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Substituent Effect on Gas Phase Basicity of cis 2-Phenyl-2-butene. Intrinsic Resonance Demand of α,α-Dialkylbenzyl Carbocations

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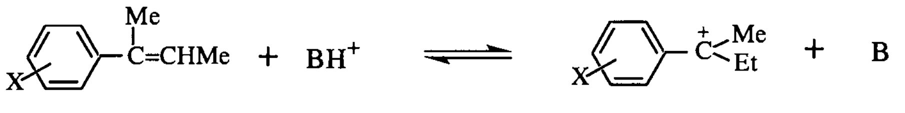
The gas phase basicities of cis 2-aryl-2-butenes have been determined by measuring proton transfer equilibria. It has been shown that the substituent effect on the stability of the conjugate acid ion of the olefin, α-ethyl-α-methylbenzyl cation, is in complete agreement with that of α-cumyl cation, suggesting that α,α-dialkyl benzyl cations seem likely to be characterized by the r value of 1.0 given by the LArSR analysis.

The substituent effects on the thermodynamic stability of benzylic carbocations determined on the basis of free energy changes of proton or halide ion transfer equilibria in the gas phase were successfully described in terms of the Yukawa-Tsuno (LArSR) Eq. 1[1-3] in a similar manner as the effects on reactivities in solution,[4-9]

$$\delta\Delta G^{o}=\rho(\sigma^{o} + r\,\Delta\bar{\sigma}_{R}^{+}) \qquad (1)$$

where the r value is a measure of the degree of π-interaction between the cationic center and the substituent, representing the resonance demand of the cationic site. The LArSR analysis for the substituent effects of a series of benzylic carbocation systems showed that the resonance demand (r) increases linearly with decreasing stability of the unsubstituted member of each series.[5,6,9,10] That is, the more stable benzylic cation has been characterized by the smaller resonance demand. In the previous study,[11] the resonance demand (r=0.87) of α-t-butyl-α-methylbenzyl cation system was however found to be smaller than 1.00 of α-cumyl cation nevertheless the stability of the parent α-t-butyl-α-methylbenzyl cation is even lower than α-cumyl cation. This result was accounted for by the reduced coplanarity between the benzene π-orbital and a vacant p-orbital due to the steric congestion around the cationic center. This helps us to make physical significance of the r value clearer and may present a practical method for estimating a torsional angle between the benzylic site and the benzene system from the change in r value determined experimentally. In order to confirm the validity of our interpretation of the reduced r value for α-t-butyl-α-methylbenzyl cation system, it is important to elucidate whether the effect of the α-t-butyl group on the r value except steric effect is equal to that of the α-methyl group as a good approximation. Therefore, we decided to examine effects of a variety of α-alkyl groups on the resonance demand of benzylic carbocations. In this study we have analyzed the substituent effect on the gas phase basicity of cis 2-phenyl-2-butene of which the conjugate acid, α-ethyl-α-methylbenzyl cation, is assumed to have a planar structure, i.e., a full conjugation system, because of sterically small size of the ethyl group at α-position.

All derivatives of cis 2-phenyl-2-butenes were prepared from the corresponding 2-phenyl-2-butanols by the dehydration with potassium hydrogen sulfate or with sulfuric acid in acetic acid, and were purified by column chromatography on silica gel or gas chromatography. Gas phase basicities (GB) of cis 2-phenyl-2-butenes were determined by measuring the equilibrium constants of the proton transfer reaction (2) at 343 K using a homemade pulsed ion cyclotron resonance spectrometer as described previously[8,12,13] and an Extrel FTMS 2000 Fourier transform mass spectrometer equipped with a 3.0 T superconducting magnet. Equilibrium constant value was obtained from the ratio of ion intensities when equilibrium was attained and from the ratio of the pressures of neutrals in the ICR cell measured by means of a Bayard-Alpert ionization gauge. Two or more reference compounds of known basicity were used for the determination of basicity of each derivative.



(2)

$$K = \frac{[BH^+][\text{olefin}]}{[\text{conjugate acid}^+][B]} \qquad (3)$$

$$\Delta G^o = -RT \ln K \qquad (4)$$

The basicity of the unsubstituted cis 2-phenyl-2-butene is found to be only 0.4 kcal mol^{-1} higher than α-methylstyrene, revealing that there is no significant difference in effect on the stability of benzylic cation between the methyl and ethyl groups at α-position. This is consistent with the observation that the basicity of the unsubstituted cis 2-phenyl-2-pentene is 0.7 kcal mol^{-1} higher than α-methylstyrene. Relative gas phase basicities of cis 2-aryl-2-butenes are summarized in Table 1. Figure 1 shows plots of the ΔGB values of cis 2-phenyl-2-butenes against the corresponding values of α-methylstyrenes. There is an excellent linear free energy relationship with a slope of unity covering a whole range of substituents, indicating that not only the contribution of the substituent field/inductive effect but also the resonance effect contribution to the stability of the conjugate acid ion is essentially the same in both systems. In other words, not only a ρ but also an r given by the LArSR

Table 1. Gas-phase Basicities of Styrene Derivatives

Subst.	cis 2-Phenyl-2-butenes[a)]	α-Methyl-styrenes [a,b)]
p-OMe	10.4	10.5
3-Cl, 4-OMe	6.4	6.7
p-Me	4.5	4.1
m-Me	1.7	1.8
H	0.0 (199.2)[c)]	0.0 (198.8)[c)]
p-Cl	0.8	0.4
m-Cl	-4.5	-4.7
m-F	-4.7	-4.7
m-CF$_3$	-6.3	-6.3
p-CF$_3$	-7.5	-7.2
cis 2-phenyl-2-pentene	199.9[c)]	

a) δΔGB / kcal mol^{-1}, 1 cal = 4.184 J. Positive value denotes greater basicity. b) Ref. 8. c) Absolute GB value anchored by GB(NH$_3$) = 195.6 kcal mol^{-1}.

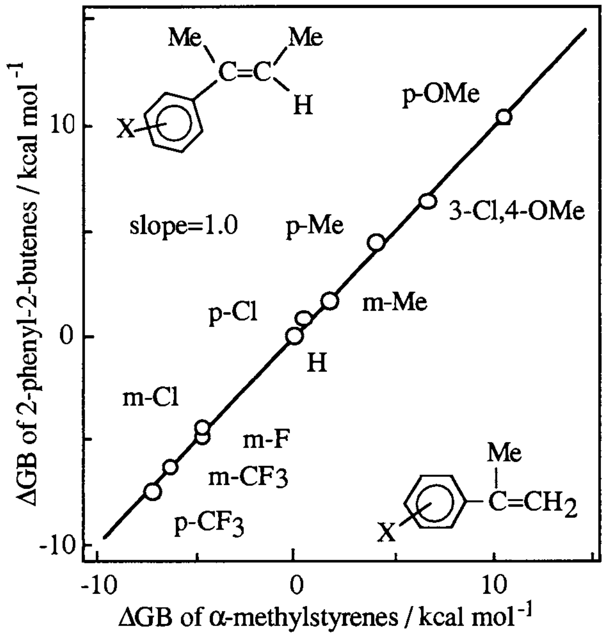


Fig. 1. Plots of ΔGB of 2-phenyl-2-butenes against the corresponding values of α-methylstyrenes.

analysis for the substituent effect on the stability of α-ethyl-α-methylbenzyl cation is in agreement with the corresponding value of α-cumyl cation, indicating that the r value is not influenced by the replacement of the methyl group at α-position by the ethyl group. This r value of 1.0 for the α-ethyl-α-methylbenzyl cation system seems to conform to the linear relationship between the resonance demand and the stability of the parent carbocation obtained from a series of benzylic carbocation systems as shown in Fig. 2 5,6,9,10) because the stability of the unsubstituted α-ethyl-α-methylbenzyl cation is very close to that of the corresponding α-cumyl cation. On the contrary, α-t-butyl-α-methylbenzyl cation in which a vacant p-orbital is assumed to be twisted from the benzene ring deviates clearly from the linear relationship. These facts lead to the conclusion that this linear relationship is not found artificially but is generally retained for the benzylic system as far as the benzene π-orbital and a vacant p-orbital lie on the same plane. That is, factors governing the resonance demand and the stability of the parent (ring substituent =H) benzylic carbocation are identical, suggesting that the origin of the resonance demand is the intrinsic stability of a benzylic cation.6,9) This linear relationship therefore presents a practical method for estimating r values of other benzylic carbocation systems from the stabilities of their parent carbocations. Since α,α-diethylbenzyl cation has been found to have similar stability to α-cumyl cation, i.e, only 0.7 kcal mol^{-1} more stable than the latter, the r value for α,α-diethylbenzyl cation is also assumed to be 1.0. Thus, the r value of 1.0 must be retained for all α,α-dialkylbenzylic carbocation system as a good approximation as far as no twisting out of the benzene ring plane occurs.

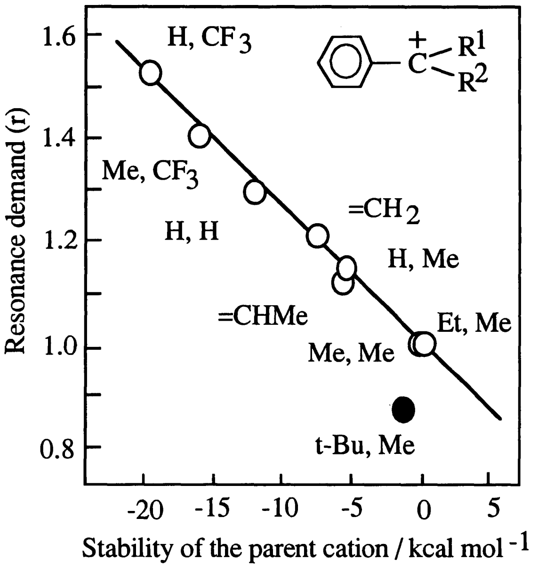


Fig. 2. Linear relationship between r values and stabilities of the unsubstituted member of each series. A closed circle denotes the twisted system.

It therefore seems likely that the r value of imaginary planar α-t-butyl-α-methylbenzyl cation is approximated by the value of α-cumyl cation. This allows us to estimate the torsional angle (θ) between the benzylic site and the benzene system from the r value of the twisted α,α-dialkylbenzyl cation and $r_{max}=1.0$ for the planar α,α-dialkylbenzyl cation by the equation $r/r_{max} = \cos\theta$, giving $\theta=29^{o}$ for α-t-butyl-α-methylbenzyl cation.11,14) In fact, the θ value of 29^{o} is in good agreement with the value based on ab initio MO calculation.14, 15) This supports that the r value is a real measure of the degree of π-interaction, overlapping of a vacant p-orbital with the benzene π-orbital.

Finally, it is of interest to note that the stability of unsubstituted α,α-dialkylbenzyl cation increases slightly as α-alkyl substituent changes from the methyl group to the ethyl group and that the t-butyl group causes relatively large decrease in stability by 1.1 kcal mol^{-1}.11) This fact is quite different from the observation for stabilities of saturated alkyl cations that hydride ion affinity of an alkyl cation increases significantly in the following order, Me_3C^+ (230.6 kcal mol^{-1}) < $Me_2(Et)C^+$ (227.2) < $Me(Et)_2C^+$ (226.3) < $Me_2(i\text{-}Pr)C^+$ (225.8).16) The same trend was observed for gas-phase basicities of alkylamines,17, 18) e.g., Me_3N (217.3 kcal mol^{-1}) < $Me_2(Et)N$ (219.7) < $Me_2(i\text{-}Pr)N$ (222.0) < $Me_2(t\text{-}Bu)N$ (224.2).19,20) Such effect of the alkyl group is also seen in the stabilization of negatively charged sites in alkoxide ions.21) These stabilization effects of α-alkyl substituents are considered to be attributed to the charge-induced dipole interaction between the polarizable alkyl substituent and the charge.[17,18,22] The present observation for the α,α-dialkylbenzyl cation reveals that the polarizability effect of α-alkyl groups is not important for the determination of the stability of the benzylic carbocations and that the lower stability of α-t-butyl-α-methylbenzyl cation than α-cumyl cation is ascribed to the reduced resonance effect of the phenyl group caused by twisting out of the benzene ring plane. The diminished contribution of polarizability effect to the stability of α,α-dialkylbenzyl cation may be accounted for by the large π-delocalization of the positive charge into the benzene ring. The magnitude of the charge-induced dipole stabilization energy decreases remarkedly with the larger distance of the charge to the center of substituent polarizability as expected from $E=-\alpha q^2/2\varepsilon R^4$, [19,22] where α is the substituent polarizability, q the charge, ε the dielectric constant, and R the distance of separation of the charge from the center of substituent polarizability. The dispersion of the positive charge into the benzene ring makes the effective distance longer, resulting in a small contribution of the charge-induced dipole stabilization. This is the case of the benzylic carbocation system where most of positive charge is delocalized into the benzene ring. On the contrary, the charge in non-conjugated systems like saturated alkyl cations and ammonium ions must mostly be localized at the ionic center atom, resulting in a greater charge-induced dipole stabilization.

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