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LIGAND CHANGE EFFECT IN CROWN ETHER PHASE TRANSFER CATALYST DURING THE REACTION BETWEEN AQUEOUS POTASSIUM THIOCYNATE AND P-NITROBENZYL BROMIDE

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ABSTRACT

Various ligands changes in phase transfer catalyst named18-Crown-6 during the reaction between Aqueous potassium thiocynate and P-Nitrobenzyl bromide resulting significantly change in reaction rate. Change in Ligand lipophilicity makes valuable impact in catalyst performance. When electron withdrawing carbonyl group function act as a ligand then lower reaction rate observed, reverse is true when electron releasing alkyl group function act as a ligand than higher reaction rate is observed.

KEYWORDS : Crown ether, Ligand Lipophilicity, Stability constants, Partitions constants, Alkylated ligand and Carbonyl Ligands

Crown ether used as Phase transfer catalyst mainly due to selective cation binding affinities and adjustable hydrophobicities.Due to this reason Crown ether consider better phase transfer catalyst in comparison to quaternary salts Phase transfer catalyst.Now a days Crown ether is widely used in API Pharma Industry to complete organic synthesis in shorter time.

The rates at which the experimental compounds catalyzed the reaction of aqueous potassium thiocyanate with P-nitrobenzyl bromide in chloroform solution were determined.The results were compare with each other and with the results of identical experiments carried out using common crown ethers as catalyst. The result of these experiment were reproducible, as is evidenced by the small difference between duplicate runs. The reaction rate are differentially related to the structures of the ligands.This correction can be explained in terms of the ligand-metal binding constants and partition coefficient of the ligands and their complexes. (Stott et al., 1980, Reed et al., 1991 & Izatt et al., 1985).

MATERIALS AND METHODS

All the reagent,substrate and solvent were obtained from commercial sources and used as received.All reactions were carried out in chloroform solution that was 0.25M in p-nitro benzyl bromide(PNBB) substrate and 0.15M in benzodioxolane (BD) (internal standard) .Prior to use, the chloroform was washed repeatly with water and dried over anhydrous Calcium chloride to remove ethanol,which is present in commercial reagent grade chloroform. To 15 ml of the stock solution substrate and standard were added 0.0001 mol(accurate 0.1 mg) of the ligand to be evaluate and an approximately equimolar amount of powered dry salt, potassium thiocyanate.The mixture was stirred for 5 min. at 1000-1500 rpm.Samples about 0.75 ml,of the chloroform layer were periodically removed and dried over anhydrous sodium sulphate and the ratio of substrate to standard was determined by NMR.The reaction rates are tabulated.

RESULTS

Catalysis by any of the alkylated Dibenzo-18-Crown-6 compounds gives rate that are 5-15% higher than those for Parent Crown.As per Reference .Dicyclohexano-18-crown-6 catalyzed the reaction more efficiently than 18-Crown-6 due to combined effect of stability and partition constants. Due to Ligand Lipophilicity Dicyclohexano-18-crown-6 accelerate the reaction 30% faster than 18-crown-6 and 80% faster than Dibenzo18-Crown-6.The lower rate observed for reaction catalyzed by Bis[(1-hydroxyethyl) benzo]18-crown-6.

DISCUSSION

Landini showed that for PTC with quaternary ammonium salts the observed rate K_{obsd} was proportional to the amount of catalyst in the organic phase This may also be assumed for PTC reactions of the crown ether. This important concentration in the latter case is that of the crown metal complex in the organic phase. Equation shows this relation.The partitioning of crown-metal complexes has been investigated and expressions for the various equilibria

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are available.The association constant for the association of the anion with the crown metal complex is assumed to be constant for out experiments.Since the total crown and metal concentrations were held constant can be reduces to be the proportionality without additional simplifying assumptions.The Reaction between potassium thiocyanate and p-nitrobenzyl bromide given below

$$K^+SCN^- + NO_2PhCH_2Br \xrightarrow{\text{Crown ether}} NO_2PhCH_2SCN + K^+Br^-$$

K_{obsd}=K[CRMA]org

CR= Crown ; M= Metal cation ; A=Anion

K_{obsd} proportional to Ks DCRMA/(1+DCR)

Ks=[CRM]org/[M]aq[CR]aq

DCR=[cr]org/[CR]aq(Crown Partition)

DCRMA=[CRMA]org/[CRMA]aq(complex Partition)

Based on the above expression it would appear that change in catalyst efficiency could be explained in terms of the legand metal complex stability constants and ligand lipophilicity.The latter factor, however is difficult to predict since changes in the same direction, but to different degrees and since changes in the two partition have opposing effect on the reaction rates. Figures 02 shows that catalysis by any of the alkylated dibenzo-18-crown-6 copmounds gives rates that are 5-15% higher than those for the parent crown. All of the alkanoyl derivations give rates only half that of the parent ligand. With the exceptions of the ethyl analogue, all the hydroxyalkyl derivatives gave the same rate as dibenzo-18-crown-6.The direction of this rate change is as would be expected on the basis of stability constants. The Ks would be lower for the electron withdrawing carbonyl function as are the observed rates of reaction for those catalysts.The reverse is true of the alkylated ligands. Although the specific stability constants of these disubstituted dibenzo-18-crown-6 ligands are not known.Their relative rate constants are similar to the relative rate constants are similar to the relative stability constants observed by Smid and co-worked for the binding of sodium ions by a similar series of 4- substituted dibenzo -15-crown -5 ligand. Thus ,not only are the directions of the difference in K_{obsd} correlated to the stability constants of the complexes, but so are the general magnitudes of those differences.

In the series of substituted dibenzo-18-crown -6 compounds the, lipophilicity of the ligands is expected to increase as the size of the hydrocarbon substituent is increased.It can be assumed then that the concentration of crown metal complex in the organic phase did not increase. In terms of the simplified expression, the lipophilicity of dibenzo-18-crown-6 is already so high that the ratio DCRMA/(1+DCR) is approaching unity, and the reaction rate is likely dependent on the complex stability constant.In fact dibenzo-18 crown-6 is reported to be almost completely in the benzene layer when partitioned between benzene and water. Thus, it is not unreasonable that increasing the lipophilcity of the ligands did not produce more efficient catalysts.

Changes in ligand lipophilicity however can have an impact in catalyst performance.This clearly manifests in the reaction rate data obtained for the simple crown ethers. Table 01, shows that observed reaction rates with these crown ethers(runs 1-3,19-20) donot correlate with reported stability constants of the potassium complexes of these ligands. The large increase in K_{obsd}. Furthermore, dicyclohexano-18-crown-6 is catalyzed the reaction more efficiently than 18-Crown-6 even through it has lower K_s. The combined effect of both stability and partition constants does provide an explanation of the observed rates however. The partition of dibenzo 18-crown-6 between benzene and water strongly favors the benzene while that of 18 crown 6 strongly favors the water. Thus although 18- crown-6 binds potassium 2.3 times better than dinenzo-18- dibenzo-18-crown-6,It is less efficient at extracting the bound potassium into the organic phase and it can only acceptable the reaction 1.4 times faster than dibenzo-18-crown-6. Reported solubilities for the common crown ether indicate that the partitioning of dicyclohexano 18 crown 6 is probably intermediate to that of 18-crown-6 and dibenzo-18-crown-6. The effect of this is also apparent in the observed reaction rates. Even through it's Ks with potassium is 110% higher than that of than dibenzo-18-crown-6, dicyclohexano-18-crown-6 is only able to accelerate the reaction 80% faster than dibenzo-18- crown-6. (Lxin et al., 2010, strasser, 1985).

The lower rates observed for reactions catalyzed by (1- hydroxyethyl) benzno 18 crown 6 (run 15 and 16) can be explained in a similar manner. The addition of two

Table 1: Liquid-Liquid phase Transfer catalyst of the reaction between aqueous potassium thiocynate and P-Nitrobenzyl bromide

Sr.No.o	Catalyst Name	Run No.	Repeatation No. (Duplicates Run)	Kobsd, 10^4 S^{-1}	K_{rel}
01	None(Without Catalyst)	-------	I	0.098	0.05
			II	0.122	
02	18-crown-6	1	I	2.97	1.44
			II	3.03	
03	Benzo-18-crown-6	2	I	2.68	1.23
			II	2.42	
04	Dibenzoenzo-18-crown-6	3	I	2.095	1.00
			II	2.072	
05	Syn-bis(Methylbenzo)18-crown-6	4	I	2.73	1.27
			II	2.56	
06	Anti-bis(Methylbenzo)18-crown-6	5	I	2.60	1.22
			II	2.48	
07	bis(Acetylbenzo)18-crown-6	6	I	1.15	0.51
			II	0.99	
08	Bis[(1-hydroxyethyl)benzo]18-crown-6	7	I	1.47	0.70
			II	1.46	
09	Bis(tert-butylbenzo18-crown-6	8	I	2.63	1.26
			II	2.60	
10	Bis(n pentylbenzo) 18-crown-6	9	I	2.50	1.15
			II	2.31	
11	Bis[(1-hydroxy isopentyl)benzo]18-crown-6	10	I	2.06	1.00
			II	2.09	
12	Bis(heptanoylbenzo) 18-crown-6	11	I	0.99	0.49
			II	1.06	
13	Bis(n-hepylbenzo) 18-crown-6	12	I	2.23	1.11
			II	2.32	
14	Bis(n-decylbenzo) 18-crown-6	13	I	2.18	1.04
			II	2.8	
15	Bis(tetradecanoylbenzo) 18-crown-6	14	I	0.93	0.50
			II	1.14	
16	Bis[(1-hydroxytetradecyl]benzo) 18-crown-6	15	I	2.09	1.03
			II	2.18	
17	Bis(n-tetradecylbenzo)- 18-crown-6	16	I	2.31	1.11
			II	2.30	
18	Dicyclohexano- 18-crown-6	17	I	3.62	1.56
			II	3.29	
19	Bis (methylcyclohexano)-18-crown-6	18	I	4.69	2.34
			II	5.05	
20	Bis(n-decylcyclohexano)- 18-crown-6	19	I	3.86	1.86
			II	3.84	

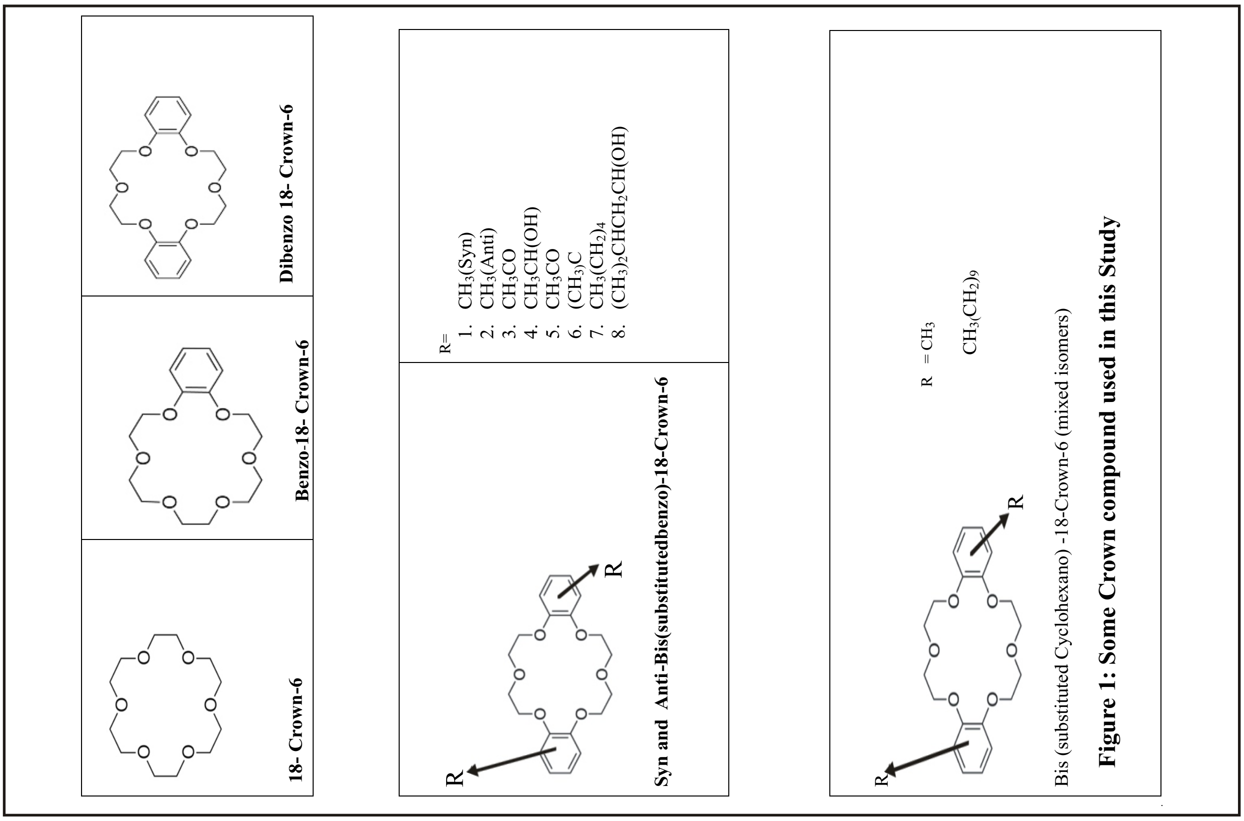

Figure 1: Some Crown compound used in this Study

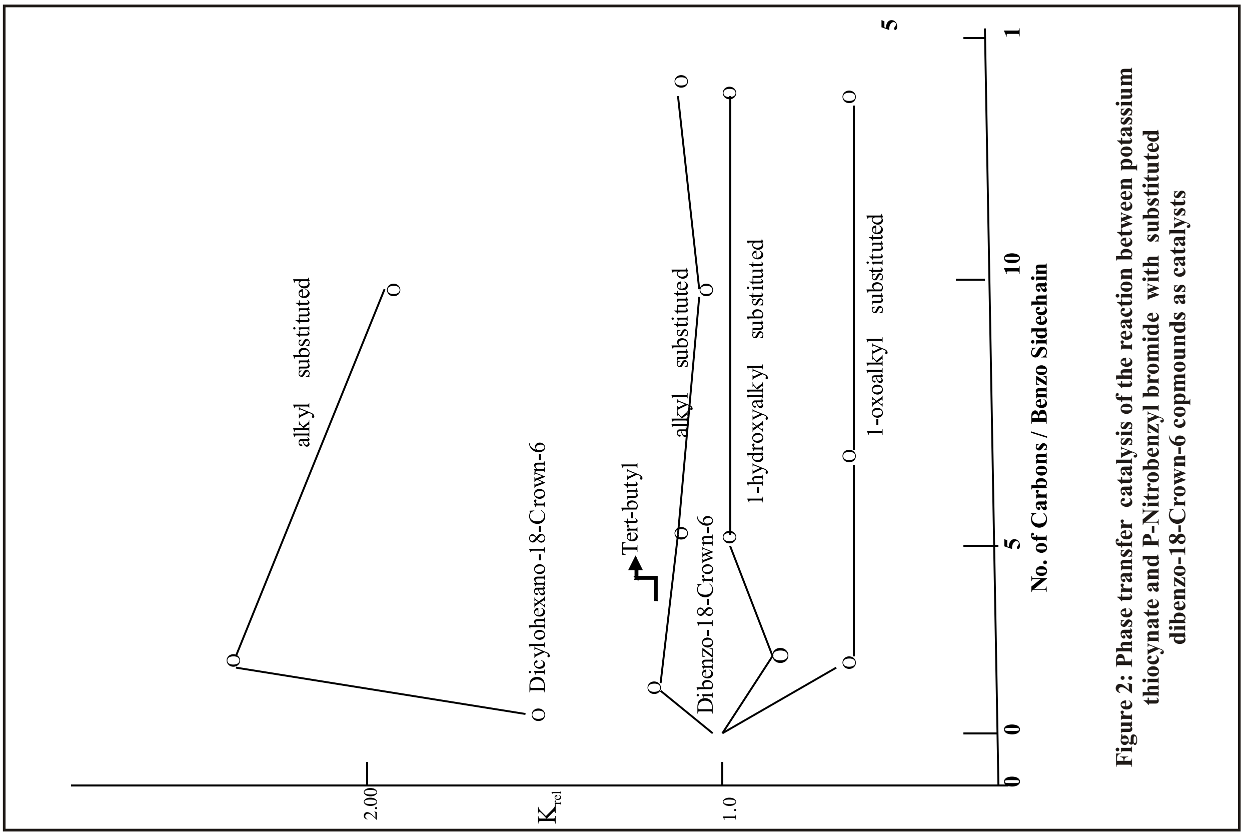

Figure 2: Phase transfer catalysis of the reaction between potassium thiocyanate and P-Nitrobenzyl bromide with substituted dibenzo-18-Crown-6 copmounds as catalysts

hydroxyl groups without the addition of substantial hydrophobic bulk to the parent dibenzo crown ether results in higher water solubility for the ligand.This result in a lower concentration of the crown lower reaction rate. Substitution by alcohols of at least five carbons has no such deleterious effect on the reaction rates.As the length of the alkyl group increases from one to ten carbon atoms the bis(n-alkylbenzo)-18 crown 6 compounds are progressively poorer catalysts. (Shamsipur et al., 1988, Izatt 1992).

All of these compounds are virtually water insoluble and are expected to have the same stability constants with potassium. Factor identified in the Expression, then are probably not responsible for the observed effect and its cause is not totally clear. It is possible those longer substituent's are more capable of interfering with the approach of the substrate molecule to the thiocyanate ion that is loosely associated with the crown metal complex. The observed decline in activity is linear and has a value of 6 x 10-6 S-1 per carbon atom in each side chain.The same effect is noticed for reactions catalyzed by alkyl substituted cyclohexane- 18 crown -6 compounds, the methyl analogue being somewhat more effective than the n-decyl compound. The activity of the tert-butyl analogue of dibenzo-18-crown-6 is higher than would be predicted.This observation tends some support to the proposed explanation.Being specially compact, the tert-butyl group is less able to interface with the approach of a substrate molecule to the face of the complex than its liner analogue.

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