CCXLI.—*The Action of Fluorine upon Aqueous Solutions of Chromium and Manganese Salts.*

By FRIEDRICH FICHTER and ERNST BRUNNER.

OUR researches on electrochemical oxidation of organic compounds have fully demonstrated the efficiency of a platinum anode as a powerful oxidising agent, and we noted especially the formation of organic peroxides and peracids, which are the intermediate products in the different forms of the Kolbe reaction. Since this effect is to be attributed to oxygen formed under a very high potential, and since there is no fundamental difference between electrochemical oxidation and ordinary chemical oxidation, we anticipated that similar results could be achieved by purely chemical means if the reagents furnished oxygen of the same high potential.

The positive end of the table of electrochemical potentials (first supplement, Deutsche Bunsen-Gesellschaft, 1915), measured in *N*-solutions of the respective salts, represents a number of such oxidising agents, several of which (*e.g.*, hydrogen peroxide, quadrivalent lead, and ozone) are frequently employed :

Lower stage of oxidation.		Higher stage of oxidation.	Potential.
$2H_2O$	⟶	$H_2O_2 + 2H^{\cdot}$	+ 1·8 volts
$Co^{\cdot\cdot}$	⟶	$Co^{\cdot\cdot\cdot}$	+ 1·8 ,,
$Pb^{\cdot\cdot}$	⟶	$Pb^{\cdot\cdot\cdot\cdot}$	+ 1·8 ,,
$O_2 + H_2O$	⟶	$O_3 + 2H^{\cdot}$	+ 1·9 ,,
$2F'$	⟶	F_2	+ 1·9 ,,

The figures in the table are somewhat uncertain, and the value for fluorine is probably too low. Von Wartenberg (*Z. anorg. Chem.*, 1926, **151**, 313) has recently found that the heat of formation of 1 g.-mol. of hydrogen fluoride in aqueous solution is equal to 74·6 Cal., instead of 50·3 Cal., the generally adopted value of Berthelot and Moissan. Latimer (*J. Amer. Chem. Soc.*, 1926, **48**, 2868) estimates the potential of gaseous fluorine to be as high as + 2·85 volts, direct measurements being impossible, since fluorine reacts instantaneously with water.

In spite of the well-known and powerful chemical affinity of fluorine, its effect upon aqueous solutions of mineral salts does not appear to have been examined by Moissan, and even Ruff, who used gaseous fluorine in the preparation of the highest fluorides of the platinum metals, does not mention its use in this way.

Our assumption that fluorine, owing to its position in the potential table, would act as the most powerful oxidising agent proved to be correct, for we have prepared crystalline potassium and ammonium persulphates by its action upon the corresponding bisulphates, and perphosphates, percarbonates, and perborates in a similar way (*Helv. Chim. Acta*, 1923, **6**, 640; 1926, **9**, 467; 1927, **10**, 549). The oxidising power of fluorine is, therefore, at least equal to that of a platinum anode. The formation of persulphates from bisulphates might be written as $2KHSO_4 + F_2 = K_2S_2O_8 + 2HF + 42{\cdot}6$ Cal., or as $2SO_4'' + F_2 = S_2O_8'' + 2F'$. If we adopt the first equation, we should write the electrochemical formation of persulphates in a similar way: $2KHSO_4 + O = K_2S_2O_8 + H_2O$, whereas the usual explanation emphasises the ionic reaction $2SO_4'' = S_2O_8'' + 2\ominus$. The difference between the two conceptions is purely formal.

The oxidising power of fluorine, however, surpasses that of a platinum anode, for by introducing it into sulphuric acid of medium concentration we obtain sulphur tetroxide ($H_2SO_4 + F_2 = SO_4 + 2HF$), a very labile compound which exists only a few hours and decomposes with evolution of ozone. Berthelot had previously obtained this tetroxide by treating a mixture of sulphur dioxide with excess of oxygen in an ozoniser. Our method gives better yields, but the tetroxide cannot be isolated from its solution. The production of ozone in the electrolysis of concentrated sulphuric acid with platinum anodes must, apparently, be explained by the intermediate formation of the same labile sulphur tetroxide.

These reactions of fluorine upon acids or anions are capable of wide extension, for we have recently found that nitric and perchloric acids furnish extremely labile peroxides or peracids. We now describe the action of fluorine upon kations of a lower valency.

Marshall discovered that a well-cooled solution of cobaltous sulphate in sulphuric acid gives, by electrolysis, the sulphate of tervalent cobalt (J., 1891, **59**, 760), and Fichter and Wolfmann (*Helv. Chim. Acta*, 1926, **9**, 1093) prepared the same salt by passing fluorine into a solution of cobaltous sulphate in sulphuric acid. The latter noted that in such cases the anion of the salt is of importance, for only the sulphate can be thus oxidised and the concentration of free sulphuric acid has to be kept between certain limits. Although this preparation of cobaltic sulphate requires a relatively high concentration of sulphuric acid, no mechanism other than the orthodox ionic explanation ($2Co^{\cdot\cdot} + F_2 = 2Co^{\cdot\cdot\cdot} + 2F'$) has hitherto been suggested, but we prefer the hypothesis that the labile sulphur tetroxide, formed by interaction of fluorine and sulphuric acid, is the true oxidising agent: $2CoSO_4 + SO_4 = Co_2(SO_4)_3$.

Our experiments with chromium salts corroborate this conception. A solution of chromium alum, acidified with very dilute sulphuric acid, is not altered by the passage of fluorine for several hours, but if the concentration of free acid is as high as 1·5*N*, a regular oxidation to chromic acid sets in, and is easily recognised by the change of colour from violet to orange-yellow. Higher concentrations of sulphuric acid up to 7·5*N* have the same effect. The oxidation is certainly indirect, for if the amount of chromic acid is determined by titration, the fresh solution, which evolves ozone, has about 1·5 times the possible oxidising power. After standing over-night or heating on a water-bath, the excess of oxidising substances is destroyed, and the solution has an oxidising value corresponding exactly to the theoretical amount of chromic acid. The oxidising substance must be sulphur tetroxide, for it is effective at 0°, whereas persulphate oxidises chromic salts only at higher temperatures.

We may conclude from these experiments that the electrochemical oxidation of chromium alum to chromic acid is also an indirect one. Since it is essential that the sulphuric acid be concentrated (Höchster Farbwerke, D.R.-P. 103,860, 1898), we suggest that this is because the acid must be strong enough to furnish sulphur tetroxide.

If a dilute solution of potassium dichromate is treated with fluorine, it becomes green and is reduced to a chromic salt, most probably the fluoride. Our crude fluorine always contains free hydrogen fluoride; the action of fluorine upon an aqueous solution furnishes hydrofluoric acid, and its concentration would be sufficient for the formation of chromic fluoride. In this case, fluorine acts as a reducing agent. This contradictory behaviour must be explained by the intermediate formation of hydrogen peroxide, thus: $2H_2O + F_2 = H_2O_2 + 2HF$. The formation of hydrogen peroxide can be detected by working with a small quantity of chromic acid and in the presence of dilute sulphuric acid; under these conditions and by proper cooling we obtain the blue perchromic acid, soluble in ether. Perchromic acid is very unstable, losing oxygen and yielding chromic salts; in this manner the reduction of dichromate can be carried out quantitatively by prolonged treatment with fluorine.

The concentrated sulphuric acid used in the oxidation of chromium alum to chromic acid fulfils two functions: first, it furnishes the sulphur tetroxide, the true oxidising agent, and, secondly, it prevents the formation of hydrogen peroxide, and hence of perchromic acid which would lead to reduction.

Both reactions which chromium compounds undergo under the influence of gaseous fluorine must be explained by intermediate products formed by the action upon water or sulphuric acid. Consequently, in oxidations with fluorine, an excess of this gas is often detrimental, for it destroys, by secondary reactions, the substances which it formed first.

The electrochemical oxidation of manganese salts has been investigated by several authors (see a review by Sem, *Z. Elektrochem.*, 1915, **21**, 425). As the action of fluorine is in most cases a true counterpart of electrochemical oxidation, we directed our attention to the similarity as well as to the difference of the two methods.

When a suspension of manganous fluoride in water is treated with a stream of fluorine, it dissolves slowly, furnishing a red liquid, from which a saturated solution of potassium fluoride precipitates the complex potassium manganifluoride, K_2MnF_5,H_2O (discovered by Christensen, *J. pr. Chem.*, 1887, **35**, 57), a pink crystalline powder. In this case, we admit the possibility of a direct oxidation without formation of an intermediate product; but the reaction is far from being complete: the formation of hydrogen peroxide can be detected from the beginning, and, moreover, we have a complicated equilibrium between manganous and manganic fluorides, hydrofluoric acid, and hydrogen peroxide, where the temperature, concentration, and duration of the treatment with fluorine are of influence. Sometimes the pink colour diminishes even during the experiment.

The formation of manganese tetrafluoride proved to be impossible by this method.

In most cases we used platinum vessels for our experiments, but the metal appeared to have a catalytic effect in decomposing salts of high valency (compare hydrogen peroxide), especially when it had lost its smoothness. To avoid this danger, we employed graphite beakers, but even with this precaution it was impossible to obtain manganese tetrafluoride. Further, a solution of the yellow complex salt, K_2MnF_6 (Weinland and Lauenstein, *Z. anorg. Chem.*, 1899, **20**, 40), was immediately reduced to the red salt by fluorine. This inability of fluorine to oxidise manganous fluoride to manganese tetrafluoride is completely parallel to the failure to effect this reaction by anodic oxidation (Mueller and Koppe, *ibid.*, 1910, **68**, 160).

Manganous sulphate, in the presence of sulphuric acid, was more readily oxidised, undoubtedly owing to the intervention of sulphur tetroxide. The formation of manganic sulphate, the first step, is easy to recognise, by the red colour. On continued passage of fluorine, this colour changes to a brownish-red and finally to a dark brown, and the oxidising power corresponds to a nearly complete transformation into the labile sulphate of quadrivalent manganese, $Mn(SO_4)_2$. If the concentration of the sulphuric acid is not high, hydrolysis sets in, and manganese dioxide is formed; but, although it is easy to obtain a yield exceeding 90%, the formation of manganese dioxide is not a certain proof of the primary formation of a salt of quadrivalent manganese, for it may be formed by hydrolysis of manganic sulphate, one-half of which is reduced to manganous sulphate and subsequently re-oxidised.

In order to bring the oxidation to the highest stage, permanganic acid, it is useful to have a low concentration of manganous ions and a high concentration of sulphuric acid, the latter being necessary to avoid the formation of hydrogen peroxide. In these circumstances, the characteristic colour of permanganate ions becomes visible the more quickly the smaller the concentration of manganous sulphate.

Manganic phosphate is very stable; a strong solution of manganous carbonate in an excess of phosphoric acid turns a deep amethyst-red on treatment with fluorine, but the oxidation is not complete. This is easy to understand, for the solution contains traces of hydrogen peroxide. We assume that fluorine acts first upon the phosphoric acid, forming monoperphosphoric acid, which readily oxidises manganous sulphate in acid solution to manganic phosphate. Schmidlin and Massini, who first prepared monoperphosphoric acid, considered the amethyst colour to be due to permanganic acid (*Ber.*, 1910, **43**, 1166), but spectrographic examination shows at once that the dark lines are lacking.

All the experiments with manganese salts and fluorine correspond exactly with the results of electrochemical oxidations. In all cases fluorine has proved to be at least as powerful an oxidising agent as a platinum anode, and our observations throw a new light on the mechanism of such oxidations, which are by no means simple. They depend largely on the anions, and also on intermediate products formed by primary oxidation of the acids, which are ignored in the theory of augmentation of positive charges (see p. 1864).

EXPERIMENTAL.

For the sake of brevity, we give for each reaction only one out of the great number of experiments carried out. (Fuller details will be published in E. Brunner's thesis.)

A. *Chrome Alum and Fluorine.*—(1) 0·9734 G. of chrome alum, 50 c.c. of water, and 2 c.c. of concentrated sulphuric acid were placed in a platinum crucible, cooled with ice, and treated with a current of fluorine during 75 minutes. The solution became orange and evolved ozone. After addition of potassium iodide and starch solution, 84·17 c.c. of 0·1*N*-thiosulphate solution were needed; this corresponds to 0·2808 g. of CrO_3, whereas the possible maximum is only 0·1949 g.

(2) 1·1365 G. of the alum and the above amounts of water and acid were treated as before. After standing over-night and being heated on the water-bath, the solution was mixed with potassium iodide and titrated with 0·1*N*-thiosulphate solution (Found: 0·2281 g. CrO_3. Calc.: 0·2276 g.).

B. *Potassium Dichromate and Fluorine.*—(1) *Formation of perchromic acid.* One drop of 0·5*N*-potassium dichromate, 40 c.c. of water, and 5 c.c. of 2*N*-sulphuric acid were placed in a platinum crucible, carefully cooled with ice and salt, and a few bubbles of fluorine introduced. By shaking with ether, previously freed from organic peroxides, the dark blue colour of perchromic acid was extracted.

(2) *Reduction to chromic fluoride.* 0·5216 G. of dichromate was dissolved in 50 c.c. of water, and, after cooling in ice, treated during 3 hours with fluorine. The green solution was partly evaporated in a platinum dish on the water-bath and then precipitated by ammonia; it furnished 0·2664 g. of chromium oxide (Calc.: 0·2695 g. Yield 98·9%).

C. *Manganous Fluoride and Fluorine.*—(1) Manganese fluoride was suspended in water, by a stirrer, in a platinum crucible, and treated with fluorine until nearly all was dissolved; the unattacked fluoride was removed by filtration through a hardened filter in a paraffined funnel, and the clear solution mixed with a saturated solution of potassium fluoride, whereupon a pale red crystalline powder separated, which was washed with very dilute hydrofluoric acid and dried at room temperature (Found: Mn, by conversion into Mn_3O_4, 22·37; active F, 7·67. Calc. for K_2MnF_5,H_2O: Mn, 22·32; active F, 7·72%).

(2) 0·6384 G. of manganous fluoride, suspended in water, cooled in ice, and treated during $1\frac{1}{2}$ hours with fluorine, dissolved and became red. After addition of potassium iodide and hydrochloric acid, it required 48·02 c.c. of 0·1*N*-thiosulphate solution, *i.e.*, yield = 69·9%.

D. *Manganous Sulphate and Fluorine.*—(1) *Formation of manganese dioxide.* 10 C.c. of a 1·11*N*-solution of manganous sulphate, with 0·3039 g. of $Mn^{\bullet\bullet}$, were treated exactly as in C(2); the solution remained colourless, but manganese dioxide was precipitated. Both the solution and the precipitate were distilled with hydrochloric acid, and the evolved chlorine was passed into a solution of potassium iodide. The liberated iodine consumed 101·2 c.c. of 0·1*N*-thiosulphate solution. If the manganous salt had been transformed completely into dioxide, 110·6 c.c. would have been needed; the yield was therefore 91·5%.

(2) *Formation of the sulphate of quadrivalent manganese.* A mixture of 2 c.c. of a 1·11*N*-solution of manganous sulphate, with 0·0608 g. of $Mn^{\cdot\cdot}$, and 4·0820 g. of concentrated sulphuric acid (95·64%) was cooled in ice and treated with fluorine during 5 hours; it became red, then browner, and finally dark brown. Concentrated hydrochloric acid and potassium iodide were added and the iodine was titrated [Found: 19·2 c.c. Calc.: 22·1 c.c. Hence yield of $Mn(SO_4)_2$ = 86·9%]. This result is probably too high, for the solution may have contained sulphur tetroxide in addition to quadrivalent manganese.

(3) *Formation of permanganic acid.* Three drops of a 1·11*N*-solution of manganous sulphate, 10 c.c. of water, and 3·3902 g. of concentrated sulphuric acid (95·64%) were treated with fluorine. After 15 minutes, the violet colour of permanganic acid appeared and became more and more distinct; the spectroscope revealed clearly the five absorption bands. With two drops of the manganous sulphate solution the violet colour appears after a few minutes; with four drops a treatment of one hour is needed, but the colour becomes very rich.

THE UNIVERSITY, BASLE.

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