KINETICS AND MECHANISM OF COMPLEXATION

BETWEEN TERT-BUTYLAMMONIUM HEXAFLUOROPHOSPHATE AND 18-CROWN-6

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The thermodynamic stability of crown ether complexes has been the subject of numerous investigations[1]. In contrast, information about the kinetic stability is scarce and mostly restricted to alkali cation complexes in polar solvents[2]. Since, however, the catalytic activity of crown ethers is most pronounced in apolar solvents[3], we have developed a method to study the kinetics of complexation in apolar media.

The method is based on the observation that the exchange of $t-BuNH_3PF_6$ between any two crown ethers, which is fast on the NMR time scale at room temperature[4], becomes sufficiently slow on cooling to produce line broadening and peak separation of the tert-butyl signal in the ^{1}H NMR spectrum. The tert-butyl groups are present in three different species: complexed with crown ether I (I.AM), with crown ether II (II.AM), and in free $t-BuNH_3PF_6$ (AM), the latter in undetectably low concentration.

$$\text{I. AM} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{I + AM} \qquad K_1 = \frac{k_{-1}}{k_1} \qquad\qquad (1)$$

$$\text{II. AM} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{II + AM} \qquad K_2 = \frac{k_{-2}}{k_2} \qquad\qquad (2)$$

When the pair of complexes is chosen in such a way that one complex (e.g. I.AM) is kinetically much more stable than the other (II.AM), the exchange between I.AM and free salt is rate determining for the overall salt exchange between the complexes, and the simple, two-site line-shape equations can be used to determine the exchange rates[5].

In this paper we will illustrate the method by the exchange of $t-BuNH_3PF_6$ between the complexes of 18-crown-6 (I, kinetically stable, $\delta_{Bu} = 1.356$) and crown ether II (kine-

tically less stable[6], δ_{Bu} = 0.825):

I   II

The lifetimes (τ) were determined from the line broadening for various concentrations between +40 and -25 ^{O}C. Experimentally we found that the reciprocal lifetime of the I.AM species was given by

$$\tau^{-1}_{I.AM} = k_1 + k_3 \, [AM] . \tag{3}$$

The dependence on the concentration of free salt (equations (5) and (6), below) indicates that, in addition to the exchange reactions (1) and (2), there is an important contribution by the bimolecular exchange between free salt and the 18-crown-6 complex:

$$I.AM + AM^* \xrightarrow{k_3} I.AM^* + AM . \tag{4}$$

The rate constants k_1 and k_3 were obtained from two series of experiments:

(i) With chloroform solutions containing the complexes I.AM and II.AM only[7], the concentration of free salt is (since $K_1 \gg K_2$)[4] approximated by

$$[AM] = \{[\,II.AM]\,/K_2\}^{\frac{1}{2}} . \tag{5}$$

From a plot of $\tau^{-1}_{I.AM}$ against $II.AM^{\frac{1}{2}}$ (Fig. 1) we obtain k_1 by extrapolation to [II.AM] = 0, while the slope yields $k_3/\sqrt{K_2}$.

(ii) With chloroform solutions containing an excess of free II ($[II]_e$) in addition to the complexes, the free salt concentration is approximated by

$$[AM] = \frac{[\,II.AM]}{K_2[II]_e} . \tag{6}$$

From a plot of $\tau^{-1}_{I.AM}$ against $[II.AM]/[II]_e$ (Fig. 1) we obtain k_1 by extrapolation to $[II.AM]/[II]_e$ = 0, while the slope gives k_3/K_2. The results obtained at 20 ^{O}C (Fig. 1) show that the k_1 values found by procedures (i) and (ii) are identical within experimental error.
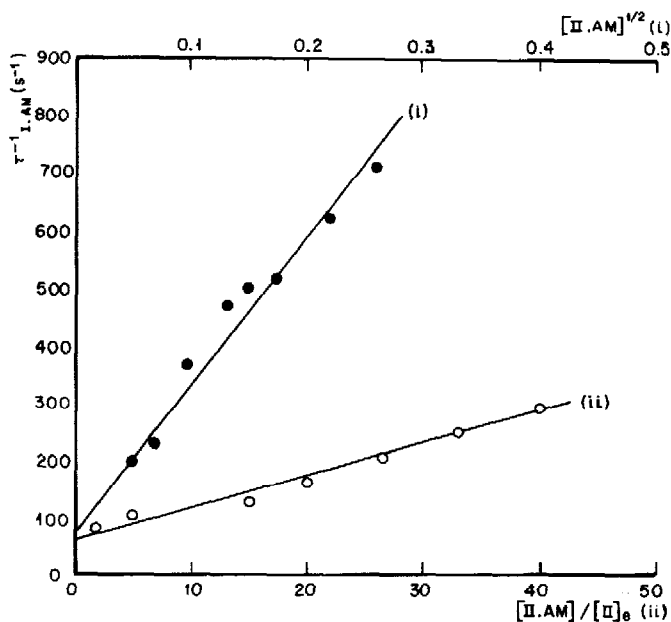
FIGURE 1
DEPENDENCE OF $\tau^{-1}{}_{I.AM}$ ON CONCENTRATION

The decomplexation of the $t\text{-}BuNH_3PF_6$ complex of 18-crown-6 is a fairly slow process ($k_1 = 70$ s^{-1} at 20 °C) with a high energy of activation ($E_a = 20.4 \pm 1$ kcal/mol).

From the slope values k_3/K_2 and $k_3/\sqrt{K_2}$, we calculated the association constant for crown ether II: $K_2 = 2.2 \times 10^5$ M^{-1} at 20 °C. Using the ratio $K_1/K_2 = 106$ previously determined[4], we obtained a value of $K_1 \approx 2.3 \times 10^7$ M^{-1} for the association constant of 18-crown-6 and $t\text{-}BuNH_3PF_6$. Combined with the rate of decomplexation this yields a complexation rate $k_{-1} = 1.6 \times 10^9$ s^{-1}, which means that the rate of complex formation is diffusion controlled.

The characteristics of the bimolecular exchange reaction are indicative of a complexation reaction: a high rate ($k_3 = 1.3 \times 10^6$ M^{-1}s^{-1} at 20 °C) and a low activation energy ($E_a = 8.1 \pm 1$ kcal/mol). It is most likely that the reaction rate k_3 reflects the formation of a 1:2 complex, an obvious intermediate[8] in the bimolecular exchange.

$$I.AM + AM^* \rightleftharpoons AM^*.I.AM \rightleftharpoons I.AM^* + AM \tag{7}$$

It is interesting to note that the bimolecular exchange according to reaction (8)

$$I.AM + II \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} II.AM + I \tag{8}$$

only becomes apparent at a relatively high concentration of II ($k_4 \approx 10^3$ M^{-1}s^{-1} at 20 $^{\circ}$C).

Our results demonstrate that <u>both</u> <u>kinetic</u> and <u>thermodynamic</u> data of crown ether complexes in apolar solvents can be obtained from simple ^{1}H NMR measurements. The reliability of this method is further illustrated by the fact that the rate of decomplexation of 18-crown-6 was independent of the choice of the weaker complex. When II.AM was replaced by the corresponding complex of dibenzo-18-crown-6, the same rate and activation parameters were obtained. We have successfully used this method to study the relationship between structure and kinetics of complexation for a series of crown ethers[9].

REFERENCES AND FOOTNOTES

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4. F. de Jong, D.N. Reinhoudt, and C.J. Smit, <u>Tetrahedron Letters</u> <u>1976</u> 1375.

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6. This has been confirmed by the independent determination of the rate of decomplexation of II[9].

7. The complexes were prepared by equilibrating 1 ml of the crown ether solution in chloroform (0.2 M) with three successive 3-ml portions of an aqueous solution of t-BuNH$_3$Cl (1.0 M) and LiPF$_6$ (1.0 M), and precipitating the complex with an excess of ether.

8. This type of 1:2 complex is exclusively formed when an excess of solid t-BuNH$_3$SCN is added to an 18-crown-6 solution in chloroform[9].

9. F. de Jong and D.N. Reinhoudt, to be published.