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# Gas Phase Basicities of Styrenes toward Trimethylsilyl Cation. Structure and Stability of $Me_3Si$-Styrene$^+$ Complexes

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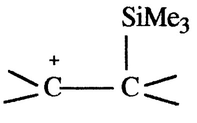
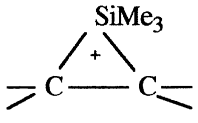
Gas phase basicities of styrenes toward $Me_3Si^+$ have been determined based on $Me_3Si^+$ transfer equilibria. The substituent effect on the stability of $Me_3Si$-styrene$^+$ complex has been analyzed by means of the LArSR Eq., giving a $\rho$ value of -5.76 and an r value of 0.41. These results imply that $Me_3Si$-styrene$^+$ complex as a long-lived ion in an ICR cell has not a classical open structure different from the protonated styrene.

There is considerable current interest in Lewis-basicity and -acidity of organic compounds in the gas phase.$^{1-6)}$ These studies provide important information on intrinsic properties of interactions of ions and neutrals as well as solvation of ions. In previous study, we have determined gas phase basicities toward $Me_3Si^+$, GB($Me_3Si^+$), for a series of acetophenones.$^{7)}$ The comparative analysis of its substituent effect with that of the corresponding $H^+$ basicity revealed that the positive charge is formed on the benzylic carbon by binding of $Me_3Si^+$ to the oxygen atom of the carbonyl group in the same manner as the protonation and that the degree of $\pi$-delocalization of the positive charge into the aryl $\pi$-system is also similar to that of the protonated ions. These results prompt us to study $Me_3Si^+$ basicities of alkenes. If the association of $Me_3Si^+$ with alkene yields the carbenium ion having the $Me_3Si$ group in a position $\beta$ to the cationic center, thermochemical data for such gaseous ions would provide a new insight into the stabilizing effect of a $\beta$-silyl group, the so-called $\beta$-silicon effect, on carbenium ion intermediates in solvolytic reactions that is one of the most interesting aspects in organosilicon chemistry.$^{8-13)}$ Recently, Li and Stone$^{14)}$ have studied thermochemical properties of several $Me_3Si$-alkene$^+$ complexes using a pulsed high pressure mass spectrometer. Hajdasz and Squire$^{15)}$ estimated from a proton affinity of trimethylvinylsilane determined by the bracketing technique that the ethyl cation is stabilized by 39 kcal mol$^{-1}$ (1 cal =4.184 J) when an H is replaced by $Me_3Si$. However, it is not confirmed well the structures of $Me_3Si$-alkene$^+$ complex and the protonated trimethylvinylsilane, i.e., a classical open structure (**1a**) or a bridged structure (**1b**). Analysis of the substituent effect on thermochemical properties of ions would give useful information for elucidating the structures of gaseous ions as well as nature of interactions of $Me_3Si^+$ and carbon bases. We have therefore studied the substituent effect on the thermodynamic stability of $Me_3Si$-styrene$^+$ complex.

$Me_3Si$-styrene$^+$ complexes can be formed by a reaction between styrenes and $Me_3Si^+$ generated from electron impact ionization of $Me_4Si$ in an ion cyclotron resonance (ICR) cell. The gas phase basicities of styrenes toward $Me_3Si^+$ have been



**1a**



**1b**

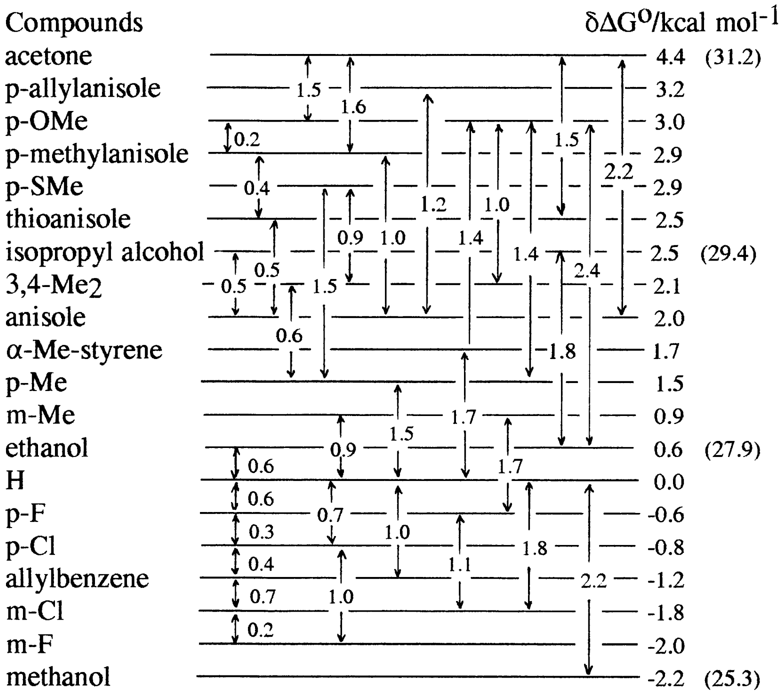


Fig. 1. Ladders of free energy changes of $Me_3Si^+$ transfer equilibria. Values in parentheses are free energy changes for the following reaction at 468 K; $Me_3Si\text{-}base^+ \longrightarrow Me_3Si^+ + base$, Ref. 3.

Table 1. Gas Phase Basicities of Styrenes toward $Me_3Si^+$ and $H^+$

| Subst. | ΔGB/kcal mol$^{-1}$ $Me_3Si^+$ | ΔGB/kcal mol$^{-1}$ $H^+$ a) |
|---|---|---|
| p-OMe | 3.0b) | 12.3 |
| p-SMe | 2.9b) | 11.5 |
| 3,4-Me$_2$ | 2.1 | 7.0 |
| p-Me | 1.5 | 5.1 |
| m-Me | 0.9 | 1.8 |
| H | 0.0 | 0.0 |
| p-F | -0.6 | 0.4 |
| p-Cl | -0.8 | -0.3 |
| m-Cl | -1.8 | -4.7 |
| m-F | -2.0 | -5.3 |

a) Ref. 16.
b) Basicity of the substituent, see text.

determined by measuring equilibrium constants of $Me_3Si^+$ transfer reaction (1) using a homemade pulsed ICR spectrometer as described previously.[7] Equilibrium constant for reaction (1) is obtained from the ratio of ion intensities of $Me_3SiB_1^+$ and $Me_3SiB_2^+$ when equilibrium has been attained and from the known pressures of neutrals in the ICR cell. Typical operating conditions are as follows, electron beam energy = 16 eV, tetramethylsilane pressure = $4\times10^{-6}$ to $1\times10^{-5}$ Torr (1 Torr = 133 Pa), the pressures of styrenes and reference bases were in a range of $2\times10^{-7}$ to $1\times10^{-6}$ Torr.

$$B_1 + Me_3SiB_2^+ \rightleftharpoons Me_3SiB_1^+ + B_2 \qquad (1)$$

Figure 1 shows ladders of interlocking basicities with respect to $Me_3Si^+$ measured at 323 K. The overlapping values reveal internal consistency for ΔG° within ±0.2 kcal mol$^{-1}$. The ΔGB values evaluated with a ladder of basicities are summarized in Table 1 together with the corresponding $H^+$ basicities[16] which are regarded as a measure of the stabilities of α-phenylethyl cations.

The plots of $Me_3Si^+$ basicity versus $H^+$ basicity for a series of styrenes in Fig. 2 show a moderately good qualitative correlation between these two quantities. For meta substituents there exists a considerably good linear relationship with a slope of 0.4. Such a limited linear relationship of non-conjugate substituents has generally been observed for the gas phase stabilities of ordinary benzylic carbocations.[17-19] With reference to this line all π-donor substituents show downward deviations. This may be indicative of that the resonance contribution of para π-donor substituent is significantly reduced in the $Me_3Si$-styrene$^+$ complex compared with that in the corresponding protonated ion. Deviations of p-methoxy and p-methylthio groups may however result from different binding site of $Me_3Si^+$ because these two substituents have high affinity toward $Me_3Si^+$. In fact, the ΔGB($Me_3Si^+$) value of p-methoxystyrenes relative to parent anisole is 1.0 kcal mol$^{-1}$, being identical to that of

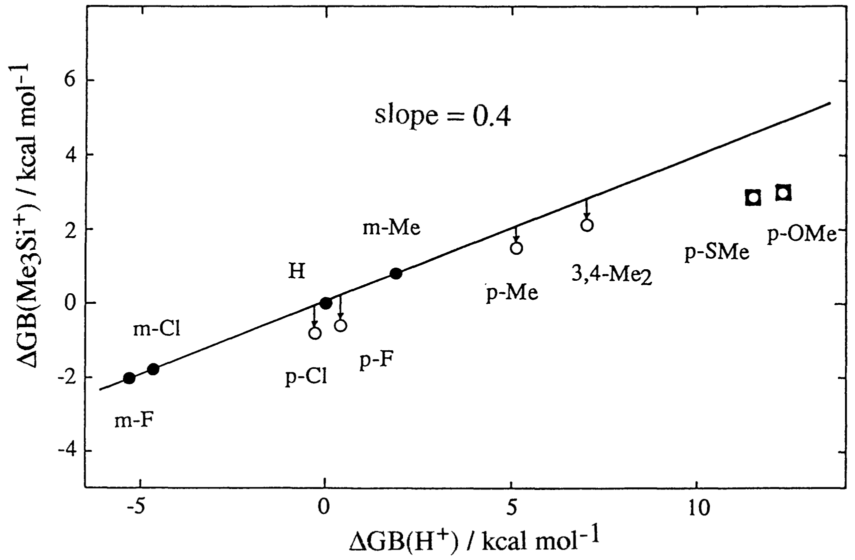


Fig. 2. The correlation between $\Delta GB(Me_3Si^+)$ and $\Delta GB(H^+)$ for m, p-substituted styrenes.

p-methylanisole in which the binding site must be the oxygen atom of the methoxy group. The $\Delta GB(Me_3Si^+)$ value of p-methylthiostyrene relative to thioanisole, 0.5 kcal mol$^{-1}$, also seems to be reasonable as the effect of the p-$CH=CH_2$ group on the $GB(Me_3Si^+)$ of thioanisole. These results suggest that the binding of $Me_3Si^+$ to these two derivatives must occur at the oxygen or sulfur atom of the substituents. Application of the LArSR Eq. 2[20, 21] to the substituent effect on the $GB(Me_3Si^+)$ of styrene excluding p-methoxy- and p-methylthiostyrenes provides an r value of 0.41 and a $\rho$ value of -5.76 (kcal mol$^{-1}$ $\sigma^{-1}$) with excellent precision (R=0.997 and SD=±0.1 kcal mol$^{-1}$). If the association of $Me_3Si^+$ with p-methoxystyrene and p-methylthiostyrene occurs at the ethylene moiety in the same manner as other derivatives, the effects of p-methoxy and p-methylthio groups on the $GB(Me_3Si^+)$ of styrene can be estimated to be 2.4 kcal mol$^{-1}$ and 1.7 kcal mol$^{-1}$, respectively, from the LArSR correlation result. These values are apparently smaller than observed values, supporting again that the binding site of these compounds is not the ethylene moiety but the methoxy and methylthio groups.

$$\Delta GB = \rho\,(\sigma^{0} + r\,\Delta\bar{\sigma}_{R}^{+}) \qquad (2)$$

The $\rho$ value of -5.76 is significantly smaller than that for the ordinary benzylic carbocations of which $\rho$ values fall into a narrow range of -13 to -14 regardless of the stability of the parent carbocation.[16-18, 22] Since the magnitude of a $\rho$ value primarily depends on the magnitude of the charge and the distance between the cationic center and the substituent,[23] the small $\rho$ value of -5.76 means that the center of the charge is far apart from the substituent compared with the case of the ordinary benzylic carbocations, suggesting that the structure of the $Me_3Si$-styrene$^+$ complex is different from that of the ordinary benzylic carbocations. In addition, the magnitude of the r value, a measure of the $\pi$-interaction between positive charge and the aryl $\pi$-system, would also provide useful information on the structure of the association complex. Although the limited number of $\pi$-donor substituents may not give a precise r value, the r value of 0.41 is distinctly smaller than that for $\alpha$-phenylethyl cation (r=1.15),[16] revealing that there is no effective $\pi$-delocalization of the positive charge into the aryl $\pi$-system. Such substituent effect behavior of the stabilities of $Me_3Si$-styrene$^+$ complexes indicates that there exists a little charge on the benzylic carbon, leading us to the conclusion that the association complex is not a classical open ion at least. The most conceivable structure of this ion is assumed to be a partially bridged one, a classical open ion at least. The most conceivable structure of this ion is assumed to be a partially bridged one, although it is not clear at present whether such small charge development at the benzylic carbon results from the bond formation between the benzylic carbon and Si or from the strong electronic interaction between the vacant 2p orbital and the $C_\beta$-Si bond.

Since the association complex formed in the gas phase may correspond to an intermediate of the $S_N1$ solvolysis of the corresponding substrate, it is instructive to compare the present result of the $Me_3Si$-styrene$^+$ complexes with that of the solvolysis. Recently, Shimizu and co-workers10) obtained a $\rho$ of -3.05 and an r of 1.05 for the solvolysis of 1-phenyl-2-(trimethylsilyl)ethyl acetates, arriving at the conclusion that this substrate must solvolyze through rate-determining formation of a classical open cation. The r value for the gaseous ion is apparently smaller than that of solvolysis transition state. On the contrary, the r values of ordinary benzylic carbocations in the gas phase were found to be in complete agreement with those for the corresponding $S_N1$ solvolysis, implying a complete similarity of structure between the transition state and the intermediate.17) The discrepancy of the r value for the present system therefore suggests a significant difference in structure between the solvolysis transition state and the stable intermediate cation.24) Consequently, the solvolysis of the present substrate may be interpreted as follows. In the rate-determining transition state bond cleavage of the leaving group proceeds without the neighboring assistance of the $\beta$-$Me_3Si$ group and after then a partially bridged ion is formed as a more stable intermediate without a significant barrier.

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