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Gas Phase Substituent Effect on Basicity of Phenylacetylene. Intrinsic Resonance Demand of Phenylvinyl Cation

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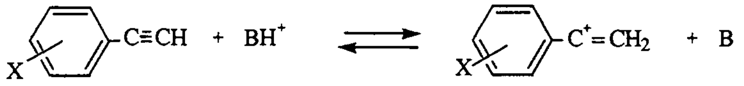
The substituent effect on gas-phase basicity of phenylacetylene has been analyzed in terms of the LArSR Eq., providing an r of 1.21 and a ρ of -14.1. The magnitude of the r is reconciled with the "resonance demand - carbocation stability relation" derived from sp^2-hybridized benzylic carbocations.

Vinylic carbocations have been no longer regarded as unusual intermediates as a result of numerous investigations.[1-4] Most of experimental information about their stabilities was derived from kinetic studies based on an assumption that the transition state of a reaction is structurally similar to a cationoid intermediate. Thermodynamic data such as proton affinities of alkynes can be regarded as a more direct measure of the stability of vinyl cations.[5] Modena, Speranza, and co-workers recently determined gas-phase basicities (GB) of phenylacetylenes and noted that the GB data were correlated linearly with σ^+.[6] We have continued to criticize σ^+ analysis on the basis of the concept of varying resonance demand in the substituent effect.[7,8] That is, application of σ^+-analysis must be restricted within the system of which resonance demand is very close to that of 1-methyl-1-phenylethyl (α-cumyl) cation even though the system of interest bears positive charge at the carbon conjugative with aryl group. This has been proved by excellent applicability of the LArSR Eq. 1[9] to a wide variety of reactions and by mechanisitic reasonableness of their correlation results.[7,8] It is, therefore, of great interest to elucidate the resonance demand of α-phenylvinyl cation in a comparison with sp^2 hybridized benzylic cations because the magnitude of resonance demand (r) itself gives important information about electronic nature of a cation. However, the available data are not sufficient for detailed LArSR analysis. Accordingly, in this study we added newly several substituents

$$\log (k/k_0) = \rho(\sigma^0 + r\Delta\bar{\sigma}^+_R) \qquad (1)$$

for aiding the correlation analysis, and also reexamined the GB values in the literature.

Gas phase basicities of substituted phenylacetylenes were determined based on proton transfer equilibria (2) using suitable reference bases of known basicity. The measurements of equilibrium constants were performed with a homemade pulsed ion cyclotron resonance spectrometer as described previously.[10,11] The GB values relative to that of unsubstituted phenylacetylene are summarized in Table 1. The GBs of several derivatives are higher by 1 to 3 kcal mol^{-1} than the corresponding values in the literature.[6] Although the reason for such disagreement is not clear, we used the data listed in Table 1 for the present analysis of the substituent effect because all GBs obtained newly or revised in this study are internally consistent with each other.



(2)

In Fig. 1 are plotted the relative GBs of phenylacetylenes against those of α-methylstyrenes which are referred to as a measure of the stability of α-cumyl cations. This corresponds to the σ^+-plot in the gas phase because the GB values of α-methylstyrenes have been correlated very well with σ^+.[11] Figure 1 shows that there exists no simple linear relationship as a whole, indicating that the stabilities of phenylvinyl cations cannot be described by a single σ^+ substituent constant set. While meta substituents provide

Table 1. Relative GB of Arylacetylenes

Subst.	ΔGB [a)] kcal mol^{-1} [b)]
p-NH_2	19.3
p-OMe	13.0 (10.0)[c)]
3-F-4-OMe	9.1
3-Cl-4-OMe	9.1
p-SMe	12.6
3-Cl-4-SMe	8.3
p-Me	5.5 (4.6)[c)]
m-Me	2.2
3,5-Me_2	4.4
p-F	0.3[c)]
m-F	-5.6[c)]
p-Cl	0.1 (-1.4)[c)]
m-Cl	-5.1 (-4.8)[c)]
m-CF_3	-6.6 (-8.0)[c)]
H	0.0 (-4.0, -4.2[c)])[d)]

a) At 323 K. b) 1 cal = 4.184 J.
c) Ref. 6. d) Relative to NH_3 (GB of NH_3 = 195.6 kcal mol^{-1}).

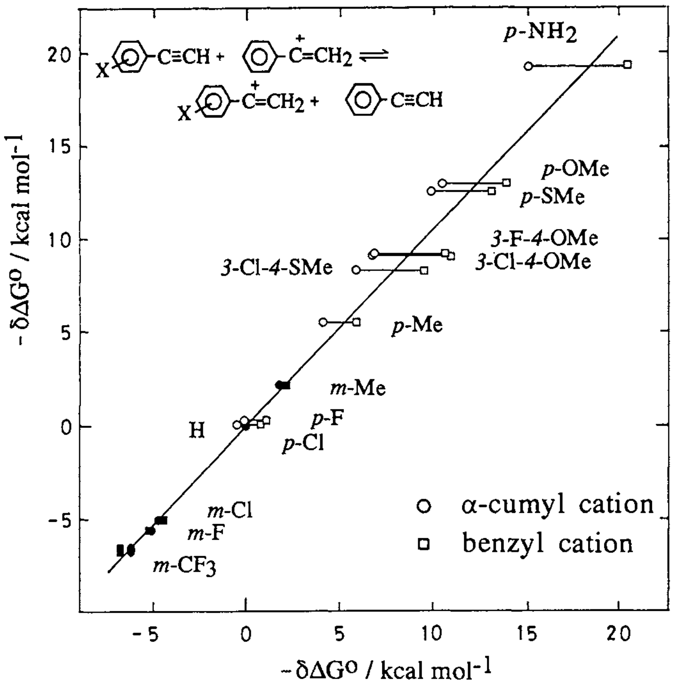


Fig. 1. Plots of stabilities of phenylvinyl cations against the corresponding α-cumyl and benzyl cations.

an excellent linear relationship with a slope of unity, all para π-donors show systematic deviations from the meta line. These upward deviations of para π-donors may be indicative of exalted resonance stabilization by such substituents in the phenylvinyl cation system compared with that in the α-cumyl one. On the contrary, the corresponding plots against stabilities of benzyl cations, which have been determined based on chloride transfer equilibria,[12)] show downward deviations of para π-donors from the meta line, suggesting in turn reduced resonance contribution in phenylvinyl cation compared with that in benzyl cation. These facts lead to a conclusion that the phenylvinyl cation system has an intermediate resonance demand between those of α-cumyl and benzyl cations.

Application of LArSR Eq. 1 to the stabilities of phenylvinyl cations gives an r of 1.21 and a ρ of -14.1 (kcal $\mathrm{mol}^{-1}\ \bar{\sigma}^{-1}$). The ρ value is equal to that of α-cumyl cation or benzyl cation as expected from Fig. 1, indicating the same response to the substituent field/inductive effects for these three systems regardless of the different stability of respective parent (ring substituent = H) carbocations. This is in accord with our observations for a series of sp^2-hybridized benzylic carbocations.[11-14)] The r value of 1.21 means that the resonance demand is greater in phenylvinyl cation than in α-cumyl cation (r=1.00). Regarding the change in the r value with the system, we have found in previous studies that its change in magnitude is related to the change of the intrinsic stability of parent carbocation of respective systems, i.e., the more unstable carbocation has the greater r value.[13)] The magnitude of the r value of phenylvinyl cation seems to be also reconciled with the variation of the r value depending on the stability of the parent carbocations. Indeed, there exists a good linear relationship between resonance demands (r) and stabilities ($\Delta G^o_{(H)}$) of parent carbocations including phenylvinyl cation as shown in Fig. 2. This supports strongly our conclusion that the resonance demand is a function of structure of a carbocation,[12-14)] and suggests that π-delocalization mechanism in the phenylvinyl cation is not of specific mode but is merely characterized by a unique position of 1.21 in a continuous spectrum of resonance demands of a series of carbocations.

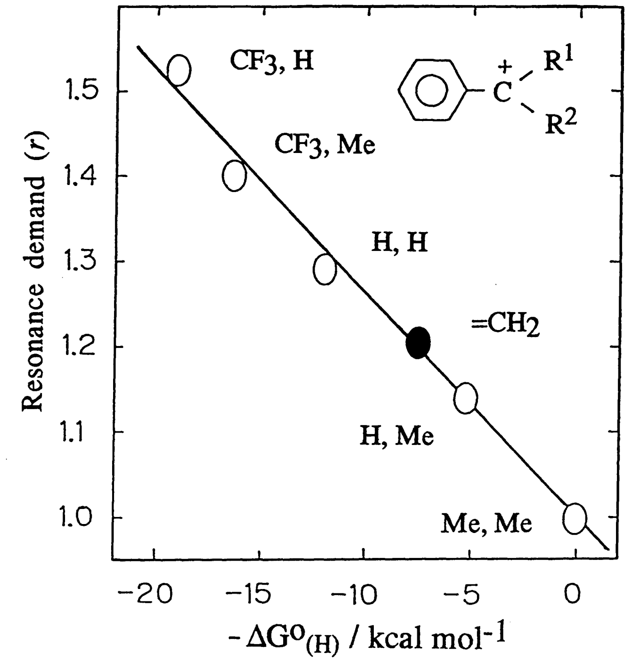


Fig. 2. Relationship between resonance demands (r) and relative stabilities of parent carbocations.

The intrinsic resonance demand of phenylvinyl cation would give an important basis for understanding of nature of vinyl cations in solution. It is of interest to compare the present result with the substituent effect on rates of acid-catalyzed hydration of phenylacetylenes,[1c,2,15] which is considered to proceed with a vinylic cation as an intermediate. Application of the LArSR Eq. 1 to rate data of the hydration of phenylacetylenes gives an r of 0.89 with a ρ of -4.17. The ρ value as large as that obtained for S_N1 solvolysis of ordinary benzylic substrates seems to be consistent with the currently accepted mechanism.[16,17] The significantly reduced ρ value of the hydration compared with that of GB can be explained in terms of solvent stabilization of the positive charge in the rate-determining transition state or the following intermediate. The magnitude of the r of 0.89 for the hydration is appreciably smaller than that for GB. Similar results were observed for the hydration of carbon-carbon double bond. The r values of the hydration were 0.74 and 0.94 for α-methylstyrene[15,17] and styrene,[19] respectively, while r=1.00 and 1.15 for the corresponding GBs. We found in earlier studies that the r values for gas-phase stabilities of sp^2-hybridized benzylic carbocations are exactly the same as those of the corresponding S_N1 solvolysis[12-14] and that the r value is independent of external stabilization of a cation through solvation.[18] Accordingly, reduced r values for the hydration suggest that the structure of the transition state is appreciably different from the corresponding cationoid intermediates with respect to π-delocalization of the positive charge, probably an asymmetrically bridged structure. Further studies must be required for clarifying in detail the nature of the transition state of the hydration of carbon-carbon triple and double bonds.

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