Revisiting Markovnikov Addition to Alkenes via Molecular Electrostatic Potential

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Molecular electrostatic potentials (MESP) surrounding the π-region of several substituted ethylenes (CH_2CHR) have been characterized by locating the most negative-valued point (V_{min}) in that region. The substituents have been classified as electron donating and withdrawing on the basis of the increase or decrease in the negative character of V_{min} in these systems as compared to ethylene. The values of V_{min} show a good linear correlation with the Hammett σ_p constants, suggesting that the substituent electronic effects in substituted ethylenes and substituted benzenes are basically similar. With electron-donating substituents, the position of MESP minimum is closer to the unsubstituted carbon facilitating the π-complex formation of it with HCl at this site. Such a regiospecific π-complex formation is found to favor the formation of Markovnikov-type transition state for the addition of HCl to CH_2CHR. For the electron-withdrawing substituents, the V_{min} location is almost equidistant and farther from the ethylenic carbon atoms. This and the less negative V_{min} values account for the less regiospecific $CH_2CHR\cdots HCl$ π-complexes as well as the transition states for the HCl addition to CH_2CHR when R is an electron-withdrawing group. The interaction energy (E_{int}) between CH_2CHR and HCl for the formation of the $CH_2CHR\cdots HCl$ π-complex shows a good linear correlation with the corresponding V_{min} value.

Introduction

It is well-known that the addition of a molecule H−X to an unsymmetric olefin CH_2CHR often occurs regiospecifically leading to the predominant formation of CH_3CHRX. This was discovered by Markovnikov in 1870 and later came to be known as Markovnikov's rule of addition,[1] which has been considered as one of the most important developments toward the modern views on organic reaction mechanisms. A typical example of Markovnikov reaction is the addition of hydrogen iodide to propene,[2] which gives 2-iodopropane as the major product and 1-iodopropane as the minor one. The ratio of 2-iodopropane and 1-iodoprapane in this reaction is found to be 1000:1. The electronic effect of the substituent R in the olefin usually termed, as the substituent effect is an important factor governing the rate of the reaction. For instance, the rate constants for the addition of HI to ethene, propene, and 2-methylpropene are in the ratio 1:90:7000 as reported by Benson and Bose.[2−4]

There are numerous simple illustrations of Markovnikov addition reactions in standard organic textbooks,[5] which often describe the mechanism that is centered on the stability of a carbocation generated by the addition of a proton to the olefin. Such ionic reaction mechanism normally holds good for ionizing polar solvents.[6] However, in the case of hydrogen bromide addition to alkenes, a free radical chain mechanism generally operates, resulting in the formation of anti-Markovnikov products.[7] In certain addition reactions, especially in the gas phase, bimolecular and trimolecular mechanisms have been suggested.[2,3,8,9] For example, the addition of hydrogen halides and other polar reagents to olefins is reported to be first order in the olefin and approximately third order in hydrogen halide, which contradicts a carbocation-based mechanism. In such reactions, the higher order in hydrogen halide was explained on the basis of the catalytic effect offered by one or more hydrogen halide molecules to the alkene−hydrogen halide complexes via hydrogen bonds.[10] Although the carbocation-based mechanism is generally acceptable for the hydrogen halide addition reactions to alkenes, the energetic aspects do

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not favor such a mechanism in the gas phase. Specifically, the combined system of the carbocation and separated anion is generally higher in energy relative to the reactants.[11a] Benson and Bose[2] from experimental studies proposed a very closely associated ion pair as the most likely transition state for the gas-phase addition reactions. Fahey and McPherson[11b] have even reported such a mechanism for the hydrochlorination of the *tert*-butylethylene and styrene in acetic acid.

There are several theoretical studies on the addition of hydrogen halides to ethylene.[12] These studies as well as the experimental works showed the formation of weakly bound T-shaped ethylene−hydrogen halide complex during the reaction.[13] This complex was further explored for the potential energy characteristics of the addition reactions.[14] Frontier molecular orbital theory is sometimes used for explaining the regioselectivities of addition reactions to olefins.[15] A recent study of Markovnikov addition by Sæthre, Thomas, and Svensson[16] showed a correlation of both regiospecificity and reactivity to core-ionization energies of the olefin carbon atoms. They also noticed that a significant difference between Markovnikov and anti-Markovnikov addition is due to the charge distribution in the initial state of the olefin and not to different ability of the molecules to delocalize the added charge in the transition state. In a more recent paper, Hessley has stressed upon the importance of the electrostatic potential as well as the electron density distribution in molecules for the better understanding and interpretation of the regiospecificity of Markovnikov reactions.[17]

A scalar property of a molecule that can be determined experimentally and used widely for understanding molecular reactivity, intermolecular interactions, molecular recognition, electrophilic reactions, and a variety of chemical phenomena[18−23] is the molecular electrostatic potential (MESP). The MESP generated by a molecule can be calculated rigorously from its electron density, $\rho(\mathbf{r})$ distribution by employing the equation

$$\mathrm{V}(\mathbf{r}) = \sum_{A}^{N} \frac{Z_{\mathrm{A}}}{|\mathbf{r} - \mathbf{R}_{\mathrm{A}}|} - \int \frac{\rho(\mathbf{r}')\mathrm{d}^3\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \qquad (1)$$

where Z_{A} is the charge on nucleus A, located at $\mathbf{R}_{\mathrm{A}}$. It is also interpreted as a quantity directly related to the interactive behavior of a molecule with a unit test positive charge.

Recent works by Gadre and co-workers[22,23] have shown that the topography mapping of the electrostatic potential of a molecule (MESP) is a succinct way to analyze the reactivity of a molecule in determining the most electrophilic site of a molecule. They have used such topographical data for predicting cooperative intermolecular interactions. An application of this approach to substituted benzenes directly led to simple explanation of the activating, deactivating, and orientation effects of substituents.[23] Even the aromaticities of polycyclic benzenoid hydrocarbons have been found to correlate very well with their MESP topography.[23] There are several examples that point out that a molecule is first "seen" via the MESP surrounding it.[19,20,22] During the initial stages of the electrophilic addition reactions to olefins, the π-electron concentration around the C═C double bond attracts the incoming electrophile for the formation of a weak π-complex. Such a complex formation will lead to the activation of the C═C bond giving rise to the addition product. It is tested and proved that MESP topography mapping of electron-rich centers is useful for understanding the weak intermolecular complexes.[22] Is it therefore possible to gain new insights into the Markovnikov addition reaction by characterizing the π-regions of the olefin via the MESP topography? If so, does it help in predicting the regioselectivity of the reaction? The present work searches the answers to these questions by studying the MESP topography of several susbstituted ethylene molecules as a first guiding step for following their addition reaction with HCl. This is later followed up by a search of the transition states by quantum-chemical methods.

Methodology

Geometries of 20 $CH_2{=}CHR$-type substituted ethylenes (R = H, CH_3, CH_2CH_3, $COCH_3$, F, $CHCH_2$, CCH, COOH, CHO, CFO, NO_2, NH_2, $NHCH_3$, $N(CH_3)_2$, $NHNH_2$, NHOH, NO, OCH_3, OCN, and OH) have been optimized at the HF/6-31G**

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level of theory using the Gaussian98[24] set of programs. The π-regions of all these systems have been characterized by carrying out the MESP topography mapping, which involves the finding of the most negative-valued MESP point due to the olefinic π-bond. This point generally termed as a critical point (CP)[25,26] shows three positive eigenvalues for the Hessian matrix, viz.

$$H_{ij} = \left[\frac{\partial^2 V(\mathbf{r})}{\partial x_i \partial x_j}\right]_{\mathrm{CP.}} \qquad (2)$$

The advantage in this approach is that the information regarding this CP (a π-CP) can be directly used for exploring the electrophilic reactivity of the system in terms of its weak as well as strong interactions with other molecules. There are also computational advantages. It has been shown that $V(\mathbf{r})$ is relatively correct to one order higher than that of the wave function used.[27] Generally, an HF wave function obtained by employing a good quality basis set is found to be accurate enough for computing $V(\mathbf{r})$ for molecules in their ground electronic state.[28] It is hoped that HF/6-31G** level calculation is sufficient for the present work involving simple systems. However, a few test cases have been studied at B3LYP/6-31G** level[29] in order to assess the importance of the electron correlation effects.

The π-complexes of all the olefinic systems with HCl are also obtained at the HF/6-31G** level by initially placing the HCl molecule near the π-CP in such a way that the hydrogen of HCl is around 1 Å away from π-CP. Selected $CH_2{=}CH$-R···HCl complexes have been further explored for obtaining the transition states corresponding to the Markovnikov as well as anti-Markovnikov-type addition of HCl to ethylenic systems. Further, starting from these transition states, an intrinsic reaction coordinate (IRC) search[30] is carried out to make sure that they are really connected to the actual reactants and products.

Results and Discussion

(a) MESP Topography. Let us start from the MESP topography corresponding to the π-region of ethylene. As expected, the MESP of this molecule is negative in the regions above and below the molecular plane corresponding to the double bond. This feature is illustrated in Figure 1 a through an MESP isosurface with value −15.00 kcal/mol. Figure 1b shows the position and values of the two most negative-valued points ($V_{\min}$) in the MESP topography. These two points are equidistant from the carbon atoms (the distance is 1.668 Å), and they possess MESP value of −23.97 kcal/mol. It is equivalent to say, from the definition of MESP, that a test positive charge will experience net interaction energy of −23.97 kcal/mol at these points. In other words, the $V_{\min}$ contains the information regarding the interactive behavior of the simplest electrophile, viz., a unit test positive charge to a double bond.

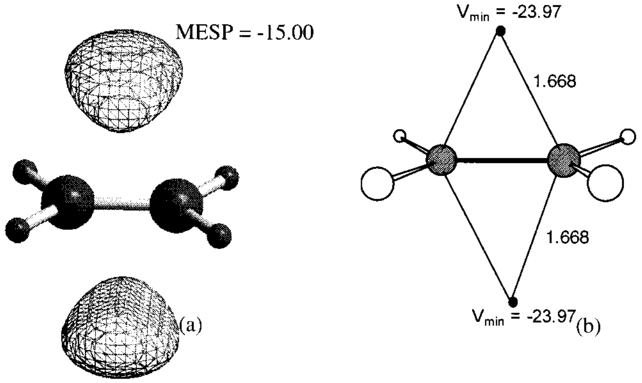

Figure 1. (a) π-Region of ethylene as seen in the MESP. (b) MESP minima of ethylene. The MESP values are in kcal/mol and distances are in Å.

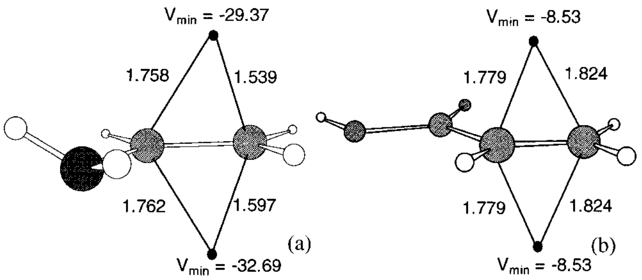

Figure 2. MESP minima, $V_{\min}$ of (a) CH_2CHNH_2 and (b) CH_2-CHCOOH. The MESP values are in kcal/mol and distances are in Å.

It would be interesting to see what happens to the position and values of $V_{\min}$ on substituting one of the hydrogens of ethylene by another atom or a functional group. Two prototype examples, viz., CH_2CHNH_2 and $CH_2CHCOOH$, are displayed in Figure 2. Since the two faces of the olefinic plane of CH_2CHNH_2 are different due to the pyramidalization of the amino group, we can locate different valued $V_{\min}$ for each face and both of them are more negative as compared to the $V_{\min}$ value of ethylene. The $V_{\min}$ values at the two faces are lower by 8.72 and 5.40 kcal/mol than the $V_{\min}$ value for the ethylene molecule (cf. Figure 1). On the basis of these $V_{\min}$ values, it can be said that the amino group acts as an electron-donating group to the ethylenic double bond. This feature is very similar to the one found in the earlier works on substituted benzenes,[23] where an electron-donating group was seen to generate more negative MESP over the benzene ring. Usually, such an observation in the case of aniline is explained on the basis of the resonance phenomenon involving the nitrogen lone pair and the aromatic ring. Unlike aniline, in the case of CH_2CHNH_2, the amino group is not planar, and therefore, the resonance mechanism may not be fully active. Even then the negative character of $V_{\min}$ is enhanced on both sides

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of the ethylenic double bond indicating that the presence of an electron-rich center like the amino group attached to an ethylenic double bond produces electron flow toward the π-region. This is found to be true for all the electron-donating groups studied herein, viz., CH_3, CH_2CH_3, NH_2, $NHCH_3$, $N(CH_3)_2$, $NHNH_2$, NHOH, OCH_3, and OH (we note here that generally the substituent classification as electron donating or withdrawing is based on the Hammett constants,[31,32] which are derived form experimental measurements carried out on substituted benzenes). One can also see from Figure 2a that the amino group substitution in ethylene shifts the V_{min} toward the unsubstituted carbon atom. A similar observation is noted for other electron-donating groups as well. This feature is very important because it hints at the regiospecificity of the attack of an electrophile to the olefinic system.

Exactly opposite trends in the values and locations of the V_{min} can be seen when the substituent is an electron-withdrawing group such as COOH. The V_{min} values in $CH_2CHCOOH$ become less negative as compared to ethylene by 15.44 kcal/mol. A further interesting feature is that these CP's are not only further away from both the carbon atoms, but also closer to the substituted carbon. A comparison of the distance of the V_{min} from both the olefinic carbon atoms in CH_2CHNH_2 and $CH_2CHCOOH$ shows that $V_{min} = -32.69$ and -29.37 kcal/mol in CH_2CHNH_2, which are closer to the unsubstituted carbon by 0.165 and 0.219 Å, respectively, and $V_{min} = -8.53$ kcal/mol in $CH_2CHCOOH$ is only 0.045 Å closer to the substituted carbon (cf. Figure 2 and Table 1). This indicates that the regiospecificity toward the electrophile is more pronounced in the CH_2CHNH_2 system. Similar observations can be made when the ethylenic substituents are CCH, CHO, $COCH_3$, NO, COF, and NO_2. The V_{min} values of $CHCH_2$-, F-, and OCN-substituted ethylenes are also less negative than the V_{min} value of CH_2CH_2, but their distance from the unsubstituted carbon is smaller than the distance from the substituted carbon. In the case of COF- and NO_2-substituted systems, positive valued V_{min} is observed over the C=C bond, indicating much strong electron withdrawal by these groups from the double bond.

In previous works,[23] a good linear relationship has been noticed between the Hammett constant of a substituent and the V_{min} values observed over the aromatic ring of the substituted benzenes. In the present work, the case studies of CH_2CHNH_2 and $CH_2CHCOOH$ systems suggest that the substituent effects in ethylenic systems are somewhat parallel to those observed for the corresponding substituted benzene systems. A test of this can be made by comparing the Hammett constants[31,32] of the substituents with the V_{min} values corresponding to the π-regions of CH_2CHR systems. Figure 3 depicts a plot of V_{min} versus the corresponding Hammett σ_p constant values. There exists a fairly good linear correlation between these two quantities confirming the similarities in the substituent electronic effects in ethylenic and aromatic systems (cf. Table 1).

Table 1. Hammett σ_p Constants of the Substituents and the V_{min} Values of CH_2CHR Systems and the Interaction Energy for the $CH_2CHR\cdots HCl$ Systems (V_{min} and E_{int} in kcal/mol)

R	V_{min}	C1⋯CP[a]	C2⋯CP[a]	Hammett constant (σ_p)	E_{int}
$N(CH_3)_2$	−32.19	1.586	1.758	−0.83[b]	−3.59
$NHCH_3$	−32.76	1.534	1.769	−0.70[c]	−3.55
NH_2	−33.07	1.539	1.758	−0.66[b]	−3.50
$NHNH_2$	−27.67	1.623	1.770	−0.55[d]	−3.03
OH	−26.54	1.606	1.795	−0.37[b]	−2.93
NHOH	−25.67	1.639	1.775	−0.34[d]	−2.69
OCH_3	−26.98	1.628	1.790	−0.27[b]	−3.02
CH_3	−25.04	1.618	1.696	−0.17[b]	−2.70
CH_2CH_3	−24.97	1.622	1.696	−0.15[b]	−2.71
$CHCH_2$	−21.90	1.682	1.724	−0.04[e]	−2.38
H	−23.97	1.668	1.668	0.00	−2.49
CCH	−15.94	1.773	1.769	0.23[f]	−1.74
F	−13.99	1.689	1.850	0.06[b]	−1.60
CHO	−5.08	1.839	1.790	0.42[g]	−0.78
COOH	−8.53	1.824	1.779	0.45[b]	−1.03
$COCH_3$	−8.16	1.798	1.759	0.50[b]	−1.07
OCN	−1.38	1.780	1.932	0.54[h]	−0.52
NO	−1.57	1.923	1.889	0.91[i]	−0.57
COF	0.38	1.914	1.843	0.70[j]	−0.30
NO_2	5.90	2.223	2.205	0.78[b]	

[a] C1⋯CP and C2⋯CP correspond to distance (in Å) of the critical point from the unsubstituted and substituted carbon atoms, respectively. [b] From ref 32b. [c] From ref 32c. [d] From ref 32d. [e] From ref 32e. [f] From ref 32f. [g] From ref 32g. [h] From ref 32h. [i] From ref 32i. [j] From ref 32j.

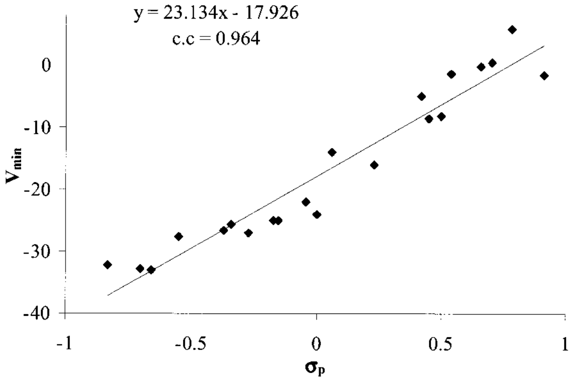

Figure 3. Correlation between the Hammett σ_p constants and the π-region MESP CPs (V_{min} in kcal/mol) of substituted ethylenes.

(b) π-Complexes of CH_2CHR with HCl. We have seen above that V_{min} in the MESP topography corresponding to the π-region of an ethylenic double bond gives a good estimate of the electron-donating and -withdrawing effect of a substituent attached to it. It is also mentioned that the values of V_{min} correspond to the energetic behavior of a test positive charge at that point. What other chemically meaningful information can be extracted from the V_{min} values? Does it simulate realistically the interactive behavior of an actual electrophilic system with the π-bond? To answer these queries, we have studied the π-complex formation of the HCl molecule with the CH_2CHR systems. Modeling of these reactions is also expected to give valuable information regarding the mechanism of electrophilic addition of HCl to a double bond[17] since the system's passage to the

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(31) Hammett, L. P. *Chem. Rev.* **1935**, *17*, 125.

(32) (a) For a survey of Hammett constants, see: Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165. (b) McDaniel, D. H.; Brown, H. C. *J. Org. Chem.* **1958**, *23*, 420. (c) Hogben, M. G.; Graham, W. A. G. *J. Am. Chem. Soc.* **1969**, *91*, 283. (d) Jaffè, H. H. *Chem. Rev.* **1953**, *53*, 191. (e) Charton, M. *Prog. Phys. Org. Chem.* **1981**, *13*, 119. (f) Landgrebe, J. A.; Rynbrandt, R. H. *J. Org. Chem.* **1966**, *31*, 2585. (g) Charton, M. *J. Org. Chem.* **1963**, *28*, 3121. (h) Perrin, D. D.; Dempsey, B.; Serjeant, E. P. *pK$_a$ Prediction for Organic Acids and Bases*; Chapman Hall: London, 1981; Appendix. (i) Belyaev, E. Y.; Tovbis, M. S.; Suboch, G. A. *Zh. Org. Khim.* **1976**, *12*, 1790EE. (j) Yagupol'sskii, L. M.; Il'chenko, A. Y.; Kondratenko, N. V. *Russ. Chem. Rev.* **1974**, *43*, 32EE.

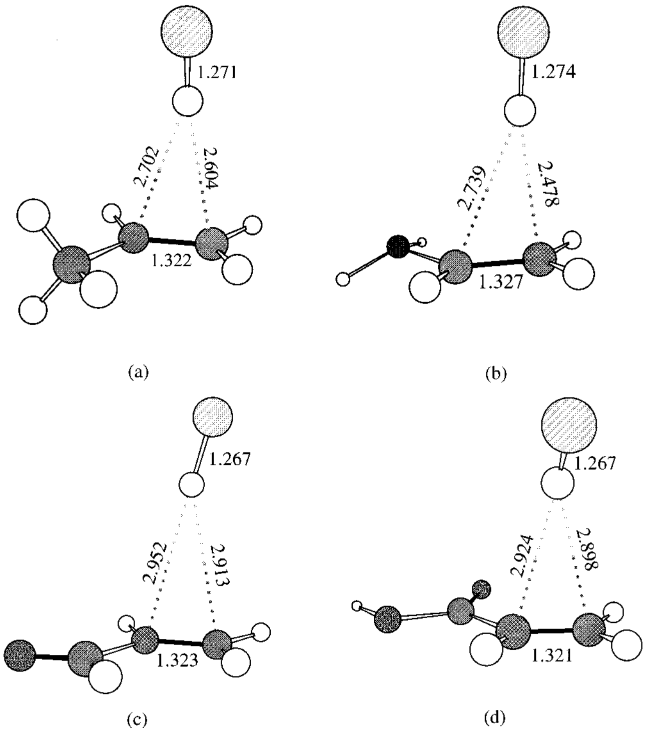

Figure 4. π-complexes of (a) CH_2CHCH_3, (b) CH_2CHNH_2, (c) CH_2CHCHO, and (d) $CH_2CHCOOH$ with HCl. Distances are in Å.

transition state for the addition reaction may be thought of as initiated from these π-complexes. Figure 4 depicts the optimized geometries of four $CH_2CHR\cdots HCl$ π-complex systems—two for electron-donating (CH_3 and NH_2) and the other two for electron-withdrawing (CHO and COOH) R substituents. The HF/6-31G** level interaction energies (E_{int}) of all the $CH_2CHR\cdots HCl$ systems are reported in Table 1. As expected, the E_{int} is found to be larger when R is an electron-donating group and the complex formation in such a case is achieved at smaller intermolecular distance as compared the situation in which R is an electron-withdrawing group. Further, a stronger π-complex formation with R as an electron-donating group also produces a slightly activated H−Cl bond. For instance, when R = CH_3 and NH_2, the H−Cl bond is elongated by 0.005 and 0.008 Å in the respective π-complexes which, in the case of a deactivating COOH group, is only 0.001 Å (1.266 Å is the uncomplexed H−Cl bond distance). A clear preference for the H of the HCl molecule toward the unsubstituted carbon atom (the Markovnikov carbon atom) can be seen from the C···H distances of $CH_2CHCH_3\cdots HCl$ and $CH_2CHNH_2\cdots HCl$. A similar but diminished effect is seen when the substituent is an electron-withdrawing group such as CHO and COOH. In fact, for strong electron-withdrawing groups such as COF and NO, the $C_{(substituted)}\cdots H$ distance is slightly smaller than the $C_{(unsubstituted)}\cdots H$ distance. These observations can be directly correlated with the location and the values of the V_{min} in the MESP topography. When the V_{min} location is away from the C=C bond and the V_{min} value is less negative as in the case of electron-withdrawing groups, the π-complex formation is found to be weak and less regiospecific. On the other hand, relatively more regiospecific and strong π-complex formation is observed when V_{min} is more negative and closer to the C=C bond as in the case of electron-donating groups. Almost a perfect linear correlation obtained between E_{int} and V_{min} (cf. Figure 5) further confirms the validity of the MESP-based arguments for studying the complex formation. It is also meaningful to say at this point that a substituent group R is an activating group toward the π-complex formation if the V_{min} of the CH_2CHR system is more negative than the V_{min} of CH_2CH_2 and otherwise it would act as a deactivating group for the same reaction. This feature is in analogy with the substituent effect as seen for the electrophilic substitution reactions of substituted benzenes.[23] Among all the substituted ethylenes studied here, the NO_2-substituted ethylene is the most deactivated system toward an electrophilic addition reaction as seen from its substantially positive V_{min} value of 5.90 kcal/mol. For this case, the π-complex formation with H−Cl was not observed. We also note that a change of level of the theory or basis set in the calculation can somewhat change the absolute values and position of the V_{min}. However, the good linear correlation of V_{min} versus σ_p as well as V_{min} versus E_{int} suggest that the relative value of V_{min} is more important than the absolute one when one compares the electronic effect of different substituents.

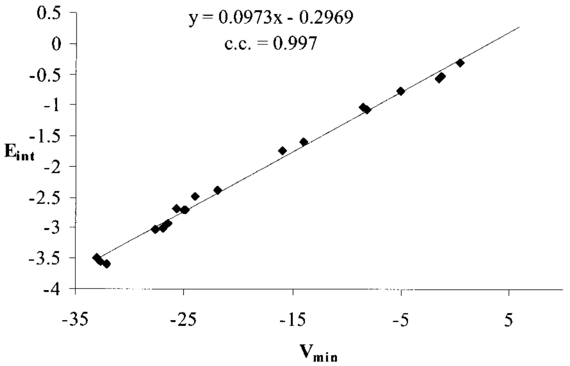

Figure 5. Correlation between the π-region MESP CPs (V_{min}) of CH_2CHR systems and the interaction energies (E_{int}) (both values are in kcal/mol) of the $CH_2CHR\cdots HCl$ systems.

(c) Transition States and IRC Calculations. The $CH_2CHR\cdots HCl$ π-complex formation would lead to the formation of the transition states corresponding to the Markovnikov or the anti-Markovnikov-type addition of the H−Cl bond to the double bond.[33] Based on the four features of the π-complexes noted for R as an activating group, viz., (i) closer approach of the HCl to the double bond, (ii) higher interaction energy, (iii) smaller $C_{(unsubstituted)}\cdots H$ distance as compared to $C_{(substituted)}\cdots H$ distance, and (iv) higher activation of H−Cl bond, we can say that a CH_2CHR system is better "prepared" for the addition reaction preferably the Makovnikov-type when R is an activating rather than a deactivating group. The validity of this statement is tested by actually computing the transition states for the Markovnikov and anti-Markovnikov-type addition reactions. Figure 6 depicts the computed transition-state geometries and the activation energies corrected by zero-point vibration energies

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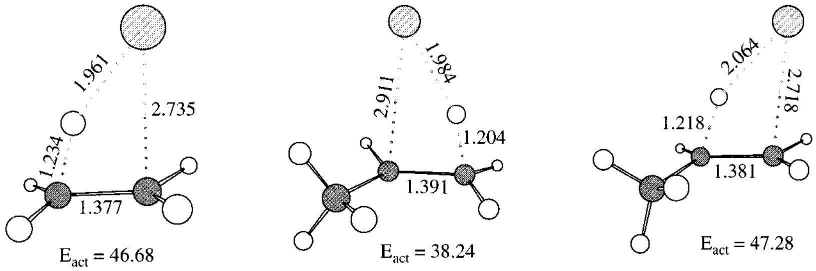
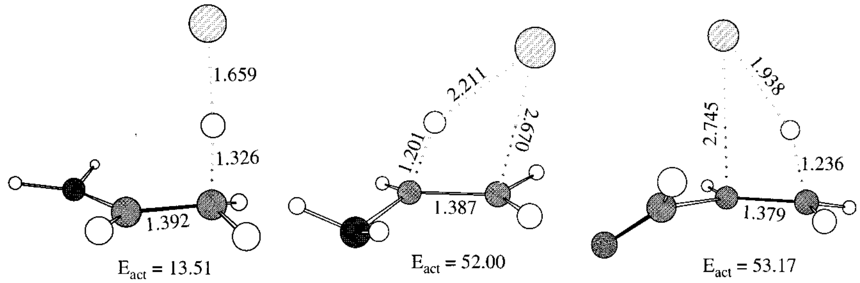
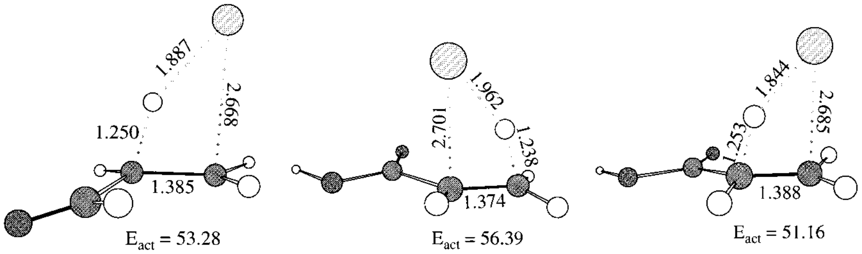
[33] (a) See 16 for experimental activation energy calculations of HCl, HBr, and HI additions to ethene, propene, and 2-methylpropene. For an earlier discussion, see: Maccoll, A. In *Studies on Chemical Structure and Reactivity*; Ridd, J. H., Ed.; Methuen: London, 1966. (b) Swinbourne, E. S. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: Amsterdam, 1972; Vol. 5, p 149. (c) Benson, S. W.; O'Neal, H. E. *Kinetic Data on Gas-Phase Unimolecular Reactions*; National Bureau of Standards: Washington, DC, 1970; NSRDS-NBS 21.



(a) CH_2CH_2....H...Cl (TS) (b) CH_2CHCH_3....H...Cl (TS1) (c) CH_2CHCH_3....H...Cl (TS2)



(d)CH_2CHNH_2....H...Cl (TS1) (e)CH_2CHNH_2....H...Cl (TS2) (f)CH_2CHCHO....H...Cl (TS1)



(g)CH_2CHCHO....H...Cl (TS2) (h)$CH_2CHCOOH$....H...Cl (TS1) (i)$CH_2CHCOOH$....H...Cl (TS2)

Figure 6. Transition-state (TS) geometries corresponding to the Markovnikov (TS1) and anti-Markovnikov-type (TS2) addition of HCl to CH_2CHR systems, where R = H, CH_3, NH_2, CHO, and COOH. The activation energies (E_{act}) in kcal/mol corrected for zero-point vibration are also depicted. Distances are in Å.

(E_{act}) for a few test cases, viz., the olefinic systems with R = H, CH_3, NH_2, CHO, and COOH. A general observation is that in all these transition states, the H−Cl bond is almost completely broken as can be seen from the large H···Cl distance (1.659 to 2.211 Å) as compared to the bond length of free HCl molecule (1.266 Å). All these transition states could be better understood by invoking its similarity to an ion pair consisting of a carbocation and a chloride anion.[2,16] From the values of E_{act}, it is quite clear that the olefins with electron donating groups prefer the Markovnikov rather than anti-Markovnikov addition and that the preferred addition needs less activation as compared to the HCl addition to ethylene. A probable reason for this result is the higher resemblance of the Markovnikov-type transition state to the corresponding π-complexes.[34] In the case of ethylenes with electron-withdrawing groups, the activation energy needed for both Markovnikov and anti-Markovnikov-type additions is almost the same but higher than that required for the HCl addition to ethylene. This result can also be correlated to the corresponding π-complexes, where in such cases a less regiospecific and weak complex is formed.

Experimental activation energies (E_{expt}) of the addition of HX to $CH_2{=}CHX$ (X is a halogen) is generally estimated from the corresponding unimolecular elimination reactions of HX from CH_3CH_2X. In the recent work of Sæthre, Thomas, and Svensson,[16] such E_{expt} values for the addition of HCl to ethene (39.7 kcal/mol), Markovnikov addition of HCl to propene (34.5 kcal/mol) and 2-methyl propene (28.5 kcal/mol), and anti-Markovnikov addition of HCl to propene (41.3 kcal/mol) and 2-methylpropene (41.7 kcal/mol) are reported. As compared to these values, the theoretical activation energies at HF/6-31G** level (E_{act}) are somewhat large for the addition of HCl to ethene (46.68 kcal/mol) and the Markovnikov (38.20 kcal/mol) and anti-Markovnikov addition of HCl propene (47.28 kcal/mol). To make a further comparison, we have also computed the HF/6-31G** level values of E_{act} for the Markovnikov (E_{act} = 29.73 kcal/mol) and anti-Markovnikov (E_{act} = 47.85 kcal/mol) addition of HCl to 2-methylpropene. Although the theoretical values of the activation energies (E_{act}) are somewhat larger than the experimental activation energies (E_{expt}), we have obtained a good linear correlation between the two (the correlation equation is $E_{act} = 1.3983(E_{expt}) - 9.9753$ and correlation coefficient = 0.9963), which suggests that the theory correctly predicts the overall trend in the values. A similar observation was also noted by Sæthre, Thomas, and Svensson[16] from their HF/D95(d,p) level theoretical estimates of the activation energies of these reactions. In fact, E_{act} at HF/6-31G** and HF/D95(d,p) was almost the same for HCl addition to ethene and for HCl addition to propene, and 2-methylpropene, the E_{act} values were

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(34) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

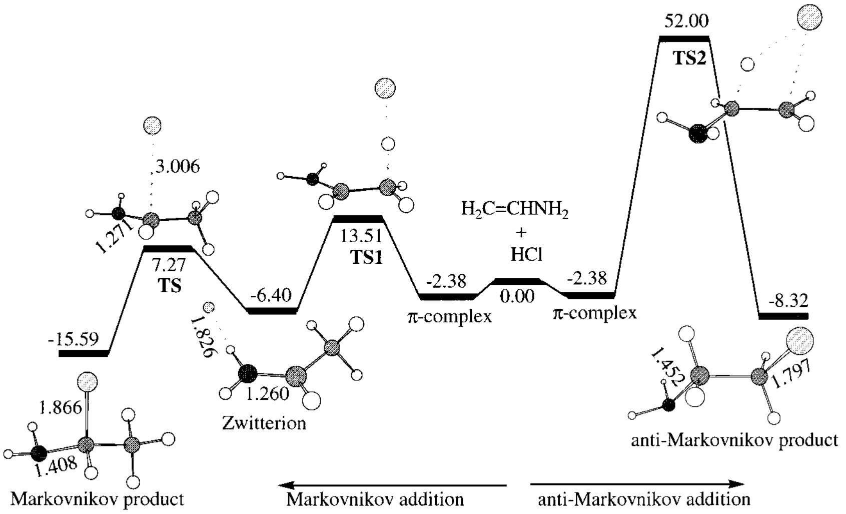

Figure 7. Markovnikov and anti-Markovnikov addition of HCl to $CH_2{=}CHNH_2$. The energy levels corrected to zero-point vibration are given in kcal/mol. The structure of the π-complex is shown in Figure 4b.

around 2.32 kcal/mol smaller than the HF/D95(d,p) level values.

We have also carried out an intrinsic reaction coordinate (IRC)[30] search starting from the transition state (TS) to find out the actual end products of the reactions. As expected, all of the TSs except the one corresponding to the Markovnikov addition of HCl to $CH_2{=}CHNH_2$ led to the corresponding π-complexes as one end product and the other end products were the usual Markovnikov and anti-Markovnikov addition products. In fact, the transition state for the Markovnikov addition of HCl to $CH_2{=}CHNH_2$ is not a classical four-center transition state thought to be characteristic of the hydrogen halide addition to ethylene.[2] The IRC search starting from this TS showed a stepwise ionic mechanism. The TS was connected to the $CH_2{=}CHNH_2{\cdots}HCl$ π-complex and a zwitterionic $CH_3{-}C^{+}(H)NH_2{\cdots}Cl^{-}$ wherein the Cl^- was attached to one of the amino hydrogens (cf. Figure 7). The formation of the usual four-center transition state was prevented due to the strong interaction of the nitrogen lone pair electrons with the vacant orbital on C^+ as is evident from the very short $C^+{-}N$ distance of 1.260 Å in the zwitterion. Further, activation of the zwitterionic system led to another TS as shown in Figure 7. The IRC calculations on this TS confirmed that it connects the zwitterionic system and the final Markovnikov product.

To check the effect of electron correlation, we have studied the systems CH_2CH_2, CH_2CHNH_2 and $CH_2CHCOOH$ as well as their π-complexes and the transition states with HCl at B3LYP/6-31G** level of theory.[29] The results obtained in this study vis-à-vis those obtained at the HF/6-31G** level of theory are summarized in Table 2. Qualitatively, there is no change in the results at both levels of theory. The electron correlation decreases the negative character of the MESP in all the systems as evident in their V_{min} values. However, the interaction energies (E_{int}) of the π-complexes are increased by 48.8, 72.4, and 76.2% in the case of $CH_2CH_2{\cdots}HCl$, $CH_2CHNH_2{\cdots}HCl$, and $CH_2CHCOOH{\cdots}HCl$, from the corresponding HF/6-31G** values. Such an increase in E_{int} is reflected in the closer approach of HCl to the olefin system for the formation of the π-complex. There is also a decrease (generally about 20−30% as compared to HF/6-31G** level) in the activation barriers of both Markovnikov and anti-Markovnikov addition reactions. In fact, the E_{act} value at B3LYP/6-31G** level for the addition of HCl to ethene is 5.49 kcal/mol smaller than the experimental activation energy estimated from the HCl elimination reaction from CH_3CH_2Cl.[16] Further, a substantial reduction in the activation barrier for the Markovnikov addition of HCl to CH_2CHNH_2 is seen, which is a change from the HF/6-31G** value of 13.51 kcal/mol to the 1.67 kcal/mol at the B3LYP/6-31G** level.

Table 2. Results Obtained at B3LYP/6-31G Level (Corresponding HF/6-31G** Values in Parentheses)[a]**

	R = H	R = NH_2	R = COOH
V_{min}	−20.21 (−23.97)	−31.75 (−33.07)	−6.59 (−8.53)
$CH_2CHR{\cdots}HCl$ distances			
C1···H (Å)	2.436 (2.698)	2.062 (2.478)	2.546 (2.898)
C2···H (Å)	2.436 (2.698)	2.497 (2.739)	2.602 (2.924)
E_{int} (kcal/mol)	3.70 (2.49)	6.03 (3.50)	1.81 (1.03)
$E_{act}(M)^b$ (kcal/mol)	34.21 (46.68)	1.67 (13.51)	39.70 (56.39)
$E_{act}(AM)^b$ (kcal/mol)	34.21 (46.68)	41.57 (52.00)	37.60 (51.16)

[a] C1 and C2 are the unsubstituted and substituted carbon atoms in the olefin. [b] M and AM denote Markovnikov and anti-Markovnikov-type transition states, respectively.

Conclusions

The subtle electronic effects occurring at the π-region of an ethylenic double bond due to the substituent attached to it are monitored by locating the most negative-valued point of the MESP (V_{min}) in that region. Substituents are classified as electron donating or withdrawing on the basis of the increase or decrease of the negative character of V_{min} as compared to that of ethylene. With electron-donating substituents, the location of V_{min} is closer to the unsubstituted carbon of the ethylenic unit, thereby enhancing the formation of the π-complex of HCl closer to that carbon. Such a regiospecific π-complex facilitates the Markovnikov-type addition of HCl to the double bond. On the other hand, a less negative value and comparatively farther away V_{min} location from the double bond explains the weak and the less regiospecific π-complex in the case of ethylenes with electron withdrawing substituents. In such cases, the addition reactions require larger activation energies and they are less regiospecific. Further, the value of $V_{\min}$ can be directly related to the interaction energy (E_{int} in kcal/mol) of the corresponding π-complex by the equation, $E_{\text{int}} = 0.0973(V_{\min}) - 0.2969$ (cf. Figure 5). One can also notice close similarities in the electronic effects of substituents when comparing the HCl addition to the substituted ethylenes and the electrophilic substitution reactions of substituted benzenes. Both the reactions are activated or deactivated in a similar manner by the substituents. The linear correlation obtained between $V_{\min}$ and σ_p further confirms this. It is well-known that in the case of electrophilic substitution reactions of substituted benzenes an electron-donating group directs the electrophile mainly toward the ortho and para carbon atoms (ortho-para orienting) and an electron-withdrawing group directs the electrophile mainly toward the meta carbon atom (meta orienting). Very similar to this, an electron-donating group can be said to be Markovnikov-orienting in the context of the HCl addition to the substituted ethylenes. Although when electron-withdrawing groups are attached to the double bond, we see the location of $V_{\min}$ nearer to the substituted carbon (anti-Markovnikov-orienting) rather than the unsubstituted carbon, we do not see a clear preference for the anti-Markovnikov addition product in the calculation. For instance, HCl addition to CH_2CHCHO is slightly favorable for the Markovnikov product but such an addition to $CH_2CHCOOH$ is favorable for an anti-Markovnikov product.

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Supporting Information Available: Cartesian coordinates of optimized geometries and energies of CH_2CHR, $CH_2CHR\cdots HCl$, and transition states at HF/6-31G** and B3LYP/6-31G** levels. This material is available free of charge via the Internet at http://pubs.acs.org.

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