The Reversible Tautomerism of 9,10-Anthraquinols

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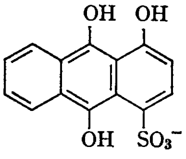
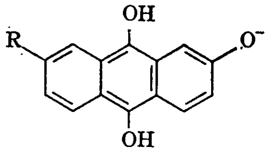
DURING investigations of the redox properties of hydroxy-9,10-anthraquinonesulphonic acids, in aqueous solution,[1] it was established that the polarographic oxidation of the anthraquinols (I and IIa), in specific pH ranges, yielded anodic waves, which were not immediately stable. The anodic limiting diffusion current gradually decreased to a lower constant value and, simultaneously, an unsymmetrical cathodic wave appeared at more negative potentials, the respective wave heights decreasing and increasing at about the same rate, until equilibrium was reached. Gill and Stonehill[2] have observed similar behaviour for (IIb), and kinetic measurements indicated that reversible rearrangement to (IVb) was responsible.

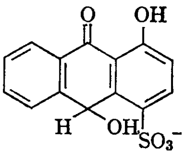
The rate of decrease of the anodic limiting currents of (I) and (IIa) has been recorded under various conditions. Only one particular acid–base form of the anthraquinol is consumed in the reaction, and at pH values where the concentration of this is not appreciable, the wave height remains constant. For (I) only the species with three undissociated hydroxy-groups (pH < 7), and for (IIa) only that with one dissociated hydroxy-group (pH 6—12) undergo conversion. The kinetics are described by the equation for a simple reversible reaction, in which the forward and reverse processes are of first order,[3] and reversible tautomerism of the anthraquinols is therefore evident. The electronic absorption spectra of (I) and (IIa), in suitable buffer solutions, were not immediately constant, but slowly varied until eventually steady characteristics were recorded. The occurrence of well-defined isosbestic points indicated that only two components were present.



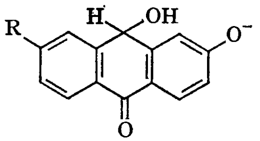
(I)



(IIa); R=SO_3^-
(IIb); R=H



(III)



(IVa); R=SO_3^-
(IVb); R=H

Gill and Stonehill[2] found that the rate of rearrangement of (IIb) was practically independent of pH, but this was definitely not the case for (I) and (IIa). Experiments in solutions of constant ionic strength and pH, but varying concentrations of buffer acid and base, confirmed the existence of general acid catalysis of the forward reaction and general base catalysis of the reverse reaction, but not for (IIa) in boric acid–sodium hydroxide buffers. This result is consistent with those for other prototropic rearrangements, but does not allow mechanistic interpretation, as the probable reaction products (III and IVa, respectively) have not been characterised. The apparent absence of general acid and base catalysis for (IIa) in borate buffers can be correlated with the known low catalytic activity of the borate anion as a base[4] and the probable mechanism of dissociation of boric acid (V). Dilute borate buffers contain only (Va) and (Vc).[5] The relatively slow rate of proton transfer by boric acid[6] and its low catalytic activity indicate that the acid dissociation is governed by an initial slow hydration step. It is a Lewis acid, like its acid halides, and does not

[1] A. D. Broadbent, Dissertation, ETH, Zürich, 1963; A. D. Broadbent and H. Zollinger, *Helv. Chim. Acta*, 1964, **47**, 2140.

[2] R. Gill and H. I. Stonehill, *J.*, 1952, 1857.

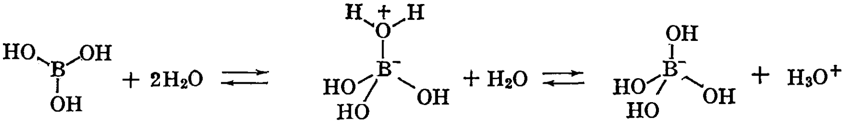
[3] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", J. Wiley and Sons, Inc., London, 1961, p. 186.

[4] R. P. Bell, D. H. Everett, and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, 1946, *A*, **186**, 443.

[5] N. Ingri, *Acta Chem. Scand.*, 1957, **11**, 1034; J. O. Edwards, G. C. Morrison, V. F. Ross, and J. W. Schulz, *J. Amer. Chem. Soc.*, 1955, **77**, 266.

[6] R. P. Bell, "The Proton in Chemistry," Methuen and Co. Ltd., London, 1958; J. Kuta, *Coll. Czech. Chem. Comm.*, 1956, **22**, 1411.

function as a direct proton donor. The ineffectiveness of the borate anion as a base catalyst can be explained by the probable strong acidity of its conjugate acid (Vb).



(Va) (Vb) (Vc)

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