

Fundamentals and Applications of Supramolecular Chemistry
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Week 08
Lecture 36

W8L36_Supramolecular chemistry of complexation of Organic Cations

Hello, everybody. So, now let us continue our discussion. So, this week we will be discussing supramolecular chemistry, which involves the recognition of organic cations and organic anions, and we will be looking at extended concepts of supramolecular chemistry.

So, until now in this syllabus, we have been focusing primarily on cationic response, which is the response of cations to different host molecules. Now, we will be discussing a different area of supramolecular chemistry, namely those involving anions. But before we proceed to anions, we would like to first take up the interaction of organic moieties and organic cations with a different kind of host molecule.

So, the supramolecular chemistry of organic cations involves host molecules. So, we will now be taking some specific cases because we have, by and large, looked at cation recognition behavior; we have looked at cryptands, we have looked at ethers, we have looked at lariat ethers, and so on and so forth.

So, let us now take up different examples. So, let us start with looking at the cryptand, and in this regard, we will be taking different kinds of cations, particularly those involving the ammonium types, where R1, R2, R3, and R4 are the different functional groups, or they can be the same functional groups and the corresponding ammonium salts of these.

So, for example, let us look at the first cryptand. We have taken the example of 2, 2, 1-cryptand where we have looked at n equal to 1. We can also have n equal to 2. In that case, it will be a 2, 2, 2-cryptand. And we can now modify this cryptand to form the following molecule.

So let us look very closely at this modified cryptand; it resembles a soccer ball, and what we have now done is add a set of nitrogen atoms here. Another arm of the nitrogen atom, which connects this nitrogen atom, is the -CH₂CH₂OCH₂CH₂- spacer.

And we can actually now represent this particular soccer ball in the following way: it has a tripodal geometry. You can see here that this is also a tripodal geometry, this is a tripodal nitrogen, and we can represent it in the following way.

So, this is a representation of the soccer ball compound where we can see the tripodal nitrogen, and now we will include the ammonium cation here to start with, which forms hydrogen bonds via N plus hydrogen bonds with the soccer ball.

So, now you can see that the ammonium ion binds to this cryptand, and this results in an increase in the pKa of the ammonium ion. That is, this particular process, where the release of the hydrogen ion has to be done by the ammonium ion.

So, now because of the complexation with the cryptand, the increase in the pKa of the ammonium ion is 6 units. That means these protons are now more strongly held by charge-assisted hydrogen bonds, and because of the strong hydrogen bonding, the hydrogens are stabilized in this particular complex. Therefore, it is very difficult to abstract this proton, thereby resulting in an increase in the pKa of the ammonium hydrogens by 6 units.

And therefore, it is very unlikely that these hydrogen atoms or hydrogen ions will now be lost because the pKa value is now increased by 6 units in comparison to the uncomplexed analog. So, this is a very interesting example where we can have ammonium ion stabilization with the soccer ball complex.

Similarly, we can look at the binding of ammonium ions with corands, where we can now draw. So, we now have this as a corand, and it undergoes complexation with the alkyl ammonium compound. So, we can draw this: the nitrogen here; these are the hydrogen bonds.

Ok. So, you have these hydrogen bonds that are present, and R is above the plane of the paper. So, it is now in a perching geometry. So, this actually sits on a perching geometry where the tripodal hydrogens of nitrogen interact via the N-H...N hydrogen bonding, and the R group sits above the plane. So, in this perching geometry via charge-assisted hydrogen bonds, the organic ammonium cation is able to stabilize itself.

Now, we can look at some thermodynamic data that is related to the complexation free energies for corand receptors with ammonium ions. So, let us look at this particular data, which is with respect to the corand receptors with the ammonium ions. Now, we will consider three such corand receptors.

This is the first corand receptor; the second corand receptor is the naphthyl fragment, and the third one is the binaphthyl moiety, where we have the methyl group here and the

methyl group is now here. So, you see that you get this orientation of this particular binaphthyl unit, and the methyl groups are now above the plane as well as below the plane.

So, we have these three host complexes, and we can look at the thermodynamic data where we can examine the complexation of these 1, 2, and 3 with the ammonium cation, with the methyl ammonium, and $R_3CNH_3^+$, where all the hydrogens have been replaced with the alkyl group. Now this value is 10.5, and this is in kilocalories per mole.

For the methyl, it is 9, 8.3, 9.5, 7.5, 6.9, 8.9, 6.9, and 6.4. So, we can see that when we go from left to right, given a particular host, when we start from ammonium to methyl ammonium to $R_3CNH_3^+$, there is a decrease in the magnitude of the complexation free energy.

And similarly, when you go from the top to the bottom, that is when you change the host from 1 to 2 to 3, again there is a decrease in the complexation free energy.

And you can see that the decrease is pronounced when going from ammonium to methyl ammonium; the decrease is 1.5 kilocalories per mole. Here you can see that the decrease is around 2 kilocal per mole, and here you can also see that the decrease is around 2 kilocal per mole.

So, there is a pronounced decrease in complexation free energy when the host changes from ammonium to methylammonium, and this difference suggests that the replacement of H with methyl, and then further on with additional CR_3 , increases the steric bulk, and hence the magnitude decreases. And when you come to this particular third host, that is, when you have the methyl complex, there are unfavorable steric interactions with your R, R, R, which are connected to carbon.

So, you can see here that when you have the R bulky groups, they will actually be interacting with the methyl groups at these two positions. So, there will be severe steric clashes between the R and the methyl groups in this position, as well as in this particular position. That results in a decreased affinity of the ammonium ions for the host complex, thereby decreasing the free energy change associated with this process.

So, we can now consider even larger size cations; we can now consider the largest size cations. Thus, complexation with larger cations.

For example, we can consider both the guanidinium cation and the imidazolium cation. So, let us first consider the guanidinium cation. So, this is guanidine; the addition of a proton makes it a cation. This is my guanidinium cation, and the corresponding imidazole has a nitrogen lone pair, and there is a lone pair here as well. So, if you add a proton, it

protonates the ring nitrogen.

This is my $C_3H_5N_2^+$. This is my imidazolium cation. So, this can also function as an organic guest molecule, and we can now look at the complementarity, the electrostatic complementarity, between one guanidinium and the host.

So, let us look at this host, which actually is a 27-membered corand. In this 27-membered corand, let us draw the structure. We have the R groups here, and we have R groups here.

So, we have got this 27-membered structure, and there are 9 oxygen atoms present. So, we call this the 27-crown-9 ether, and R here is the carboxylate anion. And we see that this has a threefold symmetry, and the guanidinium also has a threefold symmetry.

So, these two are complementary to each other; the symmetry of the guanidinium, which is the threefold symmetry, is complementary to this particular threefold symmetry. So, now it can nicely go and sit in this pocket, and it can form the hydrogen bonds here and here.

So, we can see that the hydrogen bond exists now, and the positive charge is there, and these are the $N^+ - H \cdots O$ hydrogen bonds. So, this kind of strong binding and complementarity exists between your guanidinium, and now instead of guanidinium, you can also have the imidazolium cation, which can interact by hydrogen bonds, and in this case, you will also have the $C-H \cdots O$ hydrogen bonds, which will play a role.

So, we have these very interesting interactions that are present here. Now we can go and look at the binding with lariat ethers. So here also, what are lariat ethers? Let us look at different kinds of lariat ethers. Here, it has been observed that for small-sized lariat ethers, as a function of the length of the side chain, we have a side arm in the lariat ether.

Irrespective of the length of the side arm, the magnitude of the equilibrium constant remains the same; thus, we will be looking at the values of $\log K$, which are the $\log K$ values. However, for the large-sized lariat ethers, it changes dramatically.

So, let us look at these values now. We have this lariat ether here, and R is equal to $-CH_2CH_2OMe$. So, this is the side chain, and the length of the lariat ether can increase if it goes to $-(CH_2CH_2O)_3$ and to $-(CH_2CH_2O)_5-Me$.

Now, I am considering the binding with the ammonium cation; this value is 3.06, 3.29, and 3.49. So here you can see that the binding is not very efficient.

In the case of the lariat ether, it relatively remains constant. Thus, increasing the length of this side arm does not really improve the magnitude of the binding constant. So, now

when we increase the number of oxygens by 1, and there is a CH₂-CH₂ unit increase when R is equal to CH₂-CH₂-O-Me, -(CH₂-CH₂-O)₂-, and -(CH₂-CH₂-O)₃-Me, 4 times and 5 Me. So, we take these different molecules where the length of the side chain is increasing, and we take the log K values as 3.14, 3.19, 3.38, 3.48, and 3.49.

So, you see that the magnitude remains constant, and this was the second set of lariat ethers. This was the first set of lariat ethers, and now when you go to the next set of lariat ethers, here you see the number of oxygens has increased to 5. Now when R is equal to CH₂CH₂OMe, the magnitude of log K increases by one order of magnitude; it becomes 4.2.

When it is -(CH₂CH₂O)₂-Me, it is 4.75; when it is 3Me, it is 4.56; when it is 4 Me, it is 4.4; and when it is 5 Me, it is 4.04. So, right away you can see that there is an increase in the magnitude of the log K value, an order of magnitude by which the log K value increases.

Now, why does this happen? This is based on the fact that when you have an ammonium ion now present here. So, we can see that we have the hydrogens which are interacting via hydrogen bonds. You can see that this is interacting with this. However, this hydrogen is in the vicinity of a -CH₂-CH₂- unit, so there is a steric clash.

So, it is able to maximize hydrogen bonds. So, we have these three hydrogens, and there are acceptors in the vicinity of two of these, but in this one, it essentially encounters a clash with the -CH₂CH₂- group.

On the contrary, when you consider this particular one, you will see that these hydrogens, which I am considering now in the plane, essentially form the tripodal plane. They are able to form hydrogen bonding interactions, but the one above is here. So this is my ammonium cation now. So now you can see that three of the hydrogens are able to interact with all the suitable acceptors.

This is the fourth proton, and therefore it is able to bind more efficiently via the formation of this additional N-H...O hydrogen bond. The more favorable hydrogen bonds the ammonium cation is able to participate in, along with the suitable orientation and arrangement of the acceptor atoms, depending upon the size of the lariat ether, the greater the magnitude of the binding constant will be.

And this magnitude is not going to change too much if you change the length of the side arm or the length of the side chain. If it increases, you will see that it does not really enhance much of the binding constant of this ammonium cation.

So, this lariat ether is also a very good host for encapsulating the ammonium cations. So, overall, in this lecture, we have now seen lariat ethers, corands, and cryptands functioning as suitable hosts for efficient encapsulation of organic cations.

So, now in the next lecture, we will go to anions and see what are the factors that affect anion binding, what are the size requirements are, what the electronic requirements are, the geometrical requirements of anions when they bind with a suitable host, and what the requirements on the host side are as well to have efficient anion-host binding.

Thank you.