81. *The Mechanism of Some Ionic Reactions in Aqueous Solutions.*

By Joseph Weiss.

The mechanism of the reduction of ferric chloride by stannous salts is discussed in detail and it is shown that the stannous chloride enters as the complex anion $(SnCl_4)^{2-}$ into a (two-stage) reaction of simple electron-transfer processes.

In connection with this, Shaffer's general hypothesis for oxidation–reduction processes is found not to agree with the experimental facts. All these reactions can be easily interpreted on the basis of the "one-step" mechanism of oxidation–reduction processes, excluding reactions with (multivalent) ions of the same sign which are statistically disfavoured on account of Coulombic repulsion.

The well-known reduction of ferric chloride by stannous salts was investigated first by Noyes (*Z. physikal. Chem.*, 1895, **16**, 576) and subsequently by several workers (see, *e.g.*, van 't Hoff, "Studies in Chemical Dynamics," p. 113; Timofeew, Muchin, and Gurewitsch, *Z. physikal. Chem.*, 1925, **115**, 161). More recently, Gorin (*J. Amer. Chem. Soc.*, 1936, **58**, 1787) has investigated the corresponding reaction in perchloric acid solutions. The mechanism of this simple analytical reaction is, however, still not clear. Following Noyes (*loc. cit.*), the process is often quoted as a typical example of a termolecular reaction in solution, but in the presence of hydrochloric acid or of chloride ions, which both accelerate the reaction, it appears to follow a bimolecular course. This behaviour has been attributed to "salt effects" which may be treated—as was suggested—by Brönsted's theory. Although salt effects are undoubtedly of some importance, they cannot be the true explanation, for a change in the concentration of hydrochloric acid by a factor of about 2 produces an acceleration of about 450% (cf. Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford Univ. Press, 1933, p. 220). Moreover, a salt effect would not be expected to change the order of the reaction.

It is suggested that the reason for these discrepancies lies in the usual formulation of the reaction according to

$$2Fe^{3+} + Sn^{2+} = 2Fe^{2+} + Sn^{4+} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

It is clear that if this equation did represent the reaction, an enormous Coulombic repulsion between all the positively charged ions would have to be overcome in the formation of the primary collision complex. This energy of repulsion actually enters exponentially (as a Boltzmann factor) into the expression for the reaction-velocity constant, as has also been shown by Christiansen (*Z. physikal. Chem.*, 1924, **113**, 35) in his statistical interpretation of Brönsted's theory. From the outset it is, therefore, most unlikely that the reaction will proceed according to equation (1) apart from other facts incompatible with it.

All the experimental facts can be fully explained on the basis of the following two simple reaction steps. Stannous ions, which in the presence of chloride ions show a great tendency to form complex anions (cf. Mellor, "Treatise on Inorganic Chemistry," Vol. VII, p. 424), actually enter as such into the reaction, so that reaction (1) is transformed into one between oppositely charged ions, *viz.*,

$$Fe^{3+} + (SnCl_4)^{2-} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} Fe^{2+} + (SnCl_4)^{-} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$Fe^{3+} + (SnCl_4)^{-} \xrightarrow[k_3]{} Fe^{2+} + SnCl_4 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

with the equilibrium

$$SnCl_2 + 2Cl^- \rightleftarrows (SnCl_4)^{2-} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

This simple reaction conforms to the well-known principle that all oxidation and reduction processes proceed stepwise and often simply as electron-transfer processes (cf. Haber and Weiss, *Proc. Roy. Soc.*, 1934, *A*, **147**, 332; Weiss, *Nature*, 1934, **135**, 648; *Naturwiss.*, 1935, **23**, 64). $(SnCl_4)^-$ corresponds to a tervalent tin compound, as will be obvious from the equilibrium

$$SnCl_4^- \rightleftarrows SnCl_3 + Cl^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4a)$$

The intermediate formation of such compounds in the oxidation of stannous salts has been demonstrated by Ball, Wulfkuehler, and Wingard (*J. Amer. Chem. Soc.*, 1935, **57**, 1729).

For the stationary state, the expression for the rate of the reaction can be easily derived from reactions (2) and (3) as

$$-\frac{d[Fe^{3+}]}{dt} = -2\frac{d[Sn^{II}]}{dt} = k_2[Fe^{3+}][(SnCl_4)^{2-}]\left\{\frac{k_3[Fe^{3+}]}{k_{-2}[Fe^{2+}] + k_3[Fe^{3+}]}\right\} \quad . \; . \; . \; . \; . \quad (5)$$

In neutral or slightly acid solutions only a small amount of the ferric salt will be present as Fe^{3+} on account of partial hydrolysis. Therefore, one can assume, as a first approximation, that the following relation holds :

$$k_{-2}[Fe^{2+}] > k_3[Fe^{3+}] \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

except, of course, for the initial stages, *i.e.*, before $[Fe^{2+}]$ has risen to a reasonable value. Under this condition equation (5) simplifies to

$$-d[Fe^{3+}]/dt = k_2k_3[Fe^{3+}]^2[(SnCl_4)^{2-}]/k_{-2}[Fe^{2+}] \quad . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

In this rather restricted region the reaction is approximately of the third order, but, of course, is still dependent on the concentration of the Fe^{2+}. Actually, the third-order constants as given by Noyes are not particularly good, and the initial values invariably show a strong deviation which is fully understandable. He found, however, that the third-order constants were greatly improved if he added a certain quantity of ferrous salts to the reaction mixture, right from the beginning, thus keeping approximately constant the value of the denominator in (7).

In the presence of hydrochloric acid the hydrolysis of the ferric salt is prevented. This increases the ferric ions available for the reaction and also increases the concentration of $(SnCl_4)^{2-}$ according to the equilibrium (4). Thus, at any rate for the initial stages of the reaction, the condition holds that

$$k_{-2}[Fe^{2+}] < k_3[Fe^{3+}] \quad \ldots \ldots \ldots \ldots \quad (8)$$

and consequently equation (5) simplifies to

$$-d[Fe^{3+}]/dt = k_2[Fe^{3+}][(SnCl_4)^{2-}] \quad \ldots \ldots \ldots \ldots \quad (9)$$

We see that under these conditions the reaction is bimolecular, in agreement with the experiment of Noyes (*loc. cit.*).

If the stannous chloride enters as $(SnCl_4)^{2-}$ into the reaction as suggested by the above mechanism, then the bimolecular or termolecular rate constants calculated in the ordinary way must still be proportional to the square of the chloride-ion concentration in the solution, as indicated by the equilibrium (4).

The author has calculated from Noyes's experiments (*loc. cit.*) in acid solution the values of $k_{\text{bi.}}/[Cl^-]^2$ which, if the above assumption is correct, must remain constant for a variation of the chloride-ion concentration. That this is the case is shown in Table I.

TABLE I.

Experiments in hydrochloric acid solutions.

Total (additional) concentration of Cl^- in g.-mol./l. (from $FeCl_3$ + HCl).	$k_{\text{bi.}}$.	$k_{\text{bi.}}/100[Cl^-]^2$.
$(3 \times 0{\cdot}025) + 0{\cdot}025$	1·10	1·15
$(3 \times 0{\cdot}025) + 0{\cdot}05$	1·60	1·03
$(3 \times 0{\cdot}025) + 0{\cdot}10$	2·90	0·95
$(3 \times 0{\cdot}025) + 0{\cdot}10$	3·80	1·23
$(3 \times 0{\cdot}05) + 0{\cdot}10$	5·20	0·83

Some rate constants determined by Timofeew, Muchin, and Gurewitsch (*loc. cit.*) are calculated in Table II.

TABLE II.

Experiments in neutral solution with the addition of chlorides.

Total (additional) concentration of Cl^- ions in g.-mol./l. ($FeCl_3$ + chloride).	$k_{\text{ter.}}$.	$k_{\text{ter.}}/100[Cl^-]^2$
$(3 \times 0{\cdot}0625)$	24	6·81
$(3 \times 0{\cdot}0625) + 0{\cdot}0625$	40	6·40
$(3 \times 0{\cdot}0625) + 0{\cdot}1250$	60	6·25
$(3 \times 0{\cdot}0625) + 0{\cdot}3125$	172	6·87

The constancy of the function in col. 3 over a considerable range is as good as can be expected, and it is thus clearly shown that the velocity is proportional to $[Cl^-]^2$, as follows from equilibrium (4).

The mechanism proposed above is supplementary to the work of Gorin (*loc. cit.*), who investigated the reaction in perchloric acid solution where there is no appreciable complex formation of Fe^{3+} or Sn^{2+}; this reaction was found to be slower by a factor of 10^5 to 10^6 (under similar conditions) than that in the presence of chloride ions. Gorin also concluded that the free ions do not interact with each other on account of the strong electrostatic repulsion. From the rate law :

$$d[Fe^{2+}]/dt = \text{const.}\ [Fe^{3+}][Sn^{2+}]/[H^+]^2$$

which he found to be valid for higher concentrations of ferric salt, he concluded that the time-determining process must be a reaction between $Fe(OH)_2^+$ and Sn^{2+}. Although this may be possible, the same rate law would result if the reaction took place between $Fe(OH)^{2+}$ and $Sn(OH)^+$ or Fe^{3+} and $Sn(OH)_2$ or H_2SnO_2. The latter case would be favoured by the absence of Coulombic repulsion and also it is more likely, as ferric salts are not hydrolysed to any appreciable extent at the comparatively high concentrations of free acid present in these experiments, whereas stannous salts are hydrolysed even in dilute acid solutions. The kinetics and the deviation from the simple rate law can also be explained with a two-stage electron-transfer reaction similar to the one given above. This would also readily explain why the simple bimolecular rate law is valid only for high $[Fe^{3+}]$ similar to the case of the equations (8) and (9), whereas Gorin does not give a satisfactory explanation for this.

Shaffer (*J. Amer. Chem. Soc.*, 1935, **55**, 2169; *J. Physical Chem.*, 1936, **40**, 1021) has put forward a hypothesis for oxidation–reduction processes, according to which, reactions between molecules or ions, where one component is capable of a bivalent oxidation (or reduction) but the other only of a univalent reduction (or oxidation), are greatly disfavoured or even immeasurably slow. This is obviously not true for the above reaction, for ferric salts are rapidly reduced by stannous salts in hydrochloric acid solution. From the outset the argument is invalid because all these processes go stepwise through successive univalent changes. However, even in a bimolecular reaction between equally charged ions the rate may be slowed down on account of the electrostatic repulsion, if the reducing ions cannot form an ion of opposite charge as in the reaction discussed above. It is also clear (as shown above) that the formation of the complex metal ions will depend largely on the nature of the anions present.

Shaffer gives two examples to illustrate his theory : (*a*) the oxidation of thallous salts by ceric salts; (*b*) the oxidation of titanous salts by iodine.

(*a*) It is true that the reaction between thallous ions and ceric sulphate in sulphuric acid solutions is very slow. However, the reason cannot be that given by Shaffer because, *e.g.*, the oxidation of stannous salts by ceric salts is very rapid. It is more likely that the Coulombic repulsion between thallous ions and ceric ions prevents a rapid interaction between these ions, as in this case the reducing ion is not capable of forming a complex anion as are stannous salts and some other metal salts—for instance, potassium permanganate, where the change $Mn^{VII} \longrightarrow Mn^{II}$ oxidises thallous salts quite easily, as is well known.

(*b*) In the reaction between titanous salts and molecular iodine, Shaffer's theory is also not valid, for it is well known that the first step in the reduction of iodine molecules is I_2^- (cf. Wagner, *Z. physikal. Chem.*, 1924, **113**, 261). It is more likely that in the probable mechanism, *viz.*,

$$Ti^{3+} + I_2 \rightleftarrows Ti^{4+} + I_2^- \quad \ldots\ldots\ldots \quad (10a)$$

$$Ti^{3+} + I_2^- \longrightarrow Ti^{4+} + 2I^- \quad \ldots\ldots\ldots \quad (10b)$$

the reverse process of reaction (10*a*) is fast compared with reaction (10*b*), which would fully account for the observed facts.

This state of affairs can be and is actually changed in the presence of certain oxidation–reduction catalysts, such as pyocyanine, which are well known (cf. Michaelis, *Chem. Rev.*, 1935, **16**, 243) themselves to undergo a univalent reduction–oxidation by passing through the corresponding semi-quinone stage, as has been affirmed by Shaffer (*loc. cit.*). In the presence of these catalysts, either the reverse process may be inhibited or, more probably, the mechanism is changed to an interaction between titanous salt and oxidised dye, followed by the reduced dye being reoxidised by molecular iodine. In this way iodide ions and titanic salt are formed, whereas the catalyst undergoes successive processes of reduction and oxidation.

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