

Action of X-Rays on Aqueous Solutions of Perchloric Acid

IN the study of the radiation chemistry of metal ions in solution, it may seem desirable to use perchloric acid solutions because it is generally assumed that perchlorate ions show relatively little tendency to complex formation.

However, as was found recently¹, perchlorate in aqueous solutions is decomposed by the action of X-rays into chlorate and oxygen. Fig. 1 shows that the amount of chlorate formed in the irradiation of aqueous solutions of perchloric acid by X-rays (200 kV.) is directly proportional to the concentration of the perchloric acid. While the addition of ceric salts to the solution does not influence the formation of chlorate (see Fig. 1), if ferrous salts are present in the solution, chloride is formed in an amount which is equivalent to the chlorate formed in the absence of ferrous salt, under otherwise similar conditions.

Fig. 2 shows some of the results obtained in the system ferrous perchlorate - perchloric acid. In this case, particularly at the higher perchloric acid concentrations, the results do not show the normal features of the radiation chemistry of the ferrous

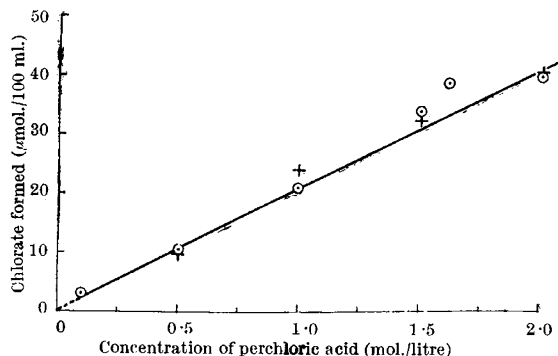


Fig. 1. Dependence of the formation of chlorate on the concentration of perchloric acid. Irradiation with X-rays (200 kV.) at constant dose of 2×10^5 e.u., in the presence of air. (1 e.u. \equiv 93 ergs/ml.) \circ , aqueous perchloric acid; +, aqueous perchloric acid in the presence of ceric perchlorate (3.17×10^{-3} M)

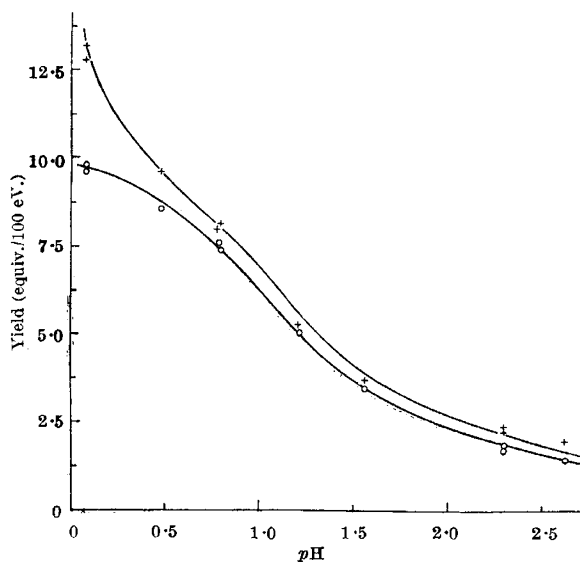


Fig. 2. Dependence of the yield of ferric salt (+) and of hydrogen (O) formed in the irradiation of ferrous perchlorate (0.01 M) in evacuated solutions at different concentrations of perchloric acid (as indicated by the pH). X-rays (200 kV.); constant dose of about 3.70×10^5 e.u.

ferric system¹. Whereas in the irradiation of ferrous sulphate in sulphuric acid solutions, *in vacuo*, the amount of hydrogen gas formed is equivalent to the amount of ferric salt produced¹, this is no longer true in perchloric acid solutions where, under similar conditions, less than the equivalent amount of hydrogen is produced.

The general conclusions which can be drawn from these results are again in agreement with the assumption that the energy absorbed by the water leads to the net decomposition: $H_2O \xrightarrow{\text{X-rays}} H + OH$, resulting in the formation of hydrogen atoms and hydroxyl radicals², which, however, under the conditions in question, seem to be unable to react with the perchlorate.

As pointed out above, the amount of chlorate formed is directly proportional to the concentration of the perchlorate. This would be in agreement with the assumption that its formation is due to a 'direct' effect, that is, to the radiation energy which is absorbed by the perchlorate itself. It is conceivable that this mechanism involves the formation of an unstable intermediate leading to the formation of chlorate (which is not influenced by ceric salts) and which in the presence of ferrous salts is further reduced to chloride.

A full account will be published elsewhere.

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¹ Rigg, T., Stein, G., and Weiss, J., *Proc. Roy. Soc., A*, **211**, 375 (1952).
² Weiss, J., *Nature*, **153**, 74 (1944).

A New Route to Oestrone

IN a recent paper, Johnson and Christiansen¹ have reported a new total synthesis of oestrone (I) from the keto-diester (II).

For a number of years we have been engaged in the study of the Friedel-Craft reaction with the view of preparing compounds of type II. We have already reported² the synthesis of 4-methyl-4-carbomethoxy-(*p*-methoxyphenyl)-cyclohexan-3-one (IV) by Friedel-Craft condensation between anisole and 4-methyl-4-carbomethoxycyclohexene-3-one (III). In the present communication, the study of the condensation of methyl 4-methyl-4-carbomethoxycyclohexene-3-one-2-acetate (V, λ_{max} , 235 m μ , $\log \epsilon$ 3.8) with anisole is reported. The reaction was carried out in the cold with a solution of (V) in anisole in a slow stream of dry hydrogen chloride and in the presence of anhydrous aluminium chloride. The condensation product, obtained as a glass, was hydrolysed and decarboxylated in 80 per cent yield to give a mixture of two isomers of 4-methyl-(*p*-methoxyphenyl)-cyclohexan-3-one-2-acetic acid (VI, A and B, melting points 208° and 135°) in the ratio 1 : 7, respectively. The isomer B was also obtained by Johnson and Christiansen by the hydrolysis of their keto-diester II (private communication). A direct comparison of the mixed melting point of our isomer B, melting point 135° with an authentic specimen, kindly supplied by Dr. W. S. Johnson, showed no depression. The recent successful conversion of (II) to oestrone (I) makes further work in this line unnecessary.

The unsaturated keto-ester (V) was prepared by the following method. Methyl hexane-1,2,6-tri-