

Markovnikov addition to alkenes. A different view from core-electron spectroscopy and theory

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Carbon 1s ionization energies for ethene, propene and 2-methylpropene have been measured in the gas phase at high resolution using synchrotron radiation and analysed by means of *ab initio* calculations. For the first time, resolution is good enough to assign ionization energies to the inequivalent carbons in propene and 2-methylpropene. A linear correlation is found between the ionization energies and activation energies for addition of the electrophiles HF, HCl, HBr and HI to these molecules. The correlation shows that both reactivity and regioselectivity are quantitatively related to core-ionization energies. Theoretical analysis of the core-ionization energies shows that the differences between ionization energies for the doubly bonded carbons are due to the charge distribution in the unionized molecule. Theoretical analysis of the transition state for addition of HCl to propene and 2-methylpropene indicates that a significant portion of the difference between Markovnikov and anti-Markovnikov addition is also due to the charge distribution in the initial state and not to different ability of the molecules to delocalize the added charge in the transition state. The increase in reactivity with the number of methyl groups is also strongly influenced by the initial-state charge distribution.

Introduction

Electrophilic reactions to alkenes are of fundamental interest in synthetic and mechanistic organic chemistry and of great importance in many industrial processes. The reactions are characterized by two important properties. These are the effects of substituents on reactivity and on orientation. With respect to reactivity, electron-withdrawing substituents decrease the reactivity and electron-donating ones increase it. With respect to orientation, addition often follows Markovnikov's rule, which, in its simplest form, is that hydrogen adds to the carbon with the most hydrogens.¹

A simple illustration of these properties is found in the series ethene, propene and 2-methylpropene, where the substituents can be regarded to be hydrogen, methyl and dimethyl. The kinetics of addition of the electrophiles HCl, HBr and HI to these molecules have been discussed by Benson and Bose.² As an example of the effect of the substituent on reactivity, their results show that the rate constants for the addition of HI to these compounds are in the ratios 1:90:7000 for ethene, propene and 2-methylpropene, respectively, at 600 K.[†] Also, their results show that the addition of HI to propene follows Markovnikov's rule; the yield of 2-iodopropane is *ca.* 1000 times as great as the yield of 1-iodopropane.²

A simple picture for this addition process has been commonly used to account for these results.^{4,5,6a,7a,8a,9a,10a} The slow step is considered to be the addition of a proton to the reacting molecule to form a positive intermediate, or carbocation. This step is followed rapidly by the addition of X[−] to form the product. The rate and regioselectivity of the reaction are determined by the energies of the possible transition states and hence by the stability of the relevant carbocations.

Whereas there is evidence for the existence of positively charged transition states in solution, this picture is an oversimplification, especially when applied to gas-phase reactions. For instance, for the reaction of HI with propene, the measured activation energy is 23.4 kcal mol^{−1} (1 cal = 4.184 J),³ whereas

the energy of the carbocation and separated anion is 134 kcal mol^{−1} relative to the reactants.[‡] It is apparent that the transition state is at a much lower energy than that of the isolated carbocation. It, therefore, cannot be an isolated carbocation, but must involve a closely associated ion pair, as has been emphasized by Benson and Bose.²

Nevertheless, the picture of the transition state as a carbocation is widely used and serves well to rationalize the observations concerning electrophilic reactions. In fact, Markovnikov's rule has been formulated in such terms: the reaction proceeds so as to form the most stable carbocation. Although the transition state may not be a carbocation, it is considered to resemble one closely enough that the factors that influence the energy of the carbocation influence the energy of the transition state in the same way, in keeping with Hammond's postulate.^{6b}

The understanding of electrophilic addition reactions and of Markovnikov's rule has therefore centred around the stability of carbocations. The facts are simple: the greater the number of alkyl groups attached to the carbon with the positive charge, the more stable the carbocation. Although many different explanations are given for this result,[§] they all seem to concur that the major effect is the ability of the substituent to delocalize the positive charge that is added when the carbocation is formed.

This emphasis on the ability of the charged molecule to delocalize its charge recurs in explanations of many properties of organic molecules—acidities, basicities, substituent effects,

[‡] Thermochemical energies are taken from standard sources and from Benson and Bose,² except for those that relate to the propyl cations, which are taken from ref. 11.

[§] Examples of different explanations are: March, ref. 6c: 'The stability order [of carbocations] can be explained by hyperconjugation and by the field effect.' Morrison and Boyd, ref. 7b: 'It may be an inductive effect; it may be a resonance effect.' Streitwieser, Heathcock and Kosower, ref. 8b: 'The order of the stability of carbocations is in large part attributed to the greater polarizability of alkyl groups compared to hydrogen.' Solomons, ref. 9b: 'Alkyl groups attached to the positive carbon atom of a carbocation delocalize the positive charge.' McMurry, ref. 10b: 'Part of the answer has to do with hyperconjugation, and part has to do with inductive effects.'

[†] Calculated from Arrhenius parameters given in ref. 3.

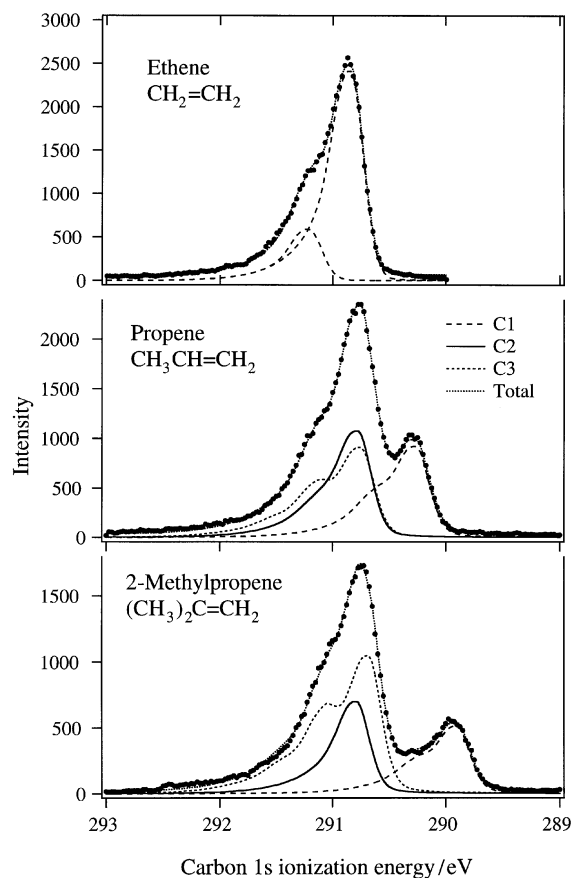


Fig. 1 Carbon 1s photoelectron spectra of ethene, propene and 2-methylpropene. The lines through the points show the results of least-squares fits to the data. The spectra of propene and 2-methylpropene were deconvoluted using results from methane and ethene to constrain the vibrational profiles.

and, as here, reactivities.^{12,13c-e,14} However, a number of studies have shown that, for many such systems, the charge distribution of the initial molecule plays a more important role in determining these properties than does the ability of the final state[¶] to disperse charge.

Here we use both theoretical calculations and relationships between activation energies for addition reactions and measured carbon core-ionization energies to investigate the addition of the electrophiles HF, HCl, HBr and HI to ethene, propene and 2-methylpropene. From these investigations we conclude that the initial-state charge distribution, which is the major factor in determining the differences in ionization energies, also must play a significant role in determining the relative activation energies for addition of HX to these alkenes or to the two different sites in propene and 2-methylpropene. This result is in accord with previous results on acidity¹² and on substituent effects in thiophene,^{13e} but not with the usual explanations of regioselectivity.

Results and discussion

Core-ionization energies and chemical properties

Our analysis begins with a consideration of carbon 1s core-ionization energies. At first glance it may not be apparent that the energies to form carbocations and the energies to remove core-electrons should be related to one another. However, a carbocation can be formed by the addition of a proton (positive charge) to a selected site in the molecule. Similarly, core-ionization, by removing an electron from an inner shell, leaves an excess positive charge at a selected site. Although the ener-

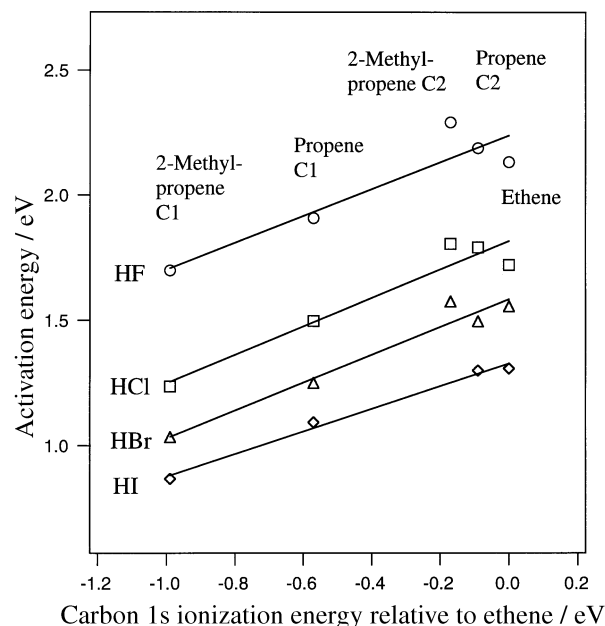


Fig. 2 Correlation between carbon 1s ionization energies and activation energies for addition of HF, HCl, HBr and HI to ethene, propene and 2-methylpropene

gies for these two processes are quite different, we can expect that the chemical factors that influence these two properties will be the same and there is a considerable body of experimental data and theoretical results that supports this view.^{12,13,15-18}

We are concerned here with electrophilic addition to ethene, propene and 2-methylpropene, and therefore with carbon 1s core-ionization energies for these molecules. Recent advances in experimental technique have made it possible to determine the small differences in ionization energies for the inequivalent, but similar carbon atoms in these molecules. These have been measured in the gas phase by high-resolution photoelectron spectroscopy at the Swedish National Synchrotron Laboratory (MAX)¹⁹ and are reported elsewhere.²⁰ Photoelectron spectra for ethene, propene and 2-methylpropene are presented in Fig. 1. The points show the experimental data and the lines represent least-squares fits to the data. The small peak seen in the ethene spectrum is due to vibrational excitation during core-ionization. The spectra of propene and 2-methylpropene were deconvoluted using peak shapes derived from the ethene spectrum and from similar measurements of methane. The peak shapes include the effects of vibrational excitation during core-ionization (predominantly CH stretching modes), instrumental resolution and lifetime broadening. The details of the fitting procedure are discussed elsewhere.²⁰ In summary, the vibrational structure that is apparent in each peak is not a free parameter in these fits, but is derived from the spectra for methane and ethene, using an appropriate theoretical model.²⁰ The areas under the peaks are constrained by the stoichiometry of the molecule. The assignment of the three groups to the inequivalent carbons in propene is based on theoretical calculations, described below, and on comparison with similar measurements on three monochloropropene isomers.^{||} For 2-methylpropene, one of the three peaks is found to have intensity twice that of the other two. This is assigned to the two equivalent methyl carbons, and the others are assigned on the basis of theory. Fig. 1 shows clearly that the effect of methyl substitution is to shift the energy of the terminal unsaturated carbon atom towards lower ionization energies. The measured shifts, relative to ethene, are summarized in Table 1. C1 denotes the

^{||} In each isomeric spectrum, one of the ionization energies is shifted to higher values by the attached chlorine, while the others are nearly unchanged.

[¶] Or transition state, in case of reactions.

Table 1 Experimental and calculated shifts in C 1s ionization energies, ΔI , initial-state potentials, ΔV , and final-state relaxation energies, ΔR , for alkenes relative to ethene^a (1 eV = 23.06 kcal mol⁻¹)

Molecule	Atom ^b	$\Delta I_{\text{expt}}/\text{eV}$	$\Delta I_{\text{calc}}/\text{eV}$	$\Delta V_{\text{calc}}/\text{eV}^c$	$\Delta R_{\text{calc}}/\text{eV}^d$
Ethene	C1	0.0	0.0	0.0	0.0
Propene	C1	-0.57	-0.59	-0.37	0.22
	C2	-0.09	-0.14	0.10	0.24
2-Methylpropene	C1	-0.99	-1.06	-0.65	0.41
	C2	-0.17	-0.27	0.21	0.48

^a $\Delta I = \Delta V - \Delta R$. ^b C1 is the terminal atom doubly bonded to C2. ^c Potential due to the charge distribution in the initial state. ^d Relaxation due to redistribution of electrons in the ionized state.

terminal unsaturated carbon, C2 the central unsaturated carbon and C3 the terminal saturated carbon(s).

As noted above, the transition state for electrophilic addition is thought to be similar to the carbocation that would be formed by addition of a proton to the appropriate atom in the molecule. The energy for this step, the activation energy, should be closely related to the proton affinity. As has been noted, the removal of a core electron also adds a positive charge at a selected atom. The energy for this process should also be related to the proton affinity. It is not surprising therefore that there exist excellent correlations between core-ionization energies and proton affinities.¹⁵ Particularly noteworthy is a correlation given by Brown and Tse,^{15j} who have plotted proton affinities for a large number and variety of oxygen-containing compounds against the oxygen 1s ionization energy of the appropriate oxygen atom. The data fit well with a straight line that has a slope of *ca.* 0.7. It is apparent that the same chemical effects influence the proton affinities as influence the core-ionization energies, but that the sensitivity of the proton affinities to these effects is less than the sensitivity of the core-ionization energies. Good correlations are also found between core-ionization energies and electronic substituent parameters of the Hammett type.¹⁶

Here we are concerned with addition of HX to ethene, propene and 2-methylpropene. There is a considerable body of relevant data available and from this we have obtained a set of activation energies for addition of HF, HCl, HBr and HI. These are obtained for Markovnikov addition in all cases and for anti-Markovnikov addition for all except addition of HI to 2-methylpropene. A discussion of our choice of activation energies is given in the Appendix and the values are presented in Table 2.

Plots of these activation energies *versus* the measured core-ionization energies are shown in Fig. 2. We see that there is a good correlation between these two quantities in the expected direction. The straight lines are least-squares fits to the points. The slopes of the lines are 0.55 for HF, 0.57 for HCl, 0.56 for HBr and 0.45 for HI. Regarding the slopes, we note the following. First, they are of order 1, in accord with our belief that the energies needed to form the carbocation and the transition state are influenced by the same factors and nearly to the same extent as are the energies to remove carbon 1s electrons. Second, in more detail, they are all somewhat less than 1, in keeping with our experience that proton affinities are less sensitive to these chemical effects than are the core-ionization energies. Third, the slopes are nearly the same as we go from HF to HI, suggesting little specific interaction between the halogen and the alkene. The halogen appears to play only the role of a carrier of the proton. The differences in positions of the three correlation lines—highest for HF and lowest for HI—are presumably related to the differences in bond dissociation energy for the hydrogen halides. Both the homolytic and heterolytic dissociation energies are greatest for HF and least for HI.

We note also that the points for the anti-Markovnikov addition at C2 fall on the same correlations with the points for addition at C1. This result further strengthens our belief that the transition-state energies and the core-ionization energies

Table 2 Experimental activation energies for addition of HF, HCl, HBr and HI to alkenes (kcal mol⁻¹)^a

Molecule	Atom ^{b,c}	HF	HCl	HBr	HI
Ethene	C1	49.1	39.7	35.9	30.2
Propene	C1	44.0	34.5	28.8	25.2
	C2	50.5	41.3	34.5	30.0
2-Methylpropene	C1	39.2	28.5	23.9	20.0
	C2	52.8	41.7	36.3	

^a Obtained from the corresponding unimolecular elimination reactions as explained in the Appendix. ^b Site of H addition. ^c C1 is the terminal atom doubly bonded to C2.

reflect the same chemical properties. It is, however, to be noted that the three points for addition of HF and HCl at C2 appear to be inversely correlated with the core-ionization energies. This inverse correlation is also apparent in *ab initio* calculations of these activation energies for the HCl addition, discussed in a subsequent section.

The factors that determine the energies

There are two factors that determine the energy involved in adding or removing a charge from a specific site on a molecule. One of these is the potential at the site; the charge must be either removed from or placed into this potential. The other is the relaxation of the other charges—electrons and nuclei—in response to the effect of the added charge.

For core electrons the appropriate relationship for the change in core-ionization energy, I , for the same element in two different sites is^{14,21} given by eqn. (1), where V is the potential energy

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

of a unit positive charge at the site of interest; it depends on the charge distribution in the neutral molecule. R represents the effect of relaxation of the other charges; it depends on the ability of the ion to delocalize the added charge *via* resonance or polarization. Related expressions have been derived for removal of protons (acidity)^{12,15e} and for addition of protons (basicity).^{15a,b,e} If we are concerned with such thermodynamic quantities as acidity, basicity or ionization energy, then R is a property of the final state. For kinetic properties such as activation energies, R refers to the transition state.

The absolute values of V depend on what process we are concerned with. Relative values (*i.e.* ΔV and ΔR), reflecting substituent effects, can be expected to be similar. This expectation is supported by theoretical calculations.¹²

Values of ΔV and ΔR have been determined experimentally from comparisons of core-ionization energies with gas-phase acidities^{12,15h,17} and from comparisons of core-ionization energies with Auger kinetic energies.^{13,18} They can also be calculated theoretically. Where both experimental and theoretical results are available, there is usually good agreement between the two methods.^{12,13h,d,e,18b} We will use the results of theoretical calculations (described below), noting that they reproduce the experimental ionization energies well and may, therefore, be expected to reproduce also the values of ΔV and ΔR .

The usual textbook treatment of such properties as acidity, basicity, substituent effects and activation energies places major emphasis on the effects of relaxation—the ability of the charged state to delocalize the charge—and little emphasis on the initial state—the potential produced by the ground-state charge distribution at the site to which the charge is to be added. However, numerous analyses that have been designed to isolate the relative importance of ΔV and ΔR show that some important chemical properties are due almost exclusively to the initial-state potential and very little to the final-state relaxation.^{12,13c-e,18} Other types of information support this view.²²

It is important therefore to analyse the data presented here to assess the contributions of ΔV and ΔR to the ionization energies and to the transition-state energies for addition of HX to these alkenes. In the following two sections we use electronic structure theory for this, first for the core-ionization energies and then for the activation energies.

Understanding the core-ionization energies

Ab initio calculations of the energies of the neutral and core-ionized molecules (at the optimized geometry of the neutral) were done at the restricted Hartree–Fock level with the MOLECULE-ALCHEMY programs** using the D95(d,p) basis set. This is the Dunning–Huzinaga double-zeta basis²³ augmented with d and p polarization functions on C ($\zeta = 0.75$) and H ($\zeta = 1.00$). The hole-state calculations for the core-ionized molecules were performed within the restricted open-shell Hartree–Fock approximation using the maximum overlap criterion.²⁴

Calculated vertical core-ionization energies were obtained as the difference between the total energies of the final core-hole state and the initial closed-shell state. These so-called Δ SCF ionization energies take into account the redistribution of electrons after ionization. The potential at the nuclei in the initial state was taken as the negative of the orbital energy.^{††} The relaxation energy was then obtained as the difference between this Koopmans' theorem energy and the calculated ionization energy.

Table 1 gives a comparison of the calculated and experimental core-ionization energies for propene and 2-methylpropene, relative to those for ethene. For propene the agreement between experiment and theory is good. For 2-methylpropene, it is less good, but the theory reproduces the essential features of the experimental results. Also included in Table 1 are the theoretical values of ΔV and ΔR , which are our principal concern here.

We consider first the decrease in ionization energy for C1 as we move from ethene to propene to 2-methylpropene. Inspection of Table 1 shows that *ca.* 60% of the change in ionization energy (ΔI) is due to a change in the initial-state charge distribution, reflected in ΔV . Less than 40% of the change is due to delocalization of the added charge in the ionic state, reflected in ΔR . This indicates an important role for the charge distribution in the neutral molecule in determining the ability of the molecule to accept positive charge at this site.

Turning now to the difference in ionization energy between C1 and C2, 0.48 for propene and 0.82 eV for 2-methylpropene, we see a more striking effect. From the theoretical numbers, we see that this is almost entirely due to ΔV —the initial state effect—and hardly at all to different abilities of the different transition states to delocalize the charge— ΔR .

Summarizing, we have seen that there are linear correlations

** The MOLECULE-ALCHEMY program package incorporates the MOLECULE integrals program written by J. Almlöf and the ALCHEMY programs written by P. Bagus, B. Liu, M. Yoshimine, A. D. McLean and modified by P. Bagus and U. Wahlgren.

†† The potential energies are not actually equal to the orbital energies. However, the shifts in potential energies, which are of more interest than absolute values, have been found to be very nearly equal to the shifts in Koopmans' theorem energies, see ref. 25.

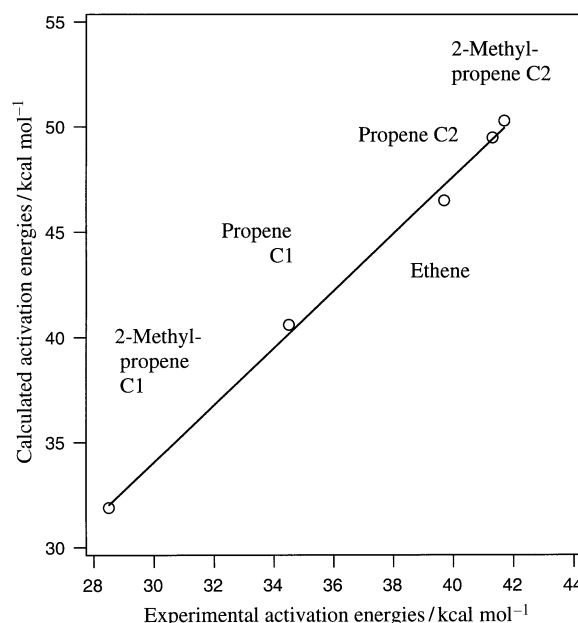


Fig. 3 Correlation between calculated and experimental activation energies for the HCl addition to ethene, propene and 2-methylpropene

between core-ionization energies and activation energies for electrophilic addition. The theoretical calculations show that the difference between the core-ionization energies is primarily due to the charge distribution in the initial state of the molecule. These observations lead us to the hypothesis that the difference in transition-state energies arises in the same way. In the following section we use theoretical calculations to investigate this hypothesis.

Understanding the activation energies

Ab initio calculations of activation energies for the HCl addition to the three alkenes have been done at the SCF-HF level. Transition-state geometries were located from analytical gradients using the GAMESS set of programs.²⁶ Hydrogen, carbon and chlorine were described by 6-31(d,p) basis sets.²⁷ Details of the calculations of geometry, saddle point localizations, reaction pathways and energy evaluations are reported elsewhere.²⁸ The theoretical activation energies, corrected for zero-point vibration, are compared with the experimental values in Table 3. For a visual comparison of experiment and theory, we have plotted the calculated activation energies *versus* the experimental values in Fig. 3.

It is apparent from Fig. 3 that the theory correctly predicts the data trend. In detail, however, the slope of the line in Fig. 3 is 1.36, indicating that the theoretical calculations overestimate both absolute and relative magnitudes of the activation energies.^{‡‡} The overall agreement gives confidence that the theory is dealing correctly with the major features of the transition state and that we can use these calculations to provide insight into the reason for the differences in activation energy for the two sites in propene and 2-methylpropene. The lack of detailed agreement indicates that we should be cautious in drawing quantitative conclusions from these results.

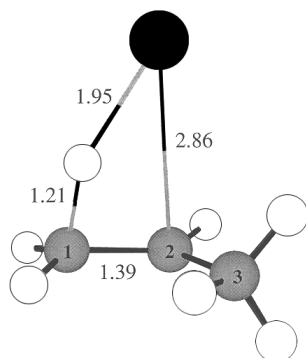
Fig. 4 shows the configuration of the transition state for addition to C1 of propene (Markovnikov addition). The configuration for addition to C2 is similar, except that the H atom is close to C2 rather than to C1. We note that the HCl bond (1.95 Å) in the transition state is much longer than it is in the free molecule (1.26 Å). The Mulliken charge for the chlorine atom in the transition state is -0.76 compared with -0.21 in the free

‡‡ Extensive calculations on the HCl addition to ethene^{28c} indicate that high-level CI calculations combined with large basis sets is necessary to improve the calculated activation energies beyond the HF results.

Table 3 Experimental, E_{expt} , and theoretical, E_{calc} , activation energies for addition of HCl to alkenes, and comparison with difference in potential energy, ΔV .

Molecule	Atom ^a	$E_{\text{expt}}/\text{kcal mol}^{-1b}$	$\Delta E_{\text{expt}}/\text{kcal mol}^{-1c}$	$E_{\text{calc}}/\text{kcal mol}^{-1d}$	$\Delta E_{\text{calc}}/\text{kcal mol}^{-1e}$	$\Delta V/\text{kcal mol}^{-1ce}$
Ethene	C1	39.7	—	46.5	—	—
Propene	C1	34.5	0.0	40.6	0.0	0.0
	C2	41.3	6.8	49.5	8.9	11.1
2-Methylpropene	C1	28.5	0.0	31.9	0.0	0.0
	C2	41.7	13.2	50.3	18.4	20.1

^a C1 is the terminal atom doubly bonded to C2. ^b Obtained as described in the Appendix. ^c Difference in energy between C2 and C1. ^d Hartree–Fock calculation corrected for zero-point energies. ^e Potential energy of a proton at distances corresponding to transition-state geometries.

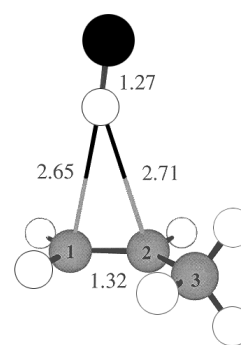
**Fig. 4** Calculated configuration of the transition state for addition of HCl to propene in the Markovnikov position

molecule. These results are consistent with the customary view that the transition state is very similar to a carbocation with an associated negative ion.

We have seen that the difference in core-ionization-energies between C1 and C2 is due primarily to the difference in electrostatic potentials at the site of the core electrons. We now consider the electrostatic potential calculated for the reactant alkene at the site that corresponds to the H atom of HCl in the activated complex. Looking first at the potentials around the propene molecule, we find that the potential at the site for addition to C1 is 0.48 V more negative than it is at the site for addition of C2. This translates into a difference of 11.1 kcal mol⁻¹ in the energy of a proton at these two sites, significantly more than the difference in activation energies. For 2-methylpropene this difference is 20.1 kcal mol⁻¹, which is also greater than the calculated difference in activation energies. The actual difference in activation energy that can be attributed to the difference in potential is somewhat less than this because the proton still carries a share of the electrons from the HCl molecule. One cannot decompose the contributions to the activation energy further than this, but it is apparent that variation in potential, arising from the charge distribution in propene, must play an important role in determining the relative stability of the two transition states.

The effect of the polarity of propene is apparent even at relatively large distances from the molecule. The transition-state calculations show the existence of a weakly bound complex between HCl and ethene and propene at a CH distance of *ca.* 2.7 Å. This is illustrated for propene in Fig. 5. In this complex the bond lengths for HCl and the alkene molecules are almost the same as for the isolated molecules. For ethene, the HCl molecule is located symmetrically, whereas for propene it is located with the proton pointed slightly toward C1 in response to the potential which becomes more negative as we go in the direction from C2 to C1 even at this distance from the carbon-carbon axis.

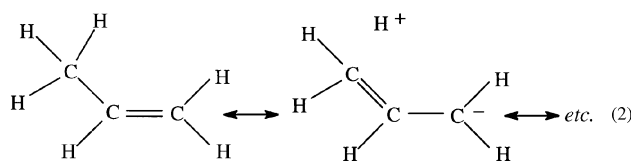
Additional evidence for the polar nature of propene and 2-methylpropene is found in the dipole moments of the species involved, since these are a measure of the charge distribution. The relevant values are 0.366 D for propene, compared with 0.084 D for propane and 0.50 D for 2-methylpropene, com-

**Fig. 5** Configuration of weakly bound complex between propene and HCl, showing orientation of the HCl towards Markovnikov addition

pared with 0.132 D for 2-methylpropane.²⁹ It is apparent that the unsaturated molecules are considerably more polar than the corresponding saturated ones.

Theoretical calculation of these moments using the D95 (d, p) basis set²³ gives 0.42 D for propene and 0.62 D for 2-methylpropene, in reasonable agreement with the experimental values. For propene, the calculation shows that the dipole moment is nearly parallel to a line joining the two terminal carbons. The negative end is at the unsaturated terminal carbon, C1, and the positive end is at the methyl carbon, C3. For 2-methylpropene, the dipole lies along the double bond (because of symmetry) with its negative end towards the unsaturated carbon.

These results suggest that electrons are transferred from the methyl end of the molecule to the unsaturated end. Hyperconjugation provides a mechanism for this process as illustrated in



eqn. (2). Thus it appears reasonable to believe that C1 is, in the initial state, more negative than C2, and, therefore, inherently more receptive to electrophilic attack.

Conclusions

The important factor that determines the reactivity and regioselectivity in the reactions considered here is the energy of the transition state relative to the energy of the separated reactants, that is, the activation energy. The fastest reactions are those with the lowest activation energies or, in equivalent terms, the most stable transition states. The simplified view of the transition state is that it is similar to a carbocation with an associated anion and that the same factors that determine the stability of carbocations determine the stability of these transition states.

As noted in the introduction, the relative stability of different carbocations is usually rationalized in terms of the ability of

the cation to delocalize the positive charge. In this view, the energy difference arises from differential response of the valence electrons to the additional charge. However, the theoretical calculations, as well as the experimental dipole moments, show that even in the neutral molecule there is significant polarization of charge. This produces a potential distribution that has a significant influence on the differences in the energy associated with protonation of different sites of the alkenes. Thus, the relative stability of the carbocations and the transition states is at least partly a result of the charge distribution in the neutral molecule and not entirely due to delocalization that takes place after addition of the positive charge.

The conclusions reached here are based on the theoretical calculations of the configurations of the transition states and the additional calculations that give the potentials at the sites of the proton in the transition states. However, it is to be noted that these conclusions were already apparent in the analysis of the core-ionization energies, which, as we have seen, reflect the activation energies. The difference in ionization energies between C1 and C2 is entirely due to differences in potential at the two carbon nuclei. In addition the differences in potential at the nuclei are very similar to the differences in potential at the site of the proton in the transition state.

We have so far considered the difference between Markovnikov and anti-Markovnikov addition—the regioselectivity of the addition. We can now use the core-ionization energies and the associated theoretical calculations to provide some insight into the reactivity differences between ethene, propene and 2-methylpropene. As has been noted above, the theoretical results for the core-ionization energies (Table 1) show that *ca.* 60% of the shift in core-ionization energy between ethene and C1 in propene is due to a change in the initial-state charge distribution, reflected in ΔV . Less than 40% is due to delocalization in the ionic state, reflected in ΔR . If we accept the view that core-ionization energies and activation energies are influenced in a similar way by similar factors, as indicated by the correlation shown in Fig. 2, we conclude that a significant proportion of the difference in reactivity between ethene and propene is due to differences in the initial-state charge distribution.

With high-resolution core-electron spectroscopy, we can measure the relative ability of a specific atom in a molecule to accept charge. These energies are seen to correlate both with reactivities (in terms of site-specific activation energies) and with thermodynamic quantities (such as site-specific energies of protonation). The recent advances in technique for inner-shell spectroscopy, which make it possible to see the differences between carbon atoms in hydrocarbons, provide promise of useful applications of this technique to problems in physical organic chemistry.

Appendix

Experimental activation energies

We are concerned with addition of HF, HCl, HBr and HI to ethene, propene and 2-methylpropene. Of these reactions only HI addition has been studied directly under ordinary laboratory conditions.^{2,3} Most of the knowledge of activation energies for the bimolecular addition reactions has come from the inverse process, *i.e.* the unimolecular elimination reactions of alkyl halides.^{30,31} From the results of these reactions, Arrhenius parameters for the addition reactions may be calculated from available thermodynamic data.² Because of considerable spread in the experimental results, we have used the elimination activation energies as recommended by Benson and O'Neal in their NBS compilation,³² where the energies were evaluated on the basis of calculated *A* factors from absolute rate theory.^{32,33} The elimination barriers for the fluoro compounds and for 1-iodopropane were not considered by Benson and O'Neal. The value for the latter was obtained from Yamada^{31,34} and corrected as described in ref. 33. Elimination activation energies for

the fluoro compounds were taken from ref. 35. The *A* factors for these reactions are close to the recommended values³³ and the energies were used as reported.

Activation energies for the addition reactions, E_{add} , were calculated from the equation $E_{\text{add}} = E_{\text{elim}} + \Delta H_{\text{rxn}} + RT$. The heat of reaction, ΔH_{rxn} , was generally obtained from experimental ΔH_f° values at 298 K³⁶ and corrected to the mean experimental temperature using constant heat capacities, C_p , as reported at 298 K.³⁷ For fluoroethane and 2-fluoro-2-methylpropane ΔH_f° values were obtained from ref. 37 and 38, respectively. ΔH_f° for 1-fluoro- and 1-bromo-2-methylpropane was estimated from the 1-chloro-2-methylpropane value using shifts for 1-fluoro- and 1-bromo-propane relative to 1-chloropropane.³⁶ The experimental uncertainty of the ΔH_f° values is generally less than 1 kcal mol⁻¹, except for 1-chloro-2-methylpropane where it is reported to be *ca.* 2 kcal mol⁻¹.³⁶

The C_p value for 2-fluoro-2-methylpropane was estimated from the 1-chloro-2-methylpropane value using the shift between 2-fluoro- and 2-chloro-propane.³⁷ Similarly, C_p values for 1-fluoro- and 1-bromo-2-methylpropane were estimated from 1-chloro-2-methylpropane using shifts for 1-fluoro and 1-bromopropane relative to 1-chloropropane.³⁷

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