have been calculated using a proton affinity for ammonia of 202 kcal/mol.¹⁶ We have used data measured at 300 K, where available, and 600 K otherwise.

Either because they were not readily available or because of insufficient volatility, we have not measured core-ionization energies for fluoro- or chloroacetic acid. The approximate energies appearing in Table II have been estimated from measurements for the corresponding ethyl esters according to the formula

$$\text{CXH}_2\text{COOH} = \left(\frac{\text{CF}_2\text{HCOOH} - \text{CH}_3\text{COOH}}{\text{CF}_2\text{HCOOC}_2\text{H}_5 - \text{CH}_3\text{COOC}_2\text{H}_5} \right) \times (\text{CXH}_2\text{COOC}_2\text{H}_5 - \text{CH}_3\text{COOC}_2\text{H}_5) + \text{CH}_3\text{COOH}$$

where each molecular symbol represents the oxygen ionization energy for the corresponding compound. If the factor given in the first parentheses were not present, this expression would be equivalent to the assumption that the shift for the acid is the same as the shift for the ester. The first factor (1.22) corrects for our empirical observation that this assumption is not correct. As a test case, this method was used to estimate the value for trifluoroacetic acid from the experimental value for its ethyl ester; the result differed by only 0.01 eV from the experimental value for trifluoroacetic acid.

The correlation between core-ionization energy and proton affinity for double-bonded oxygen is illustrated in Figure 1. The solid points represent the measurements we have made (the numbered data of Table II). The half-filled points represent the estimates for chloro- and fluoroacetic acid. The open circles represent the rest of the data available on double-bonded oxygen (except for CO₂), which are summarized in Table II.

The solid line is a least-squares fit to all of the solid points and has a slope of -1.6 ± 0.1 . We note, first, that this slope differs markedly from the value of approximately -1.0 found by others.¹⁻⁴ The reason for this difference is not in the electron spectroscopy data but rather in the proton affinities. The recent values of proton affinities presented by Yamdagni and Kebarle and by Wolf et al. disagree markedly from those used earlier. This slope of -1.6 is in strong disagreement with the simple arguments that suggest that it should be -1.0 . Apparently, the proton affinities are less sensitive to environmental changes than are the core-ionization energies.

Although only three (no. 3, 6, and 9) of the eleven points on which the solid line is based involve inductive effects, they have a strong influence on the slope and location of the line, since they are well removed from most of the other data. It is significant that the open and half-filled data, which were not used for the fit, and which represent compounds in which either relaxation effects (open) or inductive effects (half-filled) are important, all fall close to this line. We conclude that there is a single correlation between proton affinities and core-ionization energies regardless of whether the determining factor is the initial-state charge distribution or the final-state relaxation. These relationships are considered more quantitatively below.

Also shown in Figure 1 is a dashed curve representing the fit obtained by Benoit and Harrison⁵ to the carbonyl data. They included in their data the point for CO₂, which lies well off the graph to the upper left. In addition they have used a proton affinity for formaldehyde of 7.28 eV instead of 7.56 reported by Wolf et al.¹⁵ Because of the influence of these points, their line fits the data for the other carbonyl compounds poorly.

Correlation between Gas-Phase Acidities and Core-Ionization Energies. As noted above, if the inductive effect favors removal of an electron, then it hinders the removal of a proton. Thus, if the core-ionization-energy shifts are dominated by inductive effects, we will expect a positive correlation between acidity and core-ionization energy. Conversely, a large polarizability favors removal of charge of either sign. If the shifts are dominated by relaxation effects, we will expect a negative correlation between acidity and core-ionization energy.

For these comparisons, the appropriate measure of acidity is the gas-phase acidity, which is the negative of the proton affinity of the anion. In Figure 2, we have plotted the core-ionization energy for a series of compounds against this proton affinity. (We have estimated the values for the monohalogenated acids from data for the corresponding esters, using the method outlined above.) The compounds that we expect to be dominated by inductive effects are shown as the solid circles. There is the expected negative¹⁷ correlation between the proton affinity of the anion and the core-ionization energies; the slope of the solid line, which is a least-squares fit to the solid points, is -1.1 .

The two points in the lower right-hand corner of Figure 2 are for C₂H₅COOH and CH₃COOH. The difference between these two compounds should be largely due to the different polarizability of the two substituents. We expect, and find, that there is positive correlation between the anion proton affinity and ionization energy for these two compounds. The correlation is in the expected direction; both the ionization energy and anion proton affinity are lower for the molecule with the larger substituent. Unfortunately, the separation between these two points is not large enough compared to their experimental uncertainties for this to be a convincing demonstration.

We turn now to the monohalogenated acids. There is both theoretical and experimental evidence to indicate that the major differences between halogens is not in their inductive effect but in their polarizability. Davis and Shirley⁹ have calculated 0.3 eV as the inductive difference between fluorine and chlorine in carboxylic acids, but 2.5 eV as the difference due

to relaxation. Similarly, they have analyzed the Auger energies for halogenated germanes¹⁸ and have concluded that the inductive difference between fluorine and chlorine is 0.15 eV and the relaxation difference 0.36 eV. We see that the data shown in Figure 2 for the monohalogenated acids are in agreement with this idea. There is a positive correlation (with slope close to +1) between the core-ionization energy and the anion proton affinity; the acids with the most polarizable substituents have the lowest core-ionization energy and the lowest anion proton affinity (highest gas-phase acidity).

Finally, we note that the point for formic acid falls well off the correlation line. Because of the low polarizability of hydrogen compared to the other substituents, we expect that formic acid would deviate from the other compounds in the observed direction.

The contrast between Figures 1 and 2 is striking. In Figure 1, the comparison between proton affinities and core-ionization energies, the two effects work the same way on both quantities. In this case, all compounds, regardless of which effect is important, fall on the same correlation line. On the other hand, since the initial-state charge distribution has opposite effects on proton removal and electron removal, while the polarizability has the same effect, we see that there is no simple correlation between gas-phase acidity and core-ionization energy. A comparison of Figures 1 and 2 should, however, allow us to determine the relative importance of these two effects. The quantitative aspects of such a comparison are discussed below.

Quantitative Relationships between Core-Ionization Energies, Proton Affinities, and Gas-Phase Acidities. The quantitative aspects of proton affinities, gas-phase acidities, and core-ionization energies have been discussed by Davis and Shirley.⁹ We summarize their treatment.

The proton affinity of the neutral species (or basicity) is expressed in terms of two quantities: $V_B(0)$, the electrostatic potential energy at the proton site in the neutral molecule, and R_b , the relaxation energy after a proton is added at this site. We will be interested in the proton affinity relative to that of some reference compound. Expressing this quantity as ΔPA , we have

$$\Delta PA = -\Delta V_B(0) - \Delta R_b \quad (1)$$

(In this notation, a negative relative potential energy favors protonation, as does a negative relative relaxation energy.)

The acidity is expressed in terms of the proton affinity of the anion, PA_a ; the stronger the acid, the lower the value of this quantity. Like the proton affinity of the neutral species, PA_a depends on an electrostatic potential and a relaxation energy. The appropriate expression is

$$\Delta PA_a = -\Delta V_A(1) + \Delta R_a \quad (2)$$

Here $\Delta V_A(1)$ is the relative potential energy at the added proton in the neutral species and ΔR_a is the relaxation energy associated with the removal of that proton. Note that the expression for proton affinity is formulated in terms of addition of a proton to the neutral species and that for anion proton affinity in terms of removal of a proton from the neutral species.

The core-ionization energy shift is, according to the model proposed by Davis and Shirley,^{8,9} given by the expression

$$\Delta E_B = -\Delta V - \Delta R \quad (3)$$

where ΔV is the potential energy of the electron in the compound of interest relative to that in a reference compound and ΔR is the change in relaxation energy.

Equations 2 and 3 constitute two equations with four unknowns. If we can establish relationships between ΔV and $\Delta V_A(1)$ and between ΔR and ΔR_a , we can evaluate the un-

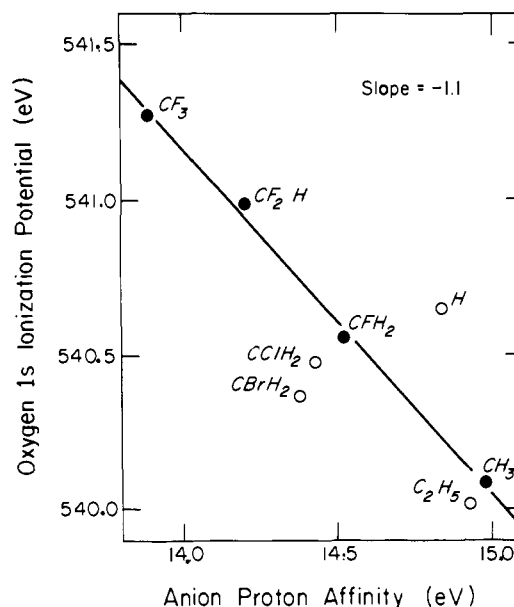


Figure 2. Correlation between hydroxyl oxygen ionization energy and anion proton affinity for carboxylic acids. Filled circles represent points for which the relative acidity and core-ionization potential are determined largely by inductive effects. The solid line is a least-squares fit to the filled points.

Table III. Calculated and Experimental Values of Inductive and Relaxation Effects (eV)

	Experimental		Theoretical ^a	
	$\Delta V_A(1)$	ΔR_a	$\Delta V_A(1)$	ΔR_a
CH ₃ COOH	0	0	0	
CFH ₂ COOH	10.3	-0.5	9.5	0.2
CF ₂ HCOOH	18.4	0.4	17.0	0.4
CF ₃ COOH	25.1	-0.1	26.6	1.4
CFH ₂ COOH	10.3	-0.5	9.5	0.2
CClH ₂ COOH	10.6	-2.2	9.8	-2.3
CBrH ₂ COOH	10.3	-3.6		
HCOOH	7.5	4.3	11.2	5.9
CH ₃ COOH	0	0	0	0
C ₂ H ₅ COOH	-0.1	-2.2	-0.2	-1.8

^a Reference 9.

known quantities. As the simplest approximation we might assume that $\Delta V = -\Delta V_A(1)$ and $\Delta R = -\Delta R_a$. In this case, the correlation between core-ionization energy and anion proton affinity would have a slope of +1 for relaxation shifts and -1 for inductive shifts. The line of Figure 2, which represents inductive shifts, has a slope of -1.1, close to the expected value of -1. The correlation shown in Figure 1, between proton affinities and core-ionization energies, suggests that the proportionality between ΔR_b and ΔR is the same as that between $\Delta V_B(0)$ and ΔV . If ΔR_a and ΔR are similarly related, then we can make the assumption that

$$\frac{\Delta R}{\Delta R_a} = \frac{\Delta V}{\Delta V_a} = -1.1 \quad (4)$$

(The effect of a different assumption is discussed below.)

With this assumption, it is possible to solve the above equations for the individual inductive and relaxation shifts. The results for $\Delta V_A(1)$ and ΔR_a are given in Table III, where they are compared with values calculated by Davis and Shirley.⁹ The agreement between the experimentally derived and the theoretically calculated results is good as to both magnitude and trends.

Before examining these results further, let us consider an

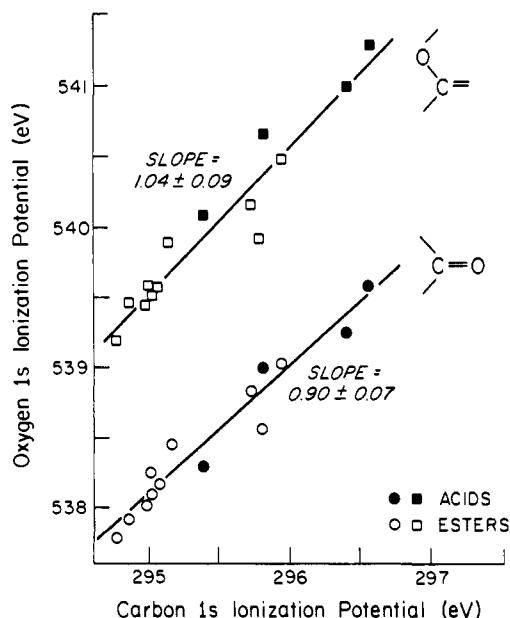


Figure 3. Correlation between carboxyl carbon ionization energy in acids and esters and the carbonyl oxygen energy (lower) or the ether oxygen energy (upper).

alternate assumption about the relationship between ΔR and ΔR_a . Davis and Shirley⁹ have suggested that $\Delta R_a \approx \Delta R_b$. Since the relationship between ΔR_b and ΔR is established by the correlation between proton affinity and core-ionization energy to be $\Delta R = -1.6\Delta R_b$, we have, with their suggestion, that $\Delta R = -1.6\Delta R_a$. Using this relationship, rather than that given in eq 4, causes a 20% reduction in the magnitude of the ΔR_a and $\Delta V_A(1)$ values. The trends remain unchanged, but the agreement with the theoretical results is not so good as before.

We now consider in more detail the results given in Table III. The first four entries give the change as hydrogens are replaced by fluorines in acetic acid. As expected, the potential at the proton site increases strongly and monotonically with fluorination. This result is consistent with the high electronegativity of fluorine. The values of ΔR_a for these compounds are of no significance, since we have assumed that ΔR_a is zero for these compounds. The small differences from zero reflect the failure of the data in Figure 2 to fall exactly on a straight line.

The next three entries in Table III show the effects of changing the single halogen from fluorine to chlorine to bromine. We see that the inductive effect, both experimentally and theoretically, is the same for these substituents. The variation is entirely in the relaxation term, which increases in magnitude with increasing polarizability of the substituent. As noted above, the Auger data of Perry and Jolly¹⁸ on GeF_4 and GeCl_4 (as analyzed by Davis and Shirley⁹) are in agreement with these conclusions. A similar treatment of the Auger data¹⁸ on GeH_3Cl and GeH_3Br shows that their inductive effects are the same and that their differences are due to the larger polarizability of bromine compared to chlorine.

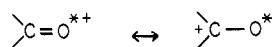
The last three entries of Table III show the effect of replacing H with CH_3 or CH_3 with C_2H_5 . For the second pair, the change is, as expected, almost entirely due to relaxation. For the first pair, we expect a large relaxation between H and CH_3 . This, in the correct direction, is found. There is, in addition, a large inductive effect, suggesting that hydrogen is more electron withdrawing than methyl when attached to a carboxyl group. The same effect can be seen from Auger data on germane and tetramethylgermane¹⁸ and on arsine and tri-

methyl arsine,⁷ although it is not so pronounced in these compounds as in the formic acid-acetic acid comparison.

Charge Rearrangement upon Protonation or Ionization. The basicity and core-ionization energy depend on the ease with which the molecule can accept positive charge. For protonation or core ionization of an oxygen atom, these properties depend not only on the oxygen atom but also on the adjacent atoms. For instance, a positive charge placed at the oxygen atom of a carbonyl group can be readily delocalized through the participation of different resonance structures. Thus, we have



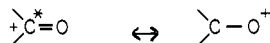
and



where O^* represents a core-ionized oxygen atom. The stability of the final state (and, hence, the proton affinity and core-ionization energy) depends not only on the stability of the two left-hand structures but also on that of those on the right. The basicity and the oxygen core-ionization energy depend, therefore, on the ease with which the adjacent carbon atom can accept positive charge.

The carbon core-ionization energy, which is easily determined, is a measure of the ease with which the carbon atom can accept positive charge. We expect, therefore, that there should be a correlation between the carbon core-ionization energy and either the proton affinity or oxygen core-ionization energy. Such a correlation is shown as the lower set of data in Figure 3. The striking feature of this figure is not that there is a linear correlation, since such relationships between the core-ionization energies of adjacent atoms are to be expected and are known,¹⁹ but rather that the slope is close to 1. This is to be contrasted with the situation for a number of molecules CH_3CXYZ where a plot of the CH_3 ionization energy vs. the CXYZ energy has a slope of only 0.165.¹⁹

The simplest explanation of the close coupling between the carbon and oxygen ionization energies in the carbonyls is that regardless of where the initial ionization is produced the positive charge is redistributed through valence rearrangement so that the final configuration is the same in either case. For ionization of the oxygen, delocalization takes place through the structures shown above. For ionization at the carbon the structures given below are important.

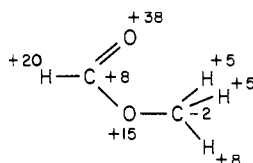


The upper set of data in Figure 3 shows the correlation between the ether-oxygen core-ionization energy and that for the carbonyl carbon. Once again we see a linear relationship with a slope close to 1. We conclude from the pair of correlations that positive charge is delocalized over the entire carboxyl group no matter where it is originally produced. (Strictly speaking these correlations suggest only that the final distribution of the positive charge is independent of its initial location. It might in each case end up concentrated on the same single atom. It is more reasonable to assume that it is spread over the entire group.) The interaction of this final charge distribution with the rest of the molecule establishes the final-state energy and, hence, the relative core-ionization. Thus, a given substituent has the same effect on the core-ionization energy regardless of where in the carboxyl group the ionization takes place.

To see if there is any theoretical basis for these ideas, we have done CNDO/2 calculations to determine the distribution of positive charge following core ionization or protonation. Core ionization is simulated by the equivalent-cores approximation: a core-ionized atom is replaced by the atom of next higher atomic number. The results of these calculations are

shown for methyl formate in Figure 4. The numbers give the change of charge (in units of 0.01 e) at the indicated sites when a positive charge is added through either core ionization or protonation. The site of core ionization is, in each case, indicated by the arrow. We see the anticipated result, namely, that the positive charge is extensively delocalized over the carboxyl group (and the adjacent hydrogen). The methyl group is only a minor participant. We have done similar calculations for methyl acetate with similar results. It is interesting to note that on protonation (Figure 4d) about 40% of the charge remains with the proton. This result may be related to the fact that the proton affinities are less sensitive to changes in the substituent than are the core-ionization energies (see Figure 1).

In addition to the correlations between core-ionization energies and proton affinities, there have been reported correlations between core-ionization energies and first ionization potentials.^{1,5,20} In the simplest approximation, the least-bound electron is considered to be in a lone-pair orbital on the carbonyl oxygen. Ionization of this electron is then similar to ionization of an oxygen core electron followed by the same sort of delocalization of charge. That the final charge is delocalized can be seen from the results of CNDO/2 calculations for HCOOCH_3 and HCOOCH_3^+ , which are shown below. The



numbers indicate the change in atomic charge (in units of 0.01 e) when the least-bound electron is removed. There is a strong similarity between this charge distribution and those shown in Figure 4.

It is less clear, however, that the initial electron is localized on the carbonyl oxygen. Calculations for the neutral molecule indicate that it is 58% on that oxygen, with the rest distributed over the rest of the carboxyl group and the adjacent hydrogen. The electron distribution is, in fact, very similar to the distribution for the positive charge shown above. Since there is, however, the very close coupling between the ionization energies for the various atoms in the carboxyl group, it is not necessary to assume that the electron is localized on the oxygen to understand the correlation between the first ionization potential and the core-ionization energies. Regardless of where in the carboxyl group the electron is initially located, it will be equally affected by changes in substituents.

Conclusions

For a series of compounds whose basicity is determined by inductive effects for some, polarization effects for others, and a mixture for still others, we have shown that there is a single linear correlation between the gas-phase proton affinity and the oxygen core-ionization energy. This result indicates that the proportionality between the strength of inductive effects on the proton affinity and the strength of inductive effects on core-ionization energies is the same as the proportionality between the corresponding strengths for relaxation effects. From the slope of the correlation line, -1.6 , we conclude that proton affinity is less strongly influenced by changes in substituent than is the core-ionization energy.

There is no simple correlation between the proton affinities of the anions and the core-ionization energies. The results are, however, consistent with an expected negative correlation between proton affinity and core-ionization energy when inductive effects are important and a positive correlation when relaxation effects are important.

These data have been analyzed quantitatively to establish the magnitudes of inductive and relaxation effects in deter-

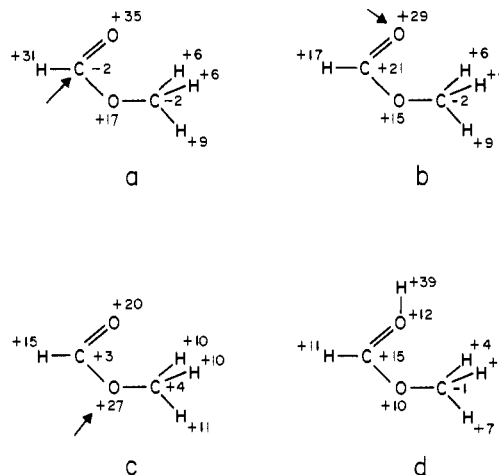


Figure 4. Distribution of positive charge by valence rearrangement when core ionization takes place at the indicated site (a, b, c) or when protonation takes place (d). Based on CNDO/2 calculations.

mining the acidities of a number of carboxylic acids. The results are in good agreement with theoretical calculations reported by Davis and Shirley⁹ and are in good agreement with chemical experience. They show the inductive effect of successive fluorination and the inductive effect of single halogenation. They further indicate that the difference between fluorine, chlorine, and bromine is not in their induction but rather in increased polarizability as we go through this series. The difference between methyl and ethyl substituents is found to be due to the large polarizability of the ethyl group, while the difference between hydrogen and an alkyl group is due to both induction and polarizability.

There are linear correlations with approximately unit slope between the core-ionization energies of the carbon and two oxygens in the carboxyl group of acids and esters. From this result we conclude that positive charge, whether produced by core ionization of one of these atoms or by protonation, is extensively delocalized throughout the carboxyl group by valence-electron rearrangement. This conclusion is supported by the results of CNDO/2 calculations.

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Bonding Energies in Association Ions of Aromatic Compounds. Correlations with Ionization Energies

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Abstract: Enthalpies of dissociation, ΔH°_D (kcal mol⁻¹), were measured by temperature studies on the equilibria $(B_1B_2)^+ \rightleftharpoons B_1^+ + B_2$ (B_1 and B_2 = benzene and substituted benzenes). It is observed that ΔH°_D is largest (16 ± 1) in symmetric association ions ($B_1 = B_2$) and decreases to 10 ± 1 as the difference in the ionization potentials of B_1 and B_2 (ΔIP , kcal mol⁻¹) increases. For example, for $(C_6H_6 \cdot C_6H_6)^+ \Delta IP = 0$, $\Delta H^\circ_D = 17.0$; for $(C_6H_6 \cdot C_6F_6)^+ \Delta IP = 16.7$, $\Delta H^\circ_D = 10.5$. Similarly, for $(1,3,5-C_6H_3(CH_3)_3 \cdot 1,3,5-C_6H_3(CH_3)_3)^+ \Delta IP = 0$, $\Delta H^\circ_D = 17.2$; while for $(1,3,5-C_6H_3(CH_3)_3 \cdot C_6H_6)^+ \Delta IP = 19.1$, $\Delta H^\circ_D = 10.6$. Weak bonding ($\Delta H^\circ_D = 11.0$) is also observed in $C_6H_7^+ \cdot C_6H_6$ where the reactant ion is not a radical and in $C_6H_6^+ \cdot c-C_6H_{12}$ ($\Delta H^\circ_D = 9.9$), where the neutral reactant lacks a π system. It is suggested that weak bonding of about 10 kcal mol⁻¹ in the latter association ions and in association ions with large ΔIP is due to electrostatic interactions, while in the aromatic association ions additional bonding of as much as 6 ± 1 kcal mol⁻¹ results from electron delocalization. The measurements were done by pulsed high-pressure mass spectrometry, utilizing soft chemical ionization by charge transfer from CS_2^+ , which should yield cyclic benzene ions in the electronic ground state.

Introduction

Bonding between radical ions and neutral aromatic molecules is of obvious interest in gaseous ion chemistry and mass spectrometry, but it is also of considerable interest in condensed phase chemistry. For example, ion-neutral interactions play a role in determining ionization potentials (IP) in the condensed phase; ionized states, in turn, contribute to conductivity in organic semiconductors.¹ Dimer cations of benzene, naphthalene, perylene, and other aromatic hydrocarbons have been observed in solutions subjected to pulse radiolysis.^{2,3} Benzene and substituted benzenes constitute an obvious and experimentally tractable model for the investigation of relationships between structure and ion-molecule interaction energies in dimer cations of aromatic compounds.

The benzene dimer cation, $(C_6H_6)_2^+$, has been observed in the gas phase by a number of research groups.⁴⁻⁶ Quantitative investigations concerning this ion dealt with the kinetics of the association of $C_6H_6^+$ with C_6H_6 ,⁷⁻⁹ as well as with the enthalpy of dissociation (ΔH°_D) of $(C_6H_6)_2^+$. ΔH°_D was measured by Field and co-workers¹⁰ to be 15 kcal mol⁻¹ using high-pressure mass spectrometry ($P = 0.5-1.5$ Torr) with a continuous mode of ion production and detection. Tiernan and co-workers,⁸ using continuous ionization and somewhat lower pressures ($P = 0.1-0.2$ Torr), obtained a value of $\Delta H^\circ_D = 8 \pm 2$ kcal mol⁻¹. Wexler and Pobo⁷ identified a negative activation energy of 10 kcal mol⁻¹ which they found in the kinetics of the formation of $(C_6H_6)_2^+$ with a lower limit for ΔH°_D . In the condensed phase, ΔH°_D was measured to be 14.8 kcal mol⁻¹ by Badger and Brocklehurst¹¹ using spectroscopic data for the transition between attractive and repulsive states of the dimer cation in solution. The difference between the reported gas-phase values of ΔH°_D may be due in part to failure to achieve equilibrium in either or both of the previous mass spectrometric measurements. Our recent experience has been that the continuous ionization methods used are notoriously unreliable. In addition, the specific identity of the $C_6H_6^+$

monomer ion, which may be a cyclic ion in either the electronic ground state or an excited state, or an acyclic ion in an undefined electronic state,^{8,12} was ambiguous in previous measurements.

We have redetermined the value of ΔH°_D for the benzene ion dimer by making a temperature study of the association equilibrium $C_6H_6^+ + C_6H_6 \rightleftharpoons (C_6H_6)_2^+$ using a time-resolved high-pressure mass spectrometric technique with which equilibrium can generally be achieved. Furthermore, to increase confidence in the identity of the $C_6H_6^+$ ion, we produced it using a mild chemical ionization method which should yield the ion with a cyclic structure in the ground electronic state. Finally, we extended these measurements to other aromatic ions and molecules.

Experimental Section

Our measurements were performed by pulsed high-pressure mass spectrometry using the Rockefeller University Chemical Physics Mass Spectrometer.^{13,14} Mixtures of the aromatic compounds of interest in a carrier gas were prepared in a gas handling system and allowed to flow into the ion source. Ionizing pulses of 600 V electrons with a duration of 20 μ s initiated reaction sequences leading to the equilibria of interest. The course of the reactions and the attainment of equilibria were monitored by recording the intensities of ions issuing from the source as a function of reaction time.

The reagent gas used was a mixture of 15-30% CS_2 and N_2 . The total pressure ranged from 0.5 to 1.5 Torr, with most measurements made at ~ 0.8 Torr. The sample of interest was an aromatic compound or a mixture of two aromatic compounds. The concentration(s) of aromatics ranged from 0.05 to 5% of the gas mixture, and they were empirically selected so that equilibrium concentrations of the ions of interest were within the dynamic range of the mass spectrometer. With these conditions, ions of the aromatic compounds are generated by the following sequence of chemical ionization processes:

