

ABSTRACT

This thesis deals with a kinetic investigation on the thallation of simple aromatic compounds in two solvent systems.

(i) In trifluoroacetic acid at 25°C the reaction of thallium trifluoroacetate with benzene and toluene is too rapid for observation by conventional kinetic procedures. It has been found that the addition of acetic acid and a wide range of other diluents causes a lowering of the rate, and the reaction has been followed in trifluoroacetic acid:acetic acid mixtures. Toluene in this system is found to react with the thallium species at a rate seven times greater than benzene and shows an isomer ratio 10 percent ortho, 3 percent meta, and 87 percent para. A primary isotope effect for both toluene and benzene has been recorded. Enhanced positional and substrate selectivity has been observed for a variety of electrophilic aromatic substitution reactions in trifluoroacetic acid. The activation parameters of thallation are of interest in this connection since they are sensitive both to temperature and dilution by acetic acid. It has been found that activation energy decreases to low values for solutions with small amounts of acetic acid but at the same time the entropy of activation becomes less favourable.

(ii) In 80 percent acetic acid 20 percent water catalysis of the reaction by perchloric and sulphuric acid has been studied. Catalysis does not depend on the acidity of the medium but is consistent with a scheme dependent on an equilibrium in which successive acetate anions are replaced by the anions of the catalyst. All the species so produced are effective electrophiles but the one which has

all the acetate anions replaced is the most reactive. The isomer distribution for sulphuric acid catalysis has also been studied and shows that there is increased selectivity towards para substitution at higher catalyst concentrations.

Thallation shows evidence of reversibility in both trifluoroacetic acid and in mineral acid catalysed reactions in acetic acid-water. In general the mechanism of thallation appears quite similar to that of the corresponding mercuration reactions.