

RAMAN EFFECT AND HYDROGEN BONDS

Part VIII. A Note on the Solutions of Coumarin in Mineral Acids

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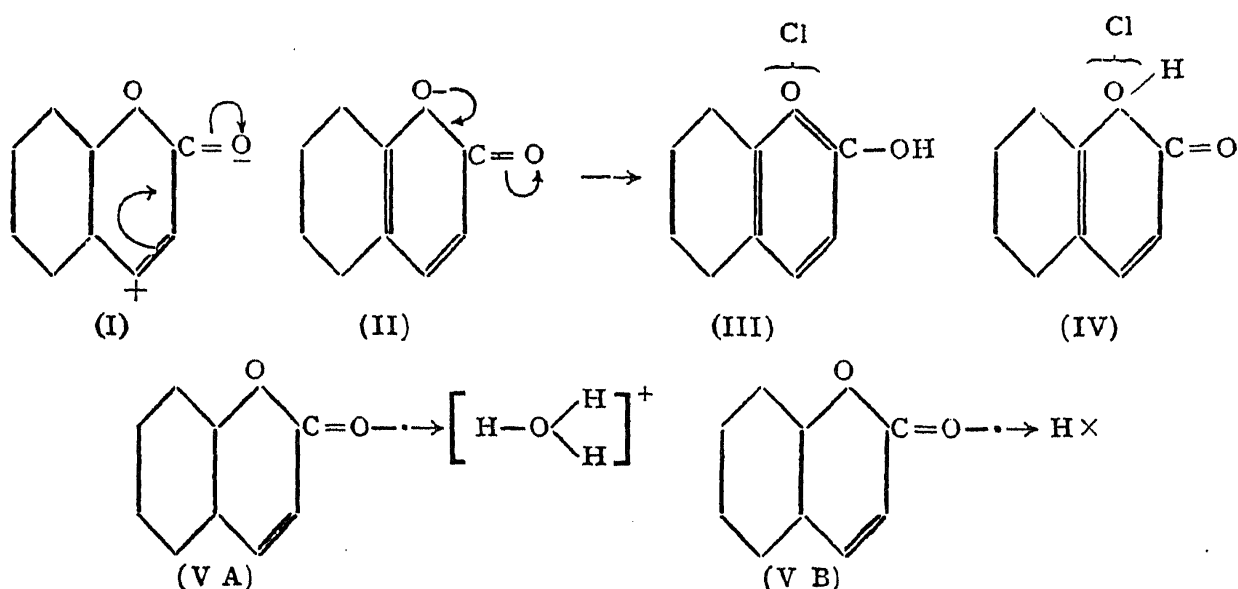
AMONG carbonyl compounds coumarin is unique in that it forms "True Hydrogen Bonds¹" with all acceptor solvents so far studied, phenol, chloroform, methyl and ethyl alcohols and acetic acid. Irrespective of the concentrations of the solutions and the capacities of the solvent molecules to form hydrogen bonds, the whole of the coumarin present enters into combination, so that in the Raman spectrum of the solutions the original carbonyl frequency of coumarin disappears completely and a modified frequency alone is present.^{2,3} In almost all other cases of carbonyl compounds the association between solute and solvent molecules is not complete and consequently both the original and modified C = O frequencies are noticed.

Though coumarin is sparingly soluble in water, considerable amount of it goes into solution in concentrated mineral acids. It dissolves up to 5% easily in cold concentrated hydrochloric acid and more of it is dissolved by the fuming acid. Concentrated nitric and sulphuric acids can dissolve much larger quantities of the solid, and solutions containing up to 50% can be easily made in the cold. On diluting the solutions with water the substance is precipitated unchanged.

In looking for an explanation of the high solubility of coumarin in aqueous mineral acids it is obvious that some kind of loose combination is involved. If an additive reaction be considered as a possibility, the capacity of the acid molecules to enter into such a reaction is dependent on the nature of the ions that they can produce. Of the two ions of the mineral acids mentioned above, the anions are more stable and the reactivity is dependent on the kationoid reactivity (electrophilic nature) of hydrogen ions. In regard to the coumarin molecule the following three centres of reactivity have to be considered : (1) the carbonyl group (C = O), (2) the ethylenic double bond (C = C) and (3) the pyrone oxygen. With reference to addition reactions, (1) is always kationoid (electrophilic), the reaction being initiated at the C atom and (2) also becomes kationoid in reactivity due to the existence of electromeric polarisation as shown in formula (I) below. Consequently these two centres of reactivity cannot be affected by the electrophilic acid reagents. Further,

the looseness of the combination involved definitely shows that addition at these centres does not take place, since additive compounds produced from ethylenic and carbonyl groups should be more stable. Regarding additive properties of (3), the pyrone oxygen, in forming oxonium salts all evidence seems to support the opinion that the oxygen and the $C=O$ group work in conjunction (see formula II) to form a hydroxypyrylium salt as shown in (III) and not a pyronium compound of type (IV). Though an oxygen atom in ether may be capable of forming oxonium salts directly, when it exists in conjugation with a carbonyl group, the two seem to function together. In this connection may be mentioned the high Raman frequency of the $C=O$ group in esters and particularly in the phenyl esters, as compared with the other types of compounds having the carbonyl group. This has been explained by us as due to the existence of polarisation similar to (II).⁴

There is a further possible mode of combination between coumarin and the mineral acids through the formation of hydrogen bonds as represented by formula (V). The question whether this happens or a hydroxy pyrylium salt is formed, can be solved by a study of the Raman spectrum of the solutions of coumarin in mineral acids. If structure (III) is formed the carbonyl frequency of coumarin should disappear, and if (V) is formed the frequency should undergo change, but should exist in the $C=O$ region.



[The symbol $\cdots\rightarrow$ is now proposed to indicate a hydrogen bond in order to distinguish it from a co-ordinate bond which is ordinarily represented by an unbroken arrow.]

Details regarding the Raman spectrum of coumarin in the solid state and in solutions in various solvents have already been given.⁵ The carbonyl frequency of the solution in a non-polar solvent, carbon tetrachloride (1742 cm.^{-1}) is taken as the standard for comparison. The pure substance

is dissolved in concentrated hydrochloric acid in the cold and a clear solution is obtained by rapidly filtering off the excess of the solid through a sintered glass funnel. A 5% solution could thus be made and employed for investigation. Though there is a good amount of continuous spectrum, the $C=C$ and $C=O$ regions are clear. It is noticed that the ethylenic frequencies are unaffected and are the same as those found in the spectrum of coumarin in carbon tetrachloride. There is a prominent $C=O$ frequency, but it has undergone a shift from 1742 to 1720 cm^{-1} and is rather diffuse. As in other solutions of this substance the original $C=O$ frequency has completely disappeared and a new one has taken its place. It could therefore be concluded that a hydroxypyrylium salt of type (III) is not formed and that the enhanced solubility of coumarin in hydrochloric acid is due to the formation of hydrogen bond as in (V).

A saturated solution of coumarin in cold concentrated nitric acid is coloured pale yellow. But a solution containing about 20-25% of coumarin is suitable for the study of the Raman spectrum and can be easily made. Almost the same results are obtained as in the case of the hydrochloric acid solution. The ethylenic frequencies are unchanged and the modified $C=O$ frequency is at 1722 cm^{-1} . The existence of complexes of type (V) involving hydrogen bonds is established in this case also.

With the concentrations of the acids employed, 33% hydrochloric acid and 68% nitric acid which approximate to 10 N, there does not seem to exist unequivocal evidence for complete ionisation. It is therefore difficult to say definitely whether structure (VA) involving hydrated hydrogen ions or (VB) involving undissociated molecules of the acids represents the correct nature of the complexes involved.

Solutions of coumarin in concentrated sulphuric acid did not give clear pictures due to the existence of continuous spectrum and some fluorescence.

Summary

The marked solubility of coumarin in aqueous mineral acids is attributed to the formation of complexes. That this takes place through hydrogen bonds is shown by a study of the Raman spectrum of these solutions wherein the carbonyl frequency is found to be considerably lowered, but still persists.

REFERENCES

1. Murty and Seshadri .. *Proc. Ind. Acad. Sci., A*, 1942, **15**, 157.
2. *Ibid.*, 1941, **14**, 601.
3. *Ibid.*, 1942, **15**, 241.
4. *Ibid.*, 1939, **10**, 315.
5. *Ibid.*, 1941, **14**, 598 ; 1938, **8**, 520.