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Substituent Effect on the Gas Phase Basicity of α, α, α-Trifluoroacetophenone. Intrinsic Nature of Resonance Demand

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Gas-phase basicities (GB) of α, α, α-trifluoroacetophenones were determined by means of the pulsed ICR spectrometer. The substituent effect on the GB was correlated in terms of the LArSR Eq. with an *r* of 1.20. The *r* values for stabilities of a series of benzylic carbocation systems, $\mathrm{ArC}^{+}(R^{1})R^{2}$, could be related to electronic effects of R^{1} and R^{2}.

In earlier studies,[1-4)] we found that the substituent effects on the basicity of the benzoyl compounds (ArCO*R*) in the gas phase as well as in aqueous solutions were described in terms of the LArSR Eq. 1.[5)]

$$\Delta \mathrm{GB} = \rho(\sigma^{\mathrm{o}} + r\Delta\bar{\sigma}_{\mathrm{R}}^{+}) \qquad (1)$$

The *r* value as a measure of π-delocalization of the positive charge in the conjugate acid ion into the aryl π-system varied significantly with the change of the *R*-substituent linked to the carbonyl carbon atom. Furthermore, it was found that the *r* values in the gas phase were in complete agreement with the corresponding values in aqueous solutions.[4,5)] From these facts we concluded that resonance demand (*r* value) was characteristic of the ion structure itself, independent of the external stabilization through solvation. It is of particular interest to examine the dependency of the *r* value on the ion structure in order to confirm the physical significance of the *r* value. The *r* values observed so far show a trend that the system possessing the greater electron-releasing *R* group has the smaller *r* value. To substantiate further quantitatively a relation between the *r* and the ion structure we have analyzed the substituent effect on the gas phase basicity of α, α, α-trifluoroacetophenone of which conjugate acid ion must be destabilized by a strong electron-withdrawing CF_3 group.

$$\mathrm{XC_6H_4CO}CF_3 + \mathrm{C_6H_5C^{+}}(CF_3)\mathrm{OH} \rightleftharpoons \mathrm{XC_6H_4C^{+}}(CF_3)\mathrm{OH} + \mathrm{C_6H_5CO}CF_3 \qquad (2)$$

Gas phase basicities were determined by measuring the proton-transfer equilibrium constant using the pulsed ion cyclotron resonance spectrometer as described previously in detail.[1)] Unsubstituted α, α, α-trifluoroacetophenone is found to have 7.7 kcal mol^{-1}

(1 cal = 4.184 J) lower basicity than benzaldehyde. This magnitude of the effect of CF_3 group on the GB is in agreement with those observed for HCO*R* (7.0) and MeOCO*R* (7.9) bases$^{6)}$ in contrast with the effects of strong π-electron donors such as NMe_2 and OMe groups,$^{7)}$ suggesting that the contribution of inductive effect of the *R* group is constant independent of the stability of the parent conjugate acid ion (*R*=H).

The relative gas-phase basicities of α, α, α-trifluoroacetophenones ($R=CF_3$) are listed in Table 1. In Fig. 1 are plotted the gas phase basicities of the CF_3 system against the corresponding acetophenones ($R=CH_3$).$^{1)}$ The *meta* substituents and *para* π-acceptor ones fall on the line with a slope of unity, indicating the same sensitivity to substituent effects for both systems in spite of the large difference in the stability of parent (ring substituent=H) carbocation. On the contrary, strong *para* π-donor substituents deviate upward by 2 to 3 kcal mol^{-1} from the line. Such deviations may be attributed to an enhanced resonance stabilization by *para* π-donor substituents in the conjugate acid of the CF_3 system compared with the corresponding CH_3 system. In fact, application of LArSR Eq. 1 to the CF_3 system provides an r=1.20 higher than that for the CH_3 system (r=0.78).$^{1)}$

Table 1. Gas Phase Basicities of α, α, α-Trifluoroacetophenones and Acetophenones

Subst.	ΔGB/kcal mol^{-1} a) CF_3	 CH_3 b)
p-OMe	10.9	8.1
p-SMe	10.0	6.7
3-Cl-4-OMe	7.8	5.4
3-F-4-OMe	7.2	
3-Cl-4-SMe	8.0	4.5
p-CH_3	4.2	3.9
p-t-Bu	6.2	5.1
3,5-Me_2	4.3	3.8
m-Me	2.4	1.8
H	0.0	0.0
	(184.4)$^{c)}$	(197.3)$^{c)}$
p-Cl	-0.6	-0.7
p-F	-0.5	-0.6
m-Cl	-3.5	-3.4
m-F	-3.7	-3.7
m-CF_3	-5.8	-5.3
p-CF_3	-6.3	-5.8

a) Positive value denotes greater basicity relative to unsubstituted derivative. b) Ref. 1. c) Absolute values converted with respect to GB(NH_3)=195.6kcal mol^{-1} (Ref.8).

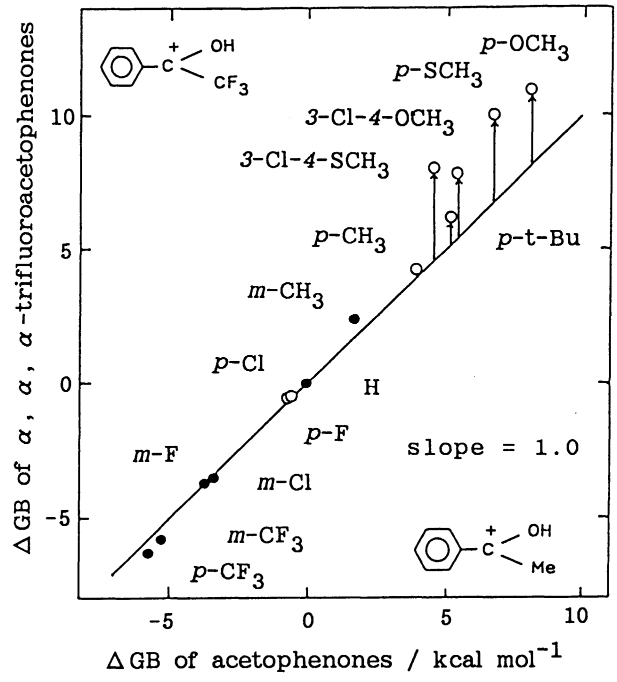

Fig. 1. Comparison of GB's between CF_3 and CH_3 systems.

Table 2. Results of LArSR Analysis for Gas Phase Basicities of Benzoyl Systems, ArCO*R*

R	ρ	*r*	GB[a)]	$\Delta\bar{\sigma}_R^+$ [b)]	$SE_{(Ph)}$ [c)]	Ref.
NMe_2	11.8	0.23	213.8	-1.30	10.8	4
OMe	11.9	0.45	195.5	-0.70	14.8	2
Me	12.3	0.78	197.3	-0.20	19.3	1
H	12.1	1.04	192.1	0.00	24.8	3
CF_3	11.5	1.20	184.4	0.00	27.1	this work

a) Gas phase basicity of parent compound (ring substituent=H), in kcal mol^{-1}. b) Resonance effect substituent constants, taken from Ref. 10. c) GB(PhCO*R*)-GB(HCO*R*).

The results of the LArSR analysis for a series of *R*-substituted benzoyl systems are summarized in Table 2. At first glance it seems that the *r* value decreases with the increasing GB of the parent compounds. However, the *R*=OCH_3 system does not satisfy such a trend, suggesting that the contribution factors determining the *r* value are somewhat different from those to the GB of the parent compound. It may be instructive to compare the *r* values with substituent constants of the *R* group. Table 2 demonstrates that the resonance effect of the *R* group is an important factor determining the *r* value. In addition, the fact that the CF_3 system has a higher *r* value than the *H* system suggests that the inductive effect of the *R* group also contributes appreciably to the variation of the *r* value. Similar dependency of the *r* value on α-substituent(s) was observed for the stabilities of benzylic carbocation system, $ArC^+(R^1)R^2$, [9-11] in which the *r* value increased up to 1.53 for a highly electron-deficient carbocation, R^1=H; R^2=CF_3.[11b] The conjugate acid ions of benzoyl compounds can be regarded as a member of benzylic carbocations having OH group as one of *R* substituents. The *r* values for all these systems except for R^1=NMe_2, R^2=OH system can be correlated in terms of a following equation with both resonance and inductive substituent constants of R^1 and R^2 as shown in Fig. 2.

$$r = 0.40\Sigma\sigma^o + 0.60\Sigma\Delta\bar{\sigma}_R^+ + 1.30 \qquad (3)$$

where $\Sigma\sigma^o = \sigma^o(R^1) + \sigma^o(R^2)$ and $\Sigma\Delta\bar{\sigma}_R^+ = \Delta\bar{\sigma}_R^+(R^1) + \Delta\bar{\sigma}_R^+(R^2)$. Clearly, the change in the *r* value that the system possessing the greater electron-releasing *R* group has the smaller *r* value can quantitatively be related with electronic effects of *R* substituents, indicating that the positive charge formed at the benzylic position is stabilized complementarily by π-delocalization into the ary π-system and into α-substituents. This supports strongly our conclusion that the *r* is inherent in an ion structure itself. The *r* value of 0.23 for the R^1=OH, R^2=NMe_2 system larger than the calculated value based on Eq. 3 suggests the reduced electron releasing effects of α-substituents. This may result from steric inhibition of resonance effect of NMe_2 group due to its bulkiness. Furthermore, we have found an excellent correlation of a different type for the benzoyl system including the NMe_2 system as shown in Fig. 3 when the *r* values are plotted against the difference in GB between PhCO*R* and HCO*R*. This indicates that the effect of phenyl group on the stability of the conjugate acid ion also reflects a degree of the π-delocalization of the positive charge into the aryl π-system. Consequently, the present results support real significance of the *r* parameter introduced into the LArSR Eq. 1.

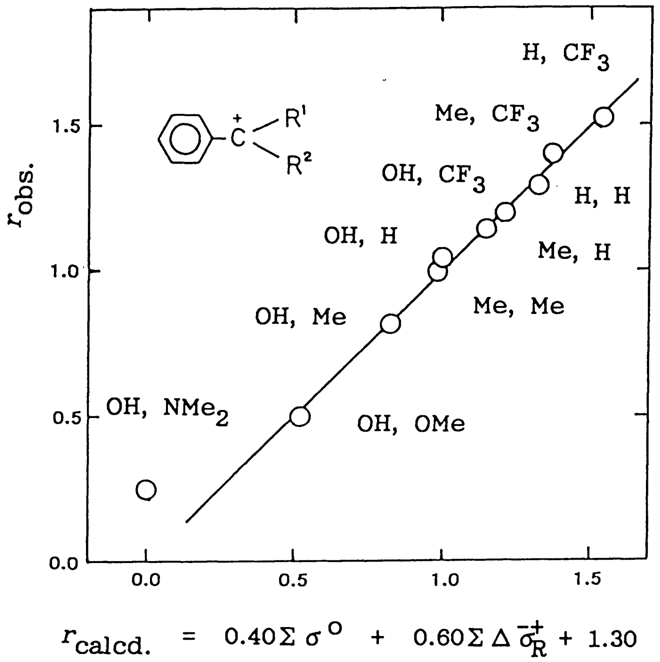

Fig. 2. Calculated vs. observed resonance demands (*r*) of benzylic cations.

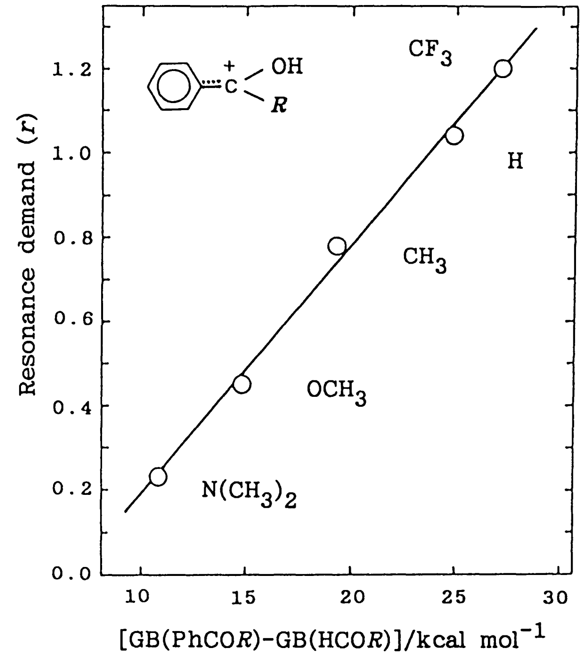

Fig. 3. Plots of the *r* values for the benzoyl system against stabilization effects of the phenyl group.

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