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Reactivity of molecules with nitrogen-containing functional groups toward H^+ and $SiMe_3^+$ ions

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The equilibrium constants of trimethylsilyl cation transfer reactions differ from those of proton transfer reactions by many orders of magnitude. The basicity of MeCN (**1**), $MeNO_2$ (**2**), and Et_2NH (**3**) in the gas phase decreases in the series **3** >> **1** > **2**, whereas the affinity of the same compounds for trimethylsilyl cation decreases in the series **1** >> **3** ≈ **2**. Semiempirical quantum-chemical MNDO calculations indicate that the formation of $MeCN{\cdot}SiMe_3^+$ ions is thermodynamically more favorable than that of $MeNH_2{\cdot}SiMe_3^+$ ions.

Key words: mass spectrometry, chemical ionization, trimethylsilyl cation, basicity, acetonitrile, nitromethane, diethylamine.

The interaction of trimethylsilyl ion with substrate molecules under conditions of chemical ionization (CI) using $SiMe_4$ as the reagent gas results in the formation of weakly excited adducts $[M+SiMe_3]^+$, and the intensities of their peaks can serve as a measure of basicity of the molecules.[1,2] Being a bulkier analog of a proton, the Me_3Si^+ ion is incapable of either migration between functional groups or chelation with them.[3] In this work, the reactivity of MeCN, $MeNO_2$, and Et_2NH molecules in the reactions of H^+ (and $SiMe_3^+$) ion transfer was studied.

Experimental

Mass spectra were recorded on a Kratos MS-30 mass spectrometer (energy of ionizing electrons 200 eV, temperature of the ion source 150 °C). The reagent gas pressure (0.2 Torr) was kept constant with the use of an external manometer mounted on the inlet system. Tetramethylsilane (Merck) of 99.7% purity was used in the experiments. Equimolar mixtures were introduced through a heated direct inlet system.

Results and Discussion

The CI mass spectra of acetonitrile (**1**), nitromethane (**2**), and diethylamine (**3**) with tetramethylsilane as the reagent gas contain only peaks of ion-adducts $[M+SiMe_3]^+$. If a mixture of compounds M^1 and M^2 is introduced simultaneously, then thermodynamically controlled reactions (1) and (2) occur in the ionization chamber of the mass spectrometer.

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$$M^1 + SiMe_3^+ \rightleftharpoons M^1 \cdot SiMe_3^+ \quad (1)$$

$$M^2 + SiMe_3^+ \rightleftharpoons M^2 \cdot SiMe_3^+ \quad (2)$$

For equimolar mixtures, the ratio of intensities of the ion peaks, $[M^1 \cdot SiMe_3^+]/[(M^2 \cdot SiMe_3^+]$, is the equilibrium constant (K_{eq}) of reaction (3).

$$M^1 \cdot SiMe_3^+ + M^2 \overset{K_{eq}}{\rightleftharpoons} M^2 \cdot SiMe_3^+ + M^1 \quad (3)$$

Thus, in contrast to the determination of basicity of molecules when attaining equilibrium in the proton transfer reaction:

$$M^1H^+ + M^2 \rightleftharpoons M^2H^+ + M^1, \quad (4)$$

high concentrations of compounds M^1 and M^2 are not required for the determination of K_{eq}, since each compound is in thermodynamical equilibrium with $SiMe_3^+$ ions.[3]

A comparison of the equilibrium constants of $SiMe_3^+$ ion transfer reactions (5—7) $K_{eq}(SiMe_3^+)$ and those of proton transfer reactions in analogous systems $K_{eq}(H^+)$[4] shows that for the compounds studied they differ in magnitude by many orders.

$$MeNO_2 \cdot SiMe_3^+ + MeCN \rightleftharpoons MeCN \cdot SiMe_3^+ + MeNO_2, \; K_{eq}(SiMe_3^+) = 2.1, \quad (5)$$

$$MeNO_2 \cdot H^+ + MeCN \rightleftharpoons MeCN \cdot H^+ + MeNO_2, \quad K_{eq}(H^+) = 10^{3.1}, \quad (5')$$

$$HNEt_2 \cdot SiMe_3^+ + MeCN \rightleftharpoons MeCN \cdot SiMe_3^+ + HNEt_2, \; K_{eq}(SiMe_3^+) = 2.0, \quad (6)$$

$$HNEt_2 \cdot H^+ + MeCN \rightleftharpoons MeCN \cdot H^+ + HNEt_2, \quad K_{eq}(H^+) = 10^{-22.7}, \quad (6')$$

$$MeNO_2 \cdot SiMe_3^+ + HNEt_2 \rightleftharpoons HNEt_2 \cdot SiMe_3^+ + MeNO_2, \; K_{eq}(SiMe_3^+) = 1.1, \quad (7)$$

$$MeNO_2 \cdot H^+ + HNEt_2 \rightleftharpoons HNEt_2 \cdot H^+ + MeNO_2, \quad K_{eq}(H^+) = 10^{25.5}. \quad (7')$$

This indicates a lower selectivity of $SiMe_3^+$ ions in reactions with functional groups.

Because of the inability of $SiMe_3^+$ ions to migrate[3] and their reduced selectivity toward functional groups, tetramethylsilane as the reagent gas has significant advantages over protic reagent gases in the study of compounds whose protonated MH^+ ions are unstable. Irrespective of the position of its primary location, the proton is capable of migrating toward a loosely bound functional group and eliminates with this group.[5,6]

Table 1. Energies of formation (ΔE_f) of complexes of compounds **1**—**3** with the $SiMe_3^+$ ion calculated by the MNDO method

Complex ions	ΔE_f /kcal mol^{-1}
$MeCN \cdot SiMe_3^+$	−45.8
$MeNO_2 \cdot SiMe_3^+$	−35.4
$MeNH_2 \cdot SiMe_3^+$	−40.0

The reactivities of H^+ and $SiMe_3^+$ ions toward the functional groups investigated differ considerably. Thus, if the basicities of the compounds studied decrease in the series **3** >> **1** > **2**, then their affinities toward the $SiMe_3^+$ ions change as follows: **1** >> **3** ≈ **2**.

The fact that $SiMe_3^+$ ions exhibit increased reactivity toward the nitrile group and decreased reactivity toward the amino group (compounds containing this group have the highest proton affinities) seems to be unexpected. However, semiempirical quantum-chemical MNDO (with full geometry optimization) calculations[7] of complexation energies of molecules containing the $[M+SiMe_3]^+$ ion show that the formation of $MeCN \cdot SiMe_3^+$ ions is thermodynamically more favorable than that of analogous $MeNH_2 \cdot SiMe_3^+$ ions, which is in accordance with the experiment and is likely due to steric effects (Table 1).

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