Radiation-induced Aliphatic Hydrogen Exchange in Aqueous Solution: Evidence for a Spur Reaction between Organic Radicals and Electrons

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Summary Stereochemical studies on cyclohexane-1,2-diols and scavenger experiments on dioxan indicate that the radiation-induced hydrogen exchange at C-H bonds involves the reaction sequence: $RH \xrightarrow{OH^\cdot} R^\cdot \xrightarrow{e^-_{aq}} R^- \xrightarrow{HTO} RT$, the first two steps of which occur in spur regions.

Aliphatic alcohols in solution in tritiated water undergo hydrogen exchange at C–H bonds under the influence of tritium-β- and γ-radiation.[1]

The original observation of the exchange[2] was unexpected and the mechanism remained puzzling. A more detailed study of certain aspects of this reaction, which we believe to be a general—though unrecognised—feature of the radiation chemistry of all aliphatic compounds in aqueous media, has been carried out on degassed solutions, and the principal conclusions are now reported.

(1) The exchange is not confined to hydroxylic substrates, but is also readily observable with dioxan as a substrate, or in dioxan–water as a solvent, with cyclohexane.

(2) The reaction is retarded not only by addition of known electron scavengers[3] (Ag^+, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, H_3O^+), as previously reported,[1] but also by species that have negligible reactivity towards solvated electrons and instead are effective scavengers of hydroxyl radicals[4] (N_3^-, Br^-, SCN^-). The manner of action of the two classes of inhibitors requires the involvement of two separately scavengeable primary radiolysis products in the sequence of reactions leading to exchange. Under our conditions such a reaction sequence can occur only in spurs. Some of the reasons for this conclusion are the form of the concentration dependence of the exchange, the dependence of the rate of exchange on the square (*not* the cube) of the tritium concentration (first-order in tracer concentration[5] and first-order in concentration of radiation source[6]) and the low steady-state bulk concentration of radical species which

renders the occurrence of encounters between two different primary radiolysis products after their diffusion out of the spur regions excessively improbable.

(3) Exchange at a chiral position (*e.g.*, α-hydrogen in *cis*- or *trans*-cyclohexane-1,2-diol) occurs with partial retention and partial inversion of configuration. Whichever diastereoisomer is used as substrate, the labelled products are formed in practically the same ratio (*trans*-diol: *cis*-diol *ca.* 3·5:1). It is concluded that the reactions of these substrates involve at least one common intermediate (or equilibrating common set of intermediates) which then goes on to the same set of products.

The results can be accommodated by a simple scheme of reactions (1) (recently considered by Kochetkov for reactions in frozen aqueous solutions of sugars but rejected for reactions in liquid solutions[7]) the first two steps of which

$$\mathrm{RH} \xrightarrow{\mathrm{OH}\cdot} \mathrm{R}\cdot \xrightarrow{\mathrm{e^-_{aq}}} \mathrm{R}^- \xrightarrow{\mathrm{HTO}} \mathrm{RT} \qquad (1)$$

we consider to take place in spurs. The scheme explains the stereochemical result since R· and R⁻ are species which are the same for parent molecules RH that differ only in the chirality of the carbon atom from which the initial hydrogen abstraction takes place. *G*-values for exchange reactions were calculated on the basis that the total number of hydrogen exchange events is equal to the number of tritium exchange events divided by the fractional abundance of tritium in the solvent, *i.e.* by neglecting isotope effects. Limiting *G*-values are 0·33 for *trans*-cyclohexane-1,2-diol (total for exchange at *all* ring positions) and *ca.* 0·44 for dioxan, for substrate concentrations of *ca.* 0·7—0·8M.

The inference that electrons can react in spurs not only with other primary radiolysis products (OH·, H_3O^+) but also with organic radicals derived from a solute has further implications in radiation chemistry. Radiation-chemical studies on 'aqueous' solutions are often carried out in the presence of *ca.* 1M methyl or ethyl alcohol.[8] It is possible that the radicals formed from these alcohols by hydrogen abstraction can, by analogy with other evidence to be presented in detail elsewhere, react with electrons before these can diffuse into the bulk of the solution. Estimates of 'early' electron yields, deduced from observed yields of identified products without consideration of radical-electron reactions, may thus be too low. Observations of hydrogen exchange, which reveal the occurrence of these processes, are thus an essential requirement in such studies.

The action of electron scavengers does not totally inhibit the exchange, even at high concentrations, and the limiting value of the rate reduction depends on the chemical identity of the scavenger. This finding provides a new line of evidence for the involvement in radical reactions of the lower-valence state of the cation inhibitor,[9] an electron transfer from which (*e.g.* $\mathrm{R}\cdot + \mathrm{Ni}^+ \rightarrow \mathrm{R}^- + \mathrm{Ni}^{2+}$) can be involved in an alternative exchange route.

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