THE PRECIPITATION OF NICKEL OXALATE

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The rate of formation of precipitates of nickel oxalate in solutions containing nickel sulfate and oxalic acid has been studied by turbidimetric and dilatometric techniques which cover successive stages of the reaction. Equations have been derived relating the rate of formation to the initial concentrations of nickel sulfate and oxalic acid in the solution. A mechanism based on the formation and subsequent rearrangement of a complex ion is suggested.

The work described in this paper is part of a general study of the properties of the oxalates of divalent heavy metals in the solid state. Nickel oxalate is an example of this class of compounds and may be prepared by the reaction in solution between a soluble nickel salt and oxalic acid.[1] This reaction does not, however, proceed by a simple ionic double decomposition mechanism; an induction period is observed and the rate of precipitation depends markedly on the concentrations of the reactants in solution. The present work was undertaken to establish these relationships.

Experimental

Stock solutions of nickel sulfate and oxalic acid of normal strength were prepared from high grade chemicals and diluted as required. When a solution of nickel sulfate of, say, 0.3 N is added to one of oxalic acid of the same strength—the order of addition is immaterial—no precipitate at first appears. After some minutes the solution becomes cloudy, the solid particles increase in size and subsequently settle out. Two techniques have been employed to follow these processes.

(i) **Turbidimetric Method.**—This method is useful for following the very early stages of the reaction which is carried out in the cell of a photoelectric colorimeter. The instrument scale, graduated logarithmically from 0 to 100, gave directly the percentage of light cut off by the solution. A green filter was used throughout and the instrument was adjusted to read zero with distilled water in the cell. The solutions were mixed in the required amounts to make up a total volume of 10 ml., the cell inserted in the colorimeter and the scale reading followed with time as the optical density of the solution increased.

As it is not possible to relate the scale reading, R, directly to the amount of precipitate present, the assumption was made that dR/dt was proportional to the rate of formation of the precipitate. The method was used only for the very early part of the reaction when no visible settling took place.

(ii) **Dilatometric Method.**—The required solutions were mixed and drawn rapidly into a dilatometer. The rate of change in volume of the reaction system as the precipitation proceeded, which is proportional to dH/dt where H is the reading of the liquid level in the capillary, was taken as a measure of the rate of precipitation. The volume of the bulb of the dilatometer was 93 ml. and the capillary diameter was 0.8 mm. The solutions and dilatometer were maintained at 20 ± 0.05°.

These two methods are complementary in that the part of the reaction measured in the colorimeter precedes that which causes a significant increase in volume in the dilatometer.

Results

In the turbidimetric experiments, the graph of the scale reading against time gave an s-shaped curve with a long central straight portion, the slope of which, S_t, was taken as the rate of formation of the precipitate. Measurements were made at five different oxalic acid concentrations. The slopes, S_t, plotted against the excess concentration of oxalic acid, C, are shown in Fig. 1. For concentrations of oxalic acid equal to or greater than those of nickel sulfate

$$S_t = h_1C + h_2 \qquad (1)$$

where h_1 and h_2 are both functions of the concentration of nickel salt, E, given by

$$h_1 = k_1E^3 \qquad (2)$$

$$h_2 = k_2E^{3/2} \qquad (3)$$

The over-all equation is, therefore

$$S_t = k_1E^3C + k_2E^{3/2} \qquad (4)$$

where $k_1 = 2820$ and $k_2 = 43.6$ when C and E are expressed as normalities and S_t as the number of scale divisions per minute.

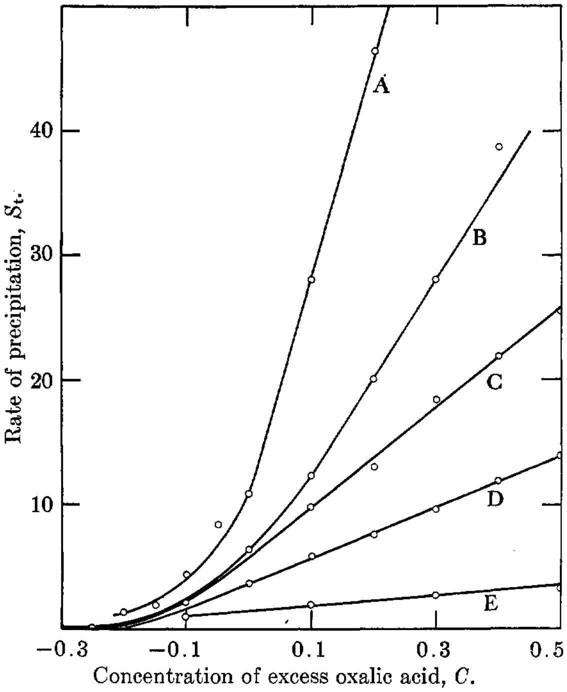

Fig. 1.—A, 0.4 N; B, 0.3 N; C, 0.25 N; D, 0.2 N; E, 0.15 N.

The dilatometric experiments were carried out on the same plan. The graph of the capillary reading against time again gave an s-shaped curve with a long central straight portion, the slope of which, S_d, was taken as the rate of formation of the precipitate. The results are shown in Fig. 2 in a manner analogous to Fig. 1. For concentrations of oxalic acid equal to or greater than those of nickel sulfate

$$S_d = h_3C + h_4 \qquad (5)$$

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[1] N. V. Sidgwick, "The Chemical Elements and their Compounds," Vol. 2, Oxford University Press, London, 1950, p. 1435.

where h_3 and h_4 are both functions of the concentration of the nickel salt, E, given by

$$h_3 = k_3E - k_4 \qquad (6)$$

and

$$h_4 = k_5E^3 \qquad (7)$$

The over-all equation is therefore

$$S_d = (k_3E - k_4)C + k_5E^3 \qquad (8)$$

where $k_3 = 16.15$, $k_4 = 2.0$ and $k_5 = 8.4$ when C and E are expressed as normalities and S_d in cm. min.$^{-1}$.

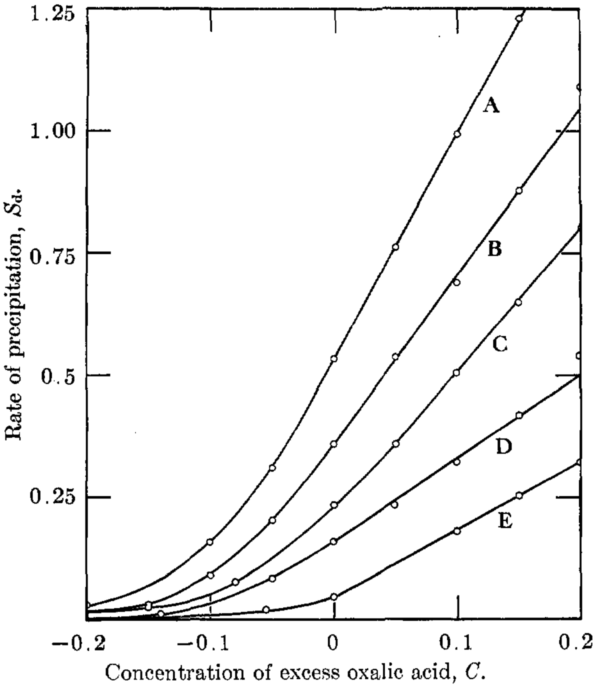

Fig. 2.—A, 0.4 N; B, 0.35 N; C, 0.3 N; D, 0.25 N; E, 0.2 N.

Equations 4 and 8 do not hold when the nickel sulfate is in excess. In these circumstances the rates tail off asymptotically with decreasing acid concentration; the induction period increases with decreasing salt and acid concentration and is considerable at the lower concentrations, especially when the salt is in excess.

Discussion

Nickel oxalate is known to exhibit a strong tendency to self-complex formation[2,3]; it is suggested, therefore, that the first step in the reaction involves the formation of a soluble complex represented by the equation

$$2NiSO_4\,(aq) + 2H_2C_2O_4\,(aq) \rightleftharpoons [Ni(C_2O_4)_2]^{=}\,Ni^{++}\,(aq) + 2H_2SO_4\,(aq)$$

The equilibrium constant is $\sim 10^{13}$,[4] so that formation of the favored complex ion would account for the existence of an induction period and for the longer periods and slower rates of precipitation in the presence of excess nickel sulfate.

In the early part of reaction studied turbidimetrically, for equinormal conditions the direct rearrangement

$$[Ni(C_2O_4)_2]^{=}\,Ni^{++}(aq) \longrightarrow 2Ni\,C_2O_4{\cdot}2H_2O(s) \qquad (5)$$

would give rise to a term in the rate equation proportional to the square root of the complex ion concentration, that is, to $E^{3/2}$. There is good evidence that this step proceeds heterogeneously on the walls of the vessel. In the presence of excess oxalic acid the complex is rendered less stable, the decomposition yielding an additional term proportional to the product of the concentration of the complex ion, E^3, and the excess oxalic acid concentration, C. These two steps account for the experimental equation 4.

In the dilatometric range the solution is already cloudy with small crystals of solid oxalate dispersed in the solution. Growth may proceed by the breakdown of the complex ion at the surface of existing crystals, giving rise to a term proportional to the concentration of the complex ion, E^3, and, in the presence of excess oxalic acid, by direct ionic addition to the existing crystals yielding a term proportional to EC. The additional retardation term, $-k_4C$ in 8 is attributed to the solubility of the freshly deposited oxalate in the solution containing excess oxalic acid. These three processes would account for the experimental equation 8.

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(2) R. Scholder, E. Gadenne and H. Niemann, *Ber.*, **60**, 1510 (1927)

(3) R. Scholder, *ibid.*, **60**, 1525 (1927).

(4) G. Sartori, *Gazz. chim. ital.*, **64**, 3 (1934).