

energy (less stability) than an isolated Kekulé structure.

The figures in Table 2 enable one to predict approximate pK_A values (in water) for bases giving rise to ionic forms of the above five types. ΔpK_A values (averaged from Table 2) would be *ortho* = + 2.5, *para* = + 4.2, *ortho-para* = + 2.3, *ortho-ortho* = + 0.5, *para-para* = + 4.5.

In this way, from the pK_A values of isoquinoline (5.33, water), phthalazine (3.47, water) and phenanthridine (3.30, 50 per cent ethanol), the pK_A values of 6-amino isoquinoline, 6-amino phthalazine and 6-amino phenanthridine may be predicted to be 9.8 (water), 8.0 (water) and 7.9 (50 per cent ethanol; see Table 1 for ΔpK_A), respectively. These three bases (*para-para*-quinonoid type) would be the strongest mono-amino derivatives in their series, since in each case no amino derivative of the *para*-quinonoid type is possible.

One of us (P. H. G.) thanks the Commonwealth Research Grant Committee of this University for a scholarship.

PETER H. GORE
JOHN N. PHILLIPS

Department of Organic Chemistry,
University of Sydney.
Oct. 6.

¹ Albert, A., and Goldacre, R., *Nature*, **153**, 467 (1944).

² Albert, A., and Goldacre, R., *J. Chem. Soc.*, 706 (1946).

³ Albert, A., Goldacre, R., and Phillips, J., *J. Chem. Soc.* (in the press).

Reaction between Hydrogen Peroxide and Iron Salts

FROM a recent discussion with J. H. Baxendale and P. George, we understand that they have from kinetic studies proposed a reaction scheme for the mechanism of the evolution of oxygen from hydrogen peroxide and ferrous ions [see p. 692 of this issue of *Nature*]. We have also obtained experimental evidence from the studies of the consumption ratios which lead to conclusions similar to theirs and which are discussed in the following.

The reaction between hydrogen peroxide and ferrous salts has been studied by Haber and Weiss¹ and certain aspects of it more recently again by Baxendale, Evans and Park². We have now studied this reaction in its dependence on pH, and we have investigated the role of the ferric ions in the hydrogen peroxide ferrous-ion reaction.

We have used a flow apparatus built on similar lines to those suggested by Schmid³, to bring about a very rapid mixing of the component solutions and thus to ensure well-defined initial concentrations of the reactants. So far, only consumption ratios ($-\Delta(\text{H}_2\text{O}_2)/-\Delta(\text{Fe}^{2+})$) have been measured.

In order to study the effect of ferric ions, we have investigated the reaction (at different pH) in the presence of (i) fluoride, (ii) pyrophosphate ions, both of which are known to form stable complexes with ferric ions, and we have convinced ourselves that these complexes are not active as catalysts. We have found that fluoride and pyrophosphate ions both decrease the consumption ratios.

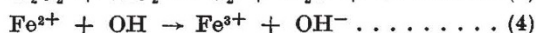
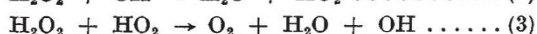
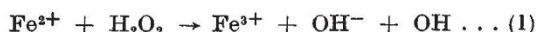
It is of importance to note that the hydrolysis products of ferric ions (which are formed if the reaction is carried out at sufficiently high pH) are themselves also practically inactive as catalysts during time intervals which are relevant for the relatively fast reaction between ferrous ions and hydrogen peroxide.

Conversely, we have been able to show that addition of ferric salts (over and above that formed by the oxidation of the ferrous salt) increases the consumption ratios. This clearly indicates that ferric ions are involved in the ferrous ion catalysis, which, however, must not be confused with the well-known relatively slow catalytic decomposition of hydrogen peroxide by ferric salt alone.

It seems that all this can be explained by a slight modification of the original scheme of Haber and Weiss by introducing into the 'ferrous ion catalysis' one of the reactions (reaction (14) of ref. 1) which has been considered previously in connexion with the 'ferric ion catalysis'.

The decrease of the consumption ratios with decreasing pH suggests further that it is the anion, O_2^- , rather than the undissociated HO_2 which enters into the reaction, the two being connected by the equilibrium $\text{HO}_2 \rightleftharpoons \text{H}^+ + \text{O}_2^-$.

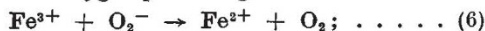
Thus in addition to the original equations:



with a possible additional chain-breaking by the interaction of two radicals, for example:



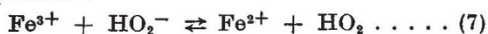
one has the oxygen-producing reaction:



which reaction, in the presence of ferric ions, largely replaces reaction (3); this, on the other hand, is of fundamental importance in the photochemical decomposition⁴ and in the decomposition of hydrogen peroxide by ionizing radiations⁵.

Reaction (6) is also of great importance in the aerobic oxidation of ferrous ions, as discussed previously⁶.

If, on the other hand, one starts with ferric ions only, the initial reaction is represented by the well-known process¹:



which, in conjunction with the oxygen-producing reaction (6) and followed by the re-oxidation of the ferrous ions according to reactions (1) and (4), gives a sufficiently complete picture of the 'ferric ion catalysis' of hydrogen peroxide as discussed in the earlier paper¹. However, in general one has to include also the reverse process of reaction (7) and the chain reactions (2) and (3) as discussed previously.

Thus the only difference compared with the previous scheme is that reaction (6) preponderates over reaction (3) if ferric ions are present.

A full account with all the experimental details will be published elsewhere.

J. WEISS
C. W. HUMPHREY

King's College,
University of Durham,
Newcastle-upon-Tyne 1.
March 16.

¹ Haber, F., and Weiss, J., *Proc. Roy. Soc., A*, **147**, 332 (1934).

² Baxendale, J. H., Evans, M. G., and Park, G. S., *Trans. Farad. Soc.*, **42**, 155 (1946).

³ Schmid, H., *Z. physik. Chem.*, **148A**, 321 (1930).

⁴ Lea, D. E., *Trans. Farad. Soc.*, **45**, 81 (1949).

⁵ Weiss, J., *Nature*, **153**, 748 (1944).

⁶ Weiss, J., *Nature*, **135**, 648 (1934); *Naturwiss.*, **23**, 64 (1935).