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Kinetics and Mechanism of Reactions Between Tetranitrodibenzo Crown Ethers and Alkali Metal Hydroxides

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The paper reports results of the kinetic and spectroscopic studies of reactions between tetranitrodibenzo crown ethers: TNDB 18C6, TNDB 24C8 and TNDB 30C10 or theirs analogs: 1,2-dimethoxy- or 1,2-diethoxybenzenes and alkali metal hydroxides: LiOH, NaOH, KOH, RbOH and CsOH in DMSO: water (95:5 v/v) mixture. These reactions lead via the non-concerted mechanism to formation of σ-adducts and complexes with metal cations.

Keywords: Kinetics, crown ethers

INTRODUCTION

Crown ethers and cryptands are characterized by a unique ability to form stable complexes with most cations, particularly with IA and IIA elements. The complexation of metal cations depends on the relative size of the cavity and the cation. 15-Crown-5 (15C5) and its derivatives have cavities 1.7-2.2 Å in diameter which matches the size of sodium cation (1.9 Å). The cavity 18-Crown-6 (18C6) and its derivatives vary in size from 2.6-3.2 Å. The size of potassium cation is (2.66 A). The size of rubidium and cesium cations are 2.96 Å and 3.38 Å, respectively. The cavity size of 24-Crown-8(24C8) is > 4 Å and 30-Crown-10(30C10) > 6 Å. One factor that affects complex stability constants is the degree of cavity-cation complementarity [1-4].

In the previous paper [5] we presented kinetic results for reactions of 4, 5-dinitrophenyl-substituted, 15- and 18-membered crown ethers: 15C5 and 18C6 with lithium, sodium, potassium and tetra-*n*-butylammonium hydroxides in DMSO: water (95:5 v/v). Nucleophilic aromatic substitution reaction of hydroxide ions with the benzene ring in the compounds was studied, along with cation complex formation. An excess of base was used relative to the amount of σ-complex which yields the dissociation of the σ-adduct.

Tetranitrodibenzo crown ethers (see Fig. 2) were studied along with, 1,2-dimethoxy- or 1,2-diethoxybenzenes (controls). Kinetic studies of the reactions of these compounds with hydroxide ions in DMSO: water (95:5 % v/v) mixed solvent were carried out.

EXPERIMENTAL

Tetranitrodibenzo crown ethers (TNDB-crown ethers) and their analogs were prepared using commercial benzocrown ethers or 1,2-dialkoxybenzenes as starting materials. Nitration of the benezene rings was accomplished according to the method of Skerret (fuming nitric acid at –30 °C (Fig. 1) [6]. Reaction products were crystallized from the ethanol-acetonitrile mixture.

The structures of the tetranitrodibenzocrown ethers (TNDB-crown and their H-NMR spectra are collected in Figure 2.

Lithium, sodium, potassium, rubidium and cesium hydroxides were obtained from commerical sources. DMSO and water were purified by the standard method [7]. Hydroxide/water solutions were prepared directly prior to measurements. The base concentration was determined by titration. The base solutions used in kinetic measurements were prepared by mixing aqueous hydroxide solutions with DMSO.

Kinetic Measurements

The kinetic runs were carried out under pseudo-first order conditions (excess base) using a stopped-flow spectrophotometer (Applied Photophysics) with the cell block thermostated ± 0.1 °C. The observed rate constants were calculated from the traces of absorbance *vs*. time.

The observed rate constant k_{obs} depends on the case concentration $k_{obs} = k[B] + k_{-}$, where k is the rate constant for the forward proton transfer reaction, k_{-} is the rate constant for the reverse proton transfer reaction and $[B]$ is the initial base concentration. Rate constants for the forward (k) reaction were calculated by linear least-square fit of the variation of k_{obs} *vs*. base concentration. The activation parameters were calculated by linear least-squares fit of ln k *vs*. $1/T$.

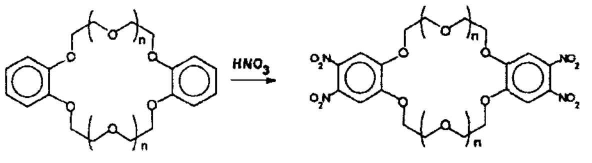
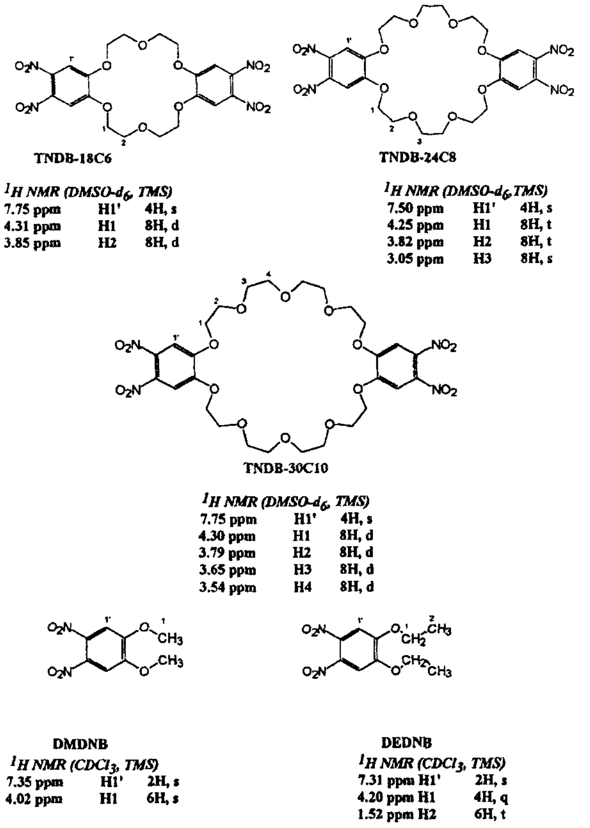


FIGURE 1



TNDB-18C6

^1H NMR (DMSO-d_6, TMS)		
7.75 ppm	H1'	4H, s
4.31 ppm	H1	8H, d
3.85 ppm	H2	8H, d

TNDB-24C8

^1H NMR (DMSO-d_6,TMS)		
7.50 ppm	H1'	4H, s
4.25 ppm	H1	8H, t
3.82 ppm	H2	8H, t
3.05 ppm	H3	8H, s

TNDB-30C10

^1H NMR (DMSO-d_6, TMS)		
7.75 ppm	H1'	4H, s
4.30 ppm	H1	8H, d
3.79 ppm	H2	8H, d
3.65 ppm	H3	8H, d
3.54 ppm	H4	8H, d

DMDNB

^1H NMR (CDCl$_3$, TMS)		
7.35 ppm	H1'	2H, s
4.02 ppm	H1	6H, s

DEDNB

^1H NMR (CDCl$_3$, TMS)		
7.31 ppm	H1'	2H, s
4.20 ppm	H1	4H, q
1.52 ppm	H2	6H, t

FIGURE 2

RESULTS AND DISCUSSION

The addition of hydroxides lithium, sodium, potassium, rubidium and cesium to TNDB-crown ethers or their analogs dissolved in DMSO-water led to formation of a colored product. Variation in the absorption spectra of TNDB-18C6 and NaOH in DMSO: water mixture as a function of time is presented in Figure 3.

The ^{1}H-NMR spectra of the crown ethers and their analogs (1,2-dimethoxy-4,5-dinitrobenzene and 1,2-diethoxy-4,5-dinitrobenzene) with NaOH in a deuterated DMSO mixture, after 30

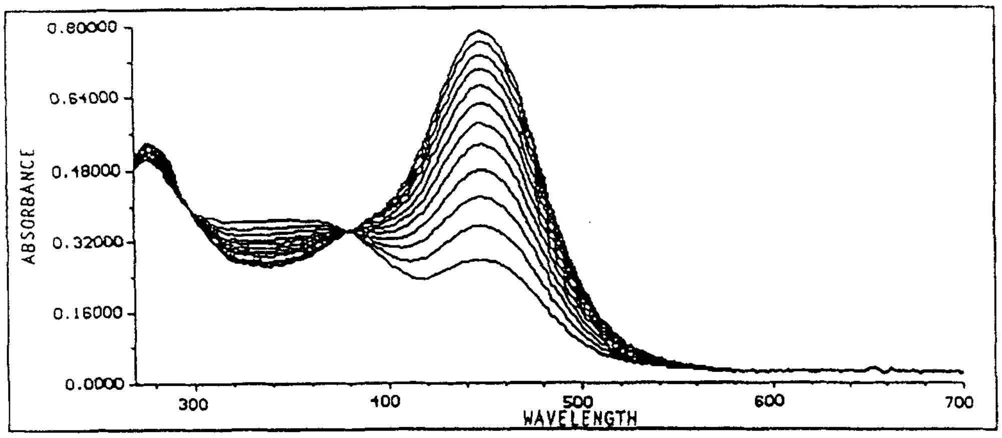


FIGURE 3 Variation of absorption spectra of TNDB 18C6/ NaOH [0.005 M] in DMSO: water mixture (95.9 v/v) as a function of time. Start time-20 s, cycle time-20 s.

minutes, showed that the colored reaction product was a σ complex, formed by nucleophilic aromatic addition. The final reaction products of 1,2-dimethoxy-4,5-dinitrobenzene–NaOD; ^{1}H NMR (DMSO-d_6, TMS; 7.30 ppm, d, 1H; 6.25 ppm, d, 1H; 4.10 ppm, s, 6H) and of TNDB 18C6 - NaOD; 1H NMR (DMSO-d_6, TMS; 7.75 ppm, s, 2H; 7.30 ppm, d, 1H; 6.20 ppm, d, 1H; 3.80–4.50 ppm, m, 16H) are presented in Figure 4.

Kinetics studies were conducted by using a spectrophotometric method for reactions of these dinitrodialkoxybenzenes and crown ethers with lithium, sodium, potassium, cesium and rubidium hydroxides in DMSO: water (95:5 v/v). All of the reactions studied were second order, i.e., first order with respect to the base and to crown ether concentrations. The process of metal cation – crown ether complex formation is faster than formation of the Meisenheimer complex and does not influence the kinetics of the σ-complex formation reaction (Fig. 5).

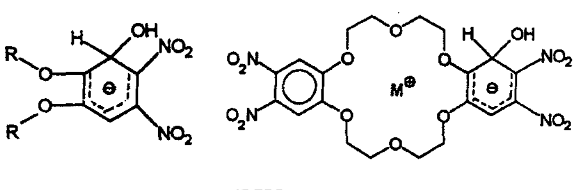


FIGURE 4

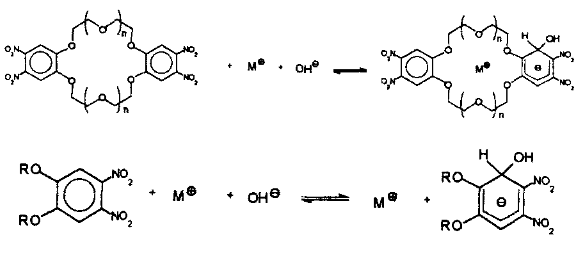


FIGURE 5

The kinetic results for reactions of dinitrodialkoxybenzenes and hydroxides collected in Tables I and II. They reveal a strong relationship between the rate constant of the reaction studied and the kind of the alkali metal hydroxides used. For the reaction of DMDNB (25 °C) with alkali metal hydroxides, the relationship between the rate constant and the kinds of bases used was as follows:

$$k_{\mathrm{LiOH}} : k_{\mathrm{NaOH}} : k_{\mathrm{KOH}} : k_{\mathrm{RbOH}} : k_{\mathrm{CsOH}} = 1 : 2 : 30 : 16 : 0.2$$

Whereas for the reaction with DEDNB (25 °C) it was:

$$k_{\mathrm{LiOH}} : k_{\mathrm{NaOH}} : k_{\mathrm{KOH}} : k_{\mathrm{RbOH}} : k_{\mathrm{CsOH}} = 1 : 1.5 : 23 : 23 : 0.2.$$

The different reactivity of alkali metal hydroxides is a result of the degree of changes in

TABLE I Kinetic parameters (± standard deviation) for reaction between 1,2-dimethoxy-4,5-dinitrobenzene (DMDNB) and MOH in DMSO: water mixture (95 : 5 v/v)

Temp. °C			10^4k_{obs} [s^{-1}]				
Base concent.	0.0050 M	0.0075 M	0.100 M	0.0125 M	0.0150 M	10^2k[$M^{-1}S^{-1}$]	10^5int [s^{-1}]
			DMDNB + LiOH				
25	–	–	–	–	–	0.69 (exp)	–
40	1.32	1.95	2.54	3.08	3.54	2.22 ± 0.1	26.0 ± 0.8
45	2.24	3.25	4.20	4.97	5.72	3.47 ± 0.1	6.0 ± 1.0
50	2.85	4.24	5.12	6.35	7.42	4.50 ± 7.0	7.0 ± 2.0
	$\Delta H^{\neq}_{25}$ [kJmol^{-1}] = 59.6 ± 8.5		$-\Delta S^{\neq}_{25}$ [Jmol^{-1}deg^{-1}] = 95.2 ± 26.9			$\Delta G^{\neq}_{25}$ [kJmol^{-1}] = 85.3 ± 8.5	
			DMDNB + NaOH				
25	0.85	1.44	1.45	2.00	2.50	1.54 ± 0.20	1.04 ± 2.2
30	1.63	2.53	3.72	4.41	5.20	3.61 ± 0.20	–1.10 ± 2.3
35	2.85	4.20	5.51	7.12	8.43	5.63 ± 0.10	–0.10 ± 1.1
40	4.30	6.40	8.90	10.62	12.71	8.42 ± 0.30	1.70 ± 2.7
45	5.57	9.15	12.50	15.62	18.95	13.20 ± 0.10	–7.50 ± 1.1
	$\Delta H^{\neq}_{25}$ [kJmol^{-1}] = 78.8 ± 7.1		$-\Delta S^{\neq}_{25}$ [Jmol^{-1}deg^{-1}] = 14.1 ± 22.9			$\Delta G^{\neq}_{25}$[kJmol^{-1}]=83.1 ± 7.1	
			DMDNB + KOH				
25	10.0	16.2	20.1	25.1	31.3	20.6 ± 0.9	–0.60 ± 0.9
30	17.2	24.7	31.0	39.5	48.0	30.6 ± 0.20	15.0 ± 10.0
35	24.2	34.1	46.5	57.0	67.3	43.6 ± 0.8	21.0 ± 9.0
40	35.0	52.5	67.0	84.0	100.5	65.0 ± 0.9	28.0 ± 10.0
45	61.0	88.0	116.2	144.2	172.0	111.2 ± 0.5	50.0 ± 5.0
	$\Delta H^{\neq}_{25}$ [kJmol^{-1}] = 62.5 ± 7.1		$-\Delta S^{\neq}_{25}$ [Jmol^{-1}deg^{-1}] = 49.1 ± 11.7			$\Delta G^{\neq}_{25}$ [kJmol^{-1}]=77.1 ± 3.6	
			DMDNB + RbOH				
25	8.3	10.2	13.5	16.4	18.7	10.8 ± 0.5	26.0 ± 5.2
30	10.5	16.3	19.8	25.5	28.6	18.2 ± 1.0	19.0 ± 11.0
35	11.5	17.5	22.5	28.5	34.2	22.6 ± 0.4	2.8 ± 3.6
40	17.3	30.2	38.1	48.3	56.0	38.2 ± 2.0	–1.6 ± 21.0
45	32.0	49.0	65.3	82.8	97.3	65.7 ± 1.0	–4.8 ± 11.0
	$\Delta H^{\neq}_{25}$ [kJmol^{-1}] = 66.0 ± 5.5		$-\Delta S^{\neq}_{25}$ [Jmol^{-1}deg^{-1}] = 42. ± 17.8			$\Delta G^{\neq}_{25}$ [kJmol^{-1}]=78.6 ± 5.5	
			DMDNB + CsOH				
25	7.22	11.34	14.91	17.00	22.15	0.14 ± 0.01	3.2 ± 10.3
30	11.47	17.28	22.35	27.11	34.10	0.22 ± 0.01	4.2 ± 8.6
35	18.23	25.93	35.10	45.35	53.14	0.36 ± 0.01	–1.5 ± 10.3
40	25.14	37.23	50.00	62.30	74.20	0.49 ± 0.01	4.9 ± 3.3
45	36.15	51.13	67.11	84.44	105.00	0.68 ± 0.02	3.6 ± 2.6
	$\Delta H^{\neq}_{25}$ [kJmol^{-1}] = 60.1 ± 3.0		$-\Delta S^{\neq}_{25}$ [Jmol^{-1}deg^{-1}] = 59.6 ± 9.9			$\Delta G^{\neq}_{25}$ [kJmol^{-1}] = 77.9 ± 3.1	

dissociation and formation of different kinds of ion pairs i.e., loose or fight depending upon charge density and ion parameters [8–10]. The highest values for rate constants were observed for the reactions with KOH.

Kinetic results for the reactions of TNDB crown ethers and the hydroxides was collected in Tables III–V.

At 25 °C, for the reaction with TNDB 18C6, the relationship between the rate constant and the bases was:

$$k_{LiOH} : k_{NaOH} : k_{KOH} : k_{RbOH} : k_{CsOH} = 1 : 37 : 97 : 43 : 19.$$

The value of the rate constant for the reaction of TNDB 18C6 is distinctly higher than for the analogous reactions with DMDNB or DEDNB. The best steric adjustment and stability of metal cation-crown ether complex was obtained for the

TABLE II Kinetic parameters (± standard deviation) for reaction between 1,2-diethoxy-4,5-dinitrobenzene (DMDNB) and MOH in DMSO: water mixture (95 : 5 v/v)

Temp. °C			$10^4 k_{obs}$ [s^{-1}]				
Base concent.	0.0050 M	0.0075 M	0.0100 M	0.0125 M	0.0150 M	$10^2 k$ [$M^{-1}s^{-1}$]	10^5 int [s^{-1}]
			DEDNB + LiOH				
25	–	–	–	–	–	0.64 (exp)	–
40	1.00	1.93	2.47	3.02	3.28	2.26 ± 0.3	0.8 ± 3.0
45	1.75	3.02	3.78	4.38	5.49	3.54 ± 0.3	2.0 ± 3.0
50	2.87	4.35	5.62	6.25	7.95	4.82 ± 0.4	6.0 ± 4.0
	$\Delta H^{\neq}_{25}$ [$kJmol^{-1}$] = 61.2 ± 6.2		$-\Delta S^{\neq}_{25}$ [$Jmol^{-1}deg^{-1}$] = 81.5 ± 6.2			$\Delta G^{\neq}_{25}$ [$kJmol^{-1}$] = 85.5 ± 6.2	
			DEDNB + NaOH				
25						1.07 (exp)	
30	0.98	1.13	1.73	2.10	2.53	1.63 ± 0.10	0.07 ± 1.5
35	1.80	2.70	3.58	4.48	5.31	3.52 ± 0.10	0.54 ± 0.3
40	3.01	4.30	5.61	7.09	8.47	5.48 ± 0.10	2.10 ± 0.9
45	4.65	6.61	8.77	10.83	12.63	8.07 ± 0.10	6.30 ± 1.4
50	6.70	9.91	12.53	16.04	19.48	12.68 ± 0.10	2.60 ± 3.8
	$\Delta H^{\neq}_{25}$ [$kJmol^{-1}$] = 78.0 ± 5.9		$-\Delta S^{\neq}_{25}$ [$Jmol^{-1}deg^{-1}$] = 21.3 ± 19.0			$\Delta G^{\neq}_{25}$ [$kJmol^{-1}$] = 84.3 ± 5.9	
			DEDNB + KOH				
25	10.0	15.3	19.0	22.1	25.4	15.0 ± 1.0	33.0 ± 10.0
30	17.2	24.7	31.0	39.5	48.0	30.6 ± 0.20	15.0 ± 10.0
35	24.2	34.1	46.5	57.0	67.3	43.6 ± 0.8	21.0 ± 9.0
40	35.0	52.5	67.0	84.0	100.5	65.0 ± 0.9	28.0 ± 10.0
45	61.0	88.0	116.2	144.2	172.0	111.2 ± 0.5	50.0 ± 5.0
	$\Delta H^{\neq}_{25}$ [$kJmol^{-1}$] = 35.0 ± 2.0		$-\Delta S^{\neq}_{25}$ [$Jmol^{-1}deg^{-1}$] = 143.6 ± 6.4			$\Delta G^{\neq}_{25}$ [$kJmol^{-1}$] = 77.9 ± 2.0	
			DEDNB + RbOH				
25	10.3	13.0	15.8	21.0	25.4	15.3 ± 1.2	18.2 ± 13.2
30	12.1	16.2	21.4	27.2	32.0	20.3 ± 0.6	14.6 ± 6.7
35	14.7	21.1	30.1	37.6	43.0	29.2 ± 1.3	0.6 ± 14.0
40	23.1	35.2	44.8	55.4	64.9	41.5 ± 1.0	32.0 ± 11.0
45	27.2	39.8	53.7	65.3	79.8	52.3 ± 0.9	8.8 ± 9.5
	$\Delta H^{\neq}_{25}$ [$kJmol^{-1}$] = 47.5 ± 1.9		$-\Delta S^{\neq}_{25}$ [$Jmol^{-1}deg^{-1}$] =102.3 ± 6.1			$\Delta G^{\neq}_{25}$ [$kJmol^{-1}$] = 77.8 ± 1.9	
			DEDNB + CsOH				
25	7.13	10.35	14.35	19.20	21.28	0.15 ± 0.01	−3.9 ± 9.8
30	10.03	15.39	20.55	26.35	30.07	0.20 ± 0.01	0 ± 7.9
35	15.33	22.47	30.10	38.14	44.21	0.29 ± 0.01	6.7 ± 7.3
40	20.35	30.01	39.15	47.35	57.18	0.36 ± 0.01	2.4 ± 6.3
45	27.48	39.71	53.77	66.34	78.12	0.51 ± 0.01	1.9 ± 8.9
	$\Delta H^{\neq}_{25}$ [$kJmol^{-1}$] = 45.4 ± 1.9		$-\Delta S^{\neq}_{25}$ [$Jmol^{-1}deg^{-1}$] = 108.8 ± 6.1			$\Delta G^{\neq}_{25}$ [$kJmol^{-1}$] = 77.8 ± 1.9	

following arrangement: potassium cation with TNDB 18C6. The highest values of rate constants for reactions of TNDB 18C6 with KOH is observed.

At 25 °C for the reaction with the crown ether characterised by larger cavity size, TNDB 24C8, the relationship between rate constant and that based used was follows:

$$k_{LiOH} : k_{NaOH} : k_{KOH} : k_{RbOH} : k_{CsOH}$$
$$= 1 : 11 : 10 : 18 : 15.$$

The dependence $k = f$ (base used) is a result of 2 : 1 cation crown ether complex formation in reactions with lithium or sodium cations and TNDB 24C10. In the case of reactions with other bases, 1 : 1 cation – crown, ether complex is formed.

For the largest crown, at 25 °C, TNDB 30C10, the relationship between the rate constant and the bases used was found to be:

$$k_{LiOH} : k_{NaOH} : k_{KOH} : k_{RbOH} : k_{CsOH}$$
$$= 1 : 8 : 10 : 5 : 9.$$

TABLE III Kinetic parameters (± standard deviation) for reaction between TNDB 18C6 and MOH in DMSO: water mixture (95 : 5 v/v)

Temp. °C			$10^4k_{obs}[s^{-1}]$				
Base concent.	0.0050 M	0.0075 M	0.100 M	0.0125 M	0.0150 M	$10^2k[M^{-1}s^{-1}]$	10^5int $[s^{-1}]$
			TNDB 18C6 + LiOH>				
25	–	–	0.26	0.33	0.39	0.026 ± 0.001	0.01 ± 0.01
45	–	–	3.78	4.38	5.49	0.048 ± 0.002	0.05 ± 0.03
60	–	–	5.62	6.25	7.95	0.084 ± 0.005	−0.01 ± 0.06
	$\Delta H^{\neq}_{25}$ [kJmol^{-1}] = 24.8 ± 2.3		$-\Delta S^{\neq}_{25}$ [Jmol^{-1}deg^{-1}] =192 ± 7			$\Delta G^{\neq}_{25}$ [kJmol^{-1}] = 82.2 ± 2.3	
			TNDB 18C6 + NaOH				
25	5.1	7.5	10.0	12.4	14.6	0.96 ± 0.01	0.3 ± 0.1
30	6.2	9.3	12.2	15.4	18.7	1.24 ± 0.02	−0.08 ± 0.17
35	8.0	13.3	16.3	21.5	25.6	1.73 ± 0.08	−0.3 ± 0.8
40	13.3	18.3	24.5	30.1	38.5	2.49 ± 0.13	0.06 ± 1.14
45	18.5	24.5	35.7	42.3	50.5	3.27 ± 0.16	1.5 ± 1.7
	$\Delta H^{\neq}_{25}$ [kJmol^{-1}] = 43.6 ± 4.6		$-\Delta S^{\neq}_{25}$ [Jmol^{-1}deg^{-1}] =100 ± 15			$\Delta G^{\neq}_{25}$ [kJmol^{-1}] = 73.3 ± 4.6	
			TNDB 18C6 + KOH				
25	13.5	18.9	24.9	32.8	38.0	2.52 ± 0.09	0.46 ± 1.0
30	20.5	27.2	37.2	46.5	56.2	3.62 ± 0.11	1.42 ± 1.2
35	25.4	37.4	48.1	60.1	72.2	4.65 ± 0.05	2.12 ± 0.6
40	32.3	47.8	62.7	79.5	94.5	6.24 ± 0.06	0.92 ± 0.7
45	43.7	63.8	85.0	106.3	124.5	8.16 ± 0.12	3.02 ± 1.3
	$\Delta H^{\neq}_{25}$ [kJmol^{-1}] = 43.2 ± 1.3		$-\Delta S^{\neq}_{25}$ [Jmol^{-1}deg^{-1}] =92 ± 4			$\Delta G^{\neq}_{25}$ [kJmol^{-1}] = 70.7 ± 1.3	
			TNDB 18C6 + RbOH				
25	6.9	9.2	12.2	15.0	18.0	1.12 ± 0.03	1.0 ± 0.4
30	9.9	13.2	18.3	25.5	27.2	1.88 ± 0.18	0.1 ± 1.9
35	13.0	18.2	25.0	30.3	37.6	2.45 ± 0.08	0.3 ± 0.8
40	17.9	27.2	35.5	44.0	51.9	3.39 ± 0.05	1.4 ± 0.6
45	26.5	38.0	50.2	62.5	75.1	4.87 ± 0.05	1.8 ± 0.5
	$\Delta H^{\neq}_{25}$ [kJmol^{-1}] = 53.2 ± 3.2		$-\Delta S^{\neq}_{25}$ [Jmol^{-1}deg^{-1}] =65 ± 10			$\Delta G^{\neq}_{25}$ [kJmol^{-1}] = 72.7 ± 3.2	
			TNDB 18C6 + CsOH				
25	2.4	3.6	4.7	6.2	7.4	0.50 ± 0.01	−0.2 ± 0.1
30	3.5	5.4	7.0	8.6	11.2	0.74 ± 0.04	−0.3 ± 0.4
35	6.0	8.5	10.8	13.3	16.0	0.99 ± 0.02	1.0 ± 0.2
40	8.5	11.5	15.5	18.2	21.6	1.32 ± 0.04	1.9 ± 0.5
45	11.4	15.6	20.6	25.9	31.4	2.01 ± 0.06	0.9 ± 0.6
	$\Delta H^{\neq}_{25}$ [kJmol^{-1}] = 50.5 ± 2.3		$-\Delta S^{\neq}_{25}$ [Jmol^{-1}deg^{-1}] =82 ± 8			$\Delta G^{\neq}_{25}$ [kJmol^{-1}] = 74.8 ± 2.3	

An influence of 2:1 cation metal – crown ether complex formation on the rate constant was observed in reactions with lithium, sodium, or potassium hydroxides. The large difference in size between the cation and the crown ether cavity is responsible for the kinetics of the reactions studied. In σ-complex formation, the kinetic macrocyclic effect takes a maximum value for arrangements characterised by the optimum adjustment of sizes of the cation and the cavity. For the following ions: Li^+, Na^+, K^+, Rb^+ and Cs^+, the hydration numbers are 25.3, 16.6, 10.5, 10.0 and 9.9, whereas the negative hydration enthalpies are 519, 406, 322, 293 and 264 [kJ mol^{-1}], respectively [11]. These values determine the activation parameters of the reactions studied.

Values of $\Delta G^{\neq}$ for reactions between crown ethers and alkali metal hydroxides are lower than for reactions of the latter with dialkoxydinitrobenzenes. For reaction with LiOH (Li^+ is characterized by the highest values of hydration

TABLE IV Kinetic parameters (± standard deviation) for reaction between TNDB 24C10 and MOH in DMSO: water mixture (95 : 5 v/v)

Temp. °C			$10^4 k_{obs}$ [s^{-1}]				
Base concent.	0.0050 M	0.0075 M	0.0100 M	0.0125 M	0.0150 M	10^2k [M^{-1}s^{-1}]	10^5int [s^{-1}]
			TNDB 24C8 + LiOH				
25	–	–	0.30	0.37	0.45	0.030 ± 0.002	−0.01 ± 0.01
45	–	–	0.47	0.57	0.65	0.036 ± 0.002	0.11 ± 0.03
60	–	–	0.69	0.86	1.00	0.062 ± 0.003	0.08 ± 0.04
	$\Delta H^{\neq}_{25}$ [kJmol^{-1}] = 13.8 ± 6.7		$-\Delta S^{\neq}_{25}$ [Jmol^{-1}deg^{-1}] =229 ± 21			$\Delta G^{\neq}_{25}$ [kJmol^{-1}] = 82.0 ± 6.7	
			TNDB 24C8 + NaOH				
25	1.6	2.6	3.4	4.2	5.0	0.34 ± 0.01	0 ± 0.1
30	2.6	4.2	5.5	7.0	8.2	0.56 ± 0.01	0 ± 0.1
35	5.1	7.6	10.2	12.7	15.3	1.02 ± 0.01	0.1 ± 0.1
40	7.6	11.5	15.1	19.0	22.5	1.49 ± 0.02	0.2 ± 0.2
45	10.5	15.7	21.5	26.5	32.5	2.19 ± 0.03	−0.6 ± 0.3
	$\Delta H^{\neq}_{25}$ [kJmol^{-1}] = 71.8 ± 3.4		$-\Delta S^{\neq}_{25}$ [Jmol^{-1}deg^{-1}] =13 ± 11			$\Delta G^{\neq}_{25}$ [kJmol^{-1}] = 75.7 ± 3.4	
			TNDB 24C8 + KOH				
25	1.6	2.2	3.0	3.7	4.5	0.29 ± 0.01	0.1 ± 0.1
30	2.7	4.0	5.2	6.2	7.7	0.49 ± 0.02	0.3 ± 0.2
35	4.0	5.8	7.4	9.81	11.8	0.78 ± 0.03	0.1 ± 0.3
40	5.6	8.5	11.3	14.3	17.0	1.14 ± 0.09	0.1 ± 0.1
45	7.5	11.3	15.4	19.3	23.3	1.58 ± 0.01	0.5 ± 0.1
	$\Delta H^{\neq}_{25}$ [kJmol^{-1}] = 64.4 ± 2.1		$-\Delta S^{\neq}_{25}$ [Jmol^{-1}deg^{-1}] =39 ± 10			$G^{\neq}_{25}$ [kJmol^{-1}] = 76.0 ± 3.0	
			TNDB 24C8 + RbOH				
25	2.9	4.2	5.8	7.0	8.4	0.55 ± 0.01	0.1 ± 0.2
30	3.8	5.8	7.7	9.6	11.6	0.78 ± 0.01	−0.1 ± 0.1
35	5.5	8.8	11.2	14.3	16.7	1.12 ± 0.03	0.1 ± 0.4
40	7.3	11.4	15.0	18.3	22.5	1.50 ± 0.02	−0.1 ± 0.2
45	9.6	15.2	20.6	26.2	31.2	2.17 ± 0.02	0.1 ± 0.3
	$\Delta H^{\neq}_{25}$ [kJmol^{-1}] = 51.1 ± 1.0		$-\Delta S^{\neq}_{25}$ [Jmol^{-1}deg^{-1}] =79 ± 3			$\Delta G^{\neq}_{25}$ [kJmol^{-1}] = 74.6 ± 1.0	
			TNDB 24C8 + CsOH				
25	2.7	3.3	4.8	6.0	7.1	0.46 ± 0.03	0.2 ± 0.3
30	3.5	5.2	6.8	8.6	10.3	0.68 ± 0.01	0.1 ± 0.1
35	5.1	7.8	10.2	12.7	15.4	1.02 ± 0.01	0.1 ± 0.1
40	7.4	11.3	14.7	18.7	22.5	1.50 ± 0.02	−0.1 ± 0.1
45	9.6	14.5	19.5	42.7	29.5	2.00 ± 0.02	−0.4 ± 0.1
	$\Delta H^{\neq}_{25}$ [kJmol^{-1}] = 56.4 ± 15		$-\Delta S^{\neq}_{25}$ [k Jmol]^{1}] =62 ± 5			$\Delta G^{\neq}_{25}$ [kJmol^{-1}] = 75.0 ± 1.5	

number of ions and negative hydration enthalpy), we observe a maximum for the free enthalpy of the activation and the largest negative value for the activation entropy describing the solvation effect.

All other reactions are also characterized by large negative values for the activation entropy. The ionic transition states of these reactions are more soluble than are the initial states. The energy barrier of the enthalpy of activation depends on the base used and upon solvation effects.

The results obtained show that the σ-complex formation process is strongly dependent on the ability of nitrophenyl crown ethers, to complex alkali metals cations. The facility of σ-complex formation increases for arrangements in which the cation is built into the crown ether structure and a hydroxyl group (OH^-) does not attack a neutral molecule, but does when the whole system is rendered positive by formation of a charged complex. The cation assisted mechanism is responsible for this process.

TABLE V Kinetic parameters (± standard deviation) for reaction between TNDB 30C10 and MOH in DMSO: water mixture (95 : 5 v/v)

Temp. °C			10^4k_{obs} [s^{-1}]				
Base concent.	0.0050 M	0.0075 M	0.100 M	0.0125 M	0.0150 M	10^2k [$M^{-1}s^{-1}$]	10^5int [s^{-1}]
			TNDB 24C8 + LiOH				
25	–	–	0.34	0.47	0.56	0.044 ± 0.005	−0.09 ± 0.06
40	–	–	0.50	0.64	0.75	0.050 ± 0.003	0.01 ± 0.04
60	–	–	0.63	0.77	0.93	0.03 ± 0.03	0.03 ± 0.03
	$\Delta H^{\neq}_{25}$ [kJmol^{-1}] = 3.0 ± 0.4		$-\Delta S^{\neq}_{25}$ [Jmol^{-1}deg^{-1}] =261 ± 1			$\Delta G^{\neq}_{25}$ [kJmol^{-1}] = 80.9 ± 0.4	
			TNDB 30C10 + NaOH				
25	1.9	2.7	3.7	4.5	5.4	0.35 ± 0.01	0.12 ± 0.07
30	4.2	6.5	8.6	11.0	12.9	0.88 ± 0.02	−0.12 ± 0.18
35	6.8	10.0	13.6	16.8	20.0	1.33 ± 0.02	0.16 ± 0.17
40	9.5	14.1	19.0	23.6	28.6	1.91 ± 0.02	−0.12 ± 0.16
45	12.1	19.0	26.4	32.5	39.7	2.75 ± 0.04	−1.50 ± 0.40
	$\Delta H^{\neq}_{25}$ [kJmol^{-1}] = 75.0 ± 9.5		$-\Delta S^{\neq}_{25}$ [Jmol^{-1}deg^{-1}] =46 ± 31			$\Delta G^{\neq}_{25}$ [kJmol^{-1}] = 76.2 ± 9.5	
			TNDB 30C10 + KOH				
25	2.0	2.7	4.5	5.5	6.2	0.45 ± 0.03	−0.4 ± 0.3
30	4.2	6.0	8.0	10.2	11.9	0.78 ± 0.17	0.2 ± 0.2
35	6.2	9.2	12.5	15.0	18.0	1.18 ± 0.03	0.4 ± 0.3
40	7.6	11.4	15.2	18.9	22.6	1.50 ± 0.01	0.1 ± 0.0
45	9.7	14.3	19.4	24.3	29.0	1.94 ± 0.02	0.0 ± 0.2
	$\Delta H^{\neq}_{25}$ [kJmol^{-1}] = 54.0 ± 5.5		$-\Delta S^{\neq}_{25}$ [Jmol^{-1}deg^{-1}] =69 ± 18			$\Delta G^{\neq}_{25}$ [kJmol^{-1}] = 74.8 ± 5.5	
			TNDB 30C10 + RbOH				
25	1.0	1.7	2.3	2.6	3.2	0.21 ± 0.02	0.21 ± 0.02
30	3.1	5.2	6.8	8.5	10.2	0.70 ± 0.02	−0.24 ± 0.20
35	5.6	8.6	11.3	14.0	16.6	1.09 ± 0.02	0.26 ± 0.18
40	7.8	11.6	15.6	19.2	23.1	1.53 ± 0.01	0.18 ± 0.13
45	11.3	15.4	20.6	25.4	30.8	1.96 ± 0.04	1.10 ± 0.50
	$\Delta H^{\neq}_{25}$ [kJmol^{-1}] = 74.0 ± 18		$-\Delta S^{\neq}_{25}$ [Jmol^{-1}deg^{-1}] =7 ± 59			$\Delta G^{\neq}_{25}$ [kJmol^{-1}] = 76.1 ± 18	
			TNDB 30C10 + CsOH				
25	2.2	3.5	4.5	5.5	6.2	0.40 ± 0.02	0.4 ± 0.3
30	2.6	4.2	5.6	7.0	8.5	0.58 ± 0.01	0.2 ± 0.1
35	3.2	5.3	7.0	8.9	11.6	0.81 ± 0.04	−0.9 ± 0.4
40	4.0	6.4	8.4	10.7	12.8	0.88 ± 0.13	−0.3 ± 0.2
45	5.0	8.2	11.0	13.5	16.5	1.13 ± 0.03	−0.5 ± 0.3
	$\Delta H^{\neq}_{25}$ [kJmol^{-1}] = 37.0 ± 4.4		$-\Delta S^{\neq}_{25}$ [Jmol^{-1}deg^{-1}] =128 ± 14			$\Delta G^{\neq}_{25}$ [kJmol^{-1}] = 75.2 ± 4.4	

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