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THE REVERSIBLE TAUTOMERISM OF 9,10-ANTHRAQUINOLS.

by A. D. Broadbent and E. F. Sommermann.
Department of Colour Chemistry, The University, Leeds 2.

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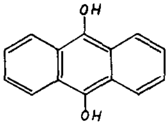
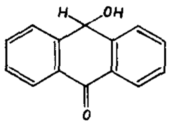
The reversible rearrangement of 9,10-anthraquinols (I) to the corresponding 9-hydroxy-10-anthrones (II) is well known. The kinetics of the tautomerism of 2-hydroxy-9,10-anthraquinol (III) were first examined by Gill and Stonehill (1). Recent measurements on aqueous solutions of sulphonated 1- and 2-hydroxy-9,10-anthraquinols showed that the foreward reaction to the 9-hydroxy-10-anthrone is subject to general acid catalysis, and the reverse reaction to general base catalysis (2). No catalytic effects were observed in boric acid buffers; there absence was correlated with the mechanism



I



II

of dissociation of boric acid. Because of this the reversible tautomerism of 2-hydroxy-9,10-anthraquinol and some of its derivatives has been reinvestigated.

The conventional polarographic technique was used to record the rate of disappearance of the anthraquinol (3). The rate curves were analysed assuming a simple reversible reaction, in which the foreward and reverse processes are of first order (4). The rate at which equilibrium is attained is highly dependent upon the nature of the buffer solution. In ethanolamine - hydrochloric acid buffers, of constant pH and ionic strength, the kinetics substantiate the assumed simple reversible reaction. The rate is directly proportional to the concentrations of buffer acid and base in the solution, and there appears to be no catalysis by the solvent (Fig. 1). In boric acid - sodium hydroxide buffer solutions, of similar pH and the same ionic strength, the rate is almost independent of the concentrations of the buffer components, over the range investigated. Analysis of the rate curves did not give the expected linear relationship (Fig. 1). Other derivatives of III (6-hydroxy- and 7-sulphonate) have also been examined. The results confirmed the existence of general acid catalysis of the foreward reaction and general base catalysis of the back reaction in the tautomeric rearrangement of these compounds, except in borate buffer solutions, where catalysis is mainly by the solvent and similar deviations from the expected kinetic behaviour arise. Although the rearrangement product has not yet been fully characterised, the following reaction mechanism seems possible.

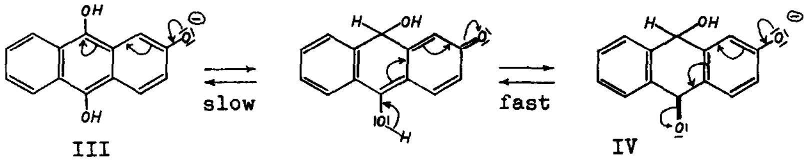
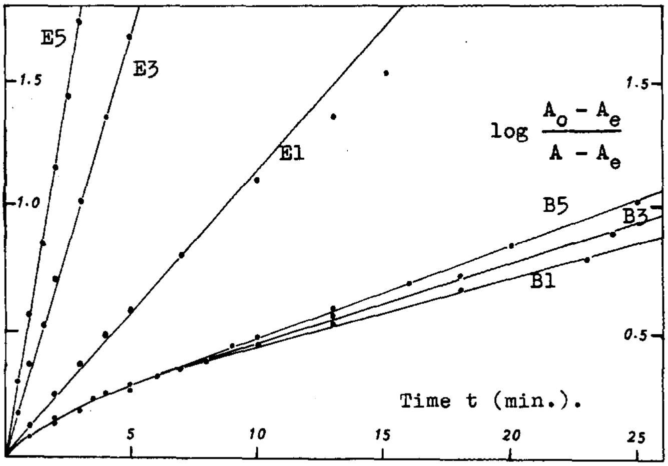


FIG. 1.

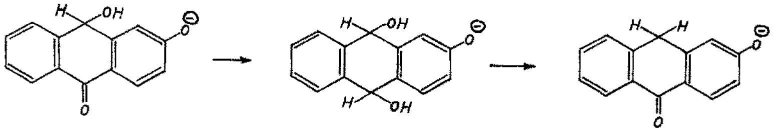


2-Hydroxy-9,10-anthraquinol (5×10^{-4}M, 25°C, pH = 9.2 - 9.4) in borate buffers (B1, B3, B5) with relative buffer component concentrations of 1, 3 and 5, and likewise in ethanolamine buffer solutions (E1, E3, E5).

Assumed kinetic equation $$2.303 \log \frac{A_o - A_e}{A - A_e} = t(k + k') \qquad (4)$$

The rapid rate of rearrangement of III, in ethanolamine buffer solutions, also manifests itself in the polarographic reduction of 2-hydroxyanthraquinone. In borate buffers a single diffusion-controlled wave is obtained, but in the ethanolamine buffers an additional wave, at more negative potentials, is observed, which has very pronounced kinetic character (3). It is caused by reduction of the rearrangement product of III, and its limiting current is governed by the rate of this reaction in the region of the electrode-solution interface. In borate buffer solutions the rearrangement is much slower, and diffusion of III away from the electrode surface is quicker than the rearrangement.

Polarography of III, in equilibrated buffer solution, gives the expected anodic diffusion wave of the anthraquinol, and, at more negative potentials, a cathodic wave, attributed to reduction of the carbonyl group in 2,9-dihydroxy-10-anthrone (IV). The latter has been shown to consist of a diffusion-controlled wave, followed by a kinetic wave at more negative potentials. The half-wave potential of the kinetic wave is very close to that of the anthrone (presumably V), prepared by chemical reduction of 2-hydroxyanthraquinone (5). This kinetic character of the more negative wave, which was proved by investigating the dependence of wave-height on temperature and mercury pressure, must be related to the mechanism of the reduction of IV to V. It would appear that its wave-height is governed by the rate of conversion of 2,9,10-trihydroxy-9,10-dihydroanthracene (VI) to V.



IV VI V

Further studies of these mechanisms are in progress[*].

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[*] F. Sommermann, Technische Hochschule, Stuttgart, Lehrstuhl für Textilchemie, Germany.