Radiation-induced Aliphatic Hydrogen Isotope Exchange between t-Butyl Alcohol and Solvent Water

By V. GOLD* and J. H. ROLSTON
(*King's College, University of London, Strand, W.C.2*)

Summary A radiation-induced aliphatic hydrogen exchange reaction has been found and certain features of its mechanism have been interpreted in terms of the formation of a solvated electron.

ON extending Gold and Gruen's study of tritium exchange between the aliphatic hydrogen atoms of t-butyl alcohol[1] present as a solute in partially aerated aqueous solution to lower concentrations of acid catalyst, we have observed the supervention of a pH-independent (between pH 6 and 12) exchange reaction. This reaction is induced by the β-radiation of tritium contained in the solvent, and represents a hitherto unrecognised radiation-induced process. This conclusion is based on (i) the observation that the extent of exchange (for small amounts of exchange) is proportional to the square of the tritium concentration in the medium (as first noted for the radiation-induced aromatic tritium exchange[2]), (ii) the retardation of the exchange reaction by substances known to be effective scavengers for reactive species formed on radiolysis of water, and (iii) exchange experiments in which the solutions were exposed to similar radiation doses (of γ-rays), over a much shorter period of time from a ^{60}Co source, which resulted in amounts of exchange proportional to the radiation dose and roughly the same *G*-value (0·11—0·13, ignoring any isotope effect).

The small difference in efficiency of metal ion scavengers ($Ag^+ \sim Cd^{2+} > Cu^{2+} > Ni^{2+}$) is more in line with their reactivity towards hydrated electrons than towards hydrogen atoms as deduced from pulse radiolysis studies.[3] (In this respect these results provide a contrast with our previous studies of the corresponding aromatic exchange reaction.[2]) If we conclude from this that the inhibition is due to competition between t-butyl alcohol and metal ions for hydrated electrons, then we calculate that the second-order rate constant for the reaction between hydrated electrons and t-butyl alcohol has a value in the region of

10^8 l mole^{-1}sec.$^{-1}$. Even high concentrations of scavenger do not entirely suppress the exchange reaction: there is a residual exchange, the rate of which is approximately proportional to the concentration of t-butyl alcohol.

As a working hypothesis we suggest that our observations are explained by the assumption that the essential step in the initiation of exchange is the formation of a solvated electron in which there is a t-butyl alcohol molecule in the solvation shell (or trapping cluster). This type of solvated electron is assumed to be formed by two routes, the main one being reaction of a hydrated electron with t-butyl alcohol (the reaction of rate constant 10^8 l mole^{-1}sec.$^{-1}$ which can be suppressed by the addition of electron scavengers) and the other route a direct radiolytic process the probability of which is only determined by the concentration of t-butyl alcohol and which is not suppressed by the added solutes. We postulate that, within the cluster of solvent molecules held to and thereby forming a trap for the electron, hydrogen exchanges take place very rapidly.

At first sight, there appears to be an inconsistency between our inference, that the reaction of t-butyl alcohol and the hydrated electron has a fairly large rate constant, and pulse radiolysis studies which suggest that alcohols are relatively inert.[4] However, the reaction which we consider as the precursor of the exchange does not destroy the solvated electron, but merely alters its state of solvation without a profound change in its optical absorption.[5] It may therefore not be easily noticed in pulse radiolysis when the rate of disappearance of the characteristic absorption spectrum is being followed.

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[1] V. Gold and L. C. Gruen, *J. Chem. Soc.* (*B*), 1966, 600.
[2] J. R. Adsetts and V. Gold, *Chem. Comm.*, 1968, 915; *J. Chem. Soc.* (*B*), 1969, 1108.
[3] M. Anbar and P. Neta, *Internat. J. Appl. Radiation Isotopes*, 1967, **18**, 493.
[4] M. Anbar, *Adv. Phys. Org. Chem.*, 1969, **7**, 115.
[5] U. Schindewolf, *Angew. Chem. Internat. Edn.*, 1968, **7**, 190.