

Table VII

solution complexes	pH range in which each com- plex prevails	solid complexes	pH for- mation value
$\text{Cu}(\text{TsglyH})_2$	$5 \leq \text{pH} \leq 7.5$	$\text{Cu}(\text{TsglyH})_2 \cdot 4\text{H}_2\text{O}$	$\text{pH} < 5$
$[\text{Cu}(\text{Tsgly})(\text{OH})]^-$	$8 \leq \text{pH} \leq 10$	$[\text{Cu}(\text{Tsgly})(\text{H}_2\text{O})_3]$	$\text{pH} > 5$
$[\text{Cu}(\text{Tsgly})(\text{OH})_2]^{2-}$	$8 \leq \text{pH} \leq 13$		
$[\text{Cu}(\text{Tsgly})_2(\text{OH})_2]^{4-}$	$10 \leq \text{pH} \leq 13$	$\text{K}_2[\text{Cu}(\text{Tsgly})_2]$	$\text{pH} > 10$

complexes are prevalent. The stability constant values of these last two complexes, very similar to one another, justify their simultaneous presence in solution and the unitary ratio of the diffusion currents of their polarographic waves.

In Table VI all the complexes present in solution and their stability constants are reported and the complexes which prevail in each pH range are underlined.

The types of complexes are in accordance with expectations on the formation of mixed copper(II) complexes in the different pH ranges.¹⁶

(b) The complexes that prevail in solution are the same ones as are isolated in the solid state in about the same condition of pH as shown in Table VII. This quite similar behavior also

(16) Souchay, P.; Lefebvre, J. In "Equilibres et Reactivite des Complexes en Solution"; Masson et Cie, Ed.; Paris; 1969; Chapter III, p 71.

supports the assignments of the coordination of the ligand in solution on the basis of the information on the structure of the solid complexes which has been previously reported.⁵

The variety of the copper(II) ion geometries in the solid complexes is not observed in solution complexes. The electronic spectra of the latter may reasonably suggest elongated octahedral geometries since water molecules present in large excess (mass effect) may occupy the coordination positions of the metal ion free from *N*-tosylglycinate or OH^- ions.

In solution the excess of water molecules enables the involvement of the SO_2 group in the copper(II) ion coordination to be excluded, since it is probably involved in strong hydrogen bonding. Its presence in the solid state may be justified as imposed by metal ion geometry or crystal packing or other causes.

However, the presence of the SO_2 group on the ligand is of fundamental importance to determining the variable coordinative ability, which permits the existence of a greater number of complexes both in solution and in the solid state. Since the sulfonyl group has a strong inductive electrophilic effect, the anion of the sulfonamide group becomes an excellent nucleophile and the substituted amino group can react further.^{17,18}

Registry No. *N*-Tosylglycine, 1080-44-0.

(17) Photaki, I. In "Topics in Sulfur Chemistry"; Senning, A., Ed.; Thieme, G. Publ.: Stuttgart, 1976; Vol. 1, p 113.

(18) Rastelli, A.; De Benedetti, P. *J. Chem. Res.* 1977, 90.

Formation Constants of Complexes between Crown Ethers and Alkali Picrates in Apolar Solvents. Application of Crown Ether Network Polymers

Roger Sinta, Peter S. Rose, and Johannes Smid*

Contribution from the Polymer Research Institute, Chemistry Department, College of Environmental Science and Forestry, State University of New York, Syracuse, New York 13210. Received January 7, 1983

Abstract: Benzo-18-crown-6 and benzo-15-crown-5 ligands anchored to cross-linked polystyrene resins were utilized to obtain quantitative information on the complexation of soluble crown ether ligands (including linear polycrown ethers) to sodium and potassium picrate in dioxane and toluene. The constant K describing the competition equilibrium $\text{Pic}^-, \text{M}^+, \text{Cr}^* + \text{L} \rightleftharpoons \text{Pic}^-, \text{M}^+, \text{L} + \text{Cr}^*$ (where L is a soluble ligand and Cr^* the immobilized crown ether) was determined spectrophotometrically. The formation constants, K_L , of the soluble $\text{Pic}^-, \text{M}^+, \text{L}$ complexes were then computed from the expression $K_L = KK_N$, where K_N denotes the known binding constant of the picrate salt to the particular crown network used. K_N , and, therefore, K_L , cannot be obtained in toluene, but the measured K values still furnish a relative scale of ligand affinities toward the picrate salt in this solvent. Use of different networks to obtain K_L and direct measurement of K_L for some of the ligands have established the reliability of the competition method as a way to obtain quantitative information on ligand interaction with ion pairs in apolar media. Values obtained for K and K_L demonstrate the sensitivity of such interactions with solvent and counterion. It is argued that the competition method is a versatile tool for studying interactions of ionic solutes with different types of ligands in apolar solvents.

Soluble as well as immobilized crown ethers, cryptands, and other cation-binding ligands have been extensively employed in studies of mediated ion transport, solute separations, and anion-activated catalysis.¹⁻⁶ Chloroform, toluene, dioxane, or similar apolar solvents are frequently chosen as the reaction medium. In

these solvents, formation constants of the ligand-ion or -ion pair complexes may easily exceed values of 10^6 M^{-1} . When complexation to an ion pair causes a significant change in its absorption spectrum, binding constants can be obtained spectrophotometrically. Such changes are sometimes observed when tight ion pairs are modified on complexation to ligand-separated ion pairs, for example, with fluorenyl and picrate salts.^{7,8} When complexation results in increased formation of free ions, conductometry can be

(1) Izatt, R. M.; Christensen, J. J., Eds. "Process in Macrocyclic Chemistry"; Wiley-Interscience: New York; Vol. I, 1981; Vol. II, 1982.

(2) Montanari, F.; Tundo, P. *J. Org. Chem.* 1981, 46, 2125.

(3) Manecke, G.; Kramer, A. *Makromol. Chem.* 1981, 182, 3017.

(4) Regen, S. L. *Angew. Chem., Int. Ed. Engl.* 1979, 18, 421.

(5) Akelah, A.; Sherrington, D. C. *Chem. Rev.* 1981, 81, 557.

(6) Blasius, E.; Janzen, K. P.; Keller, M.; Lander, H.; Nguyen-Tien, T.; Scholten, G. *Talanta* 1980, 27, 107.

(7) Takaki, U.; Hogen Esch, T. E.; Smid, J. *J. Am. Chem. Soc.* 1971, 93, 6760.

(8) Bourgoin, M.; Wong, K. H.; Hui, J. Y.; Smid, J. *J. Am. Chem. Soc.* 1975, 97, 3462.

employed to obtain ligand binding constants.^{9,10} However, in solvents such as dioxane or toluene, no free ions are formed, and ligand interaction with ionic solutes frequently yields ligand-complexed tight ion pairs without a significant change in optical spectrum. In such cases, ligand binding constants are difficult to determine, especially since it is desirable to operate at low concentrations of ionic solute in order to minimize association of ion pairs into higher aggregates.¹¹

In a recent communication¹² we demonstrated that immobilized crown ethers (Cr*) can be effectively utilized to study interactions of soluble crown ethers or other ligands with ionic solutes such as picrate salts. The method is based on forcing a solute A⁻,M⁺ complexed to a crown ether Cr* (or another ligand such as a cryptand or a podand) bound to a solvent-swollen network out into the surrounding medium by adding a ligand L which competes with Cr* for A⁻,M⁺:



If A⁻ is a chromophore, e.g., a picrate anion, K can be easily obtained by monitoring spectrophotometrically the release of A⁻,M⁺,L as a function of the concentration of added ligand L. The equilibrium constant K equals the ratio K_L/K_N , where K_L is the binding constant of A⁻,M⁺ to L and K_N that of A⁻,M⁺ to the resin-bound crown ether Cr*. Hence, by measuring K and K_N the complex formation constant K_L can be calculated. K_N values for sodium, potassium, and cesium picrate with five crown ether network polymers derived from cross-linked, chloromethylated polystyrenes have recently been determined in dioxane, tetrahydropyran, tetrahydrofuran, and 2-methyltetrahydrofuran as a function of crown structure and crown content.^{12,13} In this publication we have employed three of these networks to study the interaction of a series of soluble crown ethers to sodium and potassium picrate in dioxane and toluene. In dioxane, reliable K and K_L values can be obtained. In toluene, only K values can be measured since the insolubility of picrate salt in toluene prevents the determination of K_N . However, K values still provide us with a relative scale of ligand affinities toward ionic solutes in solvents in which solutes are insoluble in the absence of an ion-binding ligand.

Experimental Section

Materials. The synthesis and purification of the picrate salts and the crown ether network polymers have been previously described.¹³ Structures of the three networks used are shown below. Their crown content was obtained by determining in dioxane the maximum amount of picrate salt that can be bound to the network.¹³ For this purpose, sodium picrate was used for the benzo-15-crown-5 resin 5R15C5 and potassium picrate for the benzo-18-crown-6-containing networks R18C6 and 5R18C6. In these three systems, 1:1 complexes are formed exclusively, and saturation of the network by picrate salt can be readily achieved.

The crown ether compounds 15-crown-5 (15C5), 4'-methylbenzo-15-crown-5 (MB15C5), 18-crown-6 (18C6), dicyclohexano-18-crown-6 (DCH18C6 and DCH18C6-A, the cis-syn-cis isomer of DCH18C6), 4'-methylbenzo-18-crown-6 (MB18C6), and dimethyldibenzo-18-crown-6 (DMB18C6) were purified samples previously synthesized in our laboratory or obtained commercially. The crown ether 3,4-bis-(1',4',7',10',13'-pentaoxacyclopentadeca-2-ene)phenylcarboethoxy ether (bis(B15C5)), a crown with two B15C5 units joined at the 4' positions by a -CH₂OCH₂- chain, was kindly supplied to us by K. H. Wong.¹⁴ The homopolymer of 4'-vinylbenzo-15-crown-5 (P15C5) and two copolymers of this monomer with styrene (50%SP15C5 containing equal molar quantities of the two monomers, and 10%SP15C5 containing 10 mole % of the crown monomer) were also available from previous experiments.¹⁵ Dioxane and toluene were dried on LiAlH₄ and CaH₂, respectively, and carefully distilled prior to use.

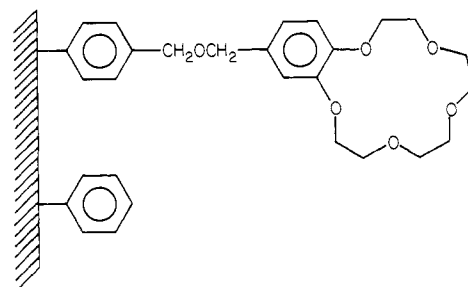
Measurements of Binding Equilibria. In a 50-mL silanized round-bottom flask provided with a fritted filter and optical cell was placed 5 mL of a picrate solution in dioxane ($\approx 10^{-4}$ M in picrate). A sufficient quantity of network (usually between 1 and 10 mg) was then added to assure that after reaching equilibrium (≈ 60 min) nearly all picrate was bound to the resin. The solution was thermostated at 25 °C, and aliquots of a concentrated solution of a crown ether (or other ligand) in dioxane were added. After each ligand addition, and after equilibrium was reached (10–20 min), the concentration of released picrate Pi⁻,M⁺,L (see eq 1) was measured on a Cary 14 or Beckman Acta M VI spectrophotometer by filtering the solution into the optical cell. After the measurement the solution was returned to the flask containing the network and an additional amount of ligand added for the next measurement.

Since alkali picrates do not dissolve in toluene it was necessary when using this solvent to solubilize the salt first with a small amount of ligand. After determining the picrate concentration, sufficient network was added to bind 80 to 90% of the salt. Then a toluene solution of the ligand is added to release the picrate again, similar as described for dioxane.

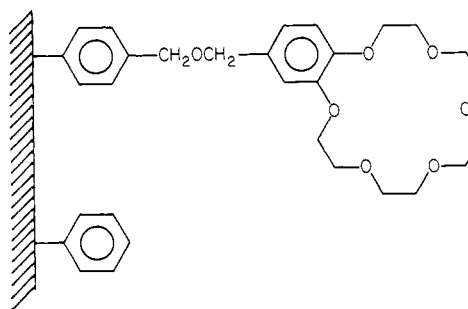
Molar absorptivities of the ligand complexes in dioxane were obtained by adding ligand to a picrate solution in dioxane, using excess ligand to assure complete conversion into the complex. In toluene, a known amount of picrate salt was completely solubilized with excess ligand, and from the recorded spectrum of the complex the molar absorptivities were calculated.

Results and Discussion

The networks used in our investigation were derived from 2% cross-linked, chloromethylated polystyrenes. Their structures are shown below. R18C6, synthesized from a polystyrene resin with



5R15C5



R18C6, 5R18C6

0.9 mequiv of C1/g of polymer was found to contain 0.70 mequiv of benzo-18-crown-6 per g of resin, about one ligand per eleven monomer base units. 5R18C6 and 5R15C5 were prepared from a resin containing 5 mequiv of C1/g of polymer. Analysis of the respective networks yielded 1.48 mequiv of benzo-18-crown-6 and 1.92 mequiv of benzo-15-crown-5 per g of resin, or about one ligand per two monomer units.¹³ With preswollen networks, equilibrium between network-bound picrate and its ligand complex in either dioxane or toluene was established in 10–20 min.

Release of the picrate complex Pi⁻,M⁺,L on addition of a ligand L to network-bound picrate Pi⁻,M⁺,Cr* is shown in eq 1. The assumption is made that Cr* and L only form 1:1 complexes with Pi⁻,M⁺, and that conditions are chosen such that the amount of uncomplexed Pi⁻,M⁺ in solution is negligibly small as compared to Pi⁻,M⁺,L. The concentration of Pi⁻,M⁺,L is determined spectrophotometrically by using the appropriate molar absorptivities. The latter, together with the absorption maxima of the Pi⁻,M⁺,L complexes, are collected in Table I. The maxima are indicative of the nature of the ion pair–ligand complexes, that is,

(9) Gilkerson, W. R.; Jackson, M. D. *J. Am. Chem. Soc.* **1979**, *101*, 4096.

(10) Ungaro, R.; El Haj, B.; Smid, J. *J. Am. Chem. Soc.* **1976**, *98*, 5198.

(11) Takaki, U.; Hogen Esch, T. E.; Smid, J. *J. Phys. Chem.* **1972**, *76*, 2152.

(12) Sinta, R.; Smid, J. *J. Am. Chem. Soc.* **1981**, *103*, 6962.

(13) Sinta, R.; Lamb, B. S.; Smid, J. *Macromolecules*, in press.

(14) Wong, K. H.; Ng, H. L. *Tetrahedron Lett.* **1979**, 4295.

(15) Shah, S. C.; Kopolow, S. L.; Smid, J. *Polymer* **1980**, *21*, 187.

Table I. Absorption Maxima and Molar Absorptivities of Alkali Picrates and Their Crown Complexes in Dioxane and Toluene at 25 °C

cation	ligand	dioxane		toluene	
		λ_m , nm	$\epsilon_m \times 10^{-4}$	λ_m , nm	$\epsilon_m \times 10^{-4}$
Na ⁺	18C6	347	1.44	360	1.45
	DCH18C6	360	1.60	360	1.45
	MB18C6	360	1.60	360	1.43
	DMB18C6	360	1.62	358	1.42
	15C5	352	1.56		
	MB15C5	352	1.50		
	bis(B15C5)	352	1.50		
K ⁺	18C6	349	1.46	360	1.56
	DCH18C6	360	1.51	360	1.56
	MB18C6	360	1.52	360	1.50
	DMB18C6	360	1.51	360	1.51
	15C5	360	1.50		
	MB15C5	360	1.50		
	bis(B15C5)	377	1.50		
	P15C5	380			
	50% SP15C5	378			
	10% SP15C5	360			

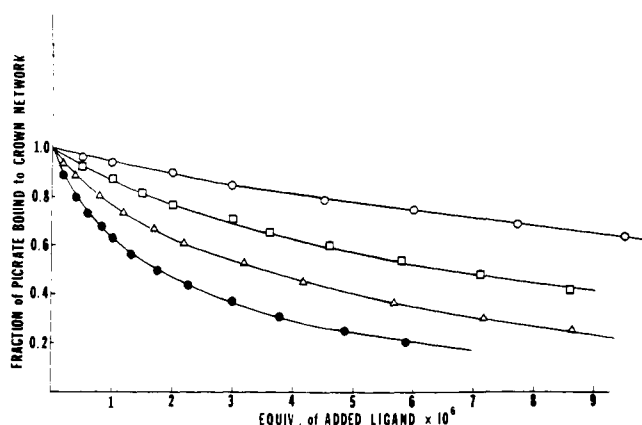


Figure 1. Decrease in the fraction of R18C6-bound potassium picrate on addition of 18C6 (●) DCH18C6 (Δ), MB18C6 (□), and DMB18C6 (○) in dioxane.

whether a ligand-complexed tight or loose ion pair is the predominant species. For example, the 15C5-type ligands, including the bis(crown ether), all give tight 1:1 ion pair complexes with sodium picrate in dioxane, λ_m being 352 nm as compared to 347 nm for the uncomplexed salt. The interionic ion pair distance appears to be enlarged for complexes with the 18C6-type ligands, λ_m being 360 nm for sodium and potassium picrate in both dioxane and toluene. The bis(crown ether) complex with potassium picrate has a λ_m of 377 nm, close to that found for the loose ion pair complexes of this salt with other bis(crown ethers) in tetrahydrofuran.⁸

The decrease in the fraction of R18C6-bound potassium picrate ($[Pi^-, M^+, Cr^* / Pi_0]$) in dioxane on addition of four 18C6-type ligands is graphically depicted in Figure 1. The quantity $[Pi^-, M^+, Cr^*]$ can be easily calculated since it equals $[Pi^-, M_0^+ - Pi^-, M^+, L]$. Inspection of these plots immediately shows that crown interaction with potassium picrate is the strongest with 18-crown-6, and decreases in the order 18C6 > DCH18C6 > MB18C6 > DMB18C6. If F_1 is the fraction of ligand L bound to picrate salt ($F_1 = [Pi^-, M^+, L] / L_0$, $[L_0]$ being the total ligand concentration), and F_2 is the fraction of network-bound crown ether Cr^* complexed to Pi^-, M^+ ion pairs ($F_2 = [Pi^-, M^+, Cr^*] / Cr_0^*$), then it can be easily verified that the following relationship holds:

$$(1/F_2) - 1 = K[(1/F_1) - 1] \quad (2)$$

Hence, a straight line passing through the origin with slope equal

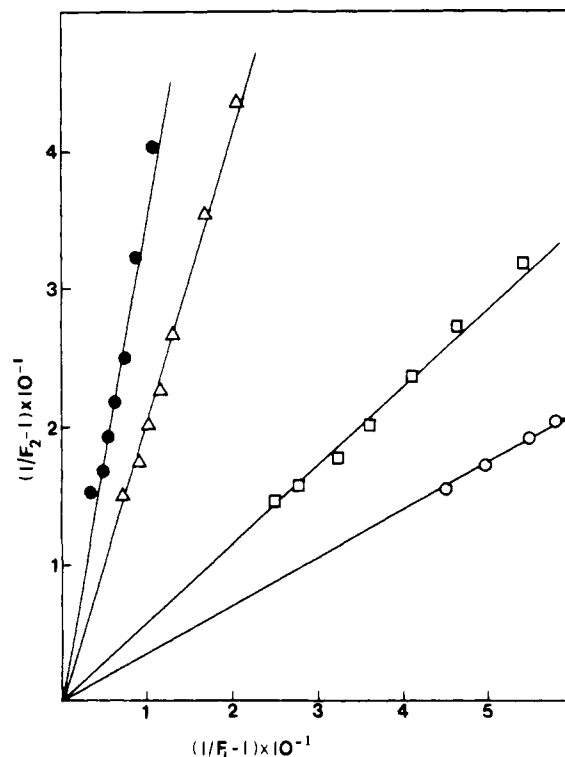


Figure 2. Plots of eq 2 for release of 5R18C6-bound potassium picrate in dioxane on addition of 18C6 (●), DCH18C6 (Δ), MB18C6 (□) and DMB18C6 (○).

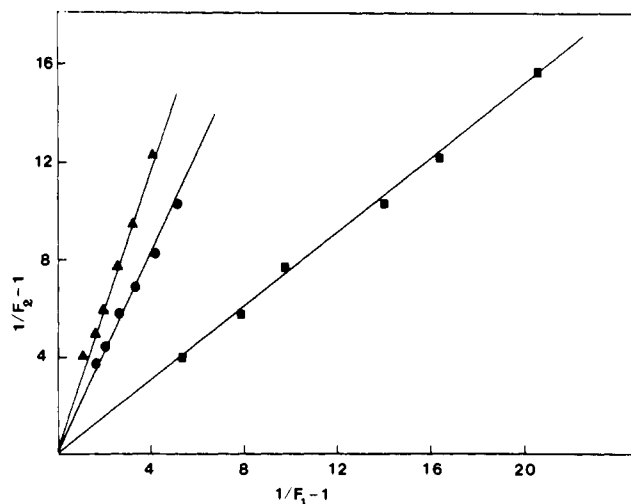
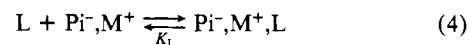
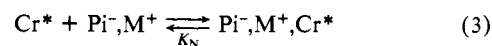


Figure 3. Plots of eq 2 for release of R18C6-bound sodium picrate in dioxane on addition of 15C5 (▲), bis(B15C5) (●) and MB15C5 (■).

to K should result by plotting $(1/F_2) - 1$ vs. $(1/F_1) - 1$. The latter variables can easily be computed from L_0 , Cr_0^* and the spectrophotometrically determined value of $[Pi^-, M^+, L]$.

Equilibrium 1 can be analyzed in terms of reactions



where

$$K = K_L / K_N \quad (5)$$

Thus, the formation constant, K_L , of the picrate-ligand complex can be calculated by determining K from this competition-type experiment with use of a network/picrate salt/solvent system for which K_N is known.

Representative $(1/F_2) - 1$ vs. $(1/F_1) - 1$ plots for several types of crown ligands are depicted in Figures 2-5. They were derived

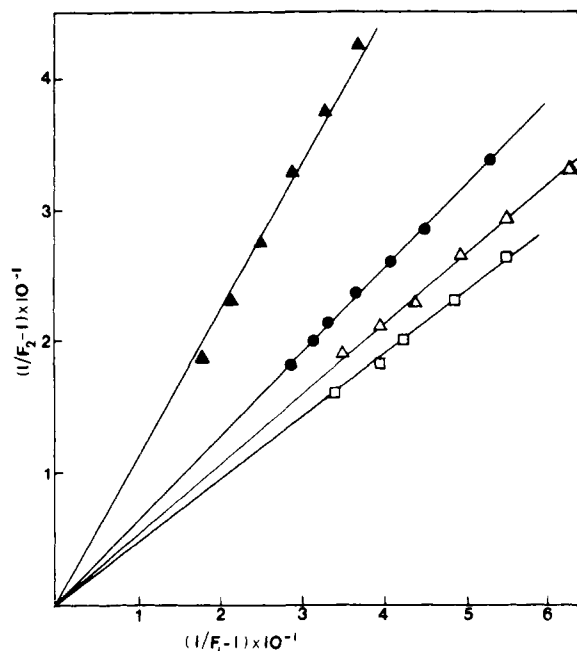


Figure 4. Plots of eq 2 for release of 5R15C5-bound sodium picrate in dioxane on addition of DCH18C6-A (▲), 18C6 (●), DCH18C6 (Δ) and MB18C6 (□).

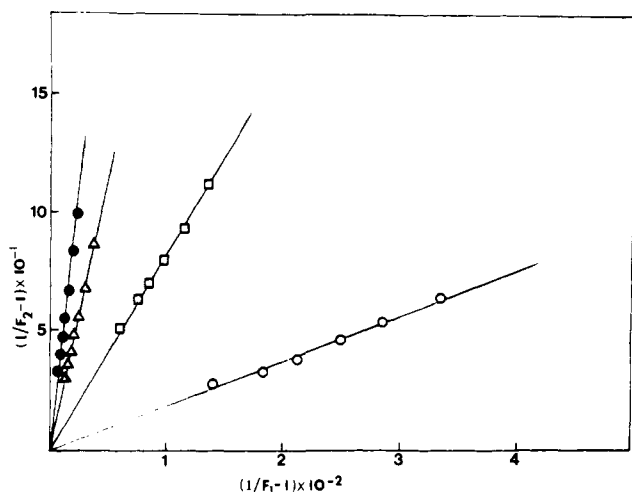


Figure 5. Plots of eq 2 for release of R18C6-bound potassium picrate in toluene on addition of 18C6 (●), DCH18C6 (Δ), MB18C6 (□), and DMB18C6 (○).

from three different networks with sodium and potassium picrate in either dioxane or toluene (plots for four 18C6-type ligands with R18C6-bound potassium picrate in dioxane were published in our preliminary communication¹²). The linearity of the plots, all of which can be extrapolated to pass through the origin, indicates that the process of picrate release by ligand can indeed be described by eq 1. In most experiments the network loading F_2 was less than 0.2. However, we have ascertained that under conditions of high network loading ($F_2 \rightarrow 1$) linear relationships were obtained with K values identical with those found at low F_2 values. This result is not surprising since binding of picrate salts to crown ether networks was shown to obey Langmuir adsorption behavior in ethereal solvents close to the point of network saturation, even for the high-capacity networks 5R15C5 and 5R18C6.^{12,13} This implies the absence of electrostatic interactions between the network-bound ion pairs. This apparently is also the case in toluene where $(1/F_2) - 1$ vs. $(1/F_1) - 1$ plots are also linear (Figure 5) but where direct binding of picrate salt to the network cannot be measured. Linearity of the plots of Figures 2–5 also implies that under our experimental conditions ($[Pi^-, M^+, L] \approx 10^{-4}$ – 10^{-5} M), formation of aggregates of the type $[Pi^-, M^+, L]_n$ does not occur

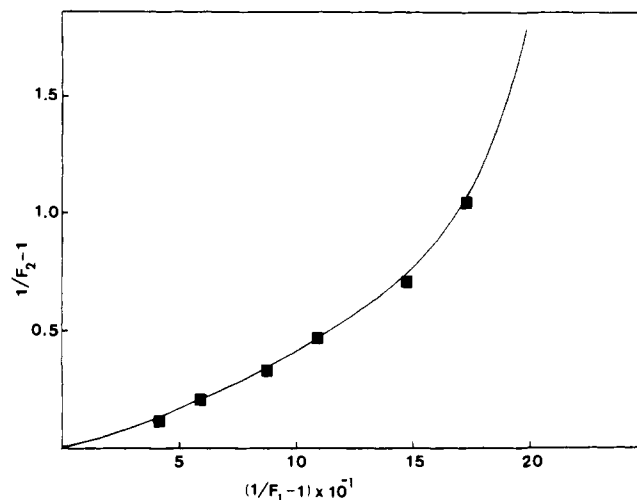


Figure 6. Plot of eq 2 for the release of R18C6-bound potassium picrate in dioxane on addition of MB15C5.

to any degree in either dioxane or toluene. Aggregation would cause additional release of network-bound picrate at high concentrations of Pi^-, M^+, L , and plots of $(1/F_2) - 1$ vs. $(1/F_1) - 1$ would curve upward at high $(1/F_1) - 1$ values.

The derivation of eq 2 assumes $[Pi^-, M^+] \ll [Pi^-, M^+, L]$. This is certainly valid in toluene where solubility of picrate salt is very low. However, in dioxane, some free picrate salt may be present if sufficient network is not added, even in the presence of added ligand. If no correction is made, points at low concentrations (low $(1/F_1) - 1$ values) fall above the line as was observed in some of our plots, since the calculated value $1/F_1 = [L_0/Pi^-, M^+, L]$ is too low. The correction can be easily made since $[Pi^-, M^+, L]$ equals the measured picrate concentration $[Pi_m]$ minus the free picrate $[Pi^-, M^+]$, the latter being given by (see also eq 3)

$$1/[Pi^-, M^+] = K_N[(1/F_2) - 1] \quad (6)$$

Application of this correction to systems where deviation from linearity was observed at low $(1/F_1) - 1$ values resulted in linear plots over the entire $(1/F_1) - 1$ region.

A more general relationship can be derived to account for any free picrate Pi^-, M^+ in solution. Since measured picrate $[Pi_m]$ equals $[Pi^-, M^+ + Pi^-, M^+, L]$, it can easily be verified that

$$[Pi_m] = [Pi^-, M^+](1 + K_L L) \quad (7)$$

and

$$[(1/F_2) - 1][Pi_m] = 1/K_N + K_L \quad (8)$$

where L is given by $[L_0] - [Pi^-, M^+, L] = [L_0] - [Pi_m] + 1/K_N - [(1/F_2) - 1]$. When the K_N value of the network is used to calculate L , linear plots with slopes identical with those derived from eq 2 are obtained by plotting $[(1/F_2) - 1][Pi_m]$ vs. L . The intercept $1/K_N$ was too small to determine K_N with any accuracy. Assuming the applicability of eq 8, one can in principle take a network of unknown K_N and determine for which set of K_N and $K_L (=KK_N)$ values, if any, the experimental data yield a linear plot.

Formation of 1:1 and 1:2 Picrate Salt-Ligand Complexes.

Addition of the ligand MB15C5 to potassium picrate bound to an R18C6 network in dioxane yields a strongly curved $(1/F_2) - 1$ vs. $(1/F_1) - 1$ plot (Figure 6). Previous studies with this ligand-salt combination in THF have shown the existence of both 1:1 ($Pi^-, M^+ + L \rightleftharpoons Pi^-, M^+, L$, λ_m 362 nm) and 1:2 complexes ($Pi^-, M^+, L + L \rightleftharpoons Pi^-, L, M^+, L$, λ_m 380 nm).^{8,16} The lower dielectric constant of dioxane is likely to make formation of the loose ion pair Pi^-, L, M^+, L more difficult. However, addition of excess MB15C5 in our system causes the absorption maximum of the picrate complex to shift to higher wavelength, suggesting formation

(16) Wong, K. H.; Bourgoign, M.; Smid, J. *J. Chem. Soc., Chem. Commun.* 1974, 715.

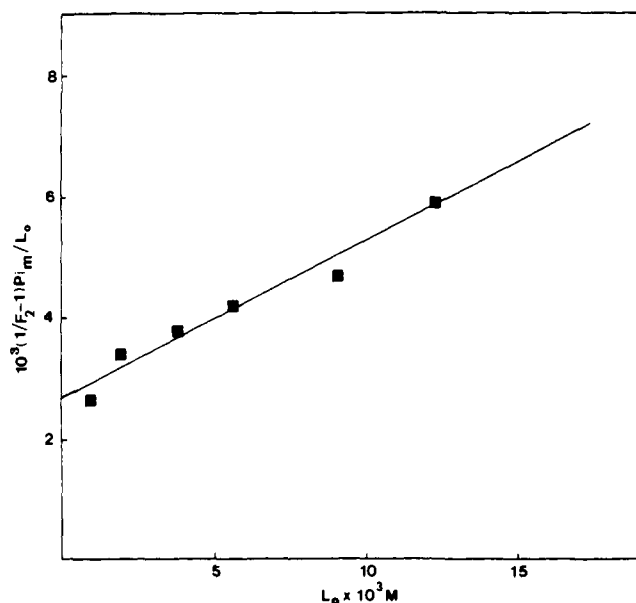


Figure 7. Plot of eq 10 with $L = [L_0]$ for R18C6-bound potassium picrate in dioxane on addition of MB15C5.

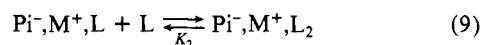
Table II. Equilibrium Constants, K , and Formation Constants, K_L , for Complexes of Potassium Picrate with Crown Ether Ligands in Dioxane at 25 °C, Using R18C6 and 5R18C6 as Network Polymers

ligand	R18C6 ^a		5R18C6 ^b	
	K	$K_L \times 10^{-4}, M^{-1}$	K	$K_L \times 10^{-4}, M^{-1}$
18C6	5.62	96.7	3.76	97.0
DCH18C6	3.13	53.8	2.19	56.5
MB18C6	0.91	15.6	0.60	15.5
DMB18C6	0.595	10.2	0.437	11.3
P15C5	1.05	18.0		
50% SP15C5	0.77	13.2		
10% SP15C5	0.453	7.8		

^a Network containing 0.70 mequiv of crown per g of polymer; $K_N = 1.72 \times 10^5 M^{-1}$.¹³ ^b Network containing 1.48 mequiv of crown per g of polymer; $K_N = 2.58 \times 10^5 M^{-1}$.¹³

of a Pi^-, M^+, L_2 complex. In such a case, picrate release at high concentration of MB15C5 will be proportional to $[MB15C5]^2$, and the plot will curve upward.

If in addition to equilibrium 1 formation of a 1:2 complex is taken into account (eq 9)



the following relationship can be derived:

$$[(1/F_2) - 1][Pi_m]/L = K + KK_2L \quad (10)$$

where $[Pi_m]$ denotes again the measured picrate concentration, i.e., $[Pi_m] = [Pi^-, M^+, L + Pi^-, M^+, L_2]$. In the reaction with MB15C5, conditions were such that $[Pi_m] \ll [L_0]$. Hence, L , which equals $[L_0] - [Pi^-, M^+, L] - 2[Pi^-, M^+, L_2]$, may be approximated by $[L_0]$. Replotting the experimental data of Figure 6 according to eq 10 (with $L = [L_0]$) yields a reasonably linear plot (see Figure 7) with $K = 0.0027$ and $K_2 = 91 M^{-1}$. A value of $91 M^{-1}$ for the formation constant of Pi^-, M^+, L_2 from the 1:1 complex Pi^-, M^+, L appears reasonable considering that direct spectrophotometric measurements of K_2 for the same system in THF as solvent yielded a value of $200 M^{-1}$.¹⁶ The formation constant K_L of the 1:1 complex equals KK_N , K_N for our system being $1.72 \times 10^5 M^{-1}$. Hence, $K_L = 460 M^{-1}$ for the 1:1 complex of MB15C5 with potassium picrate in dioxane, a value that is 340× smaller than that found for MB18C6 (Table II).

For our binding competition studies between network-bound and soluble ligands we always utilized networks that only form

Table III. Equilibrium Constants, K , and Formation Constants, K_L , for Complexes of Sodium Picrate with Crown Ether Ligands in Dioxane at 25 °C, Using R18C6 and 5R15C5 as Network Polymers

ligand	R18C6 ^a		5R15C5 ^b	
	K	$K_L \times 10^{-4}, M^{-1}$	K	$K_L \times 10^{-4}, M^{-1}$
18C6	1.34	3.46	0.617	3.58
DCH18C6	1.00	2.58	0.479	2.78
DCH18C6-A			1.11	6.44
MB18C6	0.773	2.00	0.397	2.30
DMB18C6	0.191	0.493		
15C5	2.80	7.22		
MB15C5	0.739	1.91		
bis(B15C5)	1.83	4.72 ^c		

^a Network containing 0.70 mequiv of crown per g of polymer, $K_N = 2.58 \times 10^4 M^{-1}$.¹³ ^b Network containing 1.92 mequiv of crown per g of polymer, $K_N = 5.80 \times 10^4 M^{-1}$.¹³ ^c Expressed in molar concentration of the bis compound.

Table IV. Comparison of K Values in Dioxane and Toluene for Sodium and Potassium Picrate with 18-Crown-6-Type Ligands and R18C6 as Network ($T = 25$ °C)

ligand	sodium picrate		potassium picrate	
	dioxane	toluene	dioxane	toluene
18C6	1.34	1.26	5.62	4.09
DCH18C6	1.00	1.24	3.13	2.08
MB18C6	0.773	0.67	0.908	0.60
DMB18C6	0.191	0.124	0.596	0.206

1:1 complexes with added picrate salts. Earlier investigations have shown that some network-picrate combinations form both 1:1 and 1:2 picrate-crown complexes, for example, 5R15C5 and potassium picrate.¹³ When the network forms exclusively 1:2 complexes, or when conditions are chosen under which such a network forms chiefly 1:2 complexes (usually at higher $1/F_2$ values, see ref 13), K can still be calculated from eq 2 with K_N being the intrinsic binding constant for the network. Deviation from linearity in plotting 2 may result when the network contains both 1:1 and 1:2 complexes. Therefore, in determining K or K_L values it is advisable to choose networks which form only one type of complex with the added ionic solute, preferably a 1:1 complex, and where Langmuir adsorption behavior is obeyed, e.g., Pi^-, K^+ with R18C6, or Pi^-, Na^+ with R18C6 or 5R15C5.

Equilibrium and Complex Formation Constants. Tables II, III, and IV contain the K and K_L values for complexes of a number of crown ether ligands with sodium and potassium picrate in dioxane and toluene. No K_L values can be computed in toluene since in this solvent the low solubility of picrate salts prevents direct measurements of K_N . On the basis of the accuracy of our extinction coefficients and other common experimental variables and considering the reproducibility of our measurements, the reported K values have an accuracy of about 5%.

The reliability of these data was checked in two ways. First, identical K_L values for a picrate-ligand complex should be obtained when networks with different K_N 's are employed in the determination of K . A comparison of the second and fourth columns of Table II reveals that the use of two networks differing in K_N by a factor of 1.5 (R18C6 and 5R18C6) yields an average deviation of 4% for corresponding K_L values of potassium picrate with four 18-crown-6-type ligands. Similarly, the average deviation in corresponding K_L values for sodium picrate with three 18-crown-6 ligands (Table III) is 8% when two networks (R18C6 and 5R15C5) are used differing in K_N by a factor of 2. Second, K_L can sometimes be determined directly by optical spectroscopy in systems where the conversion of Pi^-, M^+ into the complex Pi^-, M^+, L is accompanied by a significant spectral shift. Using this approach, K_L for potassium picrate and MB18C6 in dioxane (a λ_m shift from 349 to 360 nm) was found to be $1.7 \times 10^5 M^{-1}$ compared to the network value of $1.56 \times 10^5 M^{-1}$ (Table II). The same method applied to the system potassium picrate and

DMB18C6 in dioxane which yielded $K_L = 9.5 \times 10^4 \text{ M}^{-1}$ compared to $10.2 \times 10^4 \text{ M}^{-1}$ found with the network (Table III). Hence, the network method appears to provide reliable values for complex formation constants in apolar media.

K and K_L values for potassium and sodium picrate (Tables II and III) decrease in the order $18\text{C6} > \text{DCH18C6} > \text{MB18C6} > \text{DMB18C6}$, although the *cis-syn-cis* isomer DCH18C6-A of dicyclohexano-18-crown-6 in complexing sodium picrate is more effective than 18C6 (Table III). The above sequence is not unexpected when compared with binding data for the same ligands and cations in other solvents.^{1,17} It largely reflects the ring substituent effects on the basicity of the oxygen binding sites and the conformation of the crown ring. The binding constants of the four ligands in dioxane are considerably larger with the potassium salt than with the sodium salt, the respective K^+/Na^+ selectivities (i.e., $K_L(K^+)/K_L(\text{Na}^+)$) being 28, 21, 8, and 21. Complex formation constants and cation selectivities of crown ligands are sensitive functions of crown ring substituents, cavity size, solvent, and, in case of ion pair complexation, the nature of the accompanying counterion. For example, the K^+/Na^+ selectivity for picrate salts with MB18C6 is 8 in dioxane (Tables II and III), 100 in CHCl_3 (based on extraction in $\text{CHCl}_3/\text{H}_2\text{O}$, see ref 18), and only 2.1 in acetone.¹⁰ For B18C6 (no 4'-methyl substituent) the K^+/Na^+ selectivities are 2.4 in acetone¹⁰ and 2.5 in CH_3CN ,¹⁹ where the values in acetone and CH_3CN refer to free cations.

Another example of solvent and ion pairing effects on complex formation is found by comparing the binding constants of the two ligands 18C6 and 15C5 with sodium ion in different solvents. The ratio $K_L(18\text{C6})/K_L(15\text{C5})$ is 80 in propylene carbonate,²⁰ 8 in methanol,²¹ 1.3 in water,²² and 0.48 in dioxane (Table III). The reversal in dioxane may at least in part result from interference by the two ortho nitro substituents of the picrate anion. This interference is likely to affect complexation with 18C6 more than with 15C5, since effective complexation with the former ligand requires a deeper penetration of the cation into the crown cavity. For the ligands MB18C6 and MB15C5 the K_L ratios with Na^+ are 31 in acetone¹⁰ and 1.05 in dioxane (Table III). A ratio of 128 is found in acetone for the 4'-nitro derivatives of B18C6 and B15C5!¹⁰ These are just a few examples demonstrating the drastic changes that can occur in cation selectivities of crown ligands when crown ring substituents, counterions, or solvents are altered. Such effects have been discussed in more detail by several researchers.^{1,17,20}

A value $K_L = 460 \text{ M}^{-1}$ was calculated above for the 1:1 complex of MB15C5 and Pi^- , K^+ in dioxane, a system which also forms a 2:1 complex. This constant is much lower than previously estimated (10^4 M^{-1}) for this complex in THF.¹⁶ The value 10^4 M^{-1} was based on a very small change in spectral shift (5 nm) and may be substantially in error. With $K_L = 460 \text{ M}^{-1}$ one calculates a $K_L(\text{MB18C6})/K_L(\text{MB15C5})$ ratio of 340 for Pi^- , K^+ in dioxane. This value is not unreasonable since the ratio of extraction equilibrium constants for Pi^- , K^+ with these two ligands in $\text{CHCl}_3/\text{H}_2\text{O}$ (based on a 1:1 complex for MB15C5) is 580,¹⁸ while the K_L ratio for B18C6 and B15C5 in CH_3CN is 80.¹⁹ The 2:1 crown- K^+ complexes are favored at high concentrations of the 15C5-type ligands, and such ligands then become increasingly more effective complexing agents relative to that of 18C6-type ligands which only form 1:1 complexes with K^+ ions or ion pairs. Sandwich-type 2:1 crown- K^+ complexes are the predominant species with the polymeric ligands P15C5, 50% SP15C5, and 10% SP15C5 (Table II). Spectra show formation of crown-separated ion pair complexes between Pi^- , K^+ and the "bis(crown ether)" units along the polymer chain, and K_L values for these ligands

become comparable with the values for ligands such as MB18C6. Although spacing the crown ligands farther apart diminishes the probability of forming the 2:1 complexes, the styrene copolymer with 10 mol % vinylbenzo-15-crown-5 (10% SP15C5) contains sufficient crown ligands in close proximity to form 2:1 complexes.²³

It is worthwhile pointing out that the equilibrium constants, K , for Pi^- , K^+ and Pi^- , Na^+ in the R18C6/MB18C6 system are not far from unity, the respective values in dioxane being 0.91 (Table II) and 0.77 (Table III). The immobilized ligand in R18C6 closely resembles the soluble MB18C6, and a K value close to unity implies that the binding affinity of a ligand is not much different from that of its immobilized analogue, provided that the network is in a good-swelling solvent and that there is sufficient spacing between anchored ligands to minimize cooperative effects. Such effects are present in 5R18C6 where K_N is 1.5 times larger than in R18C6 and K is correspondingly lower ($K = 0.60$). Actually, the observed K value of slightly less than unity for R18C6 can be rationalized on the basis of the larger inductive effect of the CH_2OCH_3 substituent of the immobilized ligand as compared to the 4'- CH_3 of the MB18C6 ligand.

No drastic changes are evident in the relative ligand affinities of four 18C6-type ligands with respect to sodium or potassium picrate when the cation-interacting solvent dioxane is replaced by the poorly interacting solvent toluene (Table IV). Except for DCH18C6/ Pi^- , Na^+ , all K values in toluene are lower than those in dioxane, the largest decrease being a factor of 3 for DMB18C6 and Pi^- , K^+ . The linearity of the $(1/F_2) - 1$ vs. $(1/F_1) - 1$ plots, as argued earlier, implies that interactions between network-bound ion pair complexes or between the soluble complexes are minimal. The lower K values in toluene point to increased cation affinity of the network relative to that of the soluble ligands. This may be due to increased cooperativity of network ligands in their interactions with ion pairs. We are presently investigating to what extent network swelling is affecting K values and affinities of immobilized ligands.

The studies outlined here are not limited to immobilized crown ethers. We have recently applied this competition method with oligo-oxyethylene (glyme) containing networks for measuring affinities of ligands less powerful than crown ethers, for example, glymes, sulfoxides, and polyamines.²⁴ Again, linear $(1/F_2) - 1$ vs. $(1/F_1) - 1$ plots are obtained in most systems. By using the same crown ether network in competition with a relatively weakly binding crown ligand (DMB18C6) and a strongly interacting glyme ligand (glyme 9) we were able to arrive at a scale of ligand affinities with respect to sodium picrate in toluene for a series of crown ethers and glymes. Cryptand-based networks are also being explored to evaluate the affinities of the more powerful cryptand-type ligands in apolar media.

The use of more polar solvents is complicated by dissociation of the ion pair-ligand complexes into free ions. The latter species usually have much higher complexation constants with crown ethers or other ligands than the tight ion pairs prevalent in our system.⁸ In fact, some competition studies carried out in THF yielded curved $(1/F_2) - 1$ vs. $(1/F_1) - 1$ plots, probably because a considerable fraction of the picrate-crown complexes was dissociated in this solvent. Difficulties could also arise in solvents that are poor swelling agents for the polystyrene-based resins, e.g., heptane. This aspect is now being explored. In this regard, it may be advantageous to utilize crown ethers immobilized on macroporous resins or silica gel. This will expand the number of solvents in which ligand interactions with ionic solutes can be studied quantitatively by this technique. It also is likely to speed up the measurements since the time needed to reach equilibrium between salt bound to immobilized and to soluble ligand may be faster.

In conclusion, the competition method using immobilized crown ethers or other ligands yields reliable and quantitative information on formation constants of complexes between ionic solutes and a variety of ion-binding ligands in apolar media. The use of very

(17) Poonia, N. S.; Bajaj, A. V. *Chem. Rev.* **1979**, *79*, 389.

(18) Wong, K. H.; Yagi, K.; Smid, J. *J. Membr. Biol.* **1974**, *18*, 379.

(19) Hofmanova, A.; Koryta, J.; Brezina, M.; Mittal, M. L. *Inorg. Chim. Acta* **1978**, *28*, 73.

(20) Takeda, Y.; Yano, H.; Ishibashi, M.; Isozumi, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 72.

(21) Lamb, J. D.; Izatt, R. M.; Swain, C. S.; Christensen, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 475.

(22) Izatt, R. M.; Terry, R.; Haymore, B. L.; Hansen, L. D.; Dalley, N. K.; Avondelt, A. G.; Christensen, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 7620.

(23) Shah, S. C.; Kopolow, S. L.; Smid, J. *Polymer* **1980**, *21*, 188.

(24) Xu, W. Y.; Smid, J., unpublished work from this laboratory.

low solute concentrations minimizes complications arising from aggregation phenomena frequently encountered in such solvents. Although this paper only describes results with picrate salts, the method can, and is being extended to include other anions, e.g., carboxylates. It is anticipated that the data obtained for different ionic solutes as a function of solvent and network variables will be helpful in rationalizing phenomena encountered when immo-

bilized crown ethers, cryptands, or glymes are utilized in phase transfer, chromatography, or other applications.

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Registry No. Sodium picrate, 3324-58-1; potassium picrate, 573-83-1.

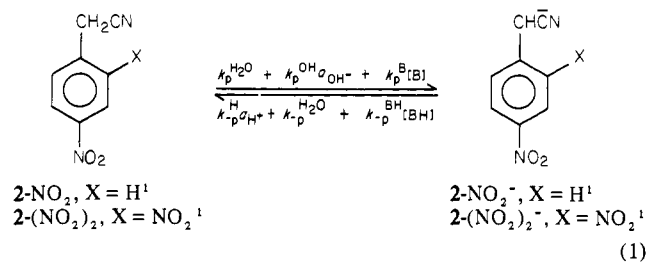
Rates of Deprotonation of (4-Nitrophenyl)acetonitrile and (2,4-Dinitrophenyl)acetonitrile in 50% Me₂SO-50% Water

Claude F. Bernasconi* and Sharon A. Hibdon

Contribution from the Thimann Laboratories of the University of California, Santa Cruz, California 95064. Received November 8, 1982

Abstract: Rates of reversible deprotonation of (2,4-dinitrophenyl)acetonitrile (2-(NO₂)₂) by OH⁻, water, piperidine, morpholine, cacodylate, acetate, formate, and chloroacetate ion and of (4-nitrophenyl)acetonitrile (2-NO₂) by OH⁻, piperidine, morpholine, *n*-butylamine, and 2-methoxyethylamine in 50% Me₂SO-50% water at 20 °C are reported. The intrinsic rate constant (in the Marcus sense) for the dinitro derivative is about 10-fold lower than that for the mononitro compound. This is consistent with the stronger charge delocalization in the anion of the dinitro compound, which leads to greater structural/electronic/solvational reorganization during the reaction. Brønsted β_B values (variation of base) for the deprotonation by piperidine and morpholine are 0.50 for 2-(NO₂)₂ and 0.74 for 2-NO₂, respectively. Brønsted α_{CH} values (variation of C-H acid) are 0.47 for deprotonation by morpholine and 0.35 for deprotonation by piperidine. The α_{CH} and β_B values indicate a charge imbalance (*I* = β_B - α_{CH} > 0) in the transition state in the sense that positive charge development on the amine nitrogen seems to be ahead of negative charge development on the C-H acid. This imbalance is of opposite sign from that reported for the deprotonation of nitroalkanes and carbonyl compounds (*I* < 0) but must nevertheless have the same origin, namely, a lag in structural/electronic/solvational reorganization behind proton transfer in the transition state. The opposite sign is a consequence of having the substituent at a different location within the molecule. The dependence of β_B on the C-H acidity and the dependence of α_{CH} on amine basicity are related by the cross-correlation coefficient *p*_{xy} = 0.053. The change in transition-state structure, which is implied by these changes in β_B and α_{CH}, can be rationalized on the basis of a More O'Ferrall-Jencks diagram, which has separate axes for proton transfer and for electronic/structural/solvational organization.

This paper reports a kinetic study of the reactions shown in eq 1 in 50% Me₂SO-50% water at 20 °C. *k*_p^{H₂O}, *k*_p^{OH⁻}, and *k*_p^B are



the rate constants for deprotonation by water, OH⁻, and buffer bases, respectively, while *k*_{-p}^H, *k*_{-p}^{H₂O}, and *k*_{-p}^{BH} refer to the microscopic reverse of the *k*_p's.

The rate of deprotonation of 2-NO₂ has first been studied in Caldin's laboratory in mixtures of ethanol and ether at -77 °C. Detritiation rates of 2-NO₂ (tritium on benzylic carbon) by a variety of bases in aqueous solution have been reported by Hibbert and Long⁴ while Walters⁵ has studied the deprotonation of 2-NO₂

in various Me₂SO-water mixtures. On the other hand, no reports on the kinetics of the proton-transfer reactions involving 2-(NO₂)₂ could be found in the literature.

The reactions of eq 1 are of interest in the context of structure-reactivity relations in proton transfer involving C-H acids.⁶ A question of particular interest is whether the second nitro group in 2-(NO₂)₂, whose effect on the p*K*_a^{CH} (2-NO₂) = 12.62 and p*K*_a^{CH} (2-(NO₂)₂) = 8.06 in 50% Me₂SO-50% water), leads to an increase in the intrinsic barrier (in the Marcus^{7,8} sense) for proton transfer. Such an effect might be expected because the added nitro group leads to a more effective delocalization of the negative charge in the anion (2-(NO₂)₂⁻), a factor that is known to increase intrinsic barriers for proton transfers.^{6,8,9} Thus, a study of 2-NO₂ and 2-(NO₂)₂ under identical conditions seemed desirable.

An additional motivation for such a study is related to our ongoing interest in structure-reactivity relationships of nucleophilic additions to activated olefins.⁹ Of particular relevance is our recent investigation of the addition of amines to α-cyano-4-nitrostilbene

(5) Walters, E. A. *J. Phys. Chem.* **1977**, *81*, 1995. (b) *ibid.* **1978**, *82*, 1219.

(6) For recent reviews, see: (a) Bell, R. P. "The Proton in Chemistry"; 2nd ed.; Cornell University Press: Ithaca, NY, 1973. (b) Hibbert, F. *Compr. Chem. Kinet.* **1977**, *8*, 97. (c) Crooks, J. E. In "Proton Transfer Reactions"; Caldin, E. F., Gold, V., Eds.; Wiley: New York, 1975; p 153.

(7) (a) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891. (b) Cohen, A. O.; Marcus, R. A. *Ibid.* **1968**, *72*, 4249.

(8) Hine, J. *Adv. Phys. Org. Chem.* **1977**, *15*, 1.

(9) For a recent review, see: Bernasconi, C. F. *Pure Appl. Chem.* **1982**, *54*, 2335.

(1) We use the symbols 2-NO₂, etc., rather than 1-NO₂, etc., for consistency and easier comparison with the symbols used in the following paper.²

(2) Bernasconi, C. F.; Murray, C. J.; Fox, J. P.; Carré, D. *J. Am. Chem. Soc.* **1983**, following article in this issue.

(3) (a) Caldin, E. F.; Harbron, E. *J. Chem. Soc.* **1962**, 2314. (b) Caldin, E. F.; Kasparian, M.; Tomalin, G. *Trans. Faraday Soc.* **1968**, *64*, 2802.

(4) Hibbert, F.; Long, F. A. *J. Am. Chem. Soc.* **1972**, *94*, 2647.