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THE ROLE OF HYDROGEN BONDING IN THE AUTOXIDATION AND ALKYLATION OF 2-NAPHTHOLS

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The powerful hydrogen bond electron donor fluoride ion assists the O-alkylation of 2-naphthols but inhibits the autoxidation of 1-alkyl-2-naphthols. These observations may be explained in terms of the nature of the OHF^- hydrogen bond.

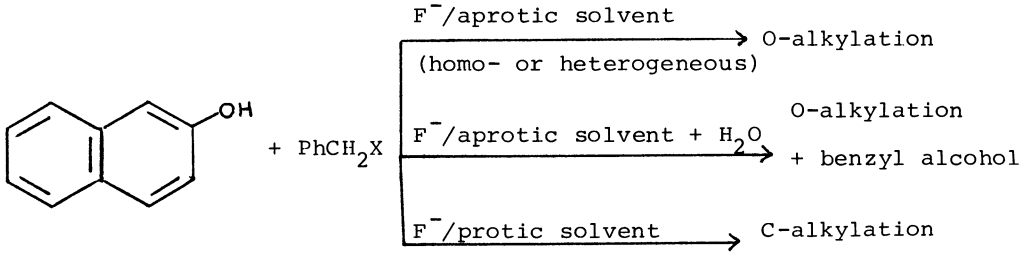
Carnduff has shown that whereas a number of 1-alkyl-2-naphthols readily undergo autoxidation at room temperature, those that possess an intramolecular H-bond to the hydroxyl hydrogen do not react under the same conditions.[1,2)]

The intramolecular H-bond might be considered as locking the acidic hydrogen and hence inhibiting its removal - a similar argument has been used to explain the lower than expected acidities of many intramolecularly H-bonded aromatic hydroxy compounds.[3)] In the light of these observations we have investigated the reactivity towards autoxidation of 1-alkyl-2-naphthols where the acidic hydrogen is in an intermolecular H-bond to the powerful H-bond electron donor fluoride ion. Strong H-bonding to fluoride is now an established method for enhancing the reactivity of protic compounds[4)] and it is tempting to suppose that autoxidations which are often base-promoted might be assisted by this type of interaction.

Fluoride disrupts the intramolecular H-bond in 1-benzyl-2-naphthol as witnessed by a large downfield shift in the ^1H n.m.r. resonance of the hydroxyl hydrogen. Reaction of 1-benzyl-2-naphthol and KF-18-crown-6 (approximately equimolar quantities) in benzene with oxygen for 10 hours resulted in no detectable change apart from the large downfield shift in the OH ^1H n.m.r. resonance. Irradiation of the mixture with u.v. had no effect. We then turned our attention to 1-isopropyl-2-naphthol which cannot form an intramolecular H-bond and should readily autoxidise.[1)] Reaction of this compound

in benzene under conditions similar to those described above but in the absence of fluoride gave a good yield of the hydroperoxide[1] but the reaction was completely stopped by the addition of fluoride.

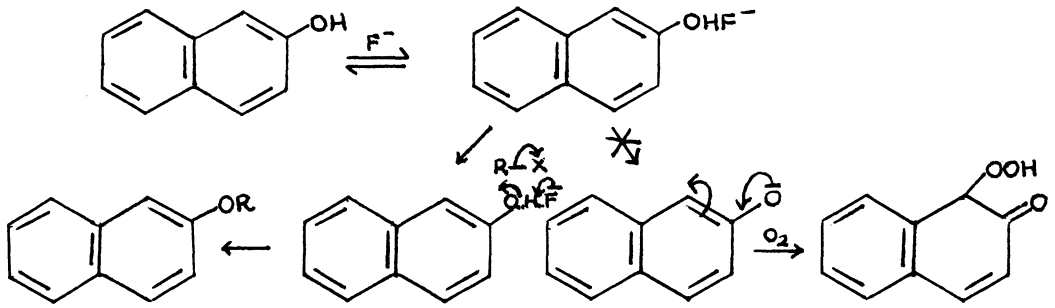
In an attempt to demonstrate that fluoride-2-naphthol complexes are indeed powerful nucleophiles towards normal electrophiles we studied the reaction of 2-naphthol with benzyl halides in the presence of fluoride. The anion of 2-naphthol is ambident and would normally be expected to undergo attack by an incoming electrophile at both the C-1 carbon and oxygen sites. H-Bonding along with several other factors has been demonstrated to have an effect on the course of 2-naphthol alkylation reactions. We have found that by using tetraethylammonium fluoride dihydrate (TEAF.$2H_2O$) in DMF or KF in DMF, 2-naphthol was readily alkylated by benzyl chloride or benzyl bromide on heating to produce the O-alkylated product only. Addition of small amounts of water to the reaction system resulted in the production of benzyl alcohol as well as the O-alkylated naphthol whereas running the reaction in kF/CF_3CH_2OH gave the C-alkylated naphthol as the only product.



The observed alkylation reactions are consistent with the concept of charge localisation within the 3 atom H-bond unit. Theoretical calculations on the charge density distributions in strongly H-bonded complexes involving fluoride clearly show significant build up of negative charge density on the electron acceptor atom at the expense of the fluoride ion and the H-bonded hydrogen.[5] Charge density changes in the rest of the complex are small and probably insignificant. Our results would seem to be consistent with the calculations in that we observe high nucleophilic reactivity at the naphthol oxygen with no apparent delocalisation of charge. In 2,2,2-trifluoroethanol, the situation is quite different and only C-alkylation is observed. This presumably results from initial deprotonation of the naphthol as dissolution of 2-naphthol in $kF-CF_3CH_2OH$ produces a deep red colouration (λ_{max} 348 nm) characteristic of the naphthol anion. It is not clear if deprotonation occurs as a result of direct attack by the fluoride anion itself or indirectly by attack by 2,2,2-trifluoroethoxide, but once the delocalisable naphthoxide anion is generated, preferential

solvation of the oxygen will cause exclusive C-alkylation to occur when the benzyl halide is introduced.[6)]

It is clear from the alkylation studies that nucleophilic activation of the naphthol does occur on H-bonding to fluoride and we must seek to explain the reduced reacticity towards oxygen in terms of different reaction mechanisms. In autoxidation reactions, oxygen can abstract a hydrogen atom and the rate of such a reaction is likely to depend to some extent on the ease of H-abstraction. This would seem to agree nicely with Carnduff's original observations on the reduced reactivity of intramolecularly H-bonded naphthols[1,2)] but can it explain the reduced reactivity of intermolecularly H-bonded naphthols when the same type of interaction enhances reactivity towards alkylation? One possible explanation is that in alkylations, attack by the electrophile occurs on the actual H-bonded complex rather than on the free anion as shown below. This is consistent with the many spectroscopic studies which show that except



under special circumstances, proton transfer does not occur between F^- and a protic molecule.[4)] Clearly oxygen cannot follow such a route and it is obviously unable to abstract a hydrogen atom from the tight OHF unit. Autoxidation can occur under basic conditions and would involve initial proton abstraction and subsequent attack by the resulting anion or molecular oxygen. For the conversion of a 2-naphthol to a hydroperoxy-naphthalenone, attack on oxygen must be preceded by delocalisation of the charge on to the C-1 carbon and this is inhibited in our systems by the charge localisation of the H-bond.

A solution of TEAF.$2H_2O$ (0.02 mol; prepared by evaporation at 30-40°C of a solution of the aqueous fluoride in excess acetonitrile under reduced pressure) and 2-naphthol (0.02 mol) in DMF (50 cm^3) was evaporated at ca 50°C under reduced pressure to remove most of the residual water. Benzyl chloride or bromide (0.02 mol) in DMF (20 cm^3) was added and the whole stirred at room temperature for 4 h. Extraction with ether followed by aqueous washing,

drying ($MgSO_4$) and evaporation of the solvent gave after purification on an alumina column, benzyl-2-naphthyl ether (0.017 mol., 85%, m.p. 98-100°C; m/e 234 (M+)). Reaction of undried TEAF or TBAF (containing ca 10 mol equiv. of H_2O) with equimolar amounts of benzyl bromide and 2-naphthol in DMF gave benzyl alcohol (25-50% yields; m/e 108 (M+)) and unreacted 2-naphthol only. Refluxing a mixture of kF (0.1 mol), 2-naphthol (0.02 mol) and benzyl bromide (0.02 mol) in DMF (100 cm^3) for 10 h gave after chromatographic separation, a 17% yield of benzyl-2-naphthyl ether and unreacted 2-naphthol only. When the same reaction was carried out using 2,2,2-trifluoroethanol as the solvent, a 44% yield of 1-benzyl-2-naphthol (m.p. 112-14°C, m/e 234 (M+)) was recovered.

In conclusion, strong H-bonding of 2-naphthols to fluoride enhances selective reactivity towards electrophilic alkylating agents by high charge localisation within the H-bond. H-bonding in general inhibits hydrogen atom abstraction and is therefore, likely to inhibit radical reactions at H-bonded centres under normal circumstances.

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