950 μmol) was added. The reaction mixture was stirred for 2 h (20 °C) and washed with H_2O (2 × 1 mL). The organic layer was separated, dried with $MgSO_4$, and concentrated. The residue was chromatographed (SiO_2, CH_2Cl_2—MeOH, 95 : 5). Oxidation by the complex with the L_1 ligand afforded compound **1** in a yield of 0.19 g (91%), R_f 0.28 ($CHCl_3$—MeOH, 9 : 1), m.p. 87—90 °C (*cf.* Ref. 1: m.p. 100—101 °C for the natural alkaloid). Oxidation by the complex with the L_2 ligand afforded compound **1** in a yield of 0.14 g (66%), m.p. 86—89 °C. Found (%): C, 52.87; H, 9.90; N, 11.01; S, 12.45. $C_{11}H_{24}N_2O_2S$. Calculated (%): C, 53.19; H, 9.74; N, 11.28; S, 12.91.

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Reactivity of functional groups toward H^+ and $SiMe_3^+$ ions

V. I. Kadentsev, A. A. Stomakhin, N. G. Kolotyrkina, and O. S. Chizhov*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 117913 Moscow, Russian Federation. Fax: +7 (095) 135 5328. E-mail: vkadents@cacr.ioc.ac.ru

No correlation was observed between the gas-phase basicities of various functional groups toward H^+ and $SiMe_3^+$ ions. Differences in the reactivity of functional groups studied toward $SiMe_3^+$ ions are smaller than those in the reactivity toward protons.

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

Previously,[1,2] it has been shown that the reactivity of $SiMe_3^+$ ions in reactions with mono-, di-, and trihaloalkanes is determined by the basicity of these molecules, *i.e.*, by their proton affinity.[3] However, studies of compounds with nitrogen-containing functional groups have shown[4] that the basicities of these compounds toward H^+ and $SiMe_3^+$ ions do not correlate (this has been confirmed by quantum-chemical calculations).

This work was carried out in a continuation of comparative studies of the reactivity of various functional groups toward H^+ and $SiMe_3^+$ ions.

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 of compounds under study were introduced through a heated direct inlet system.

Results and Discussion

The mass spectra of all compounds in the mixtures studied contain only the peaks of adduct-ions $[M \cdot SiMe_3]^+$. 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 the trimethylsilyl ion transfer reaction.[2]

$$[M^1 \cdot SiMe_3]^+ + M^2 \xrightleftharpoons{K_{eq}} [M^2 \cdot SiMe_3]^+ + M^1$$

We measured the rate constants for reactions (1)—(11).

The results obtained in this work and in our previous studies[2—4] made it possible to establish the following

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Reaction				$K_{eq}(SiMe_3)$
$CD_3COCD_3 + CH_2Cl_2 \cdot SiMe_3^+$	$\rightleftharpoons$	$CD_3COCD_3 \cdot SiMe_3^+ + CH_2Cl_2$	(1)	31.0
$CD_3COCD_3 + Et_2O \cdot SiMe_3^+$	$\rightleftharpoons$	$CD_3COCD_3 \cdot SiMe_3^+ + Et_2O$	(2)	2.3
$Et_2O + NHEt_2 \cdot SiMe_3^+$	$\rightleftharpoons$	$EtOEt \cdot SiMe_3^+ + NHEt_2$	(3)	1.3
$MeCN + {}^*C_4H_4S \cdot SiMe_3^+$	$\rightleftharpoons$	$MeCN \cdot SiMe_3^+ + C_4H_4S^*$	(4)	4.5
$MeCN + {}^{**}C_4H_4O \cdot SiMe_3^+$	$\rightleftharpoons$	$MeCN \cdot SiMe_3^+ + C_4H_4O^{**}$	(5)	4.56
$C_4H_4S + C_4H_4O \cdot SiMe_3^+$	$\rightleftharpoons$	$C_4H_4S \cdot SiMe_3^+ + C_4H_4O$	(6)	1.02
$MeNO_2 + C_4H_4O \cdot SiMe_3^+$	$\rightleftharpoons$	$MeNO_2 \cdot SiMe_3^+ + C_4H_4O$	(7)	2.9
$Et_2O + C_4H_4O \cdot SiMe_3^+$	$\rightleftharpoons$	$Et_2O \cdot SiMe_3^+ + C_4H_4O$	(8)	1.8
$NH(Et)_2 + C_4H_4O \cdot SiMe_3^+$	$\rightleftharpoons$	$NH(Et) \cdot SiMe_3^+ + C_4H_4O$	(9)	1.6
$CD_3COCD_3 + NHEt_2 \cdot SiMe_3^+$	$\rightleftharpoons$	$CD_3COCD_3 \cdot SiMe_3^+ + NHEt_2$	(10)	4.1
$C_4H_4O + CH_2Cl_2 \cdot SiMe_3^+$	$\rightleftharpoons$	$C_4H_4O \cdot SiMe_3^+ + CH_2Cl_2$	(11)	52.0

* C_4H_4S is thiophene.
** C_4H_4O is furan.

series (I) of relative affinities of the compounds listed above toward the $SiMe_3^+$ ion:

$$CD_3COCD_3 > MeCN > MeNO_2 > Et_2O > NHEt_2 > C_4H_4S \sim C_4H_4O >> CH_2I_2 > CH_2Br_2 > CH_2Cl_2 \quad (I)$$

The basicities of these compounds (series II) change as follows:

$$NHEt_2 > Et_2O > C_4H_4S \approx C_4H_4O > MeCOMe > MeCN > MeNO_2. \quad (II)$$

The equilibrium rate constants for reactions of compounds containing functional groups with N, O, or S atoms (reactions (2)—(10)) differ insignificantly (the K_{eq} values vary between 1.02 and 5.5). However, they appreciably increase on going to chloroalkanes (K_{eq} = 31.0 and 52.0 for reactions (1) and (11), respectively). Comparison of the affinity series of the molecules toward $SiMe_3^+$ and H^+ ions (I and II, respectively) indicates the absence of correlation between the corresponding values, which is due not only to steric factors.

For instance, no significant differences between steric effects of the reactions of Et_2O and $NHEt_2$ with $SiMe_3^+$ were observed; however, the basicities of these compounds toward $SiMe_3^+$ and H^+ cations are inverted.

Thus, the basicities of functional groups toward H^+ and $SiMe_3^+$ cations can likely correlate only within one homologous series.[1,2]

The observed changes in the reactivities of molecules on going from proton to trimethylsilyl cation is in agreement with the results of analogous studies of gas-phase reactions of organic compounds with metal cations.[5,6] Comparison of the $K_{eq}(SiMe_3)$ values obtained in this work with the corresponding $K_{eq}(H)$ values[1,3,7] shows that the reactivity of the molecules studied toward $SiMe_3^+$ varies in a much narrower range than the reactivity toward protons.

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