

Alkali Metal Complexes. Substitution Reactions

A. K. BANERJEE, P. KEJARIWAL and S. K. ROY

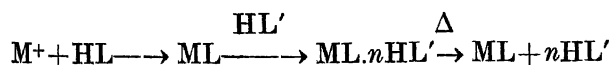
Chemistry Department, Patna University, Patna 800005

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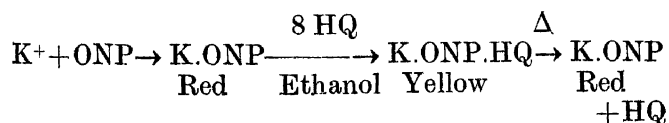
Acetylacetone and salicylaldehyde though have a higher pK value than *o*-nitrophenol, 1-nitroso-2-naphthol, isonitrosoacetophenone or salicylic acid, do not form mixed ligand complexes with alkali metal salts of the above organic acids, but completely replace the ligands and form metal salts/complexes of acetylacetone or salicylaldehyde. It is observed that these substitution reactions are not entirely dependent on pK value, but depends on the co-ordinating ability of the ligand.

The solution and thermal studies of the brown adducts of alkali-metal salts of *o*-nitrophenol and 1-nitroso-2-naphthol also support the above view.

IN our studies on the complexes of alkali metals with mixed ligands, it has been shown that adducts of the formula $ML.nHL'$ (HL and HL' are different organic acids) are formed, and one of the conditions put forward in the syntheses is that the pK value of HL' should be higher than HL , as otherwise HL' would replace the HL from the metal salt ML and form ML' .¹ These mixed complexes usually have a decomposition temperature slightly higher than the melting point of the second ligand, HL' , and break up into ML and HL' .



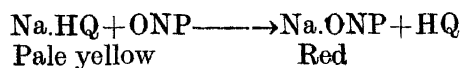
A typical example is



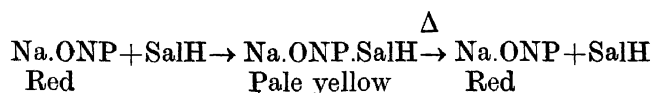
(ONP—*o*-nitrophenol; 8HQ—8-hydroxyquinoline)

8-Hydroxyquinoline melts at a temperature of 75° and the decomposition temperature of $K.ONP.HQ$ is 100°. This difference in the melting point of 8HQ and the decomposition temperature of $K.ONP.HQ$ may be due to (a) co-ordination of metal to the ligand, (b) hydrogen bonding between the ligands, (c) lattice effect and so on.

It is found that to an alkali metal salt solution of an organic acid of high pK value, if another strong organic acid is of low pK value, added then usually the alkali metal salt of the organic acid of low pK value (stronger acid) is formed; stronger acids replace the weaker ones. As a typical example to a saturated ethanol solution of $Na.HQ$, when ONP is added, $Na.ONP$ separate out from the solution.

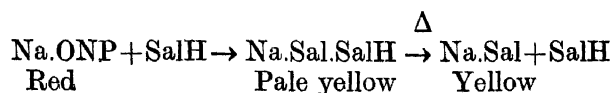


On extending the work on the synthesis of alkali metal complexes of mixed ligands with salicylaldehyde and acetylacetone, we have come across a number of compounds, which do not follow the usual rules as reported in our earlier work. As a typical example, to an ethanol solution of $Na.ONP$, when salicylaldehyde was added, it was found that a pale yellow precipitate separated out. The reaction was thought to proceed thus :

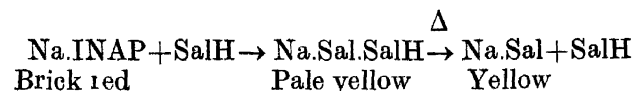


(SalH—Salicylaldehyde).

From the analytical results, I.R. spectrum and melting point of the above compound $Na.ONP.SalH$ (?), it was found that the compound is actually $Na.Sal.SalH$, and not $Na.ONP.SalH$.



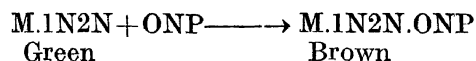
Na -isonitrosoacetophenone also gave similar reaction with salicylaldehyde.



(INAP—isonitrosoacetophenone).

According to Sidgwick and Brewer², the red coloured *o*-nitrophenolates react in the solid state with salicylaldehyde forming bright yellow powders which are absorbed salicylaldehyde on red *o*-nitrophenolates. This reaction when carried out in absolute ethanol or when red solid Na - or K -*o*-nitrophenolate was vigorously stirred in warm salicylaldehyde, it was found that salicylaldehyde completely replaced *o*-nitrophenol ligand. It was thus found that though

Further it has been found that when ONP was added to 1N2N metal salts, the same brown adducts M.1N2N.ONP separated out.



Thus it is seen that 1N2N (pK = 7.7), though have a higher pK value than ONP (pK = 7.17) form more stable salts than ONP salts. This stability may be due to greater chelating power of 1N2N over ONP towards the alkali metals. The other factors may be the hydrogen bonding between the ligands or difference in the melting point of both the ligands.

Experimental

A. *Reactions of M.ONP (I), M.1N2N (II), M.INAP (III), M.SalA (IV), M.HQ (V) with Salicylaldehyde :*

The general method of preparation was to add an excess of salicylaldehyde (mole ratio 4 : 1) to a concentrated solution/suspension of alkali metal salts of the organic acids in absolute ethanol. The mixtures were warmed for 10 min, and then on cooling deposited pale yellow compounds in every case. The compounds were filtered, washed with absolute ethanol and dried at 85°. Analyses (in Table) show them to be M.Sal.SalH.

B. *Reactions of M.1N2N (VI), M.INAP (VII), M.HQ (VIII) with acetylacetone :*

To the suspension of the alkali metal salts of the organic acids in acetone, an excess of acetylacetone (mole ratio 1 : 3) was added. The salts in suspension went into solution on warming and on cooling deposited white crystalline compounds. Again the analyses (in Table) show them to be M.acac.

C. *Reactions of M.ONP with 1N2N and M.1N2N with ONP :*

To the solutions of M.ONP/M.1N2N in absolute ethanol, solid 1N2N/ONP was added (mole ratio 1 : 3), and the mixtures were warmed on a steam-bath. On cooling the solutions, brown compounds (IX) separated out in both the cases. These brown mixed ligand complexes when heated to about 100°, break up into green coloured salt (X). The brown compounds when treated with benzene or chloroform gave green residues (X), which were found to be M.1N2N on analysis.

Acknowledgement

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References

1. A. K. BANERJEE, A. J. LAYTON, R. S. NYHOLM and MARY R. TRUTER, *J. Chem. Soc. (A)*, 1970, 292.
2. SIDGWICK and BREWER, *J. Chem. Soc.*, 1925, 2379.