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Delocalization Does Not Always Stabilize: A Quantum Chemical Analysis of α-Substituent Effects on 54 Alkyl and Vinyl Cations

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The effects of α-substituents on alkyl and vinyl cations are studied using high-level ab initio calculations. The geometries, stabilities, and electronic properties of 27 alkyl cations and 27 vinyl cations with α-substituents are computed at the B3LYP/6-311+G(d,p), MP2/6-311+G(d,p), and CBS-Q levels. The substituents studied vary from strongly destabilizing (e.g., α-CN and α-CF_3) to strongly stabilizing (e.g., α-$OSi(CH_3)_3$ and α-NH_2). The calculations show that in the case of vinyl cations the stabilization provided by the α-substituents is larger by an average value of 4 kcal/mol than for the alkyl ones. This is the result of the intrinsically lower stability of vinyl cations (on average 17 kcal/mol). However, strong inductively donating or withdrawing α-substituents show different behavior. Because of the high amount of s character in the carbon−α-substituent bond in the vinyl cations (sp hybridized), more pronounced σ effects are found than in the corresponding alkyl cations, leading to lower stabilization for inductively withdrawing α-substituents and higher stabilization for inductively donating ones. Thus, distinct effects of α-substituents on the stabilization of the cations are observed. However, no correlation is found between NBO-computed charge increases or bond-order increases at either the carbocationic center or at the α-substituent of the molecule and the stability provided by an α-substituent. This demonstrates the conceptual difference between stabilizing and electron-donating effects. Only for the C_β−H hyperconjugative effect in the vinyl systems is a correlation with the computed reaction enthalpies observed. Finally, the effect of leaving-group variation is studied. Changing the leaving group from H to Cl yields geminal effects ranging from 7 kcal/mol destabilization to 9 kcal/mol stabilization of the neutral precursor.

Introduction

Carbocations are reactive intermediates in many chemical reactions.[1] Numerous studies have been performed to generate alkyl cations and to a lesser extent vinyl cations by thermal[2] as well as photochemical[3] means and to establish the effects of α-substituents on their ease of formation and their stabilities.[4] A thorough analysis of α-substituent effects on carbocations, however, is hampered by the fact that information, experimental as well as theoretical, is available only for subsets of substituents.

In this paper, we present a comprehensive state-of-the-art quantum chemical investigation of the relative stabilities of carbocations as a function of a broad range of α-substituents ranging from strongly electron-donating to strongly electron-withdrawing. In total, 27 different α-substituents are considered for alkyl as well as vinyl cations, and the effects they exhibit on the geometries, stabilities, and electronic properties of the cations are analyzed. Several of these α-substituents have been the topic of previous studies.[5,6] The effect of the α-substituents R under study on the stability of alkyl cations **1** and vinyl cations **2** (relative to hydride transfer) is given by the reaction enthalpies (ΔH) of the isodesmic reactions[7] in eqs 1 and 2.

$$H_3C{-}CH_3 + \underset{\mathbf{1}}{H_3C{-}C(+)HR} \xrightarrow{\Delta H} H_3C{-}CH_2R + H_3C{-}C(+)H_2 \quad (1)$$

$$H_2C{=}CH_2 + \underset{\mathbf{2}}{H_2C{=}C(+)R} \xrightarrow{\Delta H} H_2C{=}CHR + H_2{=}C(+)H \quad (2)$$

R = CH_3, CH_2Y (Y = F, Cl, Br, OH, CN, and CF_3), $C(CH_3)_2$-OH, CHF_2, CF_3, CH=CH_2, C≡CH, CN, C_6H_5, *c*-C_3H_5, C(O)H COOH, F, Cl, Br, I, NH_2, OH, SH, $Si(CH_3)_3$, $OSi(CH_3)_3$, and NO_2). In two preceding papers, the theoretical level necessary to describe the thermodynamics of α-substituted alkyl and vinyl cations accurately has been assessed by comparing the ΔH results computed by several theoretical methods to all experimentally available data for the two classes of cations (six alkyl cations and five vinyl cations, respectively).[8,9] One of the conclusions of that work was that the CBS-Q method predicts the relative stabilities of all experimentally studied α-substituted cations to within experimental error. Drawbacks of this method, however, are the limited range of elements that can be studied and the impossibility of obtaining meaningful results for species

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that are not minima on the potential energy surface (vide infra). The other computational methods we used (B3LYP and MP2) each yielded some systematic errors in the sets of the experimentally studied cations. Clearly, an a priori prediction of the relative stabilities of cations **1** and **2** for a broad range of R requires an extension of the methods at hand.

B3LYP and MP2 computations have therefore been performed for the whole range of α-substituents, and CBS-Q computations, whenever feasible. From the data obtained for the common cases, a high-quality correlation between the B3LYP or MP2 data and the CBS-Q data is derived, which is used to convert B3LYP/MP2 data for the otherwise problematic cases to CBS-Q-like data. This gives a set of data that is either obtained via CBS-Q computations or has a CBS-Q-like quality for the whole set of α-substituents under study. Because CBS-Q computations do not allow for the analysis of electronic properties, the B3LYP and MP2 computations are used to study the electronic properties of the alkyl and vinyl cations and their neutral precursors with the NBO method.[10] Using these methods, the geometries, stabilities, and electronic properties of 54 α-R substituted cations are studied. In addition, the effect of changing the leaving group from H to Cl is investigated.

Computational Details

All computations were performed using the Gaussian 94 (revision D.4)[11] and Gaussian 98 (revisions A.6 and A.7)[12] suites of programs. Natural bond orbital (NBO) calculations were performed with the NBO 3.1 program[10] implemented therein.

Calculations on the species under study were performed using the B3LYP (Becke's three-parameter nonlocal exchange hybrid functional[13] with the nonlocal correlation functional of Lee et al.[14]) method, Møller−Plesset second-order perturbation theory, and the CBS-Q model chemistry method (values taken at 0 K).[15] All MP2 calculations take the correlation effects of all electrons into account. All B3LYP and MP2 computations were started by optimization using the 6-311G(d,p) basis set and were followed by single-point computations with the 6-311+G(d,p) basis set.

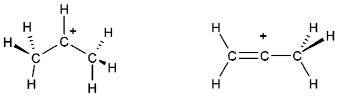
The geometries of all species under study were fully optimized. Optimizations of the parent vinyl and ethyl cations were started from a bridged (nonclassical) structure, which has previously been shown to be the global minimum.[16] For the CBS-Q calculation of the ethyl cation, the optimization and zero-point energy correction were performed at the MP2(FC)/6-31G-(d′,p′) level, instead of at the default levels (optimization at the MP2(FC)/6-31G(d′) level and zero-point energy correction[17] at the HF/6-31G(d′) level). This was necessary because the inclusion of polarization functions and electron correlation is required for a proper description of the bridged ethyl cation.[18] All optimized structures were shown to be minima on the potential energy surface via vibrational frequency computations. Next to the fully optimized structures, geometries were also considered in which constraints were used to prevent bridging and to ensure that open α-substituted cations were studied. Selected geometrical features of the species under study are discussed in the text or in the Supporting Information, whereas additionally all MP2-optimized geometries of all cations under study are available in the form of Gaussian archive files as Supporting Information. All single-point computations were performed using the SCF = tight option in Gaussian 94 or Gaussian 98.

Results and Discussion

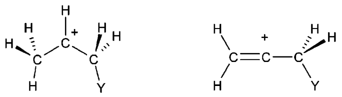
Geometries. The alkyl cations **1** and vinyl cations **2** with 27 α-substituents and their neutral precursors have been calculated using the B3LYP/6-311+G(d,p),[19] MP2/6-311+G(d,p),[19] and CBS-Q methods. Their structure and typical bond lengths (MP2 data)[20] are given in Figure 1. In the cations, compared to their neutral precursors, several structural changes have occurred. In the alkyl cations, the empty p orbital is perpendicular to the C−C(H)R plane, with the C−C−R angle close to 124° (with small variations of about 1°), and the carbocationic center is thus close to being sp^2 hybridized. The vinyl cations have the empty p orbital perpendicular to the π bond of the vinylic moiety with a C=C−R angle of 180° (± 0.5°) and are sp hybridized at the cationic center. To alleviate the destabilizing effect of the empty p orbital, two types of interactions are at work: (1) π donation from the α-substituent toward the formally positive charged carbon atom, leading to a decrease in the C−R bond length[21] and (2) hyperconjugation leading to C−H bond length increases for the C_β−H bonds present in the CH_3/CH_2 moieties of the cations or in the α-substituent, which have orbital overlap with the carbocationic center, as well as to C−C and C=C bond length decreases between C^+ and the β-carbon atoms.[22] These two effects operate simultaneously: In all cases, increases in the C_β−H bond lengths (0.02 Å) and, with three exceptions, significant decreases in the C−R bond lengths (varying from 0.06 to 0.20 Å) are observed. Only for the α-CF_3, the α-C(O)H, and the α-$Si(CH_3)_3$ substituent, C−R bond length *increases* of 0.01−0.03 Å are computed for the alkyl as well as the vinyl cations, demonstrating the lack of π donation and hyperconjugative effects for these substituents.

For 9 of the 27 α-substituents, optimization of the cations yielded at at least one theoretical level such large structural changes, by migration (α-CH_2OH, α-$C(CH_3)_2OH$, and α-$Si(CH_3)_3$) or bridging (α-CHF_2, α-CF_3, α-COH, α-COOH, α-CH_2Br, and α-NO_2), that these cations could no longer be described as α-substituted cations. The migration of hydrogen atoms or methyl groups takes place if a more stable cation will be formed; in solution, this will be an activated process, as this will also involve extensive solvent reorganization. Bridging, either of the α-substituent itself or of one of the β-hydrogen atoms, is observed both experimentally[2,3] and theoretically[5,6] for species that have destabilizing α-substituents. Because of the stabilizing effects of solvation, this phenomenon will be less pronounced in solution than in the gas phase. In addition, the presence of other more-stabilizing moieties (α-alkyl or α-phenyl) that are frequently part of experimentally studied compounds in solution[2,3] will also diminish the importance of migration/bridging. Although these migrated/bridged species are interesting in themselves, a study of the effect of α-substituents is thus limited by this phenomenon. Because the effect of α-substituents is our primary concern, only nonbridged and nonmigrated α-substituted cations are discussed; detailed information about the observed bridging and migration can be found in the Supporting Information. To prevent bridging of either the α-substituent or the β-hydrogen atoms to C^+, constraints were used during the optimization of these nine cases. In Figure 1, the geometries of these nine cations are displayed in their symmetry-constrained, open structures.

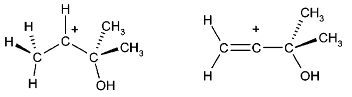
Stabilities. In our benchmark studies, it was shown that the CBS-Q method is capable of computing reaction enthalpies as depicted in eqs 1 and 2 within experimental error for all α-substituted alkyl and vinyl cations for which experimental data are available.[8,9] Therefore, the CBS-Q method is the method of choice to assess thermodynamic stability for the broad range of α-substituents studied here. The relative stabilization offered by an α-substituent R to the alkyl and vinyl cations under study was established by calculating the reaction enthalpies of eqs 1



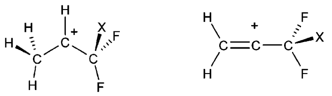
C_β–H	C–C	C–R	C_β–H	C=C	C–R
1.118	1.437	1.437	1.093	1.275	1.409



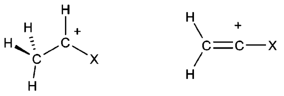
Y	C_β–H	C–C	C–R	C_β–H	C=C	C–R
F	1.120	1.434	1.449	1.096	1.274	1.427
Cl	1.121	1.436	1.440	1.096	1.274	1.413
Br	1.127	1.431	1.445[a]	1.097	1.276	1.403
OH	1.104	1.441	1.444[b]	1.095	1.275	1.419[b]
CN	1.119	1.433	1.456	1.097	1.272	1.424
CF_3	1.142	1.420	1.455	1.096	1.272	1.416



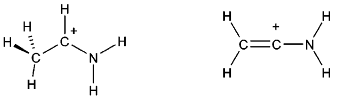
C_β–H	C–C	C–R	C_β–H	C=C	C–R
1.127	1.415	1.511[b]	1.094	1.278	1.415[b]



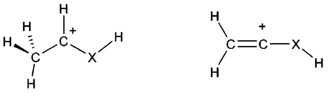
X	C_β–H	C–C	C–R	C_β–H	C=C	C–R
H	1.127	1.415	1.511[a]	1.108	1.267	1.492
F	1.132	1.408	1.529[a]	1.102	1.264	1.529



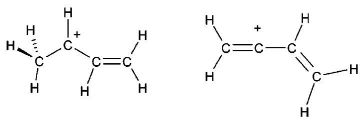
X	C_β–H	C–C	C–X	C_β–H	C=C	C–X
F	1.104	1.432	1.249	1.095	1.269	1.206
Cl	1.103	1.448	1.611	1.094	1.281	1.554
Br	1.103	1.449	1.769	1.094	1.282	1.705
I	1.102	1.457	1.944	1.093	1.286	1.884



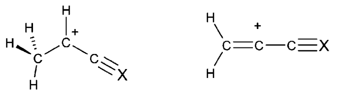
C_β–H	C–C	C–R	C_β–H	C=C	C–R
1.095	1.482	1.288	1.088	1.291	1.259



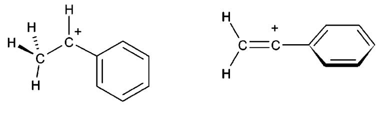
X	C_β–H	C–C	C–R	C_β–H	C=C	C–R
O	1.099	1.459	1.260	1.090	1.282	1.225
S	1.098	1.472	1.630	1.091	1.294	1.594



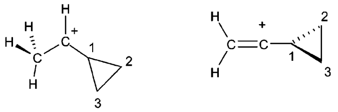
C_β–H	C–C	C–R	C_β–H	C=C	C–R
1.101	1.458	1.399	1.092	1.276	1.371



X	C_β–H	C–C	C–R	C_β–H	C=C	C–R
CH	1.104	1.455	1.374	1.094	1.286	1.331
N	1.112	1.434	1.390	1.100	1.274	1.360



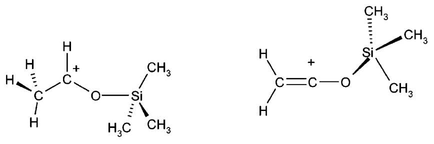
C_β–H	C–C	C–R	C_β–H	C=C	C–R
1.099	1.470	1.392	1.090	1.292	1.361



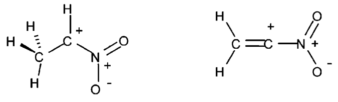
C_β–H	C–C	C–R	C_β–H	C=C	C–R
1.098	1.470	1.371	1.090	1.294	1.346

Y	C_β–H	C–C	C–Y	C_β–H	C=C	C–Y
H	1.126	1.417	1.505[a]	1.101	1.271	1.494[a]
OH	1.125	1.421	1.497[a]	1.101	1.273	1.475[a]

C_β–H	C–C	C–R	C_β–H	C=C	C–R
1.108	1.438	1.941[b]	1.098	1.282	1.910



C_β–H	C–C	C–R	C_β–H	C=C	C–R
1.097	1.469	1.243	1.085	1.295	1.197



C_β–H	C–C	C–R	C_β–H	C=C	C–R
1.097	1.474	1.423[a]	1.087	1.310	1.362[a]

Figure 1. Selected bond lengths (in Å) of the cations under study (MP2(full)/6-311G(d,p) computations). ([a]Constrained to prevent bridging, and [b]constrained to prevent migration. See the Supporting Information for more details.)

TABLE 1: Computed Reaction Enthalpies of Equations 1 and 2 for the α-Substituents under Study (CBS-Q Computations)[a]

R	alkyl	vinyl	ΔΔH[b]	R	alkyl	vinyl	ΔΔH[b]
H	0.00	0.00	0.00	F	6.95	−9.25	−16.20
CH_3	18.63	25.89	7.26	Cl	9.83	11.17	1.34
CH_2Cl	5.59	12.90	7.31	Br[h]	9.52	12.70	3.18
CH_2Br[c]	*8.66*	14.00	5.34	I[h]	13.32	20.53	7.21
CH_2OH[d]	*15.30*	*21.69*	6.39	NH_2	64.96	53.69	−11.27
$C(CH_3)_2OH$[e]	*22.71*	*25.99*	3.28	OH	37.43	25.92	−11.51
CH_2CN	−2.10	4.76	6.86	SH	36.39	38.21	1.82
CH_2CF_3	3.62	9.63	6.01	$Si(CH_3)_3$[i]	*17.30*	34.21	16.91
CH_2F	4.98	10.89	5.91	$OSi(CH_3)_3$	57.75	55.10	−2.65
CHF_2[f]	*−13.81*	−8.91	4.90	NO_2[j]	*−23.09*	*−25.44*	−2.35
CF_3[f]	*−23.56*	−16.41	7.16				
$CH{=}CH_2$	31.98	32.55	0.58				
$C{\equiv}CH$	18.17	25.64	7.48				
$C{\equiv}N$	−16.02	−11.71	4.31				
C_6H_5	36.77	54.10	17.33				
c-C_3H_5	42.97	47.06	4.11				
$C(H){=}O$[g]	*−10.25*	*−4.51*	5.74				
COOH[g]	*−8.41*	*−5.92*	2.49				

[a] CBS-Q-like data is given in italics. [b] The difference in (de)stabilization provided by the α-substituent in the alkyl and vinyl cations. [c] The C(+)−C−Br angle in the alkyl cations is constrained to 120.0°. [d] The hydrogen atoms at the α-substituent are prevented from migrating in the case of the alkyl cation by the use of symmetry. [e] The methyl groups at the α-substituent are prevented from migrating in the case of the alkyl cation by the use of symmetry. [f] The H−C−C(+) angle in the alkyl cation is constrained to 102.3°. [g] The C(+)−C−O angle is constrained to 120.0°. [h] Average of results obtained without effective core potential (ECP) and with CEP-121[33] and SDD[34] as ECPs for bromine and iodine. [i] The methyl groups are prevented from migrating by the use of symmetry. [j] The C(+)−N═O angle is constrained to 120.0°.

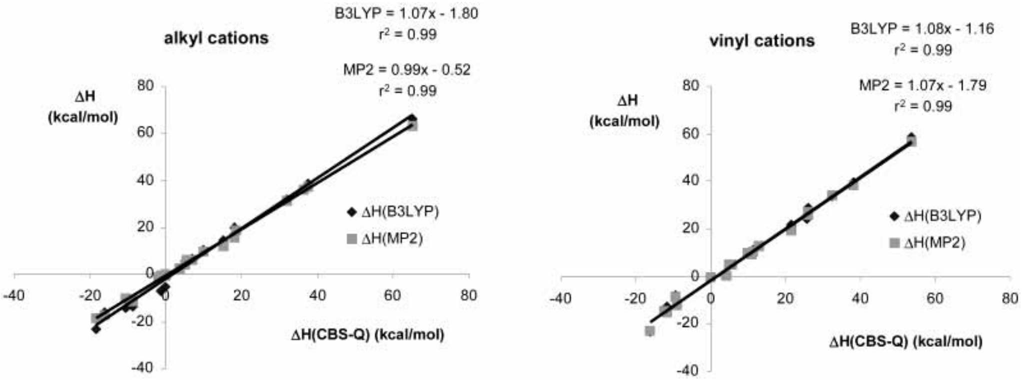


Figure 2. Correlation between B3LYP- and MP2-computed reaction enthalpies with CBS-Q-computed reaction enthalpies for the reactions depicted in eq 1 (alkyl cations, left) and eq 2 (vinyl cations, right).

and 2 for different α-substituents R. Equation 1 yields the (de)stabilization provided by the α-substituents to the alkyl cations compared to that of the alkane precursor, and eq 2 yields the corresponding property for the vinyl cations compared to that of the alkene precursor.

In Table 1, the results obtained by the CBS-Q method are given. Because of the fact that this is a composite method, it is not possible to obtain meaningful CBS-Q results for species that are not minima on the potential energy surface (e.g., the bridging species).[23] This is also the case for molecules that contain Br or I atoms because the CBS-Q method is not available for molecules that contain fourth-row elements. Nevertheless, to obtain high-quality data for these situations, the reaction enthalpies for all α-substituents under study were also computed using the B3LYP and MP2 methods with the 6-311+G(d,p) basis set.[19] The correlations between these data and the CBS-Q data for all alkyl and vinyl cations with α-substituents that can be computed with all three methods are presented in Figure 2.

The relative shortcomings of the B3LYP and MP2 computations are obvious from the observation that the slopes in Figure 2 deviate slightly from the ideal value of 1.00 and that the intercepts do not go through the origin as theoretically desired. The results of both methods do, however, show very good correlation with the CBS-Q results (r^2 > 0.98 in all cases). Using these correlations, B3LYP or MP2 results can be converted to data points with CBS-Q-like quality for those structures for which direct CBS-Q computations are not feasible. These CBS-Q-like data are used in Table 1 (printed in italics) where appropriate.

An analysis of the data in Table 1 shows that the α-substituents studied affect the stability of cations significantly, ranging from about 65 kcal/mol stabilization to 25 kcal/mol destabilization. The influence of α-substituents on a carbocation center is due to three effects: (1) inductive effects, which can be electron-donating or electron-withdrawing, (2) π donation or (partial) bridging from the α-substituents toward the cation, and (3) β-hydrogen hyperconjugative stabilization effects. These effects operate in conjunction with one another, and separation of the effects is usually not possible. In several cases, it is nevertheless obvious which effect dominates. For heteroatom α-substituents such as α-NH_2, α-OH, and α-SH, π donation clearly prevails over inductive withdrawing, whereas the carbon-based α-$CH{=}CH_2$ and α-C_6H_5 substituents are nearly only π-donating. The largest destabilizing effects are found for α-CF_3 and α-NO_2, which are both strongly inductively electron-withdrawing and not (or hardly) capable of π donation. A smaller amount of destabilization is observed for the α-CN substituent, which is both a π donor and an inductive electron-withdrawing substituent.

A clear conceptual separation of β-inductive effects from other effects is nevertheless possible. They can be studied separately by analyzing the subset of α-R = α-CH_2Y (with Y being H, halogens, OH, CN, and CF_3). The π-donation effects of the Y moiety are not expected to be important, and the hyperconjugative effects of the CH_2 moiety in the CH_2Y substituents are more or less equal for different Ys.[24] Therefore, the stabilization provided by α-CH_2Y substituents compared to that provided by α-CH_3 are a good measure of the size of the β inductive effects of the Y substituent in α-CH_2Y compared to that of H. The observed order of the β inductive effect is Y = CN > CF_3 > F > Cl > Br > OH, and it ranges from 20 to 5 kcal/mol (destabilization relative to Y = H, i.e., α-CH_3) for both the alkyl and vinyl cations. The computed reaction enthalpies do not correlate with either the electronegativity of the substituents or the inductive substituent parameters such as σ_I.[25] β inductive effects in these cations are to a good approximation additive, independent of the orientation of Y. For example, the results for the α-$CH_xF_{(3-x)}$ series of substituents show a monotonic decrease in stabilization of ~16 kcal/mol per F atom for the alkyl cations and ~15 kcal/mol per F atom for the vinyl cations. Only for the α-CF_3 substituent is some dampening of the inductive effect observed.

A remarkable β effect is the large increase in stabilization found upon changing R from α-OH to α-$OSi(CH_3)_3$, which explains the usefulness of this substituent not only as a protecting group but also as a stabilizing group in syntheses involving carbocationic intermediates.[26]

With a quantitative evaluation of the β effects at hand, a closer examination of the α effects of the substituents is now possible. An analysis of the data for the same substituents Y that were investigated for the β inductive effects positioned at the α-carbon shows that in most cases the inductive withdrawing effects are counteracted by π donation. Whereas the CN group is a better inductive electron-withdrawing group than CF_3 according to the β effects, the α-CF_3 substituent destabilizes the alkyl and vinyl cations more than α-CN does. Clearly, a rather large π donation by the α-CN substituent counteracts its electron-withdrawing inductive effect, whereas for the α-CF_3 substituent, the magnitude of the π donation is negligible. For the substituents F, Cl, Br, and OH, the stabilization decreases with increasing inductive electron-withdrawing capability, as expected. Next to this effect, however, π donation also plays an important, but not constant, role, as is clear from the C−R bond length decreases and the differences therein (e.g., a decrease of 0.20 Å for α-Br and 0.14 Å for α-F). The α-C(O)H and α-COOH substituents do not stabilize via π donation: the C−R bond length decreases between the cations, and the neutral precursor are nonexistent for α-C(O)H and small (0.02 Å) for α-COOH. The (de)stabilization by these two α-substituents is mainly the result of an inductive withdrawing effect opposed by direct interaction between the oxygen atom and the carbocationic center, present in the open as well as the bridged structures. The α-CH_2Y substituents are not capable of π donation and stabilize cations by hyperconjugative effects, which are counteracted by the previously discussed inductive effects.

The stabilization provided by α-substituents to alkyl cations and that provided to vinyl cations shows good correlation (Figure 3). The slope is almost equal to 1.00, which shows that alkyl and vinyl cations respond with similar sensitivity to changes in α-substituents. The intercept is the average of the differences $\Delta\Delta H$ between stabilization provided by a given α-substituent in the alkyl cations versus that of the vinyl cations (Table 1, columns 4 and 7). The intercept value of 4 kcal/mol shows that the stabilization by any α-substituent is on average 4 kcal/mol larger in the vinyl cations than in the alkyl cations. Because of this difference in stabilization, some borderline α-substituents such as α-CH_2CN and α-C(O)H destabilize alkyl cations, whereas they mildly stabilize vinyl cations. Four α-substituents that display the strongest inductive effects (α-F, α-OH, α-NH_2, and α-$Si(CH_3)_3$) fall off of the correlation of Figure 3 because of the different sensitivity of alkyl and vinyl cations to inductive effects (vide infra).

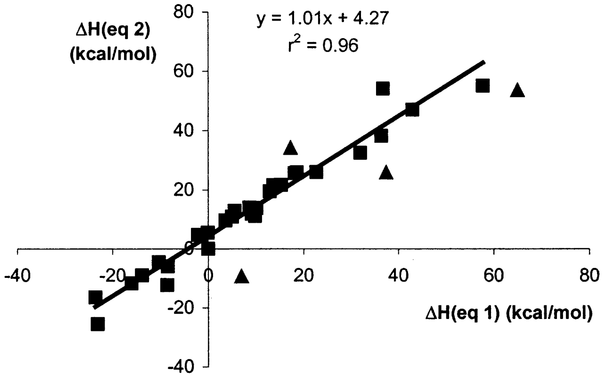


Figure 3. Correlation between the reaction enthalpies computed for the alkyl and vinyl cations (i.e., ΔH of eq 1 versus ΔH of eq 2). Four points (▲) are not included in the correlation. See text for details.

A comparison of the stability of alkyl versus vinyl cations is obtained from the isodesmic reaction in eq 3. The parent alkyl cation (R = α-H) is computed to be 17 kcal/mol more stable than the parent vinyl cation. Also, for all α-R substituted cations, higher stabilities for the alkyl systems are computed in comparison with those of the corresponding vinyl cations. The stabilities are, of course, subject to the same variation as observed for the $\Delta\Delta H$ values given in Table 1 (ΔH values of eq 3 are equal to ($\Delta\Delta H$ + 17 kcal/mol)).

$$H_2C{=}CHR + \underset{\mathbf{1}}{H_3C{-}C(+)HR} \xrightarrow{\Delta H} H_3C{-}CH_2R + \underset{\mathbf{2}}{H_2C{=}C(+)R} \quad (3)$$

The intrinsically higher instability of vinyl cations compared to that of alkyl cations explains the increased amount of stabilization (on average, 4 kcal/mol) provided to them by α-substituents. In some cases, however, vinyl cations are stabilized less by α-substituents than alkyl cations are. For example, the α-OH substituent stabilizes both alkyl and vinyl cations, but the former are more stabilized: 37 versus 26 kcal/mol (see the entry for α-OH in Table 1). This is a general trend for α-substituents, which are strongly inductively electron-withdrawing (α-F, α-OH, and α-NH_2).[5p,6d,27] Inductive effects, which are σ-effects by nature, are more pronounced for the more-electronegative sp-hybridized vinyl cations because of the higher s character of the C−R bond than for the sp^2-hybridized alkyl cations.[5p,6d,27] The higher electronegativity of the vinyl cation might manifest itself in the amount of delocalization of the positive charge, which is expected to be larger for the vinyl than for the alkyl cations. Whether this is indeed the case will be discussed in the Electronic Properties section. The most striking example is observed for the α-F substituent: the stabilizing effect in the alkyl cation is reversed to a destabilizing effect in the vinyl cation. For α-F, the stabilization provided is 16 kcal/mol lower in the vinyl cation than in the alkyl cation. The reverse effect is found for the strong inductively electron-donating α-$Si(CH_3)_3$ group: the stabilization is in this case 17

TABLE 2: Charge Increases Computed at C(+) in Both the Alkyl and the Vinyl Cations in Going from the Neutral Compound (Leaving Group: H^-) to the Corresponding Cation (MP2/6-311+G(d,p) Data)

R	alkyl	vinyl
CH_3	0.647	0.585
CH_2Cl	0.719	0.585
CH_2Br[a]	0.612	0.573
CH_2OH[b]	0.702	0.568
$C(CH3)_2OH$[c]	0.622	0.599
CH_2CN	0.633	0.598
CH_2CF_3	0.612	0.601
CH_2F	0.659	0.577
CHF_2[d]	0.714	0.623
CF_3[d]	0.666	0.618
$CH{=}CH_2$	0.492	0.440
$C{\equiv}CH$	0.542	0.704
$C{\equiv}N$	0.602	0.572
C_6H_5	0.420	0.383
c-C_3H_5	0.558	0.525
$C(H){=}O$[e]	0.664	0.656
COOH[e]	0.650	0.587
F	0.592	0.524
Cl	0.363	0.274
Br[f]	0.284	0.205
I[f]	0.193	0.123
NH_2	0.531	0.394
OH	0.242	0.125
SH	0.425	0.298
$Si(CH_3)_3$[g]	0.712	0.646
$OSi(CH_3)_3$	0.428	0.421
NO_2[h]	0.499	0.424

[a] The C(+)−C−Br angle in the alkyl cations is constrained to 120.0°. [b] The hydrogen atoms on the α-substituent are prevented from migrating in the case of the alkyl cation by the use of symmetry. [c] The methyl groups on the α-substituent are prevented from migrating in the case of the alkyl cation by the use of symmetry. [d] The H−C−C(+) angle in the alkyl cations is constrained to 102.3°. [e] The C(+)−C−O angle is constrained to 120.0°. [f] Average of results obtained with CEP-121[33] and SDD[34] as ECPs used for bromine and iodine. [g] The methyl groups are prevented from migrating by the use of symmetry. [h] The C(+)−N=O angle is constrained to 120.0°.

kcal/mol higher in the vinyl cation than in the alkyl cation. This number also shows that this is truly a σ-effect and not a difference in response to the π donation for alkyl and vinyl cations, as the α-$Si(CH_3)_3$ substituent contains no participating p electrons. Such inductive effects also play a role for all other substituents, but because these inductive effects are relatively less important because of the presence of other effects, the differences in stabilization all fall in the same range (4 kcal/mol, on average).

Electronic Properties. The electronic properties of the molecules under study were analyzed using the NBO method.[10] The NBO method was chosen over the Mulliken and AIM methods because of problems that were previously encountered with the latter two.[8,9,28] In the present study, charge and bond-order increases (i.e., the differences in charges and bond orders between the neutral molecules and the cationic species) will be used. These charge and bond-order increases show in general the same picture for the alkyl and vinyl cations, and because of that, the common features will be discussed prior to a comparison of the results found for the alkyl and vinyl cations.

In Table 2, the charge increases as obtained with the MP2 method on C^+ are given. The charge increases on R and on the CH_3 or CH_2 moieties of the alkyl and vinyl systems are given in the Supporting Information.

The general picture that emerges from the charge computations for the alkyl cations is that the charge is delocalized over the whole molecule. In the case of the carbon-based substituents, still a relative large portion of the charge is located at the carbocation center (from 0.5 for α-$CH{=}CH_2$ to 0.7 for α-CF_3 and α-C(O)H in its open form), with the exception of the α-cyclopropyl substituent in which the charge at C^+ is only 0.18 (for a discussion, see the Bond Orders section). For the α-hetero substituents, the amount of charge at C^+ is generally lower and varies from 0.2 for the α-I substituent to about 0.6 for α-F and α-$Si(CH_3)_3$. The opposite order is observed for the charge increases at the substituent R. Therefore, the amount of charge that resides on the CH_3 moiety is fairly constant (between 0.15 and 0.20 for most substituents). For the vinyl cations, similar trends are observed. Here also, more localization of the charge on the carbocation center is computed for the carbon-based substituents, and more spreading onto the α-substituent is computed for the α-hetero substituents.

Comparison of the charge distributions over the molecule for alkyl and vinyl cations with a given α-substituent shows that the amount of charge that resides on the carbocation center is smaller for the vinyl cations (on average, by −0.07) with only small variations. As a consequence, higher charge increases are computed at the α-substituent R of the vinyl cations (on average, 0.04) and at the CH_2 moiety (on average, 0.03) compared to that of the alkyl systems. This is indeed as expected on the basis of the higher electronegativity of the vinyl cation compared to that of the alkyl cation (vide supra).

In the Stabilities section, it was mentioned that inductive effects are more pronounced in vinyl cations than in alkyl cations, which leads to different stabilization effects by strong inductively withdrawing or donating α-substituents in the two systems. Therefore, with inductively withdrawing α-substituents such as α-F, α-OH, and α-NH_2, more charge development at C^+ is expected in the vinyl systems than in the alkyl ones. The opposite, a smaller charge increase on C^+, is expected in the case of α-$Si(CH_3)_3$ (a strong inductive donor). This is indeed observed for all cases but one (Table 2). The exception is the α-F substituent, for which the large inductive effect is counteracted by an even-larger π donation.

In Figure 4, two graphs are presented, illustrative of the lack of correlation between charge increases on any part of the molecule and the stabilization provided by α-substituents. This lack of correlation was observed earlier for small sets of substituents for alkyl and vinyl cations.[5a,8,9] Figure 4 shows, now also for a large set of substituents, that no correlation exists between charge increases at , for example, an α-substituent and the stability provided by such a substituent. This lack of correlation is not restricted to NBO charges, as also with the methodologically very different AIM charges no correlation was observed.[8] Even for subsets such as the halogens or the $CH_xF_{(3-x)}$ series, no good correlation is found. In the case of the halogens, some correlation ($r^2 = 0.6$) between charge and stability is observed. For the $CH_xF_{(3-x)}$ series, however, increasing the number of F atoms in the substituent has no effect on the amount of charge development at the α-substituent or at any other part of the molecule for that matter, although it has a distinct effect on the reaction enthalpies. Although delocalization of charge always diminishes the electron−electron repulsions, the simple model that the (de)stabilization of cations is solely provided by overall charge acceptance or charge donation of an α-substituent appears to oversimplify reality. The present study clearly points to the factors that yield this more complicated situation. Stabilization via electron donation can occur via π or σ donation. The stabilization obtained via donation of a certain fraction of an electron via one route does not automatically imply an equal stabilization when donation occurs via the other route. This effect combines with the phenomenon that many substituents are electron-donating in one sense and electron-withdrawing in the other. In addition, the overall stabilization that is provided will also depend on the C−R distance, the hybridization of the C^+ atom, and the C−C/C=C bond length. Therefore, even in the “simple” case of isolated compounds, as studied here, no simple relation exists

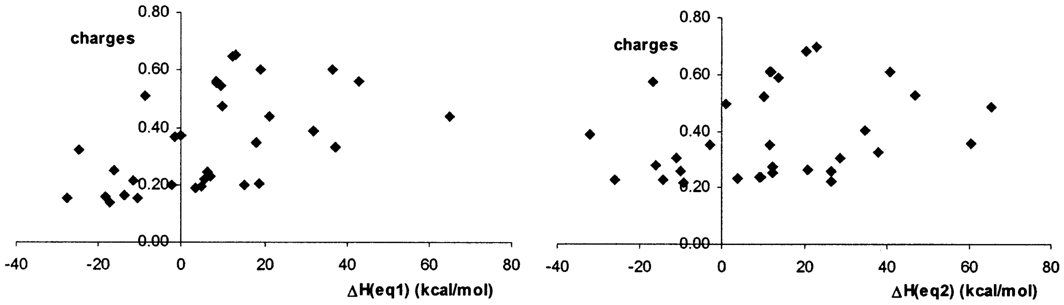


Figure 4. Lack of correlation between charge increases at the α-substituents R (B3LYP data) and the computed reaction enthalpies for the alkyl cations (Δ*H* of eq 1; left) and vinyl cations (Δ*H* of eq 2; right). MP2 data are similar.

TABLE 3: Bond-Order Increases of the C^+-R Bond in Both the Alkyl and the Vinyl Systems in Going from the Neutral Compound (Leaving Group: H^-) to the Corresponding Cation (MP2/6-311+G(d,p) Data)[a]

	alkyl	vinyl		alkyl	vinyl
R			R		
CH_3	0.19	0.20	F	0.37	0.39
CH_2Cl	0.18	0.16	Cl	0.61	0.60
CH_2Br[b]	0.14	0.18	Br[h]	0.67	0.65
CH_2OH[c]	0.15	0.17	I[h]	0.74	0.68
$C(CH3)_2OH$[d]	0.13	0.14	NH_2	0.55	0.47
CH_2CN	0.15	0.18	OH	0.76	0.67
CH_2CF_3	0.13	0.18	SH	0.67	0.56
CH_2F	0.14	0.15	$Si(CH_3)_3$[i]	−0.05	−0.08
CHF_2[e]	0.01	0.02	$OSi(CH_3)_3$	0.64	0.64
CF_3[e]	−0.07	−0.06	NO_2[j]	0.02	0.04
$CH{=}CH_2$	0.34	0.27			
$C{\equiv}CH$	0.28	0.29[f]			
$C{\equiv}N$	0.13	0.15			
C_6H_5	0.40	0.29			
c-C_3H_5	0.46	0.42			
$C(H){=}O$[g]	0.02	−0.03			
COOH[g]	−0.02	−0.02			

[a] Positive numbers indicate an increase in the bond order. [b] The C(+)−C−Br angle in the alkyl cations is constrained to 120.0°. [c] The hydrogen atoms on the α-substituent are prevented from migrating in the case of the alkyl cation by the use of symmetry. [d] The methyl groups on the α-substituent are prevented from migrating in the case of the alkyl cation by the use of symmetry. [e] The H−C−C(+) angle of the alkyl cations is constrained to 102.3°. [f] MP2(full)/6-311G(d,p) data; inclusion of diffuse functions made the NBO computations fail. [g] The C(+)−C−O angle is constrained to 120.0°. [h] Average of results obtained without effective core potential (ECP), CEP-121,[33] and SDD[34] as ECPs for bromine and iodine. [i] The methyl groups are prevented from migrating by the use of symmetry. [j] The C(+)−N=O angle is constrained to 120.0°.

between stabilization offered by an α-substituent and the total amount of electrons it donates!

Bond Orders. Three different bond-order increases in going from the neutral precursors to the cations under study are considered, namely, those of the C−R bond, the C−C or C=C bond, and the C_β−H bonds. Of these three increases, those of the C−R bond show the largest variation in the studied set of α-substituted cations and are presented in Table 3. The other data are given in the Supporting Information and will be discussed only briefly.

The effects range from −0.08 to +0.76. This indicates that in some cases the loss of the leaving group weakens the C−R bond compared to the neutral bond. In most cases, however, it strengthens the bond between the carbocation center and the substituent, sometimes even to the point that the C−R bond becomes almost a double bond. Relatively small bond-order increases are computed in the case of α-substituents that are not capable of π donation. The effects of these substituents are on the order of −0.05 to 0.2, with low values for α-CF_3 and α-CHF_2 substituents and higher values for the CH_2Y series. The largest increases are observed for α-substituents such as α-$CH{=}CH_2$, α-I, and α-SH bearing π or p electrons. The bond-order increases are higher for hetero substituents than for most carbon-based substituents: 0.6−0.7 for Cl, Br, I, NH_2, OH, and SH versus 0.3 to 0.4 for $CH{=}CH_2$ and $C{\equiv}CH$, indicating that substituents with lone-pair electrons are better π donors than α-substituents with π electrons. The relatively large stabilization provided by the α-cyclopropyl group is reflected by the significant strengthening of the C−R bond (bond-order increase = +0.46). This is coupled to the lengthening and weakening of the C^1-C^2 bond (see Figure 1, cyclopropyl substituent) and its concomitant bond-order decrease from 0.92 in the neutral to 0.67 in the cationic species. For the p/π donors but strongly electronegative α-substituents F and CN, relatively small bond-order increases are found (0.2 for α-CN and 0.3 for α-F). For the α-C(O)H and α-COOH substituents, no significant bond-order increases are observed, although these groups are in principle capable of π-electron donation. The main interaction between these substituents and the carbocation center is the donation of electron density of the doubly bound oxygen atom to the carbocation center, as is reflected in the order computed for the bonds between C^+ and that oxygen atom: 0.5−0.6 for the bridged structures and 0.2−0.3 for the open cations.

The C−C/C=C bond-order increases vary from 0.1 to 0.3. The higher values are computed for the α-CH_2R substituents, and the lower ones, for the hetero substituents. The C_β−H bond order is smaller in the cations than in their neutral precursors, and the magnitude of the decrease is rather small (0.05−0.20).

The C−R bond-order increases show very similar responses to the α-substituents in the alkyl and vinyl systems: a plot of the results for the alkyl cations versus the vinyl cations shows excellent correlation for both the B3LYP and MP2 methods (r^2 = 0.97 and 0.98, respectively; see Supporting Information). The slope obtained with either method is 0.9, which shows that vinyl cations are more susceptible to π donation than alkyl cations. This is caused by the intrinsically higher instability of vinyl cations compared to alkyl cations, which results in a larger need for stabilization. The C−C/C=C and C_β−H bond-order increases for the alkyl versus vinyl systems do not correlate well, also because of the smaller range of the effects.

The C−R and C−C/C=C bond-order increases do not show any correlation with the reaction enthalpies (plots shown in Supporting Information); only for the C_β−H bond-order decreases in the vinyl cations is a reasonable correlation observed (Figure 5). The amount of hyperconjugation (bond-order decrease) in vinyl systems is thus related to the stabilization provided by the α-substituent; the need for hyperconjugative stabilization is larger for destabilizing α-substituents. For the alkyl systems, no correlation between the C_β−H bond order and Δ*H* is observed.

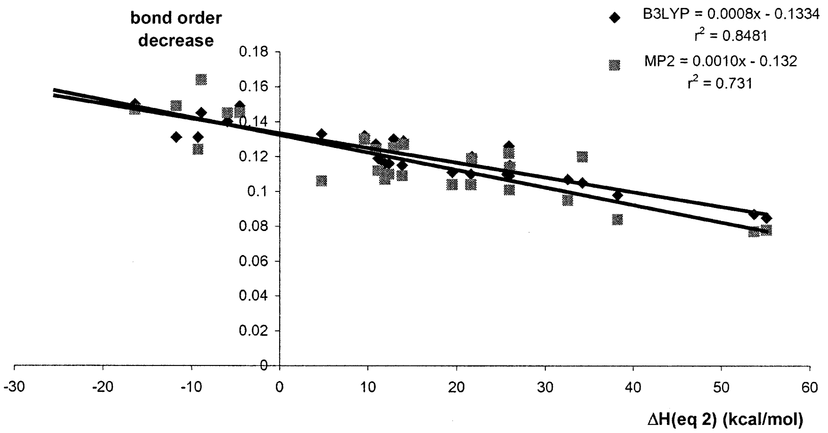


Figure 5. Correlation between the C_β−H bond-order decreases in the vinyl systems and the reaction enthalpies Δ*H* of eq 2.

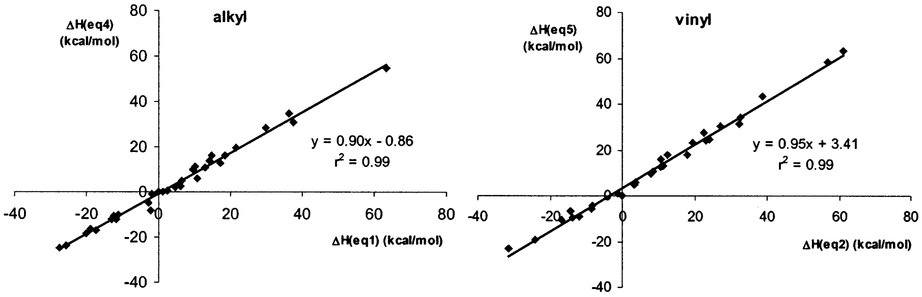


Figure 6. Correlation between the reaction enthalpies of eqs 1 and 4 and eqs 2 and 5 for H and Cl as leaving group, respectively (MP2(full)/6-311+G(d,p) data).

Leaving-Group Effect. In using isodesmic reactions such as eqs 1 and 2, the formation of a cation with a given substituent R from a neutral precursor is compared to a reference system. The computed reaction enthalpies are therefore dependent on the enthalpies of both the neutral and the cationic molecules. To assess the effect of (de)stabilization of the neutral precursors by α-substituents R, the group transferred in the isodesmic reactions is changed from H to Cl (eqs 4 and 5). Equation 4 yields (de)stabilization compared to the chloroalkane precursor, and eq 5 yields (de)stabilization compared to the chloroalkene precursor. The difference between the results for H and Cl provides information about the geminal interactions[29,30] between the α-substituent and the leaving group.

$$H_3C{-}CH_2Cl + \underset{\mathbf{1}}{H_3C{-}C(+)HR} \xrightarrow{\Delta H} H_3C{-}CHClR + H_3C{-}C(+)H_2 \quad (4)$$

$$H_2C{=}CHCl + \underset{\mathbf{2}}{H_2C{=}C(+)R} \xrightarrow{\Delta H} H_2C{=}CClR + H_2{=}C(+)H \quad (5)$$

R = CH_3, CH_2Y, (Y = F, Cl, Br, OH, CN, CF_3, $C(CH_3)_2OH$, CHF_2, and CF_3, $CH{=}CH_2$, $C{\equiv}CH$, CN, C_6H_5, *c*-C_3H_5, C(O)H, COOH, F, Cl, Br, I, NH_2, OH, SH, $Si(CH_3)_3$, $OSi(CH_3)_3$, and NO_2). The reaction enthalpies of eqs 4 and 5 have been calculated using the B3LYP and MP2 methods.[31] The results of the two methods correlate excellently (not shown). The results obtained for Cl as a leaving group are compared with those obtained for H in Figure 6. The plots show a high correlation (r^2 = 0.99) for both the alkyl and vinyl cations. The alkyl systems, however, respond differently to the change in leaving group than the vinyl systems, as is clear from the differences in slope and intercept computed for the alkyl and the vinyl systems.

For the alkyl cases, the enthalpy differences between H and Cl as leaving groups range from −4 to +9 kcal/mol. The negative values indicate that for Cl geminal effects destabilize the neutral precursor compared to H. The largest destabilizing geminal effects are found for α-COOH, α-NO_2, α-CN, and α-CF_3 (about −3 to −4 kcal/mol), all of which are substituents that also destabilize the alkyl cations. The largest stabilizing geminal effects are computed for α-NH_2 (9 kcal/mol) and α-OH (6 kcal/mol), and smaller stabilizing effects, for α-CH_3, α-CH_2OH (both 4 kcal/mol), α-$OSi(CH_3)_3$, and α-F (both 3 kcal/mol). The results for the subset of halogens are interesting: the order found is F > Cl > Br > I with α-F geminally stabilizing and the other three destabilizing (the destabilization varies from −1 to −3 kcal/mol). These effects oppose the order of electronegativity of halogen substituents. This is, however, not a general trend because for α-NH_2 and α-OH higher stabilizing effects are found than for α-F. The steric bulk of substituents has a destabilizing effect for Cl versus H as the leaving group, as can be observed for the couples α-CH_2OH/α-$C(CH_3)_2OH$ and α-OH/α-$OSi(CH_3)_3$: the more sterically demanding substituents stabilize less (3 kcal/mol). Experimentally, geminal interactions have been implied to explain the ratio in solvolysis rates of 2-CH_3- and 2-$Si(CH_3)_3$-substituted 2-chloropropanes.[30a] A similar geminal effect is found in our computations: a difference of 2.5 kcal/mol is computed, which is about 2 kcal/mol lower than the value computed in that study for the couple SiH_3/CH_3.

For the vinyl systems, a different trend is observed. For almost all α-substituents, destabilizing effects are computed upon changing the leaving group from H to Cl; however, for α-CH_3, α-CH_2OH, and α-$Si(CH_3)_3$, small stabilizing effects (1−2 kcal/mol) are calculated. The destabilizing effects range from −7 to −1 kcal/mol; the largest effect is found for α-NO_2, and somewhat smaller effects are found for α-CN, α-CF_3, α-Br, and α-I. The B3LYP and MP2 results of −4.8 and −6.0 kcal/mol, respectively, for α-CN are comparable to, although a little lower than, the previously computed value of −6.4 kcal/mol.[32] The order found for the α-halogen substituents in the alkyl cations is not observed for the vinyl cations, nor are the steric effects, which demonstrates the differences in geminal interaction between alkyl and vinyl cation precursors. Overall, the effect of the leaving group on the stability of the neutral precursors seems to be a complex combination of steric and electronic effects and is therefore hard to predict.

Conclusions

In total, the effects of 27 α-substituents on the geometries, stabilities, and electronic properties of alkyl and vinyl cations have been studied. The set ranges from strongly electron-withdrawing substituents such as α-CF_3 to strongly electron-donating ones (e.g., α-NH_2). The relative stabilities of the cations have been determined with CBS-Q or CBS-Q-like calculations using isodesmic reactions and yield an accurate data set for a broad range of α-substituents. The electronic effects of the substituents consist of π donation from the α-substituent to the carbocation center combined with inductive effects, which can be both electron-donating and electron-withdrawing in nature. The computed stabilities show that α-substituted vinyl cations are on average 17 kcal/mol less stable than their alkyl counterparts. The stabilization provided by α-substituents is larger (on average, ~4 kcal/mol) for vinyl cations than for alkyl cations to alleviate the intrinsically higher instability of the former. Only for strong inductively withdrawing α-substituents such as α-F, α-OH, and α-NH_2 is a lower stabilization by the α-substituent computed for the vinyl cations than for the alkyl ones. This is because in (sp-hybridized) vinyl cations σ effects are more pronounced because of the higher s character of the C−R bond in those cations. The strong inductively donating substituent α-$Si(CH_3)_3$ is subject to the same effect, which leads to a much higher stabilization in the vinyl cation than in the corresponding alkyl one.

The NBO-computed electronic properties show that there is no general correlation between charge increases or bond-order increases on any part of the molecule and the stability provided by an α-substituent. This demonstrates the clear conceptual difference between stabilizing and electron-donating effects.

The influence of the leaving group is studied by comparing hydrogen with chlorine as a leaving group in the isodesmic reactions. In the case of the alkyl systems, the geminal effect ranges from −4 to 9 kcal/mol and is caused by a combination of inductive and steric effects. In the vinyl systems, Cl instead of H as a leaving group leads to a destabilizing geminal effect on the order of −7 to −1 kcal/mol for almost all substituents.

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Supporting Information Available: Tables of MP2-optimized cation geometries (G98 archive files) and of all calculated NBO charges and bond orders, together with a detailed technical description of the cases in which bridging and/or migration plays a role, are available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1986; Vols 1−4. (b) Vogel, P. *Carbocation Chemistry*; Elsevier: Amsterdam, 1985. (c) *Dicoordinated Carbocations*; Rappoport, Z.; Stang, P. J., Eds.; Wiley: West Sussex, U.K., 1997. (d) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. *Vinyl Cations*; Academic Press: New York, 1979. (e) Okuyama, T. *Acc. Chem. Res.* **2002**, *35*, 12−18. See for recent theoretical case studies: (f) Werstiuk, N. H.; Wang, Y.-G. *J. Phys. Chem. A* **2001**, *105*, 11515−11523. (g) Olah, G. A.; Prakash, G. K. S.; Rasul, G. *J. Org. Chem.* **2001**, *66*, 9011−9014. (h) Vrcek, I. V.; Vrcek, V.; Siehl, H.-U. *J. Phys. Chem. A* **2002**, *106*, 1604−1611.

(2) (a) Kitamura, T.; Taniguchi, H.; Tsuno, Y. In *Dicoordinated Carbocations*; Rappoport, Z., Stang, P. J., Eds.; Wiley: West Sussex, U.K., 1997; Chapter 7. (b) Rappoport, Z. In *Reactive Intermediate;* Abramovitch, R. A., Ed.; Plenum Publishing: New York, 1983; Vol 3, Chapter 7. (c) Creary, X. *Chem. Rev.* **1991**, *91*, 1625−1678.

(3) (a) Johnston, L. J.; Kwong, P.; Shelemay, A.; Lee-Ruff, E. *J. Am. Chem. Soc.* **1993**, *115*, 1664−1669. (b) Schepp, N. P.; Wirz, J. *J. Am. Chem. Soc.* **1994**, *116*, 11749−11753 and references in these papers. (c) Lodder, G. In *Dicoordinated Carbocations*; Rappoport, Z., Stang, P. J., Eds.; Wiley: West Sussex, U.K., 1997; Chapter 8. (d) Kropp, P. J. In *CRC Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M., Song, P.-S., Eds.; CRC Press: Boca Raton, FL, 1995; Chapter 84. (e) Kitamura, T. In *CRC Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M., Song, P.-S., Eds.; CRC Press: Boca Raton, FL, 1995; Chapter 85. (f) Lodder, G.; Cornelisse, J. In *The Chemistry of Functional Groups*, Supplement D2; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1995; Chapter 16. (g) Gronheid, R.; Lodder, G.; Okuyama, T. *J. Org. Chem.* **2002**, *67*, 693−702. (h) Gronheid, R.; Lodder, G.; Ochiai, M.; Sueda, T.; Okuyama, T. *J. Am. Chem. Soc.* **2001**, *123*, 8760−8765.

(4) (a) Hammett, L. P. *Physical Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1970. (b) Ritchie, C. D. *Physical Organic Chemistry*, 2nd ed.; Marcel Dekker: New York, 1990. (c) Isaacs, N. S. *Physical Organic Chemistry*, 2nd ed.; Longman: Harlow, U.K., 1995.

(5) Previous work on alkyl cations: for references to R = H, CH_3, $CH{=}CH_2$, $C{\equiv}CH$, F, and Cl, see footnotes 8, 14, and 16 in ref 8. References to R = CH_2F: (b), (i), (n), (s), (v), (y), and (aa). References to R = CH_2Cl: (c), (i), (n), (x), and (aa). References to R = CH_2Br: (aa). References to R = CH_2OH: (b). References to R = CH_2CN: (d), (e), and (m). References to R = CH_2CF_3: (e). References to R = CHF_2: (o) and (s). References to R = CF_3: (e), (g), (h), (k), (r), (s), (z), and (ae). References to R = C_6H_5: (ad), (af), and (ah). References to R = *c*-C_3H_5: (w), (x). References to R = CN: (d), (e), (f), (g), (h), (k), (m), (r), (ae), and (af). References to R = C(O)H: (e), (g), (j), (k), (m), (q), (t), (ad), (ae), and (af). References to R = COOH: (q), (t), and (af). References to R = Br: (aa). References to R = NH_2: (a), (g), (k), (r), and (af). References to R = OH: (a), (g), (h), (k), (r), (af), and (ag). References to R = SH: (l). References to R = $Si(CH_3)_3$: (a) and (p). References to R = NO_2: (k), (ac), and (af). (a) Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 1291−1296. (b) Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 5901−5909. (c) Hopkinson, A. C.; Lien, M. H. *Theor. Chim. Acta* **1977**, *44*, 385−398. (d) Dixon, D. A.; Charlier, P. A.; Gassman, P. G. *J. Am. Chem. Soc.* **1980**, *102*, 3957−3959. (e) Paddon-Row, M. N.; Santiago, C.; Houk, K. N. *J. Am. Chem. Soc.* **1980**, *102*, 6563−6565. (f) Moffat, J. B. *Chem. Phys. Lett.* **1980**, *76*, 304−306. (g) Reynolds, W. F.; Dais, P.; Taft, R. W.; Topsom, R. D. *Tetrahedron Lett.* **1981**, *22*, 1795−1798. (h) Paddon-Row, M. N.; Houk, K. N.; Tidwell, T. T. *Tetrahedron Lett.* **1982**, *23*, 383−386. (i) Raghavachari, K.; Haddon, R. C.; Starness, W. H. *J. Am. Chem. Soc.* **1982**, *104*, 5054−5056. (j) Nobes, R. H.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1983**, *105*, 309−314. (k) Reynolds, W. F.; Dais, P.; MacIntyre, D. W.; Topsom, R. D.; Marriot, S.; Nagy-Felsobuki, E. v.; Taft, R. W. *J. Am. Chem. Soc.* **1983**, *105*, 378−384. (l) Ginsburg, J. L.; Langler, R. F. *Can. J. Chem.* **1983**, *61*, 589−593. (m) Dixon, D. A.; Eades, R. A.; Frey, R.; Gassman, P. G.; Hendewerk, M. L.; Paddon-Row, M. N.; Houk, K. N. *J. Am. Chem. Soc.* **1984**, *106*, 3885−3891. (n) Frenking, G. *Tetrahedron* **1984**, *40*, 377−379. (o) Heinis, T.; Bär, R.; Börlin, K.; Jungen, M. *Chem. Phys. Lett.* **1984**, *105*, 327−331. (p) Wierschke, S. G.; Chandrasekhar, J.; Jorgenson, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496−1500. (q) Bonnet-Delpon, D.; Charpentier-Morize, M. *Chem. Phys. Lett.* **1985**, *116*, 478−481. (r) Aissani, A. M.; Baum, J. C.; Langler, R. F.; Ginsburg, J. L. *Can. J. Chem.* **1986**, *64*, 532−538. (s) Tidwell, T. T.; Wolfe, S. *Can. J. Chem.* **1987**, *65*, 473−481. (t) Lien, M. H.; Hopkinson, A. C. *J. Am. Chem. Soc.* **1988**, *110*, 3788−3792. (u) Lien, M. H.; Hopkinson, A. C. *J. Am. Chem. Soc.* **1988**, *110*, 3788−3792. (v) Ford, G. P.; Raghuveer, K. S. *Tetrahedron* **1988**, *44*, 7489−7498. (w) Koch, W.; Liu, B.; DeFrees, D. J. *J. Am. Chem. Soc.* **1988**, *110*, 7325−7328. (x) Saunders, M.; Laidig, K. E.; Wiberg, K. B.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 7652−7659. (y) Stams, D. A.; Thomas, T. D.; Maclaren, D. C.; Ji, D.; Morton, T. H. *J. Am. Chem. Soc.* **1990**, *112*, 1427−1434. (z) Reynolds, C. H. *J. Chem. Soc., Chem. Commun.* **1990**, 1533−1535. (aa) Reynolds, C. H. *J. Am. Chem. Soc.* **1992**, *114*, 8676−8682. (ab) McAllister, M. A.; Tidwell, T. T. *Croat. Chem. Acta* **1992**, *65*, 633−653. (ac) Redfern, P. C.; Murray, J. S.; Politzer, P. *Can. J. Chem.* **1992**, *70*, 636−641. (ad) Amyes, T. L.; Richard, J. P.; Novak, M. *J. Am. Chem. Soc.* **1992**, *114*, 8032−8041. (ae) Apeloig, Y.; Biton, R.; Zuilhof, H.; Lodder, G. *Tetrahedron Lett.* **1994**, *35*, 265−268. (af) El-Nahas, A. M.; Clark, T. *J. Org. Chem.*

1995, *60*, 8023−8027. (ag) Olah, G. A.; Burrichter, A.; Rasul, G.; Yudin, A. K.; Prakash, G. K. S. *J. Org. Chem.* **1996**, *61*, 1934−1939. (ah) Reindl, B.; Clark, T.; Schleyer, P. v. R. *J. Phys. Chem. A* **1998**, *102*, 8953−8963.

(6) Previous theoretical work on vinyl cations: Apeloig, Y.; Müller, T. *Dicoordinated Carbocations*; Rappoport, Z., Stang, P. J., Eds.; Wiley: West Sussex, U.K., 1997; Chapter 2. References to R = H, CH_3, CH=CH_2, F, and Cl: see footnote 6 in ref 9. References to R = CF_3: (h), (i), and ref 5ae. References to R = C≡CH: (a), (d), and ref 5a, c. References R = CN: ref 5ae. References to R = C_6H_5: (c), (i), and (k). References to R = *c*-C_3H_5: (a). References to R = CH(=O): ref 5ae. References to R = COOH: (n). References to R = Br: (d). References to I: (m). References to R = NH_2: (b), (e), (f), (l), and ref 5a. References to R = OH: (b), ref 5a, j. References to R = SH: (g). References to R = $Si(CH_3)_3$: (d) and ref 5p. (a) Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Org. Chem.* **1977**, *42*, 3004−3011. (b) Kollman, P.; Nelson, S.; Rothenberg, S. *J. Phys. Chem.* **1978**, *82*, 1403−1406. (c) Apeloig, Y.; Franke, W.; Rappoport, Z.; Schwarz, H.; Stahl, D. *J. Am. Chem. Soc.* **1981**, *103*, 2770−2780. (d) Apeloig, Y.; Stanger, A. *J. Org. Chem.* **1982**, *46*, 1462−1468. (e) Nguyen, M. N.; Ha, T.-K. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1401−1405. (f) Würthwein, E.-U. *J. Org. Chem.* **1984**, *49*, 2971−2978. (g) Rodriquez, C. F.; Hopkinson, A. C. *Can. J. Chem.* **1987**, *65*, 1209−1213. (h) Martin, P. S.; Yates, K.: Csizmadia, I. G. *Can. J. Chem.* **1989**, *67*, 2178−2187. (i) McAllister, M.; Tidwell, T. T.; Peterson, M. R.; Csizmadia, I. G. *J. Org. Chem.* **1991**, *56*, 575−580. (j) Hamilton, T. P.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1991**, *113*, 7147−7151. (k) Hori, K.; Kamada, H.; Kobayashi, S.; Taniguchi, H. *J. Chem. Soc., Perkin Trans. 2* **1992**, 871−877. (l) Bouchoux, G.; Penaud-Berruyer, F.; Nguyen, M. T. *J. Am. Chem. Soc.* **1993**, *115*, 9728−9733. (m) Campos, P. J.; Rodríguez, M. A. *J. Chem. Soc., Chem. Commun.* **1995**, 143−144. (n) Pellicciari, R.; Natalini, B.; Sadeghpour, B. M.; Marinozzi, M.; Snyder, J. P.; Williamson, B. L.; Kuethe, J. T.; Padwa, A. *J. Am. Chem. Soc.* **1996**, *118*, 1−12.

(7) For a general description of the method, see: (a) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; pp 298−308. (b) Ponomarev, D. A.; Takhistov, V. V. *J. Chem. Educ.* **1997**, *74*, 201−203.

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

(9) Van Alem, K.; Lodder, G.; Zuilhof, H. *J. Phys. Chem. A* **2000**, *104*, 2780−2787.

(10) Glendeling, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO*, version 3.1; University of Wisconsin, 1990.

(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; 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 94*, revision D.4; Gaussian, Inc.: Pittsburgh, PA, 1995.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revisions A.6 and A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

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

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

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

(16) (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.

(17) (a) Scaled by a factor 0.9401 according to ref 17b. (b) Scott, P. A.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502−16513.

(18) (a) Ruscic, B.; Berkowitz, J.; Curtiss, L. A.; Pople, J. A. *J. Chem. Phys.* **1989**, *91*, 114−121. (b) Klopper, W.; Kutzelnigg, W. *J. Phys. Chem.* **1990**, *94*, 5625−5630. (c) Perera, S. A.; Bartlett, R. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1995**, *117*, 8476−8477.

(19) Geometry optimizations and vibrational analysis were performed using the 6-311G(d,p) basis set with either one of the methods followed by single-point computations using the 6-311+G(d,p) basis set to obtain the total energies according to refs 8 and 9.

(20) (a) MP2/6-311G(d,p) data is given because this is the best level used in this study to evaluate geometries.[20b] (b) St-Amant, A. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH: New York, 1996; Vol 7, Chapter 5.

(21) Ingold, C. K.; Ingold, E. H. *J. Chem. Soc.* **1926**, 1310−1333.

(22) Olah, G. A. *Carbocations and Electrophilic Reactions*; Verlag Chemie: Weinheim, Germany, 1973.

(23) The CBS-Q method is a composite method in which the total energy is derived via a number of steps, one of which is inclusion of a zero-point energy (ZPE) correction. For structures that are not minima on the potential energy surface, no meaningful ZPE correction is obtained, which leads to meaningless total energies.

(24) There is some variation observed in the C_β−H bond length elongations for the different α-CH_2Y substituents. These variations, however, are small (0.01 Å for the alkyl and 0.005 Å for the vinyl systems for either B3LYP or MP2) and do not show any correlation with the reaction enthalpies.

(25) Friedl, Z.; Hapala, H.; Exner, O. *Collect. Czech. Chem. Commun.* **1979**, *44*, 2928−2945.

(26) Bell, R. P. L.; Wijnberg, J. B. P. A.; de Groot, Ae. *J. Org. Chem.* **2001**, *66*, 2350−2357.

(27) Apeloig, Y.; Stanger, A. *J. Org. Chem.* **1983**, *48*, 5413.

(28) (a) The Mulliken charges and bond orders proved to be severely basis-set dependent, and the AIM method yields unrealistic negative charges on formally positively charged carbon atoms in vinyl cations.[9] (b) See also: Perrin, C. L. *J. Am. Chem. Soc.* **1991**, *113*, 2865−2868.

(29) (a) Kirmse, W.; Goer, B. *J. Am. Chem. Soc.* **1990**, *112*, 4556−4557. (b) Wu, Y.-D.; Kirmse, W.; Houk K. N. *J. Am. Chem. Soc.* **1990**, *112*, 4557−4559.

(30) (a) Apeloig, Y.; Biton, R.; Abu-Freih, A. *J. Am. Chem. Soc.* **1993**, *115*, 2522−2523. (b) Richard, J. P.; Amyes, T. L.; Rice, D. J. *J. Am. Chem. Soc.* **1993**, *115*, 2523−2524.

(31) CBS-Q computations are not performed because inclusion of an extra Cl atom will increase the computational costs drastically. Therefore, we chose to study these leaving-group effects using only the B3LYP and MP2 methods.

(32) Pasto, D. J. *J. Org. Chem.* **1992**, *57*, 1139−1145.

(33) Stevens, W. J.; Basch, H.; Krauss, M. *J. Chem. Phys.* **1984**, *81*, 6026−6033. (b) Stevens, W. J.; Krauss, M.; Basch, H.; Jasien, P. G. *Can. J. Chem.* **1992**, *70*, 612−630. (c) Cundari, T. R.; Stevens, W. J. *J. Chem. Phys.* **1993**, *98*, 5555−5565.

(34) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270−283. (b) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284−298. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299−310.