# Hydrogen Exchange in Phenylacetylene and the Hydroxide Ion Anomaly

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*Summary* The general base-catalysed exchange of acetylenic hydrogen in phenylacetylene is found to give a Brønsted correlation with unit slope and no primary isotope effect, indicating that a diffusion or rotation step following proton transfer is the rate-determining stage of this reaction; comparison of this result with the behaviour of chloroform suggests an explanation for the substantial deviations generally shown by hydronium and hydroxide ions from Brønsted plots for proton transfer to or from carbon based on other catalysts.

It has been suggested that proton transfer to carbon in aqueous solution, traditionally a slow reaction, becomes encounter-controlled when the transfer takes place to a localized electron pair, as in the trichloromethyl anion.[1] We report that reprotonation of the phenylacetylide anion, also a species with an electron pair localized on carbon, appears to be encounter-controlled as well. This result was to be expected following an earlier study,[2] but experimental difficulties in that work prevented a firm conclusion from being drawn.

We studied this reaction by measuring rates of exchange of the acetylenic hydrogen in phenylacetylene using tritium as a tracer. Rates of loss of tritium from [$^3$H]phenylacetylene, present at low concentration (*ca.* $10^{-3}$M) in wholly aqueous solutions of base, were first-order for 10—12 half-lives. The reaction is subject to general base catalysis and gives a Brønsted plot with unit slope: for the five primary amines, benzylamine, 2-methoxyethylamine, 2,2-dimethoxyethylamine, 2-cyanoethylamine, and 2,2,2-trifluoroethylamine, $\beta = 0{\cdot}97 \pm 0{\cdot}05$. Isotope effects, determined by measuring initial rates of incorporation of tritium from the solvent into phenylacetylene and [$^2$H]-phenylacetylene,[1] are within experimental error of unity: for reaction with hydroxide ion, $k_H/k_D = 0{\cdot}95 \pm 0{\cdot}09$; and for reaction with 1-methylimidazole, $k_H/k_D = 1{\cdot}17 \pm 0{\cdot}52$.

The absence of an isotope effect implies that proton transfer is not taking place in the rate-determining stage of this reaction. The unit Brønsted slope confirms this and shows further that proton transfer occurs before the rate-determining step. This information leads to the hypothesis that replacement of the original proton in the hydrogen-bonded complex between phenylacetylide ion and the protonated proton acceptor, either by diffusion apart of these two species or rotation of a new hydrogen into hydrogen-bonding position, is the slow step of the reaction, equation (1).

$$\begin{tikzcd} \mathrm{PhC{\equiv}CH + B} \arrow[r, "\rightleftharpoons" description, phantom] & \mathrm{PhC{\equiv}CH{\cdot}B} \arrow[r, "\rightleftharpoons" description, phantom] & \mathrm{PhC{\equiv}C^{-}{\cdot}HB^{+}} \arrow[d, shift left, harpoon] \\ \mathrm{PhC{\equiv}CH' + B} \arrow[r, "\rightleftharpoons" description, phantom] & \mathrm{PhC{\equiv}CH'{\cdot}B} \arrow[r, "\rightleftharpoons" description, phantom] & \mathrm{PhC{\equiv}C^{-}{\cdot}H'B^{+}} \arrow[u, shift left, harpoon, "\text{Rate-determining}"'] \end{tikzcd} \qquad (1)$$

Consistent with this mechanism is the fact that combination of the presently determined rate constants with a value of the p$K_a$ of phenylacetylene which has been in the literature for some time, 21,[3] gives specific rates of recombination of phenylacetylide and ammonium ions of the order of $10^{10}$M$^{-1}$ s$^{-1}$, which is the expected magnitude for an encounter-controlled process in aqueous solution at 25°. On the other hand, use of a recently determined value, p$K_a$ = 23·2,[4] gives rates of recombination greater than the encounter-controlled limit by several orders of magnitude; this supports the speculation[4] that assumptions regarding activity coefficient behaviour needed to reference the experimental data, which were obtained in cyclohexylamine solution, to an aqueous standard state may be invalid.

The hydroxide ion catalytic coefficient for the present reaction is anomalously low: it misses the Brønsted correlation by a factor of $10^2$. If this were not the case, general base catalysis could not have been detected, *i.e.* with $\beta = 1$ and the hydroxide ion point lying on the Brønsted line, the hydroxide ion reaction would have overwhelmed proton transfer to any other base.[1,5] The latter is, in fact, the situation claimed for the encounter-controlled hydrogen exchange of chloroform, where general base catalysis could not be observed directly but was rather inferred from other data.[1] In this respect, phenylacetylene resembles carbon acids whose deprotonation is not encounter-controlled, *i.e.* pseudo-acids from which proton transfer is slow and for which hydroxide ion is generally an anomalously poor proton acceptor. Chloroform, however, appears to be similar to "normal"[6] oxygen and nitrogen acids whose deprotonation is encounter-controlled and which give Brønsted plots with hydroxide ion either on or slightly above the line.

The fact that phenylacetylene is a poorer hydrogen bond donor than chloroform[7] suggests an explanation for this striking difference, and for the general behaviour of hydroxide and hydronium ion points in Brønsted correlations as well. Formation of an encounter complex prior to proton transfer between the hydroxide ion, which is very strongly solvated by hydrogen bonding in aqueous solution, and a pseudo-acid requires the expenditure of somewhat more energy than formation of a similar complex between the acid and most other bases. The hydroxide ion therefore generally lies below Brønsted correlation lines for systems such as these. When the proton donor can itself hydrogen bond to the proton acceptor, however, some of this energy is regained, and the behaviour of the hydroxide ion becomes less anomalous. If the proton donor is sufficiently good at forming hydrogen bonds, it may become part of the hydrogen-bonded network of the solvent, as is the case with "normal" acids, and proton transfer may then occur by the Grotthuss chain mechanism which gives the hydroxide ion an advantage over other bases. Consistent with this explanation is the fact that the hydronium ion, which is also strongly hydrated in aqueous solution, generally lies below Brønsted lines for slow proton transfer to carbon and above Brønsted lines for encounter-controlled proton transfer to "normal" bases.

A different explanation of the anomalous behaviour of the hydroxide ion toward carbon acids has been advanced.[1] That hypothesis requires solvent water to be relatively ineffective at forming a hydrogen-bonded encounter complex with the carbanion in the reverse reaction, which, *via* the equilibrium, slows down the forward process as well. It is not clear, however, why water should be a poor hydrogen bond donor relative to its $pK_a$, and this explanation also does not allow for cases where the reverse reaction does not occur but the hydroxide ion anomaly still exists, as, for example, in the halogenation of carbonyl compounds.[8]

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