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THE EFFECT OF RING SUBSTITUENTS ON THE DEDIAZOTISATION OF AROMATIC DIAZONIUM FLUORIDES

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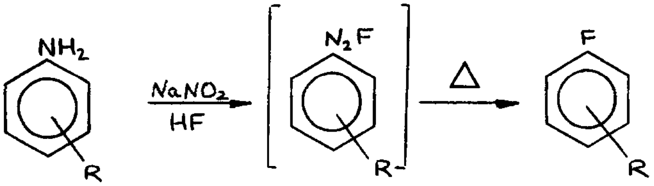
The basic reaction may be summarised as:



A range of ring substituted anilines were investigated and the group R was found to have a marked effect on the rate of dediazotisation and yield of fluoroaromatic formed. This effect was interpreted as operating in four ways:

1. Inductive. Electron donating groups (eg. Me) increased the rate of decomposition, withdrawing (eg. NO_2,-COOH) slowed it down.

2. Mesomeric. If the charge on the diazonium ion can be delocalised on to R (eg. _ortho_ and _para_-NO_2), then the rate was slowed down.

3. _Ortho_ lone pair delocalisation. If the group R was in the _ortho_ position to the diazo and had a lone pair available for donation into the outer nitrogen (eg.- NO_2, - OMe, - Hal, - OH), stabilisation occurred which prevented fluoroaromatic formation.

4. Side reactions. Some groups such as - OMe, - $COCH_3$, - Me reacted with the NOF/HF of the reaction medium.

Various methods of raising the reflux temperature of the reaction medium (addition of H_2O, NaF, glyme) in order to obtain decomposition were used. If a temperature above about 80°C was necessary to obtain this reaction, tar formation predominated.