LXXIX.—*The Action of Nitric Acid on Some Metals.*

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Investigation of the kinetics of the dissolution of metals in acids with evolution of hydrogen (compare Centnerszwer, *Z. physikal. Chem.*, 1929, *A*, **141**, 297) has shown that the reactions involved are more complex than the simple electronic exchange often represented in text-books of electrochemistry. When nitric acid is the reagent, the numerous reduction products afford even greater complexity of reaction and the matter appears to have received less attention, although it is of technical importance.

Previous investigators (Acworth and Armstrong, J., 1877, **31**, 60; Freer and Higley, *Amer. Chem. J.*, 1899, **21**, 377) have studied primarily the gaseous products of reduction of nitric acid at various concentrations by different metals (see summary by Bancroft, *J. Physical Chem.*, 1924, **28**, 474). Divers (J., 1883, **43**, 465) classified metals into two groups in respect of their action on nitric acid : copper, mercury, silver, and bismuth produce water, nitrous acid, and the nitrate of the metal, whilst zinc, cadmium, magnesium, aluminium, lead, iron, and the alkali metals do not yield nitrous acid, but give ammonia and generally also hydroxylamine. One of these groups includes metals which do not disengage hydrogen from hydrochloric acid, and the other comprises metals which do so.

For many years two rival theories have existed. According to one view, the first product of reaction of a metal such as copper with nitric acid is hydrogen, which, however, does not appear as such, but, being in the nascent state, reduces the nitric acid to a variety of reduction products depending on the conditions of reaction. In support of this, it is urged that free hydrogen is obtained when magnesium acts on very dilute nitric acid. Acworth and Armstrong (*loc. cit.*) incline to this view and write $Cu + 2HNO_3 = Cu(NO_3)_2 + 2H$ to represent the first stage. Supporters of the other view regard the metal itself as the reducing agent and deny the production of hydrogen.

In the present paper a study has been made of the influence of rotation on the rate of reaction of some metals with nitric acid, and the results show that these metals fall definitely into two groups, the members of which are respectively electronegative and electropositive to hydrogen: the hydrogen theory probably holds for the first group and the oxidation theory for the second.

EXPERIMENTAL.

The experiments described below were suggested by the accidental observation that some nitric acid in which an immersed copper sheet had been rotating for some hours had not acquired a blue colour. It was then found that Veley (*J. Soc. Chem. Ind.*, 1889, **8**, 858; *Phil. Trans.*, 1891, *A*, **182**, 279) had already observed that a rolling sphere of copper dissolved more slowly in nitric acid than a stationary sphere, and that the cause of the phenomenon was the removal of nitrous acid, which acts as an autocatalyst, from the surface of the dissolving metal.

In the following experiments, metal sheet 1 mm. thick was cut into strips 7 cm. long, which were 1 cm. wide over a length of 4 cm. and 0·6 cm. wide over the remaining 3 cm. A length of 5 cm. of the strip was immersed in the acid, so that the immersed portion comprised all the 1 cm.-wide part and 1 cm. of the 0·6 cm.-wide part. By means of a small hole bored at the upper end, the strip was screwed to a nickel rod which could be rotated at speeds up to 3000 r.p.m. by means of an electric motor. The reason for narrowing the upper portion of the strip was to reduce the area in contact with the liquid line where preferential corrosion occurs (Hedges, J., 1926, 831). The method is somewhat crude, but is probably better than the more usual way of immersing the support in the acid and covering all except the desired portion with wax or some other protective coating : small quantities of such materials may exert a profound influence on the reaction (compare Hedges and Myers, J., 1924, **125**, 604). All the nitric acid used was freed from nitrous acid by being warmed to 30° whilst a vigorous stream of air bubbles passed through it. The metals were cleaned by etching with nitric acid. The experiments were conducted in a thermostat at 30° and the loss of weight of the metal after 1 hour's immersion was determined. In general, it was found that repetitions of the same experiment gave results agreeing within 3—4%, although occasionally larger discrepancies appeared. The figures given in the tables represent the mean of two results differing by not more than 5%. This degree of concordance is quite sufficient, since the changes studied are of a much higher order.

Influence of Speed of Rotation on Rate of Dissolution.—(1) *Copper in* 25% * *nitric acid.*

Speed (r.p.m.) ...	0	80	100	180	360	450
Loss of wt. (g.) ...	1·312	0·259	0·131	0·079	0·014	0·003

The velocity of dissolution is greatly reduced by quite moderate rates of rotation, and at 450 r.p.m. has become exceedingly slow. The results indicate that the velocity of dissolution of copper in pure nitric acid is very low and that some product of the reaction which normally accumulates at the surface of the metal is an active catalyst. In the process of rotation, this catalyst is washed away from the surface as fast as it is formed, and consequently the reaction is slower than in the stationary state. If this explanation holds, it should be possible to increase greatly the velocity of dissolution of a rotating copper sheet by direct addition of the supposed catalytic reaction product to the nitric acid solution. For this purpose, experiments were conducted on the effect of adding nitrous acid (in the form of sodium nitrite) and copper nitrate at constant speed of rotation of the copper. The results are given below.

Effect of adding sodium nitrite (*constant speed* 450 *r.p.m.*).

Amt. added, %	0	0·1	0·5
Loss of wt. (g.)	0·003	0·171	0·622

Effect of adding copper nitrate (*constant speed* 360 *r.p.m.*).

Amt. added, %	0	0·2	1·0	10
Loss of wt. (g.)	0·014	0·004	0·004	0·007

Evidently, in agreement with Veley's conclusions (*loc. cit.*), nitrous acid is the reaction product responsible for the high speed of reaction in the stationary state. Copper nitrate, even in relatively

* Percentages relate to acid of *d* 1·42 (by vol.).

large amounts, did not increase the velocity of reaction, an observation which is contrary to that of Rennie, Higgin, and Cooke (J., 1908, **93**, 1162), who state that the reaction is greatly accelerated by copper nitrate. These authors did not rotate the metal but stirred the liquid—an inefficient means of replenishing the layer of liquid in contact with the solid.

(2) *Silver in 25% nitric acid.*

	Stationary.	At 450 r.p.m.	At 450 r.p.m., with 1% of $NaNO_2$.
Loss of wt. (g.)	1·174	0·000	1·187

Rotation of silver at 450 r.p.m. inhibited dissolution by nitric acid completely, and the solution gave no reaction for silver ions when tested with hydrochloric acid. Addition of 1% of sodium nitrite to the rotating system brought the velocity of dissolution to practically the same value as that of stationary silver.

(3) *Tin in 25% nitric acid.*

	Stationary.	At 450 r.p.m.	Stationary with 1% of $NaNO_2$.
Loss of wt. (g.)	0·270	0·390	0·114

(4) *Zinc in 10% nitric acid.*

	Stationary.	At 450 r.p.m.
Loss of wt. (g.)	1·476	3·222

(5) *Magnesium in 5% nitric acid.*

	Stationary.	At 450 r.p.m.	Stationary with 0·5% of $NaNO_2$.
Loss of wt. (g.)	0·270	0·480	0·240

The results for tin, zinc, and magnesium show a striking difference from those for copper and silver. The rate of dissolution is *increased* when the metal is rotated, and nitrous acid has no accelerating effect; indeed, substitution of nitrous acid for some of the nitric acid reduces the velocity of dissolution of tin.

Further Examination of the Copper–Nitric Acid System.—Veley (*loc. cit.*) found that copper did not dissolve in dilute nitric acid containing a substance such as urea which could destroy the nitrous acid as fast as it is formed. The author's experiments confirmed this observation, but also showed that copper dissolves readily in concentrated nitric acid even when saturated with urea, and that dissolution started in the dilute solutions on gentle warming. In the following experiments, concentrated nitric acid (*d* 1·42) was saturated with urea, and the solution diluted with distilled water in the proportion stated; 5 c.c. of the mixture were put into a test-tube immersed in a large beaker containing water, the temperature of which was raised by 1° per minute. A small piece of copper was dropped into the mixture at 25°.

HNO_3–CH_4ON_2 mixture, c.c.	H_2O, c.c.	Result.
5	—	Immediate dissolution.
4	1	,, ,,
3	2	Dissolution after 2—3 secs.
2	3	Dissolution after 5 secs.; reaction stopped by shaking tube.
1·5	3·5	No reaction at 25°; reaction starts at 27°, and ceases if temp. is decreased.
1	4	As in preceding case, but 37° is now the critical temperature.

Similar phenomena were observed when hydrogen peroxide or potassium permanganate was added to remove the nitrous acid, and the results indicate that these reagents are in general less effective than rapid stirring in removing the nitrous acid. In the more concentrated solutions at 25°, and in dilute solutions of nitric acid at higher temperatures, nitrous acid is produced by the reducing action of copper at a rate greater than that at which urea or hydrogen peroxide can react with it.

This conclusion made it of interest to determine whether a considerably higher speed of rotation could prevent the dissolution of copper by concentrated nitric acid (*d* 1·42), and it was found that, although the reaction could not be stopped, its velocity was greatly reduced. For this purpose, a piece of copper foil 1 cm. × 1 cm. × 0·01 cm. was pierced and suspended by a glass hook which was lowered into an empty beaker and rotated at 2000 r.p.m. Concentrated nitric acid was then poured into the beaker. At rest, a piece of metal of these dimensions dissolved completely in the acid in less than 30 seconds, but when it was rotated at 2000 r.p.m., after an interval of about 6 mins. (during which the solution developed a green colour) the foil always left the hook, being still partly undissolved. The piece of copper left had a black skin and appeared to be passive, dissolving in the acid extremely slowly even when at rest. Some specimens were not completely dissolved after 60 mins. An interesting behaviour was observed when one of these specimens was removed from the nitric acid and allowed to drain. After a few seconds, momentary effervescence appeared on the surface, the black film disappeared, and the metal was found to have lost its passivity towards nitric acid. This behaviour resembles exactly that of electrolytic iron which has been rendered passive by concentrated nitric acid, removed, and allowed to drain (Evans, J., 1927, 1020). Evans considers that the phenomenon is caused by the tendency of the protective film to leave the metal–liquid interface and collect at the air–liquid interface.

These results suggest that, in the absence of nitrous acid, nitric acid produces a protective oxide film on copper, which is thus rendered passive in a similar way to the well-known action of concentrated nitric acid on iron. The black film mentioned above resembled that observed by the author on copper which had been rendered passive by immersion in concentrated nitric acid at —11° (J., 1928, 975).

The Anodic Dissolution of Copper in Nitric Acid.—The dissolution of a copper anode in nitric acid is also affected greatly by the presence of nitrous acid. For example, during passage of a current of 50 milliamps. for 1 hour, a stationary anode lost 0·790 g. of copper, but when rotated at 400 r.p.m. it lost only 0·270 g.; when 2% of sodium nitrite was added, however, it lost 1·408 g.

In the following experiments, a rotating anode of the type previously described (J., 1927, 1028) was used, the cathode was of platinum foil, and the anode and cathode compartments were separated by means of a porous pot. The experiments were conducted in 25% nitric acid at 30°. The following table shows the loss of weight of the anode both when stationary and when rotated at 400 r.p.m. at various current densities. The last column gives the loss of weight to be expected in accordance with Faraday's law.

Current, milliamps.	Loss of weight, g.		
	Stationary.	At 400 r.p.m.	Calc.
0	1·312	0·01	0·000
25	1·158	0·096	0·592
50	0·790	0·270	1·185
100	1·000	0·280	2·369
500	1·314	0·586	11·848

It will be observed that in every case the rotating anode dissolves more slowly than the stationary anode, although at the higher current densities the difference is relatively less. At 25 milliamps. the loss is about twice as great as that calculated from Faraday's law, which means that much of the dissolution is controlled by local short-circuited electrolytic cells in the metal, the electrical energy of which is not registered on the external circuit. At higher current densities the loss is much less than that required by this law, the discrepancy increasing with the intensity of the current. In these cases, evolution of gas at the anode was observed, so that only a portion of the electrical energy is involved in the formation of cupric ions. Thus it appears that copper readily becomes passive, though incompletely so, under anodic polarisation, and the more readily so in absence of nitrous acid. At the end of the experiments, these electrodes had a black or grey film over their surface.

Difference of Potential between Stationary and Rotating Copper Anodes.—The difference of electropotential between the electrodes and a reference normal calomel electrode was measured by a static method, the measuring instrument being a string electrometer. The method was similar to that already described (J., 1927, 1077). The measurements were carried out both with stationary and with rotating (400 r.p.m.) electrodes, over the *C.D.* range 5—50 milliamps./cm^2., and throughout this range the rotating electrode was positive (noble) to the stationary electrode by 0·16 volt. This result is in the direction to be expected from the presence of an oxide film on the rotating electrode.

Discussion.

The metals investigated fall into two classes accordingly as the velocity of dissolution in nitric acid is increased or decreased by rotation. The presence of nitrous acid does not appreciably affect the rate of dissolution of members of the first group, but it accelerates very greatly that of metals of the second group. These groups are coincident with those of Divers (*loc. cit.*), who used as a basis of classification the nature of the reduction products. Members of the first group are electronegative to hydrogen, and those of the second group are electropositive.

The electronegative metals can normally displace hydrogen from acids and their behaviour provides no reason to doubt that they initially displace hydrogen from nitric acid; the hydrogen reduces the nitric acid to oxides of nitrogen and sometimes to ammonia and hydroxylamine. When the nitric acid is extremely dilute, hydrogen can be obtained in the free state by the dissolution of magnesium.

On the other hand, there is no *a priori* reason why the second group, consisting of electropositive metals, should displace hydrogen from nitric acid, since they do not do so from other acids.

The passivity phenomena observed when copper is rotated in concentrated nitric acid, the observations on the anodic dissolution of copper, the difference of potential between stationary and rotating copper electrodes, and the formation of visible black films on the copper all suggest that an oxide film is formed on copper by the action of nitric acid. There is also the fact that nitrous acid is produced and accelerates the reaction; part of this acid reacts with the copper oxide, for, particularly in the early stages, the soluble product contains green copper nitrite as well as the blue copper nitrate, and part of it is decomposed to oxides of nitrogen, which are the gases evolved.

The suggested reactions may be represented thus:

(1) $Cu + HNO_3 = CuO + HNO_2$;
(2) (a) $CuO + 2HNO_2 = Cu(NO_2)_2 + H_2O$;
(b) $CuO + 2HNO_3 = Cu(NO_3)_2 + H_2O$;
(3) $Cu(NO_2)_2 + 2HNO_3 = Cu(NO_3)_2 + 2HNO_2$;
(4) (a) $3HNO_2 = HNO_3 + 2NO + H_2O$;
(b) $HNO_2 + HNO_3 = 2NO_2 + H_2O$.

In dilute acid 4 (a) gives nitric oxide as the main product, whilst in concentrated acid 4 (b) preponderates and the main gaseous product is nitrogen peroxide: a mixture is usually produced.

If, by rotation or by addition of such a substance as urea, the nitrous acid formed in (1) can be removed continuously, the metal becomes covered with a film of copper oxide and dissolves only slowly. Nitrous acid may be said to "activate" the copper, perhaps in the same way that chlorine ions activate passive iron. In any case, the mechanism of this process of activation is not clear, but in some way the activating agent appears to loosen the protective film.

The theory outlined above supposes that cupric oxide can afford a sufficient degree of protection to the underlying metal, although ordinarily this substance is readily soluble in nitric acid. To test this point, some rough experiments were carried out on the rate of dissolution in nitric acid of samples of cupric oxide prepared in different ways. The method was to add 1 g. of the powdered oxide to 100 c.c. of 25% nitric acid, which was efficiently stirred at a constant rate by means of a glass stirrer, and to note the time taken for complete dissolution. An ordinary commercial sample dissolved in 3 mins. A sample prepared from copper sulphate by precipitation with sodium hydroxide and ignition of the residue was completely dissolved in 5 mins. A sample prepared by igniting cupric nitrate was incompletely dissolved after 60 mins. It is possible, therefore, for a form of cupric oxide to be sufficiently resistant to nitric acid to form a poorly protective film of the type required. The fact that the films are sufficiently thick to be easily visible is an indication of the low degree of protection afforded compared with that of the oxide film on passive iron. As fast as the relatively porous cupric oxide film is dissolved it is repaired by the nitric acid.

Thus, nitric acid appears to oxidise copper and silver superficially, causing them to become passive, and the action of nitrous acid, both on the ordinary chemical reaction and on the anodic dissolution, may be described as one of "activation," though in what way it removes the protective film is not at present understood.

Although in the dissolution of electronegative metals in dilute nitric acid the displacement of hydrogen appears to be the first reaction, in concentrated acid the oxidation reaction may preponderate. Tin and iron form two excellent illustrations. Tin dissolves in dilute nitric acid, giving stannous nitrate, and the hydrogen reduces the nitric acid mainly to ammonia; in concentrated nitric acid a hydrated stannic oxide is produced, but has not the requisite physical properties for forming a good protective coating. Similarly, iron dissolves readily in dilute nitric acid, but in concentrated nitric acid receives a thin film of ferric oxide which protects it from further action, and the iron is said to be passive.

Summary.

The rate of dissolution of copper and of silver in nitric acid is decreased and can be almost prevented by rotation of the metal: the cause of this phenomenon is that nitrous acid (one of the products of reaction) is not allowed to accumulate at the metal surface. Direct addition of nitrous acid causes the rotating metal to dissolve rapidly. On the other hand, tin, zinc, and magnesium dissolve more rapidly in dilute nitric acid when rotated, and nitrous acid has no accelerating effect. Copper which has been rotated rapidly in concentrated nitric acid acquires a black film and becomes "passive" towards nitric acid, dissolving slowly even when subsequently at rest: it shows passivity phenomena in other respects. A copper anode also dissolves more slowly in nitric acid when rotated than when at rest for a given current density, but addition of nitrous acid accelerates the rate of dissolution. A rotating copper anode is electropositive by 0·16 volt to a stationary copper anode. The results suggest that the first action of nitric acid on copper or silver is one of oxidation, forming an oxide film which prevents further rapid attack, *i.e.*, the metal becomes passive; nitrous acid acts as an activating agent. The initial product of reaction of tin, zinc, or magnesium with dilute nitric acid is probably hydrogen. The results are discussed in relation to the passivity of iron.

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