α-Substituted Vinyl Cations: Stabilities and Electronic Properties

Kaj van Alem and Gerrit Lodder*,†

Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502,
2300 RA Leiden, The Netherlands

Han Zuilhof*,‡

Laboratory of Organic Chemistry, Department of Biomolecular Sciences, Wageningen University,
Dreijenplein 8, 6703 HB Wageningen, The Netherlands

Received: October 6, 1999; In Final Form: January 4, 2000

Vinyl cations substituted at the α-position ($H_2C{=}C(+)R$), with R = H, $CH{=}CH_2$, CH_3, F, and Cl, and their neutral precursors ($H_2C{=}CHR$) have been studied using various quantum chemical methods to analyze the influence of these substituents on the thermodynamic stability and electronic properties. B3LYP data obtained with various basis sets are compared to those of post-HF computations, including MP2, MP4(SDQ), and QCISD(T) computations and the CBS-Q model chemistry. The results of those calculations are benchmarked against experimental results. The NBO and AIM population analysis methods are used for analysis of the electronic properties. The geometry, stability, and electronic structure of the vinyl cations under study are already accurately described at the B3LYP/6-311+G(d,p)//B3LYP/6-311G(d,p) and MP2/6-311+G(d,p)//MP2/6-311G(d,p) levels of theory. The results of the NBO calculations are shown to be preferable over AIM, since the latter, due to an artifact in that method, predicts counterintuitive charge distributions. Analysis of the reaction enthalpies and electronic properties shows the lack of correlation between the electron-donating ability of α-substituents and the stability provided by such substituents. Comparison of the results obtained for the vinyl cations with those of previously studied α-substituted ethyl cations shows a striking difference in stabilization of the two systems for R = F, destabilizing in vinyl systems, and stabilizing in ethyl systems, while the charge distributions are practically the same in these two systems. This outcome is discussed in detail.

Introduction

The possible occurrence of vinyl cations as reactive intermediates in thermal as well as in photochemical reactions, and the electronic structure of these species, have intrigued chemists for the past four decades.[1] Extensive experimental work has shown that vinyl cations can be generated from suitable precursors by both solvolysis[2] and photolysis.[3] Also, many theoretical studies on the parent vinyl cation as well as substituted vinyl cations have been published.[4]

However, no systematic, benchmarking study has been performed of the effects of a range of α-substituents on the stability and electronic properties of vinyl cations using high-level quantum chemical methods. Recently, a paper from our laboratories on the effects of α-substituents on ethyl cations was published.[5] For those ethyl cations ($H_3C{-}C(+)HR$), appropriate theoretical levels for an accurate description of the energetics of α-substitution were determined by comparison with experimental thermochemical data. Also, the best methods to describe the electronic properties of these species were established. The present paper discusses the results of an extension of this work to α-substituted vinyl cations. The emphasis is on (a) the required levels of theory to accurately describe the α-substituent effects on the stability of vinyl cations via the benchmarking of several theoretical methods against all currently available experimental thermochemical data, and (b) the electronic structure of these cations. Thermochemical data on both the neutral $H_2C{=}CHR$ molecules and the corresponding ions $H_2C{=}C(+){-}R$ are available for R = H, $CH{=}CH_2$, CH_3, Cl, and F. Therefore, a theoretical study was performed on this series of α-R-substituted neutral ethenes and corresponding vinyl cations using both B3LYP and post-HF (MP2, MP4, and QCISD(T)) methods with various basis sets (ranging from 6-31G(d) to 6-311++G(3df,3pd)), and a recently developed model chemistry (CBS-Q). These systems have all been studied by theoretical methods before,[6] but the benchmarking with regard to experimental data for this set of species, the inclusion of DFT methods, the comparative computation of all these species with all the post-HF methods used in this study, and the detailed analysis of the electronic structures are all presented for the first time. An assessment of the (de)stabilization by the α-substituents compared to hydrogen is made by calculation of the reaction enthalpy Δ*H* of the isodesmic reaction given in eq 1. Method dependencies and basis set effects, as well as the influence of the α-substituent on the reaction enthalpies and the electronic properties of the ions, are discussed.

$$CH_2{=}CHR + CH_2{=}C(+)H \xrightarrow{\Delta H} CH_2{=}CH_2 + CH_2{=}C(+){-}R \quad (1)$$

Computational Details

All computations were performed using the Gaussian 94 (revision D4) suite of programs.[7] Natural bond orbital (NBO)

---

† E-mail: Lodder@chem.leidenuniv.nl.
‡ E-mail: Zuilhof@sg1.oc.wau.nl.

10.1021/jp9935743 CCC: $19.00

calculations were performed with the NBO 3.1 program.[8] Atoms-in-molecules (AIM) calculations[9] were performed as implemented in Gaussian 94.

Calculations on the compounds under study were performed using the B3LYP (Becke's three-parameter nonlocal exchange hybrid functional[10] with the nonlocal correlation functional of Lee et al.[11]) method, Møller−Plesset second- and fourth-order perturbation theory, QCISD(T) and the CBS-Q model chemistry method.[12] All MP*n* ($n = 2, 4$) calculations take the correlation effects of all electrons into account, while for the QCISD(T) calculations a frozen core was used. In order to obtain data on the electronic structure from the MP4 calculations, only single, double, and quadruple substitutions (MP4SDQ) were considered (due to a restriction in Gaussian 94).

The geometries of all compounds under study were fully optimized. Optimizations of the parent vinyl cation were started from a bridged (nonclassical) structure, which had previously been shown to be the global minimum.[7n,o,13] All optimized structures were shown to be minima on the potential energy surface via vibrational frequency computations. Selected geometrical features of the species under study are discussed in the text, while all optimized geometries at all computational levels used are available as Supporting Information. All single-point computations were performed using the SCF═tight option in Gaussian 94.

Results and Discussion

Geometries. Full optimizations were performed on the vinyl cations of the form $H_2C{=}C(+){-}R$ ($R = CH{=}CH_2$, CH_3, Cl, and F), protonated acetylene (bridged vinyl cation) and their corresponding neutral precursors $H_2C{=}CHR$ using the 6-31G(d), 6-311G(d,p), and 6-311+G(d,p) basis sets with both the B3LYP and MP2 method. Typical geometrical features of the compounds under study are given in Figure 1, which depicts the results obtained from B3LYP/6-311G(d,p) and MP2/6-311G(d,p) computations.

For the parent vinyl cation (protonated acetylene) a symmetrically bridged structure is found to be the minimum on the potential energy surface, in accordance with previous theoretical[7n,o] and experimental[13] studies. The decrease in C═C bond length (of 0.10−0.11 Å) in going from the neutral precursor (ethene) to the vinyl cation is much larger than found for the other vinyl cations. Also, the length of the C−H bond involving the bridging hydrogen is substantially increased.

All other vinyl cations studied are linear, with shorter C−R bond lengths than in the neutral precursors. This decrease in C−R bond length ranges from 0.085 to 0.186 Å for B3LYP/6-311G(d,p), and from 0.084 to 0.175 Å for MP2/6-311G(d,p) and follows for both methods the order $CH{=}CH_2 < CH_3 < F < Cl$ (C−Cl bond length is decreased most, both in absolute and relative terms). Concomitant with this C−R bond length reduction, a reduction of the C═C bond length is found. The magnitude of this decrease is, however, smaller (0.05−0.06 Å), and the order is roughly inverse to the order of the decrease observed for the C−R bond lengths ($Cl < F < CH{=}CH_2 \approx CH_3$; in $H_2C{=}C(+){-}Cl$ the C═C bond length is reduced least). On the other hand, the $C_\beta{-}H$ bonds are elongated in the vinyl cations compared to the neutral compounds. This slight elongation (0.005 to 0.016 Å) points to hyperconjugation. The magnitude of this hyperconjugative effect is inversely related to the stability of the cation: in the most destabilized cation (vide infra), $H_2C{=}C(+){-}F$, the $C_\beta{-}H$ bonds are the longest; in the most stable one, $H_2C{=}C(+){-}CH{=}CH_2$, they are the shortest.

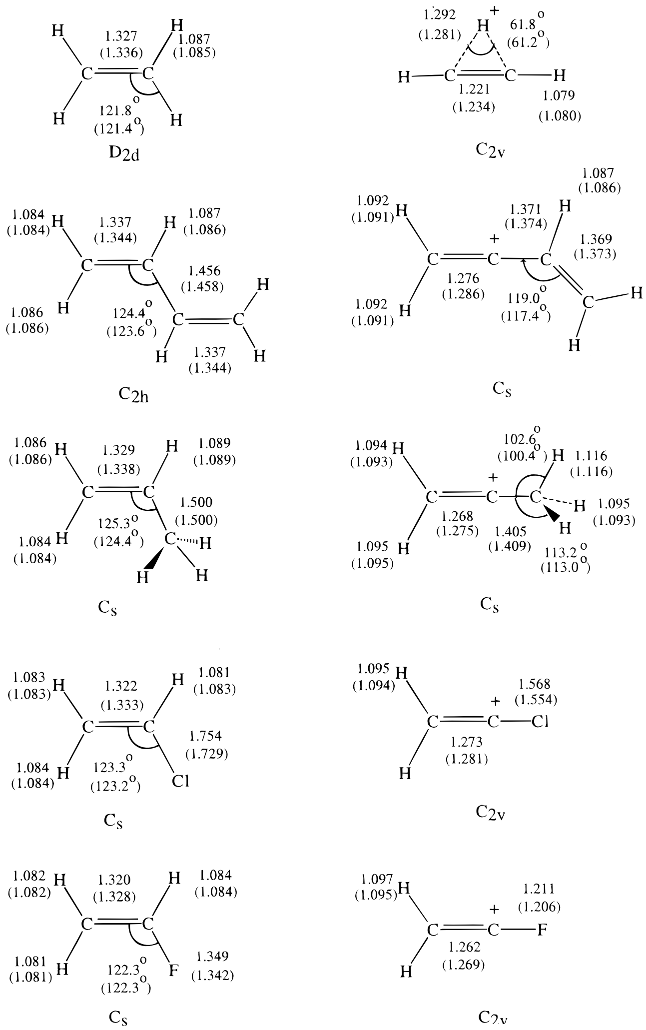

Figure 1. Typical geometrical features of compounds under study calculated at B3LYP/6-311G(d,p) and (in parentheses) MP2/6-311G-(d,p).

Comparison of the geometries of the vinyl cations and their neutral precursors optimized with B3LYP and MP2 shows that there are small but systematic differences between the two methods (Figure 1). The C═C bond lengths are with the B3LYP method calculated to be slightly shorter, up to 0.013 Å for the unsubstituted vinyl cation. For the C−R bond lengths, only marginal method dependencies are found for $R = H$, $CH{=}CH_2$, and CH_3, but for $R = Cl$ and F the method dependence is nonnegligible (albeit still small): B3LYP computations predict larger C−R bond lengths for both $R = Cl$ (0.025 and 0.014 Å for vinyl chloride and α-chlorovinyl cation, respectively) and $R = F$ (0.007 and 0.005 Å for vinyl fluoride and α-fluorovinyl cation, respectively). All other bond lengths display only insignificant differences between the two methods (<0.002 Å). Small differences are also found for the bond angles, with the B3LYP-calculated angles somewhat larger than the MP2-derived angles. However, all the observed differences in bond lengths and angles between these two methods only amount to small differences in energy: an MP2/6-311G(d,p) single-point calculation on the B3LYP/6-311G(d,p)-optimized geometry for vinyl chloride (the compound that shows the largest geometrical difference between the two methods) only differs by 0.25 kcal/mol in energy from the MP2/6-311G(d,p)//MP2/6-311G(d,p) computation.

Systematic differences are observed between the geometries obtained using different basis sets. Comparison of the 6-311G-

TABLE 1: −Δ*H* (kcal/mol) for the Isodesmic Reaction in Eq 1 Using Different Methods and Basis Sets for Substituents CH═CH$_2$, CH$_3$, Cl, and F Together with Experimental Data

		CH═CH$_2$	CH$_3$	Cl	F
1	experimental[a]	33.5	24.5	11.4	−6.7
2	B3LYP/6-31G(d)	42.26	32.76	12.99	−1.91
3	B3LYP/6-311G(d,p)	38.39	30.47	10.33	−5.20
4	B3LYP/6-311+G(d,p)[b]	38.13	30.58	11.47	−7.65
5	B3LYP/6-311+G(d,p)	38.13	30.58	11.47	−7.66
6	B3LYP/6-311++G(d,p)[c]	38.12	30.59	11.41	−7.71
7	B3LYP/6-311++G(3df,3pd)[c]	37.71	30.39	13.63	−6.54
8	MP2/6-31G(d)	33.27	23.14	6.47	−9.49
9	MP2/6-311G(d,p)	28.54	19.77	5.46	−10.11
10	MP2/6-311+G(d,p)[d]	27.95	19.72	6.13	−12.85
11	MP2/6-311+G(d,p)	27.95	19.72	6.13	−12.87
12	MP2/6-311+G(d,p)[d,e]	32.23	24.00	10.40	−8.57
13	MP4(SDQ)/6-311+G(d,p)[f]	30.99	23.52	9.32	−10.00
14	QCISD(T)/6-311+G(d,p)[f]	31.29	23.61	10.53	−9.32
15	CBS-Q	32.55	25.89	11.17	−9.25

[a] The experimental reaction enthalpies are average numbers based on experimentally determined heats of formation for the species under study.[15,16] [b] Single-point (SP) calculation on the B3LYP/6-311G(d,p)-optimized geometry. [c] SP calculation on the B3LYP/6-311+G(d,p)-optimized geometry. [d] SP calculation on the MP2/6-311G(d,p)-optimized geometry. [e] MP4(SDQ)/6-311+G(d,p)//MP2/6-311+G(d,p) calculations are used for ethene and vinyl cation. [f] SP calculation on the MP2/6-311+G(d,p)-optimized geometry.

(d,p) basis set data with those of the 6-31G(d) and 6-311+G-(d,p) basis sets shows that for R = H, CH═CH$_2$, CH$_3$, and Cl the geometries are only slightly affected by truncation of the basis set size from 6-311G(d,p) to 6-31G(d) (see Supporting Information). For R = F a significant dependence on basis set size is observed. With the 6-31G(d) basis set the C−F bond of the α-fluorovinyl cation is computed 0.011 Å (B3LYP) and 0.017 Å (MP2) longer. For the C−F bond in vinyl fluoride a corresponding method-dependent shortening (0.002 Å; B3LYP) or elongation (0.012 Å; MP2) is calculated. Basis set expansion from 6-311G(d,p) to 6-311+G(d,p) has only a marginal effect upon the geometries: no changes in bond length or bond angle larger than 0.005 Å or 0.5° and in many cases no significant changes at all are computed.

Thermodynamics. Total energies were computed using both B3LYP and post-HF methods. In the case of B3LYP basis sets ranging from 6-31G(d) to 6-311++G(3df,3pd) were used, while in the post-HF calculations the level of theory was expanded rather than the basis set,[12] so next to MP2 calculations also MP4-(SDQ) and QCISD(T) calculations were performed (see Table 1 for details on the used basis sets). The obtained total energies, corrected with a scaled[14] zero-point energy, were used to calculate the reaction enthalpies of the isodesmic reaction given in eq 1, which are presented in Table 1, together with the reaction enthalpies as derived from experimental thermochemical data.[15] Finally, the reaction enthalpies were also computed with the CBS-Q model chemistry (Table 1, entry 15).

Analysis of the reaction enthalpies shows that in most cases there is a good agreement between the calculated and experimental values.[16] Regardless of the method or basis set used, the correct order of stabilization by R is predicted (CH═CH$_2$ > CH$_3$ > Cl > F). The absolute differences between experimental and computed data do, however, show substantial method and basis set effects. The B3LYP results for R = CH═CH$_2$ and CH$_3$ are between 4.2 and 8.3 kcal/mol higher than the experimental values, while for R = Cl and F the deviations are smaller (between 0.2 and 4.8 kcal/mol). The B3LYP/6-31G(d) results show the largest error for all substituents and expansion of the basis set to 6-311G(d,p) lowers the reaction enthalpies (closer to the experimental values in all cases) by about 3 kcal/mol. For R = Cl and F, inclusion of diffuse functions improves the calculated enthalpies further, regardless of whether this inclusion of diffuse functions is used in a single-point calculation or in the geometry optimization, while for R = CH═CH$_2$ and CH$_3$ such inclusion has only a minor effect on the reaction enthalpy. Further small improvements of the calculated values can be obtained by using the 6-311++G(3df,3pd) basis set, except for R = Cl where expansion to this basis set leads in fact to larger deviations.

In contrast to B3LYP, all MP2-computed reaction enthalpies are lower than the experimental values. This deviation ranges from 0.2 (R = CH═CH$_2$) to 4.9 (R = Cl) kcal/mol for the MP2/6-31G(d) data. These relatively small deviations must result from a fortuitous partial cancellation of errors, as enlargement of the basis set size to 6-311G(d,p) or 6-311+G(d,p) results in systematically *larger* discrepancies (5−6 kcal/mol) for all substituents. This constant deviation is likely caused by a poor description of the parent (bridged) vinyl cation at the MP2 level of theory. Indeed, substitution of the energies for ethene and vinyl cation used to calculate the data of entry 10 with the MP4-(SDQ)/6-311+G(d,p) results yields reaction enthalpies that are in excellent agreement with the experimental values (within 1.9 kcal/mol; entry 12). Such excellent agreement is also obtained with the MP4(SDQ)/6-311+G(d,p), QCISD(T)/6-311+G(d,p) and CBS-Q computations, but at significantly higher computational costs. Given this result, the 6-311+G(d,p) basis set provides an overall good compromise between accuracy and computational efficiency, just as it does for the B3LYP computations. Since no significant differences in the optimized geometries are found between levels of theory that use the 6-311G(d,p) or 6-311+G(d,p) basis sets, the former can be used for all optimizations with these methods without loss of accuracy.

The results of B3LYP/6-311+G(d,p) (entry 4), corrected MP2/6-311+G(d,p) (entry 12), QCISD(T)/6-311+G(d,p) (entry 14), and CBS-Q (entry 15) calculations are plotted against the experimental values of the reaction enthalpies in Figure 2. Linear regression of the fits of the calculations vs the experiments gives for all types of calculations correlation coefficients close to unity. For the B3LYP/6-311+G(d,p) calculations the slope is 1.17, indicating that this method intrinsically overestimates the (de)-stabilizing effect of the substituents, while the intercept is close to zero (as it should be, ideally). The post-HF and the CBS-Q methods have slopes much closer to unity, but the intercepts are all further from zero than for the B3LYP/6-311+G(d,p) result, showing (a small but systematic) deviation from the experimental reaction enthalpies.

Comparison of the reaction enthalpies obtained for the α-substituted vinyl cations with those obtained for the previously studied α-substituted ethyl cations CH$_3$−C(+)HR5 shows that for R = CH═CH$_2$, CH$_3$, and Cl slightly higher stabilization energies are calculated for the vinyl cations (Table 2). Only for R = F a striking difference between the two systems is found. The α-fluoro substituent stabilizes the ethyl cation by about 7 kcal/mol, while it *destabilizes* the vinyl cation by 8 kcal/mol. The difference in stabilization is presumably related to the different hybridizations of the formally positively charged carbon atom in vinyl cations (sp) and in ethyl cations (sp^2). Because of the higher s-character in the C−R bond at sp-hybridized C$_α$ atoms than at sp^2-hybridized ones, the electronegativity of C$_α$ is higher in vinyl cations than in ethyl cations.[17] This causes inductive effects of substituents attached to sp-

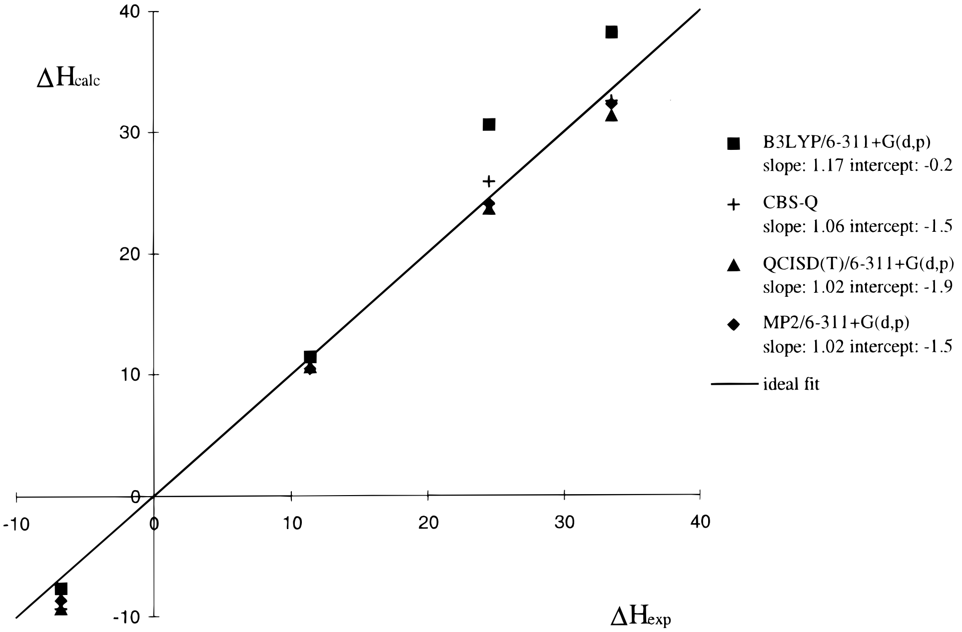

Figure 2. Calculated reaction enthalpies of eq 1 obtained using B3LYP/6-311+G(d,p) (entry 4); corrected MP2/6-311+G(d,p) (entry 12); QCISD-(T)/6-311+G(d,p) (entry 14), and CBS-Q (entry 15) versus the experimental reaction enthalpies.

TABLE 2: Reaction Enthalpies for α-Substituted Ethyl and Vinyl Compounds

	$CH{=}CH_2$	CH_3	Cl	F
B3LYP/6-311+G(d,p)				
ethyl cations[a]	37.3	23.4	10.6	7.1
vinyl cations (entry 4)	38.1	30.6	11.5	−7.7
MP2/6-311+G(d,p)				
ethyl cations[a]	30.9	17.1	9.7	6.0
vinyl cations (entry 12)	32.2	24.0	10.4	−8.6
QCISD(T)				
ethyl cations[a]	27.88	17.09	10.89	6.35
vinyl cations (entry 14)	31.29	23.61	10.53	−9.32
CBS-Q				
ethyl cations[a]	31.98	18.63	10.14	7.02
vinyl cations (entry 15)	32.55	25.89	11.17	−9.25

[a] Reaction enthalpies calculated according to ref 5.

hybridized C_α atoms to be more pronounced. The higher electronegativity manifests itself in an increased demand of stabilization of the positive charge by substituents, as becomes obvious from the higher values of ΔH in vinyl cations than in the corresponding ethyl cations (Table 2) for R = $CH{=}CH_2$, CH_3, and Cl. The difference in stabilization is smaller for R = $CH{=}CH_2$ (1.5 kcal/mol on average) than for R = CH_3 (7.0 kcal/mol on average). This is also the effect of a difference in hybridization, and thus to a difference in electronegativity, now of the substituent: sp^2 for $CH{=}CH_2$ and sp^3 for CH_3. Fluorine is a significantly stronger inductive electron-withdrawing substituent than the other three substituents. This destabilizing inductive effect is stronger in vinyl cations than the stabilization by resonance effects, which in the vinyl cations is only slightly larger (C−F bond order increases 0.37−0.40, depending on the method used; Table 5; vide infra) than in the corresponding ethyl cation (C−F bond order increases 0.34−0.38).[5] These oppositely directed effects cause the overall destabilization by α-F in vinyl cations, while they lead to an overall stabilization in ethyl cations. In comparison, for R = Cl, the inductive effects are significantly smaller due to the lower electronegativity of Cl, and the (stronger) resonance effects are in that case apparently able to compensate the differential inductive effects between α-Cl substituted ethyl and vinyl cations. As a result, the α-Cl substituent stabilizes in both the ethyl and vinyl cations, and in fact to nearly the same extent. On the basis of this analysis one would also expect differences in stabilization between ethyl and vinyl cations in the case of other α-substituents which have both stabilizing resonance and destabilizing inductive ability as e.g. the α-OH substituent.[18]

Electronic Properties. The electronic properties of the molecules under study have been analyzed using the Mulliken,[19] the NBO,[8] and the AIM[9] methods. The results of the Mulliken method show a large basis set and method dependence,[20,21] which makes them unsuitable for this purpose. They are therefore only given in the Supporting Information. The results of the NBO and AIM methods, on the other hand, are only marginally dependent on the basis set and method used. For example, the overall range in the NBO-calculated charge increases on substituent R and on the substituted carbon atom C_α on going from the neutral precursors to the α-substituted vinyl cations is less than 0.04 charge units (Table 3). A selection of the NBO-calculated charges and bond orders is depicted in Figure 3. (The choice of NBO rather than AIM data is discussed later.)

The charge delocalization onto R is largest for Cl and follows the order Cl > $CH{=}CH_2$ > F > CH_3 (Table 3). For R = Cl more than half of the positive charge is in fact found on the α-substituent, while for R = CH_3 a charge increase of only about 0.22 is observed. The charge increases at C_α follow the opposite order (CH_3 > F > $CH{=}CH_2$ > Cl) compared to the charge increase at R (Table 3). The charge increases at C_β which can be deduced from the data in Table 3, given the unity charge of the cations- are almost equal for all substituents (0.19−0.24, B3LYP; 0.16−0.21 post-HF).

In Table 4 the AIM-derived charge increases on R and C_α are given. (AIM properties could not be calculated using the 6-311++G(3df,3pd) basis set.[22]) The AIM-calculated charge increases show minor basis set effects, similar to the NBO results, with the exception that the 6-31G(d) basis set in some cases gives larger charge separations at C_α and R than the larger basis sets. The method dependency (B3LYP vs MP2) on the AIM-derived charge increseases is also small ranging from 0.003 to 0.025 for the substituents under study.

TABLE 3: Increases in NBO-Calculated Positive Charge at Substituent R and at C_α between the Neutral Species and the Corresponding Vinyl Cations

	R				C_α			
	CH═CH$_2$	CH$_3$	Cl	F	CH═CH$_2$	CH$_3$	Cl	F
B3LYP/6-31G(d)	0.422	0.234	0.522	0.239	0.377	0.514	0.239	0.497
B3LYP/6-311G(d,p)	0.402	0.223	0.519	0.247	0.415	0.544	0.257	0.502
B3LYP/6-311+G(d,p)[a]	0.403	0.224	0.522	0.258	0.413	0.539	0.252	0.499
B3LYP/6-311+G(d,p)	0.403	0.224	0.519	0.260	0.412	0.532	0.255	0.499
B3LYP/6-311++G(d,p)[b]	0.403	0.222	0.519	0.260	0.414	0.534	0.257	0.502
B3LYP/6-311++G(3df,3pd)[b]	0.401	0.220	0.518	0.256	0.419	0.539	0.258	0.508
MP2/6-31G(d)	0.420	0.220	0.538	0.248	0.406	0.560	0.253	0.521
MP2/6-311G(d,p)	0.403	0.212	0.530	0.253	0.441	0.588	0.278	0.523
MP2/6-311+G(d,p)[c]	0.404	0.212	0.532	0.263	0.440	0.585	0.274	0.524
MP2/6-311+G(d,p)	0.405	0.212	0.530	0.266	0.440	0.580	0.271	0.523
MP4(SDQ)/6-311+G(d,p)[d]	0.388	0.205	0.517	0.260	0.443	0.573	0.275	0.519

[a] Single-point (SP) calculation at the B3LYP/6-311G(d,p)-optimized geometry. [b] SP calculation at the B3LYP/6-311+G(d,p)-optimized geometry. [c] SP calculation at the MP2/6-311G(d,p)-optimized geometry. [d] SP calculation at the MP2/6-311+G(d,p)-optimized geometry.

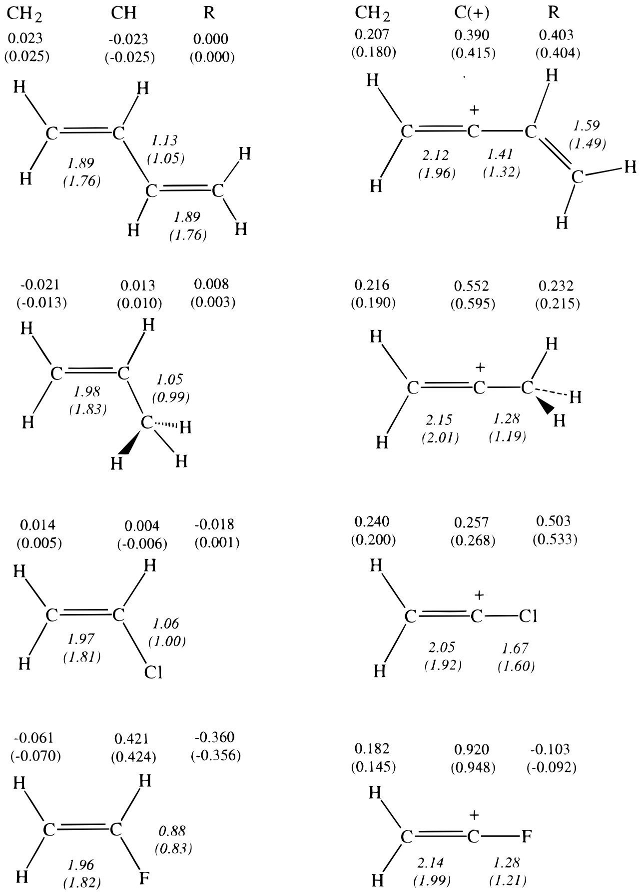

Figure 3. Typical NBO-calculated positive charges for the CH$_2$, CH, C(+) and R moieties and (in italics) bond orders computed for α-R substituted vinyl cations with R = CH═CH$_2$, CH$_3$, Cl, and F and the neutral precursors at B3LYP/6-311G(d,p) and (in parentheses) MP2/6-311G(d,p).

Nevertheless, the NBO and AIM charges show remarkable differences. For R = F, AIM charge increases of ∼0.1 are found at both C_α and R, which are substantially smaller than that computed with the NBO method. Moreover, the AIM charges at the carbon atom that is formally positively charged in the vinyl cations (C_α) show for all other substituents studied a *negative* charge development in going from the neutral compounds to the corresponding vinyl cations (Table 4). Actually, *negative* AIM charges at that atom are calculated. This observation is surprising and counterintuitive, but not without precedents: a negative charge at C_α of −0.15 was calculated using the AIM method for the vinyl cation classical (open) structure,[23] and also in the *tert*-butyl cation a negative charge of −0.10 was found.[24] As a consequence of the attribution of extra electron density at C_α large positive charge increases on R and C_β are calculated (ca. +0.6 at R and +0.7 at C_β) for all substituents, except R = F.

These unexpected negative charges might be caused by a systematic overestimation in AIM of the electron density on electronegative atoms. As the location of the zero-flux surface determines the size of the basin of an atom in a molecule in the AIM method, this also determines the amount of electron density that is attributed to that atom. This location depends not only on the electronegativity of the atoms but also on the effective nuclear charge of those atoms.[25] Such differences in effective nuclear charge cause an exaggeration of the electron density on electronegative atoms. Since the effective nuclear charge is much higher on C_α in the vinyl cations than on C_α in the neutral precursors, this results in a considerable exaggeration of the electron density on C_α, which in many cases even leads to negative charges on a formally positively charged carbon atom. The magnitude of this artifact will depend on the precise electronic structure of the cation under study, and the end result (positive or negative AIM charges on the formally positively charged carbon atom) will thus be system-dependent. For example, such counterintuitive negative charges are not computed for the previously studied α-substituted ethyl cations.[5]

The AIM and NBO methods thus differ in their predictions of the electronic structures for all α-substituted vinyl cations. This includes the degree of delocalization of the charge over the cations. According to NBO the charge increase spreads over the whole molecule. The AIM method, on the other hand, predicts, except for R = F, an alternating charge distribution with negative values on C_α and positive values on R and C_β. Besides these general differences, also the effects of substituents on the charge distribution are not the same. The order of the NBO-computed charge increase at substituent R is Cl > CH═CH$_2$ > F > CH$_3$. This contrasts with the—suspicious—AIM charge increase at R (CH═CH$_2$ > Cl > CH$_3$ > F). As can be expected, the order of charge increase at C_α differs for both methods.

The bond order increases obtained in going from the neutral molecules to the corresponding vinyl cations are given in Tables 5 and 6. The NBO- and AIM-derived bond order increases do not show any significant basis set dependence for basis sets larger than 6-31G(d). For all substituents positive bond order increases are calculated for C_α−R and C_β═C_α with both the NBO and AIM methods. The largest increase in bond order

TABLE 4: Increases in AIM-Calculated Positive Charge at Substituent R and at C_α between the Neutral Compounds and the Corresponding Vinyl Cations

	R				C_α			
	$CH{=}CH_2$	CH_3	Cl	F	$CH{=}CH_2$	CH_3	Cl	F
B3LYP/6-31G(d)	0.811	0.544	0.571	0.092	−0.397	−0.401	−0.280	0.058
B3LYP/6-311G(d,p)	0.691	0.538	0.554	0.112	−0.297	−0.252	−0.183	0.123
B3LYP/6-311+G(d,p)[a]	0.695	0.531	0.555	0.114	−0.306	−0.257	−0.189	0.118
B3LYP/6-311+G(d,p)	0.683	0.530	0.554	0.112	−0.304	−0.257	−0.189	0.122
B3LYP/6-311++G(d,p)[b]	0.695	0.531	0.554	0.117	−0.306	−0.257	−0.189	0.122
MP2/6-31G(d)	0.703	0.560	0.594	0.090	−0.428	−0.426	−0.152	0.073
MP2/6-311G(d,p)	0.695	0.546	0.565	0.109	−0.321	−0.285	−0.206	0.123
MP2/6-311+G(d,p)[c]	0.698	0.546	0.568	0.110	−0.330	−0.291	−0.208	0.128
MP2/6-311+G(d,p)	0.698	0.545	0.567	0.107	−0.329	−0.291	−0.213	0.132
MP4(SDQ)/6-311+G(d,p)[d]	0.708	0.550	0.573	0.108	−0.368	−0.322	−0.241	0.119

[a] Single-point (SP) calculation at the B3LYP/6-311G(d,p)-optimized geometry. [b] SP calculation at the B3LYP/6-311+G(d,p)-optimized geometry. [c] SP calculation at the MP2/6-311G(d,p)-optimized geometry. [d] SP calculation at the MP2/6-311+G(d,p)-optimized geometry.

TABLE 5: Increases in NBO-Calculated Bond Order between the Neutral Compounds and the Corresponding Vinyl Cations

	$C_\alpha-R$				$C_\alpha{=}C_\beta$			
	$CH{=}CH_2$	CH_3	Cl	F	$CH{=}CH_2$	CH_3	Cl	F
B3LYP/6-31G(d)	0.28	0.21	0.61	0.39	0.23	0.17	0.10	0.18
B3LYP/6-311G(d,p)	0.28	0.23	0.61	0.39	0.23	0.17	0.10	0.18
B3LYP/6-311+G(d,p)[a]	0.28	0.23	0.61	0.40	0.23	0.17	0.10	0.18
B3LYP/6-311+G(d,p)	0.28	0.22	0.61	0.40	0.23	0.17	0.10	0.18
B3LYP/6-311++G(d,p)[b]	0.28	0.22	0.61	0.40	0.23	0.17	0.10	0.17
B3LYP/6-311++G(3df,3pd)[b]	0.28	0.22	0.61	0.40	0.23	0.17	0.10	0.17
MP2/6-31G(d)	0.27	0.19	0.60	0.37	0.20	0.18	0.11	0.18
MP2/6-311G(d,p)	0.27	0.20	0.61	0.38	0.20	0.17	0.10	0.17
MP2/6-311+G(d,p)[c]	0.27	0.20	0.60	0.39	0.20	0.17	0.11	0.17
MP2/6-311+G(d,p)	0.27	0.20	0.60	0.39	0.20	0.17	0.11	0.17
MP4(SDQ)/6-311+G(d,p)[d]	0.27	0.18	0.57	0.37	0.18	0.15	0.08	0.14

[a] Single-point (SP) calculation at the B3LYP/6-311G(d,p)-optimized geometry. [b] SP calculation at the B3LYP/6-311+G(d,p)-optimized geometry. [c] SP calculation at the MP2/6-311G(d,p)-optimized geometry. [d] SP calculation at the MP2/6-311+G(d,p)-optimized geometry.

TABLE 6: Increases in AIM-Calculated Bond Order between the Neutral Compounds and the Corresponding Vinyl Cations

	$C_\alpha-R$				$C_\alpha{=}C_\beta$			
	$CH{=}CH_2$	CH_3	Cl	F	$CH{=}CH_2$	CH_3	Cl	F
B3LYP/6-31G(d)	0.32	0.17	0.60	0.18	0.12	0.11	0.05	0.04
B3LYP/6-311G(d,p)	0.31	0.19	0.60	0.21	0.16	0.17	0.12	0.09
B3LYP/6-311+G(d,p)[a]	0.31	0.19	0.59	0.21	0.17	0.17	0.12	0.09
B3LYP/6-311+G(d,p)	0.31	0.19	0.59	0.21	0.17	0.17	0.12	0.09
B3LYP/6-311++G(d,p)[b]	0.31	0.19	0.59	0.21	0.17	0.17	0.12	0.09
MP2/6-31G(d)	0.28	0.14	0.60	0.14	0.09	0.11	0.05	0.03
MP2/6-311G(d,p)	0.29	0.15	0.59	0.19	0.13	0.15	0.09	0.08
MP2/6-311+G(d,p)[c]	0.28	0.15	0.59	0.19	0.13	0.16	0.10	0.07
MP2/6-311+G(d,p)	0.28	0.16	0.58	0.19	0.13	0.16	0.10	0.07
MP4(SDQ)/6-311+G(d,p)[d]	0.27	0.13	0.56	0.18	0.09	0.13	0.05	0.02

[a] Single-point (SP) calculation at the B3LYP/6-311G(d,p)-optimized geometry. [b] SP calculation at the B3LYP/6-311+G(d,p)-optimized geometry. [c] SP calculation at the MP2/6-311G(d,p)-optimized geometry. [d] SP calculation at the MP2/6-311+G(d,p)-optimized geometry.

(+0.6) is found for $C_\alpha-Cl$, with both the NBO and AIM method. This is higher than that for $C_\alpha-CH{=}CH_2$ (+0.3), which is reflected in the change of the computed $C_\alpha-Cl$ and $C_\alpha-CH{=}CH_2$ bond lengths (see Figure 1). For R = CH_3 the smallest increase in $C_\alpha-R$ bond order is found: +0.2. For these three substituents NBO and AIM give very similar results. For R = F, however, the NBO and AIM methods differ: with NBO an increase of 0.4 is found, while with AIM an increase of only 0.2 is calculated. On the basis of the decrease in $C_\alpha-R$ bond length (both in absolute and relative terms) in going from the neutral precursors to the vinyl cations, a value between that of R = $CH{=}CH_2$ and Cl would have been expected for R = F. So again the AIM results are somewhat counterintuitive, while the NBO method yields qualitatively understandable data that fit current chemical thinking. The computed bond order increases of $C_\beta{=}C_\alpha$ are for all substituents between 0.1 and 0.2. The order found for the NBO calculations ($CH{=}CH_2 > F \approx CH_3 > Cl$) differs from the one obtained via AIM computations ($CH_3 > CH{=}CH_2 > Cl > F$), but the absolute differences are small. Neither of these orders correlates with the observed reduction in $C_\beta{=}C_\alpha$ bond lengths.

In general, it can be stated that NBO and AIM yield different results for both the total charges on an atom, and for the bond order between atoms. The first is to be expected due to the different approaches that the two methods use to divide the electron density over the atoms. Especially on account of the artifact in the AIM method, significantly deviating atomic charges are calculated. Less obvious are the reasons for the sometimes significant differences in bond order increases as computed by these methods. On the basis of the counterintuitive results obtained with the AIM method for both charges and bond orders, the use of NBO-derived electronic properties is recommended over AIM-derived electronic properties for analysis of substituted vinyl cations.

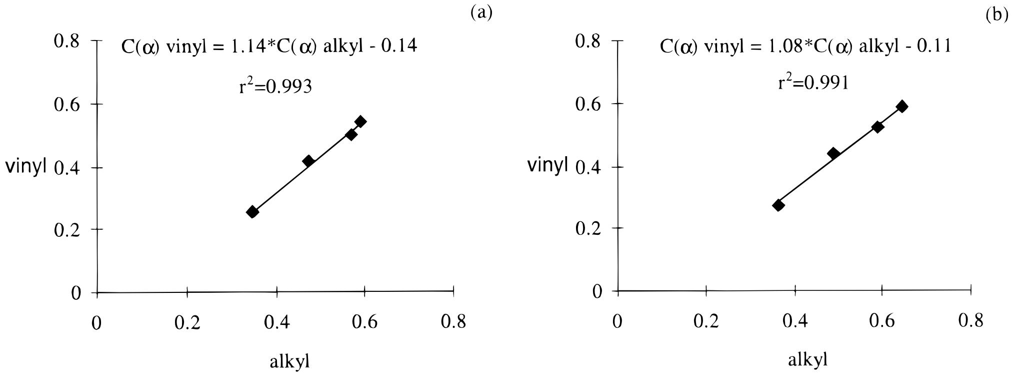

Figure 4. Charge increases on C_α for the vinyl and alkyl systems calculated using (a) B3LYP/6-311+G(d,p) and (b) MP2/6-311+G(d,p).

TABLE 7: Relative Orders Observed for Reaction Enthalpies and NBO-Derived Electronic Properties

	order[a]
reaction enthalpy	$CH{=}CH_2 > CH_3 > Cl > F$
charge increase at C_α	$CH_3 > F > CH{=}CH_2 > Cl$
charge increase at R	$Cl > CH{=}CH_2 > F > CH_3$
bond order increase between C−R	$Cl > F > CH{=}CH_2 > CH_3$
bond order increase between C═C	$CH{=}CH_2 > F \approx CH_3 > Cl$

[a] The observed orders are independent of the level of computation.

In Table 7 the orders of the NBO-computed charge and bond order increases as a function of R are given as well as the order observed for the reaction enthalpies. Analysis of those results shows that the charge increases at C_α and R and the bond order increases at C═C and C−R do *not* correlate with the reaction enthalpies of the isodesmic reaction depicted in eq 1. Such a lack of correlation has been previously observed for a series of α-R substituted vinyl cations (with R = H, CH_3, $CH{=}CH_2$, C≡CH, cyclopropyl, and phenyl).[6c] In that case the electronic properties were derived from Mulliken population analysis and the stabilities were computed at RHF/STO-3G and RHF/4-31G. The NBO method, which unlike the Mulliken analysis displays only small method and basis set dependencies, and the high levels of theory used here firmly establish that, as in the case of α-substituted ethyl cations,[5] there is no relation between the charge development on an α-substituent and the thermochemical (de)stabilization offered by that substituent. The (de)stabilization depends on the hybridization of the atoms involved, the length of the bond in the cation (both in absolute terms, and as seen in a relative sense with respect to the bond length in the corresponding neutral system), and the relative contributions of inductive and resonance effects. For example, the resonance effects may have opposite directions, which minimize the change of the overall charge on an atom, while the energetic contributions of the two may still be significantly different. As a result, simple relations between reaction enthalpy and charge increases at C_α and R may only be found for small subsets, and indeed have been recently found for the series of vinyl cations $H_2C{=}C(+){-}R$ with R = F, Cl, Br, and I.[18]

The only geometrical feature that correlates clearly with the experimentally observed reaction enthalpies of eq 1 is found in the $C_\beta H_2$ moiety. Because of hyperconjugative effects, the $C_\beta{-}H$ bonds elongate in going from the neutral molecule to the α-substituted vinyl cation (by 0.005−0.016 Å). A plot of this elongation vs the reaction enthalpies calculated for the four different substituents under study shows a clear linear correlation (r^2 = 0.96 for both B3LYP and MP2). In other words, the computed degree of hyperconjugation, reflected in $C_\beta{-}H$ bond lengths, in itself a small effect, is directly related to the reaction enthalpy of eq 1. To see whether this is a truly general result, more α-substituents have to (and will) be considered.

Finally, the charge increases at C_α and R in the vinyl system correlate well with the charge increases in the corresponding ethyl systems. A plot of these data (Figure 4) yields for MP2 and B3LYP the following result; MP2 data: charge increase on $C_\alpha^{vinyl} = 1.14$(charge increase on C_α^{ethyl}) − 0.14; $r^2 = 0.993$; B3LYP data: charge increase on $C_\alpha^{vinyl} = 1.08$(charge increase on C_α^{ethyl}) − 0.11; $r^2 = 0.991$. The generality of such correlations will be subjected to further investigations over a wider range of α-substituents.[18]

Conclusions

Computations of α-substituted vinyl cations ($H_2C{=}C(+)R$) and their neutral precursors ($H_2C{=}CHR$) were performed using B3LYP and post-HF methods with various basis sets ranging from 6-31G(d) to 6-311++G(3df,3pd) and the CBS-Q method. The electronic properties of the compounds under study at the different levels of theory were analyzed using the NBO and AIM methods.

The geometries of the vinyl cations and their neutral precursors are rather insensitive to the method or basis set used for optimization. The choice of method and basis set is of greater importance for the reaction enthalpies to determine the miminum level at which quantitative acccuracy can be obtained. To obtain this accuracy for all substituents under study the 6-311+G(d,p) basis set is needed with the B3LYP or the MP2 method, regardless of whether the geometry optimization is performed at the 6-311G(d,p) or the 6-311+G(d,p) basis set, except for R = H, where B3LYP or MP4(SDQ) instead of MP2 is needed to give sufficient accuracy.

The charge and bond order increases on going from the neutral precursors to the vinyl cations under study are analyzed using the NBO and the AIM method. Both methods show only small method and basis set dependency. The differences between the methods, however, are large. The NBO-derived charge increases are spread out over the molecule, while the AIM method predicts an alternating charge increase with positive C_β and R and for all substituents, except for R = F, negative charge increases at the carbocationic center. These counterintuitive charge increases can be the result of an overestimation of the electron density at electronegative centers in the AIM method.

The order of stabilization is invariant to the method and basis set used: $CH{=}CH_2 > CH_3 > Cl > F$. All substituents except α-fluorine are thermochemically stabilizing. In fact, an α-F substituent destabilizes vinyl cations, while for α-F a stabilizing effect was calculated for ethyl cations.[5]

The α-Cl substituent stabilizes the vinyl cation by π-donation, which is reflected in the large decrease in bond length and increase in bond order. This electron donation is larger than that offered by $CH{=}CH_2$ or CH_3, but due to the inductive effect of chlorine the amount of stabilization is less that those of the latter substituents. The α-F substituent shows also some π-donation toward the vinyl cation, but because the strong inductive effect of fluorine the α-F substituent is destabilizing.

The α-$CH{=}CH_2$ and α-CH_3 substituents strongly stabilize the vinyl cation, although in different ways. The α-$CH{=}CH_2$ substituted vinyl cation is stabilized via π-donation and can be best described as an allyl cation substituted by a methylene group. The $C_\alpha{-}R$ bond length is almost the same as the $C{=}C$ bond length in the substituent. The α-CH_3 substituent stabilizes mainly via hyperconjugation of the C−H bond in the substituent, which has maximum overlap with the empty p-orbital in the vinyl cation.

Stabilization of the vinyl cations is not only provided by most of the α-substituents, but also by hyperconjugation of the hydrogen atom at C_β, which is reflected in the elongation of the $C_\beta{-}H$ bonds and the increase of the bond order between $C_\beta{=}C_\alpha$. The extent of the $C_\beta{-}H$ bond elongation correlates well with the reaction enthalpies.

Acknowledgment. K.v.A. is grateful to The Netherlands Foundation of Chemical Research (SON) for partial funding of this research.

Supporting Information Available: Tables of Gaussian 94 archive files, zero-point energies, and all relevant charges and bond orders for all compounds studied. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Grob, C. A. Vinyl cations: how it all began. In *Dicoordinated Carbocations*; Rappoport, Z., Stang, P. J., Eds.; Wiley: West Sussex, UK, 1997; Chapter 1. (b) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. *Vinyl Cations*; Academic Press: New York, 1979.

(2) (a) Kitamura, T.; Taniguchi, H.; Tsuno, Y. *Dicoordinated Carbocations*; Rappoport, Z., Stang, P. J., Eds.; Wiley: West Sussex, UK, 1997; Chapter 7. (b) Rappoport, Z. *Reactive Intermediates;* Abramovitch, R. A., Ed.; Plenum: New York, 1983; Chapter 7, Vol. 3.

(3) (a) Lodder, G.; *Dicoordinated Carbocations*; Rappoport, Z., Stang, P. J., Eds.; Wiley: West Sussex, UK, 1997; Chapter 8. (b) Kropp, P. J. *CRC Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M., Song, P.-S., Eds.; CRC Press: Boca Raton, FL, 1995; Chapter 84. (c) Kitamura, T. *CRC Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M., Song, P.-S., Eds.; CRC Press: Boca Raton, FL, 1995; Chapter 85. (d) Lodder, G.; Cornelisse, J. *The Chemistry of Functional Groups: Supplement D2*; Patai, S., Rappoport, Z., Eds.; Wiley, Chichester, UK, 1995; Chapter 16.

(4) Apeloig, Y.; Müller, T. *Dicoordinated Carbocations*; Rappoport, Z., Stang, P. J., Eds.; Wiley: West Sussex, UK, 1997; Chapter 2.

(5) Van Alem, K.; Sudhölter, E. J. R.; Zuilhof, H. *J. Phys. Chem. A* **1998**, *102*, 10860−10868.

(6) References to R = H: (n) and (o). References to R = $CH{=}CH_2$: (c), (q), and (r). References R = CH_3: (a), (b), (c), (e), (f), (g), (h), (k), (m), and (q). References to R = Cl: (d), (l), (p), and (q). References to R = F: (b), (d), (j), and (q). (a) Radom, L.; Hariharan, P. C.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 6531−6544. (b) Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 1291−1296. (c) Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Org. Chem.* **1977**, *42*, 3004−3011. (d) Kollman, P.; Nelson, S.; Rothenberg, S. *J. Phys. Chem.* **1978**, *82*, 1403−1406. (e) Köhler, H.-J.; Lischka. H. *J. Am. Chem. Soc.* **1979**, *101*, 3479−3486. (f) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649−5657. (g) Mayr, H.; Schneider, R.; Wilhelm, D.; Schleyer, P. v. R. *J. Org. Chem.* **1981**, *46*, 5336−5340. (h) Apeloig, Y.; Stanger, A. *J. Org. Chem.* **1982**, *46*, 1462−1468. (i) Curtiss, L. A.; Pople, J. A. *Chem. Phys.* **1988**, *88*, 7405−7409. (j) Stams, D. A.; Thomas, T. D.; McLaren, D. C.; Ji, D.; Morton, T. H. *J. Am. Chem. Soc.* **1990**, *112*, 1427−1434. (k) McAllister, M.; Tidwell, T. T.; Peterson, M. R.; Csizmadia, I. G. *J. Org. Chem.* **1991**, *56*, 575−580. (l) Hamilton, T. P.; Schaefer III, H. F. *J. Am. Chem. Soc.* **1991**, *113*, 7147−7151. (m) Foresman, J. B.; Wong, M. W.; Wiberg, K. B.; Frisch, M. J. *J. Am. Chem. Soc.* **1993**, *115*, 2220−2226. (n) Tse, J. S.; Klug, D. D.; Laasonen, K. *Phys. Rev. Lett.* **1995**, *74*, 876−879. (o) Lindh, R.; Rice, J. E.; Lee, T. J. *J. Chem. Phys.* **1991**, *94*, 8008−8014. (p) Rodriquez, C. F.; Bohme, D. K.; Hopkinson, A. C. *J. Org. Chem.* **1993**, *58*, 3344−3349. (q) Apeloig, Y.; Biton, R.; Zuilhof, H.; Lodder, G. *Tetrahedron Lett.* **1994**, *35*, 265−268. (r) Cunje, A.; Rodriquez, C. F.; Lien, M. H.; Hopkinson, A. C. *J. Org. Chem.* **1996**, *61*, 5212−5220.

(7) *Gaussian 94* (Revision D4); Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A. L.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian Inc.: Pittsburgh, PA, 1995.

(8) NBO version 3.1; Glendeling, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F.

(9) Bader, R. F. W. *Acc. Chem. Res.* **1985**, *18*, 9−15. (b) Cioslowski, J.; Nanayakkara, A.; Challacombe, M. *Chem. Phys. Lett.* **1993**, *203*, 137−142.

(10) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(11) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(12) Ochterski, J. W.; Petersson, G. A.; Montgomery, J. A. *J. Chem. Phys.* **1996**, *104*, 2598−2619.

(13) (a) Bogey, M.; Cordonnier, M.; Demuynck, C.; Destombes, J. L. *Astrophys. J.* **1992**, *399*, L103−L105. (b) Bogey, M.; Bolvin, H.; Cordonnier, M.; Demuynck, C.; Destombes, J. L. *Can. J. Phys.* **1994**, *72*, 967−970.

(14) (a) Scaling factors were 0.9806 for all B3LYP calculations, 0.9661 for MP2/6-31G(d), and 0.97481 for MP2/6-311G(d,p) and MP2/6-311+G-(d,p), according to ref 14b. (b) Scott, P. A.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502−16513.

(15) The heats of formation of all neutral compounds, except vinyl fluoride, and of the vinyl cation: Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: London 1970. Vinyl fluoride: (a) Heck, A. J. R. Ph.D. Thesis, University of Amsterdam, 1993. (b) Kolesov, V. P.; Papina, T. S. *Russ. J. Phys. Chem.* **1970**, *44*, 611−613. Vinyl chloride, additional heats of formation: ref 15a. (c) Levanova, S. V.; Treger, Y. A.; Velichko, S. M.; Rozhnov, A. M. *Russ. J. Phys. Chem.* **1976**, *50*, 1148. (d) Alfassi, Z. B.; Golden, D. M.; Benson, S. W. *J. Chem. Thermodyn.* **1973**, *5*, 411−420. α-$CH{=}CH_2$ vinyl cation: (e) Lossing, F. P.; Holmes, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 6917−6920. α-CH_3 vinyl cation: ref 1b, p 7. (f) Bowers, M. T. *Gas-Phase Ion Chemistry*; Academic Press: New York, 1979; Vol. 2, Chapter 9. α-Cl vinyl cation: ref 6p. α-F vinyl cation: (g) Stams, D.; Thomas, T. D.; Maclaren, D. C.; Ji, D.; Morton T. H. *J. Am. Chem. Soc.* **1990**, *112*, 1428−1434.

(16) The experimental uncertainty for R = CH_3 is 4.9 kcal/mol.[15] For the other substituents it was not possible to determine the uncertainties, since only one experimental heat of formation, without specified experimental error, for those substituted vinyl cations is reported. Based on the experimental uncertainty for R = CH_3 and the uncertainties found for the experimental reaction enthalpies of the less elusive alkyl cations,[5] there is no reason to assume that the uncertainties for the other reaction enthalpies will be substantially lower than 5 kcal/mol. The benchmarking, however, is not performed using the reaction enthalpy data for one individual substituent, but using the data of the set of substituents (Figure 2), which partly annuls the individual uncertainties.

(17) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 1001−1012.

(18) Van Alem, K.; Zuilhof, H.; Lodder, G., manuscript in preparation.

(19) (a) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833−1840. (b) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1841−1846. (c) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 2238−2342. (d) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 2343−2346.

(20) For instance, the Mulliken-calculated charge increase on substituent R on going from the neutral precursors to the α-substituted vinyl cations changes from 0.458 to 0.262 on changing the basis set from B3LYP/6-311++G(d,p) to B3LYP/6-311++G(3df,3pd) for R = $CH{=}CH_2$ and from 0.252 to 0.663 on going from MP2/6-311G(d,p) to MP2/6-311+G(d,p) for R = CH_3, while changing these basis sets has virtually no effect on the reaction enthalpies (Table 1).

(21) Such a dependence has been noted previously.[5,21b] (b) Bachrach, S. M. *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH Publishers: New York, 1994; pp 379−390.

(22) In Gaussian 94 only basis sets with only s, p, and d functions can be used for AIM calculations.

(23) Glaser, R. *J. Phys. Chem.* **1989**, *93*, 7993−8003.

(24) Bader, R. F. W. *Can. J. Chem.* **1985**, *64*, 1036−1045.

(25) Perrin, C. L. *J. Am. Chem. Soc.* **1991**, *113*, 2865−2868.