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Substituent Effect on the Gas Phase Basicity of α-t-Butylstyrene. Coplanarity and Resonance Demand of a Benzylic Carbocation

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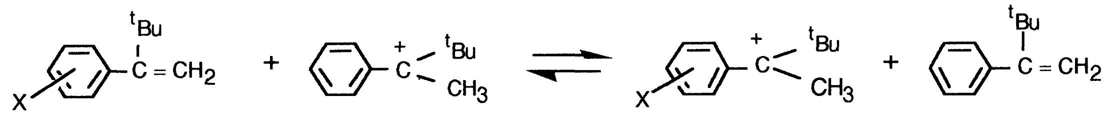
Gas phase basicities of α-t-butylstyrenes were determined based on the proton transfer equilibria. The substituent effect on the basicity has been analyzed by means of the LArSR Eq. 1, providing a ρ of -12.5 and an r of 0.86. The reduced r value relative to that for α-methylstyrene may be attributed to sterically twisting out of the coplanarity of benzene π-system in the conjugate acid ion, α-t-butyl-α-methylbenzyl cation.

Substituent effects on the thermodynamic stabilities of benzylic carbocations in the gas phase have successfully been described by the LArSR Eq. 1,[1-4)] which was derived empirically from reactivity data in solution.[5)] It was found that the r value increases significantly as the positive charge on the benzylic carbon is destabilized by the α-substituents, giving a continuous spectrum from r=1.00 for α-cumyl cation,[3)] via r=1.29 for benzyl cation[2,4)] to r ≥ 1.5 for extremely electron-deficient carbocation systems such as 1-phenyl-2,2,2-trifluoroethyl cation.[1)] The same behavior of the r value was observed for the benzylic S_N1 solvolysis and was discussed in terms of the varying extent of substituent-reaction site π-interaction in the transition state. The parameter r, an empirical measure of resonance stabilization, should be related most closely to the degree of π-overlapping of the carbocation p-orbital with the benzene π-ring, and must be reduced by sterically twisting out of the coplanarity of benzene π-system. Indeed, the solvolyses of α,α-di-t-butylbenzyl p-nitrobenzoates and α-t-butyl-α-methylbenzyl chlorides were described by the r values of 0.26 [8)] and 0.87,[9)] respectively, smaller than unity for the coplanar α-cumyl system. Furthermore, the substituent effect on the solvolysis of 4-methylbenzo-bicyclo[2.2.2]octen-1-yl triflates where no π-overlapping between the aryl π-orbital and the developing p-vacant orbital at the reaction center is possible could be described in terms of resonance un-exalted σ^o (r=0).[10)] In order to clarify further the real origin of the empirical resonance demand parameter r it is of particular importance to study the intrinsic relation between coplanarity and resonance demand for the stability of intermediates because the molecular structure of the intermediate carbocation may be defined relatively well compared with that of the transition state and because a comparison of the experimental result for the intermediates with the theoretical calculations is possible. We are therefore interested in resonance demand of a congested carbocation in the gas phase. In this study, α-t-butyl-α-methylbenzyl cation **1** has been chosen as a model of the twisted carbocation intermediate of the corresponding solvolysis because the carbocation **1** can easily be generated from α-t-butylstyrenes by protonation in the gas phase. The substituent effect for the standard free energy changes of the

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

proton transfer equilibria (2) has been analyzed on the basis of the LArSR Eq. 1.


(2)

The gas phase basicities (GB) of α-t-butylstyrenes have been determined by measuring the equilibrium constants of the proton transfer reaction at 343 K using a pulsed ion cyclotron resonance spectrometer as described previously.[2,3] Equilibrium constant value is obtained from the ratio of ion intensities when equilibrium has been 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. The unsubstituted α-t-butylstyrene was found to be less basic than α-methylstyrene by 1.1 kcal mol^{-1} (1 cal = 4.184 J), revealing that its conjugate acid ion, α-t-butyl-α-methylbenzyl cation **1**, is less stable than α-cumyl cation. The drop in stability may be ascribed to the reduced π-delocalization of the positive charge into aryl π-system caused by sterically twisting out of the benzene π-ring. Since the polarizability effect of the t-butyl group is larger than that of the methyl group,[11] the loss of 1.1 kcal mol^{-1} appears to be the minimum amount of destabilization arising from the steric inhibition of resonance effect of the phenyl group. The relative GB values are listed in Table 1 together with the corresponding values of α-methylstyrenes. Figure 1 shows plots of the ΔGB values of α-t-butylstyrenes versus α-methylstyrenes. There is no simple linear free energy relationship as a whole but is a limited linear correlation for meta substituents and para π-acceptors which have no conjugation with the positive charge. This line with a slope of 1.0 therefore suggests that the response of the stability of the conjugate acid ion to the substituent field/inductive effect is essentially the same in both systems. Since the ΔGB of α-methylstyrenes could be correlated linearly with the σ^+ substituent constant set,[3] Fig. 1 is regarded as the σ^+ plot in the gas phase. With reference to the line for non-conjugate substituents all para π–donor substituents deviate downward and the magnitude of deviations seems to be related to the ability of π-electron donating of respective substituents, suggesting that the resonance effect contribution to the stability of α-t-butyl-α-methylbenzyl cation **1** is smaller than that involved in σ^+. Application of the LArSR Eq. 1 to the substituent effect on the ΔGB of α-t-butylstyrene provides an r of 0.86

Table. 1. Relative Gas Phase Basicities of α-t-Butylstyrenes (**1**) and α-Methylstyrenes (**2**)[a]

	ΔGB/kcal mol^{-1}			ΔGB/kcal mol^{-1}	
Subst.	**1**	**2**	Subst.	**1**	**2**
p-OMe	8.6	10.5	m-Cl	-4.3	-4.7
p-SMe	8.1	10.0	m-F	-4.7	-5.1
3-Cl-4-OMe	5.5	6.7	m-CF_3	-6.0	-6.3
p-Me	3.6	4.1	p-CF_3	-7.2	-7.2
3, 5-Me	3.6	3.5	H	0.0	0.0
m-Me	2.0	1.8		(198.0)[b]	(199.1)[b]
p-F	-0.7	-0.1			

a) Ref. 3. b) Absolute GB values calculated with respect to GB of ammonia (195.6 kcal mol^{-1}).

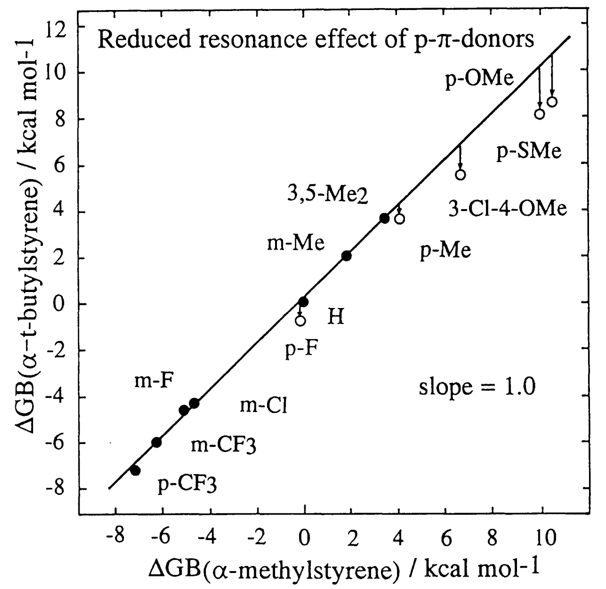


Fig. 1. Relationship of ΔGB between α-t-butylstyrene and α-methylstyrene.

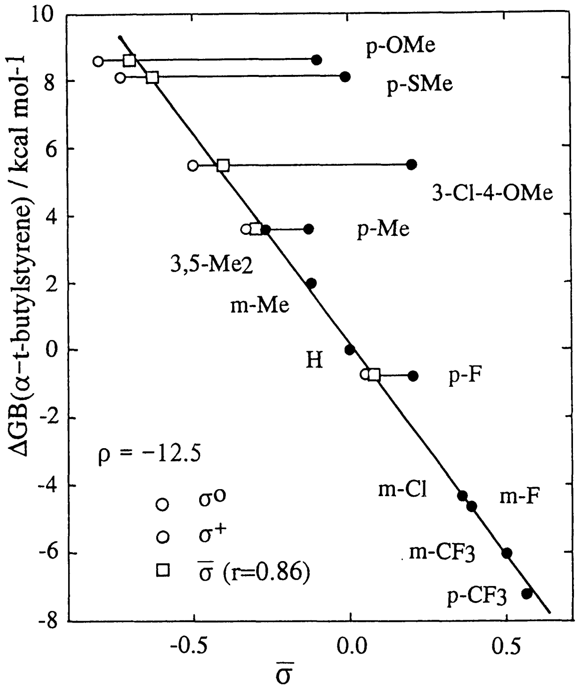


Fig. 2. LArSR plots of the substituent effect on the ΔGB of α-t-butylstyrenes.

and a ρ of -12.5 (kcal mol^{-1} $\bar{\sigma}^{-1}$) with excellent precision as shown in Fig. 2. The resonance demand parameter r is distinctly smaller than unity for α-cumyl cation, whereas a ρ of -12.5 is in agreement with that of the latter as expected from Fig. 1.

The efficiency of π-interaction between the benzene π-system and a vacant p-orbital of a carbenium ion can be accounted for in terms of $\cos^2 \theta$ where θ is the dihedral angle of twisting out of coplanarity.[12,13] Accordingly, the r value of a twisted benzylic carbocation may be related to the dihedral angle θ by a following equation,

$$r/r_{max} = \cos^2 \theta \qquad (3)$$

where r_{max} denotes the maximum resonance demand of a given carbocation. The intrinsic r_{max} value may be as reasonable approximation taken to be unity for the coplanar tertiary α,α-dialkylbenylic cation because the polarizability effect of α-substituent is not important for the determination of the r value for the stability of benzylic carbocations although polarizable α−substituents stabilizes a carbocation itself.[14] Thus, the ratio of the r values, 0.86/1.00, for the α-t-butyl-α-methylbenzyl cation can be referred to the efficiency of benzylic resonance interaction, and the torsion angle θ of 22° is given from Eq. 3. The angle is in surprisingly good agreement with the calculated angle of 20° for α-t-butyl-α-methylbenzyl cation on the basis of the ab initio MO using a STO 3G minimal basis set.[15] This agreement provides strong evidence for our characterization of the r value as a parameter reflecting the degree of resonance interaction between the aryl π-system and the cation center.

Finally, it should be noted that the r value of 0.86 obtained for the present congested carbocation system in the gas phase is identical to that for the S_N1 solvolysis of α-t-butyl-α-methylbenzyl chlorides.[9] Such agreement of the r value has generally been observed for the ordinary coplanar benzylic carbocations.[1-4] Since a carbocation generated in the gas phase may be regarded as a good model of the intermediate of the corresponding S_N1 solvolysis, the identity of the r value means that the resonance demand of the transition state is identical to that of the intermediate. This leads us to a conclusion that the degree of twisting out of coplanarity in the transition state of the congested substrate is also close to that of the intermediate although the steric interaction results in a higher activation energy of the rate-determining transition state. This suggests further that the position of the transition state relative to the intermediate along the reaction coordinate is not influenced seriously by the steric interaction.

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