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The Substituent Effect of the Methyl Group. Carbon 1s Ionization Energies, Proton Affinities, and Reactivities of the Methylbenzenes

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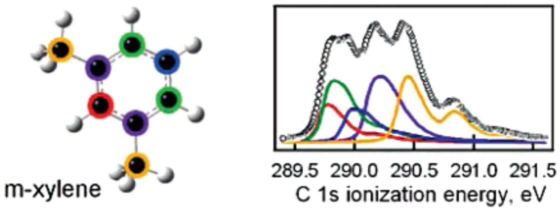

High-resolution carbon 1s photoelectron spectra have been measured for methyl-substituted benzenes. By using these data together with molecular structure calculations to predict the vibrational profiles expected in the spectra, it has been possible for the first time to assign 1s ionization energies to each of the inequivalent carbon atoms in these molecules. There exist linear correlations between the ionization energies and the energy changes for other chemical processes, such as enthalpies of protonation and activation energies for hydrogen exchange and protodesilylation. There are deviations from these correlations for sites in which hyperconjugation plays a role in the process. These can be understood by recognizing that the core-ionization energies reflect primarily the Hammett parameter σ whereas the other energies reflect σ^+. The ionization and reaction energies can be summarized compactly with a linear model in which the total effect of the substituents is equal to the sum of the effects of the individual substituents. A slightly better description is obtained with a quadratic model, which allows for interaction between the substituents.

Introduction

Substituent groups, through their ability to either withdraw or donate electrons to the rest of a molecule, can have significant effects on the chemical properties of a substance. Of particular interest are the alkyl groups, which can serve as both electron donors and electron acceptors.

The chemical effects of alkyl groups can be illustrated with a few examples. In the gas phase methanol is both a better proton donor (stronger acid) and a better proton acceptor (stronger base) than water, and ethanol is both a stronger acid and a stronger base then methanol.[1] By contrast, although acetic acid is a stronger base than formic acid and propanoic acid is a stronger base than acetic acid, both acetic acid and propanoic acid are weaker acids than formic acid. Thus the effect on acidity caused by replacing hydrogen by an alkyl group is in the opposite direction for the two classes of compounds, even though the effect on basicity is in the same direction.

For benzene, the addition of a methyl group leads to a striking increase in reactivity. For instance, the rate of hydrogen−tritium exchange is several hundred times as fast at the para position of toluene as it is for benzene.[2−4] Also, as is well known, the effect of the methyl substituent is different for different positions in the ring—for the meta position the enhancement of the rate in toluene is only a factor of 5 to 10 relative to that for benzene.[2,3] The effect of the methyl group on reactivity is reflected in the toxicity of the compounds. The exposure limit for toluene is about 100 times that for benzene,[5] presumably reflecting the higher reactivity of toluene, which can provide easier pathways for the body to dispose of this compound.

The simplest of the alkyl groups is the methyl group, which can be regarded as a prototype for the other alkyl groups. Here

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we ask two questions: what is the effect of a methyl group and how does it produce this effect. For the first question we consider carbon 1s ionization energies, proton affinities, and electrophilic reactivities as well as correlations among these quantities. All of these involve the formation of a positively charged species, either as a final state or as a transition state. For the second we consider electronegativity, polarizibility, and hyperconjugation as possible factors that lead to the effects produced by methyl substituents.

For alkanes we are concerned primarily with the effects of electronegativity and polarizibility. An investigation of the carbon 1s ionization energies of the linear alkanes[6] shows how the ionization energies are influenced by the competition between the greater electronegativity of the methyl group (relative to hydrogen) and the greater polarizibility of the methyl group. The greater electronegativity tends to increase the carbon 1s ionization energy when hydrogen is replaced by methyl, but at the same time the greater polarizibility tends to lower the ionization energy. As a result, the carbon 1s ionization energies in these hydrocarbons depend critically on the size of the molecule and the position in the carbon chain. A discussion of branched hydrocarbons will be presented later. The effects of hyperconjugation become apparent in the alkenes, alkynes, and alkadienes, which we have discussed earlier.[7−9] These studies illustrate how hyperconjugation and resonance allow charge transfer from the methyl group to the terminal unsaturated carbon (C1) in such molecules as propene, propyne, and 1,3-pentadiene. This charge transfer has significant effects on the carbon 1s ionization energies, proton affinities, and reactivities of these molecules.

Here we consider benzene and several methyl-substituted benzenes—toluene, *o*-, *m*-, and *p*-xylene, mesitylene, and 1,2,4,5-tetramethylbenzene. In these molecules, hyperconjugation plays a major role. The effects are apparent in the values of the Hammett σ values for the methyl group, -0.14 for σ_p and -0.06 for σ_m.[10] Both are negative reflecting the overall ability of the methyl group to donate electrons to the benzene ring. The larger magnitude for σ_p reflects the effect of hyperconjugation, which makes it possible for the methyl group to donate electrons to positions that are ortho and para to the methyl group but not to those that are meta to the group.

We present the results of experimental measurements of the carbon 1s ionization energies of the methyl-substituted benzenes. These energies reflect directly the ability of the molecule to accept positive charge at a specific site, and therefore, relate closely to other chemical quantities that depend on this ability, such as enthalpies of protonation (the negative of the proton affinity), rates of electrophilic reactions, and the Hammett parameters. Previous measurements on the methylbenzenes were limited to toluene and were of such low resolution that it was impossible to make any meaningful assignment of ionization energies to the chemically distinct carbon atoms on the basis of the data.[11,12] Now, with the high-resolution techniques of electron spectroscopy available at third-generation synchrotrons, aided by molecular structure theory, it is possible to use inner-shell photoelectron spectroscopy to determine the carbon 1s ionization energies of all of the chemically inequivalent carbon atoms in these molecules. Before the development of these techniques, the ability to obtain such experimental information on complex compounds did not exist.

We expect the carbon 1s ionization energies to be closely related to the enthalpies of protonation, since protonation also involves addition of a positive charge to a specific site in the molecule. Linear correlations between enthalpies of protonation and core-ionization energies are well established for nitrogen, oxygen, and a few other atoms, and these correlations have provided insight into the site of protonation and geometric changes that occur upon protonation.[13,14] However, until recently there have not been sufficiently good data available for carbon 1s ionization energies to make investigation of these relationships for carbon possible. We have, however, been able to demonstrate that such correlations exist for 1,3-butadiene and 1,3-pentadiene[9] as well as for the fluorobenzenes.[15] For the fluorobenzenes we have shown that these correlations provide insight into the π-donating effect of fluorine. We will see how similar correlations for the methyl benzenes extend those for the fluorobenzenes and provide insight into the differences between the π-donating action of the two substituents.

For core ionization, we can measure a carbon 1s ionization energy for each carbon atom in the molecule. For protonation this is not the case. In general, experimental proton affinities are known only for the most favorable site of protonation in each molecule. There exist, however, theoretical techniques that allow us to predict the proton affinities for all sites in the molecule,[16,17] and where experimental data are available, there is good agreement between theory and experiment. We will, therefore, use theoretically predicted proton affinities for comparison with the core-ionization energies.

Electrophilic reactions often involve the formation of a transition state with a localized positive charge, and we have seen elsewhere that there are correlations between these activation energies for both Markovnikov and anti-Markovnikov addition and carbon 1s ionization energies of ethene, propene, 2-methylpropene, 1,3-butadiene, and 1,3-pentadiene.[8,9] Here we consider the possibility of similar correlations between the

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carbon 1s ionization energies of the methyl-substituted benzenes and the activation energies for tritium−hydrogen exchange reactions[2,3] and for desilylation reactions.[18]

Methods and Results

Samples were obtained from commercial sources and were of greater than 98% purity. The experimental procedures for the measurements are similar to those we have described elsewhere.[6,9,15,21,22,24] Briefly, carbon 1s photoelectron spectra have been measured with an overall instrumental resolution of 70 to 80 meV, which is significantly less than the natural line width of about 100 meV. The photon energy was 330 eV. For toluene, the xylenes, and mesitylene, the measurements were made on Beamline I411 of the MAX II synchrotron,[19] and for 1,2,4,5-tetramethylbenzene they were made at Beamline 10.0.1 of the Advanced Light Source.[20] A set of measurements was made with the samples mixed with carbon dioxide to provide calibration of the energy scale and the instrumental resolution.[21,22]

The spectra contain contributions from the chemically inequivalent carbon atoms. Each kind of carbon atom produces a unique spectral pattern reflecting the vibrational excitation that occurs when that atom is core ionized. We predict these patterns using theoretical calculations based on the B3LYP density-functional method, a triple-ζ basis set, and an effective-core potential to simulate the effects of the core hole—see the Supporting Information for details of the theoretical methods. These theoretical profiles are convoluted with functions to represent the instrumental and lifetime broadening and are fit to the experimental data with only the overall intensity for each profile and its energy position as fitting parameters. This fitting procedure,[23] together with the data on carbon dioxide,[21,22] yields the adiabatic and vertical carbon 1s ionization energies.

Two features of these spectra require special comment. One is the torsional motion of the methyl groups; the other is the treatment of the carbon 1s holes on equivalent carbon atoms. A brief discussion of the effects of these on the spectra follows and more details are given in the Supporting Information. At this point it is sufficient to note that their effects, though noticeable, are small.

Torsional Motion of the Methyl Groups. In the methyl-substituted benzenes, the methyl groups are nearly free rotors, both in the ground state and in the core-ionized state. As a result, the harmonic oscillator approximation, which we have used for predicting the other vibrational excitations, is not applicable. Except for *o*-xylene, our approach has been to calculate the vibrational excitations allowing no excitation of the torsional motion. To assess the effect of the torsional motion, we calculate the torsional potentials for all species involved. Using these potentials, we obtain the wave functions for the torsional motion. From these wave functions we calculate the appropriate Franck−Condon integrals, and, hence, the degree of excitation of the torsional modes.

We consider first toluene as an example to illustrate the effect of torsional motion. Relative to what is predicted by a model that ignores this motion, inclusion of torsional motion leads to broadening of the spectra and to slight shifts in the positions of the peaks. The broadening is less than 5 meV, which is negligible in comparison with the combined effects on the line width of the instrumental and lifetime broadening (more than 100 meV). For ionization at the ipso and para positions, the shift in peak position is less than 1 meV, which is negligible. The largest shift, 3 meV, is for ionization at the meta position, and is small compared with the uncertainties in the measurements.

For *p*-xylene, we find that the effect of including torsional excitation can be described by an additivity model using the results for toluene. The largest shift due to torsional motion in *p*-xylene is 4.4 meV for C2. Assuming that a similar approach can be taken with *m*-xylene and mesitylene, we estimate that for these molecules all shifts due to torsional motion will be less than 6 meV (for C5 on *m*-xylene and C1 on mesitylene).

In *o*-xylene, the two methyl groups are adjacent to one another with the result that the additivity picture mentioned above may not be applicable. This could be especially the case for core ionization of the methyl carbons, since the positive core can interact strongly with the hydrogens of the adjacent methyl group. For this molecule, we have included the torsional excitation (calculated as described above) explicitly in the vibrational profiles used for fitting the spectrum. Comparisons of fits made with and without inclusion of this effect show that only for ionization of the methyl carbon is there a significant effect of the torsional motion. Even in this case, the effect on the energy position is only 8 meV.

We see that the effects of the torsional excitation are small in these molecules. Except for *o*-xylene, where the effect has been included explicitly, we have not included any corrections for this motion.

Equivalent Carbon Atoms. In *p*-xylene, as an example, there are three kinds of equivalent carbon atoms: the two methyl carbons, the 1 and 4 carbons, and the 2, 3, 5, and 6 carbons. At the symmetry-adapted molecular orbital level there are corresponding orbitals for the carbon 1s electrons. One pair will be plus and minus combinations of the methyl carbon 1s orbitals, another pair will be similar combinations of the 1s orbitals on the 1 and 4 carbons, and the remaining set will be four combinations of the 1s orbitals from the 2, 3, 5, and 6 carbons—approximately plus and minus combinations of orbitals on 2 and 3 and similar combinations of orbitals on 5 and 6. In this picture the carbon 1s holes produced upon ionization are delocalized over two or four atomic centers.

If the molecular orbitals are degenerate, then vibronic coupling can lead to breaking of the symmetry of the molecule.[24] In this case the carbon 1s orbitals are better described as localized orbitals. For instance, for ionization of the methyl carbon, one of these orbitals involves a core hole localized on one of the methyl carbons, with corresponding modifications of the valence electron density, bond lengths, and bond angles, primarily in the vicinity of the core hole. The other involves the 1s electrons on the other methyl carbon, whose surroundings

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will be only slightly modified from the ground state. This localized description is sufficiently accurate to describe the vibrational structure associated with ionization of the methyl and the 1,4 carbons of *p*-xylene.

Because carbon atoms 2 and 3 (as well as 5 and 6) are adjacent, the two molecular orbitals based on these atoms are not degenerate, but are split by an energy of 2β, where β is the electronic coupling integral between carbon 1s orbitals on adjacent carbon atoms, and is calculated to be 22.3 meV in benzene.[25] At the level of first-order perturbation theory, this splitting will be reflected in the vibrational excitation spectrum by a splitting of $2\beta\langle\nu_L|\nu_R\rangle$, where the term in brackets is the vibrational overlap integral between two molecules, one with the core hole on one of the equivalent carbon atoms and the other with the core hole on the other.[25−27] For the molecules of interest here, the vibrational overlap integral for the ground vibrational state of the ion is about 0.5 and lower for the excited states. As a practical matter, we have found that the effects of this interaction can be included adequately by splitting the predicted peak for the transition to the ground state into two peaks of equal intensity, separated by the appropriate amount.[25]

For carbons 2 and 3 (or 5 and 6) in *p*-xylene, this splitting is expected to be 21.6 meV. Including this in the fit gives a better fit, both visually and in terms of χ^2, but it produces negligible changes (less than 2 meV) in the peak positions.

For *o*-xylene the problem is more difficult. Although carbon atoms 3 and 6 are not equivalent to 4 and 5, the difference in carbon 1s ionization energy is predicted in a localized-hole model to be 12.5 meV, which is comparable to β. As a result, the Hartree−Fock orbitals for these hole states are delocalized over these four carbon atoms, and it becomes impossible to assign a given measured ionization energy to a localized core hole. To deal with this problem we start with a basis of localized core holes, with the energies of the C3 and C6 holes separated from those of the C4 and C5 holes by the theoretically calculated value of 12.5 meV. Adjacent carbon atoms are then coupled by the integral $\beta\langle\nu_L|\nu_R\rangle$, which is taken to be 12.3 meV for the ground ionic states and zero for the vibrationally excited states. This approach produces four predicted transitions for the ground states, with their spacing determined by the choice of parameters just mentioned and their average energy to be determined from the data. The profiles for the vibrationally excited states are taken to be as predicted from the localized hole model, but the position of these profiles relative to the average of the four ground-state energies is fixed by the theoretical results. The fit to the data obtained in this way is excellent, as can be seen in Figure 1. The fitting procedure yields energies for all of the chemically inequivalent carbons, subject to the constraint that the C3,6/C4,5 splitting is 12.5 meV. Further details on the treatment of *o*-xylene can be found in the Supporting Information.

Results

The experimental carbon 1s spectra are illustrated in Figure 1. Also included for comparison is the previously measured spectrum for benzene.[25] Here the open circles represent the experimental data and the solid black lines represent the overall least-squares fits of the vibrational profiles to the data. The individual profiles for each of the inequivalent carbons are shown in color. For *o*-xylene the profiles include one profile for the four transitions that result in ionization of carbons 3, 4, 5, and 6 (denoted as C3,4,5,6) without vibrational excitation, and one profile each for the transitions that result in ionization of C3,6 and C4,5 with vibrational excitation, as discussed above. As can be seen in each case, these calculated profiles give an excellent description of the experimental data. In some cases, such as *p*-xylene, mesitylene, and 1,2,4,5-tetramethylbenzene,

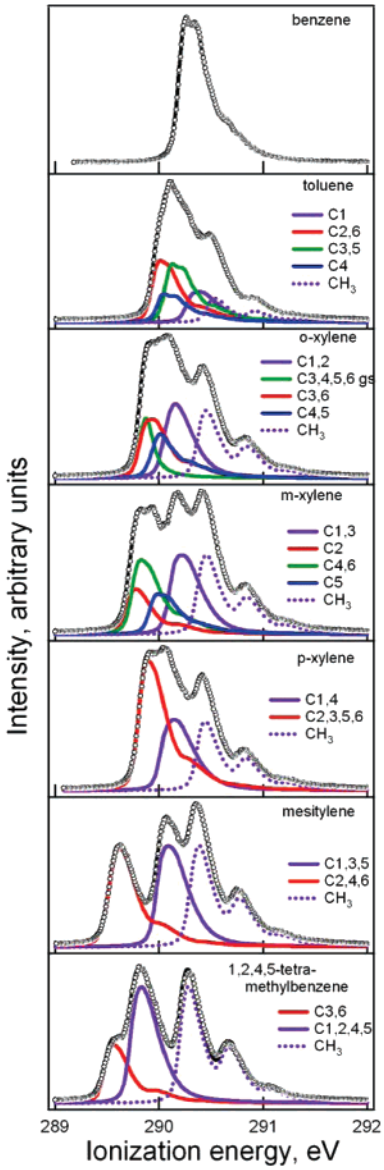

FIGURE 1. Carbon 1s photoelectron spectra of benzene and methyl-substituted benzenes. Open circles represent the experimental data and the solid black lines represent least-squares fits to the data. The components of the fits are shown in color, one profile for each kind of inequivalent carbon atom. The purple curves show the contributions from the methyl carbons (dotted) and ipso carbons (solid). Red, green, and blue curves show contributions from the other kinds of carbon. For *o*-xylene the green curve shows the contribution from the transitions to the vibrationally unexcited states resulting from ionization of C3, C4, C5, and C6.

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TABLE 1. Carbon 1s Ionization Energies (eV) for the Methyl-Substituted Benzenes

	adiabatic[a]	vertical[b]	relative adiabatic	relative theory
benzene	290.241	290.377	0.000	0.000
toluene C1	290.296	290.412	0.055	0.051
toluene C2,6	289.970	290.114	−0.271	−0.286
toluene C3,5	290.101	290.246	−0.140	−0.168
toluene C4	290.030	290.182	−0.211	−0.267
toluene CH_3	290.493	290.699	0.252	0.308
o-xylene C1,2	290.074	290.178	−0.168	−0.178
o-xylene C3,6	289.853	289.992	−0.388	−0.433
o-xylene C4,5	289.865	290.016	−0.376	−0.421
o-xylene CH_3	290.407	290.605	0.166	0.208
m-xylene C1,3	290.134	290.249	−0.107	−0.108
m-xylene C2	289.716	289.863	−0.525	−0.557
m-xylene C4,6	289.779	289.927	−0.462	−0.536
m-xylene C5	289.956	290.105	−0.285	−0.329
m-xylene CH_3	290.407	290.614	0.165	0.212
p-xylene C1,4	290.054	290.175	−0.188	−0.199
p-xylene C2,3,5,6	289.842	289.987	−0.399	−0.437
p-xylene CH_3	290.395	290.602	0.154	0.200
mesitylene C1,3,5	290.008	290.127	−0.233	−0.251
mesitylene C2,4,6	289.550	289.701	−0.691	−0.782
mesitylene CH_3	290.334	290.545	0.093	0.127
1,2,4,5-tetramethylbenzene C1,2,4,5	289.749	289.857	−0.492	−0.543
1,2,4,5-tetramethylbenzene C3,6	289.496	289.647	−0.745	−0.795
1,2,4,5-tetramethylbenzene CH_3	290.229	290.447	−0.012	0.024

[a] Ionization energy to produce the ion in its vibrational ground state. [b] Ionization energy to produce the ion with the geometry of the ground state of the un-ionized molecule.

where there are only three types of inequivalent carbon atoms, the fits are quite unambiguous. At the other extreme are toluene and *m*-xylene, each with five inequivalent carbon atoms. For both of these, the positions of the profiles for ionization of the ipso and methyl carbons are unambiguous. For *m*-xylene the positions for the C2, C4,6, and C5 profiles are also well determined. For toluene, however, three different fits give nearly the same value of χ^2. The fit shown here and used to determine the ionization energies reported here is the one that gives the lowest value of χ^2. In addition, this fit gives ionization energies that are in agreement with theoretical predictions.

The measured ionization energies obtained from these data are summarized in Table 1. Two ionization energies are given for each compound. The first is the adiabatic ionization energy, which is the ionization energy to produce the ion in its vibrational ground state; this is obtained directly from the fitting procedure discussed above. The second is the vertical ionization energy, which represents the energy needed to produce the ion in the same geometry as that of the neutral molecule. This is obtained from the adiabatic ionization energy by adding the average vibrational excitation, which, in turn, is obtained from the theoretically calculated profile. Also shown are the shifts in the adiabatic ionization energies relative to that of benzene.

The uncertainty in the absolute ionization energies is essentially that of the ionization energy of the calibrant, carbon dioxide—about 0.03 eV.[22] The uncertainties in the relative values are smaller than this. Comparisons with theoretically calculated ionization energies and consideration of the systematic behavior of the ionization energies indicate that the relative uncertainties may be as small as 0.01 eV. To allow for the possibility that these are less than 0.01 eV, we have reported our results to three decimal places.

The same theoretical calculations that predict the vibrational profiles also predict the relative carbon 1s ionization energies; these are given in the last column of Table 1. Comparison of the theoretical and experimental ionization energies shows good agreement, except that the theoretical approach predicts shifts in the ionization energy that are about 12% larger than observed. After allowing for this systematic trend, we find that the experimental and theoretical ionization-energy shifts agree with a root-mean-square deviation of 0.016 eV. Since this result reflects errors in both the theory and the experiment (which are uncorrelated), we can conclude that the error in the relative experimental values is no more than this.

Discussion

Proton Affinities, Activation Energies, and Core-Ionization Energies. Many chemical processes involve adding a positive charge at a particular site in a molecule. Among these are core ionization, protonation, and electrophilic reactions. Although the absolute energies (ionization energies, proton affinities, and activation energies) for these processes are quite different, the changes in these energies brought about by substituents that are remote to the site of charge addition may be expected to correlate linearly with one another. Correlations between core-ionization energies and proton affinities have been long known for oxygen[13] and nitrogen,[14d] and have been used to provide information on site of protonation and on geometric rearrangements that occur upon protonation.[14] Recently we have shown that linear correlations exist between carbon 1s ionization energies and enthalpies of protonation.[9,15] In addition, we have demonstrated that there are linear correlations between core-ionization energies and the activation energies for electrophilic addition in alkenes.[8] We now consider such correlations for the methyl-substituted benzenes.

For the carbon 1s ionization energies, we have used the experimental adiabatic energies from Table 1. Experimental enthalpies of protonation are not known for all of the sites and for these we use theoretically predicted values, using the method proposed by Maksič et al.,[17] which has been found to reproduce known enthalpies of protonation quite well. This method involves calculation of the optimum geometry and zero-point energies for the relevant molecular species at the Hartree−Fock level using the 6-31G(d) basis set. Then using the optimized geometries, the energies are recalculated using the MP2 method and the 6-31G(d,p) basis set. These energies are combined with the zero-pont energies (scaled by the empirical factor of 0.89) to give the value of $\Delta E°_0$ (which is equal to $\Delta H°_0$). The calculated values are given in the Supporting Information.

In addition to proton affinities and carbon 1s ionization energies, we consider the activation energies for two reactions that involve addition of a proton at a particular site in a substituted benzene ring. These are (1) the hydrogen exchange reaction, in which a tritium atom that is attached to one of the ring carbons of a methylbenzene molecule is replaced by a hydrogen atom,[3] and (2) the desilylation reaction, in which a trimethylsilyl group attached to a methylbenzene is replaced by hydrogen.[18] If we ignore pre-exponential factors that affect the rates,[28] then we can obtain relative activation energies, $\delta E_{act,i}$, from the reported rate constants for these reactions by using the relationship

$$\delta E_{\mathrm{act},i} = -RT \ln(k_i/k_{\mathrm{H}})$$

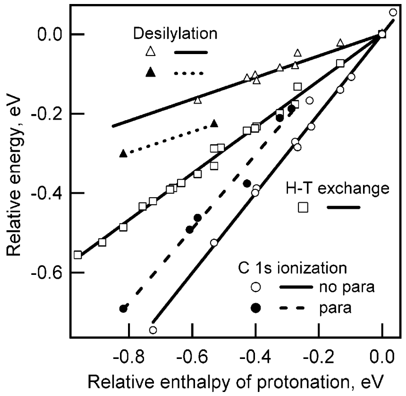

FIGURE 2. Relative energies of activation and relative carbon 1s ionization energies plotted against relative enthalpies of protonation for methyl-substituted benzenes. Triangles are for desilylation; the solid triangles are for compounds in which there are two methyl groups ortho to the trimethylsilyl group. Squares are for the hydrogen−tritium exchange reaction. Circles are for carbon 1s ionization energies. The open circles are for compounds in which there are no methyl groups para to the ionized carbon. The closed circles are for compounds in which there is a methyl group para to the ionized carbon. The lines show least-squares fits of straight lines to different sets of the data.

where k_i is the measured rate constant for a methyl-substituted benzene with substituent pattern i and k_H is the rate constant for benzene. The correlations among these various processes are shown in Figure 2, where we have plotted the relative activation energies for the two reactions and the relative measured carbon 1s ionization energies against the relative enthalpies of protonation for a number of methyl-substituted benzenes.

We see first that there is an excellent correlation between the activation energies for hydrogen−tritium exchange (squares in Figure 2) and the enthalpies of protonation. For this correlation the value of R^2 is 0.9989 and the rms deviation of the data from the correlation line is 0.011 eV. This deviation corresponds to being able to predict the exchange rate from the gas-phase proton affinity within a factor of 1.5 (compared to a factor of more than 10^8 for the range of rates considered). The slope of the correlation line is 0.58, or fairly close to 1. That there is such a good correlation between the energies for these two processes is not surprising. The transition state for the exchange reaction presumably resembles the protonated species, with an energy that is related to the gas-phase proton affinity as modified by the dielectric effect of the solvent or by the sharing of the incoming proton and the outgoing triton between the benzene ring and the solvating molecules.

For the desilylation reaction (triangles in Figure 2) there are two distinct correlations. The lower one (solid triangles) represents the data for *m*-xylene and mesitylene with the trimethylsilyl group ortho to two methyl groups. In this case, the activation energy is strongly influenced by steric effects.[18] This produces a decrease in the activation energy of about 0.08 eV, which corresponds to a factor of about 20 in the rate. If a correction is made for this, then the points for *m*-xylene and mesitylene fall on the line with the other data. However, the overall correlation ($R^2 = 0.9886$) is not so good as for the hydrogen−tritium exchange reaction.

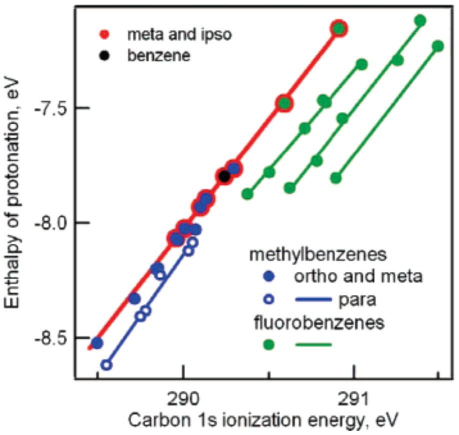

FIGURE 3. Enthalpy of protonation of benzene (black), fluorobenzenes (green), and methylbenzenes (blue) plotted against the carbon 1s ionization energies measured for the carbon at the site of protonation. Points encircled in red are for protonation/ionization at sites with no substituents either ortho or para to the site. The open blue circles are for protonation/ionization at sites with a methyl group para to the site.

For the carbon 1s ionization energies, there are also two correlation lines, one for cases where there is a methyl group para to the site of ionization (such as C4 in toluene or C4,6 in *m*-xylene) and another for all other cases. It is apparent that methyl substituents can have effects on the carbon 1s ionization energies that are different from their effects on the proton affinities or the rates of hydrogen exchange. We now consider the possible origin of these differences.

In investigating correlations between proton affinities and carbon 1s ionization energies for benzene and the fluorobenzenes we found that there is a single correlation line when the fluorine is meta to the site of protonation.[15] However, if we include the results for ortho and para substituents, these fall on three different lines, more or less parallel to the line for meta substituents, but displaced from it. The displacement is proportional to the number of ortho or para substituents. These results were interpreted to indicate that fluorine is a better π electron donor to an added proton at the ortho and para positions than it is to a positive charge at the center of the ortho and para carbon atoms. This difference arises because the protonated species has hydrogen atoms above and below the plane of the molecule. These can participate in the π molecular orbital system, and are, therefore, effective π-electron acceptors.

In Figure 3, we show this correlation, extended with the data on the methyl-substituted benzenes. Here we have plotted the enthalpy for protonation at a particular site in the molecule versus the ionization energy for removal of a carbon 1s electron from the same site. The points circled in red are those for which there are no substituents either ortho or para to the site of protonation. For these, we expect no direct effects of hyperconjugation. The red line in Figure 3 represents a least-squares fit of a straight line to these points. It fits the data quite well ($R^2 = 0.9991$, rms $= 0.0092$ eV) and has a slope of 0.95. Thus, if we restrict ourselves to situations where there is no direct contribution from hyperconjugation, there is an excellent

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(28) The major contribution to the pre-exponential factor is probably from changes in the symmetry number upon protonation. In the reaction for replacement of tritium by a proton in C_6H_5T, the change in symmetry number between the starting molecule and the transition state is from 2 to 1, leading to a factor of 2 effect on the rate. For the other molecules, either there is a similar change or no change in the symmetry number. A factor of 2 in the rate corresponds to 0.02 eV in energy, which is small compared with the 0.55 eV range in activation energies observed for these reactions.

TABLE 2. Additivity Coefficients (eV) for the Effect of Methyl and Fluoro Substituents on the Carbon 1s Ionization Energies, Enthalpies of Protonation, and Activation Energies of Substituted Benzenes[a]

		methyl				fluoro	
		ionization	protonation	hydrogen exchange	desilylation	ionization	protonation
linear coefficients							
α	ipso	0.046(5)	0.036(2)			2.504(7)	0.854(6)
	ortho	−0.264(3)	−0.279(2)	−0.174(2)	−0.084(3)	0.249(4)	0.014(4)
	meta	−0.143(3)	−0.132(1)	−0.068(2)	−0.026(3)	0.332(4)	0.312(3)
	para	−0.226(5)	−0.321(3)	−0.193(3)	−0.084(3)	0.120(7)	−0.072(6)
quadratic coefficients							
β	ortho−ortho		0.013(2)	0.010(2)	−0.027(3)		0.019(4)
	meta−meta		0.000(2)	0.002(2)			
γ	ipso-ortho	0.050(8)	0.017(4)				−0.115(4)
	ipso-para						−0.062(7)
	ortho-meta	0.017(3)	0.017(1)	0.009(1)			
	ortho-para	0.031(6)	0.019(2)	0.016(1)			
	meta−para		0.027(3)	0.017(2)			−0.027(4)
goodness of fit							
adjusted R^2		0.9986	0.9997	0.99985	0.9968	0.9998	0.9993
rms		0.008	0.004	0.004	0.005	0.020	0.012

[a] Uncertainties in the last digit are shown in parentheses. Where no value is shown, the coefficient is not statistically significant.

correlation between these energies. This correlation is comparable in quality to that seen for the hydrogen−tritium exchange reactions.

The data for the fluorobenzenes are shown in green, and we see the displacement of the data for which there are fluorines either ortho or para to the site of protonation/ionization. The three successive lines are for one, two, or three fluorines in these positions. The methylbenzenes, in blue, show a similar but much less pronounced effect. Only for the para data (open circles) is there a significant displacement from the red line, and even here, it is less than the corresponding displacement for the fluorobenzenes.

Before considering these correlations further, we show that these results can be summarized compactly in a few additivity coefficients. With these coefficients we can obtain a relatively simple picture of these correlations. These are discussed below.

Additivity of Substituent Effects. The effects of multiple substituents have often been described in terms of an additivity model. That is, the total effect of all the substituents is considered to be the sum of independent effects of the individual substituents. Previously we have shown that the ionization energies and proton affinities of the fluorobenzenes can be summarized with an additivity relationship:

$$\Delta E_r = \sum_i n_i \alpha_{ir} + \sum_i \left(n_i(n_i - 1)\beta_{ir} + \sum_{j>i} n_i n_j \gamma_{ijr} \right)$$

where ΔE_r is the energy (or enthalpy) change for reaction r (ionization or protonation) relative to that of some reference compound (benzene, in this case). The number of substituents of type i (ipso, ortho, meta, or para) is given by n_i. The coefficients α, β, and γ are characteristic of the substituent, its position, and the reaction. The first term in this expression represents the linear additive effect of the substituents, and in most treatments of additivity this is the only term considered. The second represents, to first approximation, interactions between the substituents that lead to departure from additivity. In practice, these quadratic terms are small and often insignificant.

Using the measured adiabatic ionization energies from Table 1 and the calculated enthalpies of protonation we have used least-squares fitting to determine the coefficients for the effect of a methyl substituent on the carbon 1s ionization energies and on the enthalpies of protonation in benzene. These are summarized in Table 2, together with the previously determined values for fluorine. Also included in Table 2 are coefficients for the two reactions discussed above.

The additivity model gives a very accurate description of the energy shifts. In each case, the value of R^2, adjusted for the degrees of freedom, is greater than 0.99. With the coefficients shown, the additivity model describes the carbon 1s ionization energies of the methylbenzenes with an rms deviation of 8 meV and the enthalpies of protonation with an rms deviation of 4 meV. Similar results are obtained for the fluorobenzenes. It is to be noted that, except for the desilylation reaction, the quadratic coefficients are generally small in comparison with the linear coefficients for the same process. Even if the quadratic coefficients are omitted, the model still describes most of the results well, with an rms deviation of 18 meV for the ionization energies and 19 meV for the enthalpies of protonation. For the desilylation reaction the ortho−ortho coefficient is large, reflecting the steric effect discussed above.

The linear additivity coefficients for *o*-, *m*-, and *p*-methyl substituents are all negative, regardless of the process, reflecting the electron donating power of the methyl group. By contrast, all but one of the linear coefficients for fluorine are positive, reflecting the electron withdrawing power of fluorine. For both methyl and fluoro substituents, the ortho and para coefficients for all processes are negative relative to the meta coefficients. This difference reflects the effects of hyperconjugation (methyl) and conjugation (fluoro), which allow the substituents to act as electron donors to positions that are ortho and para to the substituent, but not to positions that are meta. Comparing the ortho coefficients with the para coefficients, we see that for the methyl group they are of comparable magnitude.

The linear additivity coefficients are summarized compactly in Figure 4, where we have plotted the coefficients for the two reactions and for the carbon 1s ionization energies against the coefficients for the enthalpy of protonation. The lines shown in the figure are straight-line fits that are constrained to go through the origin, which is the point for unsubstituted benzene. For the carbon 1s ionization energies, only the points for meta substituents are used for determining the line.

In Figure 4 we see that the points for the hydrogen exchange and the desilylation reactions all fall on straight lines regardless

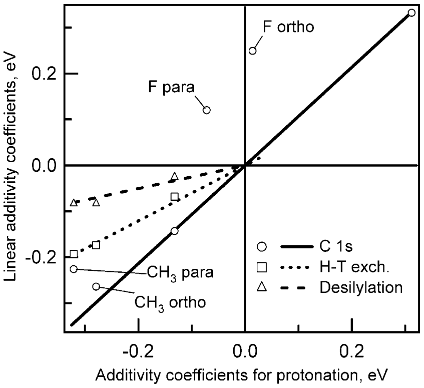

FIGURE 4. Linear additivity coefficients for desilylation (triangles), hydrogen−tritium exchange (squares), and carbon 1s ionization (circles) plotted against the coefficients for the enthalpy of protonation.

of whether there are hyperconjugative effects (ortho and para substituents) or not (meta substituents). For the core-ionization energies, however, it is apparent that the points for ortho and para substituents fall above the correlation line defined by the meta substituents. This is, of course, the same effect that has been seen in Figures 2 and 3, illustrated more compactly in terms of the additivity coefficients. As already noted, it arises because the protonated part of the molecule (whether in the gas phase or in solution) is a better π-electron acceptor than is a core-ionized carbon atom at the same site.

The solid line in Figure 4, which passes through the origin (benzene) and the points for methyl and fluoro substituents in the meta position, has a slope of 1.07, or very close to 1. Thus, the effect of a substituent in the meta position, where there are no effects of conjugation or hyperconjugation, is nearly the same for core ionization as it is for protonation. The slopes of the dotted and dashed lines, for the two reactions, are significantly less than 1, presumably reflecting the effect of the dielectric solvent on the electrostatic energies of the transition state or the effect of solvent molecules on the configuration of the transition state.

It is to be noted in Figure 4 that the displacement of the points for ortho and para substituents from the solid line is significantly greater for fluorine than it is for methyl. This effect is also apparent in Figure 3, where we see that the green lines, representing the effects of one or more fluorines in the ortho or para positions are more displaced from the red line (no conjugation) than are the open blue circles (methyl in the para position) or the points for a methyl in the ortho position. Evidently fluorine can respond to the demand created by the added proton and the modified π system more effectively than can a methyl group.

Most of these observations can be understood in terms of Hammett parameters. In the protonated species the two hydrogens above and below the plane give rise to a π orbital that can conjugate with the π orbitals on the substituent. As a result, it is expected that the enthalpies of protonation will correlate with σ^+, and this is indeed the case, as has been shown by McKelvey et al.[29] Such a correlation can be seen in Figure 5a, where we have plotted the enthalpies for protonation at the para position for a number of substituted benzenes[30] versus the Hammett parameter.[10] In this figure (similar to Figure 1 from McKelvey et al.), the open circles indicate the values for para substituents plotted against σ_p^+, whereas the triangles show the same data plotted against σ_p. It is apparent that the data correlate reasonably well with σ_p^+, but poorly with σ_p. The solid circles show the data for meta substituents plotted against σ_m. These show a correlation similar to that seen for the para substituents.

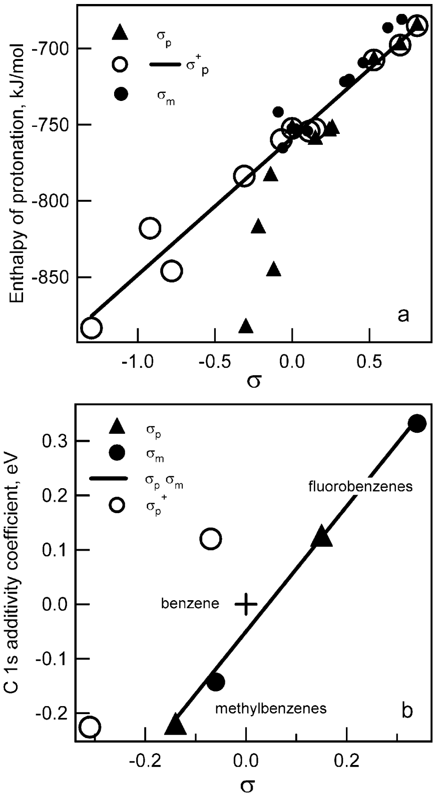

FIGURE 5. Enthalpy of protonation (a) and carbon 1s additivity coefficient (b) versus Hammett σ: circles, para substituents vs σ_p^+; triangles, para substituents vs σ_p; and solid circles, meta substituents vs σ_m.

By contrast, for carbon 1s ionization the effect of conjugation between the ionized carbon and the substituent is already included in σ. As a result, we expect that the carbon 1s ionization energies will correlate with σ, and this has been shown to be the case by Lindberg et al.[31] Such a correlation is shown in Figure 5b, where we have plotted the coefficients from Table 2 versus σ (meta or para, as appropriate) and against σ^+. It is apparent that the core-ionization energies correlate well with σ, but poorly with σ^+, as expected.

Conclusion

The carbon 1s ionization energies of the methyl- and fluoro-substituted benzenes are found to be closely related to the energies for other chemical processes that involve addition of a positive charge to a specific site in the benzene ring, such as protonation, hydrogen/tritium exchange, or protodesilylation. There are linear correlations among these energies, but also there are deviations from these correlations where hyperconjugation or conjugation can play a role in the process or if steric effects

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(29) McKelvey, J. M.; Alexandratos, S.; Streitwieser, A., Jr.; Abboud, J. L. M.; Hehre, W. J. *J. Am. Chem. Soc.* **1976**, *98*, 244−246.

(30) C_6H_5X, with X = H, CH_3, CH_3O, NH_2, NO_2, F, Cl, Br, CN, OH, and CF_3. The proton affinities have been calculated by the method described in ref 17. The calculated values are given in the Supporting Information.

(31) Lindberg, B.; Svensson, S.; Malmquist, P. Å.; Basilier, E.; Gelius, U.; Siegbahn, K. *Chem. Phys. Lett.* **1976**, *40*, 175−179.

are important. The deviations can be understood by recognizing that the ionization energies reflect primarily the Hammett parameter σ, whereas the other reaction energies reflect primarily σ^+. Additivity relationships provide a convenient and accurate way of summarizing the energies for the different processes.

In particular, we see excellent linear correlations between gas-phase enthalpies of protonation and the activation energies for solution reactions involving a protonated transition state. Thus, the gas-phase enthalpy of protonation is a predictor for the relative rates of these reactions. There is also an excellent correlation between the enthalpies of protonation and the carbon 1s ionization energies for cases where there are no substituents either ortho or para to the site of protonation or ionization. The correlation lines for the cases where there are ortho and para substituents are displaced from the line for meta substituents because of the effects of hyperconjugation (for methyl substituents) and conjugation (for fluoro substituents), which allow donation of electrons to the ortho and para positions, but not to the meta position. In the protonated species there is a pair of hydrogens above and below the plane of the molecule leading to a more extensive π-orbital structure in the protonated species than in the core-ionized species. As a result, the substituent is more effective with respect to protonation than it is to core ionization. Comparison of the energetics of these two processes thus provides insight into this difference.

Here we have focused on the role that hyperconjugation plays in the substituent effect of the methyl group. In a future paper we will consider the molecules $CH_n(CH_3)_{4-n}$ ($n = 0$ to 4), where the principal effects on the carbon 1s ionization energy are the electronegativity difference between hydrogen and the methyl group and the higher polarizibility of the methyl group.

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Supporting Information Available: Details of the theoretical methods, description of the method for dealing with vibronic coupling in *o*-xylene, calculated enthalpies of protonation, and theoretically calculated positions of the atoms in the molecules considered. This material is available free of charge via the Internet at http://pubs.acs.org.

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