# Relative Ease of Formation of Carbonium Ions and Vinyl Cations in Electrophilic Additions

**Keith Yates,* George H. Schmid, Thomas W. Regulski,**
**Dennis G. Garratt, Hei-Wun Leung, and Robert McDonald**

*Contribution from the Department of Chemistry, University of Toronto,*
*Toronto 181, Canada.* *Received June 1, 1972*

**Abstract:** The rates of addition of $Cl_2$ and $Br_2$ in acetic acid, ArSCl in tetrachloroethane, and $H_3O^+$ in 48.7% aqueous $H_2SO_4$ have been measured for the following olefin–acetylene pairs: (i) styrene–phenylacetylene, (ii) 1-phenylpropene–1-phenylpropyne, (iii) 1-hexene–1-hexyne, and (iv) 3-hexene–3-hexyne. The rate ratio $k_{\text{olefin}}/k_{\text{acetylene}}$ is found to be: $Br_2$, $2 \times 10^3$–$4 \times 10^5$; $Cl_2$, $6 \times 10^2$–$5 \times 10^5$; ArSCl, 2–200; and $H_3O^+$, 0.6–17. This range of $10^6$ in the relative reactivities of double and triple bonds toward typical electrophiles is completely unexpected in terms of our knowledge of the stabilities of the ionic intermediates being formed. By changing the solvent, the difference in bromination rates between styrene and phenylacetylene can be made to vary by a factor of $10^5$. Thus $k_{\text{styrene}}/k_{\text{phenylacetylene}}$ changes from 2590 in acetic acid to 0.67 in water indicating that solvation effects in these reactions are very important.

Electrophilic additions to olefinic systems have been the subject of considerable study.[1] The analogous additions[2] to acetylenic systems have received much less attention. Because of the current interest in vinyl cations (or disubstituted carbonium ions) *vis-à-vis* normal trisubstituted carbonium ions, we have made a comparative study of the reactivities of various olefins and acetylenes toward four typical electrophilic reagents: bromine, chlorine, arenesulfenyl chloride, and protons.

The principal difference between these two types of electrophilic addition (*i.e.*, olefinic and acetylenic) reactions should lie mainly in the different stabilities of the cations being formed in the rate-determining step of the addition, *e.g.*, substituted carbonium ions *vs.* substituted vinyl cations, which may be either open or bridged.

Studies of product stereochemistry indicate that phenyl substitution leads to open ion intermediates[3,4] (except for sulfenyl halide addition),[5,6] whereas exclusive alkyl substitution leads to bridged ions[3,4,7] (except for proton addition).

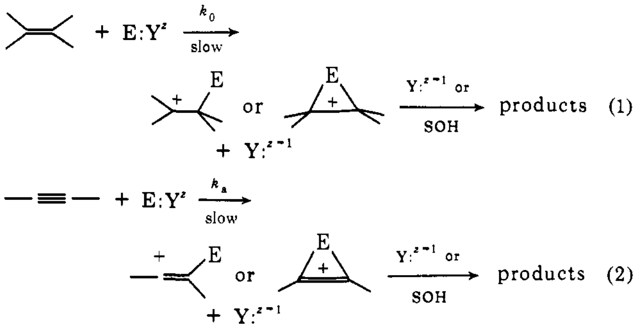
Considering the relative stabilities of carbonium ions and vinyl cations, it can be estimated from thermochemical data[8,9] that for the simplest case, acetylene *vs.* ethylene, it should be about 6 kcal more difficult to add a proton to acetylene to form the vinyl cation than to add a proton to ethylene to form the ethyl cation. Similar estimates based on electron impact studies[10] place the difficulty of formation of vinyl cations at about 10–20 kcal[2] above formation of the corresponding carbonium ion. Evidence from solvolytic studies of alkyl and vinyl systems[11] indicates a difference of the order of 8–11 kcal in $\Delta F^{\ddagger}$ for the two types of system.

Thus for the reactions we are considering it might be expected that acetylenes would react at least five powers of ten more slowly than the corresponding olefins toward typical electrophiles and possibly even much more slowly.

Our results indicate that these expectations about the relative ease of formation of the different cationic intermediates are not realized under all experimental conditions.

## Results and Discussion

The electrophilic addition reactions under investigation can be represented by the general reactions in eq 1 and 2. In the olefin reactions, the products have been



E=Br, Cl, ArS, or H; $Y:^{z-1}$=$Br^-$, $Cl^-$, $Cl^-$, $H_2O$

shown to be either simple addition products (*e.g.*, dihalides, chloroarenesulfenates, alcohols) or those arising from solvent incorporation (*e.g.*, acetoxy halides, halohydrins). With acetylenic substrates the simple addition products are stable to further reaction, unless enolic, but the solvent-incorporated products are always enolic and yield carbonyl compounds on work-up.

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(1) R. C. Fahey, *Top. Stereochem.*, **3**, 237 (1968).

(2) G. Modena and V. Tonellato, *Advan. Phys. Org. Chem.*, **9**, 185 (1971).

(3) J. H. Rolston and K. Yates, *J. Amer. Chem. Soc.*, **91**, 1469, 1477 (1969).

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(5) G. H. Schmid and V. M. Csizmadia, *Chem. Ind.* (*London*), 1811 (1968).

(6) G. H. Schmid and M. Heinola, *J. Amer. Chem. Soc.*, **90**, 3466 (1968).

(7) G. H. Schmid and V. M. Csizmadia, *Can. J. Chem.*, **44**, 1338 (1966).

(8) (a) F. P. Lossing, *ibid.*, **49**, 3571 (1971); (b) F. P. Lossing and G. P. Semeluk, *ibid.*, **48**, 955 (1970).

(9) "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, U. S. Government Printing Office, Washington, D. C., 1969.

(10) See the review by H. G. Richey and J. M. Richey, "Carbonium Ions," Vol. 2, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, p 899.

(11) S. I. Miller and D. A. Kaufman, *J. Amer. Chem. Soc.*, **90**, 7282 (1968); Z. Rappoport and A. Gal, *ibid.*, **91**, 5246 (1969); P. E. Peterson and J. M. Indelicato, *ibid.*, **91**, 6194 (1969); W. M. Jones and D. D. Maness, *ibid.*, **92**, 5457 (1970).

**Table I.** Rates of Electrophilic Additions

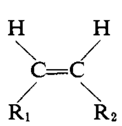
| | Bromination in acetic acid | | Chlorination in acetic acid | | 4-Chlorobenzenesulfenyl chloride in TCE | | Hydration in aqueous solution | | |
|---|---|---|---|---|---|---|---|---|---|
| Substrate | $k_{\mathrm{obsd}}$, $M^{-1}$ sec$^{-1}$ | $k_o/k_a$ | $k_{\mathrm{obsd}}$, $M^{-1}$ sec$^{-1}$ | $k_o/k_a$ | $k_{\mathrm{obsd}}$, $M^{-1}$ sec$^{-1}$ | $k_o/k_a$ | $k_{\mathrm{obsd}}$, sec$^{-1}$ | $k_o/k_a$ | Ref |
| PhCH=CH$_2$ | 11.2 | | $7.2 \times 10^3$ | | 62.2 | | $45.8 \times 10^{-5\,a}$ | | *d* |
| | | | | | | | $2.04 \times 10^{-3\,b}$ | | *g* |
| | | 2,590 | | 720 | | 186 | $1.22 \times 10^{-3\,c}$ | | *g* |
| PhC≡CH | $4.33 \times 10^{-3}$ | | 10 | | 0.334 | | $83 \times 10^{-5\,a}$ | 0.55[a] | *e* |
| | | | | | | | $3.1 \times 10^{-3\,b}$ | 0.65[b] | *f*, *g* |
| | | | | | | | $1.89 \times 10^{-3\,c}$ | 0.65[c] | *g* |
| PhCH=CHCH$_3$ | 8.9 (*c*)[h] | | $1.45 \times 10^4$ (*c*) | | 43 (*c*) | 5.2 (*c*) | Cis isomerizes to trans | | |
| | | | | | 117.7 (*t*) | 14.1 (*t*) | | | |
| | | 3,620 (*c*) | | 617 (*c*) | | | $2 \times 10^{-4\,b}$ (*t*) | | |
| | 31.7 (*t*)[i] | | >10$^5$ (*t*) | | | | | | |
| PhC≡CCH$_3$ | $2.4 \times 10^{-3}$ | 5,000 (*t*) | 23.5 | >4,000 (*t*) | 8.34 | | $1.31 \times 10^{-4\,b}$ | 1.5 (*t*) | *g* |
| *n*-BuCH=CH | 31.7 | | $7.67 \times 10^3$ | | 133 | | $1.94 \times 10^{-4\,b}$ | | |
| | | 182,000 | | 530,000 | | 84.3 | | 3.6 | *g* |
| *n*-BuC≡CH | $1.74 \times 10^{-4}$ | | $1.45 \times 10^{-2}$ | | 1.41 | | $5.35 \times 10^{-5\,b}$ | | |
| EtCH=CHEt | $2.17 \times 10^3$ (*c*) | | >10$^5$ (*c*) | | 3563 (*c*) | | $3.16 \times 10^{-4}$ (*c*) | | |
| | | 372,000 (*c*) | | ~100,000 (*c* & *t*) | | 14.0 (*c*) | | 13.9 (*c*) | *g* |
| | $1.96 \times 10^3$ (*t*) | | >10$^5$ (*t*) | | 388 (*t*) | | $3.75 \times 10^{-4}$ (*t*) | | |
| EtC≡CEt | $5.84 \times 10^{-3}$ | 336,000 (*t*) | 5.0 | | 255 | 1.5 (*t*) | $2.26 \times 10^{-5}$ | 16.6 (*t*) | *g* |

[a] Extrapolated to an equivalent acidity in aqueous $HClO_4$ and $H_2SO_4$-HOAc. [b] 48.7% aq $H_2SO_4$. [c] 47% aq $H_2SO_4$ with 3% MeOH. [d] W. M. Schubert and B. Lamm, *J. Amer. Chem. Soc.*, **88**, 120 (1966). [e] C. Eaborn, R. W. Bott, and D. R. W. Walton, *J. Chem. Soc.*, 384 (1965). [f] D. S. Noyce and M. D. Schiavelli, *J. Amer. Chem. Soc.*, **90**, 1020 (1968). [g] This work. [h] *c* = *cis*. [i] *t* = *trans*.

Studies of product stereochemistry have shown that the ionic intermediates for each type of substrate can be represented either as open ions or bridged ions, depending on the particular substituents in the substrate and on the nature of the electrophile.

At the low concentrations of electrophile maintained in the present study, the kinetics are simple, first order in olefin or acetylene and first order in electrophile. The kinetics were generally measured under pseudo-first-order conditions, using at least a 50-fold excess of organic substrate over electrophile, except in the hydration reactions where the acid concentration was kept constant.

**Bromination.** The rates of bromination of the following pairs of similarly substituted olefins and acetylenes were measured in anhydrous acetic acid at 25° using a combination of standard potentiometric, spectrophotometric, and stopped-flow techniques, as described in the Experimental Section.



Ia-d

$R_1C{\equiv}CR_2$

IIa-d

a, $R_1$ = Ph; $R_2$ = H
b, $R_1$ = Ph; $R_2$ = Me (cis and trans)
c, $R_1$ = *n*-Bu; $R_2$ = H
d, $R_1$ = Et; $R_2$ = Et (cis and trans)

The rate constants are listed in Table I (some of these values have been reported previously[4]), from which it can be seen that the olefins add bromine fairly rapidly ($k_o \sim 10$–$10^3$ $M^{-1}$ sec$^{-1}$), whereas the acetylenes generally react much more slowly ($k_a \sim 10^{-3}$–$10^{-4}$ $M^{-1}$ sec$^{-1}$). The rate ratios $k_o/k_a$, based on similarly substituted unsaturated systems, are very large. Thus a given olefin can react with bromine under these conditions anywhere from several thousand to several hundred thousand times as rapidly as the correspondingly substituted acetylene. It can be noted that bromine shows much greater selectivity toward alkenes (Ic–d) over alkynes (IIc–d), than toward arenes (Ia–b) over arynes (IIa–b). The above results are semiquantitatively in accord with the expected greater ease of formation of carbonium ions over vinyl cations, based on thermochemical and mass spectrometric results, and also in agreement with the known greater ease of formation of carbonium ions over vinyl cations in solvolytic reactions.

**Chlorination.** The corresponding rates of chlorine addition, also in anhydrous acetic acid, at 25° were determined in a similar way, and the rate constants are listed in Table I. The chlorine additions to olefins are even more rapid ($k_o \sim 10^3$–$10^4$ $M^{-1}$ sec$^{-1}$) than in the previous case, and in fact *trans*-1-phenylpropene (Ib, trans) reacted too fast to obtain an accurate rate constant even using the stopped-flow technique. Again the acetylenes react more slowly, although they chlorinate significantly more rapidly ($k_a \sim 10^{-2}$–$10$ $M^{-1}$ sec$^{-1}$) than they brominate.

The relative reactivities, based on $k_o/k_a$ for similarly substituted systems, again show that the double bonds add chlorine much more rapidly than corresponding substituted triple bonds. In this case also, the values of the ratio $k_o/k_a$ vary in a similar way with structure, with chlorine showing a much greater selectivity toward olefins in the alkyl-substituted series, than in the phenyl-substituted series. The results are again in accord with expectations about the relative stabilities of carbonium ion and vinyl cation intermediates and presumably of the transition states which precede them.

**Arenesulfenation.** The rates of reaction of the same substrates (Ia–d, IIa–d) with a typical arenesulfenyl halide (4-chlorobenzenesulfenyl chloride) were investigated in tetrachloroethane as solvent at 25°, using similar kinetic methods. The rate constants obtained are listed in Table I (some of these values have been reported previously[5,6]). It can be seen that although these additions are in general fairly rapid, the olefins react more slowly with ArSCl than with $Cl_2$. Also values of the ratio $k_o/k_a$ are significantly lower than for either $Cl_2$ or $Br_2$ additions. Nonetheless, in each case, the olefin adds 4-chlorobenzenesulfenyl chloride anywhere from about 2 to 200 times as rapidly as the corresponding acetylene. The previously noted structural dependence of electrophile selectivity toward olefins is not observed for this type of addition. Both of these facts can probably be attributed to the much greater bridging ability of sulfur over either bromine or chlorine, manifest in the general trans stereospecificity of ArSCl additions which is not generally observed for $Cl_2$ and $Br_2$ additions. Such a strong neighboring group effect would be expected to reduce stability differences between carbonium ion and vinyl cation type intermediates, as the bridging atom acquires a greater share of the developing positive charge.

**Hydration.** Since the rate-determining step in hydration of olefins and acetylenes has been shown to be proton transfer,[12-14] these reactions can be regarded analogously as electrophilic additions of $H_3O^+$, at least in aqueous solution.

Only values of the rate constants for the hydration of substrates Ia and IIa have already been reported. These were repeated and hydration rate constants for the remaining substrates (Ib–d, IIb–d) also determined at 25° in a common solvent, namely 48% aqueous sulfuric acid. The rate constants are collected in Table I.

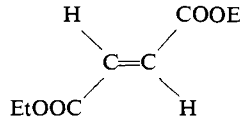
There are two very striking differences between these rates of $H_3O^+$ attack and those of the other electrophiles $Br_2$, $Cl_2$, and ArSCl. Firstly, the hydration reactions are in general much slower, with rate constants in the range $10^{-3}$–$10^{-5}$ $sec^{-1}$.[15] Secondly, and more striking is the fact that the olefin to acetylene reactivity ratios are in general close to unity, and in some cases the acetylene even reacts more rapidly than the corresponding olefin.

The general low reactivity of both olefins and acetylenes toward hydration is made even more striking by the fact that the other types of electrophilic additions were carried out in weakly polar solvents, and the rate constants for these processes would have been even higher, if they too could have been measured in aqueous solution. Thus the contrast between the rates of various electrophilic additions to the same set of substrates, as shown by an overall range of rate constants of $10^{10}$ in Table I, would be even more marked if all the rates could be investigated in the same solvent. This low reactivity toward $H_3O^+$ can be attributed mainly to the fact that hydration does not involve a similar ion-forming process to those in the other additions and that the electrophilic species $H_3O^+$ is a much more stable entity in aqueous solution than the organic ions being generated in the rate-determining step.[16]

However the change in *relative* reactivity of olefins and acetylenes in going from $Cl_2$, $Br_2$, and ArSCl to $H_3O^+$ is more remarkable. The values of $k_o/k_a$ for the various systems, listed in Table I, show a range from 500,000, in favor of the olefin as the most reactive system in some cases, to 0.6, in favor of the acetylene in others. This range of $10^6$ in the relative reactivities of double and triple bonds toward typical electrophiles is completely unexpected and is very difficult to explain in terms of what is known about the stabilities of the ionic intermediates being formed. For example, although solvolysis is not the exact microscopic reverse of electrophilic addition, the ionic intermediates generated in each type of reaction are formally very similar. However $S_N1$ solvolyses of vinyl derivatives, whatever the leaving group, are always much slower than the analogous reactions of saturated systems.[11] This difference in reactivity is usually of the order of several powers of ten, and is generally explained by the instability of the vinyl cations being formed, with respect to the corresponding carbonium ion intermediates.

**Solvent Effects.** Since the rates of reaction of the four electrophiles investigated were measured in different media, it is important to try to assess the influence of solvent polarity on both the absolute, and more particularly, the relative reactivities of olefins and acetylenes. It is well known that typical electrophilic additions (of $Br_2$, $Cl_2$, and to a less extent ArSCl) are markedly accelerated by polar solvents such as water and methanol, relative to their rates in the more commonly used weakly polar media such as acetic acid and haloalkanes. This creates experimental difficulties, since the rates are often sufficiently high, even in acetic acid, to require use of the stopped-flow approach. It was therefore decided to compare directly the rates of bromination of two highly deactivated substrates, diethyl fumarate and diethyl acetylenedicarboxylate. (Bromination was chosen as a typical electrophilic addition which is capable of showing great selectivity between olefins and acetylenes.) The rate constants for bromination of these two deactivated substrates at 25° in water are given in Table II. These values show that the very high rate differences between typical ole-

Table II. Bromination of Diethyl Fumarate and Diethyl Acetylenedicarboxylate in Water at 25°

| | | $k_{obsd}$, $M^{-1}$ $sec^{-1}$ | $k_o/k_a$ |
|---|---|---|---|
|  | $\xrightarrow[H_2O]{Br_2}$ | $1.34 \times 10^{-3}$ | 0.6 |
| EtOOCC≡CCOOEt | $\xrightarrow[H_2O]{Br_2}$ | $2.33 \times 10^{-3}$ | |

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(12) W. M. Schubert and B. Lamm, *J. Amer. Chem. Soc.*, **88**, 120 (1966).

(13) C. Eaborn, R. W. Bott, and D. R. W. Walton, *J. Chem. Soc.*, 384 (1965).

(14) D. S. Noyce and M. D. Schiavelli, *J. Amer. Chem. Soc.*, **90**, 1020 (1968).

(15) Rate constants for acid-catalyzed hydration reactions have previously been reported as pseudo-first-order rate constants, and this practice is followed here. This does not affect relative rate comparisons of olefins and acetylenes, since the acid concentration is the same in each case. Further, comparisons of absolute reactivities are little affected by this practice since division of $k_{obsd}$ (in $sec^{-1}$) by the acid concentration ($M$ = 6.8) to obtain $k_2$ in $M^{-1}$ $sec^{-1}$ involves a relatively small change compared with the range of reactivities involved here.

(16) Alternatively, a consideration of the differences in the bond energies[17] of the bond being broken in the electrophile and that being formed to carbon in the rate-determining step shows that hydration should be more difficult than bromination, chlorination, or arenesulfenation.

(17) C. T. Mortimer, "Reaction Heats and Bond Strength," Pergamon Press, London, 1962; "Handbook of Chemistry and Physics," Chemical Rubber Co., Cleveland, Ohio, 1971; C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, pp 48–50.

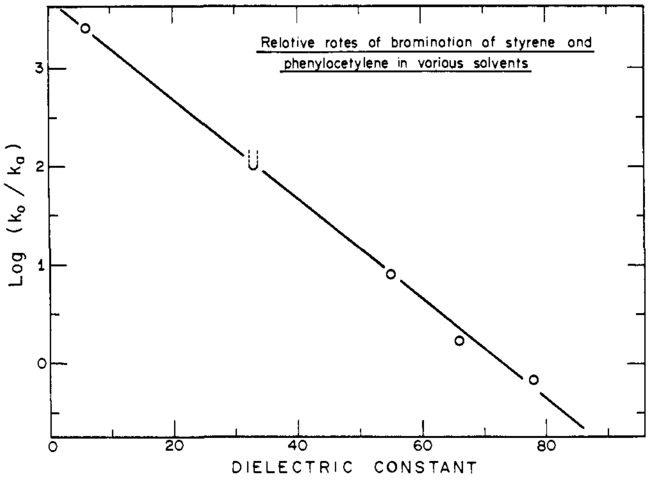

Figure 1. Plot of log $k_{\mathrm{olefin}}/k_{\mathrm{acetylene}}$ for bromine additions as a function of solvent dielectric constant.

fins and acetylenes, as shown for acetic acid in Table I, essentially disappear in aqueous solution. Thus it appears that solvation effects on the carbonium ions and vinyl cations being formed in the rate-determining steps of these reactions are capable of equalizing the ease of formation of the corresponding transition states; or alternately the mechanism changes to a nucleophilic addition in the addition to these unreactive olefins.

To investigate these possibilities further we have examined the relative rates of bromination in aqueous solution of two reactive systems, styrene (Ia) and phenylacetylene (IIa), whose reactivities in acetic acid have already been measured ($k_o/k_a = 2590$). This required use of a competition method, whereby equimolar excesses of Ia and IIa were allowed to react with an inadequate supply of $Br_2$, in each solvent. Analysis of product mixtures by glc and nmr gave the relative rates $k_o/k_a$ shown in Table III. It is clear from these results that as solvent polarity increases, the relative reactivity of olefin to acetylene sharply decreases. Ultimately in the most polar solvent used, water, the phenylacetylene actually brominates more rapidly than the styrene. This corresponds closely to the type of situation already reported for the hydration of the same two substrates, also in aqueous solution. These results suggest that the bromine addition is occurring by the same electrophilic mechanism in all solvents. However hydrolysis of the adducts in water produces bromide ion which can remove bromine and form tribromide ion. If this occurs the kinetics could change by incursion of a third-order mechanism.[4] In order to rule out this possibility a competition experiment was carried out in the presence of silver nitrate to remove any bromide ion formed. The results are given in Table III. The small change in $k_{\mathrm{styrene}}/k_{\mathrm{phenylacetylene}}$ is consistent with all bromination reactions occurring by the same mechanism.

Table III. Solvent Effect on Relative Bromination Rates of Styrene and Phenylacetylene

| Solvent | Dielectric constant | $R^c$ | $k_{\mathrm{Ia}}/k_{\mathrm{IIa}}{}^d$ |
|---|---|---|---|
| HAc | 6 | | 2590 |
| MeOH | 33 | $\geq 10^2$ | $\gtrsim 10^2$ |
| 50% MeOH–$H_2O$ | $55^a$ | 8.0 | 17.2 |
| 30% MeOH–$H_2O$ | $66^a$ | 1.7 | 2.3 |
| $H_2O$ | 78 | $0.67\ (0.61)^b$ | $0.63\ (0.54)^b$ |

[a] Taken from the work of G. Akerlöf, *J. Amer. Chem. Soc.*, **54**, 4130 (1932). [b] Reaction carried out in presence of excess silver nitrate. [c] Product ratio of styrene to phenylacetylene. [d] Calculated using the Ingold–Shaw equation (*J. Chem. Soc.*, 2918 (1927)).

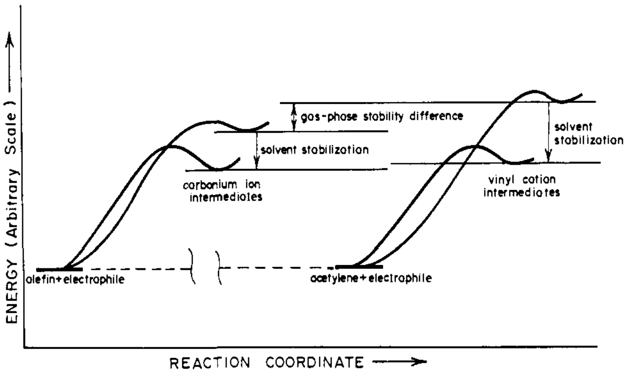

Figure 2. Schematic representation of the relative ease of formation of carbonium ion and vinyl cation intermediates in gas phase and solvent stabilized electrophilic additions.

The relationship between relative reactivity and solvent polarity is a direct one, as shown by Figure 1 where log $k_o/k_a$ is plotted as a function of solvent dielectric constant. It is clear from the linear relationship obtained[18] that, as the ion-solvating ability of the medium increases, the acetylene is able to compete more effectively for available electrophile. We believe that the variations in relative reactivity described in this paper for two series of analogously substituted substrates are without parallel in organic chemistry. We know of no reported case where solvent effects alone can invert relative rate factors as large as $10^5$ in favor of one type of substrate over another.

## Conclusions

It is evident that solvation effects in these reactions are very important and that the large differences in ease of formation of carbonium ion intermediates and vinyl cation intermediates, expected from gas-phase results and observed in weakly polar solvents, completely disappear in aqueous solution. This is somewhat surprising for several reasons.

Firstly, vinyl or carbonium ion type intermediates are not expected to be strongly solvated by specific interactions with solvents such as water. If they were capable of strong hydrogen bond interactions it would be the carbonium ions which would be favored. It therefore appears that the equalization of reactivity found in water is mainly a consequence of the effect of the high dielectric constant of the reaction medium on carbonium or vinyl ion formation and possibly of the ability of water to solvate the counterion species formed as the bond is broken in the electrophilic reagent, *i.e.*, $Br^-$, $Cl^-$, or in the case of hydration, $H_2O$.

Secondly, as the diagram in Figure 2 shows, the trend toward equalization of reactivity produced by going from the gas phase to a poor solvent, then to a good solvent, necessarily implies an earlier transition state for electrophilic additions in strongly polar sol-

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[18] A similar linear relationship is obtained between log $k_o/k_a$ and Winstein's $Y$ values for the same set of solvents.

vents. (Note that electrophilic additions in general are strongly accelerated by increased solvent polarity, or in other words, $\Delta F^{\neq}$ is decreased strongly.) Thus for either bromination or hydration in aqueous solution, an earlier transition state is implied. This is at variance with Brønsted $\alpha$'s for typical olefin hydration reactions[19,20] which are in the range 0.6–0.8, implying a high degree of proton transfer at the transition state, or in other words a late transition state. It can only be concluded, as recently suggested by Bordwell,[21] that Brønsted $\alpha$'s are not necessarily very good criteria of the degree of advancement of transition states in acid-catalyzed reactions, such as hydration of olefins and acetylenes.

Thirdly, the Hammett $\rho$ values for typical electrophilic additions are somewhat difficult to interpret. Available values are shown in Table IV. The general similarity of most of the $\rho$ values, being between $-3.2$ and $-4.8$ in the majority of cases, indicates that the degree of charge development at the benzylic carbon atom is not too different for any of the electrophiles studied, except sulfenyl halide. The low value for sulfur is a consequence of the strong bridging ability of this atom, which reduces charge on $C_\alpha$ and hence reduces ring substituent effects. However the general similarity of the $\rho$ values for $Cl_2$, $Br_2$, and $H_3O^+$ is very surprising in terms of their known bridging abilities (*i.e.*, Br > Cl ≫ H). At first glance it seems equally surprising that the $\rho$ values are relatively insensitive to medium effects. However in view of previous comments about the probably nonspecific nature of solvent effects on the ease of vinyl cation and carbonium ion formation, this similarity may be quite reasonable.[22]

**Table IV.** Summary of $\rho$ Values[a] for Electrophilic Additions

| Electrophile | System | Solvent | $\rho$ | Ref |
|---|---|---|---|---|
| $H_3O^+$ | $PhC{\equiv}CCOPh$ | $H_2O\text{-}H_2SO_4$ | $-4.21$ | *f* |
| | $PhC{\equiv}CCOOH$ | $H_2O\text{-}H_2SO_4$ | $-4.77$ | *g* |
| | $PhC{\equiv}CH$ | $H_2O\text{-}H_2SO_4$ | $-3.84$ | 14 |
| | $PhC{\equiv}CH$ | $HAc\text{-}H_2SO_4$ | $-4.3$ | 13 |
| | $PhCH{=}CH_2$ | $H_2O\text{-}HClO_4$ | $-3.58$ | *h* |
| | $PhCH{=}CH_2$ | $H_2O\text{-}H_2SO_4$ | $-4.00$ | *i* |
| | $PhMeC{=}CH_2$ | $H_2O\text{-}H_2SO_4$ | $-3.27$ | *j* |
| | $PhMeC{=}CH_2$ | $H_2O\text{-}H_2SO_4$ | $-3.27$ | *i* |
| $Cl_2$ | $PhCH{=}CH_2$ | HAc | $-3.2$ | *k* |
| | $PhCH{=}CHCOOH(t)$ | HAc | $-4.46$ | *l* |
| | $PhCH{=}CHCOOMe\ (t)$ | HAc | $-4.46$ | *l* |
| | $PhCH{=}CHCOPh$ | HAc | $-3.59$ | *l* |
| $Br_2$ | $PhCH{=}CH_2\ (k_2)$ | HAc | $-4.87$ | *m* |
| | $PhCH{=}CH_2(k_3)^d$ | HAc | $-4.38$ | *n* |
| | $PhCH{=}CH_2\ (k_g)^e$ | MeOH | $-4.20$ | *o* |
| | $PhC{\equiv}CH$ | HAc | $-5.17$ | 4 |
| ArSCl | $PhCH{=}CH_2{}^b$ | HAc | $-2.4^c$ | *p* |

[a] Based on equation $\log k/k_0 = \rho\sigma^+$ except where noted. [b] 2,4-Dinitrobenzenesulfenyl chloride. [c] Based on $\sigma$-substituent scale. [d] Based on third-order bromination rate. [e] Based on global rate with added LiBr. [f] D. S. Noyce and K. E. DeBruin, *J. Amer. Chem. Soc.*, **90**, 372 (1968). [g] D. S. Noyce, M. A. Matesich, and P. E. Peterson, *ibid.*, **89**, 6225 (1967). [h] W. M. Schubert and J. R. Keeffe, *ibid.*, **94**, 559 (1972). [i] J. P. Durand, M. Davidson, M. Hellin, and F. Coussemant, *Bull. Soc. Chim. Fr.*, 52 (1966). [j] N. C. Deno, F. A. Kish, and H. J. Peterson, *J. Amer. Chem. Soc.*, **87**, 2157 (1965). [k] H. W. Leung and K. Yates, unpublished results. [l] $\rho^+$ calculated from the work of P. W. Robertson, *et al.*, as tabulated by P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier, New York, N. Y., 1966, pp 84–85. [m] J. A. Pincock and K. Yates, *Can. J. Chem.*, **48**, 2944 (1970); J. H. Rolston and K. Yates, *J. Amer. Chem. Soc.*, **91**, 1483 (1969). [n] R. McDonald, S. Shapiro, and K. Yates, unpublished results. [o] J. E. Dubois and A. Schwarcz, *Tetrahedron Lett.*, 2167 (1964). [p] N. Kharasch and W. L. Orr, *J. Amer. Chem. Soc.*, **78**, 1201 (1956).

An unexplained phenomenon is why vinyl cation instability is always so manifest in solvolytic reactions, yet so variable in its effects on electrophilic additions. It seems clear that the mechanistic processes by which carbonium ions and vinyl cations can be formed in solvolysis and electrophilic addition reactions, although formally very closely related in a microscopic reversibility sense, must be fundamentally very different. This problem is under current investigation in our laboratories.

## Experimental Section

**Materials.** All olefins and acetylenes are commercially available and were distilled before use. The sulfuric acid solutions were prepared by diluting C.I.L. reagent grade sulfuric acid with distilled water. The density of the solution was then measured on an Anton Paar digital precision density meter (Model DMA02C) and converted to per cent $H_2SO_4$ by weight. 1,1,2,2-Tetrachloroethane[23] and acetic acid[8] were purified as previously reported.

**Kinetics. Bromination.** The rates of addition to acetylenes were measured as previously reported,[24] while the rates of addition to olefins were measured using the stopped-flow method. The consumption of bromine was measured by the decrease in absorption at 490 mμ.

**Arenesulfenation.** The rates of addition to the olefins and acetylenes were measured by the stopped-flow method as previously reported.[23]

**Chlorination.** The rates of addition to the olefins and acetylenes were measured using a Durrum-Gibson stopped-flow spectrophotometric system. The consumption of chlorine was measured by the decrease in the absorption at 321 mμ.[25]

**Hydration.** The rates of hydration were measured by observing the decrease in the concentration of olefin or acetylene with a Unicam SP800 spectrophotometer equipped with a SP825 Programme Controller, scale expander, and recorder. The wavelengths monitored for the various substrates are tabulated in Table V.

**Table V.** Wavelengths Used for Kinetic Measurements

| Substrate | λ, mμ | Substrate | λ, mμ |
|---|---|---|---|
| Styrene | 248 | *trans*-3-Hexene | 200 |
| *cis*-1-Phenylpropene | 241 | Phenylacetylene | 239 |
| *trans*-1-Phenylpropene | 251 | 1-Phenylpropyne | 238 |
| 1-Hexene | 196 | 1-Hexyne | 196 |
| *cis*-3-Hexene | 200 | 3-Hexyne | 198 |

A standard solution for a kinetic run was prepared by adding the proper amount of substrate to a 10-ml volumetric flask and then diluting to the mark with a 48.7% $H_2SO_4$ solution equilibrated at 25°. Rate constants were obtained either by plotting $\log (A - A_\infty)$ *vs.* time or by using the method of Guggenheim. All measurements were taken at a temperature of 25 ± 0.005° with each rate constant calculated from an average of three or more separate determinations.

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(22) If solvent stabilization involved a specific interaction, such as hydrogen bond formation, this form of external stabilization might be expected to reduce the role of internal (substituent) stabilization and hence the magnitude of $\rho$. However if solvent stabilization were of a more general nature, based simply on the dielectric properties of the medium, then the role of internal stabilization, and hence the $\rho$ value, might be relatively unaffected.

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**Table VI.** Reaction Products from the Halogen Competition Reactions

| Solvent | Styrene adducts,[a] % | Phenylacetylene adducts,[b] % | $k_o/k_a$ |
|---|---|---|---|
| $H_2O$ | 40 | 60 | 0.7 |
| 70% $H_2O$-MeOH | 62.5 | 37.5 | 1.7 |
| 50% $H_2O$-MeOH | 88.2 | 11.8 | 7.5 |
| MeOH | >99 | <1 | $>10^2$ |
| HAc | >99 | <1 | 2590[c] |

[a] Dibromide and solvent incorporated products. [b] Mono- and dibromo ketones; it is assumed that enolic monobromides react much faster than either styrene or phenylacetylene and hence consumption of a second molecule of $Br_2$ by these species does not affect the competition. [c] Ratio calculated from actual rate constants.

**Competition Rate Ratios.** Into a 250–5000-ml one-necked flask was placed a predetermined volume of solvent saturated with oxygen, styrene (2.60 mmol), and phenylacetylene (2.60 mmol). The solution was mixed and the flask covered to exclude light. A competitive amount (2.50 mmol) of a bromine solution was added dropwise and with stirring over a 15 min period. The solution was then extracted twice with pentane and the extract dried ($MgSO_4$). The organic layer was condensed and product analysis was accomplished by glc and nmr. Products were determined by the α- or β-proton resonances for the styrene adducts and by the ortho benzene ring protons of the ketones or the olefinic proton resonance of the acetylene adduct where appropriate. Table VI summarizes the products formed in each competitive reaction.

In order to establish the stability of the products in water and to discount any possible product equilibrium which could be present a control experiment was performed. Styrene and bromine were reacted in an aqueous medium. After the reaction was complete, phenylacetylene was added and stirred for 1 hr. The reaction mixture was worked-up and analyzed by nmr. The product distribution revealed that under the conditions of the competition reactions, the products formed were stable and no product equilibrium existed between olefin and acetylene.

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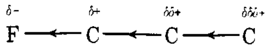
# The Conformational Dependence of the Inductive Effect in the σ-Electron System as Studied by Carbon-13 Nuclear Magnetic Resonance

**Isao Morishima,*[1a] Kenichi Yoshikawa,[1a] Koji Okada,[1a] Teijiro Yonezawa,[1a] and Kojitsu Goto[1b]**

*Contribution from the Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan, and JEOL Inc., Akishima, Tokyo, Japan.* *Received March 6, 1972*

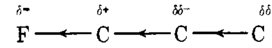
**Abstract:** The $^{13}C$ chemical shifts induced by the protonation in the trifluoroacetic acid solution have been measured for various aliphatic amines and N-heterocyclic six-membered ring compounds. The protonation-induced $^{13}C$ shifts are proved to exhibit marked structural and conformational dependences. These results are fairly well interpreted in terms of the charge densities on the carbon skeleton obtained by the semiempirical molecular orbital calculations and are discussed in relation to stereospecificity of the inductive effect in the σ-electron system.

Studies of the electronic inductive effect in the π-electron system have long been carried out experimentally and theoretically. However, the problem of the σ-inductive effect has been less studied. Elucidation of the structural and conformational dependences of the electronic structures of the σ-electron system is one of the essential problems in understanding various stereochemical problems in organic chemistry. The present study is concerned with delineating stereospecificity of the electronic inductive effect in the σ-electron system. A couple of decades ago, Ingold[2] suggested that an electron-withdrawing substituent, such as the fluorine atom, makes the atom of the σ skeleton positive, and that this effect is diminished gradually along the σ chain.



$$\overset{\delta-}{F}\longleftarrow\overset{\delta+}{C}\longleftarrow\overset{\delta\delta+}{C}\longleftarrow\overset{\delta\delta\delta+}{C}$$

In contrast to this, Pople, *et al.*,[3] using the CNDO–SCF molecular orbital calculations, suggested that the inductive effect induced by such an electronegative substituent alternates and attenuates along the σ skeleton.



$$\overset{\delta-}{F}\longleftarrow\overset{\delta+}{C}\longleftarrow\overset{\delta\delta-}{C}\longleftarrow\overset{\delta\delta\delta+}{C}$$

Although the concept of the σ-inductive effect has been well accepted in organic chemistry, the mode and mechanism of the transmission of the σ-inductive effect along the saturated molecules are still open to further experimental and theoretical investigations. In this sense, it seems worthwhile to examine experimentally these two aspects of the σ inductive effect and to investigate the consequences of conformational change in the σ skeleton.

It is well established that the $^{13}C$ chemical shift is quite a sensitive probe for detecting the structural and electronic perturbations around a carbon atom.

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(1) (a) Kyoto University; (b) JEOL Inc.

(2) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell and Sons, London, 1953.

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