CHEMISTRY

The Coloured Product of the Sakaguchi Reaction

WE have already reported¹ that the coloured product of the Sakaguchi reaction² (between arginine and α -naphthol) behaves as a typical acid-base indicator, being red in alkali and yellow³ in acid. It has now been found that the compound behaves as an oxidation-reduction indicator also.

Long strips of Whatman No. 1 filter paper (3 in. $\times$ 22 in.) were soaked in a 0.4 per cent solution of arginine hydrochloride, and dried. Colour was then developed, as described earlier^{1,3}, by dipping first in a solution of 100 mgm. α -naphthol, 1 gm. urea and 2.5 gm. potassium hydroxide in 100 ml. ethanol, and finally in a solution of 0.75 gm. bromine in 100 ml. 5 per cent aqueous potassium hydroxide. The colour was dissolved in a minimum quantity of water and the solution, after being acidified with hydrochloric acid (pH 2-3), was left overnight in a refrigerator. By washing the resulting dark precipitate with cold acidified water and then extracting repeatedly with ether, considerable purification of the compound was achieved.

It was observed that on adding a few drops of a freshly prepared solution of sodium dithionite to a dilute and slightly alkaline solution of the above substance, the red colour of the solution was instantly discharged. On shaking the solution gently in air, however, the colour reappeared. This reversible process could be repeated a large number of times with the same solution. When acidified, the yellow colour of the solution could be similarly discharged by dithionite and restored by shaking in air. These results were a clear indication of the redox nature of the compound. It was found that the compound could also be reduced to the leuco form by stannous chloride, but not by ascorbic acid or cysteine.

It appears from these observations that the coloured product of the Sakaguchi reaction has probably a quinonimine portion as its chief chromophore. If so then, in view of our recent finding⁴ that this reaction is in fact a general reaction of phenolic compounds but is specific for *para*-unsubstituted phenols (a few *p*-halophenols, which gave the reaction, were the sole exception to this rule), the compound must have a *p*-quinonoid structure (as distinct from an *o*-quinonoid one). It would thus appear that the mechanism of colour formation in the Sakaguchi reaction is presumably an oxidative coupling between a guanido compound and a phenol, somewhat as in the formation of an indophenol.

Although the present finding, together with the *para*-unsubstituted-phenol specificity of the reaction⁴, practically confirms our earlier suggestion regarding a *para*-linkage in the compound¹, it is clear, since the compound behaves as a redox system both in acid and alkali and so must have a quinonoid structure in either, that the variation of its colour in acid and alkali is not due to isomerization between a benzenoid and a quinonoid form as suggested earlier¹ but is due to other factors.

The final purification of the compound is in progress with a view to its complete characterization. These results, including the exact redox potential of the fully purified compound, will be published later elsewhere.

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³ Bhattacharya, K. R., Datta, J., and Roy, D. K., *Arch. Biochem. Biophys.* (in the press).

⁴ Bhattacharya, K. R., and Datta, J., *Proc. Forty-sixth Indian Sci. Congr., Part 3, Abstracts*, 155 (1959).

Reaction-directing Properties of Non-enzymic Macromolecules: Pyrogallol Oxidation in the System Iron(III)-Cellulose

ALTHOUGH the plant cell wall is regarded as an inert substance, mechanical in function, recent studies have demonstrated wall polysaccharides to be active sites (matrices) in the directed polymerization of 4-hydroxyphenylpropene derivatives (such as eugenol) to lignins¹. Other investigations have shown the peroxidation of pyrogallol catalysed by iron(III) to be enhanced by low concentrations of non-enzymic deoxyribonucleic acid², and have emphasized both the qualitative and quantitative effects accruing from addition of solid surfaces to various chemical or biochemical systems³⁻⁶.

To extend these views on the catalytic activity of biopolymer surfaces, the system iron(III)-cellulose has been included among those studied as an oxidase model and for its possible direct significance in biocatalysis as well.

Among the experimental procedures employed, variables other than cellulose have included concentrations of pyrogallol/hydrogen peroxide (constant molar ratio maintained at 1:5) and iron(III). The formation of coloured oxidation products from pyrogallol at 0.1 and 1.0 m.mole/20 ml. (after incubation in darkness, at $24 \pm 1^\circ$ C. in 0.025 *M* potassium dihydrogen phosphate for 100 hr.) was accelerated

Fig. 1