# Gas-phase Acidity of $CH_3X$ [X = $P(CH_3)_2$, $SCH_3$, F, Cl, Br, or I] Compounds

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Proton abstraction from $(CH_3)_3P$, $CH_3SCH_3$, $CH_3Cl$, $CH_3Br$, and $CH_3I$ in the gas phase has been investigated with the use of Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. The gas-phase acidities of the three former compounds are reported to be $\Delta G^\circ_{acid}[(CH_3)_3P]$ 1 606 ± 8 kJ mol$^{-1}$; $\Delta G^\circ_{acid}(CH_3SCH_3)$ 1 616 ± 8 kJ mol$^{-1}$; and $\Delta G^\circ_{acid}(CH_3Cl)$ 1 628 ± 12 kJ mol$^{-1}$. The competition between proton abstraction and $S_N2$ substitution in the reactions of different anions with $CH_3F$, $CH_3Cl$, $CH_3Br$, and $CH_3I$ has been determined. Based upon these kinetic experiments, it is concluded that the gas-phase acidity increases down the series $CH_3F$, $CH_3Cl$, $CH_3Br$, $CH_3I$. The reactions of $(CH_3)_2PCH_2^-$, $ClCH_2^-$, and $BrCH_2^-$ ions with various molecules are described.

Carbanions bearing an α-heteroatom are of theoretical interest and, as regards organometallic compounds, of synthetic importance.[1–14] It is widely recognized that second-row elements like sulphur stabilize an adjacent carbanionic centre more effectively than their first-row counterparts.[1,3–8,10,13–15] *Ab initio* calculations indicate that this is not caused by overlap between the carbanionic lone-pair and a low lying vacant 3*d* orbital on the sulphur atom.[4–7,10] Instead, the stabilization of the negative charge in the $RSCH_2^-$ (R = H, $CH_3$) ions has been explained by the polarizability of the sulphur atom and overlap between the carbanionic lone-pair and the $\sigma^*$ orbital of the S–R bond.[5–7,13,14]

Determination of substituent effects on carbanions in solution is complicated by counterion and solvents effects. Generation of free carbanions, however, can be achieved in the gas phase.[16,17] With respect to α-heteroatom carbanions, attention has been paid to the gas-phase acidity of $(CH_3)_3B$[18] and reactions of some silicon-stabilized carbanions with $N_2O$.[19] Recently, we reported on the gas-phase acidity of $CH_3SCH_3$ and the methyl group in $C_6H_5SCH_3$.[15] The present work has been undertaken in order to determine the gas-phase acidity of $(CH_3)_3P$ and $CH_3Cl$. Furthermore, the present article is concerned with the relative acidity of $CH_3F$, $CH_3Cl$, $CH_3Br$, and $CH_3I$. Previous related work has indicated that the relative acidity of the three former compounds was $CH_3F < CH_3Cl \simeq$ - $CH_3Br$.[20] The present results obtained with the use of Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry[21–23] show that the acidity increases down the series: $CH_3F$, $CH_3Cl$, $CH_3Br$, $CH_3I$.

## Results

$(CH_3)_3P$.—The $NH_2^-$, $C_2H_5NH^-$, $(CH_3)_2N^-$, $C_2H_5(CH_3)N^-$, and $CH_3SCH_2^-$ ions react exclusively and irreversibly with $(CH_3)_3P$ through proton abstraction. In the $HO^-$–$H_2O$–$(CH_3)_3P$ system equilibrium (1) in Table 1 is observed. Based upon the data in Table 1 and $\Delta G^\circ_{acid}(H_2O)$ 1 607 ± 4 kJ mol$^{-1}$ [24] the $\Delta G^\circ_{acid}$ value for $(CH_3)_3P$ becomes 1 606 ± 8 kJ mol$^{-1}$.

In the $DO^-$–$D_2O$–$(CH_3)_3P$ system up to eight hydrogen atoms in the $[M - H]^-$ ion from $(CH_3)_3P$ can be exchanged for deuterium atoms. The conjugate base of $(CH_3)_3P$, however, reacts with $D_2O$ to regenerate $DO^-$ ions and after a given time the relative abundances of the $^2H_0$—$^2H_8$ ions remain constant. The $[M - H]^-$ ion reacts with $N_2O$ and $CF_2O$ as shown in equations (i) and (ii).[25,26] These results indicate that proton abstraction from $(CH_3)_3P$ results in a primary carbanion as given in equilibrium (1) in Table 1 and equations (i) and (ii).

$$\underset{m/z\ 75}{(CH_3)_2PCH_2^-} + N_2O \longrightarrow \underset{m/z\ 101}{(CH_3)_2P\bar{C}{=}\overset{+}{N}{=}\bar{N}} + H_2O \qquad \text{(i)}$$

$$\underset{m/z\ 75}{(CH_3)_2PCH_2^-} + CF_2O \longrightarrow \underset{m/z\ 101}{(CH_3)_2P\bar{C}{=}C{=}O} + 2\,HF \qquad \text{(ii)}$$

$CH_3SCH_3$.—The gas-phase acidity of this compound was measured previously relative to that of $H_2O$ as being 1 615 ± 8 kJ mol$^{-1}$.[15] In order to measure the gas-phase acidity of $CH_3SCH_3$ relative to another reference acid, the gas-phase acidity of $C_2H_5NHCH_3$ was determined by studying equilibrium (2) in Table 1. Based upon the data in Table 1 and $\Delta G^\circ_{acid}[(CH_3)_2NH]$ 1 628 ± 8 kJ mol$^{-1}$ [17] the $\Delta G^\circ_{acid}$ value for $C_2H_5(CH_3)NH$ becomes 1 621 ± 8 kJ mol$^{-1}$. Relative to this acid $\Delta G^\circ_{acid}(CH_3SCH_3)$ is measured to be 1 617 ± 8 kJ mol$^{-1}$ (Table 1) in agreement with the value reported previously.[15]

$CH_3X$ (X = F, Cl, Br, I).—The initial product ion distribution in the reactions of various anions with the methyl halides are collected in Table 2. The values for the relative importance of proton transfer and $X^-$ ion formation have been determined by extrapolation to zero reaction time. This proved

**Table 1.** Equilibria studied in this work

| Equilibrium[a] | $K$ | $\Delta\Delta G^\circ_{acid} = RT\ln(K)$[b]/ kJ mol$^{-1}$ | No. of experiments |
|---|---|---|---|
| (1) $HO^- + (CH_3)_3P \rightleftharpoons H_2O + (CH_3)_2PCH_2^-$ | 1.5 ± 0.2 | −1.0 ± 0.3 | 8 |
| (2) $(CH_3)_2N^- + C_2H_5NHCH_3 \rightleftharpoons (CH_3)_2NH + C_2H_5\bar{N}CH_3$ | 20 ± 4 | −7 ± 1 | 3 |
| (3) $C_2H_5\bar{N}CH_3 + CH_3SCH_3 \rightleftharpoons C_2H_5NHCH_3 + CH_3SCH_2^-$ | 5.8 ± 0.8 | −4.4 ± 0.3 | 4 |

[a] The reactions were studied from either side of the equations and different partial pressures of the acids were used. [b] The temperature of the system is assumed to be 298 K.

**Table 2.** Relative importance of proton transfer and $X^-$ ion formation in the reactions of anions with $CH_3X$ ($X = F, Cl, Br, I$)

| System | $PA(A^-)$[a]/ kJ mol$^{-1}$ | Proton transfer[b] (%) | $X^-$[b] (%) | $\Delta H_r^\circ$ for $S_N2$[c] substitution/ kJ mol$^{-1}$ | $\Delta G_r^\circ$ for α-elimination[d]/ kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| $CH_3F$[e] | | | | | |
| $NH_2^-$ | 1 689 | 0 | 100 | −112 | 190 |
| $CH_3Cl$ | | | | | |
| $NH_2^-$ | | 68 | 32 | −281 | 20 |
| $C_2H_5NH^-$ | 1 671 | 52 | 48 | −288 | 39 |
| $(CH_3)_2N^-$ | 1 659 | 24 | 76 | −280 | |
| $C_2H_5(CH_3)N^-$ | 1 653[f] | 0 | 100 | −273 | |
| $HO^-$ | 1 635 | 0 | 100 | −210 | |
| $CH_3Br$ | | | | | |
| $NH_2^-$ | | 55 | 45 | −308 | −7 |
| $C_2H_5NH^-$ | | 44 | 56 | −315 | 11 |
| $(CH_3)_2N^-$ | | 39 | 61 | −307 | |
| $C_2H_5(CH_3)N^-$ | | 26 | 74 | −301 | |
| $HO^-$ | | 0 | 100 | −237 | |
| $CH_3I$ | | | | | |
| $NH_2^-$ | | 49 | 51 | −338 | −37 |
| $C_2H_5NH^-$ | | 52 | 48 | −345 | −18 |
| $(CH_3)_2N^-$ | | 50 | 50 | −338 | −13 |
| $HO^-$ | | 53 | 47 | −267 | 13 |
| $CH_3O^-$ | 1 587 | 0 | 100 | −242 | 62 |

[a] Values taken from ref. 17. [b] Initial product ion distributions (see text). The reproducibility is *ca.* 5%. The actual error is 10–15% of the percentages given. [c] Estimated using data from refs. 17 and 27. [d] Estimated using data from refs. 17 and 27 and from the footnote at the bottom of this page. [e] See also ref. 20. [f] This work.

**Table 3.** Relative abundance of the ${}^{35}Cl^-/{}^{37}Cl^-$ and the ${}^{79}Br^-/{}^{81}Br^-$ ions formed in the reactions of ${}^{-}CH_2{}^{35}Cl$ and ${}^{-}CH_2{}^{79}Br$, respectively, with the molecules present in the system

| System[a] | Product ions[b] | |
|---|---|---|
| ${}^{-}CH_2{}^{35}Cl$ | ${}^{35}Cl^-$ (%) | ${}^{37}Cl^-$ (%) |
| $CH_3Cl, NH_3$[c] | 85 | 15 |
| $CH_3Cl, NH_3, C_2H_5NH_2$[d] | 90 | 10 |
| $CH_3Cl, NH_3, (CH_3)_2NH$[d] | 93 | 7 |
| ${}^{-}CH_2{}^{79}Br$ | ${}^{79}Br^-$ (%) | ${}^{81}Br^-$ (%) |
| $CH_3Br, NH_3$[c] | 62 | 38 |
| $CH_3Br, NH_3, C_2H_5NH_2$[d] | 78 | 22 |
| $CH_3Br, NH_3, (CH_3)_2NH$[d] | 82 | 18 |

[a] See text. [b] Determined after most of the ${}^{-}CH_2X$ ions have reacted. [c] $p(CH_3X) \simeq 3 \times 10^{-5}$ Pa; $p(NH_3) \simeq 8 \times 10^{-5}$ Pa. [d] $p(CH_3X) \simeq 3 \times 10^{-5}$ Pa; $p(NH_3) \simeq 4 \times 10^{-5}$ Pa; $p(\text{amine}) \simeq 4 \times 10^{-5}$ Pa.

necessary because the ${}^{-}CH_2X$ ions react with the molecules present in the system. Isolation and subsequent reactions of the ${}^{-}CH_2{}^{35}Cl$ ion with the molecules present show that no ${}^{-}CH_2{}^{37}Cl$ ions are being formed. The ${}^{-}CH_2{}^{35}Cl$ ions, however, react to produce more abundant ${}^{35}Cl^-$ ions than expected from reaction (iv) (see Table 3). This can be explained by the

$$\begin{array}{ll} {}^{-}CH_2{}^{35}Cl + CH_3Cl & \left\{ \begin{array}{lll} \not\rightarrow CH_3{}^{35}Cl + {}^{-}CH_2Cl & & \text{(iii)} \\ & m/z\ 49, 51 & \\ \rightarrow C_2H_5{}^{35}Cl + Cl^- & & \text{(iv)} \\ & m/z\ 35, 37 & \end{array} \right. \\ m/z\ 49 & \end{array}$$

occurrence of reaction (v). When the difference in acidity between $CH_3Cl$ and the amine is decreased, then reaction (v) becomes more important relative to reaction (iv) (Table 3). Similar observations are made for the ${}^{-}CH_2{}^{79}Br$ ion (Table 3). These results parallel those previously obtained and discussed for the cases of 2-, 3-, and 4-fluoroanisole.[28] In the present cases no hydrogen–deuterium exchange is observed when ${}^{-}CH_2Cl$ or ${}^{-}CH_2Br$ reacts with $ND_3$ and only traces of exchange are observed with $C_2H_5ND_2$ or $(CH_3)_2ND$ (prepared *in situ* by reaction of $ND_3$ with the amines). This indicates that the competition between proton transfer and $S_N2$ substitution depends upon the internal energy of the $[R_2N^- \cdot CH_3X]^*$ complex.[29]

$$\begin{array}{l} {}^{-}CH_2{}^{35}Cl + R_2NH \rightleftharpoons [{}^{-}CH_2{}^{35}Cl \cdot R_2NH]^* \rightleftharpoons \\ m/z\ 49 \\ \qquad [CH_3{}^{35}Cl \cdot R_2N^-]^* \longrightarrow {}^{35}Cl^- + R_2NCH_3 \quad \text{(v)} \\ \qquad\qquad\qquad\qquad\quad m/z\ 35 \end{array}$$

In principle, the $X^-$ ions can be formed by either an $S_N2$ substitution or an α-elimination. The latter process can be excluded on the basis of energetic considerations for most of the systems studied (Table 2). The reaction, however, becomes energetically possible in the cases of strongly basic anions reacting with $CH_3Br$ and $CH_3I$. No conclusions regarding the

$$\begin{array}{llr} NH_2^- + CH_3I \longrightarrow NH_3 + CH_2 + \; I^- & & \text{(vi)} \\ m/z\ 16 \qquad\qquad\qquad\qquad\quad m/z\ 127 & & \\ \qquad \Delta H_r^\circ \; -1 \text{ kJ mol}^{-1}\,* & & \\ \qquad \Delta G_r^\circ \; -37 \text{ kJ mol}^{-1}\,* & & \end{array}$$

significance of α-elimination can be reached on the basis of the present results.

In the $(CH_3)_2N^-$–$(CH_3)_2NH$–$CH_3Cl$ system proton transfer is observed to occur in both directions of equation (vii). The

$$\begin{array}{lr} (CH_3)_2N^- + CH_3Cl \rightleftharpoons (CH_3)_2NH + {}^{-}CH_2Cl & \text{(vii)} \\ m/z\ 44 \qquad\qquad\qquad\qquad\qquad\quad m/z\ 49, 51 & \end{array}$$

occurrence of $S_N2$ substitution in competition with proton transfer (Table 2) hampers any quantitative studies of reaction (vii). The $\Delta G^\circ_{\text{acid}}(CH_3Cl)$, however, can be placed close to the value for $(CH_3)_2NH$.

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* Estimated using data from refs. 17 and 27. The entropies of the halide ions were estimated upon the assumption that $\Delta S_{\text{acid}}(HX) = 76.6$ J mol$^{-1}$ K$^{-1}$, which is the value for HCl (see ref. 30).

**Table 4.** Estimated thermochemical data for $CH_3Cl$, $CH_3SCH_3$, $(CH_3)_3P$, and $C_2H_5NHCH_3$

| System | $\Delta G^\circ_{acid}$ [a]/kJ mol$^{-1}$ | $\Delta S^\circ_{acid}$ [b]/J mol$^{-1}$ K$^{-1}$ | $\Delta H^\circ_{acid}$ = PA(anion)[c]/ kJ mol$^{-1}$ | Decrease in PA[d]/ kJ mol$^{-1}$ | $\Delta H^\circ_f$(anion)[e]/ kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| $CH_3Cl$[f] | 1 628 ± 12 | 97 ± 8 | 1 657 ± 12 | 86 ± 12 | 39 ± 12 |
| $CH_3SCH_3$[g] | 1 616 ± 8 | 101 ± 8 | 1 646 ± 8 | 97 ± 8 | 72 ± 8 |
| $(CH_3)_3P$[h] | 1 606 ± 8 | 102 ± 8 | 1 637 ± 8 | 106 ± 8 | 4 ± 8 |
| $C_2H_5NHCH_3$[i] | 1 621 ± 8 | 108 ± 8 | 1 653 ± 8 | — | 69 ± 8 |

[a] See text. [b] Estimated using the procedure outlined in refs. 17 and 30. [c] Temperature assumed to be 298 K. [d] Relative to $CH_3^-$ [PA($CH_3^-$) = 1 743 kJ mol$^{-1}$ [17]]. [e] Estimated using data in Table 1 and refs. 17 and 27. [f] $\Delta G^\circ_{acid}$ ($CH_3Cl$) assumed to be equal to $\Delta G^\circ_{acid}[(CH_3)_2NH]$ = 1 628 ± 8 kJ mol$^{-1}$ [see text and equation (vii)]. [g] Average of the values obtained relative to $H_2O$ (ref. 15) and $C_2H_5NHCH_3$ (see text). [h] Relative to $H_2O$. [i] Relative to $(CH_3)_2NH$.

The results in Table 2 are corroborated by the observation of reactions (viii) and (ix). These reactions are observed only to a minor extent, the main reaction being $S_N2$ substitution.

$$\underset{m/z\ 49,\ 51}{{}^-CH_2Cl} + CH_3Br \underset{\nleftarrow}{\rightarrow} CH_3Cl + \underset{m/z\ 93,\ 95}{{}^-CH_2Br} \quad \text{(viii)}$$

$$\underset{m/z\ 93,\ 95}{{}^-CH_2Br} + CH_3I \underset{\nleftarrow}{\rightarrow} CH_3Br + \underset{m/z\ 141}{{}^-CH_2I} \quad \text{(ix)}$$

## Discussion

The $\Delta G^\circ_{acid}$ values are collected in Table 4. The $\Delta H^\circ_{acid}$ values have been obtained using estimated $\Delta S^\circ_{acid}$ values (Table 4).[17,30] According to equation (x) the gas-phase acidity of an

$$\Delta H^\circ_{acid}(AH) = D(A\text{-}H) - EA(A^\bullet) + IP(H) \quad \text{(x)}$$

acid AH is determined by the strength of the A-H bond and the electron affinity, EA, of the A$^\bullet$ radical. In general, increase in gas-phase acidity can be caused by a decrease in *D*(A-H) and/or an increase in EA(A$^\bullet$).

For the methyl halides the C–H bond strength changes only slightly down the series.[31] The major factor responsible for the observed increase in acidity down the series [see Table 2 and equations (viii) and (ix)] is, therefore, the EA($^\bullet CH_2X$) or in other words the stability of these $^-CH_2X$ carbanions.

For $CH_3SCH_3$ and $(CH_3)_3P$ data on the *D*(C-H) are lacking. Recent solution-phase e.s.r. studies predict that the *D*($RSCH_2$-H) is *ca.* 8 kJ mol$^{-1}$ lower than the value for the equivalent bonds in ethers.[32] The increased acidity of $CH_3SCH_3$ and $(CH_3)_3P$ relative to that of their first-row counterparts* is mainly determined, therefore, by the increased stability of the carbanions.

The present results do not offer insight in the mechanism(s) by which the charge is stabilized within the carbanions. It should be mentioned that the relative acidities of the methyl halides follow the atomic polarizabilities of the halogen atoms: F(0.49 Å$^3$), Cl(2.31 Å$^3$), Br(3.55 Å$^3$), and I(5.87 Å$^3$).[33] If it is assumed that this relationship is simple, then it can be expected that the largest difference will be observed when going from $CH_3F$ to $CH_3Cl$ and from $CH_3Br$ to $CH_3I$.

The results in Table 2 do not allow for an accurate estimate of the $\Delta H^\circ_{acid}$ values for $CH_3F$, $CH_3Br$, and $CH_3I$. Rough estimates on the basis of the occurrence–non-occurrence of proton abstraction give as results: $\Delta H^\circ_{acid}(CH_3F)$ *ca.* 1 716; $\Delta H^\circ_{acid}(CH_3Br)$ *ca.* 1 644; and $\Delta H^\circ_{acid}(CH_3I)$ *ca.* 1 611 kJ mol$^{-1}$. These estimates together with the results in Table 4 seem to indicate that the largest increase in acidity occurs when going from $CH_3F$ to $CH_3Cl$ and from $CH_3Br$ to $CH_3I$.

Within the series $CH_3Cl$, $CH_3SCH_3$, $(CH_3)_3P$ it is not possible to ascertain whether the increase in acidity (Table 4) is caused by the heteroatoms themselves or by the increased number of methyl groups. It can be mentioned that a methyl group β to the acidic site can increase the acidity (*e.g.* $C_2H_5OH$ is *ca.* 13 kJ mol$^{-1}$ more acidic than $CH_3OH$ in the gas phase).[17]

The results in Table 4 can be contrasted with recent *ab initio* calculations on α-heteroatom carbanions.[14] These calculations predict the proton affinities of $^-CH_2Cl$, $^-CH_2SH$, and $^-CH_2PH_2$ to decrease relative to that for $CH_3^-$ by 59 to 105, 88, and 96 kJ mol$^{-1}$, respectively. The minor difference between these values and the experimental ones for $CH_3SCH_2^-$ and $(CH_3)_2PCH_2^-$ can be explained by the replacement of methyl groups for hydrogen atoms in the calculations.

## Experimental

Experiments were performed with a home-made FT-ICR mass spectrometer. The basic hardware,[34] software,[35] and the general operation procedure of the instrument[36,37] have been described previously. The total pressure was kept in the range 0.5—1.0 × $10^{-4}$ Pa. The ratio of the partial pressures of $CH_3X$, $NH_3$, and HA (conjugate acid of the anion of interest) was generally 0.5—1.0:1.0:0.5—1.0. The pressures were measured with an ionization gauge placed in a side arm of the main pumping line. The ionization gauge was calibrated against a MKS baratron (type 170 M, head type 94 AH-1) placed in the same side arm using $N_2$ as calibrant.

The primary reactant ions $NH_2^-$ and $HO^-$ were generated by dissociative resonance capture of electrons (electron energy in brackets) by $NH_3$ (5 eV) and $H_2O$ (6 eV, $HO^-$ is formed *via* $H^-$). The other reactant ions were formed by exothermic proton transfer to $NH_2^-$. Ion ejection and ion isolation were achieved as described previously.[35b,36–38] Initial product ion distributions and equilibrium constants were determined by monitoring the abundances of the ions present in the cell as a function of reaction time. In the case of $CH_3I$ the cross section for formation of $I^-$ by dissociative resonance capture of electrons is high and even minor amounts of electrons trapped in the cell will give rise to abundant $I^-$ ions. The relative abundance of the $^-CH_2I$ and $I^-$ ions formed in reaction of a particular reactant ion with $CH_3I$ was determined, therefore, as the difference between a spectrum without and a spectrum with ejection of the reactant ion. Correction for variation of the total ion current expressed as the sum of the ion abundances was achieved by normalizing this sum of abundances. The pressures used to calculate the equilibrium constants were measured with the ionization gauge. These pressures were used because oversaturation of the ionization gauge at pressures larger than

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* The gas-phase acidities of $CH_3OCH_3$ and $(CH_3)_3N$ are unknown but can be expected to be between the values for $CH_4$ ($\Delta H^\circ_{acid}$ 1 743 kJ mol$^{-1}$) and $NH_3$ ($\Delta H^\circ_{acid}$ 1 689 kJ mol$^{-1}$).[17]

$10^{-2}$ Pa led to a non-linear correlation with the baratron readings in most cases tried.

*Materials.*—The majority of the chemicals used was commercially available. The $(CH_3)_3P$ compound was prepared *in vacuo* by thermal decomposition of $(CH_3)_3P{\cdot}AgI$ (Janssen Chimica).

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