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Bifunctional sulfur-silicon podands as new nucleophilic ionophores in acyl transfer reactions. Influence of monovalent cations on the reaction kinetics

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Abstract: Two bifunctional sulfur-silicon nucleophilic ionophores 3-(trimethoxysilyl)-propanethiol (Nu1) and 3-(tri-2-methoxyethoxysilyl)-propanethiol (Nu2) were used as reagents in the acyl transfer reaction studied by kinetic methods. Nuclear magnetic resonance (NMR) and electro-spray ionisation mass spectrometry (ESI MS) were used for determination of the stoichiometry and stability constants of the complexes made by the podands and lithium or sodium ions in acetonitrile solution.

Keywords: Si-podand, 3-(trimethoxysililo)-propanethiol, 3-(tri-2-methoxyethoxysililo)-propanethiol, acyl transfer reaction, ionophores

1 Introduction

The di- and tripodands with boron, phosphorus, sulfur or silicon as a central atom (Fig. 1) were previously studied by spectroscopic methods [1–9]. Stable complexes form between the ions and neutral molecules. In the presence of protons, ions or small organic molecules, podands with $CH_3(OCH_2CH_2O)_n$ substituents can form host-guest complexes in molec-

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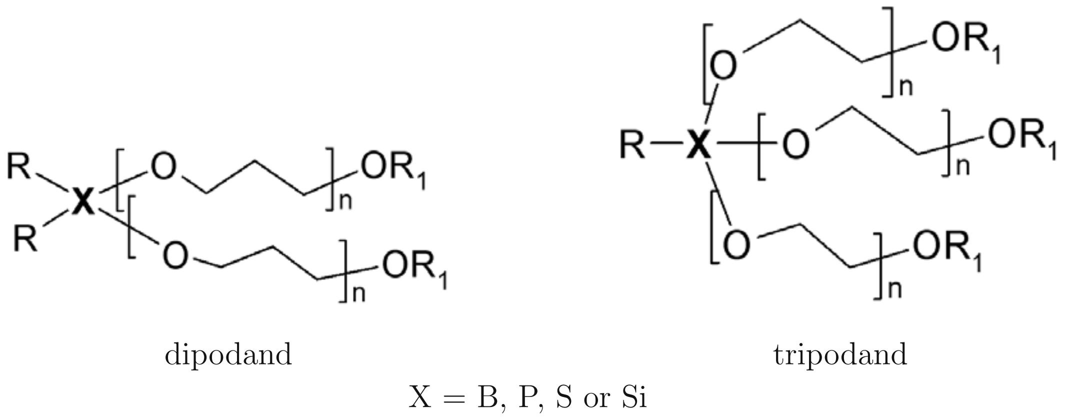
ular channels or cavities. Systems of this type were successfully applied in phase transfer catalysis or as specific solvents in organic reactions [5–9].



dipodand

tripodand

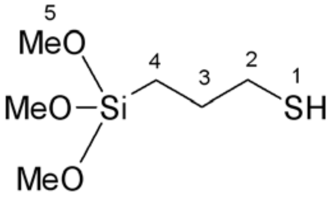
X = B, P, S or Si

Fig. 1 Di- and tri-podands with polyoxaalkyl substituents.

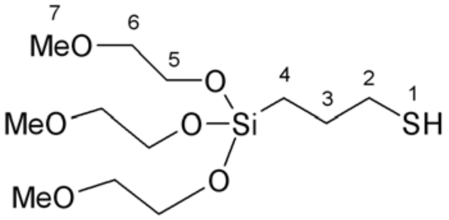
The bifunctional podands 3-(trimethoxysilyl)-propanethiol (Nu1) and 3-(tri-2-methoxyethoxysilyl)-propanethiol (Nu2) comprise a new class of reagents in organic chemistry characterized by two different functional groups. The -S-H functional group determines the nucleophilic character of the molecule and the $Si(OR)_3$ functional group permits complexation of ions and small neutral molecules as well as formation of dimers and polymers in the presence of water. The bifunctional character of the molecules studied promotes the formation of organic monolayer films on the surface of silver by self-assembly. Further modifications of such monolayers were produced through formation of complexes with different metals on the surfaces [10].

The effect of different factors determining the mechanism of the proton, electron, methyl group or acyl group transfer has been an important problem of contemporary chemistry and biochemistry [11–16]. For the last few years, this group has conducted research on the mechanism of the acyl transfer reaction [17–25]. By systematically investigating the formation of the guest-host type between multiple nucleophiles and different ions, a particularly strong effect of alkali metal ions on the kinetics of the acyl group transfer reaction was observed [26].

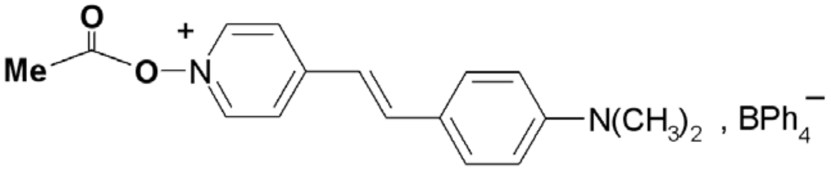
This manuscript presents the nucleophilic properties of the ionophores studied, determined by nuclear magnetic resonance (NMR) and electro-spray ionisation mass spectrometry (ESI MS) methods. Moreover, the kinetics and mechanisms of acyl transfer reactions to bifunctional podands from 4-(2-(4-dimethylaminophenyl)ethenyl)-1-acetoxypyridinium tetraphenylborate (El) in acetonitrile are discussed. In earlier publications from this research group, 4-(2-(4-dimethylaminophenyl)ethenyl)-1-acetoxypyridinium tetraphenylborate (El) was used as a model system in investigation of the acyl group transfer reaction [17–21]. The compounds studied in this research formed complexes with different ions as ionophores. The effect of alkaline ions on the kinetics of the reactions of interest was analysed and discussed. The structures of the two Nu1 and Nu2 nucleophilic ionophores and the El electrophilic molecule used in the kinetic studies are illustrated in Fig. 2.



Nu1



Nu2



El

Fig. 2 Compounds studied.

2 Experimental

2.1 Synthesis

The compound 3-(trimethoxysilyl)-propanethiol (Nu1) was used as commercial product (Aldrich) after vacuum distillation. 3-(Tri-2-methoxyethoxysilyl)-propanethiol (Nu2) was prepared in high yield (ca 90 %) by transesterification reaction of 3-(trimethoxysilyl)-propanethiol (Nu1) with ethylene glycol monomethylether with dibuthyltin oxide as a catalyst in benzene as solvent. The obtained product was purified by vacuum distillation. The electrophile: 4-(2-(4-dimethylaminophenyl)ethenyl)-1-acetoxypyridinium tetraphenylborate (E1) was synthesised by the procedure described earlier [24].

2.2 Preparation of complexes

Me_4NClO_4, $LiClO_4$ and $NaClO_4$ were used as commercial products. Lithium and sodium salts were used after drying for 6h at 100 °C. The solutions of the complexes for ESIMS studies were obtained by dissolving the respective salts and nucleophiles in acetonitrile as a solvent.

2.3 NMR measurements

^{1}H, ^{23}Na and ^{7}Li NMR spectra were recorded using a Varian Gemini 300 spectrometer, operating at 300.075, 79.371 and 116.619 MHz, respectively. Detailed acquisition parameters were reported elsewhere [19]. All spectra were measured in CD_3CN at 25 °C. The concentration of podands was prepared to be 0.1 M. Samples were prepared in an anhydrous atmosphere using carefully dried $LiClO_4$ and $NaClO_4$. The rate constants of complex formation between podands and ions (log K) were determined from the value of the chemical shift measured for a lithium or sodium ion [27, 28].

2.4 Mass spectrometry

The ESI MS spectra were recorded on a Waters/Micromass (Manchester, UK) ZQ mass spectrometer equipped with a Harvard Apparatus syringe pump. The measurements were conducted for the acetonitrile solutions of Nu1 or Nu2 (5×10^{-4} mol dm^{-3}) with Li$^+$ and Na$^+$ cations (10^{-3} mol dm^{-3}) added separately. The samples were infused into the ESI source using the Harvard pump at a flow rate 20 μdm^3 min^{-1}. The capillary, lens, and extractor ESI source potentials were set at 3 kV, 0.5 kV, and 4 V, respectively. In the ESI mass spectra, the cone voltage was 30 V. The source temperature was 120 °C and the desolvation temperature was 300 °C. Nitrogen was used as the nebulizing and desolvation gas at flow-rates of 80 and 300 dm^3 h^{-1}, respectively.

2.5 Kinetic studies

The acyl transfer reaction between Nu1 or Nu2 and El was studied by the kinetic method. The kinetic runs were conducted using a diode array spectrophotometer (Hewlett Packard) with the cell block thermostated to ±0.1 °C. The kinetic runs were completed under pseudo-first-order conditions with the nucleophile concentration in large excess relative to that of E1 ($1\text{x}10^{-4}$ M) and a constant concentration of MClO$_4$ (0.05 M), where M=Li, Na or Me$_4$N. The observed rate constants were calculated from the traces of product exhibiting absorbance at a wavelength of 520 nm as time was varied. The observed rate constant, k$_{obs,}$ depends on the initial nucleophile (Nu) concentration and is given by the equation:

$$k_{obs} = k[Nu] + k_{-} \tag{1}$$

The second order rate constants for the forward (k) reactions were calculated by linear least-squares fit of the variation of k$_{obs}$ with the concentration of the nucleophiles. The activation parameters were calculated by linear least-squares fit of ln k plotted against 1/T.

3 Results and discussion

The ^{1}H NMR chemical shifts for obtained compounds Nu1 and Nu2 are collected in Table 1.

ESI mass spectrometric results obtained for the complexes of Nu1 and Nu2 with various monovalent metal cations are shown in Table 2. The ESI MS spectra recorded in the negative ion mode (m/z = (Nu-H)$^-$) for the nucleophile solutions, Nu1 and Nu2, in acetonitrile exhibited signals that were assigned to the deprotonated molecules of podands. Addition of lithium or sodium ions into the nucleophile solutions caused the appearance of strong peaks observed in the positive ion mode, m/z = (Nu$_{1or2}$+M)$^+$, that

Table 1 ^{1}H NMR chemical shifts of silicon-sulfur podands.

Compounds	^{1}H NMR chemical shift [ppm]						
	H_1	H_2	H_3	H_4	H_5	H_6	H_7
Nu1	1.34 (t)	2.55 (q)	1.72 (m)	0.75 (m)	3.57 (s)	-	-
Nu2	1.32 (t)	2.51 (q)	1.73 (m)	0.75 (m)	3.70 (m)	3.52 (m)	3.25 (s)

(s) – singlet, (m) – multiplet, (t) – triplet, (q) – quintet

Table 2 ESI mass spectrometry data for complexes of nucleophiles with lithium or sodium cations.

Cation	m/z	
	Nu1	Nu2
–	195 $(Nu\text{-}H)^-$	327 $(Nu\text{-}H)^-$
Li+	203 $(NuLi)^+$ 399 $(Nu_2Li)^+$	335 $(NuLi)^+$
Na+	219 $(NuNa)^+$ 415 $(Nu_2Na)^+$	351 $(NuNa)^+$

were assigned to the relevant complexes formed. The Nu2 podand is an ionophore with the polyoxaalkyl substituents, $CH_3OCH_2CH_2O$, and was observed to form the 1:1 complex only with lithium and sodium ions in acetonitrile, while Nu1, having the substituent CH_3O, formed two types of complexes, 1:1 and 2:1, with monovalent ions.

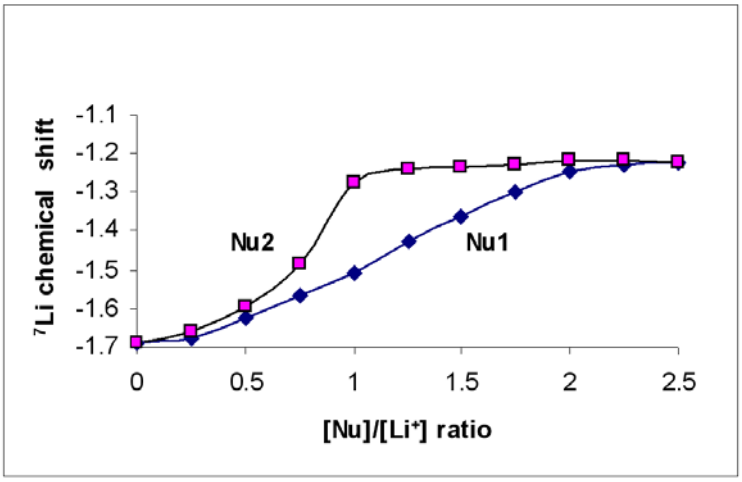


Fig. 3 Variation in the ^{7}Li chemical shifts as function of [Nu]/[Li$^+$] ratio for Nu1 orNu2.

The NMR titration of nucleophile solutions by solutions of $LiClO_4$ and $NaClO_4$ in acetonitrile was illustrated in Figs. 3 and 4, respectively. For the systems studied, the NMR titration curves were different for Nu1 than for Nu2. Nu2 formed only the 1:1 complex with lithium or sodium cations, while Nu1 formed the 1:1 and 2:1 complexes

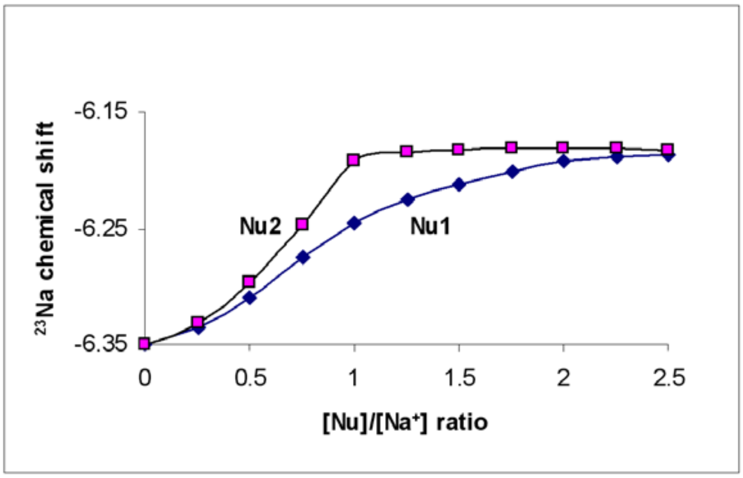


Fig. 4 Variation in the ^{23}Na chemical shifts as function of [Nu]/[Na$^+$] ratio for Nu1 or Nu2.

with both lithium and sodium cations. The chemical shift in the spectra of complexes with lithium and sodium ions, described as a function of the [Nu]/[M$^+$] ratio, was constant for Nu1 when the [Nu]/[M$^+$] ratio was equal to 2, while for Nu2 the chemical shift was constant when the [Nu]/[M$^+$] ratio was equal to 1. The logK values for 1:1 and 2:1 complexes were calculated from the NMR titration experiment (Table 3).

Table 3 Stability constants measured in acetonitrile for 1:1 (logK$_1$) and 1:2 (log K$_2$) complexes [Nu:M$^+$] between podands and lithium or sodium ions.

	[Nu1 : Li$^+$]	[Nu1 : Na$^+$]	[Nu2 : Li$^+$]	[Nu2 : Na$^+$]
logK$_1$	0.8 ± 0.4	0.6 ± 0.4	2.8 ± 0.2	2.3 ± 0.2
logK$_2$	0.8 ± 0.4	1.0 ± 0.4	–	–

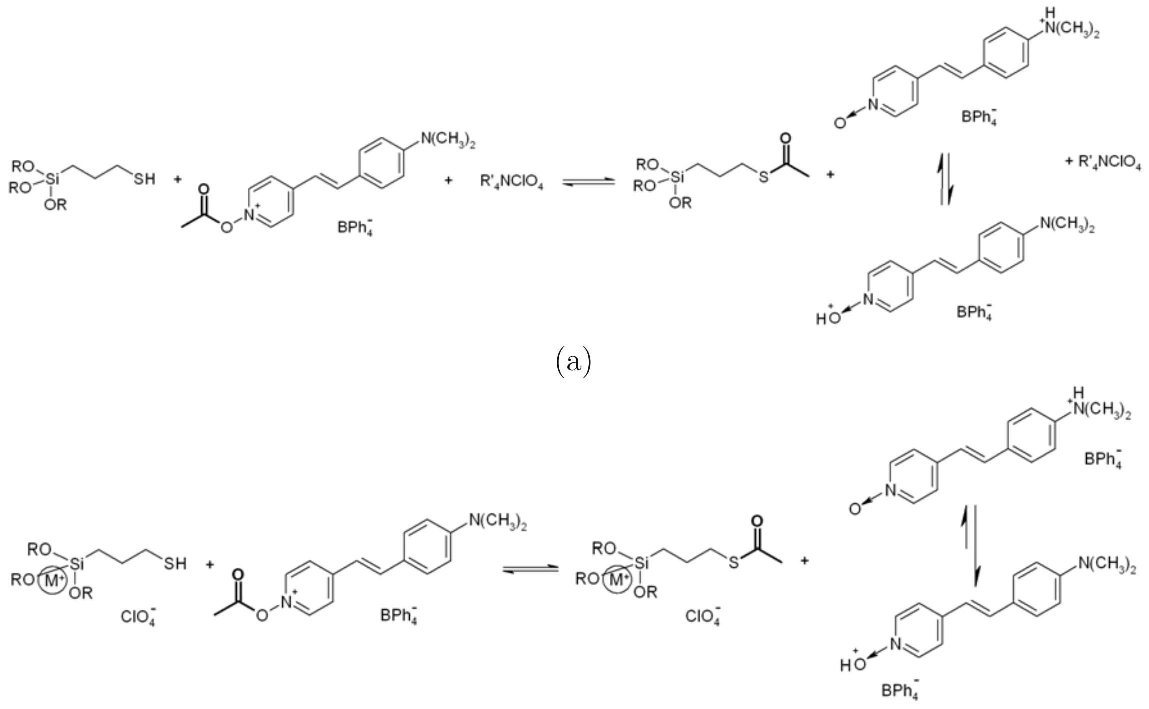
The proposed structures of the 1:1 and 2:1 complexes of $RSi(OCH_2CH_2O)_2CH_3$ with Li+ cations, where R=Et or Ph, were presented in a previous publication [29]. The influence of the R group on the structures of the complexes was not significant. The ionophoric properties were determined by the number of oxygen atoms in the polyoxaalkyl chains of the podand.

The Nu1 complexes with lithium and sodium ions of the 1:1 and 2:1 stoichiometry were characterised by similar stability constants that were low in magnitude. However, the complexes formed between Nu2 and the same ions were strong. The PM5 (parametric method 5) semiempirical calculations for Nu1 and Nu2 [16] revealed the occurrence of a hydrogen bond -S-H...O (ca. 2.60 Å) in the podand molecules studied. The stabilization of the Nu2 molecule by the two types of hydrogen bonds, -S-H...O-Me and -S-H.....O-Si-, was greater than that of Nu1, which implied that the sulfur atom of Nu1 was more nucleophilic than the sulfur atom of Nu2.

The compounds having thiol groups were acyl group acceptors. Thus, the bifunctional sulfur-silicon podands had the same properties. The -S-H groups of podands were acceptors that participated in the acylation reaction in the presence of donors containing the -COMe group.

The kinetics acyl transfer reactions between Nu1 or Nu2 and El were also studied by ultraviolet-visible (UV-VIS) spectroscopy. The influence of the ions on the kinetics of the transfer of the acyl group to the ionophores was studied. The spectrometric and NMR methods demonstrated that the use of the ionophores promoted the formation of stable complexes with metal ions. Two types of the reactions and possible reaction pathways were proposed (Fig. 5.). The rate constants (k) and activation parameters of the reaction conducted in acetonitrile between Nu1 + El (Table 4), and between Nu2 + El (Table 5) were measured.

The high value calculated for the equilibrium constant of the reaction, K = k/k$_-$, implied that the k- values (backward reactions) were relatively insignificant.



(a)

(b)

Fig. 5 Mechanism of acyl transfer processes conducted in acetonitrile when (a) the nucleophilic ionophores do not form complexes with the ion; and (b) the nucleophilic ionophores form complexes with the ion.

Two types of reactions were observed. The first type was the reaction that occurred when the salts did not form complexes with the ionophores, while the second type of reaction was observed when lithium or sodium perchlorate formed complexes with ionophoric substrates. The secondary rate constant of the acyl group transfer reaction conducted in the presence of Me_4NClO_4 at 25 °C was 2.7 times greater for Nu1 than for Nu2. Therefore, Nu1 was a stronger nucleophile than Nu2.

Table 4 Rate constants (k) and activation parameters (± standard deviation) of the reaction between Nu1 and El in acetonitrile.

Temp.	10^6 k $_{obs}$ (s^{-1})			10^4k (M^{-1} s^{-1})	ΔH≠ (kJ mol $^{-1}$)	ΔS≠ (J mol $^{-1}$ deg $^{-1}$)	ΔG≠ (kJ mol $^{-1}$)
[Nu1] M	0.01 M	0.02 M	0.04 M				
Nu1+El + Me_4NClO_4(0.05M)							
25 °C	600	1120	2070	487.9 ± 1.3	17.4 ± 1.2	-212 ± 4	80.5 ± 1.2
35 °C	986	1650	2940	650.4 ± 3.4			
45 °C	1462	2321	3900	809.4 ± 6.7			
Nu1+El + $LiClO_4$ (0.05M)							
25 °C	48	94	178	43.1 ± 6.1	19.8 ± 6.7	-224 ±22	86.5 ± 6.7
35 °C	80	141	279	66.7 ± 1.1			
45 °C	122	212	352	75.7 ± 5.2			
Nu1+El + $NaClO_4$ (0.05M)							
25 °C	63	116	220	52.3 ± 1.2	11.0 ± 1.7	-252 ± 5	86.1 ± 1.7
35 °C	90	154	284	64.7 ± 2.5			
45 °C	142	220	363	73.6 ± 6.9			

Table 5 Rate constants (k) and activation parameters (± standard deviation) of the reaction between Nu2 and El in acetonitrile.

Temp.	10^6 k $_{obs}$ (s^{-1})			10^4k (M^{-1} s^{-1})	ΔH≠ (kJ mol $^{-1}$)	ΔS≠ (J mol $^{-1}$ deg $^{-1}$)	ΔG≠ (kJ mol $^{-1}$)
[Nu1] M	0.01 M	0.02 M	0.04 M				
Nu1+El + Me_4NClO_4(0.05M)							
25 °C	230	406	770	180 ± 2	24.3 ± 3.4	-197 ± 11	83.1 ± 3.4
35 °C	520	755	1230	237 ± 3			
45 °C	712	1062	1775	355 ± 3			
Nu2 +El+ $LiClO_4$ (0.05M)							
25 °C	47	87	170	41.2 ± 0.5	26.7 ± 4.0	-201 ± 13	86.6 ± 4.0
35 °C	76	144	274	65.9 ± 0.1			
45 °C	130	220	390	86.4 ± 0.5			
Nu2+El+ $NaClO_4$ (0.05M)							
25 °C	25	68	149	41.2 ± 0.5	18.2 ± 1.0	-230 ± 3	86.7 ± 1.0
35 °C	71	130	223	52.6 ± 0.2			
45 °C	120	195	330	69.6 ± 0.1			

The value calculated for $\Delta G^{\neq}$ that described the combined changes in entropy and enthalpy in the acyl group transfer reaction to Nu2 was 2.6 kJ mol^{-1} greater than the value measured for the reaction with Nu1. The difference resulted from the difference in the potential barrier height between the two reactions ($\Delta H^{\neq}$=69 kJ mol^{-1}) and from a significant contribution of the entropy effect ($T\Delta S^{\neq}$=4.3 kJ mol^{-1}). The acyl group transfer reaction from the electrophile to podands in the presence of cations not undergoing complexation was controlled by entropy. In this reaction, a significant change in solvation was observed between the initial and the transient state. Additionally, $\Delta S^{\neq}$ was composed of large, negative values.

The secondary rate constants decreased significantly in the reaction between the salt containing ions capable of complex formation and the ionophores of podands. In the type of reaction in which the Nu-M^+ complex formed, the nucleophilic character of the sulfur atom, influencing the acyl group transfer constant, decreased. In the reactions in which the cations formed complexes, the value of $\Delta G^{\neq}$ was 6.0 times or 3.5 kJ mol-1 greather than for reactions in which the cations were not able to form complexes with the ionophores Nu1 or Nu2. For reactions conducted in the presence of lithium ions in both systems (with Nu1 and Nu2), the potential barrier increased by 2.4 kJ mol^{-1}. In the presence of sodium ions the, value $\Delta H^{\neq}$ decreased by 5.5 and 6.4 times, respectively, for Nu1 and Nu2.

The formation of complexes of the ionophore and lithium or sodium ions has no significant effect on the differences in solvation between the initial and transient state.. In the reactions in which complexes formed, the transient state was better solvated than in the reactions conducted in the presence of the ammonium salt.

The mechanism of the acyl group transfer was coupled with the proton transfer from S-H onto the basic oxygen atom, O←N-, and partly to the other basic centre of the molecule, the NMe_2 group. The formation of complexes between the ionophore and the ions present in the solution significantly affected the kinetics of the acyl group transfer reaction and thus can provide an effective method for controlling the reaction kinetics.

4 Conclusion

Investigation of reactions with participation of nucleophilic ionophores permits explanation of the effect of complexation processes on the direction of the reaction. The kinetics of the acyl transfer reaction was determined by the metal cations that did not take part in the process through a metal, cation-assisted, mechanism. The complex formation was related to changes in the electron density and charge distribution.

Complex formation can be an effective method for controlling the course of chemical reactions. Control of chemical reactions by the conscientious formation of complexes is a less complicated approach than proposed previously as it does not involve the need to change the solvent or introduce new substituents.

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