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Reactivity and Core-Ionization Energies in Conjugated Dienes. Carbon 1s Photoelectron Spectroscopy of 1,3-Pentadiene

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The high-resolution carbon 1s photoelectron spectrum of *trans*-1,3-pentadiene has been resolved into contributions from the five inequivalent carbon atoms, and carbon 1s ionization energies have been assigned to each of these atoms. Spectra have also been measured for propene and 1,3-butadiene at better resolution than has previously been available. The ionization energies for the sp^2 carbons are found to correlate well with activation energies for electrophilic addition and with proton affinities. Comparing the results for 1,3-pentadiene with those for ethene, propene, and 1,3-butadiene as well as with results of theoretical calculations makes it is possible to assess the effect of the terminal methyl group in 1,3-pentadiene. As in propene, the methyl group contributes electrons to the β carbon through the π system. In addition, there is a significant (though smaller) contribution from the methyl group to the terminal (δ) CH$_2$ carbon, also through the π system. Most of the effect of the methyl group is present in the ground-state molecule. There are only relatively small contributions from the methyl group to the ionization energies from redistribution of charge in the π system in response to the removal of a core electron. In addition to these specific effects, there is an overall decrease in average ionization energy as the size of the molecule increases as well as effects that are specific to the conjugated systems in 1,3-butadiene and 1,3-pentadiene. The results provide insight into the reactivity and regioselectivity of conjugated dienes.

Introduction

Inner-shell ionization energies of atoms in molecules provide local probes of the charge distribution in molecules and of the ability of a molecule to accept charge. As such, they can be related to and can provide insight into such chemical properties as electronegativity, acidity, basicity, proton affinities, reactivity, and regioselectivity of reactions. Recently the availability of third generation synchrotrons and high-resolution electron-energy analyzers has opened new opportunities, especially with respect to hydrocarbons and the hydrocarbon portions of molecules with heteroatoms. As a result, the past few years have seen a number of studies of such compounds, often with emphasis on relating the carbon 1s ionization energies to other, possibly more familiar, chemical properties.[1−13]

For molecules with double bonds there is a close relationship between carbon 1s ionization energies and the activation energies of electrophilic addition reactions.[14] This is expected since in both cases a positive charge is added to a selected site in the molecule. In the one case, electrophilic reaction leads to formation of a carbocation by addition of a proton or other positive substituent. In the other, ionization produces a positive center by removing an inner-shell electron. Although the energies of these two processes are different, the chemical effects that influence them are similar. This similarity has been demonstrated for the series ethene, propene, and 2-methylpropene, where both reactivity and regiospecificity were found to be quantitatively related to the carbon 1s ionization energies.[14] An additional and striking finding of that investigation was that these properties are determined to a large extent by the charge distribution in the ground state of the molecules and not by different ability of the molecules to delocalize the added charge in the transition state.

Our interest here is to extend these investigations to *trans*-1,3-pentadiene and its relation to propene and 1,3-butadiene. 1,3-Butadiene and 1,3-pentadiene are representatives of the family of 1,3-alkadienes, which have been extensively investigated both experimentally and theoretically.[15−21] Interest in these substances arises in part because of their use in the polymer industry and in part because of their ability to participate in Diels−Alder reactions, which are of great importance in synthesis. Of special interest is the effect of the methyl group at the end of the conjugated chain. This is not readily predicted, since it may be felt at both the β and δ positions (C3 and C1).[20] It will be seen that the effect of the methyl group on the C1s ionization energies is primarily determined by the ground-state charge distribution. In addition, however, in 1,3-pentadiene and in 1,3-butadiene resonance in the conjugated system allows delocalization of the added charge, thus both lowering the ionization energy and making these molecules more susceptible to electrophilic attack.

In earlier studies of propene[3] and propyne[4] it was found that the carbon 1s ionization energies of the terminal CH$_2$ and CH groups were shifted to low values by the presence of the methyl group. This result was interpreted in terms of contributions from hyperconjugation through forms such as $^-H_2C{-}CH{=}CH_3^+$ for propene and $^-HC{=}C{=}CH_3^+$ for propyne in which negative charge is transferred from the methyl group to the terminal

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carbon through the π system. It is of interest to see whether similar resonance structures such as $^{-}\mathrm{H_2C{-}CH{=}CH{-}CH{=}CH_3}^{+}$ in 1,3-pentadiene are also important. In such a case, the effect of the methyl group is transmitted from one end of the molecule to the other through the conjugated π system. Toward that end, we have measured the carbon 1s photoelectron spectrum of this molecule with sufficiently high resolution that it is possible to determine the contribution to the spectrum from each of the five inequivalent carbon atoms, and, hence, to determine the carbon 1s ionization energy for each carbon. Since 1,3-pentadiene shares common features with 1,3-butadiene, we have remeasured the carbon 1s photoelectron spectrum for this molecule as well as that of propene at higher resolution than was previously available. From these results, together with those of the linear alkanes,[5] we can assess the contributions from molecular size, relative electronegativities of carbon and hydrogen, and resonance. From the analysis, we are able to conclude that the methyl carbon does contribute electrons to C1 of 1,3-pentadiene, although not so strongly as to C3 (for which the resonance is similar to that seen in propene). In addition, we find an excellent correlation between the core-ionization energies in 1,3-pentadiene and the activation energies for addition of HCl at the different sites of this molecule as well as an excellent correlation between the ionization energies and proton affinities.

Procedures

Experimental. The carbon 1s photoelectron spectra of propene, 1,3-butadiene, and *trans*-1,3-pentadiene have been measured in the gas phase at either the Advanced Light Source (Beamline 10.0.1) or the MAX II synchrotron (Beamline I411). The photon energy was 330 eV. In each case, the photoelectrons were analyzed in a Scienta SES 200 analyzer. The measurements were made at different times, and the conditions were not the same for the different runs. For propene the overall instrumental resolution was 55 meV, for butadiene nearly 80 meV, and for pentadiene 65 meV. In all cases the instrumental resolution was less than the natural line width of the core hole, about 100 meV. Calibration of the spectra was done by measurement of a mixture of the sample with either CF_4 or CO_2. The known adiabatic ionization energies of CO_2 and CF_4 were used as standards.[22] The measured spectra are shown in Figure 1, where the experimental points are represented by the open circles. The lines represent least-squares fits to the data, discussed below.

Core-ionization is accompanied by vibrational excitation, and, for the most part, each chemically unique carbon atom produces a unique vibrational excitation spectrum. For instance, ionization of a methyl carbon shows strong excitation of the carbon−hydrogen stretching mode because there are three carbon−hydrogen bonds that are affected by the core ionization. This will be less pronounced for a carbon with only two hydrogen atoms attached (the terminal CH_2 carbons for the molecules considered here), and weak if there is only one hydrogen atom. There will also be contributions from carbon−carbon stretching modes and from a variety of bending modes. The vibrational profiles are calculated from electronic structure theory using procedures that are discussed in detail elsewhere.[12] Briefly, we calculate the optimized geometry, vibrational frequencies, and normal modes. From these, we calculate Franck−Condon factors for all significant vibrational excitations, including combination modes. This procedure has been found to give good descriptions of the vibrational excitation that accompanies carbon 1s ionization. For each molecule there is one calculated profile for each kind of carbon atom. These are fit to the measured spectra with only a flat background, the height of each profile, and the adiabatic (threshold) transition energy of each profile as fitting parameters. For propene and 1,3-pentadiene the areas of the component profiles were constrained to be equal. The least-squares procedure takes into account the instrumental broadening by convoluting the profile with a Gaussian function, as well as the additional broadening of the peak that results from interaction between the Auger and photoelectrons that are emitted during core ionization.[23] The line shape given by eq 12 from van der Straten et al.[24] with a Lorentzian line width of 100 meV[25] was used to describe this interaction.

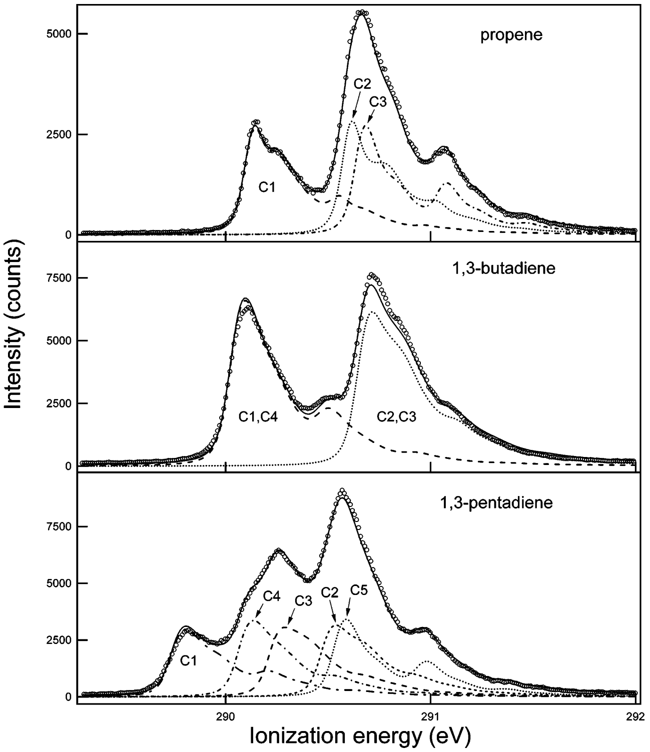

Figure 1. Experimental carbon 1s photoelectron spectra of propene, 1,3-butadiene, and 1,3-pentadiene. Open circles show the data. Solid lines represent least-squares fits to the data. Dashed and dotted lines show the contributions from individual carbon atoms.

The solid lines in Figure 1 show the overall spectra as determined from this least-squares procedure and the dashed and dotted lines show the individual components. It can be seen that there is good agreement between the experimentally measured data and the solid lines. For propene and 1,3-butadiene there is no ambiguity about the fits. For 1,3-pentadiene, the profiles calculated for C2, C3, and C4 are similar, so there is a question about which profile should be assigned to which part of the spectrum. We have considered a number of possible initial guesses for the least-squares routine, including all of the possible permutations of C2, C3, and C4. These fits show that the only ambiguity arises in the ordering of ionization energies for C2 and C3. The fit shown in Figure 1 is the one that gives the lowest value of χ^2. The ionization energies obtained in this fit are in good agreement with theoretical predictions, as can be seen in Figure 2, where we have plotted the measured core-ionization energies versus the values predicted by theoretical calculations, discussed below. In this graph the solid points show the values we have obtained from our fits. The two open circles show the results if we switch the initial guesses for C2 and C3 in the least-squares fit. It is apparent that the results of this choice are in unacceptable disagreement with the theoretical predictions.

Theoretical. The theoretical procedures used for modeling the vibrational profiles are described elsewhere and will not be

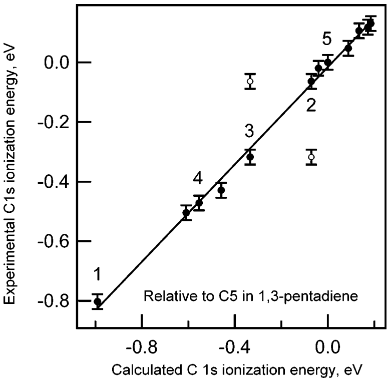

Figure 2. Comparison of measured and predicted relative carbon 1s ionization energies. The numbered points refer to the five carbon atoms in 1,3-pentadiene. Solid points represent the results derived from our fits. The two open circles represent results obtained using an initial guess in the least-squares fitting routine that reverses the order of C2 and C3.

repeated here.[12] The Gaussian set of programs was used,[26] and the calculations have been carried out with the B3LYP method using a triple-ζ basis set. For the core-ionized molecules the ionized carbon atom was represented by an effective core potential. Details of the basis set and effective-core potential are given in ref 5.

The calculations for the core-ionized states give the relative carbon 1s ionization energies of the different carbon atoms; these are listed in the Supporting Information. The calculated and experimental values are compared in Figure 2, where it can be seen that they agree well, except that theory overestimates the relative ionization energies consistently by about 20%. The straight line in Figure 2 represents a linear regression of the experimental values onto the calculated values. It has a slope of 0.82. This is a common feature of such calculations;[12] the trends are predicted correctly but the slopes differ from 1. Aside from this systematic effect, the agreement between theory and experiment is good; the regression line has an R^2 value of 0.996 and the root-mean-square deviation of the experimental points from the regression line is only 21 meV. This general agreement between theory and experiment corroborates the assignments of ionization energies that are based on the fits of the vibrational profiles to the measured spectra.

Additional calculations have been made at the Hartree−Fock and MP2 levels of theory to determine the effects of the ground-state charge distribution on the ionization energies. For this purpose, we have used the extended Koopmans theorem developed by Børve and Thomas.[27] These calculations were carried out at the geometry determined in the B3LYP optimizations.

We have also calculated transition-state energies for the addition of HCl across the double bonds in 1,3-pentadiene and 1,3-butadiene. For these calculations we have augmented the basis sets for HCl and for the sp^2 carbons in 1,3-pentadiene with additional diffuse functions.[28] We find that this procedure gives calculated transition-state energies that are in near agreement with experimentally derived activation energies for addition of HCl to ethene, propene, and 2-methylpropene.[14,29] In addition, we have calculated protonation energies for adding a proton to carbon atoms 1 and 4 in 1,3-pentadiene and to carbon atom 1 in 1,3-butadiene. The procedure used reproduces the experimental proton affinities[30] of ethene, propene, 2-methylpropene, and 1,3-butadiene reasonably well. The calculated activation energies and proton affinities are given in the supporting material.

TABLE 1: Experimental Adiabatic and Vertical Carbon 1s Ionization Energies, eV

		ionization energy, eV		
molecule	atom	adiabatic	vertical	relative[a]
ethane[b]	C1	290.545	290.714	0.000
ethene[b]	C1	290.695	290.823	0.150
propene	C1	290.136	290.230	−0.266
	C2	290.612	290.759	0.210
	C3	290.671	290.863	0.269
1,3-butadiene	C1,C4	290.060	290.245	−0.243
	C2,C3	290.683	290.845	0.380
1,3-pentadiene	C1	289.762	289.973	−0.474
	C2	290.501	290.661	0.265
	C3	290.247	290.412	0.011
	C4	290.093	290.250	−0.143
	C5	290.565	290.756	0.329

[a] Relative to average ionization energy for the linear alkane (ref 5) with the same number of carbon atoms: ethane = 290.545 eV; propane = 290.402 eV; *n*-butane = 290.301 eV; *n*-pentane = 290.236 eV. [b] Reference 22.

Results and Discussion

The measured carbon 1s ionization energies are listed in Table 1. Also listed here for reference are the ionization energies for ethane and ethene.[22] For each carbon atom, two values are given. The adiabatic value is the ionization energy for producing the ion in its ground vibrational state and is determined from the fits outlined above. The vertical ionization energy is the ionization energy to produce the ion with the same geometry as that of the ground state. It is determined by averaging over the vibrational profile. Older measurements made at lower resolution have generally reported the vertical ionization energy. Our results for propene are on the average about 40 meV lower than those reported previously,[3] and our analysis assigns a lower ionization energy to C2 than to C3 (in contrast to the previous result). Because of the higher resolution now available, we are able to get a better determination of the energies for this closely spaced pair. Our values for the vertical ionization energies in 1,3-butadiene are on the average in good agreement with earlier measurements[1,2] made at lower resolution, but give a splitting between the inequivalent carbon atoms of 0.60 eV, compared with 0.64 eV for the earlier measurements. On the basis of our experience with other measurements of this type,[22] we estimate the absolute uncertainty in these measurements to be 0.03 eV. The relative uncertainty is difficult to estimate, but it is probably not less than 0.01 eV. Because of the uncertainty in this quantity, we retain 3 decimal places for the results given in Table 1.

Core-ionization Energies, Reactivity, and Proton Affinity. The lowest ionization energies for 1,3-pentadiene are those for C1 and C4, the δ and α carbons. These are also the most reactive sites for electrophilic attack, as can be seen, for example, from the rates of addition of CH_3OCl across the double bond.[19] In this molecule, the chlorine atom is slightly positive and in the transition state attaches preferentially at the sites that most readily accept positive charge, which are also the sites where the carbon 1s ionization energy is the lowest. Addition of the chlorine at C1 is 65 times as probable as addition at C4, qualitatively in keeping with the result that the ionization energy of C1 is 0.33 eV less than that of C4. Addition of chlorine at C2 or C3 is not observed, and this is in keeping with the higher ionization energies of these atoms. Turning to differences in reactivity between different compounds, we note that the rate of addition of 4-chlorobenzene sulfenyl chloride is nine times faster with 1,3-pentadiene than with 1,3-butadiene.[20] Correspondingly, the C1 ionization energy of 1,3-pentadiene is 0.30

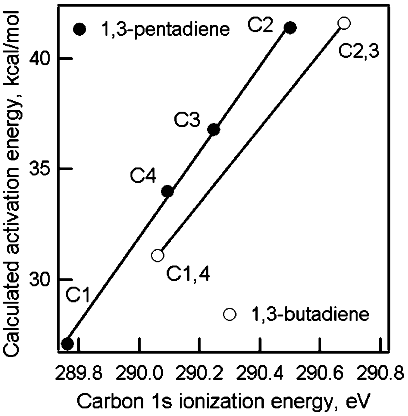

Figure 3. Calculated activation energies for addition of HCl to 1,3-pentadiene (closed circles) and 1,3-butadiene (open circles) plotted against the carbon 1s core-ionization energies. Labels indicate the carbon to which the hydrogen adds or from which a core electron is ionized. The lines are least-squares fit to the data.

eV lower than that of 1,3-butadiene. Thus the core-ionization energies reflect the reactivity.

We can obtain a more quantitative view of the relationship between reactivity and core-ionization energy by considering the activation energy for addition of HCl across the double bond. For such addition in ethene, propene, and 2-methylpropene there is a linear correlation between the carbon 1s ionization energies and the experimentally determined activation energies.[14] Since comparable experimental data are not available for 1,3-pentadiene, we use theoretically calculated transition-state energies for this purpose. As noted above, the theoretical procedure used here gives excellent agreement between the theoretical and experimental energies for ethene, propene, and 2-methylpropene. The correlations between the activation energies and the ionization energies for 1,3-pentadiene and 1,3-butadiene are shown in Figure 3. In this figure the labels indicate the site of core ionization, on one hand, and the site to which the hydrogen atom adds, on the other. The straight lines represent least-squares fits.

A comparison of the results for 1,3-pentadiene with those for 1,3-butadiene, as illustrated in Figure 3, shows the effect of the added methyl group. First, for C1, which is at the opposite end of the molecule from the methyl group, both the activation energy and the ionization energy are significantly lower in 1,3-pentadiene than in 1,3-butadiene. By contrast, the activation energy for C4, which is equivalent to C1 in butadiene, is increased by the addition of the methyl group. For C3, both the activation energy and the ionization energy are lowered by the addition of the methyl group, with the result that the significant difference between C3 and C4 in 1,3-butadiene is greatly reduced in 1,3-pentadiene.

Another quantitative view of the relation between core-ionization energies and reactivities is found by considering proton affinities. Since core-ionization and protonation both involve adding a positive charge at a specific site, we can expect there to be a correlation between proton affinities and core-ionization energies. Such correlations are well established for protonation/ionization at oxygen, nitrogen, and other heteratoms,[31] but, to our knowledge, have not been reported for protonation of carbon. Such a correlation is shown in Figure 4, where we have plotted theoretically calculated protonation enthalpies for 1,3-pentadiene at the 1 and 4 positions and for 1,3-butadiene at the 1 position versus the corresponding experimental carbon 1s ionization energies. As in Figure 3, the straight line represents a least-squares fit.

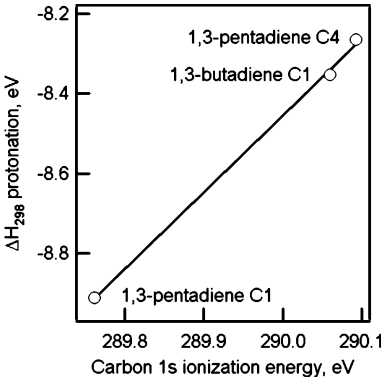

Figure 4. Protonation enthalpy plotted against carbon 1s ionization energy.

We cannot fail to note the excellence of the correlation for 1,3-pentadiene shown in Figure 3 and for both pentadiene and butadiene in Figure 4. We also note that the correlation for 1,3-butadiene in Figure 3 is similar to but displaced from that for 1,3-pentadiene. Although we might expect a correlation since the processes all involve adding a positive charge at a selected carbon, the three processes are intrinsically quite different, involving significantly different geometric changes. Nevertheless, the correlations are excellent. Noteworthy are the results for C1 in 1,3-butadiene and for C4 in 1,3-pentadiene, where we see nearly equal ionization energies, nearly equal proton affinities, and similar values of the activation energy.

The slope of the line for 1,3-pentadiene in Figure 3 (after converting to a common set of units) is 0.85, similar to the value of 0.57 found for ethene, propene, and 2-methylpropene.[14] For the correlation shown in Figure 4, the slope is 1.9. Recapitulating the discussion from ref 14, we note the following. First, the slopes of these correlations are of order 1, suggesting that the transition-state energies, protonation energies, and core-ionization energies are influenced by the same factors and to more or less the same extent. Second, the slopes for the transition-state energies are somewhat less than 1, indicating that the transition-state energy is less sensitive to these factors than is the core-ionization energy. This is not surprising, since core-ionization involves a highly localized charge at the center of interest, while the transition state involves bringing the positive end of a dipole close to this center.

It is important to note, in addition, that the slope of 0.85 for 1,3-pentadiene is indeed different from that for ethene, propene, and 2-methylpropene, 0.57. If we add points for other compounds to Figures 3 and 4, such as those for 1,3-butadiene in Figure 3, we find that, although there is still an overall correlation, there is also considerable scatter. Thus, there appear to be additional influences that are specific to the type of molecule under consideration, and some of these are discussed in the overview, below.

Systematics of the Ionization Energies. The systematic behavior of the ionization energies can be seen in Figure 5A, where we have plotted the carbon 1s ionization energies for ethene, propene, 1,3-butadiene, and 1,3-pentadiene against the number of carbon atoms in the molecule. Also included in this figure is a solid line showing the average carbon 1s ionization energy of the linear alkanes as a function of the number of carbon atoms.[5] It is apparent that there is a decrease in the average energy as the size of the molecule increases. This reflects the increasing polarizibility of the molecule with increasing size. To remove this size effect and focus on the specific effects of adding a methyl group and on the effects of conjugation, we show in Figure 5B the ionization energies

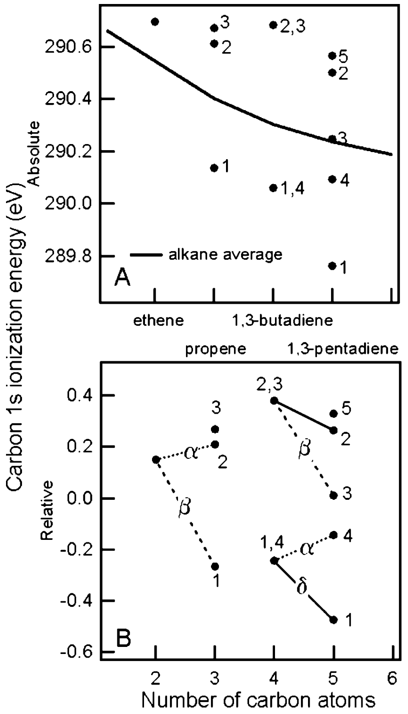

Figure 5. A. Carbon 1s ionization energies plotted against number of carbons in the molecule. Solid line shows the average ionization energy for linear alkanes. B. Carbon 1s ionization energies relative to the average for linear alkanes. Lines show the effect of adding a methyl group to the end of the molecule.

relative to the average alkane energies. These relative energies are listed in Table 1.

In the left half of Figure 5B, we see the effect of replacing one of the hydrogen atoms in ethene with a methyl group to make propene. For the carbon α to the methyl group, C2, the ionization energy increases slightly, by 0.06 eV. This difference is very close to the corresponding difference, 0.085 eV, between the ionization energy of C2 in propane and the average ionization energy in propane. In the alkanes this shift arises because a hydrogen atom in ethane has been replaced by a substituent with higher electronegativity, namely a carbon atom or the methyl group, and it is likely that the same effect accounts for the shift observed for propene. For the carbon that is *β* to the methyl group, C1, the ionization energy decreases significantly. This effect has been attributed to the effect of resonance that transfers negative charge from the methyl group to the terminal CH_2 group, as illustrated in **1c**.[3,14]

$$\underset{\textbf{1a}}{CH_2{=}CH{-}CH_3} \leftrightarrow \underset{\textbf{1b}}{{}^{-}CH_2{-}C^{+}H{-}CH_3} \leftrightarrow \underset{\textbf{1c}}{{}^{-}CH_2{-}CH{=}CH_3{}^{+}}$$

There may also be contributions from **1b**, but insofar as the charge on C2 is stabilized by polarization of the methyl group, it is difficult to distinguish between **1b** and **1c**. Comparison of Mulliken populations for propane and propene suggests that **1c** is more important than **1b**. We note also that the ionization energy for C3 in propene is 0.33 eV more positive than in propane, suggesting that electrons have been withdrawn from C3 in propene, as in **1c**. The net effect of **1b** and **1c** is that additional negative charge at the CH_2 group lowers the ionization energy of the 1s electron.

We can also anticipate that there are contributions from similar resonances in the core-ionized molecule:

$$\underset{\textbf{2a}}{{}^{+}C^{*}H_2{=}CH{-}CH_3} \leftrightarrow \underset{\textbf{2b}}{C^{*}H_2{-}C^{+}H{-}CH_3} \leftrightarrow \underset{\textbf{2c}}{C^{*}H_2{-}CH{=}CH_3{}^{+}}$$

where the asterisk indicates the core-ionized carbon atom. The right-hand forms, by allowing the positive charge to delocalize, lower the energy of the ionized state and, hence, lower the ionization energy. We will see below that the effect illustrated in **1** (initial-state effect) appears to be more important than that shown in **2**.

In the right half of Figure 5B, we see the effect of adding a methyl group to 1,3-butadiene to make 1,3-pentadiene. For C4 (α to the methyl group) and C3 (*β* to the methyl group) the effects are nearly identical to those for propene, as can be seen by comparing the two dotted lines labeled α with one another or the lines labeled *β* with one another. Of particular interest is the line labeled *δ*, which shows the effect on C1 of 1,3-butadiene of adding a methyl group to the opposite end of the molecule. The shift in ionization energy, −0.23 eV, is more than half the value of −0.37 eV for the shift at the *β* carbon. Thus, the substituent effect of the methyl group is transmitted with reasonably good efficiency through the conjugated system of the molecule.

Also noteworthy in Figure 5B is the large decrease in ionization energy for the terminal carbon, C1, as we go from ethene to 1,3-butadiene. This can be associated with the conjugated system of bonds in butadiene. We will see below that this large shift arises primarily because of charge delocalization in the ionized molecule that is made possible by resonance in the conjugated double bonds.

Charge Distribution in the Initial State and Charge Redistribution in the Final State. As indicated in the discussion above of the resonance forms for propene and its ion, the inner-shell ionization energies may depend on both the charge distribution in the initial molecule, as in **1**, and the charge rearrangement that accompanies ionization, as in **2**. Quantitatively we can write[4]

$$\Delta I = \Delta V - \Delta R \qquad (1)$$

where ΔI is the ionization energy relative to some standard, ΔV is the shift in the initial-state effect relative to the same standard, and ΔR represents the effect of charge redistribution. ΔR is given a negative sign to reflect that the relaxation of the charge distribution in response to the creation of a core hole lowers the ionization energy.

It is to be noted that an expression similar to eq 1 can also describe the interaction of molecules with one another, as, for instance, in the transition state for addition of HCl to an olefin. In this case, the first term describes the electrostatic interaction of two frozen molecular charge distributions while the second describes the effect of exchange interaction, mutual polarization, and covalency between the molecules.[32]

ΔV. Values of ΔV can be estimated from either changes in Koopmans theorem energies, $-\Delta\epsilon$, or changes in the potential, ΔU, at the carbon atom of interest. Since both of these methods have drawbacks, we use instead the extended Koopmans theorem developed by Børve and Thomas.[27] As a practical matter, the different methods give very similar results provided that we compare carbon atoms with the same hybridization. Because of this dependence on hybridization, which is not fully understood, we give values of ΔV (and, hence, also ΔR) relative to ethene for sp^2 carbon atoms and relative to ethane for sp^3 carbon atoms. The calculated values of ΔV are listed in Table 2; the estimated uncertainty in these is about 15 meV.[27]

TABLE 2: Values of ΔV, ΔR, and ΔI. Relative to Ethene, Except for C3 in Propene and C5 in 1,3-Pentadiene, Which Are Relative to Ethane (eV)

	H/C[a]	ΔV	$\delta\Delta V$[b]	ΔR	ΔI
ethene	2	0		0	0
propene	2	0.05 (avg)		0.22 (avg)	
C1		−0.27		0.29	−0.56
C2		0.13		0.22	−0.08
C3		0.29[c]		0.16[c]	0.13[c]
1,3-butadiene	1.5	0.18 (avg)		0.50 (avg)	
C1,C4	2	0.04		0.68	−0.64
C2,C3	1	0.31		0.32	−0.01
1,3-pentadiene	1.6	0.18 (avg)		0.58 (avg)	
C1		−0.11	−0.16	0.82	−0.93
C2		0.20	−0.11	0.40	−0.19
C3		0.06	−0.25	0.51	−0.45
C4		0.20	0.16	0.80	−0.60
C5		0.37[c]		0.35[c]	0.02[c]

[a] Ratio of hydrogen to carbon. [b] Relative to equivalent carbon in 1,3-butadine. [c] Relative to ethane.

The average value of ΔV for each molecule reflects the hydrogen/carbon ratio of the molecule. Carbon is slightly more electronegative than hydrogen and, hence, withdraws negative charge from the hydrogen atoms. The higher the hydrogen/carbon ratio the larger this effect, as can be seen from comparing the hydrogen/carbon ratio with the average value of ΔV shown in Table 2. Within each molecule, the individual values of ΔV reflect the charge distribution within the molecule, and we consider these now.

The values of ΔV for C3 and C1 in propene, +0.29 eV for C3 and −0.27 eV for C1, reflect the contribution from **1c**, which transfers electrons from the methyl group to the terminal methylene group via the π molecular orbital. This phenomenon has been discussed earlier in the context of both propene[3] and propyne.[4] The positive value of 0.13 eV for ΔV at C2 reflects the replacement of a hydrogen atom in ethene by the more electronegative methyl group in propene. This shift of +0.13 eV is comparable to the shifts in ΔV between methane and ethane (+0.12 eV[5]) or between ethane and C2 in propane (0.18 eV[5]), which involve the same substitution. Thus, the methyl group is serving as both an electron acceptor (through the σ bond with the α carbon) and as an electron donor (through the π bond to the β carbon).

In 1,3-butadiene, the hydrogen atoms do not contribute to the π orbitals, and, therefore, structures of the type **1c** are not significant. Thus, ΔV reflects primarily of the number of hydrogen atoms attached to each carbon. For C1 and C4 this is two, as in ethene, and we see that the shift in V relative to ethene for these carbons is small. C2 and C3 are similar to C2 in propene, which shows the effect of replacing a hydrogen atom with a more electronegative carbon atom. The value of ΔV of 0.31 eV for C2 and C3 in butadiene is, however, noticeably larger than the value of 0.13 eV for C2 in propene.

In 1,3-pentadiene we see the combination of the effects that have been noted for propene and 1,3-butadiene. The methyl group (C5) shows a positive value of ΔV, which, as is the case for propene, can be attributed to resonance transfer of electrons from the methyl group to C1 and C3, as illustrated in **3**.

$CH_2{=}CH{-}CH{=}CH{-}CH_3 \leftrightarrow$

3a

$CH_2{=}CH{-}CH^-{-}CH{=}CH_3^+ \leftrightarrow$

3b

$^-CH_2{-}CH{=}CH{-}CH{=}CH_3^+$

3c

As a result of this transfer, C1 and C3 are expected to have lower ionization energies than in 1,3-butadiene. This effect can be seen in Table 2 in the column headed $\delta\Delta V$, where the values of ΔV for 1,3-pentadiene are given relative to those in 1,3-butadiene. We see that C1 (−0.16 eV) and C3 (−0.25 eV) are indeed negative relative to those for 1,3-butadiene. C4 has become positive compared to C4 in 1,2-butadiene because of the replacement of a hydrogen atom by a methyl group, just as in propene. That C2 in 1,3-pentadiene is somewhat negative relative to C2 in 1,3-butadiene is not readily explained, since there is no obvious way for the methyl group to contribute electrons at this position.

ΔR. Values of ΔR, have been determined from the experimental shifts in the adiabatic ionization energy, ΔI, and the calculated values of ΔV using eq 1. They, along with the values of ΔI, are listed in Table 2. We note that there is a significant increase in the average relaxation energy as the size of the molecule increases, reflecting the relationship between polarizibility and molecular size. We now consider the individual values of ΔR for each molecule.

The average value of ΔR for propene (0.22 eV relative to ethene) differs only slightly from the average for propane (0.18 eV relative to ethane[5]). This near equality suggests that most of the relaxation effects in propene arise from the extra polarizibility that comes with increased size. Of interest is the value of 0.29 eV for C1, which, by using these values, can be separated into a contribution of 0.18 to 0.22 eV due to overall polarizibility, ΔR_{pol}, and one of 0.07 to 0.11 eV from the charge rearrangements shown in **2**, ΔR_{res}. The value of −0.27 eV for ΔV at this position reflects contributions to the ionization energy from the initial-state structures **1**. The three quantities ΔV, ΔR_{pol}, and ΔR_{res} combine according to eq 1 to give the overall shift in ionization energy of −0.56 eV. From this analysis it appears that the effect of resonance on the initial-state charge distribution (ΔV) is much more important than its effect on charge rearrangement (Δ_{res}). Similar conclusions were reached in an earlier discussion of propene.[14]

Both types of carbon in 1,3-butadiene show large values of the relaxation energy. Part of this is due to the size of the molecule, and it is, therefore, more instructive to subtract from these the average values of the relaxation energy of butane relative to ethane.[5] When this is done, we find that the relaxation for C2 and C3, the central carbons, is only 0.03 eV. However, for the terminal CH_2 groups, ΔR on this scale is 0.40 eV, or quite significant. This large relaxation can be attributed to a resonance contribution from

$$^+C^*H_2{=}CH{-}CH{=}CH_2 \leftrightarrow C^*H_2{-}CH{=}CH{-}CH_2^+$$

4a **4b**

which delocalizes part of the positive charge of the core hole from one end of the molecule to the other.

For 1,3-pentadiene, ΔR is large for all carbons. It is useful to think of it as resulting from three sources. First are those that arise because of the similarity between 1,3-pentadiene and 1,3-butadiene, ΔR(butadiene). Second are those that arise because pentadiene is larger than butadiene; we may equate this difference to the difference between the average value of R for pentane and that for butane, 0.09 eV.[5] Finally, there is the specific contribution from the extra methyl group (in addition to the effect that arises from its addition to the size of the molecule), ΔR(methyl). Thus

$$\Delta R_i(\text{pentadiene}) = \Delta R_i(\text{butadiene}) + 0.09\ \text{eV} + \Delta R_i(\text{methyl})$$

where the index i refers to one of the carbon atoms and ranges from 1 to 4. Using the values of ΔR(pentadiene) and ΔR(butadiene) from Table 2, we can calculate values for ΔR(methyl). These are 0.05 eV for C1, −0.01 eV for C2, 0.11 eV for C3, and 0.04 eV for C4. For C3, which occupies the same relationship to the methyl groups as C1 in propene, the relaxation energy (on this basis) is the same as for C1 in propene, that is 0.11 eV. This reflects the contribution to relaxation from the resonance structures

$$\underset{\textbf{5a}}{CH_2{=}CH{-}C^{*+}H{=}CH{-}CH_3} \leftrightarrow \underset{\textbf{5b}}{CH_2{=}CH{-}C^{*}H{-}CH{=}CH_3^{+}}$$

At C1, C2, and C4, the specific effect of the methyl group on the relaxation is small. At C1, this contribution, which can be attributed to the resonance

$$\underset{\textbf{6a}}{C^{*+}H_2{=}CH{-}CH{=}CH{-}CH_3} \leftrightarrow \underset{\textbf{6b}}{C^{*}H_2{-}CH{=}CH{-}CH{=}CH_3^{+}}$$

is only 0.05 eV.

As is the case for propene, the overall contributions to the ionization energy shifts from resonance relaxation in the ionized state (0.11 eV for C3 and 0.05 eV for C1) are less significant than the contribution from the ground-state charge distribution ($\Delta V = -0.25$ eV for C3 and −0.16 eV for C1). Thus, the added methyl group in both propene and 1,3-pentadiene shows its effect primarily through its influence on the ground-state charge distribution in the molecule.

Overview

We see that the carbon 1s ionization energies are influenced by a number of factors: the overall size of the molecule, the relative electronegativities of carbon and hydrogen, and contributions from resonance. That these are important is not surprising, since they are effects that have long been recognized. In addition, we see that there are, in some cases, striking correlations between the carbon 1s ionization energies and measures of chemical reactivity such as activation energies and proton affinities. These correlations suggest a close connection between the factors that influence the inner-shell ionization energies and those that influence reactivity.

Of particular interest is the transmission of the effect of the methyl group in 1,3-pentadiene to the terminal CH_2 group. After correcting for the influence of molecular size and effects that are specific to the conjugated system in 1,3-butadiene, the relative ionization energies given in Table 1 indicate that the effect of the methyl group on the ionization energy of this carbon is to shift it by −0.23 eV. Although smaller in magnitude than the corresponding shift in propene relative to ethene (−0.42 eV) or the shift for the C3 carbon in 1,3-pentadiene (−0.37 eV), it is significant. This shift for C1 can be seen to arise primarily from the effect on the initial-state charge distribution of the resonance illustrated in **3c**. To a lesser extent, there is also a possible contribution from charge redistribution of the type illustrated in **6b**.

A similar effect of the methyl group is seen in the comparisons of activation energies (Figure 3) and proton affinities (Figure 4) of 1,3-butadiene and 1,3-pentadiene. The effect of the methyl group added at C4 is to increase the reactivity and proton affinity at C1.

The picture of the influence of the methyl group when it is attached to ethene to form propene or to 1,3-butadiene to form 1,3-pentadiene is that there is resonance transfer of electrons from the methyl group to the β carbon (via resonances **1c** and **3b**). In the conjugated system, there is then additional transfer to the δ carbon (**3c**). This charge redistribution leads to a lowering of the carbon 1s ionization energy of these carbons. When a carbon 1s electron is ionized from one of these positions, there is charge redistribution via resonances **2bc**, **5b**, and **6b**, but this effect is smaller than that of the initial-state charge distribution.

We see that there are excellent correlations between core-ionization energies, proton affinities, and activation energies for electrophilic addition. That such correlations exist among electrical effects is not new. For instance, Benson and Bose[33] found linear correlations between the activation energies and such electrical parameters as the molar refraction and the first ionization potential of the molecule. These relationships are similar to linear-free energy relationships, and, to first approximation can be described in the same way. Thus, for each type of electrical effect, core-ionization energy, proton affinity, activation energy, we can assign a parameter, ρ, that describes how the energy for the process responds to an electrical influence. Then for each site in a molecule we can assign a parameter, σ, that describes the intensity of electrical effect at this site. The resultant effect on the energy is then equal to $\sigma\rho$. Within this framework, the energies associated with one kind of electrical effect will be proportional to the energies associated with any other electrical effect.

As one well knows, this picture is much too simple. Electrical effects cannot be described by a single variable, and typical discussions of this problem involve three[34] or four[35] variables. Here there are effects due to at least three different variables: electronegativity, polarizibility, and resonance. We can see the influence, for instance, of polarizibility in Figures 3 and 4. In Figure 3 (activation energy versus ionization energy), the correlation for 1,3-butadiene is displaced from the correlation for 1,3-pentadiene, whereas in Figure 4 all points fall on a single line. The difference may be in how the probe interacts with the polarizibility of the molecule. In Figure 4 the probes, a localized electron removed or a localized proton added, are both point charges; in this case, the interaction energy between the probe and the polarizible surroundings goes as $1/r^4$, where r is the distance between the point charge and a point in the surroundings. In Figure 3, the probe, HCl, might better be described as a dipole, and for a dipole the interaction energy scales as $1/r^6$ rather than $1/r^4$, with the consequence that the point charge is affected by a larger volume than is the dipole. Thus, polarization will reduce the ionization energy more than it reduces the activation energy. Qualitatively, this is the effect seen in Figure 3.

Despite this reservation, the correlations suggest that core-ionization energies, proton affinities, and activation energies are governed by similar influences. For the methyl group in propene and 1,3-pentadiene, we see that its effect on core-ionization energies is mostly due to its effect on the initial-state charge distribution. The portion of its effect that can be attributed to charge redistribution via resonance in the ionized state is relatively small. It is not unreasonable to extend this view to its effect on proton affinities and activation energy, and to conclude that the influence of the methyl group on these energies also arises from its effect on the ground-state charge distribution.

Traditionally orientation and reactivity for electrophilic addition reactions have been explained by considering the stability of the carbocation formed in the transition state. In this view, attack takes place preferentially at the end carbons of butadiene, C1 and C4, because at these positions the cation can be stabilized by resonance delocalization of the positive charge. In 1,3-pentadiene attack at C1 is preferred over attack at C4 because the resulting carbocation forms a resonance hybrid of two contributing secondary cations, whereas attack at C4 gives a hybrid of one secondary and one primary cation.[19] Thus, in the language of electron spectroscopy, the reactivity is determined by the final-state relaxation energy.

The analysis of the ionization energies shows that this picture may be too simple. Inspection of ΔV and ΔR for butadiene in Table 2 shows that these contribute about equally to the ionization difference between C1/C4 and C2/C3. Specifically, the ionization energy difference is 0.63 eV, of which 0.27 eV arises from ΔV and 0.36 eV from ΔR. Since the activation energies and ionization energies correlate well with one another, it is reasonable to suppose that the activation energies are influenced in the same way, and, accordingly, that the initial-state charge distribution plays a significant role in determining the regioselectivity of electrophilic addition in 1,3-butadiene.

In 1,3-pentadiene, C1 and C4 are no longer equivalent and C1 is the preferred site for electrophilic attack as well as the site with the lowest ionization energy. Inspection of the values given in Table 2 shows that the difference of 0.33 eV in ionization energy between these two sites is almost entirely due to ΔV (0.31 eV) and only negligibly to ΔR (0.02 eV). It is reasonable to suppose that the relative activation energies are determined in the same way, and, therefore, depend primarily on the initial-state charge distributions rather than on the ability of the carbocations to delocalize charge.

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Supporting Information Available: Details of the basis sets and diffuse wave functions. Numerical results for calculated ionization energies, activation energies, and proton affinities. This material is available free of charge via the Internet at http://pubs.acs.org.

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