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Gas Phase Basicities of Phenylacetylenes. Intrinsic Resonance Demand of the 1-Phenylvinyl Cation[1)]

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Gas-phase basicities (GB) of a series of substituted phenylacetylenes were determined by measuring the standard free energy changes of proton transfer equilibria using a pulsed ion cyclotron resonance mass spectrometer. The LArSR analysis of the substituent effect on the GB values gave an r^+ value of 1.18 and a ρ value of -14.0. The r^+ value is significantly larger than that obtained for the GB of α-methylstyrenes but is smaller than that for chloride ion affinities of benzyl cations, while the ρ value is similar in the three systems. This means that the 1-phenylvinyl cation has an intermediate resonance demand between those of the α-cumyl cation and the benzyl cation. Further, the r^+ value of 1.18 for 1-phenylvinyl cation obeys the same "resonance demand vs. carbocation stability" relationship observed for a series of ordinary sp^2-hybridized benzylic carbocations. This reveals that the π-delocalization mechanism in the vinyl cation system has no unique feature but it is a part of a continuous spectrum of resonance demands of varying benzylic carbocations characterized by $r^+=1.18$. A comparison of the present GB values with the substituent effect for the acid-catalyzed hydration of phenylacetylenes in solution has shown that the r^+ value is perceptibly smaller in the latter case. This suggests that the π-delocalization in the transition state differs considerably from that of the stable phenylvinyl cation intermediate. This is in contrast to the situation in the $\mathrm{S_N1}$ solvolysis where the r^+ value is identical to the value characteristic for the formation of the fully developed carbocation.

Electrophilic additions to alkynes or solvolysis of vinylic substrates have been extensively studied in the last 30 years and intermediate vinylic carbocations are no longer regarded as unusual species.[2)] Much attention has been paid to the energetics and the structures of vinyl cations. Most of the information about their stabilities was derived from kinetic studies on carbocation-forming reactions on the assumption that the transition states of these reactions were structurally similar to the vinyl cation intermediates. In particular, the substituent effect analysis of the solvolysis rates of the precursors vinyl halides and arenesulfonates has played an important role in clarifying the electronic properties of vinyl cations.[3—5)]

Mass spectrometric or ion cyclotron spectroscopic studies can provide more direct information on the thermodynamic properties of vinyl cations.[6)] For example, gas-phase basicity of alkynes, defined as the negative of the standard free energy change for protonation reaction (1), can give the intrinsic stabilities of the desired vinyl cations, because proton transfer equilibrium constants are mainly determined by the free energy differences between ionic species.

$$-\mathrm{C{\equiv}C}- + \mathrm{H}^+ \rightarrow -\mathrm{C^+{=}CH}- \qquad (1)$$

$$-\Delta G^\circ = \mathrm{GB}$$

Modena, Speranza, and co-workers[7)] measured the gas-phase basicities (GB) of a series of substituted phenylacetylenes and noticed that the ρ^+ value of -10.0 obtained from the GB vs. σ^+ plot is equal to that obtained from a similar GB vs. σ^+ plot for the styrene system, in spite of the fact that substituted phenylacetylenes are consistently less basic than the corresponding styrenes by a few kcal mol^{-1}. Based on the concept of varying resonance demand in the substituent effect, we criticized the unrestricted application of the σ^+ substituent constant scale to benzylic cation systems.[8—13)] Application of such σ^+-analysis must be restricted to systems where the resonance demand is quite close to that of the α-cumyl (1-methyl-1-phenylethyl) cation, even though the system of interest bears a positive charge at the carbon conjugated with the aryl group. This restriction is based on the excellent applicability of the LArSR Eq. 2 to a wide variety of reactions and on the mechanistic validity of their correlation results.[9—13)]

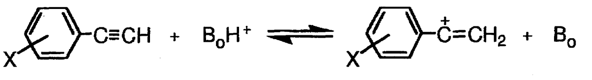
$$-\delta\Delta G^\circ = \rho(\sigma^\circ + r^+\Delta\overline{\sigma}^+_{\mathrm{R}}) \qquad (2)$$

In Eq. 2 σ° and $\Delta\overline{\sigma}^+_{\mathrm{R}}$ are a normal substituent constant and a resonance substituent constant ($=\sigma^+-\sigma^\circ$), respectively, r^+ is a resonance demand parameter indicating the degree of the π-interaction between a *para* π-donor substituent and the positive charge, and ρ is a susceptibility parameter.

Recently, we applied this analysis successfully to substituent effects on the stability of benzylic carbocations in the gas phase, and found that the resonance demand parameter (r^+) varied significantly with the system, i.e., from $r^+=1.00$[14)] for the α-cumyl cation via $r^+=1.29$[15)] for the benzyl cation to $r^+=1.53$[16] for the 2,2,2-trifluoro-1-phenylethyl cation. Moreover, the change in the magnitude of r^+ was found to be linearly related to the change of the intrinsic stability of the parent carbocation of the respective systems.[16] It is, therefore, of interest to investigate the resonance demand of 1-phenylvinyl cation in comparison with the analogous sp^2 hybridized benzylic cations. However, since the available data were not sufficient for a detailed analysis by means of Eq. 2, we undertook new measurements for a variety of substituted phenylacetylenes and re-examined the literature GB values in order to enable the correlation analysis.

Results and Discussion

The relative gas-phase basicities of substituted phenylacetylenes were obtained by measuring the standard free energy changes of the proton transfer equilibria Eq. 3 using reference bases (B_o) of known basicity.



(3)

The standard free energy changes for individual equilibria are summarized in Table 1. The uncertainly in most of the ΔG° values may be estimated to be ≤ 0.2 kcal mol^{-1}. These ΔG° values were converted to absolute GB scale in reference to GB(NH$_3$) of 195.6 kcal mol^{-1}.[17] The GB values of several derivatives were determined previously by Marcuzzi et al.[7] using the same techniques and the results are also given in Table 1. Although their data are mostly consistent (<1 kcal mol^{-1}) with our corresponding new values, there is a larger discrepancy of 2.2 kcal mol^{-1} for the *p*-MeO derivative which is clearly above the experimental uncertainly. Since most of the GB values of the reference bases used for the present determinations are in good agreement with the values cited in their study, the disagreement is not due to the basicity scale of the reference bases. Since the reason for this disagreement is unclear, for analysis of the substituent effect we prefer to use only the present data which were obtained under the same conditions.

p-Aminophenylacetylene may have two basic sites, i.e., the amino nitrogen atom and the acetylenic carbon. The GB value of 210.9 kcal mol^{-1} obtained for *p*-aminophenylacetylene is significantly greater than that of aniline (202.5 kcal mol^{-1} [17]) where protonation occurs at the amino group. If protonation of *p*-aminophenylacetylene occurs at the amino group, the higher GB value than aniline requires that the *p*-C≡CH group will stabilize the anilinium ion by 8.4 kcal mol^{-1}. This is highly unlikely, since this group is usually regarded as an electron acceptor that destabilizes a positive charge,[18] hence leading to a decreased basicity. We therefore assume that protonation must occur at the acetylene group to give a vinyl cation. No such difficulty in assigning the protonation site exists for other substituted phenylacetylenes because the substituents are less basic than C≡CH. These assignments of protonation site are consistent with the substituent effect analysis discussed below. The GB values relative to unsubstituted phenylacetylene are given in Table 2.

The relative GBs of arylacetylenes are plotted in Fig. 1 against the corresponding GB values of 1-methylstyrenes which measure the relative stabilities of the formed α-cumyl cations. Since we have recently shown a surprising excellent linear relationship for the gas phase stabilities of α-cumyl cations against ordinary solution σ^+ values,[14] there is no difficulty in defining a gas-phase σ^+ scale based on the stabilities of these cations. Thus, the GB vs. GB plot of substituted phenylacetylenes against α-cumyl cations corresponds to a σ^+-plot in the gas phase. Figure 1 shows clearly that a simple linear relationship do not exist between these two quantities for the whole set of substituents, suggesting that the stabilities of 1-phenylvinyl cations cannot be described by a single set of σ^+ substituent constants. While *meta* substituents provide an excellent linear relationship with a slope of 1.07, all *para* π-donors show systematic positive deviations from the *meta* line, i.e., the stronger *para* π-donor substituents cause the greater stabilization, whereas *p*-MeO, 3-Cl-4-MeO, and 3-F-4-MeO which have an identical resonance effect show deviations of similar magnitude. Although proton transfer equilibria are determined by the free energy differences between neutral molecule and the charged molecules, the charged form produces most of substituent effects on basicity and acidity.[6d] These deviations may therefore be indicative of an exalted resonance effect of such substituents in the phenylvinyl cation system compared with that in the α-cumyl system. In fact, the upward deviations of *para* π-donors from *meta*-line correlate nicely with the resonance effect substituent constants, $\Delta\bar{\sigma}^+_R$ (Eq. 4).

$$\Delta GB_{(\text{phenylacetylenes})} - 1.07\Delta GB_{(\alpha-\text{methylstyrenes})} = -2.66\Delta\bar{\sigma}^+_R \quad (4)$$

In contrast, the ΔG° vs. ΔG° plot of 1-phenylvinyl cations

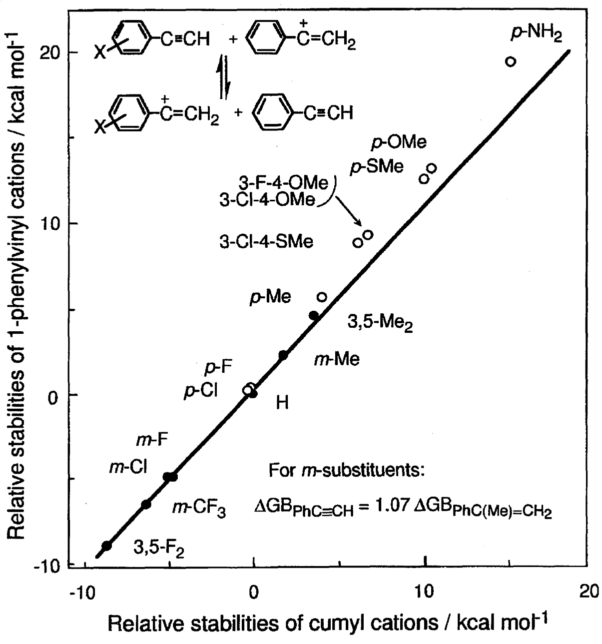


Fig. 1. Plot of ΔGB values of 1-phenylacetylenes against ΔGB values of 1-methylstyrenes.

Table 1. Standard Free Energy Changes of Proton Transfer Equilibria[a]

$$\mathrm{ArC{\equiv}CH + B_oH^+ \rightleftharpoons ArC^+{=}CH_2 + B_o}$$

Substituted phenylacetylene	Reference base (B_o)	[GB/kcal mol^{-1}][b]	$-\Delta G^\circ$[c]	Selected GB[d]	Lit 7[e]
p-NH_2	3-Acetylpyridine	[209.4]	1.5	210.9	
	1,3-Dimethyl-2-imidazolidone	[210.3]	0.6		
	i-$PrNH_2$	[211.0]	−0.2		
p-OMe	2-Fluoropyridine	[202.9]	1.6	204.6	202.4
	2-Pyrrolidone	[204.3]	0.7		
	$(MeO)_3PO$	[204.9]	−0.7		
p-SMe	2-Fluoropyridine	[202.9]	1.2	204.0	
	DMF	[203.6]	0.3		
	$(MeO)_3PO$	[204.9]	−0.8		
3-Cl-4-OMe	Acetylacetone	[199.3]	1.4	200.7	
	2-Cyanopyridine	[200.0]	0.4		
	3-Cyanopyridine	[201.3]	−0.4		
3-F-4-OMe	Acetylacetone	[199.3]	1.4	200.7	
	2-Cyanopyridine	[200.0]	0.6		
	3-Cyanopyridine	[201.3]	−0.4		
3-Cl-4-SMe	*i*-Pr_2O	[197.6]	2.6	200.3	
	t-Bu_2CO	[198.1]	2.3		
p-Me	Pr_2CO	[195.1]	1.9	197.1	196.8
	cyclo-Pr(Me)CO	[196.3]	0.9		
	p-Tolualdehyde	[196.6]	0.3		
	i-Pr_2O	[197.6]	−0.4		
m-Me	EtOAc	[192.0]	1.6	193.8	
	Pr_2O	[193.9]	0.2		
	Cyclohexanone	[194.0]	−0.2		
3,5-Me_2	Pr_2O	[193.9]	2.4	196.0	
	Pr_2CO	[195.1]	0.9		
	i-Pr_2CO	[196.1]	−0.1		
p-F	THF	[190.4]	1.3	191.8	192.5
	$(MeO)_2CO$	[191.4]	0.4		
p-Cl	THF	[190.4]	1.2	191.7	190.8
	$(MeO)_2CO$	[191.4]	0.3		
H	THF	[190.4]	1.0	191.6	192.2
	$(MeO)_2CO$	[191.4]	0.3		(191.4)[f]
	EtOAc	[192.0]	−0.2		
m-Cl	1,4-Dioxane	[185.1]	1.5	186.7	187.4
	i-PrCN	[185.7]	1.2		
m-F	1,4-Dioxane	[185.1]	1.5	186.6	186.6
	HCO_2Pr	[185.8]	1.1		
	i-PrCN	[185.7]	1.0		
	HCO_2Bu	[186.0]	0.5		
m-CF_3	EtCN	[183.6]	1.4	185.0	184.2
	i-PrCHO	[184.0]	0.5		
	HCO_2Et	[184.6]	0.4		
	PrCN	[184.9]	0.3		
3,5-F_2	PrOH	[182.0]	0.6	182.7	
	PrCHO	[183.0]	−0.2		

a) All values in kcal mol^{-1} (1 cal=4.184 J). b) GB values of reference bases, anchored by NH_3 (195.6). Taken from Refs. 6d and 17 and private communication from R. W. Taft. c) Directly measured standard free energy changes for the proton transfer equilibrium between a given and standard bases at 343 K. The positive sign of ΔG° means that the given phenylacetylene is stronger base than the reference base. d) Selected GB values of substituted phenylacetylenes. e) GB values anchored by GB(NH_3)=196.4. f) Calculated using GB(NH_3)=195.6 kcal mol^{-1}.

against benzyl cations[15] shows downward deviations of strong *para* π-donors from the unity slope *meta* line, as seen in Fig. 2. This trend indicates a reduced resonance stabilization of *para* π-donor substituents in the phenylvinyl cation compared with that in the benzyl cation. We conclude that the resonance demand of the phenylvinyl cation system has an intermediate value between the α-cumyl and the benzyl cations.

Table 2. Relative GB Values of Substituted Phenylacetylenes and Substituent Constants[a)] Used for LArSR Analysis

Subst.	ΔGB	$\sigma^{\circ}_{(g)}$	$\Delta\bar{\sigma}^{+}_{R(g)}$	Subst.	ΔGB	$\sigma^{\circ}_{(g)}$	$\Delta\bar{\sigma}^{+}_{R(g)}$
p-NH_2	19.3	−0.19	−1.00	*m*-Me	2.2	−0.12	0.00
p-OMe	13.0	−0.10	−0.70	*p*-F	0.2	0.20	−0.17
3-F-4-OMe	9.1	0.22	−0.72	*p*-Cl	0.1	0.20	−0.15
3-Cl-4-OMe	9.1	0.22	−0.72	*m*-Cl	−4.9	0.36	0.00
p-SMe	12.4	0.04	−0.73	*m*-F	−5.0	0.39	0.00
3-Cl-4-SMe	8.7	0.25	−0.73	*m*-CF_3	−6.6	0.50	0.00
p-Me	5.5	−0.13	−0.20	3,5-F_2	−8.9	0.65	0.00
3,5-Me_2	4.4	−0.28	0.00	H	0.0	0.00	0.00

a) Taken from Refs. 14 and 15c.

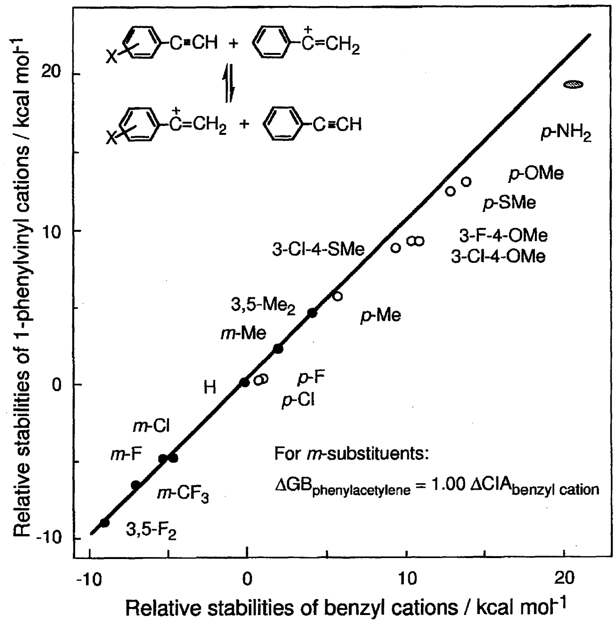


Fig. 2. Plot of ΔGB values of phenylacetylenes against ΔCIA (chloride ion affinity) values of benzyl cations. ΔCIA (20.4) of *p*-aminobenzyl cation was estimated based on the LArSR correlation ($\rho=-13.9$ and $r^{+}=1.29$) using $\sigma^{\circ}=-0.19$ and $\Delta\bar{\sigma}^{+}_{R}=-1.00$ for *p*-NH_2.[15)]

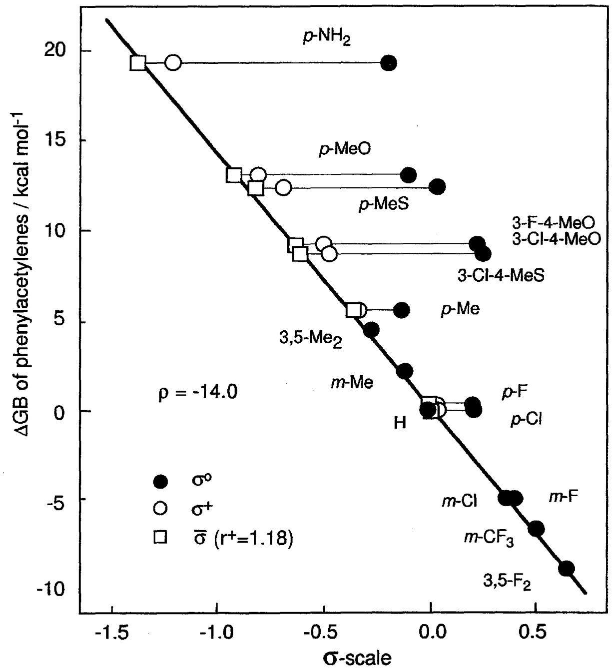


Fig. 3. LArSR plot of relative stabilities of *m*,*p*-substituted phenylvinyl cations. ●; σ°, ○; σ^{+}, □; $\bar{\sigma}$ (r=1.18).

Application of LArSR Eq. 2 to the stabilities of 1-phenylvinyl cations gave an r^{+} of 1.18 and a ρ of −14.0 with high precision (correlation coefficient=0.999 and a standard deviation=±0.3 kcal mol^{-1}), as shown in Fig. 3.[19)] This ρ value is quite similar to those for the equilibrium formation of the α-cumyl and the benzyl cations, indicating an identical sensitivity to the substituent field/inductive effects for the three systems in spite of the 7.5 kcal mol^{-1} lower stability of 1-phenylvinyl cation than that of the α-cumyl cation and the 4.5 kcal mol^{-1} higher stability than that of the benzyl cation.[15c)] The near constancy of the ρ value on changing the system is in accord with our previous observations for a series of ordinary sp^{2}-hybridized benzylic cations, where the stability of the parent carbocation (ring substituent=H) varies by > 19 kcal mol^{-1} between the α-cumyl cation and the 1-phenyl-2,2,2-trifluoroethyl cation.[14—16,20,21)] These results reveal that the ρ value is (a) independent of the stability of the parent carbocation, if the positive charge is formed at the benzylic carbon atom, and (b) appears to be insensitive to difference in hybridization of the central carbon of the ion.

In previous studies, we found that the r^{+} value varies significantly with the system, i.e., from α-cumyl cation (r^{+}=1.00)[14)] via benzyl cation (r^{+}=1.29)[15)] to 1-phenyl-2,2,2-trifluoroethyl cation (r=1.53),[16)] and that it linearly correlates with the intrinsic stability of the parent carbocations of the respective systems.[16)] The r^{+} of 1.18 for the 1-phenylvinyl cation also fits this correlation, as shown in Fig. 4. The resonance demand of the 1-phenylvinyl cation is somewhat higher than that of the 1-phenylethyl cation; this exalted r^{+} value is consistent with the 2.2 kcal mol^{-1} lower stability of the former cation compared with the latter cation (Fig. 4). This result might be attributed to the higher electronegativity of the sp hybridized carbon linked to the central carbon than of the sp^{2} hybridized carbon.

The GB of the phenylacetylene is 45.5 kcal mol^{-1} greater than that of acetylene, while the corresponding values of styrene and α-methylstyrene are 38.8 and 27.4 kcal mol^{-1} larger

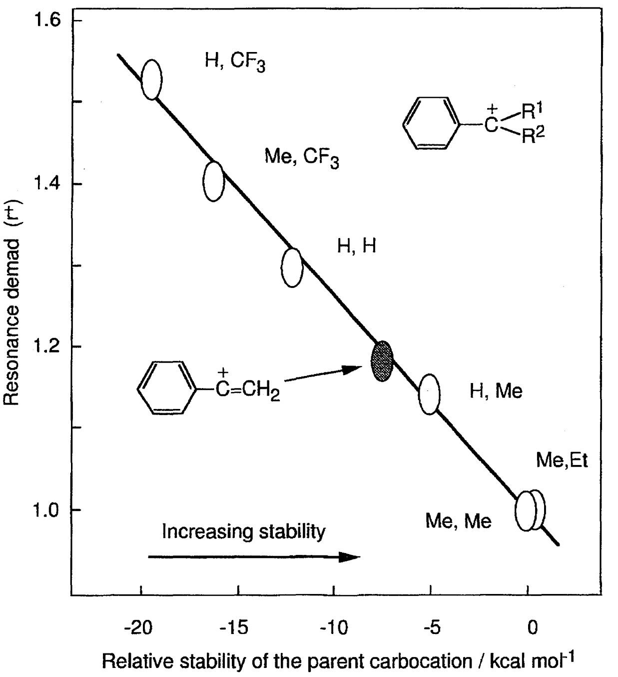
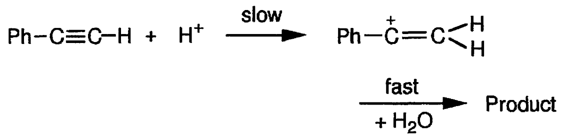


Fig. 4. Relationship between resonance demands (r^+) and relative stabilities of parent carbocations.

relative to ethylene and propene, respectively (Table 3). This indicates that the resonance stabilization by the phenyl group in a carbocation decreases significantly in order of 1-phenylvinyl cation > 1-phenylethyl cation > α-cumyl cation. This order also is the same as that of the r^+ values obtained for phenyl substituted carbocations, i.e., the system which gains the higher stabilization of the positive charge from the phenyl group has the larger r^+ value. This supports again our concept that the r^+ value is a parameter measuring the degree of the π-interaction between the substituted phenyl ring and the positive charge at the benzylic carbon.[9—14] In conclusion, the π-delocalization mechanism in the vinyl cation system resembles that in the sp^2-hybridized cations and is characterized by an r^+ value of 1.18 within the continuous spectrum of resonance demands of benzylic carbocations.

The present gas phase intrinsic stabilities of vinylic cations are important for understanding the nature of vinyl cations in solution. Although thermodynamic data for proton-transfer equilibrium of the present system cannot be obtained in solution, one may be able to evaluate from kinetic data the relative stabilities of relevant vinyl cations in solution when the latter are formed in the rate-determining step. It is therefore of interest to compare the substituent effect of GBs referred to relative stabilities of intermediate vinyl cations with the substituent effect on the acid-catalyzed hydration of phenylacetylenes, where triple bond protonation to give a vinyl cation is assumed to be rate-determining (Eq. 5).[2e,3,22)]



$$\text{Ph–C}\equiv\text{C–H} + \text{H}^+ \xrightarrow{\text{slow}} \text{Ph–}\overset{+}{\text{C}}\text{=C}{<}^{\text{H}}_{\text{H}} \xrightarrow[+\text{H}_2\text{O}]{\text{fast}} \text{Product} \qquad (5)$$

Application of the LArSR Eq. 1 to the available data of hydration of phenylacetylenes in acetic acid–water–sulfuric acid gives $r^+=0.87$ and $\rho=-4.3$.[23)] That the magnitude of ρ is as large as that obtained for S_N1 solvolysis of ordinary benzylic substrates is consistent with the currently accepted mechanism of a rate-determining formation of 1-phenylvinyl cation.[24,25)] The lower ρ value for the hydration compared with that of the GB may be reasonably attributed to solvent stabilization of the positive charge developed in the rate-determining transition state. The r^+ value for the hydration is noticeably smaller than that obtained for the equilibrium formation of the corresponding vinyl cation in the gas phase. Similar reduction of the r^+ values are observed for other acid-catalyzed hydrations of carbon–carbon double bonds, as summarized in Table 4.

There are slight differences in the r^+ value obtained for the styrene system when different data sets are used. Such differences may be partially due to the absence of suitable substituents in some data sets for a proper regression calculations based on Eq. 2. Nevertheless, all r^+ values for the hydration are clearly smaller than those observed for the corresponding carbocation stability in the gas phase. One may expect that stabilization of the transition state by solvation should result in a similar behavior of the r^+ and the ρ values.

However, we have recently found in comparison of effects of ring-substituents on basicities of benzoyl compounds, ArCOY in solution and in the gas phase that the magnitude of the r^+ is independent of a large external stabilization through solvation and that only the ρ value is sensitive to solvent stabilization of the positive charge.[26—28)] If this applies in our system, the smaller r^+ value for the hydration is unlikely to result from solvent stabilization of the transition state. In contrast, our previous studies showed that the r^+ value for the substituent effect on the gas-phase stability of sp^2-hybridized benzylic carbocations is identical with that for the S_N1 solvolysis of the corresponding precursors.[15,16,21)] This trend also seems to hold for the present vinyl cation system, because correlation with $\overline{\sigma}$ ($r^+=1.18$) gives a better linear correlation ($\rho=-4.1$, correlation coefficient=0.998) for describing the substituent effect on the solvolysis of the corre-

Table 3. Gas-Phase Basicities of Ethylenes and Acetylenes

Base	CH≡CH	PhC≡CH	CH_2=CH_2	PhCH=CH_2	MeCH=CH_2	PhC(Me)=CH_2
GB[a)]	146.1[b)]	191.6	155.6[b)]	193.9[b)]	171.7[b)]	199.1[b)]
ΔGB[c)]		45.5		38.3		27.4

a) In kcal mol^{-1}. b) Ref. 17a. c) Effect of the phenyl group on the gas phase basicity, $GB_{(\text{phenyl substituted derivative})}-GB_{(\text{unsubstituted derivative})}$.

Table 4. LArSR Correlation Results for Acid-Catalyzed Hydration of Triple Bond and Double Bond and for Gas Phase Basicity

	Hydration (log k/k_o)[a)]		Gas-phase basicity		
System	$-\rho_{hyd}$	r^+_{hyd}	$-\rho_{gas}$[j)]	r^+_{gas}	r^+_{hyd}/r^+_{gas}
PhC≡CH	4.30[b)]	0.87[b)]	14.0 (10.2)	1.18	0.74
	4.20[c,b)]	0.92[c,d)]			0.78
$PhCH=CH_2$	3.11[c)]	0.80[c)]	13.8 (10.1)[k)]	1.14[k)]	0.83
	3.94[e)]	0.70[e)]			0.61
	3.30[f)]	0.79[f)]			0.69
	3.56[g)]	0.94[g)]			0.82
	5.45[h)]	0.67[h)]			0.59
$PhC(Me)=CH_2$	3.36[i)]	0.74[i)]	13.0 (9.5)[l)]	1.00[l)]	0.74

a) Calculated using data in the literature. In aq H_2SO_4 at 25 °C otherwise noted. b) In acetic acid–water–sulfuric acid at 50.2 °C. Ref. 3. c) Ref. 2e. d) Ref. 24. e) J. C. Simandoux, B. Tork, M. Hellin, and F. Coussemant, *Bull. Soc. Chim. Fr.*, **1972**, 4402. f) Ref. 25. g) In $HClO_4$ at 25 °C, W. M. Schubert and J. R. Keeffe, *J. Am. Chem. Soc.*, **94**, 559 (1972). h) The addition of CF_3COOH in CCl_4, A. D. Allen, M. Rosenbaum, N. O. L. Seto, and T. T. Tidwell, *J. Org. Chem.*, **47**, 4234 (1982). i) Ref. 20. j) Values in parentheses are ρ for (log K/K_o). k) Ref. 21. l) Ref. 14.

sponding α-styryl tosylates[29)] in 80% aq ethanol compared with correlation with $\sigma^+(r^+=1.00)$, although only limited data are available. These findings reveal that the extent of the π-delocalization of the positive charge in the transition state of the S_N1 solvolysis must be very similar to that of the intermediate carbocation, including vinyl cations.

Accordingly, the discrepancy between the r^+ values for hydration and the GB for the phenylacetylene and styrene systems leads us to a conclusion that the structure of the transition state of the acid-catalyzed hydration is appreciably different from that of the corresponding stable cationoid intermediates with respect to π-delocalization of the positive charge, in contrast to the S_N1 solvolysis. Although α-Brönsted values and solvent kinetic isotope effects ($k_{H_2SO_4}/k_{D_2SO_4}$) reveal that the activated complex for proton transfer reactions closely resembles the final product (vinyl cation),[24)] it appears likely that the positive charge developed by protonation is still localized in part in the C_β carbon and a new C–H bond in the rate-determining transition state, which will result in a reduced π-delocalization of the positive charge into the benzene ring. For further understanding of the nature of the transition state, theoretical calculations including solvent molecules will be helpful.

Experimental

Materials. Substituted phenylacetylenes were prepared by the conventional route, involving dehydrochlorination of the mixture of chlorostyrenes obtained from the appropriate ketones and phosphorus pentachloride, and were purified by GLC or LPC. Physical properties of all compounds except the new ones lined below are in agreement with those in the literature.[3)]

3-Chloro-4-methoxy: Mp 102.5—103.5 °C; IR (Nujol) 2040 cm^{-1} (C≡CH); ^1H NMR (CCl_4) δ=7.47—6.67 (3H, m, Ar), 3.84 (3H, s, OCH_3), 2.87 (1H, s, C≡CH). Found: C, 64.74; H, 4.27%. Calcd for C_9H_7ClO: C, 64.88, H, 4.24%.

3-Fluoro-4-methoxy: Mp 37.5—38.5 °C; IR (Nujol) 2100 cm^{-1} (C≡CH); ^1H NMR (CCl_4) δ=7.22—6.65 (3H, m, Ar), 3.84 (3H, s, OCH_3), 2.87 (1H, s, C≡CH). Found: C, 71.72; H, 4.70%. Calcd for C_9H_7FO: C, 71.99; H, 4.70%.

3-Chloro-4-methylthio: IR (neat) 2115 cm^{-1} (C≡CH); ^1H NMR (CCl_4) δ=7.42—6.93 (3H, m, Ar), 2.97 (1H, s, C≡CH), 2.44 (3H, s, SCH_3). Found: 59.10; H, 3.87%. Calcd for C_9H_7ClS: C, 59.18; H, 3.86%.

p-Methylthio: IR (neat) 2135 cm^{-1} (C≡CH); ^1H NMR (CCl_4) δ=7.45, 7.31, 7.20, 7.05 (4H, A_2B_2, Ar), 2.89 (1H, s, C≡CH), and 2.44 (3H, s, SCH_3). Found: C, 72.19; H, 5.43%. Calcd for C_9H_8S: C, 72.93; H, 5.44%.

p-Aminophenylacetylene was prepared by reduction of the corresponding *p*-nitro compound with zinc in concd aqueous ammonia: mp 100. 1 °C (lit,[4b)] mp 99 °C). 3,5-Difluorophenylacetylene was prepared by desilylation of 1-(3,5-difluorophenyl)-2-trimethylsilylacetylene, which was prepared by coupling of 3,5-difluorobromobenzene with trimethylsilylacetylene in the presence of bis(triphenylphosphine)palladium(II) dichloride.[30)] IR (neat) 2180 cm^{-1} (C≡CH); ^1H NMR ($CDCl_3$) δ=6.92 (2H, m, Ar), 6.74 (1H, m), 3.06 (1H, s, C≡CH). Found: C, 69.38; H, 2.90%. Calcd for $C_8H_4F_2$: C, 69.57; H, 2.92%. Each sample was subjected to several freeze-pump-thaw cycles on the ICR inlet vacuum system to remove entrapped impurities.

Measurements. The equilibrium constant measurements were performed on a homemade pulsed ion cyclotron resonance mass spectrometer equipped with a capacitance bridge detector[31)] and several data were recorded on an Extrel FTMS 2001 spectrometer. Details of the experimental techniques used for the measurements of the equilibrium constants (K) for the proton transfer reaction (6), where B refers to a given substituted phenylacetylene and B_o is a reference base, were described previously.[14)]

$$B + B_oH^+ \rightleftharpoons BH^+ + B_o \qquad (6)$$

$$K = [B_o/B] \cdot [BH^+/B_oH^+] \qquad (7)$$

$$\Delta G^\circ = -RT \ln K \qquad (8)$$

All measurements were performed at 70 °C at constant magnet field strength of 1.3 or 3 T (for an Extrel FTMS 2001). The pressures of the neutral reactants were measured by means of a Bayard–Alpert type ionization gauge with appropriate correction factors being applied to correct the gauge readings for the different ionization cross sections of various compounds.[32,33)] Overall pressures of the reagents were maintained at 1 to 3×10^{-4} Pa by controlled rates through leak valves (Anelva) from a parallel inlet manifold into the vacuum chamber. After a reaction period of 1 to 3 s depending upon the reactant, the equilibrium was attained and the relative abundance of BH^+ and B_oH^+ was measured by signal intensities of ICR spectra. Each experiment was performed at several ratios of partial pressures and at different overall pressures. Arithmetic mean values of K from Eq. 7 were used for the calculation of ΔG° at 343 K (Eq. 8) with an average uncertainly of ±0.2 kcal mol^{-1} in most of these cases. More than two reference compounds were used to insure the internal consistency of the data. The GB values for the reference compounds were taken from the literature.[6d,17)]

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