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SUBSTITUENT EFFECTS ON THE GAS PHASE BASICITIES OF ACETOPHENONES

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Abstract: The gas phase basicities of m- and p-substituted acetophenones have been determined by the ion cyclotron resonance (ICR) equilibrium constant method. The application of the LArSR Eq. to these substituent effects provides a ρ=12.2 and an r^+=0.76 with excellent precision.

Our LArSR Eq.(1), a multi-parameter extension of the Hammett equation, has been applied to a large variety of diverse reactions in solution with excellent precision.[1-3] The most significant feature of the LArSR Eq. is the introduction of an $r^{\pm}$ parameter which is taken as a measure of the π-interaction

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

between the aryl π-system and the reaction center in the rate-determining transition state. However, the complexity of the reaction mechanism especially arising from the kinetic involvement of solvent may cause serious controversies on the proper interpretation of an r value.[4] For this reason, the substituent effects on the free energy changes for proton transfer equilibrium (2) in the gas phase is particularly important in order to validate our LArSR treatment, since here substituent effects depend only on the inherent stability of the ions without solvation. Accurate scales of relative gas phase basicities of

$$B_1 + B_2H^+ \rightleftarrows B_1H^+ + B_2 \qquad (2)$$

numerous organic compounds have been available for several years,5) but there is no detailed analysis focussed on substituent effects on gas phase basicities.[6,7] We have, therefore, determined the free energy changes for the proton transfer equilibrium (3) between a series of acetophenones and their protonated conjugate acids in the gas phase since the corresponding equilibrium in aqueous solution had been successfully correlated in terms of the LArSR Eq. (1) as a model of benzylic cation reactions.[2,3]

$$XC_6H_4COCH_3 + C_6H_5C(CH_3)OH^+ \rightleftarrows XC_6H_4C(CH_3)OH^+ + C_6H_5COCH_3 \qquad (3)$$

The standard free energy changes for the proton transfer reaction were obtained by measuring the equilibrium constants by means of the pulsed ICR mass spectrometer built in our laboratory.[8] The relative basicities of a variety of acetophenones are summarized in Table 1 (relative to the parent molecule).

There exists a roughly linear free energy relationship between the gas phase and solution basicities[9] of acetophenones. The scatter in the relationship appears to reflect specific aqueous solvent effects. The relationship is described by an equation, $\delta\Delta G^o_{(g)}=4.06\delta\Delta G^o_{(aq)} + 0.4$, with a satisfactory precision (R=0.990), excluding particular substituents which behave as strong hydrogen bond donors or acceptors in solution. A similar linear relationship between the gas and solution phase basicities was observed for α-methylstyrenes[7] and pyridines.[11] The existence of such linear free energy relationships suggests that substituent effects in the gas phase can be analyzed by the conventional method used for analyses of reactivities in solution.

In Fig. 1 the gas phase basicities of acetophenones are plotted against σ^+ values and the gas phase basicities of the corresponding pyridines. The quality of the fit of the σ^+ correlation is unsatisfactory at the acceptable level of precision of the correlation analysis of substituent effects. A partial linear relationship is observed only for the meta substituents and the para π-acceptor substituents with a significant deviation for the para π-donors. While the scatter may be attributed mostly to solvent effects on the substituent constant values determined from reactivities in aqueous solution, all of the deviations of the strong para π-donor substituents from the line should not be attributed to solvent effects alone. From the plot against the gas phase basicities of pyridines, which is absolutely free from solvent effects on substituent constants, we see that all meta substituents give an

Table 1. Relative Gas Phase Basicities[a] of Substituted Acetophenones

Subst.	$\delta\Delta G^o$	Subst.	$\delta\Delta G^o$	Subst.	$\delta\Delta G^o$
p-NMe_2	-18.1	m-SCH_3	-1.3	p-CF_3	5.8
p-NH_2	-11.4	p-CH_3	-3.9	m-CF_3	5.3
p-OCH_3	-8.1	m-CH_3	-1.7	p-CN	8.2
m-OCH_3	-2.4	p-t-Bu	-5.1	m-CN	8.1
p-OH	-5.4	m,m-Me_2	-3.8	p-NO_2	8.8
m-OH	-0.6	p-F	0.6	m-NO_2	8.4
p-OCH_3-m-Cl	-5.4	m-F	3.7	p-$COCH_3$	1.2
p-OC_2H_4-m	-9.9	p-Cl	0.7	p-CO_2CH_3	1.8
p-SCH_3	-6.5	m-Cl	3.4		

a) In kcal/mol at 343K. Gas phase basicity of unsubstituted acetophenone is -1.7 kcal/mol relative to ammonia (ref. 10). A negative sign denotes greater basicity than for the unsubstituted acetophenone, and vice versa.

excellent linear relationship and all π-donor para substituents significantly deviate downward from this meta line. This clearly indicates more enhanced resonance stabilization with π-donor para substituents in the acetophenone than in the pyridine systems. In fact, it appears that the magnitudes of the enhancements are related to the resonance substituent constants ($\Delta\bar{\sigma}_R{}^+$) of the respective susbtituents. Such reaction dependency of the resonance effect contribution is in accord with the fundamental idea of the varying resonance demand of our LArSR equation, suggesting the applicability of this analysis to substituent effects in the gas phase.

Application of the LArSR equation to the acetophenone data provides an $r^+=0.76$ and a $\rho=12.2$ using standard substituent parameters derived from reactivities in solution, excluding a few substituents which are particularly

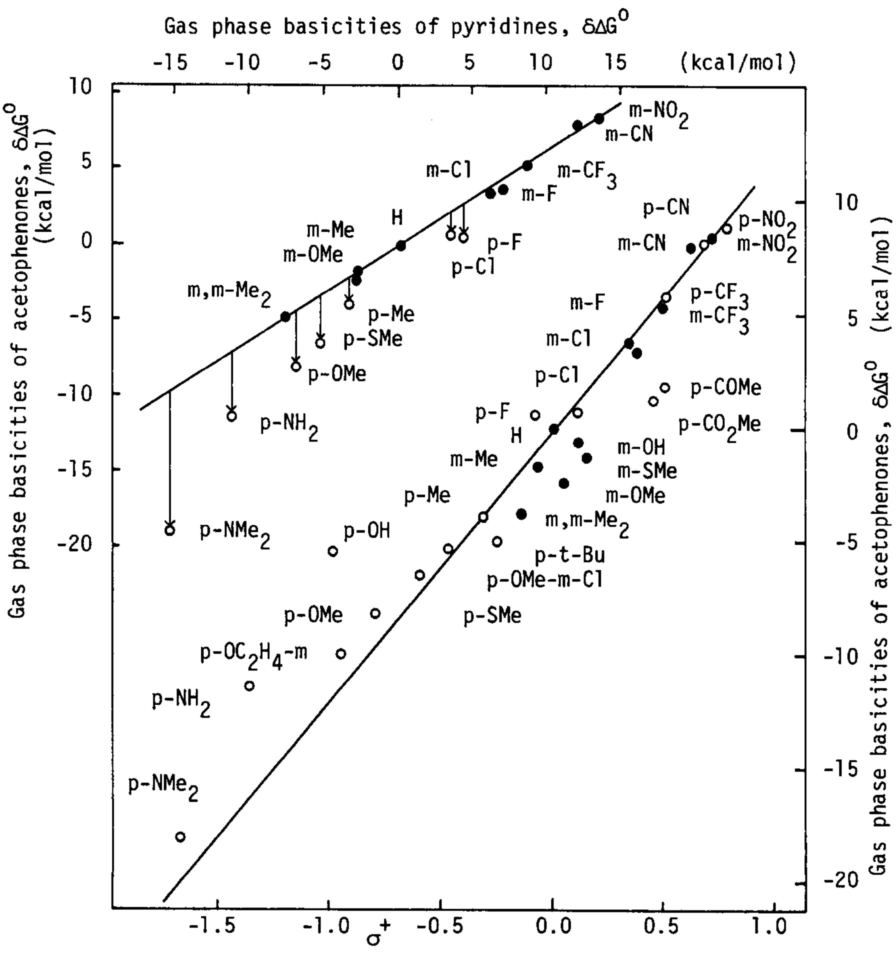

Fig. 1. Plots of gas phase basicities of acetophenones against σ^+ (lower) and the corresponding pyridines (upper).

sensitive to aqueous solvent effects. The correlation coefficient for this fit is 0.998 and the standard deviation is ±0.4 kcal/mol.[12] The unique r^+ value of 0.76 indicates a smaller contribution of the resonance effects of π-donor substituents relative to the inductive/field one than the resonance contribution in the σ^+ value (r^+=1.00 by definition). The concept of varying resonance demand in the LArSR Eq. is therefore an essential requirement in the analyses of substituent effects in the gas phase as well as in solution.

It should be particularly noted that the r^+ value of 0.76 obtained in the gas phase is identical with the r^+ value of 0.76 obtained from an analysis of the aqueous solution basicity[3] as expected from the existence of the linear relationship between both phases. This suggests that the blend of resonance effect and inductive/field contribution is inherent in the internal stabilization of the system and insensitive even to the large external stabilization provided through solvation. In contrast the ρ value of 12.2 is significantly greater by a factor of four than that obtained in aqueous solution, indicating that the ρ value reflects the solvent stabilization of the positive charge on the ion.

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