Concerning the π-Complex Mechanism for Aromatic Substitution. Detritiation in Trifluoromethanesulphonic Acid

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Summary Aromatic hydrogen exchange in trifluoromethanesulphonic acid occurs 10^{11} times faster than in trifluoroacetic acid, but gives no indication of a change to the π-complex mechanism of electrophilic substitution.

A π-COMPLEX mechanism for electrophilic aromatic substitution has been proposed because of the low selectivity between aromatic substrates under competitive conditions,[1] and has been supported by kinetic studies of individual isomers.[2] The former results have been argued to be due to mixing control[3] and the kinetic data in the latter experiments may be unsatisfactory.[4]

If a π-complex mechanism can apply to electrophilic substitution then as the reactivity of the electrophile increases, the mechanism should become more evident. Of all electrophilic aromatic substitutions, hydrogen exchange has been studied under the widest range of conditions and a wide range of electrophile reactivity,[5] but shows no evidence of the low selectivity required by a π-complex mechanism. More recently Olah *et al.*[6] have carried out benzylations in which the reactivity of the incipient benzyl cation was slightly modified by substituents in the aromatic ring. They believed that the resultant change in the reactivity pattern was due to the incursion of the π-complex mechanism (though mixing control could also account for them).

We have now carried out kinetic studies of hydrogen exchange of benzene and chlorobenzene under conditions ranging from anhydrous trifluoroacetic acid to anhydrous trifluoromethanesulphonic acid which bring about very large changes in reaction rate; it should be noted that questions concerning mixing control do not apply here. From our rate data we are able to show that at 70°, benzene undergoes exchange $2{\cdot}2 \times 10^{11}$ times faster in the latter acid compared to the former. This is certainly the largest variation in electrophile reactivity that has been produced for hydrogen exchange and probably so for any substitution. It is interesting to examine what happens to the selectivity under these conditions.

First it is necessary to correct the observed partial rate factors for the temperature difference and to do this we have used the $\rho' T' = \rho'' T''$ relationship, which we have found to be followed in hydrogen exchange with great accuracy over at least 125° temperature range. In the anhydrous sulphonic acid at $-40°$ the observed partial rate factors for chlorobenzene are: *ortho*, 0·005; *meta*, 0·000345; *para*, 0·018 which corrected to 70° are 0·0275, 0·0045, and 0·0645 respectively. There is thus some change in selectivity, the *ortho*- and *para*-position being more, and the *meta*-position less deactivating than for exchange in trifluoroacetic acid for which the values are 0·041, 0·00131, and 0·176.[7] This is not unexpected however as the electrophile in the stronger acid will have less demand for the $+E$ effect of the substituent, and this notion is supported by the greater change in reactivity at the *para*- than at the *ortho*-position. This condition will not apply to the *meta*-substituent which probably gives the most accurate indication of the change in selectivity and shows the ρ-factor to be reduced by *ca.* 20%. This modest reduction is quite consistent with the high reactivity of trifluoromethanesulphonic acid and there is no evidence at this stage of a change to a π-complex mechanism.

The H_0 acidity function value for trifluoromethanesulphonic acid has recently been determined[8] as $-15{\cdot}07$. The value for trifluoroacetic acid is *ca.* $-3{\cdot}0$,[9] so the difference is *ca.* 12 units and it is therefore noteworthy that the exchange rate is increased by almost twelve powers of 10. This correlation provides strong evidence for our supposition that the increase in rate arises from an increase in the reactivity of the electrophile rather than from a medium effect. Additional confirmation comes from the fact that the principal increase in rate on changing from trifluoroacetic acid to trifluoromethanesulphonic acid occurs on addition of small amounts of the latter to the former *i.e.* in the region where the medium composition is almost unaltered.

We thank the S.R.C. for financial support.

(*Received, 29th August* 1973; *Com.* 1220.)

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