Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Eitner, Krystian , Bartl, Franz , Brzezinski, BogumiŁ and Schroeder, Grzegorz(2001) 'Kinetics of the Protonation of Macrocyclic Amines in the Presence of Monovalent Cations in Aqueous Solution', Supramolecular Chemistry, 13: 5, 627 — 635

To link to this Article: DOI: 10.1080/10610270108039796

URL: http://dx.doi.org/10.1080/10610270108039796

SUPRAMOLECULAR CHEMISTRY, Vol. 13, pp. 627-635
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Kinetics of the Protonation of Macrocyclic Amines in the Presence of Monovalent Cations in Aqueous Solution

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(Received 13 February 2001)

For macrocyclic bases such as: 1-aza-15-crown-5 (N15C5),1,4,10-trioxa-7,13-diazacyclopentadecan (21), 1,7,10,16-tetraoxa-4,13-diazacyclooctadecan (22) and 1, 4, 7, 13, 16-pentaoxa-10, 19-diazacycloheneicosane (23), the kinetics of deprotonation and protonation reactions in the presence of monovalent cations was studied using the temperature jump technique. For the sake of comparison, the measurements were also performed for 1,4-diazabicyclo[2,2,2]octane (DABCO) base, which does not form complexes with monovalent cations. The monovalent cations affect the temperature dependence of the kinetic parameters of deprotonation. They also affect the activation parameters, which is shown by a distribution of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values, but do not influence the value of $\Delta G^{\neq}$.

Keywords: Macrocyclic bases; Kinetic parameters; Reaction of deprotonation; pK$_a$ values; Temperature jump technique

1. INTRODUCTION

The formation of complexes between the crown ethers or cryptands (macrocyclic and macrobicyclic ligands) and protons or the monovalent cations is discussed in detail in Ref. [1]. In our previous papers the behaviour of protonated and crown ethers and cryptands complexed by protons and metal cations was studied by spectroscopic methods [2-4]. In these papers we have demonstrated that proton and metal ion fluctuate in the circular multiminima cation potential, whereas the size of the cation and the size of the crown influence the properties of these complexes. If one or more N-atoms are present in the crown, the proton is always localised at one N-atom and the system no longer shows proton polarizability. The monovalent cations, however, are not localised at N-atom and show the so-called Zundel's polarizability [5-8].

The obtained pK$_a$ values of protonated and diprotonated cryptands (Scheme 1) indicate that the protonation favours the endo conformations of these compounds. NMR [9, 10] and

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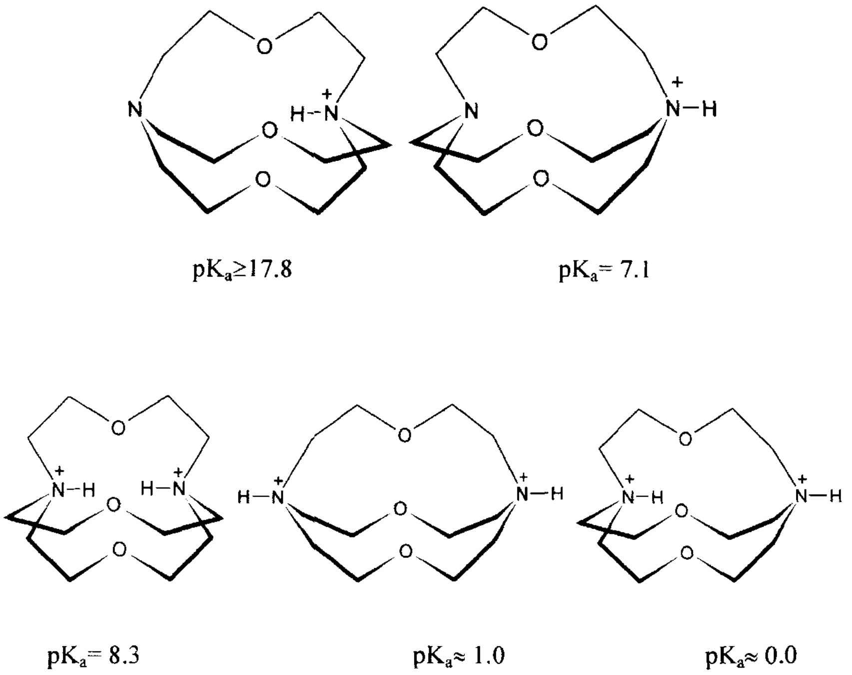
*Corresponding author.



SCHEME 1 The pK_a values for protonated and diprotonated isomers of cryptand.

stopped-flow [11–13] techniques have been used to study the kinetics of complex formation between cryptands and metal ions of groups 1A and 2A, while the temperature jump technique [14] has been used in the studies of protonation of cryptands.

Up to now protonation and deprotonation reactions of cryptands have been extensively studied. This paper reports a study of the proton transfer reaction of the cryptands and other azamacrocyclic compounds, in water solution and in the presence of group 1A cations forming stable complexes with them, by the temperature jump technique.

2. EXPERIMENTAL

The compounds studied were commercial products from Merck or Fluka and were used without any further purification.

The pK_a measurements were made using the standard potentiometric procedure.

Kinetic measurements were carried out using a temperature-jump instrument (Hi-Tech Scientific) based on the method of Joule heating. The instrument is described in Ref. [15]. The temperature jump is generated by the discharge of a 0.04 μF high voltage capacitor charged to 12 kV, through the solution. The ionic strength of the water solution is maintained at $0.05\,\mathrm{mol\,dm^{-3}}$ with salts (tetramethylammonium or metal perchlorates). The rise time is of the order of a few microseconds (about 5 μs). About $0.1\,\mathrm{cm^{-3}}$ of the solution is heated, the temperature rise being 10°C. Reactions of proton transfer are monitored spectrophotometrically and recorded on an attached computer system. Phenolphthalein was used to monitor the reaction ($\lambda = 540\,\mathrm{nm}$). In all cases simple exponential curves were observed. Two exemplary curves of the repeated reaction are given in Figure 1.

The rate constants were calculated from the exponential curves using the end-point method (program IS-2 Software Suite-HI-TECH).

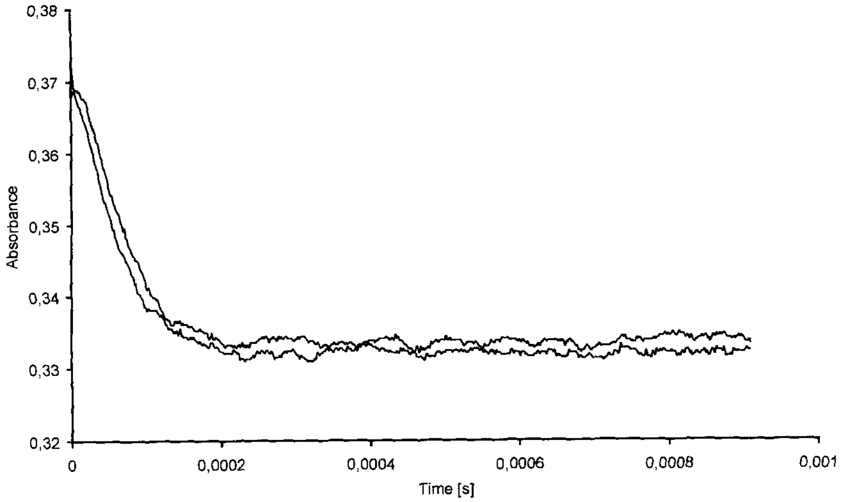


FIGURE 1 Two repeated relaxation curves of the deprotonation of the protonated N15C5 – K^+ complex in water solution induced by the 10°C temperature jump.

Second order rate constants (k_{-1}) for deprotonation reaction were calculated by linear least-squares fit of the variation of k_{obs} *vs.* proton concentration.

The activation parameters ($\Delta H^{\neq}$ and $\Delta S^{\neq}$) and the standard deviation were determined using the Eyring equation $[k = (k_B/h)\exp(\Delta S^{\neq}/R)\exp(-\Delta H^{\neq}/RT)]$ by linear least-squares fit of $\ln k/T$ *vs.* $1/T$. The $\Delta G^{\neq}$ values were calculated by the Gibbs-Helmhotz relation ($\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$) for the temperature 298 K.

The protonation rate constants were calculated from. $K = k/k_{-1}$ equation, where K is the equilibrium constant and k and k_{-1} are rate constants of the protonation and deprotonation reactions, respectively.

3. RESULTS AND DISCUSSION

The formulae of the compounds studied and their abbreviations are given in Table I.

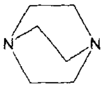
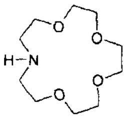
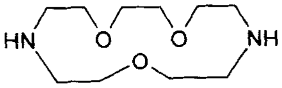
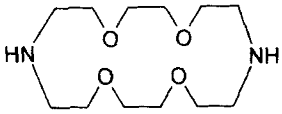
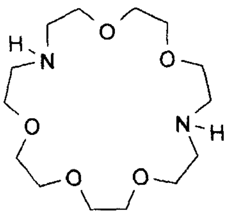
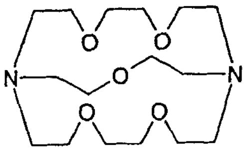
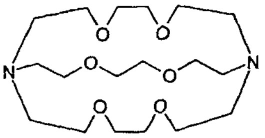
The relaxation time for the proton transfer process in the temperature-jump experiment depends only on the concentration of the hydroxide ion. The equilibrium involved is:

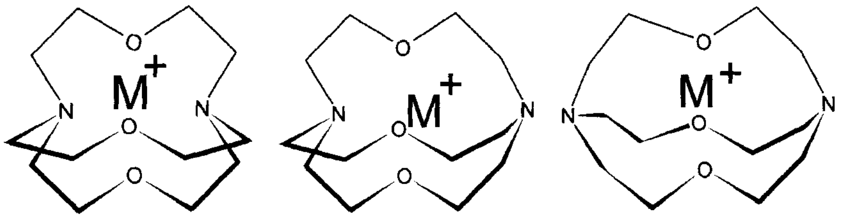
$$\text{Cryp-N} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Cryp-N}^+\text{-H} + HO^-$$

The conformation changes (exo, endo forms) do not play a significant role in this process. This is obvious because the protonation occurs only on one nitrogen atom of the cryptand and not within the ligand cavity and the relaxation time characteristic of the cryptand inversion is about two orders of magnitude faster than the relaxation time in the temperature-jump experiment [15–17]. On the other hand the rate constants k_{-1} in the case of cryptands are 3–7 orders of magnitude lower than those obtained for the deprotonation reaction of protonated aliphatic amines by HO^- groups excluding any significant participation of exo conformation of the protonated ligands [1].

In the presence of metal ions of group 1A the protonation and deprotonation of the cryptands may occur in the endo–endo conformation (Scheme 2), because only such structures of metal cryptates were found [1, 18–21].

TABLE I The compounds studied and their abbreviations

Compounds	Abbreviation
 1,4-diazabicyclo[2,2,2]octane	DABCO
 1-aza-15-crown-5	N15C5
 1,4,10-trioxa-7,13-diazacyclopentadecan	21
 1,7,10,16-tetraoxa-4,13-diazacyclooctadecan	22
 1,4,7,13,16-pentaoxa-10,19-diazacycloheneicosane	23
 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8,8,5]-tricosane	221
 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]-hexacosan	222



endo-endo endo-exo exo-exo

SCHEME 2 The endo-endo, endo-exo and exo-exo forms of complexed cryptand.

For bases other than cryptands studied in this paper, the protonation and deprotonation were much easier due to the lower energy barriers of conformation changes of these molecules. The effects observed for the cryptands are also important in the other systems studied.

The pK_{a1} values of the measured studied compounds in solutions of 0.05 mol dm^{-3} metal or $N(CH_3)_4^+$ perchlorates are summarised in Table II. Analogous measurements were previously made for some other systems and the results are collected in Table III. A comparison of the data given in Tables II and III demonstrates that the formation of the metal cation complexes with macrocyclic bases causes a decrease in the pK_{a1} value. This means that the value of this parameter can be a measure of the strength of such a complexation.

In the case of DABCO no complexation of cations occurs and, therefore, the pK_{a1} values of DABCO in the solutions including tetramethylammonium cation and other monovalent cations are almost the same. In all other cases the pK_{a1} values for the bases complexed with cations are clearly lower than those for the mixtures including $^+NMe_4$ cations. The greatest differences are observed for 221 and 222 cryptands as well as for 22 and 21 macrocyclic bases. In the protonated macrocyclic base the proton is localised at the nitrogen atom in the cavity of ligands and it is hydrogen-bonded with oxygen atoms. The cation complexation starts with the addition of metal cations to the solution of the protonated macrocyclic base and due to this effect the conformation changes so that the proton is localised at the nitrogen atom out of the ligand cavity (Scheme 3).

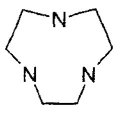
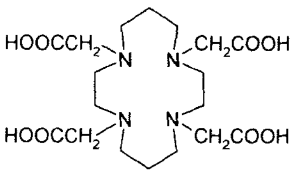
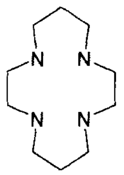
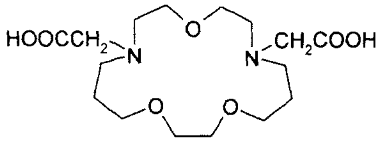
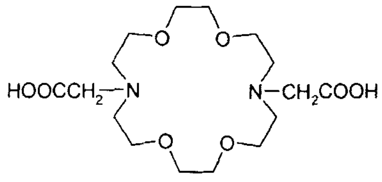
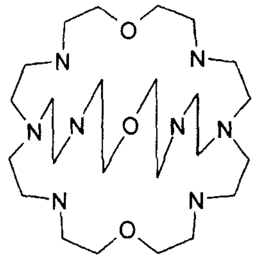
TABLE II First pK_{a1} values at 25°C of macrocyclic base in water solution in the presence of monovalent metal cations. Concentration of $MClO_4$ = 0.05 mol dm^{-3}

	pK_{a1}			
Compound	NMe_4^+	Li^+	Na^+	K^+
DABCO	12.51	12.50	12.52	12.49
N15C5	11.65	11.65	11.58	11.46
21	9.59	9.43	9.38	9.33
22	9.92	9.73	9.66	9.52
23	10.34	10.25	10.24	10.11
221	10.91	10.67	9.89	9.78
222	9.86	9.78	9.54	9.02

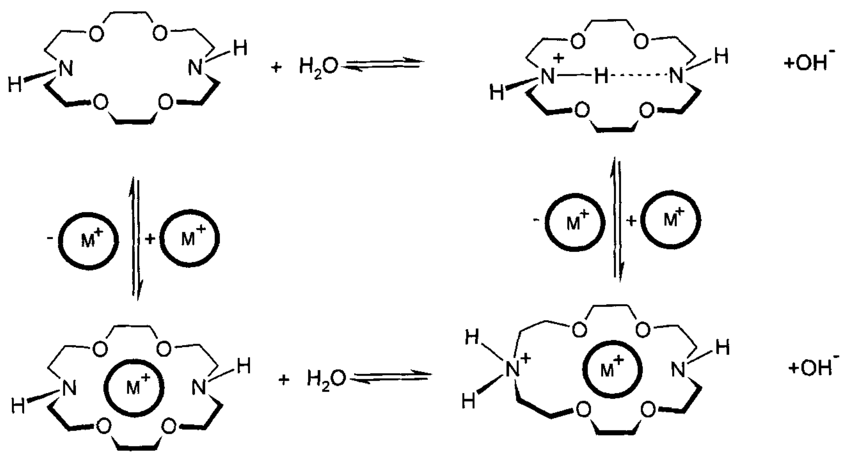
The kinetic and activation parameters of the deprotonation reaction in the 0.05 mol dm^{-3} $Me_4N^+ClO_4^-$ water solution are collected in Tables IV and V, respectively. A comparison of these data in Tables IV and V with the pK_{a1} values (Tabs. II and III) reveals that there is no correlation between these parameters. The $\Delta S^{\neq}$ values, shown in Table V are positive. A positive $\Delta S^{\neq}$ indicates that the transition state is looser than the starting material. For the reaction in solution, however, the positive $\Delta S^{\neq}$ values demonstrate that the transition state is more poorly solvated than the initial state, because of higher polarity of the latter state to the former. In contrast, the values of $\Delta H^{\neq}$ are relatively high indicating that the dissociation of the proton from the N^+—H bond (protonated base) is not easy.

The kinetic and activation parameters of the deprotonation reaction of the macrocyclic base

TABLE III pK_a values of amines in the presence of various metal cations in water solution at 25°C

Compounds	pK_a	Salts	Ref.
	10.80	0.2 mol dm^{-3} $NaClO_4$	[22, 23]
	10.94	0.5 mol dm^{-3} KNO_3	[24]
	12.09	0.1 mol dm^{-3} Me_4NNO_3	[25, 26]
	11.36	0.1 mol dm^{-3} KCl	[27]
	11.22	0.1 mol dm^{-3} KNO_3	[25, 26]
	11.78	0.1 mol dm^{-3} $NaClO_4$	[29, 28]
	11.54	0.1 mol dm^{-3} KNO_3	[30, 31]
	9.07	0.1 mol dm^{-3} Me_4NNO_3	[32]
	8.63	0.1 mol dm^{-3} KNO_3	
	8.45	0.1 mol dm^{-3} Me_4NNO_3	[33]
	9.04	0.1 mol dm^{-3} $NaNO_3$	[34]
	8.02	0.1 mol dm^{-3} KNO_3	[35]
	10.29	1.0 mol dm^{-3} NaBr	[36, 37]
	9.89	0.1 mol dm^{-3} KCl	[36]
	9.93	0.1 mol dm^{-3} KNO_3	[37]

in the 0.05 mol dm^{-3} $M^+ClO_4^-$ salt water solution are given in Tables VI and VII, respectively. A comparison of the rate constants of the deprotonation reactions of protonated amines in the presence of metal cations at 25°C with those obtained for $Me_4N^+ClO_4^-$ in water solutions (Tab. IV) shows only small differences. But these values depend strongly on the metal cation



SCHEME 3 Equilibria of the protonation and deprotonation reaction in the presence of monovalent metal cations, in the water solutions.

TABLE IV The k_{-1} kinetic data for the reactions between amines (0.005 mol * dm^{-3}) and water in the 0.05 mol * dm^{-3} $Me_4N^+ClO_4^-$ solution

Compounds	Temp. (°C)	Rate constant of deprotonation 10^{-6} (mol^{-1} dm^3 s^{-1})
DABCO	25.0	0.871
	30.0	1.115
	40.0	2.214
	50.0	3.536
N15C5	25.0	1.432
	30.0	2.147
	40.0	3.865
	50.0	5.998
21	25.0	0.995
	30.0	1.540
	40.0	3.250
	50.0	5.554
22	25.0	1.012
	30.0	1.588
	40.0	3.148
	50.0	5.899
23	25.0	1.999
	30.0	2.843
	40.0	5.121
	50.0	8.230
221	25.0	1.255
	30.0	1.768
	40.0	3.120
	50.0	4.856
222	25.0	2.670
	30.0	3.244
	40.0	5.445
	50.0	9.780

TABLE V The activation parameters (± standard deviation) for the reactions between amines and water in 0.05 mol * dm^{-3} $Me_4N^+ClO_4^-$ solution

	Activation parameters of deprotonation amines (25°C)		
Compounds	$\Delta H^{\#}_{[Me_4N^+]}$ [kJ mol^{-1}]	$\Delta S^{\#}_{[Me_4N^+]}$ [J $mol^{-1}K^{-1}$]	$\Delta G^{\#}_{[Me_4N^+]}$ [kJ mol^{-1}]
DABCO	43.6 ± 2.3	15 ± 7	39.2 ± 2.3
N15C5	42.9 ± 3.0	17 ± 10	37.8 ± 3.0
21	52.7 ± 3.0	47 ± 10	38.7 ± 3.0
22	53.3 ± 1.8	49 ± 6	38.7 ± 1.8
23	42.7 ± 1.7	19 ± 6	37.0 ± 1.7
221	40.7 ± 1,9	9 ± 6	38.2 ± 1,9
222	39.3 ± 2.5	10 ± 8	36.5 ± 2.5

used. The influence of the metal cations is manifested by a variation of the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values (Tab. VII). The most interesting cases are these for which the $\Delta S^{\neq}$ values are negative. In these cases the cations are strongest complexed by the ligands of bases. The $\Delta H^{\neq}$ values decrease with increasing radius of the metal cation. In the case of DABCO, which does not form complexes with the metal cation, such effects are not observed. For all systems studied the $\Delta G^{\neq}$ values are comparable. The measure of the metal cation influence on the proton transfer

TABLE VI The k_{-1} kinetic data for the reactions between amines ($0.005\,mol*dm^{-3}$) and water in $0.05\,mol*dm^{-3}$ $M^+ClO_4^-$ solution (where $M^+ = Li^+, Na^+, K^+$ cations)

Compounds	Temp. (°C)	Rate constant of deprotonation $10^{-6}k_{-1}$ ($mol^{-1}dm^3s^{-1}$)
DABCO + Li^+	25.0	0.879
	30.0	1.129
	40.0	2.249
	50.0	3.613
DABCO + Na^+	25.0	0.936
	30.0	1.214
	40.0	2.251
	50.0	3.817
DABCO + K^+	25.0	0.850
	30.0	1.110
	40.0	2.158
	50.0	3.643
N15C5 + Li^+	25.0	1.328
	30.0	1.548
	40.0	2.934
	50.0	4.589
N15C5 + Na^+	25.0	1.328
	30.0	1.834
	40.0	2.934
	50.0	4.215
N15C5 + K^+	25.0	1.498
	30.0	1.954
	40.0	3.187
	50.0	4.100
22 + Li^+	25.0	1.340
	30.0	1.961
	40.0	3.500
	50.0	6.598
22 + Na^+	25.0	1.311
	30.0	1.555
	40.0	2.993
	50.0	4.933
22 + K^+	25.0	1.592
	30.0	1.911
	40.0	3.148
	50.0	4.735
23 + Li^+	25.0	2.347
	30.0	2.955
	40.0	4.566
	50.0	7.821
23 + Na^+	25.0	2.099
	30.0	2.578
	40.0	4.002
	50.0	6.010
23 + K^+	25.0	2.454
	30.0	2.843
	40.0	4.799
	50.0	6.162

TABLE VII The activation parameters (± standard deviation) for the reactions between amines and water in $0.05\,mol*dm^{-3}$ $M^+ClO_4^-$ solution, where $M^+ = Li^+, Na^+, K^+$ cations

	Activation parameters of deprotonation reactions (25°C)		
Compounds	$\Delta H^{\#}_{[M^+]}$ [kJ mol^{-1}]	$\Delta S^{\#}_{[M^+]}$ [J $mol^{-1}K^{-1}$]	$\Delta G^{\#}_{[M^+]}$ [kJ mol^{-1}]
DABCO + Li^+	44.0 ± 2.3	16 ± 7	39.2 ± 2.3
DABCO + Na^+	43.1 ± 1.0	13 ± 3	39.0 ± 1.0
DABCO + K^+	45.0 ± 1.4	19 ± 5	39.2 ± 1.4
N15C5 + Li^+	39.0 ± 3.0	2 ± 9	38.2 ± 3.0
N15C5 + Na^+	34.1 ± 2.3	−13 ± 7	38.0 ± 2.3
N15C5 + K^+	30.2 ± 3.2	−25 ± 10	37.7 ± 3.2
22 + Li^+	48.0 ± 1.3	33 ± 4	38.0 ± 1.3
22 + Na^+	41.4 ± 3.0	11 ± 9	38.3 ± 3.0
22 + K^+	33.1 ± 1.2	−16 ± 4	38.0 ± 1.2
23 + Li^+	36.0 ± 2.0	−4 ± 6	37.0 ± 2.0
23 + Na^+	31.4 ± 0.4	−19 ± 1	37.0 ± 0.4
23 + K^+	29.0 ± 3.0	−27 ± 10	37.0 ± 3.0

TABLE VIII Rate constant for the protonation reactions between amines and water in $0.05\,mol*dm^{-3}$ $M^+ClO_4^-$ solution at 25°C (where $M^+ = NMe_4^+$, Li^+, Na^+ and K^+ cations)

	k (s^{-1})			
Amines	NMe_4^+	Li^+	Na^+	K^+
DABCO	28185	27796	30994	26268
N15C5	6397	5932	5049	4320
21	39			
22	85	72	60	53
23	437	417	365	316
221	1020			
222	193			

reaction is the difference observed between the activation parameters for the studied reaction at the presence and absence of the metal cation. With increasing radius of the cation the $\Delta[\Delta H^{\neq}]$ and $\Delta[\Delta S^{\neq}]$ values decreasing strongly. The strogest influence on the proton transfer reaction is observed for the reaction if the K^+ cations are present in the solution. The $\Delta[\Delta G^{\neq}]$ values are comparable for all systems and independent on the cation.

In Table VIII the rate constants for the protonation reaction of macrocyclic bases at 25°C are collected. These values are much lower than those obtained for the rate constant of deprotonation process and are strongly dependent on the cation.

Acknowledgement

Financial assistance of the Polish Committee for Scientific Research (KBN) within the Research Project 3T09A 018 17 is gratefully acknowledged.

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