1,2-Hydrogen Shifts during Acid-catalysed Hydrogen Exchange

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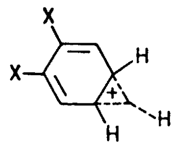
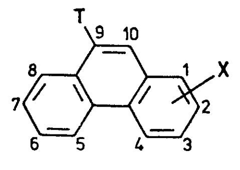
Summary The first example of a 1,2-hydrogen shift accompanying acid-catalysed hydrogen exchange has been observed during detritiation of methyl-substituted 9-tritiated phenanthrenes.



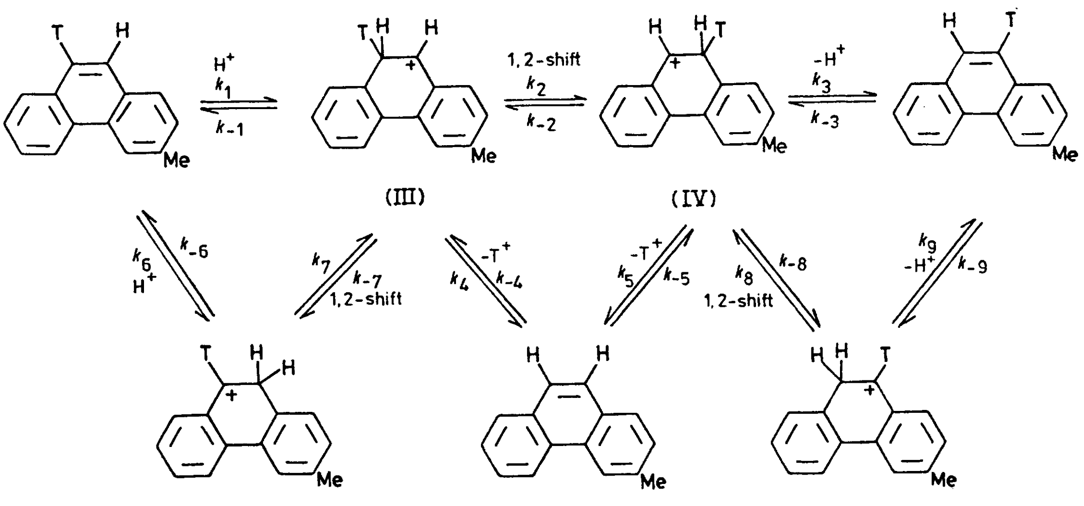
(I) X = F or Me



(II) X = 1 to 8-Me

In superacids, *o*-difluorobenzene and *o*-xylene form stable protonated species which undergo 1,2-hydrogen shifts, the benzenonium ion (I) being postulated as the intermediate.[1] Rate coefficients for such shifts have been measured for a number of symmetrically substituted aromatics in superacids.[2] Such shifts have not previously been observed during kinetic studies of acid-catalysed hydrogen exchange, though one of us has tentatively suggested that they could account for some anomalies in exchange rate data.[3] We now report the first unambiguous example of a 1,2-hydrogen shift accompanying detritiation in anhydrous trifluoroacetic acid.

Detritiation of *X*-methyl-[9-^{3}H]phenanthrenes (II, X = 1—8) gave good first-order kinetics in each case except for the 3-methyl compound where the exchange rate coefficient decreased with time. The 3-methyl compound is considerably more reactive than the other isomers because the transition state has *p*-quinonoid character. The rate coefficients for exchange of all the isomers (with the exception of the 6-methyl compound) are in agreement with theoretical predictions, and parallel the rate data for exchange at the analogous positions in methylnaphthalenes.[4] By contrast, the 6-methyl compound is too reactive, and indeed more reactive than the 5- and 7-methyl compounds in which the methyl groups are conjugated with the reaction site. This result is clearly anomalous, and coupled with the non-linearity of the first-order plot for exchange of the 3-methyl compound, shows that a 1,2-hydrogen shift is taking place across the 9,10-bond (Scheme). Because the bond-making and bond-breaking processes in the 1,2-shift are virtually equivalent, the effect of differences in zero point energies of the bonds made and broken will be minimal, so that the possible 1,2-shifts will take place at comparable rates. Moreover, since the 3-methyl compound undergoes exchange at the 9-position faster than does the 6-methyl compound, it follows that k_4 is faster than k_5, and likewise that $k_1 \approx k_{-9}$ are faster than $k_6 \approx k_{-3}$. The consequences of these equilibria are two-fold: (i) Exchange of the 3-methyl compound can take place not only by the normal route ($k_1 \rightarrow k_4$), but also by the routes $k_6 \rightarrow k_7 \rightarrow k_4$ and $k_1 \rightarrow k_2 \rightarrow k_5$ both of which will produce a slower rate of exchange. In addition the intermediate (IV) will tend to return to 6-methyl-[9-^{3}H]-phenanthrene rather than to 3-methylphenanthrene, *i.e.* an appreciable concentration of the less reactive 6-methyl-[9-^{3}H]phenanthrene will be obtained and the observed kinetic form then follows. (ii) Exchange of the 6-methyl compound can take place not only by the normal route ($k_{-3} \rightarrow k_5$) but also by routes $k_{-3} \rightarrow k_2 \rightarrow k_4$ and ($k_{-9} \rightarrow k_8 \rightarrow k_5$). Since route k_4 is faster than k_5, and k_{-9} is faster than k_{-3}, it follows that the observed rate of exchange will be anomalously high. Although some of the 6-methyl compound can isomerise to the 3-methyl compound, the latter will then exchange rapidly, and no curvature of the first-order kinetic plot will result.



SCHEME

The ease of the rearrangement evidently arises from the near-equivalence of the intermediates (III) and (IV), so that there will be a small energy barrier for their interconversion. Olah and Mo showed that the activation energy for the 1,2-shift from the 4- to the identical 5-position in *o*-difluorobenzene was only half that for the non-equivalent 3- to 4-shift.[1] Clearly when considering exchange rate data, the possibility of 1,2-shifts between near-equivalent positions must be considered. The shift across the 9,10-bond in phenanthrene is especially favourable not only because of symmetry considerations, but because the benzenoid character of the two terminal rings is preserved. Consequently the shift of both alkyl and aryl groups across the 9,10-bond of phenanthrenonium ions has been detected in superacids,[5] and it is significant that a methyl group shifts some 7 × 10^4 times faster across the 9,10-bond of the 9,9,10-trimethylphenanthrenonium ion, than across the 1,2-bond of the heptamethylbenzenonium ion (both in superacids, at 0 °C)[5] even though the latter cation should be the more stable.

Our kinetic data indicate that *ca.* 10% of the 3- and 6-methyl isomers become effectively interconverted. The exchange data for the other isomers are not significantly affected by the other isomerisations that must take place (*i.e.* $1 \rightleftharpoons 8$, $2 \rightleftharpoons 7$, $4 \rightleftharpoons 5$) because the reactivities of each pair are closely similar. 1,2-Shifts of the electrophile in alkylation,[5] sulphonation,[5] and nitration[6] in superacids have previously been detected and clearly are relevant to the fact that such migrations interfere with kinetic studies under normal conditions;[7] many of these shifts can be expected to be sterically accelerated. The possibility of 1,2-shifts now has to be considered in evaluating kinetic data for hydrogen exchange, but just as the latter is not sterically sensitive (except in a few special cases) so neither should be the 1,2-shift and the latter is therefore unlikely to be significant except under very favourable circumstances such as those described here.

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