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Gas Phase Basicities of α-Trimethylsilylstyrenes. Intrinsic Effect of α-Trimethylsilyl Group on the Stability of Carbenium Ions

Masaaki MISHIMA, Toshifumi ARIGA,† Yuho TSUNO,*
Kazutoshi IKENAGA,†† and Kiyoshi KIKUKAWA†††
Institute for Molecular Science, Myodaiji, Okazaki 444
†Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashi-ku, Fukuoka 812
††Department of Industrial Chemistry, Kumamoto Institute of Technology, Ikeda, Kumamoto 860
†††Department of Industrial Chemistry, Faculty of Engineering, Kinki University in Kyushu, Kayanomori, Iizuka 820

Gas phase basicities of α-trimethylsilylstyrenes have been determined by measuring proton transfer equilibrium constants. Basicity of α-trimethylsilylstyrene was found to be comparable to that of α-alkylstyrene, suggesting that α-trimethylsilyl group as well as α-alkyl group stabilizes a carbenium ion.

There is current interest in effects of silyl substituents on the stability of carbenium ions which are believed to be intermediates in reactions of organosilicons.[1] Experimental and theoretical studies have been carried out extensively but the effect of α-silyl substituents is even qualitatively unclear.[2-4] For example, no detectable reaction of $(CH_3)_3SiCH_2X$ (X=Br, Cl) was observed in aqueous solvents,[5] and 1-phenyl-1-(trimethylsilyl)ethyl[6] and α-trimethylsilybenzyl derivatives[7] solvolyze ca. 10^4 times slower than the corresponding methyl-substituted ones. On the other hand, 2-trimethylsilyl-2-adamantyl p-nitrobenzoate and the corresponding 2-methyl-2-adamantyl derivative solvolyze at essentially the same rate in 97% trifluoroethanol.[8] α-Trimethylsilylvinyl triflates solvolyze even faster than the corresponding alkyl substituted derivatives.[9] Such discrepancies in effects of α-silyl substituents on solvolysis rates may have been attributed to mechanistic complexities and the destabilization of the ground state.[8,10] Recently ab initio MO calculations for simple model systems reveal that α-silyl substituents destabilize significantly carbenium ions relative to alkyl groups.[2,4a] However, there is virtually no quantitative measurement in the gas phase of the stabilization energy on carbenium ions resulting from α-silyl substituents. In order to elucidate intrinsic effect of α-silyl substituents we have therefore decided to determine gas phase basicities (GB) of

α-trimethylsilylstyrenes of which conjugate acids are expected to be 1-aryl-1-(trimethylsilyl)ethyl cations.

Gas phase basicities have been determined by measuring proton transfer equilibrium constants by means of a pulsed ICR spectrometer constructed in our laboratory as described previously.[11,12] Gas phase basicity values of α-trimethylsilylstyrenes measured

$$ArC(SiMe_3)=CH_2 + BH^+ \rightleftharpoons ArC^+(Me)SiMe_3 + B \quad (1)$$

relative to suitable reference bases are converted to absolute scales with respect to ammonia (GB=195.6 kcal mol^{-1}, 1 cal=4.184 J) as listed in Table 1. Unfortunately gas phase basicity values could not be obtained for several α-trimethylsilylstyrenes having an

Table 1. Free Energy Changes of Proton Transfer Equilibria (1)

Subst.[a]	B[b]	ΔG^o [c]	GB [d]
p-OCH_3	2-chloropyridine	-1.1	
	$CH_3CON(CH_3)_2$	0.6	208.0
p-CH_3	2-cyanopyridine	-1.9	
	3-cyanopyridine	-0.6	202.8
	4-cyanopyridine	0.2	
m-Me	i-Pr_2O	-2.4	
	acetylacetone	-0.6	
	2-cyanopyridine	0.0	199.9
p-F	i-Pr_2O	-0.3	
	i-Pr_2CO	-2.0	198.0
H	i-Pr_2O	-0.7	
	acetylacetone	0.9	198.4

a) 1-Aryl-1-(trimethylsilyl)ethylenes. b) Reference bases. GB values (in kcal mol^{-1}) are as follows; 2-chloropyridine; 206.6, $CH_3CON(CH_3)_2$; 208.4, 2-cyanopyridine; 200.0, 3-cyanopyridine; 201.3, 4-cyanopyridine; 202.1, i-Pr_2O; 197.6, i-Pr_2CO; 196.0, acetylacetone; 199.3. c) Free energy changes of a reaction (1) at 308 K, in kcal mol^{-1}. d) Averaged GB values converted with respect to GB(NH_3)=195.6 kcal mol^{-1}. Positive values denote greater basicity.

Table 2. Gas Phase Basicities of α-Trimethylsilylstyrenes and the Corresponding α-Methylstyrenes[a]

	p-OMe	*p*-Me	*m*-Me	*p*-F	H
System	ΔGB/kcal mol^{-1}				
Ar-C($SiMe_3$)=CH_2	9.6	4.4	1.5	-0.4	0.0
Ar-C(Me)=CH_2	10.5	4.1	1.8	-0.1	0.0[b]

a) Ref. 12. b) Absolute GB = 199.1 kcal mol^{-1} (Ref. 13).

$PhC(SiMe_3)=CH_2 + PhCH^+Me \rightleftharpoons PhC^+(SiMe_3)Me + PhCH=CH_2$ $\Delta G^o = -4.5$

$PhC(SiMe_3)=CH_2 + PhC^+(t\text{-}Bu)Me \rightleftharpoons PhC^+(SiMe_3)Me + PhC(t\text{-}Bu)=CH_2$ $\Delta G^o = -0.2$[14]

$PhC(SiMe_3)=CH_2 + PhC^+Me_2 \rightleftharpoons PhC^+(SiMe_3)Me + PhC(Me)=CH_2$ $\Delta G^o = 0.7$

electron-withdrawing substituent because of experimental difficulties.

Comparison of GB value of α-trimethylsilylstyrene with those of relevant bases reveals that 1-trimethylsilylstyrene is clearly more basic than styrene and comparable to those of α-alkylstyrenes. If the protonation to α-trimethylsilylstyrene yields 1-phenyl-1-(trimethylsilyl)ethyl cation (1), this result will lead us to an important conclusion that the stabilization effect of α-trimethylsilyl on the carbenium ions is not different from that of alkyl groups. Accordingly, it is particularly important to examine whether the conjugate acid ion of α-trimethylsilylstyrene is 1 or its isomeric ions (2 and 3). For this purpose effect of ring-substituents on the basicity of α-trimethylsilylstyrene has been studied. In the cases of 2-phenyl-2-(trimethylsilyl)ethyl cation (2) and the siliceni-

$PhC^+(CH_3)Si(CH_3)_3$ (1) $PhCH(SiMe_3)CH_2^+$ (2) $PhC(CH_3)_2Si^+(CH_3)_2$ (3)

um cation (3) ring substituents would not affect significantly the stability of the ion because the carbon atom or the silicon atom bearing positive charge is insulated from the phenyl ring by an sp^3 carbon atom while the stability of 1 must be sensitive to the ring substituent as well as that of ordinary benzylic cations. Table 2 exhibits clearly that the substituent effect on the basicity of α-trimethylsilylstyrenes is as large as that of the corresponding α-methylstyrene of which conjugate acid ion is α-cumyl cation. This fact supports that the structure of the conjugate acid ion of α-trimethylsilylstyrene is 1.

It is noteworthy that the substituent effect on the stability of 1 is very similar to that on α-cumyl cation. This suggests that resonance effect of para π-donor substituents contribute to the stability of 1 in the same degree as that in α-cumyl cation. In other words, there is no difference in resonance demand (r), a measure of π-interaction between the positive charge and aryl π-system given by the LArSR analysis,[15] between 1 and α−cumyl cation (r=1.00).[12] In the previous studies on gaseous stabilities of

$$\delta \Delta G^o = \rho(\sigma^o + r \Delta \bar{\sigma}_R^+) \qquad (2)$$

benzylic carbenium ions we found that the resonance demand (r) varies significantly with the system and that its change is related with electronic effects of α-substituent(s) attached to the benzylic carbon atom, i.e., the destabilized carbenium ion by electron-withdrawing α-substituent(s) has the greater r value, e.g., r values for 1-aryl-2,2,2-trifluoroethyl cation and 1-aryl-1-trifluoromethylethyl cation are 1.53 and 1.40, respectively.[16] In conclusion, a striking resemblance of the substituent effect in addition to the stability of the parent carbenium ion (ring substituent = H) between 1 and α-cumyl cation suggests that the effect of trimethylsilyl group on the stability of benzylic carbenium ion is close to that of methyl group. This is in a sharp contrast with theoretical

calculations that α-silyl substituents destabilize significantly carbenium ions compared with alkyl substituents[2,4] although it is unclear whether or not calculation results for simple model systems are applicable to the present system.

The present result may further lead us to a suggestion with regard to α-silicon effect on reactions of organosilicon compounds. That is, it seems that the extremely low reactivity in the solvolysis of α-trimethylsilyl substrates compared with the corresponding alkyl substituted substrates is attributed to the destabilization of the ionizing process due to exalted steric constrain and desolvation by bulkiness of trimethylsilyl group rather than the stabilities of their intermediate carbocations. This may be supported by the fact that 1-phenyl-1-(trimethylsilyl)ethyl and 1-t-butyl-1-phenylethyl substrates solvolyze at the essentially same rate.[7] Thus, one must use with caution rates of solvolysis as a measure of intrinsic stabilities of carbenium ions.

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