Binding interaction of the trimethylgermyl cation with acetophenones in the gas phase†

PERKIN 2

Mustanir and Masaaki Mishima *

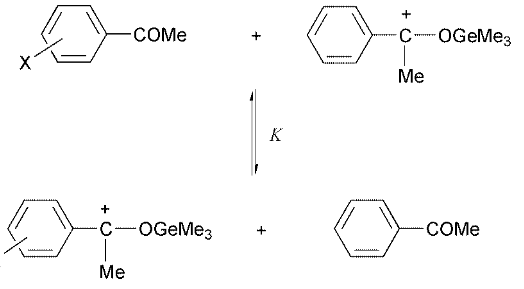
Institute for Fundamental Research of Organic Chemistry and Department of Chemistry and Physics of Condensed Matter, Graduate School of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

Received (in Cambridge, UK) 13th November 2000, Accepted 22nd March 2001
First published as an Advance Article on the web 20th April 2001

The gas-phase basicities towards the trimethylgermyl cation, GB(Me_3Ge^+), were determined for a series of acetophenones by measuring the equilibrium constants of trimethylgermyl cation transfer reactions. The effects of ring substituents on the Me_3Ge^+ basicities are excellently correlated in terms of the Yukawa–Tsuno equation, giving a ρ value of -7.1 and an r^+ value of 0.71. These results suggest that the binding interaction of Me_3Ge^+ with the O atom of the carbonyl group of the acetophenones has a pronounced covalent character, resulting in the development of a positive charge at the benzylic carbon atom, although the delocalization of the positive charge into the benzene ring is slightly smaller than that for protonation. This feature of the adduct ion with Me_3Ge^+ resembles that for the Me_3Si^+ adduct ions and is consistent with results obtained by theoretical calculations at the DFT B3LYP/6-31+G* level of theory.

Introduction

Germanium and silicon are below carbon in group 14 of the periodic table, and are more electropositive. Hence, their cations should be more accessible than carbocations.[1] Nevertheless, until now only a few silyl cations have been isolated in the condensed phase by using very weakly nucleophilic counterions and by protecting the Si^+ environment from the anion and solvent with a bulky group.[2] More recently, Sekiguchi *et al.* first isolated a free germyl cation,[3] namely, a cyclotrigermenium cation in which there is extra stabilization due to the two π-electron delocalization in addition to the hindering of the Ge^+ environment by bulky groups. These difficulties come from their high electrophilicity, which allows them to interact with a wide variety of both π- and σ-electron donors, such as solvents and counter ions.[3] The gas-phase basicities (GB) towards these Lewis cations are a good model for understanding the intrinsic nature of the binding interactions between Lewis cations and electron-pair donors.[4–6] From this point of view, we recently analyzed the substituent effects on the gas-phase basicities toward Me_3Si^+ of oxygen bases such as acetophenone and benzaldehyde and nitrogen bases such as pyridines and anilines.[7] These substituent effects could be related to the nature of the bond between Si and the oxygen or nitrogen atoms of the neutral molecules because there are no complexities arising from the variation of the steric environment at the binding site, which often causes significant disparities in the basicity order between Lewis cation and proton basicities.[7–9] The ρ values given by Hammett-type correlation were found to be close to those for the proton basicities, though the degree of delocalization of the positive charge formed at the binding site into the aromatic moiety is slightly reduced in the Me_3Si^+ adduct ions compared with that in the protonated ones. From these results and from density functional theory (DFT) calculations we concluded that the binding interactions of Me_3Si^+ with O and N atoms of organic bases have a pronounced covalent character to a degree similar to that of a proton. The same analysis will be applicable to the substituent effect for germyl cation basicities. In this paper, we report the substituent effect on the gas-phase basicity (GB) of acetophenone towards Me_3Ge^+. The relative GB(Me_3Ge^+) values were determined by measuring the Me_3Ge^+ transfer equilibrium (1) in the gas phase in the same manner as for the basicities towards Me_3Si^+ described previously.[5]



(1)

Results and discussion

The relative basicities towards Me_3Ge^+ for a series of acetophenones were determined as shown on the ladder of interconnected $\Delta G°$ values in Fig. 1. The scale covers a range of 14.3 kcal mol^{-1} from *p*-trifluoromethylacetophenone to pyridine. Comparisons of overlapping and successive steps on the ladder demonstrate an internal consistency of ±0.2 kcal mol^{-1} in most cases. The values for several organic bases other than acetophenones were also determined for comparison. These relative basicities towards Me_3Ge^+ are summarized in Table 1 along with the corresponding values towards H^+ and Me_3Si^+.

The GB(Me_3Ge^+) values increase in the order acetophenone < 2,6-dimethylpyridine ≈ aniline < *N*,*N*-dimethylaniline < pyridine, while GB(H^+) increases in the order acetophenone < aniline < pyridine < *N*,*N*-dimethylaniline < 2,6-dimethylpyridine. There is obviously a difference in the basicity order between Me_3Ge^+ and H^+. A similar difference in basicity order was observed for a comparison of Me_3Si^+ and H^+ basicities.[5]

---

† Electronic supplementary information (ESI) available: further computational details on the adducts of substituted acetophenones and the trimethylgermyl cation. See http://www.rsc.org/suppdata/p2/b0/b0090611/

DOI: 10.1039/b0090611

Table 1 Gas-phase basicities of some organic bases toward Me_3Ge^+, Me_3Si^+, and H^+

Base	ΔGB/kcal mol^{-1} [a] H^+ [b]	Me_3Si^+ [c]	Me_3Ge^+
Pyridine	0.0	0.0	0.0
N,*N*-Dimethylaniline	2.3	−7.6	−4.9
Aniline	−10.6	−11.5	−8.8
Acetophenone	−15.7	−9.3	−9.5
2,6-Dimethylpyridine	7.8	−6.8	−8.7

[a] Relative to pyridine. Negative values denote weaker bases. [b] Ref. 10. [c] Ref. 7.

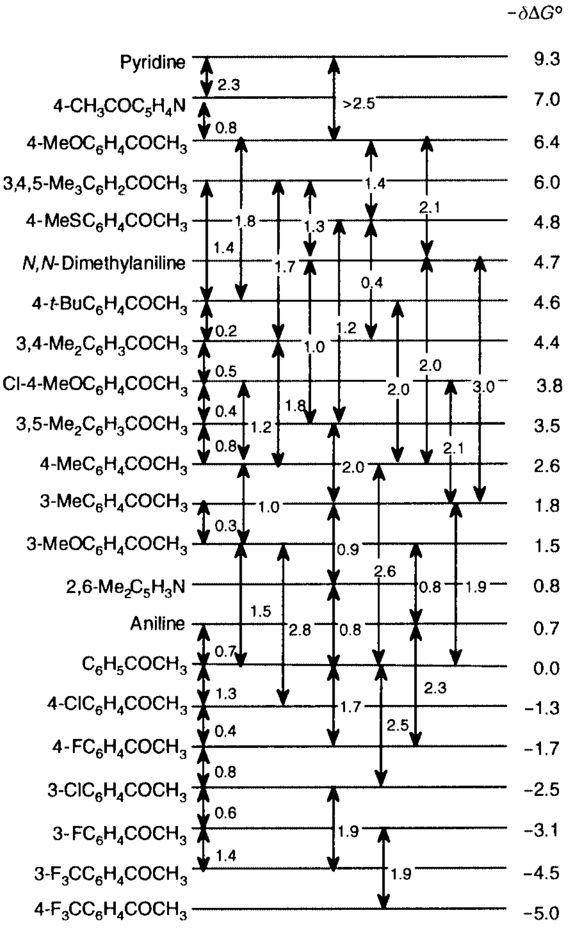


Fig. 1 Ladder of $\Delta G°$ for Me_3Ge^+ transfer equilibria at 334 K (kcal mol^{-1}). Each double arrow indicates the result of one equilibrium measurement of the indicated pair of reactants.

The ΔGB value of 2,6-dimethylpyridine relative to pyridine decreases significantly from 7.8 for H^+ to −6.8 for Me_3Si^+ to −8.7 for Me_3Ge^+. This order seems to be in agreement with the increasing size of the Lewis cation. This suggests that different steric environments of the binding sites lead to different structural effects on the basicities. Thus, comparative analysis, which is often applied to studies of interactions between Lewis cations and electron donors, must be used with caution so as not to lead to erroneous conclusions. The effects of substituents in the *meta* or *para* position of the benzene ring should be free from such difficulties. In addition, the analysis of the substituent effect provides useful information on the structures of the adduct ions and the binding site

Substituent effect

The relative basicities of substituted acetophenones towards Me_3Ge^+ are summarized in Table 2 along with literature results for H^+ and Me_3Si^+. The $\Delta GB(Me_3Ge^+)$ values of acetophenones are plotted against the corresponding H^+ basicities in Fig. 2. When the correlation is limited to *meta* substituents and *para* electron-withdrawing groups, there is an excellent linear correlation with a slope of 0.82. With respect to this line, strong π-donor substituents tend to deviate downwards. This feature is quite similar to the observation for the corresponding Me_3Si^+ basicities. In fact, there is a good linear relationship between Me_3Ge^+ and Me_3Si^+ as shown in Fig. 3. The existence of such linear relationships suggests that the binding site of Me_3Ge^+ with acetophenones is the oxygen atom of the carbonyl group in a manner similar to that for the proton and Me_3Si^+. The acetophenone substituent effects on basicity towards Me_3Ge^+ can, therefore, be analyzed by means of the Yukawa–Tsuno (Y–T) equation [eqn. (2)],[11] in the same way as for the basicities

Table 2 Relative basicities of substituted acetophenones toward H^+, Me_3Si^+, and Me_3Ge^+

Substituent	ΔGB/kcal mol^{-1} H^+ [a]	Me_3Si^+ [b]	Me_3Ge^+
4-OCH$_3$	8.1	6.8	6.4
3,4,5-Me$_3$	—	—	6.1
4-SCH$_3$	6.5	5.8	4.9
4-*t*-Bu	5.0	—	4.6
3,4-Me$_2$	5.1	4.8	4.4
3-Cl-4-OCH$_3$	5.4	4.4	3.8
3,5-Me$_2$	3.9	—	3.6
4-CH$_3$	4.0	3.1	2.6
3-CH$_3$	1.7	1.9	1.8
3-OCH$_3$	2.7	—	1.5
H	0.0	0.0	0.0
4-Cl	−0.6	−1.1	−1.3
4-F	−0.6	−1.1	−1.7
3-Cl	−3.3	−3.3	−2.5
3-F	−3.7	−3.6	−3.1
3-CF$_3$	−5.3	−5.3	−4.5
4-CF$_3$	−5.8	−5.6	−5.0

[a] Ref. 12. [b] Ref. 7.

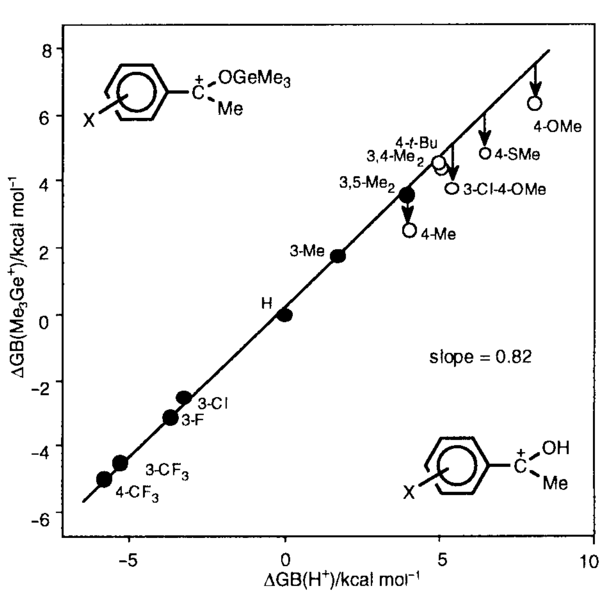


Fig. 2 Plot of $\Delta GB(Me_3Ge^+)$ *vs.* $\Delta GB(H^+)$ for acetophenones.

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

towards Me_3Si^+ and H^+, where $\sigma°$ and $\Delta\bar{\sigma}_R^+$ are the normal substituent constant and the resonance substituent constant, respectively, and r^+ is the resonance demand parameter representing the degree of the π-delocalization of the positive charge

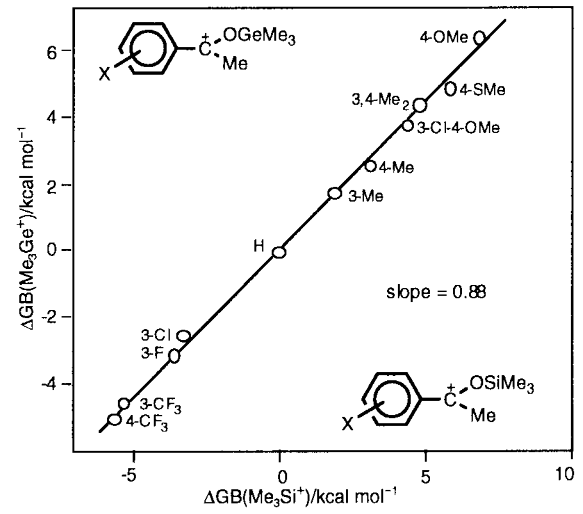


Fig. 3 Plot of ΔGB(Me$_3$Ge$^+$) *vs.* ΔGB(Me$_3$Si$^+$) for acetophenones.

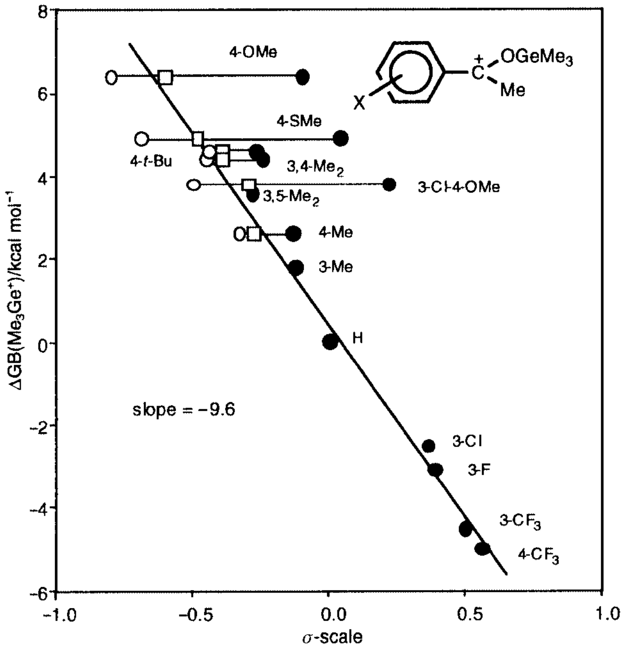
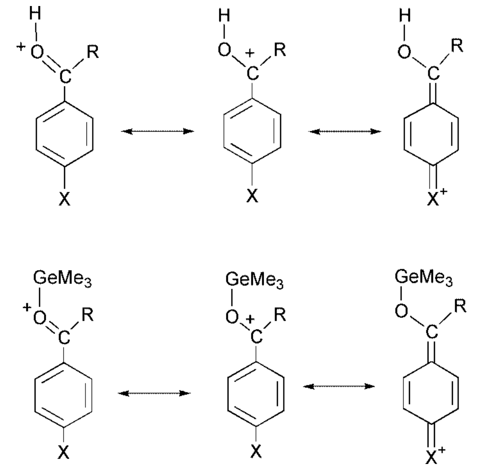


Fig. 4 The Y–T plot for ΔGB(Me$_3$Ge$^+$) of acetophenones. Closed circles, σ°; open circles, σ^+; squares, $\bar{\sigma}$ at $r^+ = 0.71$.

Table 3 The Y–T correlation results for gas-phase basicities of acetophenones

Lewis cation	$-\rho^c$	r^+	R^d
H^{+a}	8.83 (11.6)	0.82	0.999
Me$_3$Si^{+b}	8.09 (11.0)	0.75	0.998
Me$_3$Ge$^+$	7.13 (9.7)	0.71	0.996

[a] Ref. 12. [b] Ref. 7. [c] Values in parentheses are obtained by multiplying the ρ of log K/K_0 by the factor $2.303RT/1000$, *i.e.*, units of kcal mol^{-1} σ^{-1}. [d] Correlation coefficient.



Scheme 1

into the aryl π-system. Application of the Y–T equation [eqn. (2)] to the substituent effect provides a ρ value of −7.1 and an r^+ value of 0.71 with satisfactory precision ($R = 0.996$) as shown in Fig. 4.[13] An r^+ of 0.71 and a ρ of −7.1 indicate clearly the development of a large positive charge at the benzylic carbon in the Me$_3$Ge$^+$ adduct ion, suggesting that the binding interaction between Me$_3$Ge$^+$ and the oxygen atom of the carbonyl group has covalent character and that the positive charge formed at the carbon atom is delocalized into the *para* π-donor substituents through a resonance effect in a manner similar to that found for protonation as shown in Scheme 1. The ρ and r^+ values however are somewhat smaller than those obtained for protonation. Table 3 summarizes the results of Y–T analysis for the H$^+$, Me$_3$Si$^+$, and Me$_3$Ge$^+$ basicities of acetophenones. The ρ values decrease in the order H$^+$ > Me$_3$Si$^+$ > Me$_3$Ge$^+$. Since the ρ value can be considered a measure of the magnitude of the charge developed at the benzylic carbon, a decreasing ρ value along the series H$^+$ > Me$_3$Si$^+$ > Me$_3$Ge$^+$ indicates decreasing charge at the benzylic carbon along this series, *i.e.*, more positive charge is localized at the Lewis cation moiety of the adduct ions compared with that in the case of protonation. The smallest ρ value for the Me$_3$Ge$^+$ basicity may not be surprising. The Me$_3$Ge group is a huge and polarizable substituent, and hence will most readily accept some charge. The decrease in the ρ value is also consistent with the increase in electropositivity of the element of the Lewis cation. Similarly, the r^+ value decreases in the order H$^+$ > Me$_3$Si$^+$ > Me$_3$Ge$^+$. Since the r^+ value represents the degree of charge delocalization into the aromatic π-system, the variation of the r^+ value can be related to the electron supply from the substituent bonded to the benzylic carbon. In our previous studies on the proton basicities of benzoyl compounds,[12] it was found that the r^+ value for a system in which the conjugate acid ion is stabilized by an electron-releasing group attached to the central carbon atom tends to be smaller than that for a system destabilized by an electron-attracting group, *i.e.*, 0.23 for *N*,*N*-dimethylbenzamides[14] and 1.20 for α,α,α-trifluoroacetophenones.[15] Accordingly, the finding that the r^+ values for the acetophenone basicities towards Me$_3$Ge$^+$ and Me$_3$Si$^+$ are smaller than those towards H$^+$ suggests that the OGeMe$_3$ and OSiMe$_3$ groups in the limiting structure of the adduct ions can stabilize the positive charge at the benzylic carbon more effectively than the OH group can. A larger electron-releasing ability of the OGeMe$_3$ group is not unexpected, because Ge is less electronegative than H. The adduct ions of acetophenones with Me$_3$Ge$^+$ and with Me$_3$Si$^+$ can be regarded as a kind of benzylic carbocation. These results lead us to the conclusion that the binding interaction between Me$_3$Ge$^+$ and the oxygen atom of the carbonyl group must have a pronounced covalent character, *i.e.* to a degree similar to that for the proton. This is consistent with the conclusion that at low temperatures (298–373 K) the association adducts of Me$_3$C$^+$ with a neutral base exist in a covalently bound form characterized by larger $-\Delta H$ and $-\Delta S$ values, which shifts to an electrostatically bound isomer characterized by lower $-\Delta H$ and $-\Delta S$ values at higher temperatures.[16] However, the possibility of an electrostatically bound form in an adduct of Me$_3$Ge$^+$ with acetophenone at high temperatures cannot be excluded because the present experimental data have been obtained at low temperature (323 K). In conclusion, a covalently bound form of adduct ion seems to be common nature for C$^+$, Si$^+$, and Ge$^+$ at low temperature.

Table 4 Calculated relative basicities[a] of substituted acetophenones towards Me_3Ge^+, Me_3Si^+, and H^+ at B3LYP/6-31+G*//B3LYP/6-31+G*

	Me_3Ge^+		Me_3Si^+	H^+
Substituent	GB[b]	ΔGB	ΔGB[c]	ΔGB[c]
4-NH_2	48.96	8.81	10.47	14.76
4-OCH_3	45.87	5.72	6.86	9.31
4-CH_3	42.32	2.17	3.03	4.78
H	40.15	0.00	0.00	0.00
3-F	36.97	−3.19	−2.62	−4.55
3-Cl	36.48	−3.67	−3.21	−4.06
3-CF_3	33.51	−6.64	−5.81	−6.92
4-CF_3	32.96	−7.19	−6.40	−7.64

[a] All values in kcal mol^{-1}. [b] Free energy changes for isodesmic reaction (3). [c] Ref. 7.

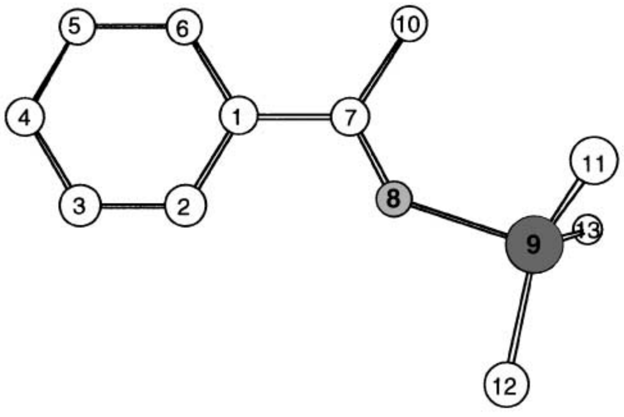


Fig. 5 Numbering of atoms for adduct ions of acetophenone with Me_3Ge^+. Hydrogen atoms are not shown.

Theoretical calculations

Although many structures may be drawn for the adduct ions of Me_3Ge^+ with acetophenone, the covalently bound adduct ion shown in Fig. 5 represents the global minimum on the potential energy surface calculated at the PM3 level. The DFT calculations were therefore carried out for the covalently bound Me_3Ge^+ adduct ions. Since the DFT calculations at the B3LYP/6-31+G*//B3LYP/6-31+G* level of theory were useful for predicting the relative Me_3Si^+ basicity for bases that are closely related in structure,[5] the same level of theory was used for the present calculations. Vibrational normal mode analyses were performed at the same level to ensure that each optimized structure was a true minimum on the potential energy surface and also to calculate the thermal correlation needed to obtain the Gibbs free energies. The GB values of acetophenones towards Me_3Ge^+ are free energy changes of an isodesmic reaction (3)

$$XC_6H_4COCH_3 + Me_3Ge^+ \rightleftharpoons XC_6H_4C(CH_3)OGeMe_3^+ \quad (3)$$

and are obtained using the calculated free energy of the respective species. The free energies of neutral acetophenones needed for this calculation were available from earlier work.[7] The calculated $GB(Me_3Ge^+)$ and relative values (ΔGB) are summarized in Table 4 along with the corresponding values for H^+ and Me_3Si^+.

$$GB = -\Delta G° = G°(XC_6H_4C(CH_3)OGeMe_3^+) - G°(XC_6H_4COCH_3) - G°(Me_3Ge^+) \quad (4)$$

Energies. There is a satisfactorily linear relationship between the calculated $\Delta GB(Me_3Ge^+)$ and the corresponding experimental values as given by eqn. (5). Although the theoretical

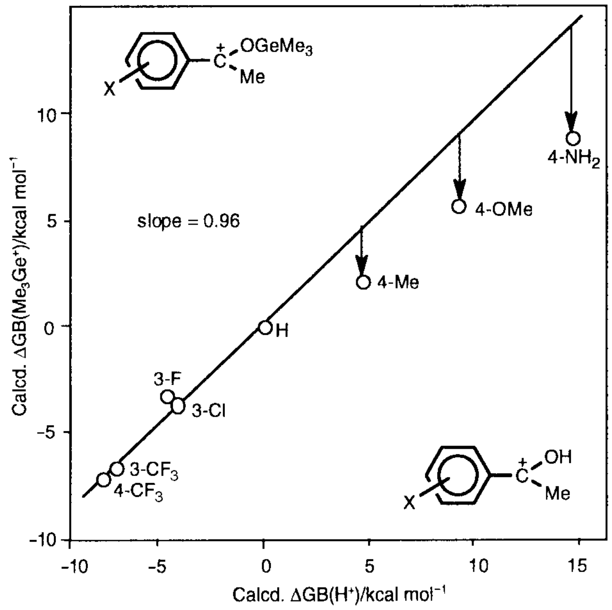


Fig. 6 Plot of calculated $\Delta GB(Me_3Ge^+)$ against calculated $\Delta GB(H^+)$.

$$\Delta GB(Me_3Ge^+)_{calcd} = 1.12\Delta GB(Me_3Ge^+)_{obsd} - 0.8\ (R = 0.987) \quad (5)$$

calculation of free energy changes at the present level of theory does not perfectly reproduce the experimental values, it is interesting to compare $\Delta GB(Me_3Ge^+)_{calcd}$ with $\Delta GB(H^+)_{calcd}$ calculated at the same level of theory because factors resulting in differences between the calculated and observed basicities may be cancelled out.

Fig. 6 shows a plot of the calculated basicities of acetophenones towards Me_3Ge^+ against the corresponding basicities towards H^+. It is found that non-conjugating substituents give a linear relationship with a slope of 0.96 and *para* strong π-donor substituents clearly show negative deviations from this line. This trend is in agreement with the experimental observation, although the magnitude of the deviations is somewhat larger than those in Fig. 2. These negative deviations for strong π-donors are again attributed to the reduced resonance effect in the Me_3Ge^+ adduct ions.

Geometries. The dihedral angles ∠C2C1C7O8 and ∠C2C1C7C10 of the Me_3Ge^+ adduct ions are 0° and 180°, respectively, being the same as those for neutral acetophenones (see the numbering of atoms in Fig. 5). The bond angles around C7, *i.e.*, ∠C1C7O8, ∠C1C7C10, and ∠O8C7C10, are also in agreement with those of the neutral species within ±2°. This suggests that the geometrical changes caused by the binding with Me_3Ge^+ are mostly due to electronic effects rather than to the steric effects of a large Me_3Ge^+ fragment. Tables 5 and 6 summarize the selected bond lengths along with the corresponding values for H^+ and Me_3Si^+ adduct ions. The C1–C7 and C2–C3 (C5–C6) bonds shorten and C7–O8 lengthens when the Me_3Ge^+ binds to the O atom of the carbonyl group. These changes in bond length are similar to those caused by binding with H^+ or Me_3Si^+, although the changes are somewhat smaller than those for protonation. Such variations in the bond lengths are in accord with the general prediction of resonance theory for the charge-delocalized benzylic cation, *i.e.*, the positive charge formed at the benzylic carbon atom can be delocalized into the benzene ring through resonance interaction (Scheme 2). The C1–C7 bond length is the most sensitive structural index for this resonance interaction and the C7–O8 bond length reflects the degree of electron supply by the OR group. The C1–C7 and C7–O8 bond lengths of substituted acetophenones and

Table 5 Selected bond lengths[a] of adduct ions of acetophenones optimized at the B3LYP/6-31+G* level

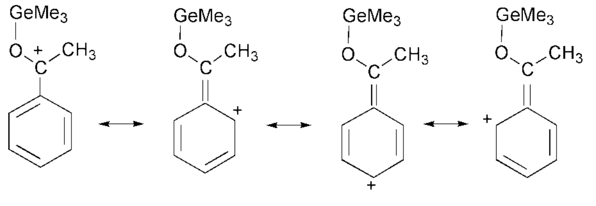
		Adduct ions with Lewis cation		
Bond	Neutral[b]	$H^{+\,b}$	$Me_3Si^{+\,b}$	Me_3Ge^+
C1–C2	1.405	1.424	1.417	1.415
C2–C3	1.397	1.386	1.389	1.390
C3–C4	1.397	1.403	1.401	1.401
C4–C5	1.404	1.405	1.402	1.402
C5–C6	1.393	1.384	1.387	1.388
C6–C1	1.406	1.424	1.418	1.418
C1–C7	1.500	1.423	1.445	1.451
C7–O8	1.224	1.312	1.279	1.271

[a] In Å. [b] Taken from ref. 7.

Table 6 C1–C7 and C7–O8 bond lengths[a] of substituted acetophenones and their adduct ions optimized at the B3LYP/6-31+G* level

		Adduct ions with Lewis cation		
Substituent	Neutral[b]	$H^{+\,b}$	$Me_3Si^{+\,b}$	Me_3Ge^+
C1–C7				
4-NH_2	1.486	1.400	1.418	1.423
4-OCH_3	1.492	1.407	1.426	1.433
4-CH_3	1.498	1.416	1.438	1.443
H	1.500	1.423	1.445	1.451
3-F	1.504	1.428	1.450	1.455
3-Cl	1.504	1.427	1.449	1.454
3-CF_3	1.504	1.428	1.451	1.456
4-CF_3	1.505	1.428	1.452	1.457
C7–O8				
4-NH_2	1.228	1.328	1.300	1.291
4-OCH_3	1.226	1.323	1.293	1.280
4-CH_3	1.225	1.316	1.283	1.275
H	1.224	1.312	1.279	1.271
3-F	1.223	1.305	1.276	1.268
3-Cl	1.223	1.306	1.277	1.268
3-CF_3	1.222	1.305	1.276	1.268
4-CF_3	1.223	1.308	1.275	1.267

[a] In Å. [b] Ref. 7.



Scheme 2

their adduct ions with Me_3Ge^+, Me_3Si^+, and H^+ are listed in Table 6. The C1–C7 bond shortens in the order neutral > Ge^+ > Si^+ > H^+ for all derivatives, and the C7–O8 bond in turn lengthens in this order. The shorter C1–C7 bond indicates the increase in resonance interaction between the benzylic carbon atom and the benzene ring in this order, and the longer C7–O8 bond indicates the decrease in π-interaction between the lone pair electrons at the oxygen atom and the charged carbon atom. The variation of ring substituents in the respective series also causes similar changes in the bond length, *e.g.* the C1–C7 bond shortens and the C7–O8 bond lengthens when the substituent on the benzene ring becomes a greater π-donor. The decreasing C1–C7 bond is again related to increasing π-delocalization of charge into the benzene ring in line with predictions by resonance theory, and this decreases the positive charge at the benzylic carbon atom, resulting in the increase of the C7–O8 bond length. Thus, the calculated geometrical features of the adduct ions are in complete agreement with the conclusions obtained from the variation in the r^+ value.

Conclusions

The substituent effects on the GB(Me_3Ge^+) of acetophenone are characterized by a ρ value of −9.7 and an r^+ value of 0.71. This result suggests that the binding interaction of Me_3Ge^+ with the O atom of the carbonyl group of acetophenones has a pronounced covalent character resulting in the development of a positive charge at the benzylic carbon atom, although the delocalization of the positive charge into the benzene ring is slightly smaller than that found for protonation. This feature of the adduct ion with Me_3Ge^+ resembles that for the Me_3Si^+ adduct ions and is consistent with the results obtained by theoretical calculations at the DFT B3LYP/6-31+G* level of theory. The adduct ions of acetophenones with Me_3Ge^+ and with Me_3Si^+ can be regarded as a kind of benzylic carbocation.

Experimental

ICR measurements

Equilibrium-constant measurements were performed on an Extrel FTMS 2001 (Fourier transform ion cyclotron resonance, FT-ICR) spectrometer equipped with a dual-cell system. Details of the experimental techniques used for measuring the equilibrium constants (K) for the Me_3Ge^+ transfer reaction (6),

$$B + B_oGeMe_3^+ \rightleftharpoons BGeMe_3^+ + B_o \qquad (6)$$

where B refers to a given base and B_o is a reference base, were similar to those used for the previously described proton-transfer measurements.[12] Only significant changes and/or additional procedures are given here. All measurements were performed at 50 °C at a constant magnetic field strength of 3.0 T. The pressures of the 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.[17] The overall pressures of the reagents were maintained at 1 to 3×10^{-4} Pa by controlled rates through leak valves (Anelva) from a parallel inlet manifold into the reaction cell in the vacuum chamber. Tetramethylgermane was introduced into an ionization cell at 5–10 × 10^{-4} Pa using a pulsed valve. Me_3Ge^+ generated by electron-impact ionization of tetramethylgermane was transferred to a reaction cell. After a reaction period of 1 to 3 s, depending upon the reactant, equilibrium was attained and the relative abundance of $BSiMe_3^+$ and $B_oSiMe_3^+$ was measured on the basis of the signal intensities of the ICR spectra. Each experiment was performed at several ratios of partial pressures and at different overall pressures. The arithmetic mean values of K from eqn. (7) were used to calculate $\Delta G°$ at 343 K [eqn. (8)] with an average uncertainty

$$K = [B_o/B][BGeMe_3^+/B_oGeMe_3^+] \qquad (7)$$

$$\Delta G° = -RT \ln K \qquad (8)$$

of ± 0.3 kcal mol^{-1} in most cases. More than two reference compounds were used to ensure the internal consistency of the data. The occurrence of the Me_3Ge^+-transfer reaction was examined by an ion-eject experiment using the SWIFT technique.[18]

Chemicals

Most of the compounds used in this study were commercial samples. Others were available from our previous studies.[12] The materials were purified by distillation or recrystallization, and were degassed prior to use by several freeze–pump–thaw cycles on the sample-inlet system of the ICR spectrometer. Tetramethylgermane was obtained from Tokyo Kasei Kogyo Co., Ltd. and used without further purification.

DFT calculations

DFT calculations were carried out using the Gaussian 98 program[19] suite. The geometries were fully optimized at the B3LYP/6-31+G* level of theory with normal convergence. The zero-point vibrational energies were calculated from the B3LYP/6-31+G* harmonic frequencies. The force-constant matrices obtained for the stationary points were confirmed to have the correct number of negative eigenvalues (zero for equilibrium structures). The zero-point energies used to obtain the Gibbs free energies were unscaled.

References

1 C. Maerker, J. Kapp and P. v. R. Schleyer, in *Organosilicon Chemistry II*, ed. N. Auner and J. Weis, VCH, Weinheim, 1996, p. 329; P. D. Lickiss, in *The Chemistry of Organic Silicon Compounds*, Vol. 2, ed. Z. Rappoport and Y. Apeloig, Wiley Interscience, Chichester, 1997, ch. 13.

2 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; C. A. Reed, *Acc. Chem. Res.*, 1998, **31**, 325; 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.

3 A. Sekiguchi, M. Tsukamoto and M. Ichinohe, *Science*, 1997, **275**, 60.

4 I. A. Blair and J. H. Bowie, *Aust. J. Chem.*, 1979, **32**, 1389; V. J. Trenery and G. Klass, *Org. Mass Spectrom.*, 1981, **16**, 344; J. A. Stone and D. E. Splinter, *Int. J. Mass Spectrom. Ion Processes*, 1984, **59**, 169; A. C. M. Wojtyniak and J. A. Stone, *Int. J. Mass Spectrom. Ion Processes*, 1986, **74**, 59; J. A. Stone and A. C. M. Wojtyniak, *Can. J. Chem.*, 1986, **64**, 575; J. A. Stone and W. J. Wytenberg, *Can. J. Chem.*, 1987, **65**, 2146; A. C. M. Wojtyniak, K. Li and J. A. Stone, *Can. J. Chem.*, 1987, **65**, 2849; D. Hajdasz and R. Squires, *J. Chem. Soc.*, *Chem. Commun.*, 1988, 1212; X. Li and J. A. Stone, *J. Am. Chem. Soc.*, 1989, **111**, 5586; X. Li and J. A. Stone, *Int. J. Mass Spectrom. Ion Processes*, 1990, **101**, 149; J. M. Stone and J. A. Stone, *Int. J. Mass Spectrom. Ion Processes*, 1991, **109**, 247.

5 V. C. Trenerry, G. Klass, J. H. Bowie and I. A. Blair, *J. Chem. Res.* (*S*), 1991, 386.

6 M. Mishima, C. H. Kang, M. Fujio and Y. Tsuno, *Chem. Lett.*, 1991, 493.

7 Mustanir, K. Shimada, F. Ohta and M. Mishima, *Bull. Chem. Soc. Jpn.,* 2000, **73,** 1845.

8 R. W. Taft, F. Anvia, J.-F. Gal, S. Walsh, M. Capon, M. C. Holmes, K. Hosn, G. Oloumi, R. Vasanwala and S. Yazdani, *Pure Appl. Chem.*, 1990, **62**, 17.

9 J.-F. Gal and P.-C. Maria, *Prog. Phys. Org. Chem.*, 1990, **18**, 159.

10 E. P. L. Hunter and S. G. Lias, *J. Phys. Chem. Ref. Data*, 1998, **27**, 413.

11 For a review, Y. Tsuno and M. Fujio, *Chem. Soc. Rev.*, 1996, **25**, 129.

12 M. Mishima, Mustanir, M. Fujio and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 2009.

13 The substituent constant values used in the present analysis were taken from ref. 12.

14 M. Mishima, M. Fujio, N. Shimizu and Y. Tsuno, *Tetrahedron Lett.*, 1986, **27**, 939.

15 M. Mishima, M. Fujio and Y. Tsuno, *Chem. Lett.*, 1990, 2281.

16 K. Norrman and T. B. McMahon, *J. Am. Chem. Soc.*, 1996, **118**, 2449.

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

18 A. G. Marshall, T.-C. L. Wang and T. L. Ricca, *J. Am. Chem. Soc.*, 1985, **107**, 7983; R. B. Cody, *Analysis*, 1990, **16**, 30; S. Guan and A. G. Marshall, *Int. J. Mass Spectrom. Ion Processes*, 1997, **157/158**, 5.

19 Gaussian 98, Revision A.5, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian Inc., Pittsburgh PA, 1998.