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SUBSTITUENT EFFECTS ON THE GAS PHASE BASICITIES OF METHYL BENZOATES. EFFECTS OF RESONANCE DEMAND ON SUSBTITUENT EFFECTS

Masaaki MISHIMA, Mizue FUJIO, and Yuho TSUNO*
Department of Chemistry, Faculty of Science,
Kyushu University 33, Hakozaki, Higashiku,
Fukuoka, 812 Japan

Abstract: The gas phase basicities of m,p-substituted methyl benzoates have been determined by means of the pulsed ICR mass spectrometer. LArSR analysis of the subtituent effect provides a smaller r^+ of 0.45 compared to that of acetophenone basicities, indicating a reduced resonance demand of the conjugate acid ion of methyl benzoate.

In the preceding paper,[1] we reported that the substituent effect on the gas phase basicity of acetophenone as analyzed in terms of our LArSR Eq. (1)[2,3] gave a ρ=12 and an r^+=0.76. This r^+ value of 0.76 indicates a smaller contribution of resonance effects of π-donor substituents relative to inductive/field one than the resonance contribution in the σ^+ substituent constant (r^+=1.00 by definition), suggesting that the dual parameter treatment is an essential requirement in the analyses of substituent effects in the gas phase as well as in solution. In order to confirm further the validity of our LArSR treatment

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

and its applicability to the analysis of substituent effects in the gas phase, it is important to study the effects of resonance demand on the substituent effects since the unique r^+ parameter in the LArSR Eq. is taken as a measure of π-electronic interaction between any π-system and the reaction center. For this purpose, it is desirable to examine the effects of common substituent Y on substituent effects of free energy changes (basicities) for proton transfer equilibrium (2) of Y-substituted benzoyl system (ArCOY) in the gas phase. In this system the resonance demand varies with Y substituent since the positive charge of the conjugate acid of benzoyl compounds would be stabilized by aryl and Y-substituent as anticipated from studies in solution.[3,4] In this paper, we report the substituent effect on the gas phase basicity of methyl benzoate ($Y=OCH_3$) in comparison with that on acetophenone ($Y=CH_3$).

$$XC_6H_4COY + C_6H_5C(Y)OH^+ \rightleftarrows XC_6H_4C(Y)OH^+ + C_6H_5COY \qquad (2)$$

Gas phase basicities were determined by measuring the proton transfer equilibrium constant using the pulsed ICR mass spectrometer as reported previously.[5] The relative basicities of substituted methyl benzoates (relative to the parent molecule) are summarized in Table 1 together with those of acetophenones.[1] In Fig. 1 are plotted the gas phase basicities of methyl benzoates against the corresponding acetophenones. Apparently, there is no simple linear relationship. However, the meta substituents and the π-acceptor para substituents provide an excellent linear free energy relationship of unit slope, indicating the same sensitivity to substituent field/inductive effects for both systems regardless of the greater π-donor ability of the OMe than of the Me group. On the other hand, the -R para substituents deviate upward by 1-3 kcal/mol from the unit line, suggesting a smaller resonance stabilization by such substituents in the conjugate acid of methyl benzoate than that of acetophenone. In fact, the magnitude of the upward deviations of π-donor para substituents appears to be related to the resonance effect substituent constant ($\Delta\bar{\sigma}_R^{+}$) of the respective substituents.

LArSR analysis of the substituent effect on the basicities of methyl benzoates provides a $\rho=11.9$ and an $r^{+}=0.45$ with excellent precision. In this application of LArSR Eq., the substituent parameters used are the standard values[3,6] for most substituents but modified values are used for p-NH_2, p-OH p-CO_2Me, and p-CHO groups because of lack of solvent effects in the gas phase.[7]

Table 1. Relative Gas Phase Basicities ($\delta\Delta G^{o}$)[a] of Substituted Methyl Benzoates (Y=OMe) and Acetophenones (Y=Me) at 343K

Subst.	Y=OMe	Y=Me	Subst.	Y=OMe	Y=Me
p-NMe_2	—	-18.1	p-F	2.2	0.6
p-NH_2	-8.0	-11.4	m-F	4.2	3.7
p-OMe	-4.8	-8.1	p-Cl	2.0	0.7
m-OMe	-1.5	-2.4	m-Cl	3.6	3.4
p-OMe-m-Cl	-1.9	-5.4	p-CF_3	5.7	5.8
p-SMe	-3.3	-6.5	m-CF_3	5.5	5.3
m-SMe	-0.7	-1.3	p-CN	8.1	8.2
p-SMe-m-Cl	-1.4	—	m-CN	7.9	8.1
p-OH	-3.1	-5.4	p-NO_2	8.9	8.8
m-OH	0.2	-0.6	m-NO_2	8.4	8.4
p-Me	-2.3	-3.9	p-CO_2Me	1.7[b]	1.2
m-Me	-1.4	-1.7	p-COMe	—	1.8[b]
p-t-Bu	-4.1	-5.1	p-CHO	4.2	—
m,m-Me_2	-2.9	-3.8	H	(-0.1)[c]	(-1.7)[c,d]

a) In kcal/mol, a negative sign denotes greater basicity. b) Applied with a statistical correction. c) Values relative to ammonia. d) Ref. 8.

The r^+ value of 0.45 for the methyl benzoate series clearly indicates that the subtituent effect on the gas phase basicity of methyl benzoate cannot be described in terms of the usual single set of substituent constants, either σ^+ or σ referred to r^+=1.00 or 0.26, respectively. The results of this LArSR analysis for the relevant systems in the gas phase (Table 2) also indicates that the ρ value is nearly constant, while the r^+ value varies dramatically with the change of Y substituent. The sensitivity of stabilization by field/inductive effect is not influenced by Y-substituent. The magnitaude and order of decrease in the r^+ value is in agreement with the order of increasing π-donor ability of the Y susbtituent ($\Delta\bar{\sigma}_R{}^+$= H;0.00, CH_3;-0.187, OCH_3;-0.678), suggesting that the r^+ value is influenced mainly by the resonance effect of the Y-substituent rather than its inductive/field one. This is further confirmed by the fact that a much smaller r^+ value (≈0.3) is obtained for the gas phase basicities of N,N-dimethylbenzamide series (Y=NMe_2).[9] It is likely that the r^+ parameter for these proton transfer equilibria is related to the resonance demand of the reaction center independent of the ρ value. These results strongly support the validity of our LArSR treatment.

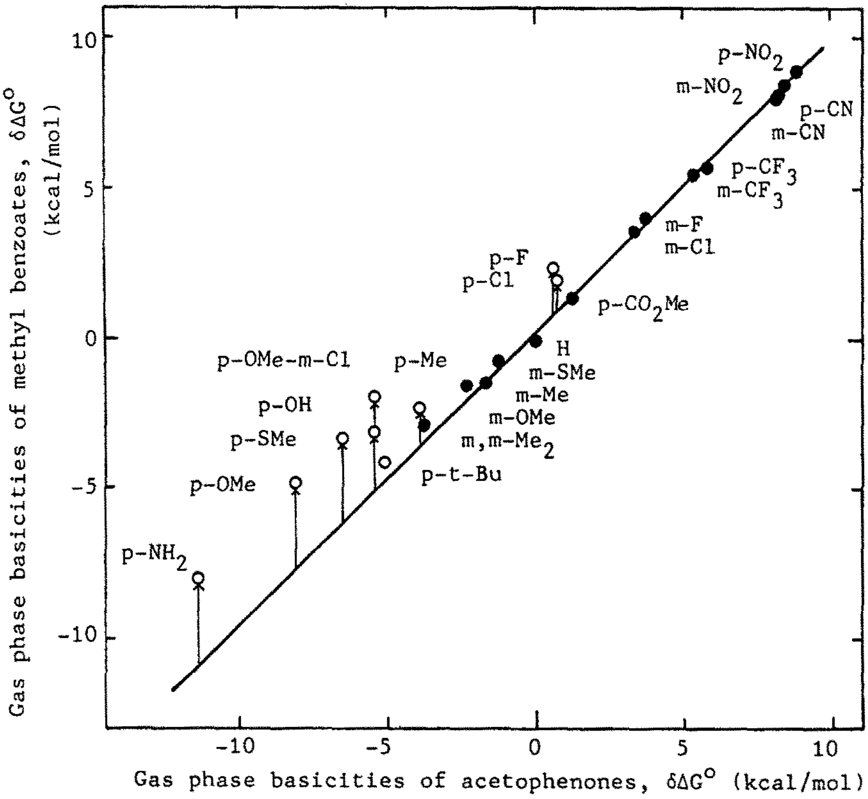

Fig. 1. Plots of relative gas phase basicities of substituted methyl benzoates against the corresponding acetophenones.

Table 2. Results of LArSR Aanalyses for Gas Phase Basicities of ArCOY

Y	ρ	r^+	c	SD	R	n	note
OMe	11.9	0.45	-0.2	±0.3	0.998	18	this work
Me	12.3	0.78	-0.5	±0.3	0.999	17	10
H	12.1	1.04	-0.3	±0.3	0.999	16	11

Finally, a comparison of the LArSR correlations for the basicities of the ArCOY systems between aqueous solution[3,12] and the gas phase provides new insights into the solvent effects on proton transfer equilibria. The r^+ values in solution (Y=H; 1.16, Me; 0.76, OH; 0.55) are very close to those in the gas phase, indicating that the r^+ value is insensitive to solvent effects. This suggests that the blend of resonance effect and inductive/field conribution depends on the inherent intramolecular stabilization of the ion regardless of the large external stabilization through solvation. In constrast the ρ values in the aqueous solution (Y=H; 2.41, Me; 3.00, OH; 1.56) are significantly smaller than those in the gas phase, reflecting the solvent stabilization of positive charge in the ion. Furthermore, the solvent attenuation factor (ρ_g/ρ_{aq}) seems to depend on the reaction system. A more comprehensive and detailed discussion of solvent effects based on gas phase studies will be presented in forthcoming papers.

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