R–O$_2$ bond strengths increase with the size (or perhaps the structure) of the R group, a trend that is suggested by our first two studies of these equilibria, but which is not predicted by group additivity concepts. These additional studies are in progress.

Complexation of *tert*-Butylammonium Perchlorate by Crown Ethers in Polar Solvents Studied by ¹H NMR Spectroscopy

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Abstract: Association constants of complexes of *tert*-butylammonium perchlorate and 1,3-xylyl-18-crown-5 and 18-crown-6 have been determined by ¹H NMR spectroscopy at various temperatures (240–306.5 K) and in different polar solvents (methanol-d_4, acetone-d_6, and acetonitrile-d_3). For 1,3-xylyl-18-crown-5 the association constants could be determined directly from the observed change of the chemical shifts of the *tert*-butyl protons at increasing crown ether concentration. On the other hand, the association constants with 18-crown-6 were deduced from chemical shift changes of the *tert*-butyl protons in a series of competition experiments. At similar conditions the association constants with 18-crown-6 were always found greater than for 1,3-xylyl-18-crown-5. In general the association constants increase from methanol < acetone < acetonitrile and at decreasing temperature. From this temperature dependence the thermodynamic values of enthalpy and entropy change ($\Delta H°$ and $\Delta S°$) upon complexation were derived. The kinetic stability of the complexes between *tert*-butylammonium perchlorate and 18-crown-6 in methanol, acetone, and acetonitrile and with 1,3-xylyl-18-crown-5 in acetone could also be determined at the coalescence temperature T_c. For 1,3-xylyl-18-crown-5·*tert*-butylammonium perchlorate in acetone at T_c = 183 K, the Gibbs free energy of activation was found to be ΔG^* = 8.8 kcal mol⁻¹. The change of kinetic stability of 18-crown-6·*tert*-butylammonium perchlorate in different solvents parallels the observed change of association constants.

Crown ethers can form complexes with inorganic and organic cations[1] and with neutral molecules.[2] Stabilities of these complexes may vary over a large range and depend on the nature of the guest, the nature of the host, and the solvent. To date the complexation of aryl- and alkylammonium salts by crown ethers in *apolar* solvents has been studied by Cram and co-workers,[3–6] Stoddart and co-workers,[7–9] Sutherland and co-workers,[10–13] Bradshaw and Baxter,[14] and de Jong and Reinhoudt.[15–17] Since the salts are sparingly soluble in apolar solvents, only indirect methods, e.g., extraction experiments,[3–6] or competition experiments[15–17] can be used. The disadvantage of the extraction method, however, is that for crown ethers with a cavity of ring size larger than 21 ring atoms, water can interfere in the complexation.[16] A ¹H NMR method has been developed to determine the association constant of the 1,3-xylyl-18-crown-5·*t*-BuNH$_3$PF$_6$ complex in a *homogeneous* chloroform phase using kinetic techniques.[15] This method is based on the fact that the rate of the exchange of *t*-BuNH$_3$PF$_6$ between the 1,3-xylyl-18-crown-5·*t*-BuNH$_3$PF$_6$ complex and the kinetically more stable 18-crown-6·*t*-BuNH$_3$PF$_6$ complex changes with variation in the concentration. These determinations are possible because of differences in the chemical shift of the *t*-Bu group in the two complexes. Combining these results with the independently determined *relative* association constants of the 18-crown-6·*t*-BuNH$_3$PF$_6$ and the corresponding 1,3-xylyl-18-crown-5 complex, the absolute association constant of the 18-crown-6 complex was determined.[17] In polar solvents such as methanol, in which the salts are soluble, the association constants of complexes between crown ethers and alkylammonium salts have been determined directly using calorimetry by Izatt et al.[18] They have studied the effect of the alkyl groups of the

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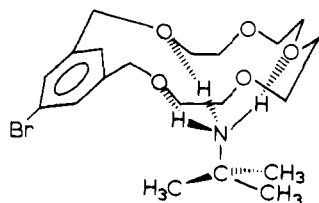
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Figure 1. A schematic representation of the molecular structure of the *p*-bromo-1,3-xylyl-18-crown-5·*t*-BuNH₃PF₆ complex deduced from X-ray diffraction data (see ref 19).

alkylammonium salts on the complexation with 18-crown-6 in methanol.

In our study a *direct* ^1H *NMR method* for the determination of association constants of crown ether complexes of ammonium salts is described that can be used in *polar* solvents. The association constants of the 1,3-xylyl-18-crown-5·*t*-BuNH₃ClO₄ complex are calculated *directly* from the chemical shift difference of the *t*-Bu group of the *salt* in the 1,3-xylyl-18-crown-5 *complex* and in the *free form*. Secondly, the determination of the kinetic stabilities in the same solvents is described. This allows for a correlation between kinetic and thermodynamic data.
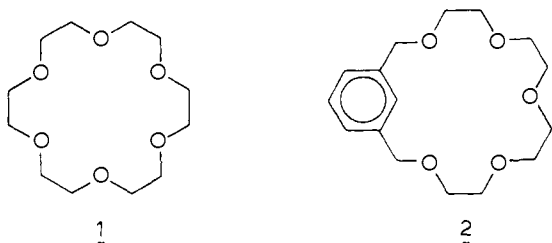
Results

All ^1H NMR spectra were recorded on a Bruker 80-MHz apparatus with a B-VT-1000 temperature accessor. The temperature was verified with a thermocouple. Me₄Si was used as the internal standard. 18-Crown-6 was prepared according to Johns et al.[19] The compound was purified by precipitation of the 18-crown-6/nitromethane (1:2) complex in diethyl ether/nitromethane (10:1 v/v) mixture. The pure compound was obtained by decomposition of the complex in vacuo and distillation under reduced pressure under nitrogen (yield 30%, mp 38–39 °C).

1,3-Xylyl-18-crown-5 was prepared according to Reinhoudt et al.[20] *t*-BuNH₃ClO₄ was prepared according to Kyba et al.[4]

1,3-Xylyl-18-crown-5·*t*-BuNH₃ClO₄. For a series of samples in which the salt concentration was approximately 0.1 M and the crown ether concentration varied from 0.0 to approximately 0.4 M, the chemical shift of the *t*-Bu group was determined at different temperatures. At each temperature the association constant was calculated by minimizing the function $F = \sum_i (\delta_{obsd,i} - X_{f,i}\delta_f - (1 - X_{f,i})\delta_c)^2$ for K and δ_c (see eq 1).

The *t*-Bu group of free *t*-BuNH₃ClO₄ shows an absorption of 109.1 Hz (δ 1.36 ppm) in the ^1H NMR spectrum in CD₃OD at 306.5 K. In the presence of 1,3-xylyl-18-crown-5 an upfield shift is observed, due to complexation of the salt by the crown ether. A similar effect has been observed in *t*-BuNH₃X complexation with 1,3-xylyl-18-crown-5 in chloroform.[3,15] The upfield shift has been attributed to the fact that in the complex the *t*-Bu group is located in the shielding zone of the aromatic nucleus of the crown ether. This interpretation is supported by X-ray analysis of *p*-bromo-1,3-xylyl-18-crown-5·*t*-BuNH₃PF₆.[21] A schematic representation of the structure of the complex is given in Figure 1. The chemical shifts of the *t*-Bu group of a number of mixtures with different ratios of crown ether and salt concentrations and at various temperatures are shown in Figure 2. As can be seen at lower temperatures as well as upon addition of more crown

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Table I. Association Constants of the 1,3-Xylyl-18-crown-5·*t*-BuNH₃ClO₄ Complex in CD₃OD at Different Temperatures

T (K)	K (L mol⁻¹)^a	δ_f (Hz)^b	δ_c (Hz)^c
306.5	3.8	109.1	67.6
291.0	5.8	108.6	66.5
276.0	8.5	107.9	64.7
260.5	12.4	107.2	62.3
240.0	22.7	106.2	60.7

^{a}Accuracy ±5%. ^{b}Chemical shift of the *t*-Bu group of free *t*-BuNH₃ClO₄ as determined. ^{c}Chemical shift of the *t*-Bu group of 1,3-xylyl-18-crown-5·*t*-BuNH₃ClO₄ as calculated.

Table II. Association Constants of the 1,3-Xylyl-18-crown-5·*t*-BuNH₃ClO₄ Complex in Acetone-d_6 at Different Temperatures

T (K)	K (L mol⁻¹)^a	δ_f (Hz)^b	δ_c (Hz)^c
306.5	51	123.5	73.9
291.0	78	123.5	71.9
276.0	118	123.3	69.7
260.5	171	123.5	68.2
240.0	240	123.3	66.8

^{a}Accuracy ±5%. ^{b}Chemical shift of the *t*-Bu group of free *t*-BuNH₃ClO₄ as determined. ^{c}Chemical shift of the *t*-Bu group of 1,3-xylyl-18-crown-5·*t*-BuNH₃ClO₄ as calculated.

Table III. Association Constants of the 1,3-Xylyl-18-crown-5·*t*-BuNH₃ClO₄ Complex in CD₃CN at Different Temperatures

T (K)	K (L mol⁻¹)^a	δ_f (Hz)^b	δ_c (Hz)^c
306.5	65	109.6	64.3
291.0	84	109.5	63.0
276.0	105	108.7	61.9
260.5	127	108.2	60.9
240.0	162	107.5	59.9

^{a}Accuracy ±5%. ^{b}Chemical shift of the *t*-Bu group of free *t*-BuNH₃ClO₄ as determined. ^{c}Chemical shift of the *t*-Bu group of 1,3-xylyl-18-crown-5·*t*-BuNH₃ClO₄ as calculated.

ether, a larger upfield shift was observed that can be attributed in both cases to an increased association. The observed chemical shift of the *t*-Bu group in all the samples is the weighted average of the chemical shift of free *t*-BuNH₃ClO₄ and the chemical shift of the *t*-Bu group in the crown ether complex (eq 1) under conditions of fast exchange on the NMR time scale:

$$\delta_{obsd} = X_f\delta_f + (1 - X_f)\delta_c \qquad (1)$$

where δ_{obsd} = observed chemical shift of the *t*-Bu group, δ_f = chemical shift of the *t*-Bu group of free *t*-BuNH₃ClO₄, δ_c = chemical shift of the *t*-Bu group in the 1,3-xylyl-18-crown-5 complex, and $X_f = [t\text{-BuNH}_3\text{ClO}_4]/[t\text{-BuNH}_3\text{ClO}_4]_0$. When the host and guest are present in a 1:1 ratio at 306.5 K, the chemical shift is approximately 99 Hz, while for a ratio of 4:1 (crown ether: salt) a chemical shift of about 85 Hz was observed. This indicates that the 1:1 complex of 1,3-xylyl-18-crown-5·*t*-BuNH₃ClO₄ at 306.5 K is considerably dissociated in CD₃OD.

The calculated association constants and calculated chemical shifts of the *tert*-butyl hydrogen atoms in the complexed form (δ_c) are given in Table I. As expected, a decrease in temperature results in an increased association constant.

From a plot of ln K *vs.* T^{-1} (Figure 3) the enthalpy and entropy of complexation were determined using the equation:
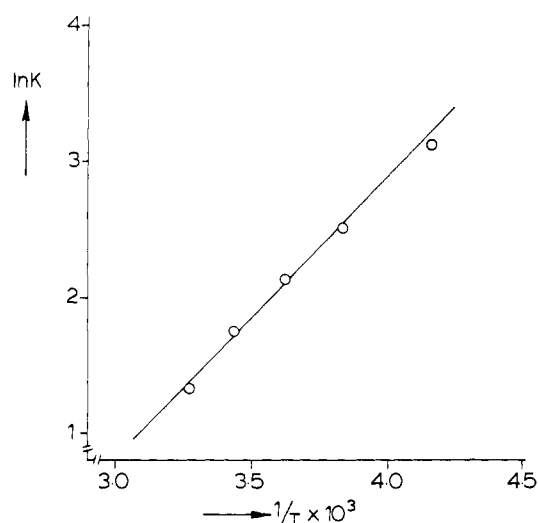
$$\ln K = \Delta S°/R - \Delta H°/RT \qquad (2)$$

The same experiments were performed in acetone-d_6 and acetonitrile-d_3. The association constants of 1,3-xylyl-18-crown-5 with *t*-BuNH₃ClO₄ in CD₃COCD₃ and CD₃CN are presented in Tables II and III, respectively. These constants are considerably larger in these solvents than in methanol. The calculated enthalpy and entropy of formation are summarized in Table IV.

18-Crown-6·*t*-BuNH₃ClO₄. The association constants of *t*-BuNH₃ClO₄ and 18-crown-6 have been determined in a compe-
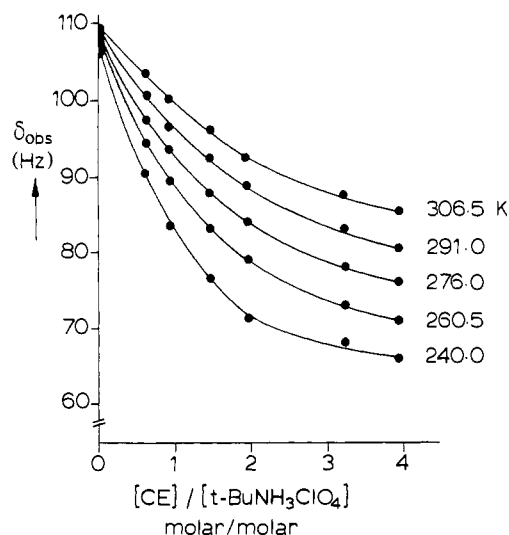
Figure 2. Observed chemical shifts of the *t*-Bu group of a solution of *t*-BuNH₃ClO₄ and 1,3-xylyl-18-crown-5 in CD₃OD at different temperatures as a function of the crown ether:salt ratio. [*t*-BuNH₃ClO₄] = 0.103 mol L⁻¹ and [1,3-xylyl-18-crown-5] = 0.094–0.404 mol L⁻¹.

Figure 3. Plot of ln *K* vs. T^{-1} for the 1,3-xylyl-18-crown-5·*t*-BuNH₃ClO₄ complex in CD₃OD.

Table IV. Enthalpy and Entropy of Formation of the 1,3-Xylyl-18-crown-5·*t*-BuNH₃ClO₄ and the 18-Crown-6·*t*-BuNH₃ClO₄ Complexes in Different Solvents

solvent	1,3-xylyl-18-crown-5		18-crown-6	
	$\Delta H°$ (kcal/mol)	$\Delta S°$ (cal/mol K)	$\Delta H°$ (kcal/mol)	$\Delta S°$ (cal/mol K)
CD₃OD	−4.0 ± 0.2	−10.5 ± 0.7	−4.6 ± 0.3	−3.9 ± 0.7
(CD₃)₂C=O	−3.4 ± 0.4	−3.0 ± 1.3	−5.4 ± 0.5	−0.7 ± 1.7
CD₃CN	−2.0 ± 0.2	2.0 ± 0.6	−1.6 ± 0.2	10.7 ± 2.0

tition experiment with 1,3-xylyl-18-crown-5 under conditions of neglible free salt concentrations.

When 18-crown-6 was added to a 0.1 M solution of *t*-BuNH₃ClO₄ in methanol-d_4, a downfield shift of the absorption of the *t*-Bu group was observed. At lower temperatures (276, 260.5, 240 K) the chemical shift did not change any more when approximately a 1:1 ratio of 18-crown-6 and *t*-BuNH₃ClO₄ was reached. At higher temperatures (306.5, 291 K) an excess of crown ether (threefold) was needed to reach this point. This means that at a 1:1 ratio the complex is partly dissociated at these temperatures. This limiting value corresponds with the chemical shift of the *t*-Bu group in the 18-crown-6·*t*-BuNH₃ClO₄ complex. The chemical shifts of the *t*-Bu group in the 18-crown-6·*t*-BuNH₃ClO₄ complex in methanol-d_4, acetone-d_6, and aceto-

Table V. Chemical Shifts of the *t*-Bu Group of *t*-BuNH₃ClO₄ (δ_f)[a] and of the *t*-Bu Group of the 18-Crown-6·*t*-BuNH₃ClO₄ Complex (δ_c)[a] in Different Solvents at Different Temperatures

solvent		temp (K)				
		306.5	291.0	276.0	260.5	240.0
CD₃OD	δ_f	109.1	108.6	107.9	107.2	106.2
	δ_c	112.1	111.8	111.3	110.1	110.8
(CD₃)₂C=O	δ_f	123.5	123.5	123.3	123.5	123.3
	δ_c	115.0	114.8	114.5	114.5	114.5
CD₃CN	δ_f	109.6	109.5	108.7	108.2	107.5
	δ_c	108.6	108.4	108.2	108.2	107.9

[a] In Hz.

nitrile-d_3 are presented in Table V. In acetone and acetonitrile contrary to methanol an upfield shift was observed. It can be seen that the difference between the chemical shift of the *t*-Bu group in the free form and the complexed form decreases in the order acetone > methanol > acetonitrile. For all the solvents, however, the differences were found to be too small for obtaining reliable association constants.

On the other hand, the difference between the chemical shift of the *t*-Bu group in 1,3-xylyl-18-crown-5·*t*-BuNH₃ClO₄ and in 18-crown-6·*t*-BuNH₃ClO₄ is considerable in all the solvents. This observation can be used for the determination of the association constants and the thermodynamic parameters of the 18-crown-6·*t*-BuNH₃ClO₄ complex *by a competition method*. We have used a similar competition method before[17] to determine the association constants of *t*-BuNH₃PF₆ with a series of crown ethers relative to 1,3-xylyl-18-crown-5 in the apolar solvent chloroform.

In a representative competition experiment 18-crown-6 and 1,3-xylyl-18-crown-5 competed for complexation with *t*-BuNH₃ClO₄. The total crown ether concentration was kept larger than the total salt concentration in order to make the free salt concentration negligible. Consequently the observed chemical shift of the *t*-Bu group is the weighted average value of the salt in the 18-crown-6 complex and in the 1,3-xylyl-18-crown-5 complex under conditions of fast exchange.

$$\delta_{obsd} = X_{18C6}\delta_{18C6} + X_{1,3X18C5}\delta_{1,3X18C5} \tag{3a}$$

$$X_{18C6} = (\delta_{obsd} - \delta_{1,3X18C5})/(\delta_{18C6} - \delta_{1,3X18C5}) \tag{3b}$$

where δ_{obsd} = observed chemical shift of the *t*-Bu group, δ_{18C6} = chemical shift of the *t*-Bu group of 18-crown-6·*t*-BuNH₃ClO₄, $\delta_{1,3X18C5}$ = chemical shift of the *t*-Bu group of 1,3-xylyl-18-crown-5·*t*-BuNH₃ClO₄, X_{18C6} = [18-crown-6·*t*-BuNH₃ClO₄]/[*t*-BuNH₃ClO₄]₀, and $X_{1,3X18C5}$ = [1,3-xylyl-18-crown-5·*t*-BuNH₃ClO₄]/[*t*-BuNH₃ClO₄]₀ = 1 − X_{18C6}.

From the observed chemical shift it is possible to calculate the concentrations of the complexes of *t*-BuNH₃ClO₄ with 18-crown-6 and 1,3-xylyl-18-crown-5. With these concentrations the free crown ether concentrations and the relative association constant, as defined in eq 4, can be calculated. From the relative association constant and the known association constant of the 1,3-xylyl-18-crown-5·*t*-BuNH₃ClO₄ complex (vide supra) the association constant of the 18-crown-6·*t*-BuNH₃ClO₄ complex was calculated.

$$K_{rel} = K_{18C6}/K_{1,3X18C5} =$$
$$\frac{[18\text{-crown-6·}t\text{-BuNH}_3\text{ClO}_4][1,3\text{-xylyl-18-crown-5}]}{[18\text{-crown-6}][1,3\text{-xylyl-18-crown-5·}t\text{-BuNH}_3\text{ClO}_4]} \tag{4}$$

where K_{rel} = relative association constant, K_{18C6} = association constant of the 18-crown-6·*t*-BuNH₃ClO₄ complex, and $K_{1,3X18C5}$ = association constant of the 1,3-xylyl-18-crown-5·*t*-BuNH₃ClO₄ complex.

The observed chemical shift of the *t*-Bu group of *t*-BuNH₃ClO₄ in a methanol-d_4 solution at 306.5 K containing *t*-BuNH₃ClO₄ (0.103 mol L⁻¹), 1,3-xylyl-18-crown-5 (0.404 mol L⁻¹), and 18-crown-6 (0.158 mol L⁻¹) was found to be 108.4 Hz. This indicates that the association constant of the 18-crown-6·*t*-BuNH₃ClO₄ complex must be larger than K_a of the corresponding 1,3-xylyl-18-crown-5 complex. The observed chemical shift is almost equal to the chemical shift of the *t*-Bu group of the 18-crown-6·*t*-

Table VI. Association Constants of the 18-Crown-6·*t*-BuNH$_3$ClO$_4$ Complex in Different Solvents at Different Temperatures

|	K (L mol^{-1})^a		
T (K)	CD$_3$OD	(CD$_3$)$_2$C=O	CD$_3$CN
306.5	260	4450	2950
291.0	370	8000	3500
276.0	620	14000	4300
260.5	960	21000	4700

^{a}Accuracy ±15%.

BuNH$_3$ClO$_4$ complex, even though an excess of 1,3-xylyl-18-crown-5 was present in solution. According to eq 3 the concentrations of the species present were calculated: [18-crown-6·*t*-BuNH$_3$ClO$_4$] = 0.0942 mol L^{-1}, [18-crown-6] = 0.0641 mol L^{-1}, [1,3-xylyl-18-crown-5·*t*-BuNH$_3$ClO$_4$] = 0.0085 mol L^{-1}, and [1,3-xylyl-18-crown-5] = 0.396 mol L^{-1}. This gave a relative association constant of 68 and an association constant of 260 L mol^{-1} for the 18-crown-6·*t*-BuNH$_3$ClO$_4$ complex.

In acetone-d_6 a larger relative association constant was found at 306.5 K, K_{rel} = 87, whereas in acetonitrile-d_3 a smaller relative association constant was found, K_{rel} = 45. The results of the determinations of the association constants of 18-crown-6 with *t*-BuNH$_3$ClO$_4$ in methanol-d_4, acetone-d_6, and acetonitrile-d_3 at different temperatures are presented in Table VI, and the values of the enthalpy and entropy of complex formation are given in Table IV.

**Kinetic Stabilities of the 18-Crown-6·*t*-BuNH$_3$ClO$_4$ and the 1,3-Xylyl-18-crown-5·*t*-BuNH$_3$ClO$_4$ Complexes in Polar Solvents.** In the experiments for the determination of the association constants and thermodynamic parameters described above, the exchange of *t*-BuNH$_3$ClO$_4$ between the free salt and the 1,3-xylyl-18-crown-5·*t*-BuNH$_3$ClO$_4$ complex, between the free salt and the 18-crown-6·*t*-BuNH$_3$ClO$_4$ complex, and between the two complexes was fast on the ^{1}H NMR time scale. However, in a few cases, lowering of the temperature revealed line-broadening of both the *t*-Bu group and the NH$_3$ group, indicating a slow exchange between the mentioned sites on the ^{1}H NMR time scale. If a solution of *t*-BuNH$_3$ClO$_4$ and 18-crown-6 in acetone-d_6 in a 2:1 ratio was lowered in temperature, a line-broadening of the absorptions of both the *t*-Bu group and the NH$_3$ group was observed (Figure 4). When the temperature was further lowered, two absorptions at 122.3 and 114.7 Hz, corresponding to the *t*-Bu group in free *t*-BuNH$_3$ClO$_4$ and the 18-crown-6·*t*-BuNH$_3$ClO$_4$ complex, respectively, and two absorptions at 8 and 7 ppm, corresponding to the free NH$_3$ group and the complexed NH$_3$ group, respectively, were observed. The free energy of activation ($\Delta G^{\ddagger}$) of the exchange process, as described by eq 5, was calcu-

18-crown-6·*t*-BuNH$_3$ClO$_4$ + *t*-BuNH$_3$ClO$_4$* $\rightleftarrows$
    18-crown-6·*t*-BuNH$_3$ClO$_4$* + *t*-BuNH$_3$ClO$_4$ (5)
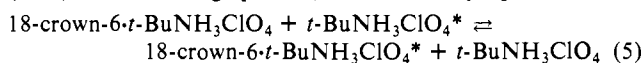
lated at the coalescence temperature (221 K) of the *t*-Bu probe by the use of eq 6 to give $\Delta G^{\ddagger}$ = 11.5 kcal/mol.

The same phenomena were observed for a solution of *t*-BuNH$_3$ClO$_4$ and 1,3-xylyl-18-crown-5 in a 2:1 ratio in acetone-d_6 (Figure 5). However, in that case coalescence was observed at a much lower temperature, 183 K. Even at 175 K the absorptions of the *t*-Bu group in the free and complexed state were still not completely separated, and for this reason an accurate $\Delta G^{\ddagger}$ value at the coalescence temperature could not be determined. Subsequently a solution containing *an excess* of 1,3-xylyl-18-crown-5 was lowered in temperature. Under these conditions at lower temperature the fraction of associated *t*-BuNH$_3$ClO$_4$ increases as shown by the appearance of only one absorption at 65.7 Hz from 203 to 178 K for the *t*-Bu group of the salt. This value corresponds to the chemical shift of the *t*-Bu group in the 1,3-xylyl-18-crown-5·*t*-BuNH$_3$ClO$_4$ complex. Independently the chemical shift of the *t*-Bu group of a solution of the free salt was shown to be 122.8 Hz at 183 K. Using these data a free energy of activation of exchange at the coalescence temperature could be calculated according to eq 6^{22,23} ($\Delta G^{\ddagger}$ = 8.8 kcal/mol). Also

$$\Delta G^{\ddagger} = 4.57 T_c (9.97 + \log (T_c/\Delta \nu)) \text{ cal/mol} \qquad (6)$$
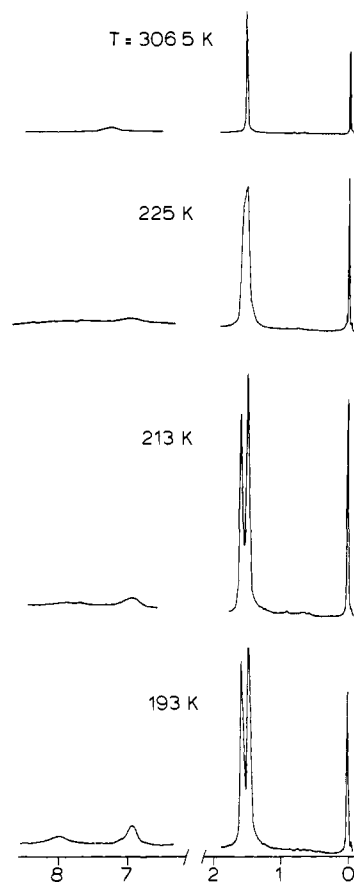
Figure 4. Temperature-dependent ^{1}H NMR spectra of 18-crown-6 (0.1 mol L^{-1}) and *t*-BuNH$_3$ClO$_4$ (0.2 mol L^{-1}) in acetone-d_6.
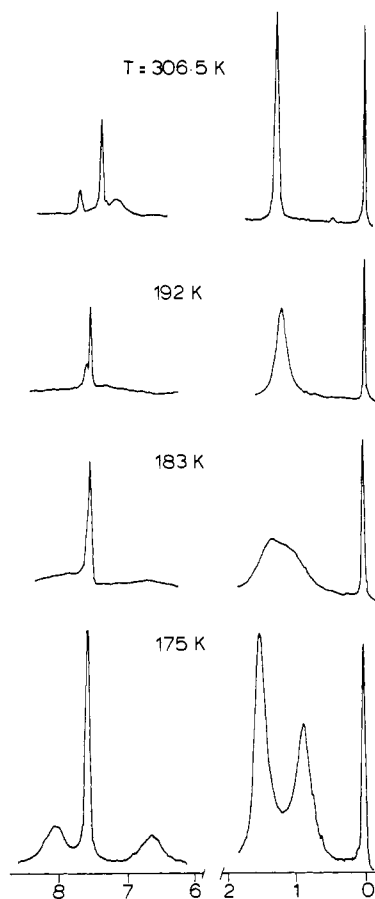
Figure 5. Temperature-dependent ^{1}H NMR spectra of 1,3-xylyl-18-crown-5 (0.1 mol L^{-1}) and *t*-BuNH$_3$ClO$_4$ (0.2 mol L^{-1}) in acetone-d_6.

Table VII. $\Delta G^{\ddagger}$ Values of the Exchange of *t*-BuNH₃ClO₄ of the Complexes in Different Solvents at the Coalescence Temperatures
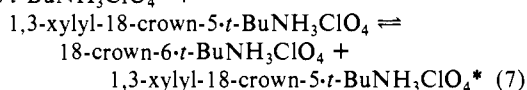
solvent	18-crown-6 $\Delta G^{\ddagger}_d$ (T_c (K))	1,3-xylyl-18-crown-5 $\Delta G^{\ddagger}$ (T_c (K))
CD₃OD	10.3 (211)	
(CD₃)₂C=O	11.5 (221)	8.8 (183)
CD₃CN	11.0 (227)	

in this case line-broadening of the NH₃ moiety and finally two separate absorptions of the NH₃ group at 8.0 and 6.6 ppm for the free and complexed form, respectively, were observed when the temperature was lowered (compare with Figure 5).[25]
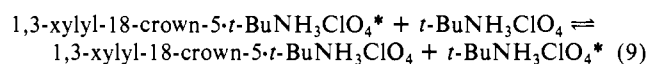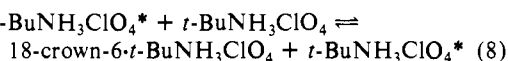
In methanol and acetonitrile the free energy of activation of exchange of *t*-BuNH₃ClO₄ between the free state and the complexed state could not be determined. In the case of 18-crown-6 the difference between the chemical shifts of the *t*-Bu group of the free and complexed form is too small, while in the case of 1,3-xylyl-18-crown-5 at the lowest possible temperature the exchange is still fast on the ¹H NMR time scale.

This problem was circumvented in the case of 18-crown-6 using a *kinetic competition* experiment using a kinetically less stable complex as a source of salt.[26] When the temperature of a solution of *t*-BuNH₃ClO₄ (0.10 mol L⁻¹), 1,3-xylyl-18-crown-5 (0.25 mol L⁻¹), and 18-crown-6 (0.05 mol L⁻¹) in methanol-*d₄* was lowered, line-broadening of the absorption of the *t*-Bu group was observed. Further lowering of the temperature to 190 K resulted in two separate signals of the *t*-Bu group, one for the 18-crown-6 complex (106.2 Hz) and one for the 1,3-xylyl-18-crown-5 complex (60.1 Hz). Coalescence was observed at 211 K. At this temperature a free energy of activation of exchange of *t*-BuNH₃ClO₄ was calculated using eq 6: $\Delta G^{\ddagger}$ = 10.3 kcal/mol. In the same way a $\Delta G^{\ddagger}$ = 11.0 kcal/mol was calculated for the exchange in acetonitrile (coalescence temperature was 227 K and $\Delta\nu$ = 47 Hz).

The overall exchange as observed in the competition experiment is described by eq 7, which is a combination of two equilibria (eq

18-crown-6·*t*-BuNH₃ClO₄* +

    1,3-xylyl-18-crown-5·*t*-BuNH₃ClO₄ ⇌

        18-crown-6·*t*-BuNH₃ClO₄ +

            1,3-xylyl-18-crown-5·*t*-BuNH₃ClO₄*   (7)

8 and 9). Equation 9 describes the exchange of the salt between

18-crown-6·*t*-BuNH₃ClO₄* + *t*-BuNH₃ClO₄ ⇌

    18-crown-6·*t*-BuNH₃ClO₄ + *t*-BuNH₃ClO₄*   (8)

1,3-xylyl-18-crown-5·*t*-BuNH₃ClO₄* + *t*-BuNH₃ClO₄ ⇌

    1,3-xylyl-18-crown-5·*t*-BuNH₃ClO₄ + *t*-BuNH₃ClO₄*   (9)

the free state and the 1,3-xylyl-18-crown-5 complex. Because this process is still fast on the ¹H NMR time scale (vide supra) in both methanol and acetonitrile, the exchange of the salt as described by eq 8 is the rate-determining step in the overall exchange process. The $\Delta G^{\ddagger}$ of this process can thus entirely be attributed to the exchange process of *t*-BuNH₃ClO₄ in the free state and the 18-

crown-6 complex. The $\Delta G^{\ddagger}$ values of exchange of *t*-BuNH₃ClO₄ for the different complexes are summarized in Table VII.

Discussion

From the obtained results a number of conclusions can be drawn. Firstly, in all the solvents studied both the thermodynamic and kinetic stability of the 18-crown-6·*t*-BuNH₃ClO₄ complex is larger than that for the corresponding 1,3-xylyl-18-crown-5 complex, as was also found for *t*-BuNH₃X salts in chloroform.[3] The lack of one oxygen–ammonium electrostatic interaction in the 1,3-xylyl-18-crown-5 complex compared with the 18-crown-6 complex is the possible origin of the observations. The thermodynamic stabilities of both complexes in the three solvents decreases in the order acetone > acetonitrile > methanol at $T <$ 276 K. At $T > 291$ K the order of acetonitrile and acetone is reversed for the complexation of *t*-BuNH₃ClO₄ with 1,3-xylyl-18-crown-5. From the $\Delta H°$ and $\Delta S°$ contribution to the $\Delta G°$ it can be concluded that both complexes are enthalpy stabilized in the solvents studied (Table IV). In methanol and acetone the overall $\Delta S°$ is negative, as expected for a complexation process. However, in acetonitrile a *positive* $\Delta S°$ has been measured. This observation strongly indicates significant solvent reorganization upon complex formation. Compared to the other two solvents, the enthalpy of complex formation is smaller in this case. This effect is more pronounced for the 18-crown-6·*t*-BuNH₃ClO₄ complex than for the 1,3-xylyl-18-crown-5·*t*-BuNH₃ClO₄ complex.

For the $\Delta S°$ of complexation, besides the entropy change upon bringing two components together, mainly two other contributions are responsible: firstly, desolvation of the components prior to complexation; secondly, conformational change of the crown ether prior to complexation. Because the desolvation of *t*-BuNH₃ClO₄ involved in the formation of both the complexes will be the same, the less favorable entropy change for the 1,3-xylyl-18-crown-5·*t*-BuNH₃ClO₄ complex probably can be attributed to the conformational change of 1,3-xylyl-18-crown-5 prior to complexation. This applies for all the solvents studied. Therefore, the entropy change of formation is always relatively in favor of the 18-crown-6·*t*-BuNH₃ClO₄ complex.

Compared with the enthalpy change in acetone and methanol, the enthalpy change in acetonitrile is considerably lower for both complexes. The difference is greater for the 18-crown-6 complex than for the 1,3-xylyl-18-crown-5 complex. A possible explanation for this observation might be the fact that 18-crown-6 can form a complex with acetonitrile via hydrogen bonds.[2] This means that these bonds have to be broken before *t*-BuNH₃ClO₄ can complex with 18-crown-6, resulting in a reduction of the overall enthalpy change of complexation.

The kinetic stability of the 18-crown-6·*t*-BuNH₃ClO₄ complex could be determined in all the solvents. The kinetic stabilities of the complex in the different solvents decreases in the order acetone > acetonitrile > methanol, which is the same order as is found for the thermodynamic stability at $T < 276$ K. The kinetic stability of the 1,3-xylyl-18-crown-5·*t*-BuNH₃ClO₄ complex could only be determined in acetone. This complex is 2.7 kcal/mol kinetically less stable than the corresponding 18-crown-6 complex. In acetonitrile and methanol the complex is kinetically less stable (in any case less than 10.9 and 8.4 kcal/mol, respectively). The data show that a thermodynamic more stable complex is also kinetically more stable.

The results presented in this study clearly show that the ¹H NMR spectroscopy can be a valuable tool for the determination of both the thermodynamic and kinetic stabilities of complexes of crown ethers where substantial changes of the chemical shifts of either the guest or the crown ether are observed upon complexation.

(22) Günther, H. "NMR Spektroscopie"; Thieme Verlag: Stuttgart, 1973; p 248.

(23) For the decomplexation of the 1,3-xylyl-18-crown-5-*t*-BuNH₃ClO₄ complex in CD₂Cl₂,[1,15-17] we have determined recently that the $\Delta G^{\ddagger}$ value at coalescence temperature (217 K) calculated from eq 6 ($\Delta G^{\ddagger}$ = 11.8 ± 0.4 kcal mol⁻¹) is not different with the experimental error from the value calculated from the $\Delta H^{\ddagger}$ = 19.2 kcal mol⁻¹ and $\Delta S^{\ddagger}$ = 37 cal mol⁻¹ K⁻¹ values that are obtained from a full-line-shape analysis.[24]

(24) (a) Sutherland, I. O. "Annual Reports on NMR Spectroscopy"; Mooney, E. F., Ed.; Academic Press: London, 1971; Vol. 4. (b) Binsch, G., *Top. Stereochem.* **1968,** *3,* 97. (c) de Boer, J. A. A., Ph.D. Thesis, Twente University of Technology, 1984.

(25) It was also observed that at these low temperatures the absorption of the ArCH₂ group is no longer a singlet but an AB quartet due to the lowering of the rate of exchange of the *t*-BuNH₃⁺ group at either side of the crown ether. This phenomenon is usually interpreted in the literature as slow "back to face" exchange.

(26) de Jong et al.[15] have used this method to study the kinetics of the 18-crown-6-*t*-BuNH₃PF₆ complex in chloroform.