Experimental and theoretical study on thermodynamic stabilities of silyl cations. Substituent effect on the stability of dimethylphenylsilyl cation in the gas phase†

Hirotaka Tashiro,[a] Kiyoshi Kikukawa,[a] Kazutoshi Ikenaga,[b] Nobujiro Shimizu[c] and Masaaki Mishima*[c]

[a] *Department of Industrial Chemistry, Graduate School of Advanced Technology, Kinki Univ. in Kyushu, Iizuka 820-0055, Japan*
[b] *Department of Industrial Chemistry, Kumamoto Institute of Technology, Kumamoto 860-0082, Japan*
[c] *Department of Chemistry, Graduate School of Science and Institute for Fundamental Research of Organic Chemistry, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan*

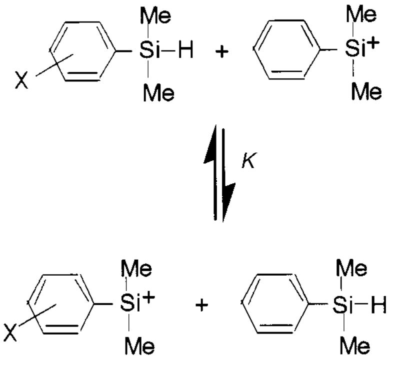
Received (in Cambridge) 8th July 1998, Accepted 21st September 1998

Thermodynamic stabilities of aryldimethylsilyl cations were determined by measuring equilibrium constants of hydride-transfer reaction in the gas phase using a FT ion cyclotron resonance spectrometer. An application of the Yukawa–Tsuno equation to the substituent effect gave a ρ of -5.87 and an r^+ of 0.29. Both r^+ and ρ values are significantly smaller than those for a carbon analog, α-cumyl cation. The same trend was observed for the results of *ab initio* calculations. In addition, the r^+ value of 0.3 for gaseous silyl cations agrees with that observed for the kinetics of the hydride-transfer reaction from aryldimethylsilanes to diarylcarbenium ions in dichloromethane. It is concluded that the dimethylphenylsilyl cation is characterized by no significant π-delocalization of the positive charge into the benzene ring in addition to a small ρ value compared to that of the α-cumyl cation.

Introduction

Three-coordinate silicon cations (silyl cations) analogous to carbenium ions have attracted continuous interest for almost half a century.[1,2] Characterization of silyl cations in condensed phases has remained one of the most difficult subjects in silicon chemistry until very recently.[3–5] On the other hand, the existence of the silyl cations in the gas phase, in contrast to those in solution, is well established from the early mass spectrometric studies.[6,7] A recent determination by FT ion cyclotron resonance spectroscopy of the hydride affinities of simple silyl cations showed that silyl cations are thermodynamically more stable than the corresponding carbocations,[8] which is consistent with the results of theoretical calculations.[9] The results of *ab initio* calculations suggested further that π-donor substituents, which directly link to the cationic silicon atom, are only 30–40% as effective in stabilizing silyl cations as in stabilizing their carbocation analogs.[10] With respect to this prediction, an interesting experimental result in condensed phases was recently reported by Mayr and co-workers.[11] They investigated kinetics of hydride-transfer reactions of hydrosilanes to carbocations in dichloromethane, and found that the reactivities of aryldimethylsilanes were linearly correlated with σ, not with σ^+. If the formation of silyl cations is involved in the rate-determining process, this result suggests that the π-delocalization of the positive charge is not significant in the silyl cation compared to the corresponding carbocation analogs, α-cumyl cations, where the substituent effect is correlated with σ^+.

In recent studies, we reported that carbocations in the gas phase are a good model for intermediates of carbocation-formation reactions in solution, such as S_N1 solvolysis.[12–16] Analysis of the substituent effects on the thermodynamic stabilities of benzylic carbocations given by the proton- and halide-transfer equilibria provided important information regarding the intrinsic nature of the π-interaction between the substituent and the positively charged center atom. In this study, we have therefore measured equilibrium constants of hydride-transfer reaction (1) in order to determine a quantitative scale of thermodynamic stabilities of aryldimethylsilyl cations, which allows us to analyze the substituent effect of their stabilities in detail. This would also give a useful basis for interpretation of kinetic results of hydride-transfer reactions in condensed phases, because such thermochemical quantities in the gas phase are absolutely free from mechanistic complexities, counter-anion and solvent.



(1)

Scheme 1

Ab initio calculations were also conducted for these hydride-transfer reactions for comparison with the experimental thermodynamic stabilities of $PhSi^+Me_2$ ions determined in the gas phase.

---

† Optimized geometries and energies are available as supplementary data (SUPPL. NO 57440, pp. 4) from the British Library. For details of the Supplementary Publications Scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 2*, available *via* the RSC Web page (http://www.rsc.org/authors).

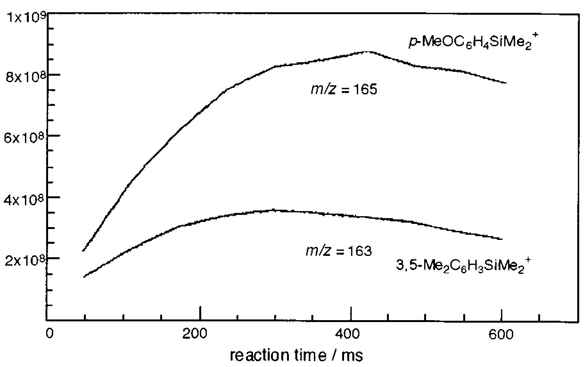


Fig. 1 Time plot of $m/z = 135$ and 165 ions formed by electron-impact ionization of a binary mixture of dimethylphenylsilane and dimethyl(*p*-methoxyphenyl)silane.

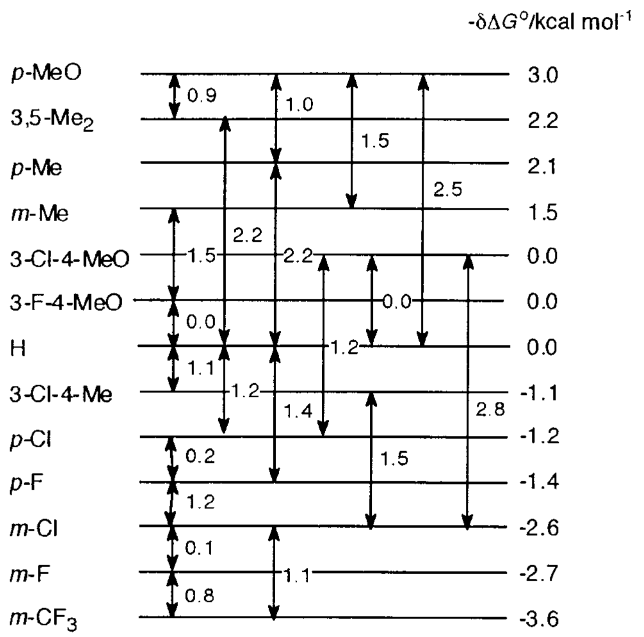


Fig. 2 Ladder of free energy changes for hydride-transfer equilibria.

Table 1 Relative stabilities of aryldimethylsilyl cations and α-cumyl cations and substituent constants[a] used for correlation analysis

Subst.	$-\delta\Delta G^{o}(\mathrm{Si}^+)$[b]	$-\delta\Delta G^{o}(\mathrm{C}^+)$[c]	σ^{o}	$\Delta\bar{\sigma}_R^+$
p-MeO	3.0	10.5	−0.10	−0.70
3,5-$\mathrm{Me_2}$	2.2	3.5	−0.28	0.00
p-Me	2.1	4.1	−0.13	−0.20
m-Me	1.5	1.8	−0.12	0.00
3-Cl-4-MeO	0.0	6.7	0.22	−0.72
3-F-4-MeO	0.0	6.7	0.22	−0.72
H	0.0	0.0	0.00	0.00
3-Cl-4-Me	−1.1	−0.7	0.25	−0.20
p-Cl	−1.2	−4.0	0.20	−0.15
p-F	−1.4	−0.1	0.20	−0.17
m-Cl	−2.6	−4.7	0.36	0.00
m-F	−2.7	−5.1	0.39	0.00
m-$\mathrm{CF_3}$	−3.6	−6.3	0.50	0.00

[a] Taken from ref. 14. [b] Negative of the free energy changes of the hydride-transfer reaction (1), in kcal mol^{-1}. [c] Relative gas phase basicities of α-methylstyrenes, in kcal mol^{-1}. Taken from ref. 13.

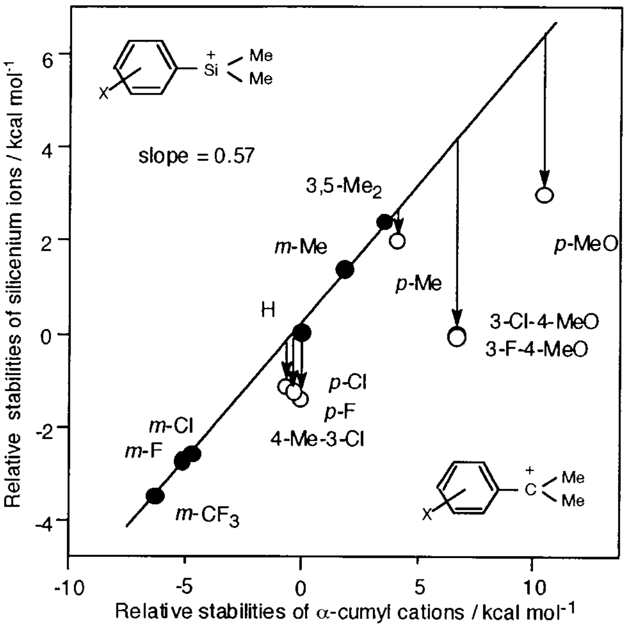


Fig. 3 Plot of relative stabilities of aryldimethylsilyl cations against those of α-cumyl cations. Closed circles; *meta* substituents, open circles; *para* π-donor substituents.

Results and discussion

The ion intensities in a typical run for a binary mixture of dimethyl(3,5-dimethylphenyl)silane and dimethyl(*p*-methoxyphenyl)silane vary with time as shown in Fig. 1. The relative intensity of the signals of $m/z = 163$ and 165, which correspond to respective silyl cations formed by loss of a hydrogen, is constant at a reaction time longer than 500 ms. This means that equilibrium has been attained. The equilibrium constant value can be calculated from the relative ion-abundances and relative partial pressures of neutrals. In this way, the standard free energy changes were determined for respective hydride-transfer equilibria, giving the ladder of hydride affinities of silyl cations as shown in Fig. 2.

Substituent effect

The relative hydride affinities of silyl cations are given in Table 1 together with relative gas-phase basicities of α-methylstyrenes as a measure of stabilities of α-cumyl cations. Fig. 3 shows the plot of the relative stabilities of aryldimethylsilyl cations against those of the corresponding α-cumyl cations. There is obviously no simple linear relationship between these two quantities. A good linear relationship with a slope of 0.57 is, however, observed for *meta* substituents, and all *para* π-donor substituents significantly deviate downward from this line. The slope of 0.57 indicates that the response of the stability of the silyl cation to a *meta* substituent is significantly smaller than that in the α-cumyl cation. It should be noted that the *p*-methoxy, 3-fluoro-4-methoxy and 3-chloro-4-methoxy groups, which are equally strong π-electron-donors, show larger downward deviations than other *para*-substituents having small π-electron-donating ability. The magnitude of deviations seems to be proportional to the π-electron-donating ability of respective substituents. This suggests that the contribution of the resonance effect in the dimethylphenylsilyl cation must be significantly smaller than that in the α-cumyl cation.

In order to estimate quantitatively the degree of resonance contribution involved in the substituent effect, extended Hammett-type linear free energy relationships have generally been used.[17] In particular, the Yukawa–Tsuno equation (2)[18]

$$\log K/K_o = -1000\ \delta\Delta G^{o}/2.303RT = \rho(\sigma^{o} + r^{+}\ \Delta\bar{\sigma}_R^{+}) \quad (2)$$

has successfully been applied to substituent effects on the stability of benzylic carbocations in the gas phase as well as reactivities in solution.[12–16]

In eqn. (2) σ^{o} and $\Delta\bar{\sigma}_R^{+}$ are a normal substituent constant and a resonance substituent constant ($= \sigma^{+} - \sigma^{o}$), respectively. The

Table 2 Some selected bond lengths (Å) and angles (°) of optimized structures at RHF/6-31G* level for aryldimethylsilyl cations and α-cumyl cations

	C1C2[a] (C1C6)	C2C3[a] (C5C6)	C3C4[a] (C4C5)	C1Si/C1C7	∠C2C1SiC9/∠C2C1C7C9
Silyl cation					
H	1.410	1.377	1.391	1.798	180.0
p-MeO	1.418	1.366	1.406	1.779	180.0
Silane					
H	1.397	1.386	1.386	1.890	
p-MeO	1.396	1.383	1.389	1.883	
Cumyl cation					
H	1.424	1.369	1.395	1.400	175.0
p-MeO	1.437	1.354	1.418	1.381	176.9
Cumene					
H	1.389	1.387	1.383	1.523	
p-MeO	1.394	1.379	1.390	1.522	

[a] Average of two bonds.

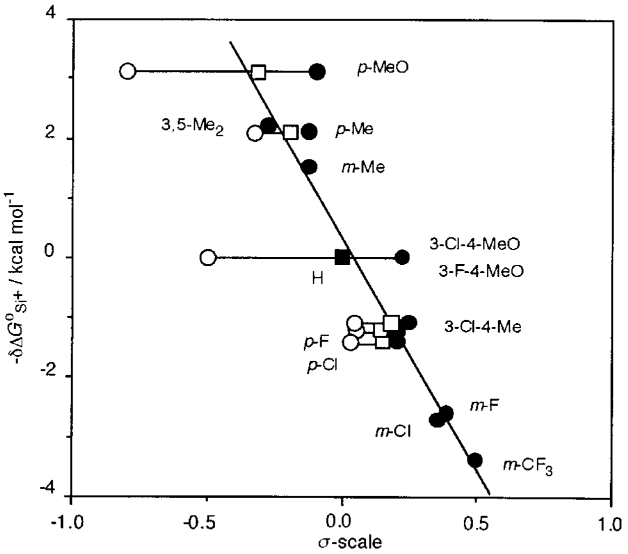
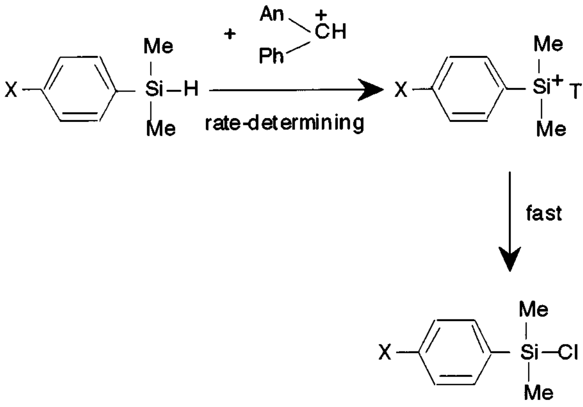


Fig. 4 The Y–T plot for the substituent effect on the stability of dimethylphenylsilyl cation. Closed circles; σ^o, open circles; σ^+, squares; $\bar{\sigma}$ at $r^+ = 0.29$.

r^+ parameter represents the degree of the π-interaction between a *para* π-donor substituent and the positive charge. An application of the Yukawa–Tsuno equation (2) to the substituent effect for the equilibrium constant of reaction (1) provided a ρ of -5.8 and an r^+ of 0.29 with satisfactory precision (SD = ±0.2 and $R = 0.991$), as shown in Fig. 4. This r^+ value is much smaller than unity for the α-cumyl cation and is comparable to that involved in σ_p value ($r^+ = 0.28$). The small r^+ value clearly indicates that π-delocalization of a positive charge is not important in the silyl cation. The previous studies on the substituent effects of benzylic carbocations showed that the r^+ value decreases significantly as a carbocation is stabilized by the substituents linked to the benzylic carbon, *e.g.*, a very small r^+ value of 0.23 was observed for the highly stabilized carbocation, 1-*N*,*N*-dimethylamino-1-hydroxybenzyl cation,[19] while $r^+ = 1.53$ was obtained for the highly destabilized 2,2,2-trifluoro-1-phenylethyl cation.[15] The small r^+ value observed for the dimethylphenylsilyl cation indeed seems to be consistent with this trend in the r^+ value because the silyl cations are significantly more stable than the corresponding carbocations, *e.g.*, hydride affinities of H_2MeSi^+, HMe_2Si^+ and Me_3Si^+ are smaller than the corresponding carbon analogs by 24.6, 21.4 and 13.1 kcal mol^{-1}, respectively.[8] *Ab initio* MO calculation as discussed later shows that $PhSiMe_2^+$ is 12.6 kcal mol^{-1} more stable than $PhCMe_2^+$. In addition, the ρ value of -5.8 is distinctly smaller than that observed for the ordinary benzylic carbocations, indicating that the response of the polar effect is reduced in the silyl cation compared to the corresponding carbon analog.

Mayr *et al.*[11] recently reported that the substituent effect on the reactivity of a hydride-transfer reaction from aryldimethylsilanes to diarylcarbenium ions in dichloromethane are correlated with σ, which corresponds to $r^+ = 0.28$ according to the Yukawa–Tsuno equation (2), giving a ρ value of -2.46.



(3)

Similar correlation results were also reported in an early study of the hydride-transfer reactions of hydrosilanes.[20] Both r^+ and ρ values for these reactions are significantly smaller than those observed for the corresponding carbocation analogs, *e.g.*, S_N1 solvolysis of α-cumyl chlorides. Furthermore, the magnitude of this r^+ value is in complete agreement with that of the gaseous silyl cation obtained in this study. Such agreement of the r^+ value was also observed for a comparison between substituent effects of benzylic carbocation stabilities in the gas-phase and the S_N1 solvolysis of the corresponding precursors.[14–16] Thus, the identity of the r^+ value leads us to the conclusion that the transition structure of the rate-determining step can be approximated by the intermediate silyl cations.

Theoretical calculations

The selected geometric parameters of the optimized structures of aryldimethylsilyl cations, α-cumyl cations and the corresponding neutral molecules at the RHF/6-31G* level are given in Table 2. These geometries were identified by means of a full

Table 3 Relative stabilities[a] of aryldimethylsilyl cations and cumyl cations calculated at MP2/6-31G*//HF/6-31G*

	$ArSi(CH_3)_2^+$		$ArC(CH_3)_2^+$	
Subst. (X)	$-\Delta E^b$	$-\delta\Delta G^{oc}$	$-\Delta E^b$	$-\delta\Delta G^{oc}$
p-MeO	5.97	6.52	11.69	11.42
3-Cl-4-MeO	2.03	0.66	6.54	6.80
p-Me	2.72	2.97	4.55	4.09
m-Me	1.77	1.38	2.42	1.87
H	0.00	0.00	0.00	0.00
p-F	−2.24	−2.23	−1.05	−1.04
m-F	−3.96	−3.94	−4.95	−4.99
m-CF_3	−6.61	−7.00	−8.29	−8.94

[a] Energy changes of isodesmic reactions (5) or (6). [b] Included zero point energy correction. [c] Thermal correction to Gibbs free energy was applied, see text.

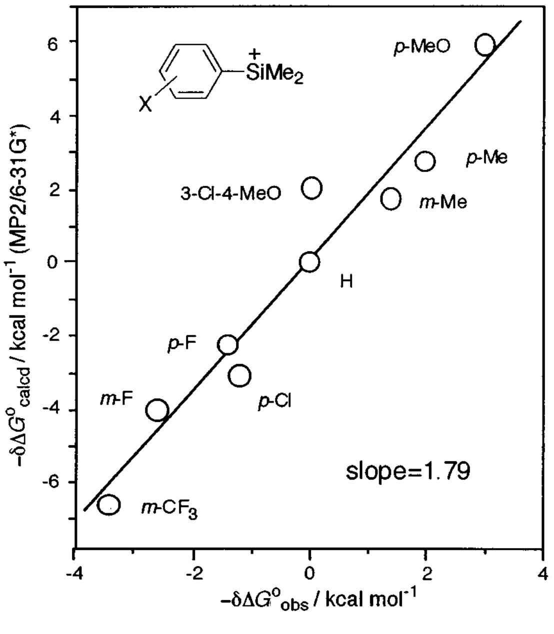


Fig. 5 Calculated $-\delta\Delta G^o$ *vs.* experimental $-\delta\Delta G^o$ for aryldimethylsilyl cations.

analysis of the vibrational modes at those stationary points. The single point calculations at MP2/6-31G* were carried out on the geometries at RHF/6-31+G*.

Energies. The energy change of the isodesmic reaction (4) gives a measure of stabilities of the silyl cations relative to the corresponding carbocation analogs.

$$XC_6H_4C(Me)_2^+ + XC_6H_4Si(Me)_2H = XC_6H_4Si(Me)_2^+ + XC_6H_4C(Me)_2H \quad (4)$$

The calculated energy changes for reaction (4) are −6.6, −7.9, −10.1, −11.9, −12.6, −11.4, −13.7 and −14.4 kcal mol^{-1} for *p*-MeO, 3-Cl-4-MeO, *p*-Me, *m*-Me, H, *p*-F, *m*-F and *m*-CF_3, respectively. All values are negative, *i.e.*, exothermic, indicating that aryldimethylsilyl cations are more stable than the corresponding α-cumyl cations. The higher stability of the silyl cation relative to the carbon analog is understandable because silicon is more electropositive and more polarizable compared to the carbon atom. In addition, the exothermicity is found to increase as the substituent changes from electron-releasing to electron-withdrawing group. This trend is consistent with that of the experimental hydride affinity values for the simple alkyl system.[8]

The substituent effect on the stability of dimethylphenylsilyl cation can be obtained by the isodesmic reaction (5) using the

$$C_6H_5Si(Me)_2^+ + XC_6H_4Si(Me)_2H = XC_6H_4Si(Me)_2^+ + C_6H_5Si(Me)_2H \quad (5)$$

calculated total energies of neutral hydrosilanes and the corresponding silyl cations. In order to compare directly with cation stabilities determined experimentally, which are free energy changes of hydride transfer reaction, thermal correction to Gibbs free energy obtained by frequency calculations at HF/6-31G* was applied to the energies calculated at MP2/6-31G*//HF/6-31G*.[21] The results are given in Table 3 together with the corresponding values for α-cumyl cations given by reaction (6).

$$C_6H_5C(Me)_2^+ + XC_6H_4C(Me)_2H = XC_6H_4C(Me)_2^+ + C_6H_5C(Me)_2H \quad (6)$$

A good linear relationship between the calculated and observed stabilities for the cumyl cation was obtained; $-\delta\Delta G^o_{calcd} = -1.12\ \delta\Delta G^o_{obs} - 0.26$ ($R = 0.994$). Similarly, a linear relationship was observed for the aryldimethylsilyl cation; $-\delta\Delta G^o_{calcd} = -1.79\ \delta\Delta G^o_{obs} + 0.06$ ($R = 0.970$). The precision of the correlation is not as good as that for the cumyl cation, as shown in Fig. 5. The slope larger than unity suggests that the calculations at the present level of theory overestimate the interaction between the substituent and the positive charge on the silicon atom. However, a comparison of the calculated stabilities between both cation series is informative, because the common factors involved in these calculations should be cancelled out. In Fig. 6 are plotted the calculated relative stabilities of dimethylphenylsilyl cations against α-cumyl cations. One can easily find a similarity between this figure and Fig. 3 for experimental values. That is, non-conjugative *meta* substituents give a linear correlation with a slope of 0.78, and strong π-donor substituents deviate downward from the line. Although the slope is somewhat larger than that observed for experimental values, it is obvious that the dimethylphenylsilyl cation is characterized by the lower response to substituent effect and by the smaller resonance contribution compared to the α-cumyl cation.

Geometries. The calculated geometries of silyl cations may provide further information regarding the π-interaction between silicon and the aryl group, because the resonance interaction in the conjugated π-system should lead to changes in structural parameters such as bond lengths. A dihedral angle of C2C1SiC7 is 180° for all substituted dimethylphenylsilyl cations, indicating that these silyl cations are planar. The planar structure allows effective overlapping between a vacant p-orbital of silicon and the benzene π-orbital. The C2C3 (C5C6) and C1-Si bonds shorten and the C1C2 (C1C6) and C3C4 (C4C5) bonds lengthen compared to the respective bonds of the corresponding neutral molecule, suggesting the presence of a resonance interaction between a positive charge on Si and the benzene ring according to the resonance theory. The changes in bond length are, however, considerably smaller than those in the α-cumyl cation. In addition, when a hydrogen at position 4 is replaced by the methoxy group, the changes of these bond lengths are smaller than the corresponding changes in the α-cumyl cation system. This result indicates a small contribution of resonance interaction in the silyl cation. This is consistent with the experimental result that the silyl cation is characterized by a small r^+ value.

Charges. Fig. 7 shows the Mulliken charges on respective positions of dimethylphenylsilyl cation and α-cumyl cation. The positive charges developed at the *ortho* and *para* positions are smaller than those in the α-cumyl cation, indicating the reduced π-delocalization of the positive charge in the silyl cation. This is consistent with the small r^+ value observed for the silyl cation. Most importantly, only 10% of the positive

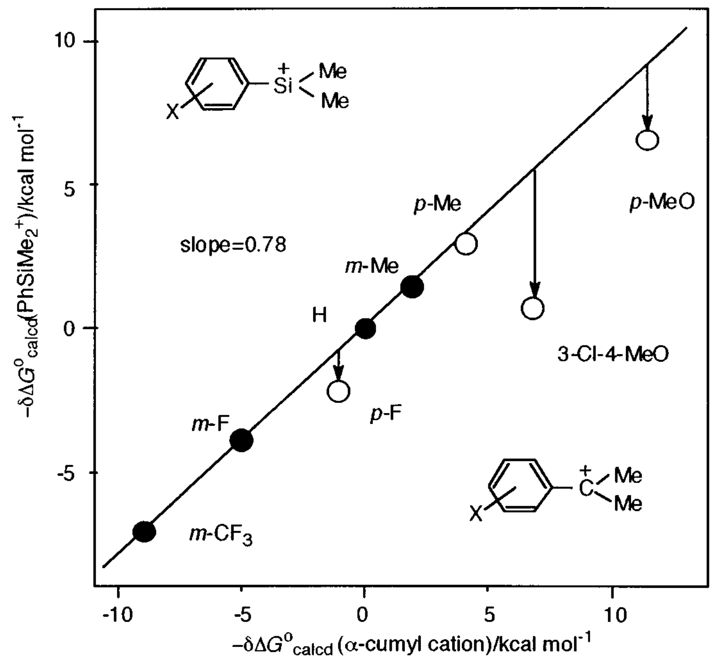
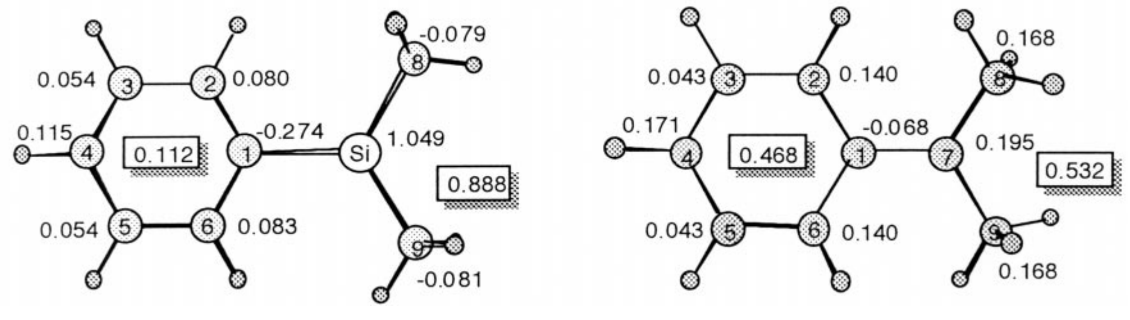


Fig. 6 Plot of calculated $-\delta\Delta G^o$, aryldimethylsilyl cations *vs.* α-cumyl cations. Closed circles; *meta* substituents, open circles; *para* π-donor substituents.



Dimethylphenylsilyl cation

α-Cumyl cation

Fig. 7 Atomic charges given by Mulliken population analysis. Atomic charges on each position with a hydrogen are summed into heavy atoms.

charge in the silyl cation is delocalized into the benzene ring and the rest of the positive charge is localized at the dimethylsilyl moiety, while half the charge is delocalized into the benzene ring in the α-cumyl cation. Such a small distribution of the positive charge into the benzene ring would result in the low response of the stability of the silyl cation to the change of the substituent, being consistent with the small ρ value.

Conclusions

Both results of analysis of substituent effects on the stability of silyl cation in the gas phase and the theoretical calculations showed consistently that the positive charge in the silyl cation is mostly localized at the silicon atom and that only a small amount of the charge is delocalized into the aryl π-system, although the silyl cation has a planar structure which is favorable for effective overlapping between a vacant p-orbital of silicon and the benzene π-orbital. The poor p–π overlap between Si and π-donor substituent is an essential feature in the silyl cation. The identity of the r^+ value between the arylsilyl cation in the gas phase and the hydride-transfer reaction from arylsilanes to carbocations revealed that the transition structure of the rate-determining step is close to the intermediate silyl cations. The smaller ρ value may be attributed to a highly localized charge at the Si atom and a longer Ph–Si bond.

Experimental

Chemicals

The silanes were either commercially available or synthesized by a Grignard reaction of the corresponding bromides with chlorodimethylsilane in ether,[22] and were purified by GLC just before use. The NMR and mass spectra of these arylsilanes, recorded on JEOL JNM-EX400 and Extrel FTMS 2001 instruments, respectively, were both consistent with the proposed structures. Physical properties of all compounds except the derivatives listed below were in agreement with those in the literature.[23–25] The ^{1}H NMR and mass spectra for the other compounds are as follows. *m*-Chloro, δ_H (400 MHz; CDCl$_3$; Me$_4$Si) 0.3 (6H, m, SiMe$_2$), 4.4 (1H, m, SiH), 7.1–7.4 (4H, m, Ph). M^+(EI) 170.0312. $C_8H_{11}ClSi$ requires 170.0313. 3-Chloro-4-methoxy, δ_H 0.3 (6H, m, SiMe$_2$), 3.8 (3H, s, Me), 4.4 (1H, m, SiH), 6.9–7.3 (3H, m, Ph). M^+ 200.0415. $C_9H_{13}ClSi$ requires 200.0419. 3,5-Dimethyl, δ_H 0.3 (6H, m, SiMe$_2$), 2.3 (6H, s, Me), 4.4 (1H, m, SiH), 6.9–7.3 (3H, m, Ph). M^+ 164.1011. $C_{10}H_{16}Si$ requires 164.1016. 3-Fluoro-4-methoxy, δ_H 0.3 (6H, m, SiMe$_2$), 3.8 (3H, s, OMe), 4.4 (1H, m, SiH), 6.9–7.3 (3H, m, Ph). M^+ 184.0709. $C_9H_{13}FOSi$ requires 184.0714. 3-Chloro-4-methyl, δ_H 0.3 (6H, m, SiMe$_2$), 2.4 (3H, s, Me), 4.4 (1H, m, SiH), 7.0–7.4 (3H, m, Ph). M^+ 184.0477. $C_9H_{13}ClSi$ requires 184.0470.

ICR measurements

The equilibrium constant measurements were performed on an Extrel FTMS 2001 spectrometer. Details of the experimental techniques used for the measurements of the equilibrium constants (K) for the hydride-transfer reaction (6) are the same as those for the proton-transfer reaction described previously.[26] Only significant changes and/or additional procedures will be given here.

$$RH + R_o^+ \rightleftharpoons R^+ + R_oH \qquad (7)$$

$$K = [R_oH/RH][R^+/R_o^+] \qquad (8)$$

$$\Delta G^o = -RT \ln K \qquad (9)$$

All measurements were performed at 50 °C at a 3 T uniform magnetic field strength. The pressures of neutral reactants were measured by means of a Bayard–Alpert type ionization gauge with appropriate correction factors being applied to correct the gauge readings for the different ionization cross sections of various compounds.[27] In order to minimize the formation of dimer ions overall pressures of the reactants were maintained at the low range of 10^{-7} to 10^{-8} Torr by controlled rates through leak valves from a parallel inlet manifold into the vacuum chamber. The gas-phase hydride-transfer reactions were initiated by a 5 ms pulse of a relatively low energy electron beam (8–12 eV) through the ICR cell. After a reaction period of 0.5 to 2 s depending upon the reactant, the equilibrium was attained and the relative abundance of R^+ and R_o^+ was measured by signal intensities of ICR spectra. Each measurement was performed at several ratios of partial pressures and at different overall pressures. Arithmetic mean values of K from eqn. (8) were used for the calculation of ΔG^o at 343 K [eqn. (9)] with an average uncertainty of ± 0.2 kcal mol^{-1} in most of these cases. The occurrence of the hydride-transfer reaction was examined by the ion-eject experiment using the SWIFT technique.[28] Each sample was subjected to several freeze-pump-thaw cycles on the ICR inlet vacuum system to remove entrapped impurities.

Calculations

All calculations were performed with the Gaussian 94 program.[29] Aryldimethylsilyl cations, α-cumyl cations, and the corresponding neutral derivatives were fully optimized at the RHF/6-31G* level and were identified by means of a full analysis of the vibrational modes at those stationary points. To improve the calculated energies electron-correlation contributions were estimated by the Møller–Plesset perturbation theory;[30] single point MP2 calculations were also carried out at the 6-31G* basis set using the frozen-core approximation. Thermal corrections to Gibbs free energy evaluated at the HF/6-31G* level were applied to a total energy of a single point MP2 calculation for comparison with the experimental free energy changes.[21]

Acknowledgements

The authors gratefully acknowledge support for this research by a Grant-in-Aid for Scientific Research from the Ministry of Education.

References

1 J. B. Lambert and W. J. Schulz, Jr., in *The Chemistry of Organic Silicon Compounds*, eds. S. Patai and Z. Rappoport, Wiley Interscience, Chichester, 1989, ch. 16, p. 1007 and references cited therein.

2 P. D. Lickiss, in *The Chemistry of Organic Silicon Compounds*, vol. 2, eds. Z. Rappoport and Y. Apeloig, Wiley Interscience, Chichester, 1998, ch. 13.

3 J. B. Lambert, S. Zhang, J. C. L. Stern and J. C. Huffman, *Science*, 1993, **260**, 1917; J. B. Lambert, L. Kania and S. Zhang, *Chem. Rev.*, 1995, **95**, 1191; J. B. Lambert and Y. Zhao, *Angew. Chem.*, *Int. Ed. Engl.*, 1997, **36**, 400.

4 C. A. Reed, Z. Xie, R. Bau and R. Benesi, *Science*, 1993, **262**, 402; Z. Xie, J. Mannung, R. W. Reed, R. Mathur, P. D. W. Boyd, A. Benesi and C. A. Reed, *J. Am. Chem. Soc.*, 1996, **118**, 2922.

5 H.-U. Steinberger, T. Muller, N. Auner, C. Maerker and P. v. R. Schleyer, *Angew. Chem.*, *Int. Ed. Engl.*, 1997, **36**, 626; P. v. R. Schleyer, *Science*, 1997, **275**, 39.

6 H. Schwarz, in *The Chemistry of Organic Silicon Compounds*, eds. S. Patai and Z. Rappoport, Wiley Interscience, Chichester, 1989, ch. 7, pp. 445–510.

7 C. Maerker, J. Kapp and P. v. R. Schleyer, in *Organosilicon Chemistry II*, eds. N. Auner and J. Weis, VCH, Weinheim, 1996, pp. 329–359.

8 S. K. Shin and J. L. Beauchamp, *J. Am. Chem. Soc.*, 1989, **111**, 900.

9 Y. Apeloig, in *Heteroatom Chemistry*, eds. E. Block, VCH, Weinheim, 1990, p. 27.

10 Y. Apeloig, in *The Chemistry of Organic Silicon Compounds*, eds. S. Patai and Z. Rappoport, Wiley Interscience, Chichester, 1989, p. 57.

11 H. Mayr, N. Basso and G. Hagen, *J. Am. Chem. Soc.*, 1992, **114**, 3060.

12 M. Mishima, S. Usui, M. Fujio and Y. Tsuno, *Nippon Kagaku Kaishi*, 1989, 1269 (*Chem. Abstr.*, 1990, **112**, 118179z).

13 M. Mishima, S. Usui, M. Fujio and Y. Tsuno, *Nippon Kagaku Kaishi*, 1989, 1262 (*Chem. Abstr.*, 1990, **112**, 118178y).

14 M. Mishima, K. Arima, H. Inoue, S. Usui, M. Fujio and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 3199.

15 M. Mishima, H. Inoue, S. Itai, M. Fujio and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 3273.

16 M. Mishima, H. Inoue, M. Fujio and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 1163.

17 J. Shorter, *Correlation Analysis of Organic Reactivity*, Research Studies Press, John Wiley and Sons, Chichester, 1982.

18 Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, 1959, **32**, 971; Y. Yukawa, Y. Tsuno and M. Sawada, *Bull. Chem. Soc. Jpn.*, 1966, **39**, 2274; Y. Tsuno and M. Fujio, *Chem. Soc. Rev.*, 1996, **25**, 129.

19 M. Mishima, M. Fujio, N. Shimizu and Y. Tsuno, *Mem. Fac. Sci., Kyushu Univ.*, *Ser. C*, 1988, **16**(2), 207 (*Chem. Abstr.*, 1989, **110**, 172599h).

20 P. A. Carey and C.-L. Hsu, *J. Organomet. Chem.*, 1969, **19**, 29.

21 The frequency calculations of cumyl cation and cumene at MP2/6-31G*//MP2/6-31G* gave the sum of electronic and thermal free energies of −347.964578 (au) and −348.809324, respectively. These quantities led to 0.2 kcal mol^{-1} lower HIA than that obtained by applying the thermal correction evaluated at HF/6-31G*//HF/6-31G* to the electronic energy calculated at MP2/6-31G*//HF/6-31G*. This indicates that the present approximation for the thermal correction to Gibbs free energy seems to be acceptable.

22 R. A. Bekeser and F. J. Riel, *J. Am. Chem. Soc.*, 1951, **73**, 3472.

23 J. Hetflejs, F. Mares and V. Chvalovsky, *Coll. Czech. Chem. Commun.*, 1965, **30**, 1643.

24 D. Seyferh, R. Damrauer, J. Yick-Pui Mui and F. T. Jula, *J. Am. Chem. Soc.*, 1968, **90**, 2944.

25 V. Bazant, V. Chvalovsky and J. Rathousky, *Organosilicon Compounds*, Academia, Prague, 1965, vol. 2, p. 261.

26 M. Mishima, M. Fujio and Y. Tsuno, *Mem. Fac. Sci., Kyushu Univ.*, *Ser. C*, 1984, **14**(2), 365 (*Chem. Abstr.*, 1985, **102**, 61712e).

27 J. E. Bartmess and R. M. Georgiadis, *Vacuum*, 1983, **33**, 149; K. J. Miller, *J. Am. Chem. Soc.*, 1990, **112**, 8533.

28 A. G. Marshall, T.-C. L. Wang and T. L. Ricca, *J. Am. Chem. Soc.*, 1985, **107**, 7983; R. B. Cody, *Analysis*, 1988, **16**, 30; S. Guan and A. G. Marshall, *Int. J. Mass Spectrom. Ion Process*, 1997, **157/158**, 5.

29 Gaussian 94, Revision C.2, M.J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1995.

30 C. Møller and M. S. Plesset, *Phys. Rev.*, 1934, **46**, 618.

Paper 8/05314F