1118 Bull. Chem. Soc. Jpn. Vol. 79, No. 7, 1118–1125 (2006)

# Stability of Complexes of Phenylacetylides and Benzyl Alkoxides with Methanol in the Gas Phase. Acid–Base Correlation in the Ionic Hydrogen-Bond Strength

**Mustanir,**[1,†] **Mio Matsuoka,**[1] **Masaaki Mishima,***[1,2] **and Heinz Koch**[3]

[1]Department of Chemistry and Physics of Condensed Matter, Graduate School of Sciences, Kyushu University,
6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581

[2]Institute for Materials Chemistry and Engineering, Kyushu University,
6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581

[3]Department of Chemistry, Ithaca College, Ithaca, NY 14850, U. S. A.

Received January 10, 2006; E-mail: mishima@ms.ifoc.kyushu-u.ac.jp

The thermodynamic stabilities of methanol-bound phenylacetylides and benzyl alkoxides were determined using a FT-ICR mass spectrometer. The complexation energies between anions and methanol were evaluated from the thermochemical cycle. The complexation energy decreases linearly with increasing acidity of the conjugate acid of an anion, giving slopes of 0.54 and 0.61 for phenylacetylide– and benzyl alkoxide–methanol complexes, respectively. These results show that the linear relationship between the complexation energy and acid–base energetics appears to be a general property in the anion–neutral molecule complexes, but the magnitude of the slope of the linear relationships is not simply related to the structure of the hydrogen-bonded complexes.

Hydrogen bonds are one of the most important noncovalent interactions.[1] To predict the ability of hydrogen bonds to stabilize ions is especially important and essential in a wide variety of chemical phenomena such as the solvation of ions,[2] enzymatic catalysis in biological processes,[3–5] and molecular recognition.[6] The stability of ionic hydrogen-bonded complexes appears to be related to the acidity of the donor and the basicity of the acceptor. Indeed, linear relationships between the hydrogen-bonding energy and the difference in acidity and basicity of the neutral and ion have been frequently observed.[7–14] Such linear relationships are useful to predict the stabilities and structures of these complexes. However, these correlations are known only for a limited range of structural types, e.g., simple aliphatic alcohols, amines, carboxylic acids, etc. That is, most of the complexes that have been studied so far involve electronegative nitrogen and oxygen for both positive and negative ions in addition to structural similarity.[9,11] Recently, the generality of a linear relationship between hydrogen-bonding strength and acidity or basicity of their components has been questioned.[15,16] Brauman and Chabinyc reported that acetylides with basicities over 8 kcal mol$^{-1}$ have the same complexation energy with methanol. The complexation energy of phenylacetylide with aliphatic alcohols, which is regarded as a complimentary system, increases with increasing acidity of alcohols and gives a linear relationship between the complexation energy and the acidity of aliphatic alcohols with a slope of 0.5.[9] From these results they claimed that the existence of a linear relationship between acid–base energetic and complexation energy is a property of the specific system and not a general one. They stated further that these linear correlations cannot be used to infer structural information about the complexes.[16] However, the acetylene compounds studied were limited to only four compounds that are composed of phenylacetylides and aliphatic acetylenes, and there exists a large difference in structure. To examine whether linear relationships as a general property exist between the hydrogen-bond energies and the acidity of hydrogen-bond donors or the basicity of the hydrogen-bond acceptors, it is important to understand the nature of the ionic hydrogen bond. We, therefore, studied the gas-phase stability of ionic hydrogen-bonded complexes of methanol with *m*- and *p*-substituted phenylacetylides and benzyl alkoxides whose basicities can be varied widely by the ring-substituents. Since these complexes have the substituents remote from the binding site with methanol, the complexation energy of the anion with methanol and the acidity of the conjugate acid are expected to be influenced only by the polar effect of the substituent without any additional factors such as effects arising from the steric environment at the binding site.

## Results and Discussion

**Stability of Methanol-Bound Anion Complexes.** Anion–methanol complexes were prepared by an exchange reaction with a methanol–methoxide complex, which was synthesized by the Riveros reaction of methoxide with methyl formate (Scheme 1).[17] The equilibrium constants for the binding of methanol to phenylacetylides and benzyl alkoxides were measured relative to $[\mathrm{MeO{\cdots}HOMe}]^-$. Figure 1 shows the ladder of $\Delta G^\circ_{\mathrm{eq}}$ measured for respective equilibrium reactions (3),

---

[†] Present address: Department of Chemistry, Faculty of Science, Syiah Kuala University, Banda Aceh 23111, Indonesia

doi:10.1246/bcsj.79.1118

$$CH_3ONO + e^- \xrightarrow[\text{ionization}]{\text{electron}} CH_3O^- + NO \qquad (1)$$

$$CH_3O^- + HCO_2CH_3 \longrightarrow CH_3O^- \cdots HOCH_3 + CO \qquad (2)$$

$$CH_3O^- \cdots HOCH_3 + A\text{-}H \overset{\Delta G_{eq}}{\rightleftharpoons} A^- \cdots HOCH_3 + CH_3OH \qquad (3)$$

Scheme 1.

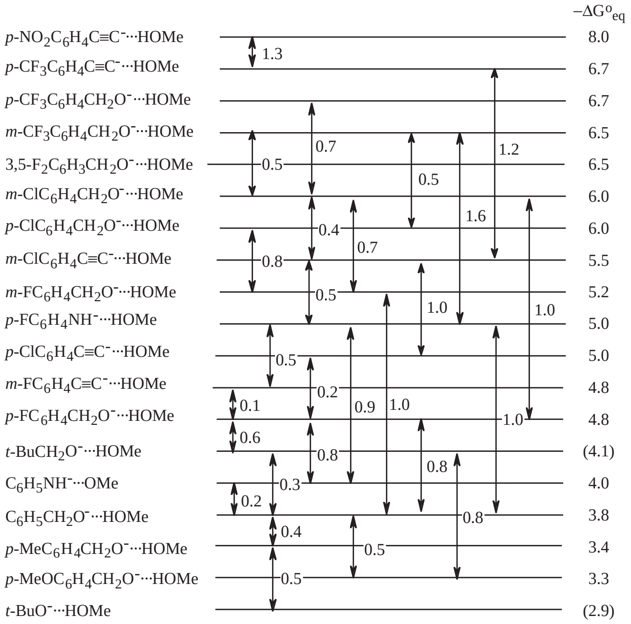

Fig. 1. Ladder of complexation equilibria of hydrogen-bonded complexes. All values are given in kcal mol$^{-1}$ (1 kcal = 4.184 kJ). $\Delta G^\circ_{eq}$ values are relative to [MeOH···OMe]$^-$. Values in parentheses are taken from Ref. 9.

where AH is the conjugate acid of an anion A of interest. All the values of $\Delta G^\circ_{eq}$ given in Fig. 1 were anchored by the values of [$t$-BuCH$_2$O···HOMe]$^-$ and [$t$-BuO···HOMe]$^-$, 2.9 and 4.1 kcal mol$^{-1}$, respectively, reported by Bartmess and co-workers.[9]

These $\Delta G^\circ_{eq}$ values and the gas-phase acidities of the corresponding conjugate acids are summarized in Table 1. The $\Delta G^\circ_{eq}$ value of $-2.8$ kcal mol$^{-1}$ (1 kcal = 4.184 kJ) is used for the methanol-transfer equilibrium between the phenylacetylide–methanol complex and methoxide–methanol one. Brauman and Chabinyc.[16] reported this value as $-1.9$ kcal mol$^{-1}$; however, the $\Delta G^\circ_{eq}$ values of $-1.80$ and $-2.74$ kcal mol$^{-1}$ reported for $p$-tolylacetylide–methanol and phenylacetylide–methanol complexes, respectively, and $\Delta G^\circ_{eq} = 1.1$ kcal mol$^{-1}$ for the equilibrium reaction between $p$-tolylacetylide–methanol and phenylacetylide–methanol complexes give a $\Delta G^\circ_{eq}$ value of $-2.8$ kcal mol$^{-1}$ for the phenylacetylide–methanol complex as an internally consistent value. This revised value also agrees with the value reported previously by Bartmess and co-workers.[9]

Table 1. Free Energies for the Equilibrium, Complexation Energies, and Gas-Phase Acidities, in kcal mol$^{-1}$

| R in R$^-$–HOMe | $-\Delta G^\circ_{eq}$ [a] | $-\Delta G^\circ_{0,1}$ [b] | $\Delta G^\circ_{acid}$ [c] |
|---|---|---|---|
| *Acetylides* | | | |
| $p$-MeC$_6$H$_4$C≡C | 1.8 | 10.2 | 363.2 |
| PhC≡C | 2.8[d] | 10.1 | 362.1 |
| $m$-FC$_6$H$_4$C≡C | 4.8 | 8.1 | 358.1 |
| $p$-ClC$_6$H$_4$C≡C | 5.0 | 7.5 | 357.3 |
| $m$-ClC$_6$H$_4$C≡C | 5.5 | 7.6 | 356.8 |
| $p$-CF$_3$C$_6$H$_4$C≡C | 6.7 | 5.6 | 353.7 |
| $p$-NO$_2$C$_6$H$_4$C≡C | 8.0 | 3.1 | 349.9 |
| HC≡C | −2.8[d] | 10.9 | 369.8 |
| $t$-BuC≡C | −5.1[d] | 11.5 | 371.4 |
| *Alkoxides* | | | |
| $p$-MeOC$_6$H$_4$CH$_2$O | 3.3 | 11.6 | 363.1 |
| $p$-MeC$_6$H$_4$CH$_2$O | 3.4 | 12.5 | 363.9 |
| C$_6$H$_5$CH$_2$O | 3.8 | 11.9 | 362.9 |
| $p$-FC$_6$H$_4$CH$_2$O | 4.8 | 9.4 | 359.4 |
| $m$-FC$_6$H$_4$CH$_2$O | 5.2 | 8.6 | 358.2 |
| $p$-ClC$_6$H$_4$CH$_2$O | 6.0 | 9.0 | 357.8 |
| $m$-ClC$_6$H$_4$CH$_2$O | 6.0 | 8.5 | 357.3 |
| 3,5-F$_2$C$_6$H$_4$CH$_2$O | 6.5 | 7.5 | 355.8 |
| $m$-CF$_3$C$_6$H$_4$CH$_2$O | 6.5 | 7.1 | 355.3 |
| $p$-CF$_3$C$_6$H$_4$CH$_2$O | 6.7 | 6.6 | 354.7 |
| MeO | 0.0 | 20.3 | 375.1 |
| EtO | 1.4[e] | 18.3[f] | 371.7 |
| $n$-PrO | 2.4[e] | 17.0[f] | 369.4 |
| $t$-BuO | 2.9[e] | 16.2[f] | 368.1 |

a) Free energy changes for the equilibrium reaction (3). b) Free energy changes for formation anion–methanol complex (7). c) Gas-phase acidities of the conjugate acids, taken from Refs. 18 and 19. d) Taken from Ref. 16, see the text. e) Taken from Ref. 9. f) Revised values in this study using $\Delta G^\circ_{acid}$ in Ref. 19.

$$AH + [MeO\cdots HOMe]^- = [A\cdots HOMe] + MeOH \qquad (4)$$

$$MeO^- + MeOH = [MeO\cdots HOMe]^- \qquad (5)$$

$$A^- + MeOH = AH + MeO^- \qquad (6)$$

$$A^- + MeOH = [A\cdots HOMe]^- \qquad (7)$$

Scheme 2.

Although the complexation energies for [A···HOMe]$^-$ cannot directly be measured due to the preferential proton-transfer reaction because phenylacetylenes and benzyl alcohols are stronger acids than methanol by 10 kcal mol$^{-1}$ or more, the complexation energies can be derived from the thermochemical cycle (Scheme 2). That is, the observed $\Delta G^\circ_{eq}$ were corrected for the difference in acidity between the entering and departing acids to give the relative hydrogen-bond energies, where the $\Delta G^\circ(5)$ value of $-20.3$ kcal mol$^{-1}$ was used for forming the [MeO$^-$···HOMe] complex.[10] The $\Delta G^\circ(6)$ values, acidity of AH relative to methanol, are available from our previous studies[18] and the literature.[19] Then, the complexation energies of [A···HOMe]$^-$ can be derived from this thermochemical cycle. The $\Delta G^\circ(7)$ values are denoted as $\Delta G^\circ_{0,1}$ in defining the thermochemistry of bonding the first neutral molecule to the bare ion. The obtained values of $\Delta G^\circ_{0,1}$ are also summarized in Table 1. Although the $\Delta S^\circ_{0,1}$ value is needed to derive $\Delta H^\circ_{0,1}$ from $\Delta G^\circ_{0,1}$, accurate estimation of the entropies of

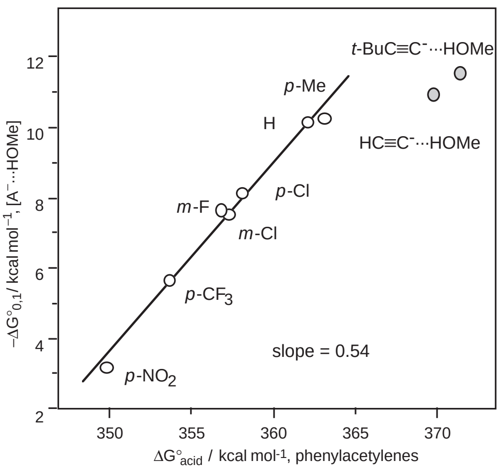

Fig. 2. Plot of complexation energy of *m*,*p*-substituted phenylacetylides with methanol against acidity of phenylacetylenes.[18]

ion-molecule complexes is difficult.[8b,9] It is generally considered that the variation of the entropies with structure is relatively small, particularly for structurally similar complexes.[9] Therefore, we use the values of $\Delta G^{\circ}{}_{0,1}$ for the present discussion on substituent effects on the hydrogen-bonding strength as the values equivalent to $\Delta H^{\circ}{}_{0,1}$.

**Phenylacetylide–Methanol Complexes.** The $\Delta G^{\circ}{}_{0,1}$ values for forming phenylacetylide–methanol complexes are plotted against the gas-phase acidities of the corresponding phenylacetylenes in Fig. 2, which cover a range of 10 kcal mol$^{-1}$ in the acidity scale.

The complexation energy increases linearly with decreasing acidities of neutrals (increasing basicities of phenylacetylides). The least-squares regression of the plot gives a slope of 0.54 with a correlation coefficient of 0.992.

$$-\Delta G^{\circ}{}_{0,1} = 0.54\Delta G^{\circ}{}_{\text{acid}} - 185.8. \quad (8)$$

It is apparent that the complexation energy of phenylacetylide with methanol varies with the acid strength of the corresponding neutrals. This result is in contrast to the conclusion obtained by Brauman and Chabinyc that all the acetylides have the same complexation energy with methanol regardless of the difference in acidity of acetylenes.[16] However, the use of the revised $\Delta G^{\circ}{}_{\text{eq}}$ value of $-2.8$ kcal mol$^{-1}$ for the phenylacetylide–methanol complex leads to the $\Delta G^{\circ}{}_{0,1}$ value of $-10.1$ kcal mol$^{-1}$ for the $\text{PhC}{\equiv}\text{C}^{-}\cdots\text{HOMe}$, which is smaller than that for $\text{HC}{\equiv}\text{C}^{-}\cdots\text{HOMe}$ complex. These values indicate that phenylacetylide, of which the conjugate acid is a stronger acid than acetylene, has a smaller complexation energy with methanol than acetylide, being consistent with our present result. Furthermore, it seems that there is an alternative linear relationship for acetylene and *t*-butylacetylene parallel to the line obtained for the phenylacetylide complex system. Such family-dependent linear correlations have frequently been observed for aliphatic alkoxide–alcohol and carboxylate–alcohol complexes.[11,12] If the correlation is limited to the four acetylene derivatives used for the analysis by Brauman and Chabinyc i.e., *p*-tolylacetylide, phenylacetylide, acetylide, and *t*-butylacetylide, a slope of 0.14 is obtained. This value is much smaller than the present value for the phenylacetylide system.

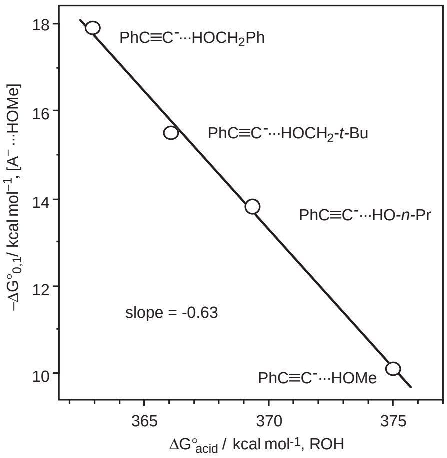

Fig. 3. Plot of complexation energy of phenylacetylide with aliphatic alcohols against acidity of alcohols, data taken from Ref. 19.

This suggests that it is important to study the complexation energies of compounds that have a similar framework to avoid an artificial conclusion. A plot of the $\Delta G^{\circ}{}_{0,1}$ for complementary phenylacetylide–aliphatic alcohol complexes ($\text{C}_6\text{H}_5\text{C}{\equiv}\text{CHOR}^{-}$) vs gas-phase acidities of the alcohol (ROH) was found to give a similar linear relationship with a slope of $-0.63$ based on the compiled values in the literature (Fig. 3).[19] These results indicate that the complexation energies for both systems vary apparently with the basicity of anions and acidity of aliphatic alcohols.

**Benzyl Alkoxide–Methanol Complexes.** The corresponding plot for the benzyl alkoxide–methanol complexes is shown in Fig. 4. One again finds that there is an excellent linear relationship with a slope of 0.61.

$$-\Delta G^{\circ}{}_{0,1} = 0.61\Delta G^{\circ}{}_{\text{acid}} - 209.6. \quad (R = 0.994) \quad (9)$$

The value of the slope for the benzyl alkoxide–methanol complex is nearly the same as that obtained for the aliphatic alkoxide–methanol complexes [$\text{RO}^{-}\cdots\text{HOMe}$], $-\Delta G^{\circ}{}_{0,1} = 0.56\Delta G^{\circ}{}_{\text{acid}} + 190.0$ ($R = 0.996$), but each system appears to conform to a different linear relationship. Bartmess and co-workers reported a value of 0.44 for a similar system.[9] More recently a value of 0.5 was obtained for the $[\text{ROHCF}_3]^{-}$ complex with a structure that is assumed to be [$\text{RO}^{-}\cdots\text{HCF}_3$], although this is not the alkoxide–alcohol complex system.[15] These results again indicate that in all the systems the complexation energies of alkoxides with alcohols change with the basicity of their anions (acidity of alcohols).

**Relationship between Acid–Base Properties and Hydrogen-Bond Strength.** Our experimental results show that the complexation energy for $\text{XC}_6\text{H}_4\text{C}{\equiv}\text{C}^{-}\cdots\text{HOMe}$ varies with the acidity of $\text{XC}_6\text{H}_4\text{C}{\equiv}\text{CH}$ in a similar manner to the complexation energy for benzyl alkoxide–alcohol complexes. The value of the slope for such a linear correlation has been widely suggested to indicate the degree of proton transfer in the complex, analogous to the interpretation of a Brønsted coefficient for kinetic data.[3,8a,8c,20,21] According to this hypothesis, the slopes of 0.5 to 0.6 observed for phenylacetylide–methanol and benzyl alkoxide–methanol complexes suggest that a proton is equally shared by the two bases involved in $[\text{PhC}{\equiv}\text{C}\cdots\text{H}\cdots\text{OCH}_3]^{-}$ and

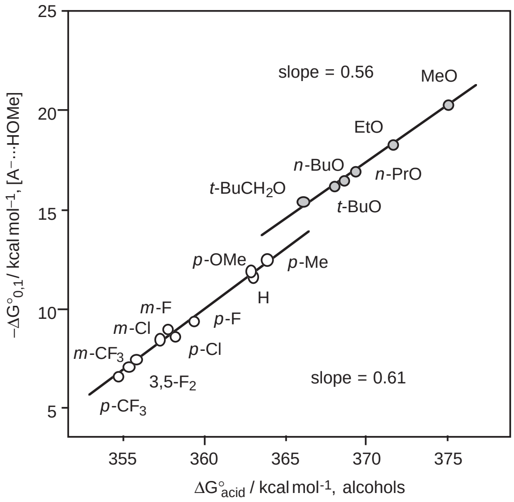

Fig. 4. Plot of complexation energy of substituted benzyl alkoxide with methanol against acidity of benzyl alcohols (open circles) and the corresponding plot for the aliphatic alkoxide–methanol complexes (closed circles).

$[PhCH_2O\cdots H\cdots OCH_3]^-$. This assumption may be consistent with the slope of −0.6 observed for the complementary system, $[PhC{\equiv}C\cdots H\cdots OR]^-$. Theoretical calculations for some systems support a low barrier surface with an equally shared proton.[22] However, fewer computational studies of asymmetric systems have been performed to examine whether this interpretation is general.[23] In the asymmetric systems the difference in acidity of the two acids would reflect in the structure of the hydrogen-bonded complexes. Indeed, the calculated structure of the $[PhC{\equiv}CHOCH_3]^-$ complex was found to be $[PhC{\equiv}C\cdots HOCH_3]^-$ and there is no stable structure of $[PhC{\equiv}CH\cdots OCH_3]^-$,[16] being consistent with the fact that phenylacetylene is a stronger acid than methanol by 13 kcal mol$^{-1}$. On the other hand, the structure of $MeO^-\cdots HCF_3$ is assumed to be more stable than $MeOH\cdots CF_3{}^-$, although $HCF_3$ is a stronger acid than MeOH.[15] These results suggest that the value of the slope for the correlation between the complexation energy and acidity is not related to the structure of the complex and is not an indication of the degree of proton transfer in the complex.

Theoretical calculations would be informative to further understand the relationship between the complexation energy and acid–base energetics. Gas-phase acidities of substituted phenylacetylenes and benzyl alcohols were calculated previously at the MP2/6-311++G**//B3LYP/6-311++G** level of theory.[18] The calculations of the methanol-bound complexes were, therefore, performed at the same level of theory. Stationary points were confirmed by vibrational frequency analyses. The calculated relative complexation energies and gas-phase acidities were converted into the absolute scale using the experimental $\Delta G^\circ_{0,1}$ and $\Delta G^\circ_{acid}$ values for the complexation energy of $[MeOHOMe]^-$ and acidity of methanol, respectively. These results are summarized in Table 2.

Optimized structures of the complexes showed that $[ArC{\equiv}C\cdots HOCH_3]^-$ and $[ArCH_2O\cdots HOCH_3]^-$ are the only stable structures on their potential surfaces. The structures of $[ArC{\equiv}CH\cdots OCH_3]^-$ and $[ArCH_2OH\cdots OCH_3]^-$ were not found as a stationary point. While the calculated gas-phase acidities were in good agreement with the experimental values as reported in the previous paper,[18] the calculated complexation energies do not agree with the experimental values. In Fig. 5 are plotted the calculated complexation energies against the calculated acidities. There are two linear relationships for the respective anion–methanol complex series. The values of the slopes are significantly smaller than the experimental values. The exis-

Table 2. DFT Calculation Results for Complexation Energies and Gas-Phase Acidities[a)]

| | $[XC_6H_4C{\equiv}CHOMe]^-$ | | $[XC_6H_4CH_2OHOMe]^-$ | |
|---|---|---|---|---|
| X | $-\Delta G^\circ_{0,1}$ | $\Delta G^\circ_{acid}$ | $-\Delta G^\circ_{0,1}$ | $\Delta G^\circ_{acid}$ |
| p-Me | 10.5 | 364.2 | 15.9 | 362.9 |
| m-Me | 10.7 | 363.8 | 16.5 | 362.7 |
| H | 10.4 | 363.3 | 15.9 | 362.0 |
| p-F | 10.4 | 361.0 | 15.3 | 359.1 |
| p-Cl | 10.3 | 359.8 | 15.1 | 357.5 |
| m-F | 10.0 | 359.7 | 15.1 | 358.1 |
| m-Cl | 9.9 | 358.9 | 15.7 | 357.7 |
| m-CF$_3$ | 9.6 | 356.0 | 15.2 | 354.8 |
| p-CF$_3$ | 9.9 | 355.5 | 14.7 | 354.2 |
| m-NO$_2$ | 9.2 | 353.6 | 14.7 | 351.9 |
| p-NO$_2$ | 8.8 | 351.9 | 14.0 | 351.6 |
| 3,5-F$_2$ | | | 14.7 | 354.5 |
| | $[AHOMe]^-$ | | | |
| MeO | 20.3[b)] | 375.1[b)] | | |
| EtO | 18.0 | 372.4 | | |
| i-PrO | 17.1 | 369.8 | | |
| HC≡C | 11.9 | 371.3 | | |

a) Energies calculated at the MP2//6-311++G**//B3LYP/6-311++G** level of theory with zero-point energy corrections scaled by 0.98 in kcal mol$^{-1}$. The absolute values are anchored by the experimental $\Delta G^\circ_{0,1}$ values for MeOHOMe and $\Delta G_{acid}$ for MeOH. b) Taken from Ref. 19.

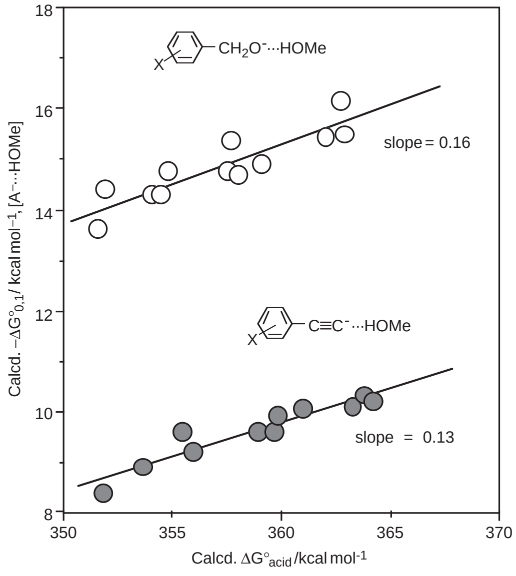

Fig. 5. Plots of calculated complexation energies vs calculated acidities for phenylacetylide (closed circles) and benzyl alkoxide (open circles) systems, MP2/6-311++G**//B3LYP/6-311++G**.

Table 3. Selected NPA Charges of Phenylacetylides and Benzyl Alkoxides

| | $XC_6H_4C{\equiv}C^-$ | | | $XC_6H_4CH_2O^-$ | | | |
|---|---|---|---|---|---|---|---|
| X | Ar[a)] | C(7) | C(8) | Ar[a)] | C(7) | O(8) | $CH_2O$[a)] |
| *p*-Me | −0.179 | −0.515 | −0.306 | −0.181 | 0.117 | −1.032 | −0.819 |
| *m*-Me | −0.186 | −0.517 | −0.297 | −0.183 | 0.116 | −1.030 | −0.817 |
| H | −0.185 | −0.517 | −0.298 | −0.183 | 0.116 | −1.031 | −0.817 |
| *p*-F | −0.182 | −0.523 | −0.295 | −0.188 | 0.119 | −1.030 | −0.812 |
| *p*-Cl | −0.196 | −0.527 | −0.277 | −0.191 | 0.115 | −1.027 | −0.809 |
| *m*-F | −0.202 | −0.528 | −0.270 | −0.193 | 0.114 | −1.027 | −0.807 |
| *m*-Cl | −0.204 | −0.529 | −0.267 | −0.197 | 0.116 | −1.026 | −0.803 |
| *m*-$CF_3$ | −0.204 | −0.533 | −0.263 | −0.197 | 0.114 | −1.026 | −0.803 |
| *p*-$CF_3$ | −0.221 | −0.535 | −0.244 | −0.197 | 0.109 | −1.023 | −0.803 |
| *m*-$NO_2$ | −0.212 | −0.539 | −0.249 | −0.202 | 0.111 | −1.026 | −0.798 |
| *p*-$NO_2$ | −0.266 | −0.538 | −0.196 | −0.206 | 0.101 | −1.017 | −0.794 |
| 3,5-$F_2$ | | | | −0.204 | 0.112 | −1.023 | −0.796 |

a) Summed NPA charges of the aromatic and $CH_2O$ moieties, respectively.

Table 4. Selected NPA Charges of Anion–Methanol Complexes

$[XC_6H_4C{\equiv}CHOMe]^-$

| X in $XC_6H_4$ | Ar[a)] | C(7) | C(8) | H(9) | OMe[a)] |
|---|---|---|---|---|---|
| *p*-Me | −0.147 | −0.424 | −0.331 | 0.522 | −0.621 |
| *m*-Me | −0.152 | −0.426 | −0.324 | 0.522 | −0.621 |
| H | −0.152 | −0.427 | −0.324 | 0.522 | −0.620 |
| *p*-F | −0.150 | −0.432 | −0.322 | 0.522 | −0.618 |
| *p*-Cl | −0.162 | −0.438 | −0.307 | 0.522 | −0.615 |
| *m*-F | −0.167 | −0.440 | −0.301 | 0.522 | −0.615 |
| *m*-Cl | −0.169 | −0.441 | −0.299 | 0.522 | −0.613 |
| *m*-$CF_3$ | −0.170 | −0.446 | −0.295 | 0.522 | −0.611 |
| *p*-$CF_3$ | −0.184 | −0.450 | −0.280 | 0.522 | −0.608 |
| *m*-$NO_2$ | −0.178 | −0.454 | −0.284 | 0.522 | −0.607 |
| *p*-$NO_2$ | −0.220 | −0.461 | −0.242 | 0.522 | −0.598 |

$[XC_6H_4CH_2OHOMe]^-$

| X in $XC_6H_4$ | Ar[a)] | C(7) | O(8) | $CH_2O$[a)] | H(9) | OMe[a)] |
|---|---|---|---|---|---|---|
| *p*-Me | −0.144 | 0.097 | −1.014 | −0.760 | 0.541 | −0.637 |
| *m*-Me | −0.146 | 0.094 | −1.013 | −0.757 | 0.541 | −0.638 |
| H | −0.145 | 0.095 | −1.014 | −0.759 | 0.541 | −0.636 |
| *p*-F | −0.151 | 0.099 | −1.016 | −0.758 | 0.540 | −0.632 |
| *p*-Cl | −0.155 | 0.096 | −1.015 | −0.757 | 0.540 | −0.629 |
| *m*-F | −0.156 | 0.094 | −1.014 | −0.754 | 0.540 | −0.630 |
| *m*-Cl | −0.161 | 0.095 | −1.013 | −0.751 | 0.540 | −0.628 |
| *m*-$CF_3$ | −0.161 | 0.095 | −1.015 | −0.753 | 0.540 | −0.626 |
| *p*-$CF_3$ | −0.160 | 0.090 | −1.014 | −0.755 | 0.540 | −0.625 |
| *m*-$NO_2$ | −0.168 | 0.095 | −1.018 | −0.753 | 0.540 | −0.619 |
| *p*-$NO_2$ | −0.170 | 0.085 | −1.013 | −0.753 | 0.539 | −0.617 |
| 3,5-$F_2$ | −0.166 | 0.092 | −1.013 | −0.749 | 0.540 | −0.624 |

a) Summed NPA charges of the aromatic, $CH_2O$, and OMe moieties, respectively.

tence of a linear relationship, however, suggests that the polar substituent provides a similar stabilizing effect to the anion and the hydrogen-bonded complex, being consistent with the present experimental results.

Although the calculations at the present level of theory are not sufficient to reproduce the complexation energies, the charge distribution and geometrical features of the complexes would be helpful to understand the substituent effect on the stability of the ionic hydrogen-bonded complex. In particular, it is interesting to examine the change in charge distribution in the complexes and anions with the substituent because the ionic hydrogen-bonding interaction would primarily be controlled by the electrostatic interaction. The selected charges obtained by natural population analysis are summarized in Tables 3 and 4. The natural charges (NPA) shown in Fig. 6 indicate that the hydrogen atom intervening between the PhC≡C and $OCH_3$ moieties in the $[PhC{\equiv}C–H–OMe]^-$ complex has +0.5 charge, and that 60% of the total negative charge exists in the PhC≡C

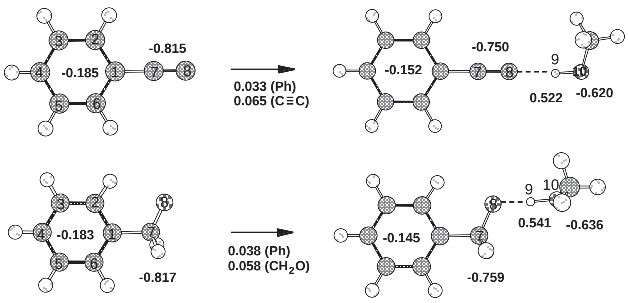

Fig. 6. Group natural charges of anions and complexes and the change of natural charge on formation of the methanol-bonded complex (MP2/6-311++G**//B3LYP/6-311++G**).

moiety, with the rest of the negative charge present in the $OCH_3$ moiety. A similar distribution of the charge is observed for the $[PhCH_2O–HOMe]^-$ complex. The change in charge distribution upon formation of the anion–methanol complex shows that the negative charge in the benzene ring decreases only 0.03 to 0.04. The negative charge at the C≡C and $CH_2O$ moieties decreases by 0.06. These changes in the charges indicate that formation of the anion–methanol complex causes a shift of the negative charge from an anion to methanol only by 10% in both systems.

The present experimental results indicate that the ability of substituted phenylacetylides to accept hydrogen bonds varies with their basicity in the same manner as that of benzyl alkoxides. Our recent analysis of the substituent effect on the gas-phase acidity of phenylacetylenes showed that there is no $\pi$-delocalization of the negative charge at the terminal carbon of the phenylacetylide into the benzene $\pi$-system as well as the benzyl alkoxide system, in which the aromatic $\pi$-system is insulated from the negative charge by the methylene group.[18] That is, phenylacetylide is a charge-localized anion as well as benzyl alkoxide.[24] Accordingly, the present results appear to indicate that there is no $\pi$-delocalization of the negative charge in the phenylacetylide–methanol complex. This is consistent with the concept that the dominant contribution to the hydrogen bond in the phenylacetylide is expected to be the interaction with the charge at the sp orbital on the terminal carbon. We therefore expect that the charge distribution at the terminal carbon or oxygen should be perturbed by the substituent in a similar manner as their anions do. However, the ab initio study showed that the charge at the oxygen for free alkoxide does not appear to change with basicity and that there is a charge shift from the carbon bonded to the oxygen into the substituents with little change at the oxygen.[25] Accordingly, it may be suitable to see the change in group charge distribution rather than the charge at the terminal atom bonded to methanol to investigate the relationship between the complexation energy and the charge distribution. The group charge of the aromatic moiety in the phenylacetylide–methanol complex is found to be linearly correlated with that in the phenylacetylide, $\Sigma q(\text{Ar, complex}) = 0.85\,\Sigma q(\text{Ar, anion}) + 4.062$ ($R = 0.998$). Similarly, the charge of the aromatic moiety in the $ArCH_2O–HOMe$ complex has the same response to the substituent as that of the anion, $\Sigma q(\text{Ar, complex}) = 1.06\,\Sigma q(\text{Ar, anion}) + 4.720$ ($R = 0.995$). These results indicate that the polar effect of the substituent transmits to the benzene ring in the anion–methanol complex in the same manner as that in the anion. Furthermore, it is found that the observed complexation energy is related to the group charge of the HOMe moiety in the complex which corresponds to the shifted charge from an anion to methanol upon formation of an anion–methanol complex (Fig. 7).

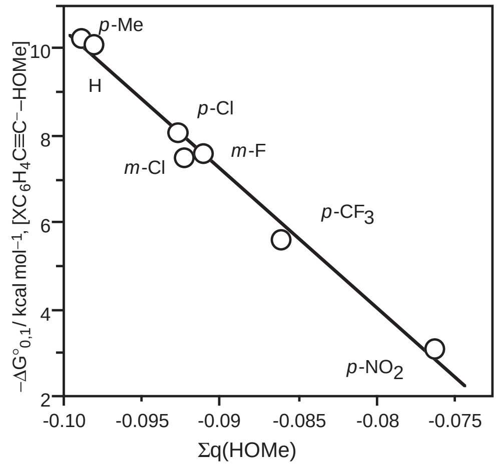

Fig. 7. Plot of observed $\Delta G°_{0,1}$ vs Σq(HOMe) for $ArC^-\equiv C\cdots HOMe$.

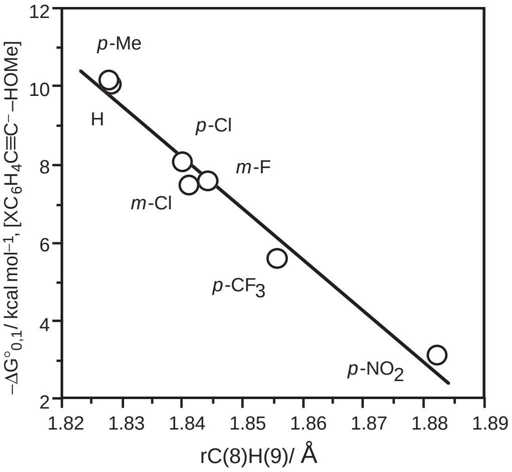

Fig. 8. Plot of observed $\Delta G°_{0,1}$ vs bond length of C(8)H(9) for $ArC\equiv C^-\cdots HOMe$.

$ArC\equiv C^-\cdots HOMe$;

$$\Delta G_{0,1} = 21.6 + 321\,\Sigma q[\text{HOMe}]. \quad (R = 0.992) \tag{10}$$

$ArCH_2O^-\cdots HOMe$;

$$\Delta G_{0,1} = 31.7 + 455\,\Sigma q[\text{HOMe}]. \quad (R = 0.974) \tag{11}$$

The larger charge transfer from the $ArCH_2O$ and ArC≡C anions to the HOMe moiety upon formation of the anion–methanol complex results in the stronger hydrogen bonding. Such charge distribution in the complex would also be reflected in the geometrical features. In fact, the experimental $\Delta G_{0,1}$ values are linearly correlated with the calculated bond lengths of C(8)H(9) in the phenylacetylide–methanol complex and O(8)-H(9) in the benzyl alkoxide–methanol complex as follows (Fig. 8).

$$\text{ArC}{\equiv}\text{C}^-\cdots\text{HOMe};$$
$$-\Delta G_{0,1} = -130r + 248. \quad (R = 0.987) \tag{12}$$
$$\text{ArCH}_2\text{O}^-\cdots\text{HOMe};$$
$$-\Delta G_{0,1} = -169r + 264. \quad (R = 0.949) \tag{13}$$

Complementarily to the bond length of C(8)H(9) in the phenylacetylide–methanol complex, the bond length of H(9)O(10) in the HOMe moiety of the complex changes with the substituent, though less sensitively. That is, the increase in hydrogen-bond strength causes the C(8)H(9) bond to shorten, the H(9)O(10) bond to lengthen, and the C(8)O(10) to shorten. Similarly, the corresponding bond lengths in the benzyl alkoxide–methanol complex change with the substituent. These results suggest that there are no essential differences in the charge distributions and in geometrical features between these two anion–methanol complexes. This is consistent with the experimental results that the substituent effect on the complexation energy is similar in both systems.

In connection with the smaller substituent effect for the complexation energy than that for the basicity of the anion, the slopes of 0.5 to 0.6 were observed for a relationship between complexation energy and acidity. It is noteworthy that the group charges of the C≡C and $CH_2O$ moieties in the complexes show a lower response to the substituent than that in the anion, while the group charge of the aromatic moiety has a similar response to the substituent in the anion as noted above.

$$\Sigma q[\text{C}{\equiv}\text{C, complex}]$$
$$= -0.279 + 0.58\,\Sigma q[\text{C}{\equiv}\text{C, anion}]. \quad (R = 0.997) \tag{14}$$
$$\Sigma q[\text{CH}_2\text{O, complex}]$$
$$= -0.476 + 0.35\,\Sigma q[\text{CH}_2\text{O, anion}]. \quad (R = 0.875) \tag{15}$$

This may be consistent with the result that the charge distribution at the C≡C and $CH_2O$ moieties decreases upon formation of the complex (see Fig. 6). The lower response would be related to a smaller substituent effect on the complexation energy than that for a proton transfer or basicity of an anion, because the complexation energy is the energy difference between an anion and the corresponding anion–methanol complex. We believe that this trend in the charge distribution is general for the anion–methanol complex, although the degree of the charge distribution may depend on the level of theory used for calculations. In conclusion, the substituent effect on the complexation energy for the phenylacetylide and benzyl alkoxide would be related to the charge distribution in the complexes. Further study is of course necessary to clarify the real meaning of the value of the slope for a linear relationship between the ionic hydrogen-bond strength and the acid–base energetics. At least, it may reveal that the value of the slope does not indicate the position of the hydrogen on the potential surface of the proton transfer as a Brønsted coefficient for kinetic data of acid-catalyzed reactions.

## Conclusion

We have presented a linear relationship between acid–base thermochemistry and hydrogen-bond strength for a substituted phenylacetylide–methanol complex as well as the complementary phenylacetylide–aliphatic alcohol complex and alkoxide–alcohol complex. Such relationships are held to be intrinsic in these systems as a general property. The magnitude of a slope for the acid–base correlation in the ionic hydrogen-bond strength is not related simply to the structure of hydrogen-bonded complexes, but also depends on the charge distribution in the hydrogen-bonded complex. This indicates that the value of the slope for such a linear correlation cannot be interpreted as an indication of the degree of proton transfer along with the potential surface.

## Experimental

**Chemicals.** Substituted phenylacetylenes and benzyl alcohols used in this study were available from our previous study[26] and from commercial sources. All chemicals were purified by gas chromatography and their purities were checked by $^1$H NMR and mass spectra in the positive mode on a FT-ICR spectrometer. Methyl nitrite, which was generated from 2-adamantyl nitrite and methanol, was used to give $CH_3O^-$ by an electron impact. The 2-adamantyl nitrite was prepared as follows.[27] In a 200 mL three-necked round-bottomed flask were placed 4.5 g (0.066 mol) of $NaNO_2$, 10 g (0.066 mol) of 2-adamantanol, and 50 mL of 10% aqueous THF. To this solution an equivalent of 2 M $H_2SO_4$ was added over 1.5 h at 0 °C. After stirring for 3 h, a small amount of ether was added. The organic layer was removed and was dried over anhydrous magnesium sulfate. The solvent was evaporated to give a light yellow powder (9.7 g yield, 81%). mp 40–45 °C. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 1.56–2.10 (m, 14H), 5.54 (s, 1H).

**Gas-Phase Equilibrium Measurement.** The gas-phase equilibrium measurements were performed on an Extrel FTMS 2001 Fourier transform mass spectrometer. Details of the spectrometer have been given previously.[28] The temperature in the ICR cell is estimated to be 330 K. The background pressures were below $1 \times 10^{-8}$ Torr (1 Torr = 133 Pa), and operating total pressures were in the range of $1 \times 10^{-6}$ to $3 \times 10^{-6}$ Torr. The pressures of the neutral reactants were measured by means of a Bayard–Alpert type ionization gauge applying the appropriate correction factors to correct the gauge readings for the different ionization cross sections of various compounds.[29]

The relative $\Delta G^\circ_{0,1}$ values were obtained by using methyl formate ester as a precursor to generate an original monosolvated ion, $[\text{MeOHOMe}]^-$.[9,16] The sequence of reactions was used to create the monosolvated species. The methoxide ion, generated by dissociative electron-impact in $CH_3ONO$, reacts with $HCO_2Me$ to generate $[\text{MeOHOMe}]^-$, Eq. 16. Equilibrium constants, $K_{\text{eq}}$, of alcohol-exchange for the reaction (19) were determined in the same way as those for acidity measurements. This equilibrium was confirmed by an ion-eject experiment using the SWIFT technique.[30] From $\Delta G^\circ_{\text{eq}}$ and $\Delta G^\circ_{\text{acid}}$, the $\Delta G^\circ_{0,1}$ value were calculated by using thermochemical cycles (Scheme 2).

$$\text{MeO}^- + \text{HCO}_2\text{Me} \rightarrow [\text{MeOHOMe}]^- + \text{CO}, \tag{16}$$
$$[\text{MeOHOMe}]^- + \text{HA}^1 \rightarrow [\text{MeOHA}^1]^- + \text{MeOH}, \tag{17}$$
$$[\text{MeOHOMe}]^- + \text{HA}^2 \rightarrow [\text{MeOHA}^2]^- + \text{MeOH}, \tag{18}$$
$$[\text{MeOHA}^1]^- + \text{HA}^2 \overset{K}{\rightleftharpoons} [\text{MeOHA}^2]^- + \text{HA}^1. \tag{19}$$

**Calculations.** DFT and MP2 calculations were carried out using the Gaussian 98 program.[31] The geometries were fully optimized at the B3LYP/6-311++G** level of theory. 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. A single point calculation was carried out at MP2/6-311++G** using geometries calculated at the B3LYP/

6-311++G** level. Zero-point energies were scaled by 0.981 for use in thermochemical calculations.[32]

The authors gratefully acknowledge support for this research by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology and by the Joint Project of Chemical Synthesis Core Research Institutes.

### Supporting Information

Selected bond lengths of optimized structures for anion–methanol complexes (Table S1). This material is available free of charge on the web at: http://www.csj.jp/journals/bcsj/.

### References

1 a) E. V. Anslyn, D. A. Dougherty, *Modern Physical Organic Chemistry*, Univ. Science Books, Sausalito, **2005**, p. 168. b) G. C. Pimentel, A. L. McClellan, in *The Hydrogen Bond*, ed. by W. H. Freeman & Co., San Francisco, **1960**.

2 W. Jorgensen, *Adv. Chem. Phys.* **1988**, *70*, 469.

3 C. L. Perrin, J. B. Nielson, *Annu. Rev. Phys. Chem.* **1997**, *48*, 511.

4 W. P. Jencks, *Catalysis in Chemistry and Enzymology*, Dower Pub., New York, **1979**.

5 C. Walsh, *Enzymatic Reaction Mechanisms*, W. H. Freeman & Co., San Francisco, **1979**.

6 J.-M. Lehn, in *Comprehensive Supramolecular Chemistry*, ed. by J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle, Pergamon, New York, **1996**.

7 a) M. Arhadi, R. Yamdagni, P. Kebarle, *J. Phys. Chem.* **1970**, *74*, 1475. b) R. Yamdagni, P. Kebarle, *J. Am. Chem. Soc.* **1971**, *93*, 7139. c) P. Kebarle, *Annu. Rev. Phys. Chem.* **1977**, *28*, 445. d) P. Kebarle, W. R. Davidson, M. French, J. B. Cumming, T. B. McMahon, *Faraday Discuss. Chem. Soc.* **1978**, *64*, 220. e) A. T. Vlades, J. S. Klassen, P. Kebarle, *J. Am. Chem. Soc.* **1995**, *117*, 10563.

8 a) J. W. Larson, T. B. McMahon, *J. Am. Chem. Soc.* **1983**, *105*, 2944. b) J. W. Larson, T. B. McMahon, *J. Am. Chem. Soc.* **1984**, *106*, 517. c) J. W. Larson, T. B. McMahon, *J. Am. Chem. Soc.* **1987**, *109*, 6230.

9 G. Caldwell, M. D. Rozeboom, J. P. Kiplinger, J. E. Bartmess, *J. Am. Chem. Soc.* **1984**, *106*, 4660.

10 a) M. Moet-Ner, *J. Am. Chem. Soc.* **1984**, *106*, 1257. b) M. Moet-Ner, L. W. Sieck, *J. Phys. Chem.* **1986**, *90*, 6687. c) M. Moet-Ner, L. W. Sieck, *J. Am. Chem. Soc.* **1986**, *108*, 7525.

11 M. M. Kreevoy, T. M. Liang, *J. Am. Chem. Soc.* **1980**, *102*, 3315.

12 M. Moet-Ner, *J. Am. Chem. Soc.* **1988**, *110*, 3858.

13 S.-O. Shan, S. Loh, D. Herschlag, *Science* **1996**, *272*, 97.

14 N. Stahl, W. P. Jencks, *J. Am. Chem. Soc.* **1985**, *108*, 4196.

15 M. L. Chabinyc, J. I. Brauman, *J. Am. Chem. Soc.* **1998**, *120*, 10863.

16 a) M. L. Chabinyc, J. I. Brauman, *J. Phys. Chem. A* **1999**, *103*, 9163. b) M. L. Chabinyc, J. I. Brauman, *J. Am. Chem. Soc.* **2000**, *122*, 5371.

17 a) L. K. Blair, P. C. Isolani, J. M. Riveros, *J. Am. Chem. Soc.* **1973**, *95*, 1057. b) R. T. McIver, J. A. Scott, J. M. Riveros, *J. Am. Chem. Soc.* **1973**, *95*, 2706.

18 M. Matsuoka, Mustanir, S. Than, M. Mishima, *Bull. Chem. Soc. Jpn.* **2005**, *78*, 147.

19 J. E. Bartmess, Negative Ion Energetics Data in *NIST Standard References Database Number 69*, ed. by P. J. Linstrom, W. G. Mallard, NIST, Gaithersburg, MD, **2003**, p. 20899 (http://webbook.nist.gov).

20 J. B. Cumming, M. A. French, P. Kebarle, *J. Am. Chem. Soc.* **1977**, *99*, 6999.

21 S. Scheiner, In *Hydrogen Bonding: A Theoretical Perspective*, Oxford University Press, Oxford, **1977**.

22 S. Wolfe, S. Hoz, C.-K. Kim, K. Yang, *J. Am. Chem. Soc.* **1990**, *112*, 4186.

23 H. Z. Cao, M. Allavena, O. Tapia, E. M. Evleth, *J. Phys. Chem.* **1985**, *89*, 1581.

24 A. J. Kresge, M. F. Powell, *J. Org. Chem.* **1986**, *51*, 822.

25 K. B. Wiberg, *J. Am. Chem. Soc.* **1990**, *112*, 3379.

26 M. Mishima, T. Ariga, T. Matsumoto, S. Kobayashi, H. Taniguchi, M. Fujio, Y. Tsuno, Z. Rappoport, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 445.

27 G. Caldwell, J. E. Bartmess, *Org. Mass Spectrom.* **1982**, *17*, 456.

28 M. Mishima, M. Matsuoka, Y.-X. Leib, Z. Rappoport, *J. Org. Chem.* **2004**, *69*, 5947.

29 a) J. E. Bartmess, R. M. Georgiadis, *Vacuum* **1983**, *33*, 149. b) K. J. Miller, *J. Am. Chem. Soc.* **1990**, *112*, 8533.

30 a) A. G. Marshall, T.-C. L. Wang, T. L. Ricca, *J. Am. Chem. Soc.* **1985**, *107*, 7983. b) S. Guan, A. G. Marshall, *Int. J. Mass Spectrom. Ion Processes* **1996**, *157/158*, 5.

31 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, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98, Revision A.5*, Gaussian, Inc., Pittsburgh PA, **1998**.

32 A. P. Scott, L. Radom, *J. Phys. Chem.* **1996**, *100*, 16502.