HYDROGEN FLUORIDE AS A CONDENSING AGENT

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The structures, H_2F_2 H_6F_6 and HF, which have at various times been assigned to gaseous hydrogen fluoride have been shown by recent electron diffraction measurements to be incorrect and incomplete. The new data indicate that the gas consists of polymers of indefinite length arranged in zig-zag fashion.

The use of hydrogen fluoride has been exploited mainly in connection with catalysis. It has been found that the catalytic alkylation of benzene can be effected in its presence. A great variety of alkylating agents can be used including olefins, alcohols, halides, ethers and esters. With the latter, acylation can also be accomplished simultaneously. As a rule tertiary and secondary halides, acohols and ethers will react at room temperature, whereas with the compounds of the primary type elevated temperatures are necessary.

It has also been observed that acylations occur in the presence of this catalyst. For example, acetophenone was produced from the interaction of acetic anhydride with benzene at 100° in the presence of hydrogen fluoride. Some acylations may proceed at ordinary temperatures. Generally polycyclic rings must be present before reaction will take place under the milder procedure. The simpler aromatic rings are acylated at 100°. Acid chlorides, anhydrides or carboxylic acids themselves are all equally capable of undergoing this reaction.

The mechanism of the alkylation reaction is as yet unknown. On the basis of present evidence it is fairly certain that neither olefins nor fluorides may act as the active intermediates in the condensation. It is proposed that a carbonium ion resulting from the ionization of the alkylating agent is the one that so far most satisfactorily accounts for all the observations. The ionization may proceed in the following manner;

$$RX + HF \leftrightarrows R{-}X{\rightarrow}H{-}F \rightleftarrows R^+ + X{\rightarrow}H{-}F^-$$
$$R^+ + C_6H_6 \longrightarrow R{-}C_6H_5 + H^+$$

Existing evidence seems to indicate that to a large extent the stability of the $X{\rightarrow}H{-}F^-$ ion determines the ease with which the reaction proceeds.