

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_o/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 alkynes¹ 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

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

alkene/alkyne	conditions	k_o/k_a	ref
<i>n</i> -BuCH=CH ₂ /	48% H ₂ SO ₄ , 25 °C	3.6	9
<i>n</i> -BuC≡CH	CF ₃ CO ₂ H, 60 °C	5.3	7
<i>trans</i> -EtCH=CHEt/	48.7% H ₂ SO ₄ , 25 °C	16.6	9
EtC≡CEt	CF ₃ CO ₂ H, 60 °C	2.6	7
<i>cis</i> -EtCH=CHEt/	48.7% H ₂ SO ₄ , 25 °C	13.9	9
EtC≡CEt			
EtOCH=CH ₂ /	aqueous buffers, 25 °C	5.5 × 10	
EtOC≡CH		10 ⁻³	
PhCH=CH ₂ ^a /	48.7% H ₂ SO ₄ , 25 °C	0.65	9
PhC≡CH ^b	0.8 M CF ₃ CO ₂ H in CCl ₄ , 30 °C	0.8	11
	HCl in CH ₃ CO ₂ H, 25 °C	~3	8

^a Solvent kinetic isotope effect, $k_{H_2O}/k_{D_2O} = 2.27$ (4.6 M HClO₄, 25 °C, ref 5); $\rho(\sigma^+) = 3.7$ (48% H₂SO₄, 25 °C, ref 6 and 11). ^b $k_{H_2O}/k_{D_2O} = 2.5$ (34% H₂SO₄, 25 °C, ref 4); $\rho(\sigma^+) = 4.1$ (48% H₂SO₄, 25 °C; data from ref 11).

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.

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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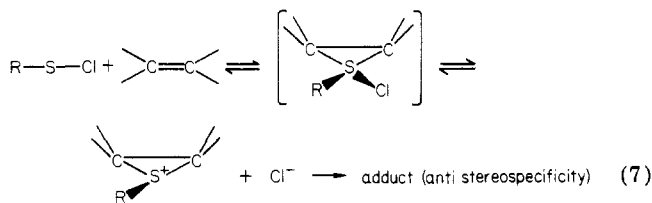
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structures of the substrates. In the case of aryl-substituted substrates the relative reactivity is unaffected by solvent changes, as expected from the fact that, in the rate-limiting step of the reaction, the solvation requirements of the small halide 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 explained²⁴ 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 estimated²⁴ to increase on going from $\text{CF}_3\text{CO}_2\text{H}$ (1) to HCO_2H (9), H_2O (25), 50% MeOH (90), $\text{CH}_3\text{CO}_2\text{H}$ (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 alkenes²⁸ and alkynes²⁹ 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.

Sulfonyl Halide Additions. The addition of sulfonyl 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 sulfonyl halide to the π system to give a sulfurane-like transition state or intermediate³² 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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(32) The hypothesis that the products of additions of sulfonyl halides to both alkenes and alkynes may be formed directly from the sulfurane-like intermediate was also advanced.³¹

Table V
Relative Reactivities of Alkenes and Alkynes in the
Addition of 4-Chlorobenzenesulfonyl Chloride^a

substrates	k_o/k_a
$\text{CH}_2=\text{CH}_2/\text{CH}\equiv\text{CH}$	2.82×10^5
$n\text{-BuCH}=\text{CH}_2/n\text{-BuC}\equiv\text{CH}$	84
$\text{trans-EtCH}=\text{CHEt}/\text{EtC}\equiv\text{CEt}$	1.5
$\text{cis-EtCH}=\text{CHEt}/\text{EtC}\equiv\text{CEt}$	14
$\text{PhCH}=\text{CH}_2/\text{PhC}\equiv\text{CH}$	1.86×10^2
$\text{trans-PhCH}=\text{CHMe}/\text{PhC}\equiv\text{CMe}$	14
$\text{cis-PhCH}=\text{CHMe}/\text{PhC}\equiv\text{CMe}$	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
$\text{CH}_3\dot{\text{C}}\text{HCH}_3$	225 ^c	250 ^f	181 ^d
$\text{CH}_3\dot{\text{C}}\equiv\text{CH}_2$	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 $\text{C}_3\text{H}_7^+ + \text{H}^- \rightarrow \text{C}_3\text{H}_8$. ^g Evaluated for the reaction $\text{C}_3\text{H}_5^+ + \text{H}^- \rightarrow \text{C}_3\text{H}_6$.

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 reminiscent 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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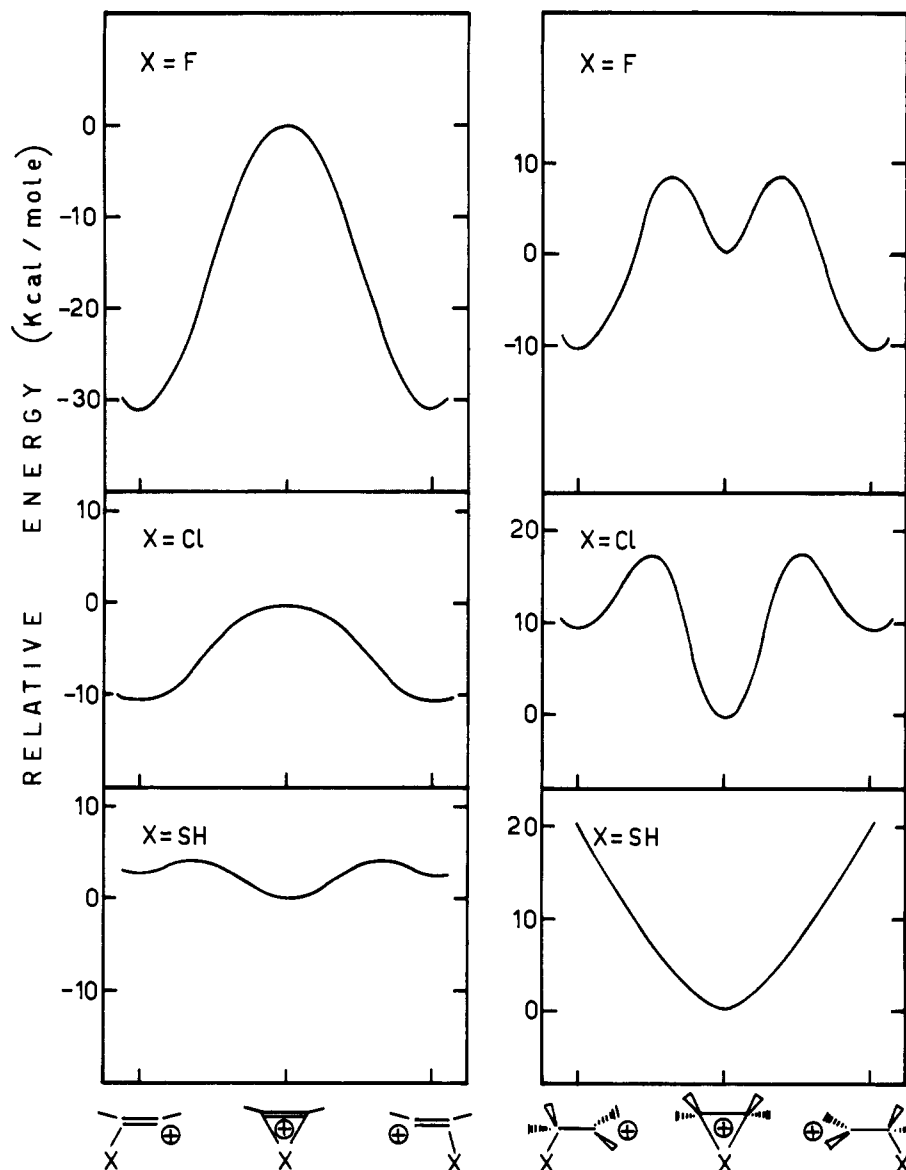


Figure 1. Energy profiles for the conversion of β -X-substituted vinyl cations and carbenium ions into the corresponding bridged ions as determined by ab initio computations.

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 non-classical 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 detected⁴⁰ 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 identified⁴¹ with certainty by NMR, whereas early reports⁴² on the detection of α -arylvinyli 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 sulfonyl derivatives is different: several thiuranium 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 geometries

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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 saturated⁴⁶ and the unsaturated⁴⁷ 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 thiiranium⁴⁸ and thiirenium⁴⁹ 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 sulfonyl halides; (c) halogens and sulfonyl sulfur are much better bridging atoms for cations derived from alkenes than those de-

rived 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 C₃ 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 10⁵–10⁸ 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 contradictory⁵¹ 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 sulfonyl 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_o/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_o/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 chlorine⁵³ 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 allowed⁵⁴ when the two molecules have sufficiently different polarity.

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¹³C NMR Chemical Shifts and the Microstructure of Polymers

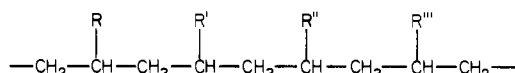
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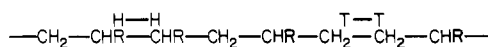
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Just as the primary structures of proteins determine their biological functions, so too the microstructures of synthetic polymers fundamentally influence their unique physical properties. Whether a polymer is an amorphous glassy or rubbery solid with 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



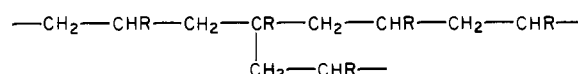
the types and distribution of side chain substituents R, R', R'', R''', etc. must be specified along with their configurational arrangement, or stereosequence, as illustrated in Figure 1 for polypropylene, where all R, R', R'', R''', etc., are methyl groups. Furthermore, in terms of physical properties it is also important to know if head-to-head (H-H) or tail-to-tail (T-T) monomer addition



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or any branching occurs during polymerization.



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 ¹H and ¹³C, which possess spin and are common to synthetic polymers, ¹H initially served as the spin probe in NMR polymer studies. However, though ¹H is more abundant than ¹³C, ¹H NMR spectra of polymers suffer from a narrow dispersion of chemical shifts and extensive ¹H-¹H spin-spin coupling. ¹³C NMR as currently practiced does not suffer from these difficulties.

The advent of proton-decoupled spectra recorded in the Fourier transform mode has catapulted ¹³C 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 structures⁵ produced by other than head-to-tail

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