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Relative Reactivities of Carbon–Carbon Double and Triple Bonds toward Electrophiles

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An unsettled question of basic organic chemistry is the relative reactivity of C–C double vs. triple bonds toward electrophiles. The higher electron density (two π bonds) of the triple bond would suggest a higher reactivity for alkynes than for alkenes whereas ionization potential (IP) data, 0.5–1 eV higher for acetylene than for ethylene derivatives of similar structure, would suggest the opposite. Reactivity data are no less contradictory: relative rates of pairs of equally substituted olefins and acetylenes, k_0/k_a, have been reported to range from 10^8 to 10^{-2}, depending mainly on the nature of the electrophilic reagent but also on the structure of the unsaturated substrates and, in some cases, on the solvent.

Although mechanistic studies on electrophilic additions to alkynes[1] are not as abundant as those for alkenes,[2] enough data are now available for a critical comparative analysis.

On the whole, kinetic and stereochemical evidence indicate very similar, sometimes identical, mechanistic features for electrophilic additions to double and triple bonds. The question then arises: what factors or fine mechanistic details are responsible for the large changes in the relative reactivities observed? It is the purpose of this Account to outline an answer to such a question.

For simplicity, let us arbitrarily subdivide electrophilic reagents and their reactions toward unsaturated C–C bonds into two main classes, depending on the observed reactivity ratios: *class A*: electrophiles that react with alkenes at similar or even slower rates than with corresponding alkynes; *class B*: electrophiles that react much faster with alkenes than with alkynes.

Table I
Relative Reactivity of Alkenes and Alkynes in Hydratio Hydration and Acid Addition Reactions

alkene/alkyne	conditions	$k_{\mathrm{o}}/k_{\mathrm{a}}$	ref
n-BuCH=CH_2/	48% H_2SO_4, 25 °C	3.6	9
n-BuC≡CH	CF_3CO_2H, 60 °C	5.3	7
trans-EtCH=CHEt/	48.7% H_2SO_4, 25 °C	16.6	9
EtC≡CEt	CF_3CO_2H, 60 °C	2.6	7
cis-EtCH=CHEt/ EtC≡CEt	48.7% H_2SO_4, 25 °C	13.9	9
EtOCH=CH_2/ EtOC≡CH	aqueous buffers, 25 °C	5.5×10^{-3}	10
PhCH=CH_2[a]/	48.7% H_2SO_4, 25 °C	0.65	9
PhC≡CH[b]	0.8 M CF_3CO_2H in CCl_4, 30 °C	0.8	11
	HCl in CH_3CO_2H, 25 °C	~3	8

[a] Solvent kinetic isotope effect, $k_{H_2O}/k_{D_2O} = 2.27$ (4.6 M $HClO_4$, 25 °C, ref 5); ρ (σ^+) = 3.7 (48% H_2SO_4, 25 °C, ref 6 and 11). [b] $k_{H_2O}/k_{D_2O} = 2.5$ (34% H_2SO_4, 25 °C, ref 4); ρ (σ^+) = 4.1 (48% H_2SO_4, 25 °C; data from ref 11).

Class A Reagents: Low Reactivity Ratio Electrophiles

Proton Addition (Acid-Catalyzed Hydration, Addition of Acids). The acid-catalyzed hydration reactions of alkenes and alkynes show similar mechanistic features. The observation of general acid catalysis,[3-5] the kinetic isotope effect,[4,5] and substituent effects[4,5,6] clearly indicate that these reactions for both substrates proceed via rate-limiting protonation of the

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(2) For a recent review, see G. H. Schmid and D. G. Garratt in "The Chemistry of Functional Groups. Supplement A. The Chemistry of Double-Bonded Functional Groups", Part 2, S. Patai, Ed., Wiley-Interscience, London, 1977, p 725.

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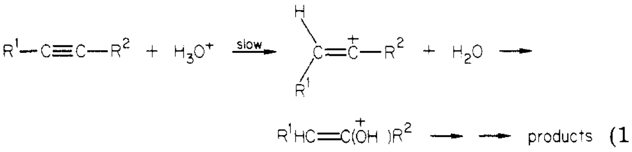
multiple bond (see eq 1 for the hydration of alkynes) and that the transition states must resemble, respectively, carbenium ions or vinyl cations. Studies on carboxylic acid[7] and hydrogen halide[8] additions suggest a similar mechanistic pattern.


(1)

The reactivity ratios, k_o/k_a, for cognate pairs of alkenes and alkynes (see Table I) are always small and become smaller with increasing reactivity.[9] Consistent with this is the circumstance that larger substituent effects are usually observed for alkynes than for alkenes. The relative reactivities, k_o/k_a, are remarkably unaffected by medium effects (thus, in Table I compare $k_{\mathrm{styrene}}/k_{\mathrm{phenylacetylene}}$ for hydration in aqueous H_2SO_4 and for the addition of CF_3CO_3H in CCl_4). This is a point of interest since it has been suggested[10,11] that the low k_o/k_a observed in acid-catalyzed hydrations, at variance with the high k_o/k_a for halogenations, could be due to differential solvation effects since the former reactions are usually performed in highly polar solvents and the latter in weakly polar ones.

The solvation requirements for the protonation of double and triple bonds have been evaluated[12,13] by the use of the Bunnett and Olsen[14] equation (eq 2). The

$$\log (k_\psi) + H_o = \phi_{\neq}(H_o + \log C_{\mathrm{H^+}}) + \log k_o \qquad (2)$$

solvation parameter $\phi_{\neq}$, which may be evaluated by measuring the rate constant for hydration, k_ψ, at several acid concentrations, is directly related, through eq 3,

$$\log f_{\mathrm{H^+}} - \log (f_{\neq}/f_s) = (\phi_{\neq} - 1)(H_o + \log C_{\mathrm{H^+}}) \qquad (3)$$

to the activity coefficients of both the transition state, $f_{\neq}$, and the substrate, f_s, and hence to the free energies of desolvation of the transition state and the substrate on going from dilute aqueous solutions to a given acid concentration.

In the case of the styrene–phenylacetylene pair, the activity coefficients of the substrates have been directly measured and found to undergo modest and similar changes on changing the acid concentration; quite likely, this is also the case for the other pairs. Hence one may infer that the $\phi_{\neq}$ values essentially depend on the quantity $\log f_{\neq}$ (see eq 3). These values (Table II), although changing with structural variation of the substrates, are very similar for each pair investigated. It follows that there is no major differential solvent effect favoring triple bond protonation on going from dilute aqueous solutions to concentrated sulfuric acid solutions. It may therefore be concluded from the similarity of the rates and of the $\phi_{\neq}$ mechanistic parameter that the proton affinities or, in other words, the free energies of protonation of double and triple bonds in solution are closely similar for structurally similar alkenes and alkynes.

Table II
Acidity Dependence[a] (eq 2) of the Rates of Hydration in Aqueous H_2SO_4, 25 °C, of Substituted Styrenes ($XC_6H_4CH=CH_2$, S) and Phenylacetylenes ($XC_6H_4C\equiv CH$, PA)

substrate	X	$\phi_{\neq}$	$-\log k_o$	k_o/k_a[b]
S	*p*-OMe	−0.54	4.38	0.21[c]
PA		−0.67	3.67	
S	X=*p*-Me	−0.34	5.50	0.24[d]
PA		−0.58	5.25	
S	X=H	−0.31	6.60	0.56[d]
PA		−0.44	6.55	
S	X=*p*-Cl	−0.28	6.95	0.76[d]
PA		−0.29	6.85	

[a] Data from ref 11. [b] Evaluated by interpolation of data measured for acid concentration close to those indicated (see *c* and *d*). [c] In 16% H_2SO_4. [d] In 38% H_2SO_4.

Carbenium Ion Additions (Addition of Alkyl Halides). The addition of carbenium ions to alkenes to form more extended carbenium ions is a well-documented reaction,[15] as it is the basis of important industrial processes such as the cationic polymerization or alkylation of alkenes with olefins. Relatively fewer studies have been reported on the analogous addition to alkynes.[16] However, the available data show a close similarity between the two unsaturated systems.

The mechanism of the addition to alkynes was investigated only recently.[17,18] In these studies, most of the addition reactions were carried out under Friedel–Crafts conditions, using alkyl or phenylalkyl chlorides and bromides in the presence of a Lewis acid as precursors of carbenium ions. The instability of acetylenes under electrophilic conditions (e.g., toward strong Lewis acids) limited the choice of alkylating agents to those that give relatively stable carbenium ions (*tert*-butyl, diphenylmethyl, benzyl) that may be generated under mild conditions. From both phenyl- and alkyl-substituted acetylenes, good yields of 1:1 adducts were obtained in the presence of $ZnCl_2$ or $ZnBr_2$ in boiling dichloromethane, with complete Markovnikov regioselectivity.

The results were consistent with a mechanism of addition[19] involving, in a first, rate-determining step, the attack of the carbenium ion on the triple bond to give a vinyl cation, which in a subsequent fast step is captured by the nucleophile (Cl^- or Br^-, complexed by the catalyst) (eq 4). The intermediate vinyl cation may

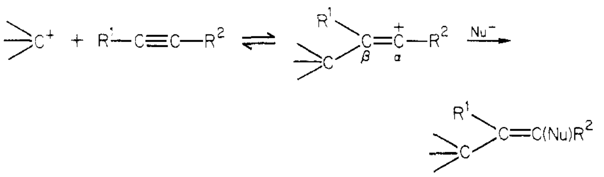

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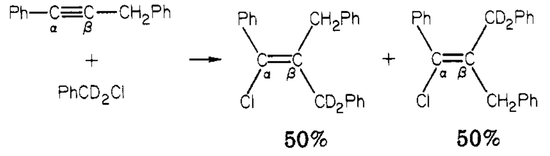
Table III
Relative Reactivities of Phenyl-Substituted Alkenes and Alkynes toward Carbenium Ions under Friedel-Crafts Conditions[a,b]

substrates	alkyl chloride	k_o/k_a
$\mathrm{PhCH{=}CH_2/PhC{\equiv}CH}$	$\mathrm{Ph_2CHCl}$	3.8
trans-$\mathrm{PhCH{=}CHMe/PhC{\equiv}CMe}$	$\mathrm{Ph_2CHCl}$	2.0
cis-$\mathrm{PhCH{=}CHMe/PhC{\equiv}CMe}$	$\mathrm{Ph_2CHCl}$	0.29
trans-$\mathrm{PhCH{=}CHPh/PhC{\equiv}CPh}$	$\mathrm{Ph_2CHCl}$	0.33
	PhCH(Me)Cl	0.40
cis-$\mathrm{PhCH{=}CHPh/PhC{\equiv}CPh}$	$\mathrm{Ph_2CHCl}$	0.003
	PhCH(Me)Cl	0.11

[a] From competition experiments (ref 26). [b] Conditions: $\mathrm{CH_2Cl_2}$, 40 °C, in the presence of anhydrous $\mathrm{ZnCl_2}$.

also suffer an intramolecular nucleophilic attack, giving a product of cyclization,[20] or undergo proton loss (in case R^1 = H) to give a disubstituted acetylene.[17]

Further support to this mechanism was given by stereochemical data, which showed[17-20] that the ratio between the isomeric products was always related to the size of the β groups of the vinyl cation intermediate, independently of the electrophilic species involved. A limiting and self-evident example[19] is reported in eq 5.



(5)

The mechanism outlined in eq 4, however, is fully valid only for the addition of carbenium ions to phenyl-substituted acetylenes. In the addition of carbenium ions to alkyl-substituted acetylenes,[18] for which a decreased stereoselectivity was observed for terminal alkynes in respect to disubstituted ones (whereas the "rule" of the relative size of β groups would suggest the opposite), and in the addition of hydrogen chloride to phenylacetylenes,[19,21] where a prevailing syn addition was observed in weakly polar solvents, other mechanistic patterns seem to participate. This calls for caution in overgeneralizing the suggested mechanism.

For this reason, the study of the relative reactivity of alkenes and alkynes toward carbenium ions was carried out only with phenyl-substituted substrates and under the same conditions used in the stereochemical study. Direct measurement of the reaction rates for both unsaturated systems was prevented by the heterogeneous nature of the reaction. The relative reactivities of pairs of olefins and acetylenes bearing the same substituents were therefore obtained by a competition method[22] (Table III).

Although the structural variations in the ethylenic and acetylenic substrates are rather limited, the results tabulated show quite clearly that, under the conditions adopted, the two unsaturated substrates have very similar reactivity unless some specific factors enter into play. The unusually low reactivity ratio for the pair *cis*-stilbene/diphenylacetylene toward diphenylmethyl carbenium ions represents such a case. However, the reactivity ratio *cis*-stilbene/*trans*-stilbene is also very low (0.01), and this suggests that the reaction of *cis*-stilbene is retarded by steric hindrance. Indeed with a smaller carbenium ion (1-phenylethyl) the steric effect appears to be smaller.

Table IV
Relative Reactivities, k_o/k_a, for the Bromination[a], at 25 °C

	styrene	*cis*-3-hexene	1-hexene
solvents	phenylacetylene	3-hexyne	1-hexyne
$\mathrm{CH_3CO_2H}$	2.6×10^3 (7.2×10^2)[b]	3.7×10^5 (*ca.* 10^5)[b]	6.5×10^4 (5.3×10^5)[b]
$\mathrm{HCO_2H}$			4.9×10^6
$\mathrm{CF_3CO_2H}$			4.6×10^7
MeOH	1.3×10^3	7.8×10^4	4.1×10^3
50% MeOH	1.5×10^3		5.0×10^5
$\mathrm{H_2O}$	$\sim 0.4 \times 10^3$		1.7×10^6

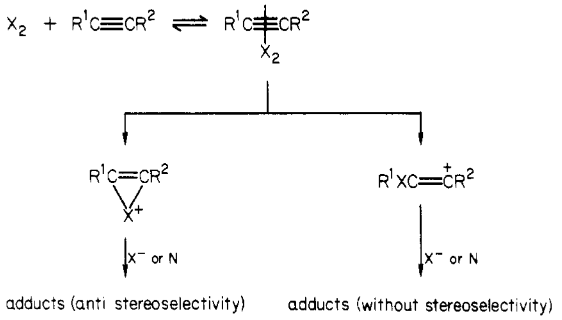
[a] Unless otherwise indicated; ref 24. [b] Chlorination; ref 9.

The partial conclusion that can be drawn at this point is that the reactivity of carbenium ions parallels that of the proton.

Class B Reagents: High Reactivity Ratio Electrophiles

Halogen Additions. The overall picture emerging from recent mechanistic studies[23-29] on the addition of halogens (mostly bromine and chlorine) to multiple C–C bonds indicates a substantial analogy between alkenes and alkynes. There are, however, also differences, as discussed below.

At least for dilute solutions,[30] the generally accepted mechanism for both alkenes and alkynes involves the rate-determining formation of a cationic intermediate, cyclic in many cases, which then yields the final adducts by reaction with available nucleophiles (see eq 6 for the addition to acetylenes). A π complex[26] is likely to be the precursor of the ionic intermediates. The rate-limiting step somewhat resembles that of an S_N1 process. Table IV shows relative reactivity data for a few pairs of alkenes and alkynes.



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The solvent effect on the k_o/k_a ratios depends on the

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(30) In relatively more concentrated solutions of halogens or when halide ions are present, different mechanisms may prevail such a concerted termolecular Ad_E3 reaction.[25]

structures of the substrates. In the case of aryl-substituted substrates the relative reactivity is unaffected by solvent changes, as expected from the fact that, in the rate-limiting step of the reaction, the solvation requirements of the small halide anion should be largely dominant over those of the large cationic partner. However, alkene/alkyne reactivity ratios for alkyl-substituted derivatives are strongly solvent dependent. The results have been explained[24] by assuming that nucleophilic assistance by the solvent is a very important kinetic factor in the case of alkynes and not in the case of alkenes. Thus, for the bromination of 1-hexyne, the relative rates of electrophilic attack with nucleophilic assistance by the solvent and of electrophilic attack without solvent assistance (the k_s/k_c ratio) were estimated[24] to increase on going from CF_3CO_2H (1) to HCO_2H (9), H_2O (25), 50% MeOH (90), CH_3CO_2H (700), 80% MeOH (1300), and MeOH (11 000).

The bridged or open structure of the cationic intermediate is often inferred[25a,27] from the stereochemical outcome of the reaction: a stereoselective anti addition is generally taken as evidence for a bridged ion. However, the stereochemical results by themselves cannot distinguish between the rate-limiting formation of an open or a bridged ion and the formation of such species after the rate-limiting step. More telling on that matter are the substituent effects. In the case of aryl-substituted alkenes and alkynes, the large negative ρ values[24,25] (σ^+) clearly suggest an open or asymmetrically partially bridged transition state and cationic intermediates. The substituent effects on alkyl-substituted alkenes[28] and alkynes[29] rather suggest the formation of bridged ions for both unsaturated systems. To sum up, the available evidence suggests that the cationic intermediates may have a geometry varying from fully bridged to open, depending on a delicate balance in which the nature of the halogen and the very nature of the substrate (double or triple bond, kind of substituent) play specific roles.

Within such a complex balance, olefins appear to be much better suited than acetylenes to react with halogen.

Sulfenyl Halide Additions. The addition of sulfenyl halides, particularly chlorides, to alkenes and alkynes has been thoroughly studied and recently reviewed.[31] Both reactions are assumed to occur via addition of the undissociated sulfenyl halide to the π system to give a sulfurane-like transition state or intermediate[32] which evolves to a thiiranium or thiirenium ion and eventually to the final products (see eq 7 for addition to alkenes).

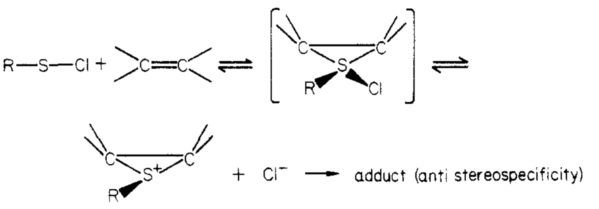

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Table V
Relative Reactivities of Alkenes and Alkynes in the Addition of 4-Chlorobenzenesulfenyl Chloride[a]

substrates	k_o/k_a
$CH_2=CH_2/CH\equiv CH$	2.82×10^5
n-BuCH=CH_2/*n*-BuC≡CH	84
trans-EtCH=CHEt/EtC≡CEt	1.5
cis-EtCH=CHEt/EtC≡CEt	14
PhCH=CH_2/PhC≡CH	1.86×10^2
trans-PhCH=CHMe/PhC≡CMe	14
cis-PhCH=CHMe/PhC≡CMe	5

[a] In 1,1,2,2-tetrachlorethane at 25 °C. Data from ref 9 and 33.

Table VI
Thermodynamic Data For $C_3H_7^+$ and $C_3H_5^+$ Ions

	IP[a]	HA(R⁺)[b]	PA[b]
$CH_3\overset{+}{C}HCH_3$	225[c]	250[f]	181[d]
$CH_3\overset{+}{C}=CH_2$	239[d]	266[g]	174[e]

[a] From ref 36. [b] From ref 35. [c] From C_3H_8. [d] From C_3H_6. [e] From C_3H_4. [f] Evaluated for the reaction $C_3H_7^+ + H^- \rightarrow C_3H_8$. [g] Evaluated for the reaction $C_3H_5^+ + H^- \rightarrow C_3H_6$.

Relative reactivity data[12,33] are reported in Table V. The k_o/k_a ratios are smaller than those observed in halogenation reactions and depend dramatically upon the structure. The relative reactivity is very large for the parent pair, ethylene and acetylene, decreases in the case of monoalkyl-substituted substrates, and becomes rather small with dialkyl derivatives. This is reminescent of the very large effect of *C*-alkyl substitution on the stability of thiirenium ions.[34]

Relative Stabilities of the Cationic Intermediates

The suggested mechanisms of electrophilic additions to double and triple bonds involve the formation of cationic intermediates. Since it is assumed that the transition states of these reactions are structurally similar to such intermediates, it follows that their properties are relevant to a discussion on the relative reactivities of olefins and acetylenes.

Carbenium Ions and Vinyl Cations: Thermodynamic Data. Thermodynamic data are available for the gas phase. Proton affinity (PA), hydride affinity (HA(R⁺)), and IP data from equilibrium cyclotron resonance and photoelectron spectroscopy measurements have been recently reported[35,36] for simple alkenes and alkynes. Data for C_3 ions are shown in Table VI. Thus, HA(R⁺) values indicate that it requires 16 kcal/mol more energy to form the 2-propenyl cation by hydride abstraction from propene than to form the 2-propyl cation from propane. On the other hand, PA data indicate that it requires 7 kcal/mol more energy to form the 2-propenyl cation by protonation of propyne than to form the 2-propyl cation from propene. We comment further on these data below.

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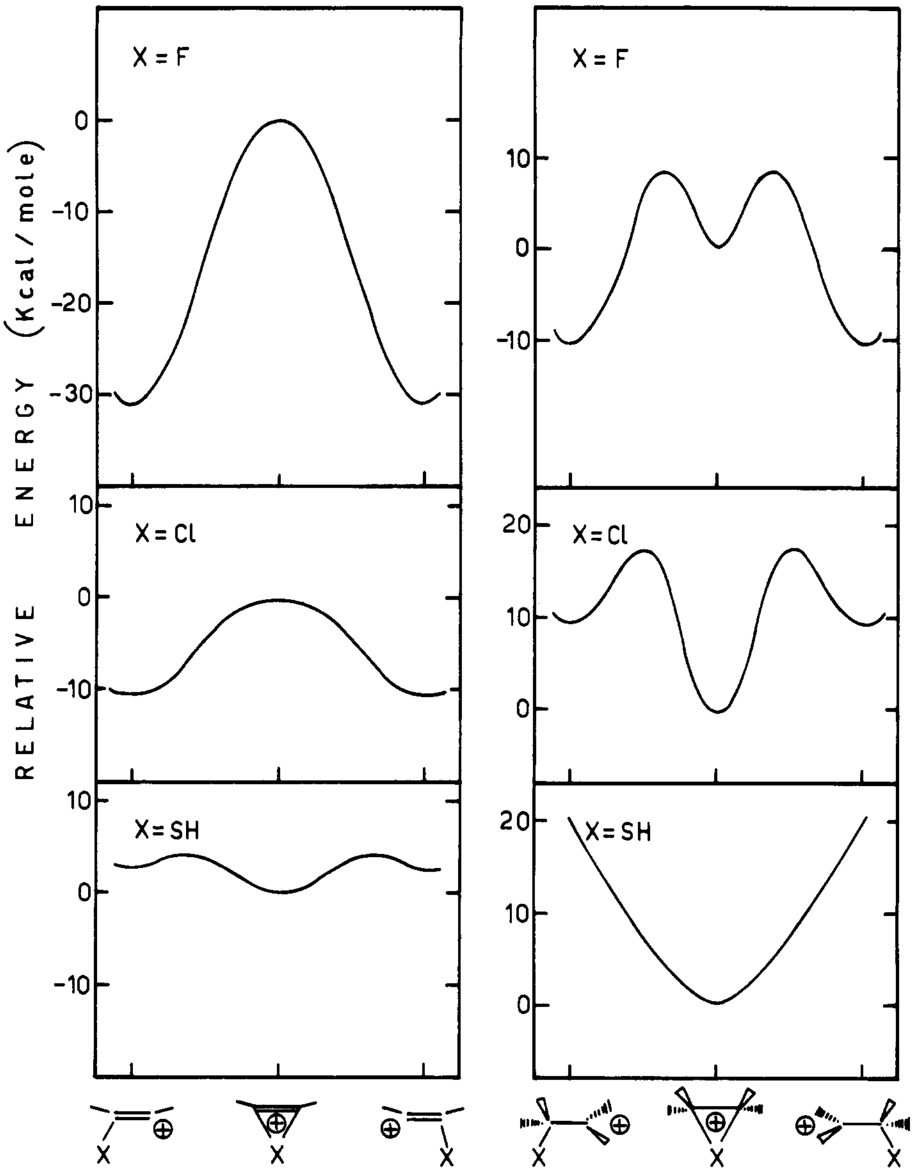

Figure 1. Energy profiles for the conversion of β-X-substituted vinyl cations and carbenium ions into the corresponding bridged ions as determined by ab initio computations.

Open and Bridged Cations. *Spectral Evidence.* Studies in superacid systems have allowed the identification, mainly by NMR techniques, of numerous carbenium ions as relatively stable species.[37] Evidence has been reported of bridged structures with hydrogen or (saturated) carbon as bridging atoms (hydrido-bridged cycloalkyl cations,[38] norbornyl and other nonclassical carbenium ions[37,39]) but not for simple open-chain systems. Apparently, neither hydrogen nor carbon is particularly able to stabilize bridged ions. Both bridged and open structures have been detected[40] for cations derived from addition of halogens to olefins. The available evidence indicates that the geometry depends on structural factors and that bromine-bridged ions are more stable than the corresponding chlorine-bridged derivatives.

On the other hand, in the domain of vinyl cations, only the ferrocenyl vinyl cation has been identified[41] with certainty by NMR, whereas early reports[42] on the detection of α-arylvinyl cations have been recently questioned.[43] No evidence has so far been reported on the existence as stable species of cations formed by addition of halogens to acetylenes.

The case of the cationic intermediates in the addition of sulfenyl derivatives is different: several thiiranium and thiirenium ions have been detected by spectroscopic methods, and a few have been isolated as rather stable salts.[34,44] No evidence for cations of open structure has been reported.

Theoretical Computation. Ab initio calculations allow a fairly accurate evaluation of both the geome-

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trical structures and the energies of small molecules. Several studies, carried out at different levels of accuracy, have been reported for most of the parent compounds of interest in the present discussion.

In the case of hydrogen or carbon as the potentially bridging atom, the energies of open and bridged ions are calculated to be roughly the same.[45] Depending on the computational methods used, either geometry may be the more stable but, more importantly, the same trend is obtained for the saturated and for the unsaturated pairs.

On the contrary, with halogen atoms, the difference between the saturated[46] and the unsaturated[47] series is quite substantial (see Figure 1); in the former case bridged ions lie always in a potential minimum, in the latter case, with both fluorine and chlorine, the bridged structure lies at a potential maximum, i.e., it is an unstable species. No data are available for brominated ions, although no dramatic changes should be expected.

In the case of thiocations a certain degree of parallelism returns: both thiiranium[48] and thiirenium[49] ions are calculated to be more stable than the corresponding open ions although the difference between bridged and open geometries is larger for the alkene-derived than for the alkyne-derived systems.

The comparison of the outcome of theoretical computations with experimental results in condensed phases should be undertaken with caution because the former refer to "model" compounds and the latter to real molecules; moreover, the solvation energies of the individual species may be different enough to change even the order of the relative stabilities,[50] although this should not be the case for the system under discussion.[51] However, it is interesting to notice that there is a close correspondence between the relative stabilities of open and bridged ions shown by the calculations and our arbitrary classification of class A and class B reagents.

Conclusions

The main features emerging from the above analysis are the following: (a) the nucleophilicity of a C–C triple bond toward external electrophiles may be as high as or higher than that of a double bond; (b) large reactivity ratios, k_o/k_a, are, however, observed in the addition of halogens and, to a lesser extent, of sulfenyl halides; (c) halogens and sulfenyl sulfur are much better bridging atoms for cations derived from alkenes than those derived from alkynes; (d) substituent effects on reactivity in electrophilic additions are larger for alkynes than for alkenes, and much more so for the least substituted molecules; (e) the relative reactivities are not very sensitive to solvent effects except when solvent nucleophilic assistance comes into play, as in the bromination of alkyl-substituted derivatives.

The core of the problem is the discrepancy between points a and b, which perhaps may be solved by taking into account point c. We suggest that the "normal" behavior of the unsaturated systems is that manifested in the addition of the proton and carbenium ions, where open cations are involved, and, by inference, in the addition of electrophiles with poor bridging ability. The very high k_o/k_a values observed in the halogenation of simple alkyl derivatives have, then, to be related to the bridging ability of these electrophiles.

Further Considerations

This suggestion implies that the formation of open vinyl cations via electrophilic additions to alkynes is almost as facile as the formation of carbenium ions from alkenes, even though the ease of formation of the two types of cations by solvolytic processes is quite different. Independent support for this hypothesis is offered by a closer analysis of the gas-phase data. As reported in Table VI for the case of C_3 ions, the hydride ion affinity of 2-propenyl cation is 16 kcal/mol higher than that of 2-propyl cation, whereas the proton affinity of propyne is only 7 kcal/mol less than that of propene; the difference may be expected to decrease on going to more complex molecules (aryl derivatives, ethers, thioethers, etc.). Furthermore, these differences in energy are considerably attenuated on going from gas to condensed phase. Indeed, the protonation of simple alkynes in solution is only slightly slower (less than 1 kcal/mol higher activation energy) than that of the corresponding alkenes, and the S_N1 reactions of vinyl derivatives are 10^5–10^8 times slower (7–11 kcal/mol higher activation energy) than those of the corresponding alkyl derivatives.[1,52] It is to be noticed that the commonly observed compression of energy differences of ions in the liquid phase compared to the gas phase, due to nonspecific solvation, is not contradictory[51] of the virtual absence of more specific solvent effect in electrophilic additions to double and triple bonds as discussed above.

The energies of formation of carbenium ions or vinyl cations, whether by solvolysis of alkyl or vinyl substrates or by cation addition to alkenes or alkynes, are a composite of several factors, such as ground-state energies, bond energies, etc. The experimental kinetic outcome—the relative reactivities toward electrophiles of cognate pairs of alkenes and alkynes—depends on a complex balance of factors, which happens to be almost even when the electrophiles are the proton or a carbenium ion and the systems are moderately substituted.

Such a balance has to break down in halogen additions proceeding through bridged cations such as those to alkyl-substituted derivatives. In this case, the stabilization by bridging of the ions derived from alkenes is much larger than of those derived from alkynes. In line with the above arguments is also the behavior toward sulfenyl halides of alkenes and alkynes which react

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via stable bridged ions. Although thiiranium ions are more stable than the corresponding thiirenium ions, smaller differences in the k_0/k_a ratios than in halogen additions are expected and were indeed observed.

The case of halogen addition to aryl derivatives that seemingly occur via open ions, yet with large k_0/k_a ratios (ca. 10^3), seemingly defies the above rationale. Here, other factors are probably involved: the differential electronic effect of the β-halogen linked to the intermediates,[23b,24] the different stability of the π complex precursors,[26c] the partial bridging of the transition states,[24] and differences in bonding energies could substantially favor the reactivity of alkenes over that of alkynes.

Finally, we wish to emphasize that the mechanism of electrophilic addition must be fully demonstrated before one undertakes to interpret the relative reactivities of alkenes and alkynes, since different modes of reaction may prevail. As an example, the syn additions of hydrogen halides[8,21,27] and chlorine[53] in nonpolar or weakly polar solvents have been explained in terms of syn-oriented tight ion pairs which collapse to products before equilibration is attained. However, there is not, as yet, enough evidence to rule out an alternative mechanism, a formally forbidden $2\sigma + 2\pi$ suprafacial cycloaddition, which may become allowed[54] when the two molecules have sufficiently different polarity.

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^{13}C NMR Chemical Shifts and the Microstructure of Polymers

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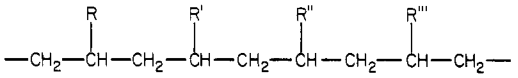
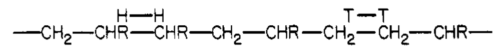
Just as the primary structures of proteins determine their biological functions, so too the microstructures of synthetic polymers fundamentally influence their unique physical properties. Whether a polymer is an amorphous glassy or rubbery solid with the ability to deform under stress without rupture or a crystalline solid possessing dimensional stability and high tensile strength depends on its microstructure, i.e., the detailed architecture of its long chains.

To determine the microstructure of the schematic vinyl polymer



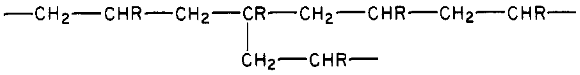
$$-CH_2-\overset{R}{\overset{|}{C}}H-CH_2-\overset{R'}{\overset{|}{C}}H-CH_2-\overset{R''}{\overset{|}{C}}H-CH_2-\overset{R'''}{\overset{|}{C}}H-CH_2-$$

the types and distribution of side chain substituents R, R′, R″, R‴, etc. must be specified along with their configurational arrangement, or stereosequence, as illustrated in Figure 1 for polypropylene, where all R, R′, R″, R‴, etc., are methyl groups. Furthermore, in terms of physical properties it is also important to know if head-to-head (H–H) or tail-to-tail (T–T) monomer addition



$$-CH_2-\overset{H-H}{CHR-CHR}-CH_2-CHR-\overset{T-T}{CH_2-CH_2}-CHR-$$

or any branching occurs during polymerization.



$$-CH_2-CHR-CH_2-\underset{CH_2-CHR-}{\underset{|}{C}R}-CH_2-CHR-CH_2-CHR-$$

Aside from X-ray diffraction studies of stereoregular, crystallizable polymers, there was no method for the direct experimental measurement of vinyl polymer stereosequence until the technique of high-resolution NMR was applied to polymers.[1] Of the two nuclei ^{1}H and ^{13}C, which possess spin and are common to synthetic polymers, ^{1}H initially served as the spin probe in NMR polymer studies. However, though ^{1}H is more abundant than ^{13}C, ^{1}H NMR spectra of polymers suffer from a narrow dispersion of chemical shifts and extensive ^{1}H–^{1}H spin–spin coupling. ^{13}C NMR as currently practiced does not suffer from these difficulties.

The advent of proton-decoupled spectra recorded in the Fourier transform mode has catapulted ^{13}C NMR spectroscopy into the position as the method of choice for determining polymer microstructure.[2-4] The distribution of monomer units in binary and ternary copolymers,[3,4] the stereoregularity of asymmetric vinyl polymers,[4] the amounts and types of vinyl polymer defect structures[5] produced by other than head-to-tail

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