obtained. As much as approximately 40 mole % ZnO can be dissolved in NiO forming a solid solution of (Ni, Zn)O whereby the cubic NiO lattice is maintained. As the reaction proceeds, the lattice constant increases due to the larger Zn ion. The maximum increase in lattice constant for a 40 mole % dissolution of ZnO is about 0.05 Å. The parabolic law of diffusion expressed the behavior of the reaction and from time dependent reaction studies the activation energy of this reaction has been determined to be E = 17,200 cal./mole = 0.75 e.v. The mechanism of the reaction is explained on the basis of defect structure formation in the NiO and ZnO lattice at elevated temperatures.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE CITY COLLEGE OF NEW YORK]

The Mechanism of the Precipitation of Magnesium Oxalate from Supersaturated Solutions

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The precipitation of magnesium oxalate from supersaturated solution, after the formation of nuclei, is first order with respect to the concentration of magnesium oxalate. The reaction leading to the formation of nuclei is third order. Also, the conductivity and the pH of the solution do not change during the formation of embryos and the precipitation. The following mechanism is therefore proposed: $Mg^{2+} + C_2O_4^{2-} = MgC_2O_4$ rapid, $MgC_2O_4 + MgC_2O_4 = (MgC_2O_4)_2$ rapid and complete, $(MgC_2O_4)_2 + MgC_2O_4 \rightarrow (MgC_2O_4)_3$ slow, $(MgC_2O_4)_3 + MgC_2O_4$ = individual crystals. The composition of the critical nuclei corresponds to $(MgC_2O_4)_2$.

Introduction

The comparatively slow rate of precipitation of magnesium oxalate from its supersaturated solutions has long been used as the basis of the separation of calcium ions from magnesium ions in analytical chemistry. Several studies of the characteristics of supersaturated solutions of magnesium oxalate have been made[2] but none deal with the mechanism of the reaction involved. An investigation of the kinetics of the precipitation of magnesium oxalate has therefore been undertaken.

From an analysis of the data on the solubility of magnesium oxalate in salt solutions and the conductivity of magnesium oxalate solutions, Pedersen[3] has concluded that magnesium and oxalate ions are in equilibrium with undissociated magnesium oxalate. Since crystallization ultimately occurs from the association of ions or molecules, we postulated the following general mechanism: magnesium and oxalate ions combine to form undissociated magnesium oxalate. Magnesium oxalate then associates stepwise to form the critical nuclei, each of which adds one more molecule of magnesium oxalate and become nuclei. Precipitation then occurs on each nucleus producing individual crystals. This mechanism also embodies the views of Reiss and LaMer[4] on the theory of nucleation and the production of homogeneous colloidal systems. Conductivity and pH measurements as a function of time were therefore made to determine the rate controlling step. The time lag, the period between the initial mixing of reactants and initial appearance of crystals, were measured to determine the order of the reaction leading to the formation of nuclei. The concentration of oxalate in solution was measured as a function of time to determine the order of the precipitation reaction.

Experimental

Stock Solutions.—All materials used were of reagent grade. Magnesium chloride was standardized by the Fajans method for chloride using dichlorofluorescein indicator. Ceric solution, prepared from ceric ammonium sulfate, was standardized against primary standard sodium oxalate, using excess ceric solution, warming to 50°, back titrating with ferrous sulfate to a slight excess, and then titrating the ferrous with the ceric solution in the presence of ferroin indicator.[5] The ceric–ferrous titer was determined each day the ferrous solution, prepared from ferrous ammonium sulfate, was used.

Potassium oxalate was standardized with the ceric solution. Buffer solution was prepared by titrating 244.7 g. of sodium acetate dissolved in water with concentrated acetic acid to pH 5.50, determined with pH meter, and then diluting to one liter.

Procedures.—Aliquot portions of standardized magnesium chloride and potassium oxalate solutions were mixed and diluted. pH and resistance measurements were then made prior to and during precipitation. Leeds and Northrup number 7662 pH meter and Industrial Instruments conductivity bridge model RC–BC were used for these measurements.

For the kinetic measurements, the aliquot portions were mixed with 5.0 ml. of standardized buffer solution, a weighed quantity of sodium sulfate, and water to a total volume of 205 ml. The sodium sulfate was added to maintain a constant ionic strength of 0.94; pH was constant at 5.70 ± 0.05; for all measurements, temperature was maintained at 25.00 ± 0.07°. At various time intervals, aliquot (10.00 ml.) portions of solution were filtered through a medium sintered glass filter, acidified and titrated with standardized ceric solution.

The duration from initial mixing to initial appearance of crystals was determined from a plot of the log of the concentration of magnesium oxalate against the time. The slope is zero initially since, during the formation of nuclei, the concentration of magnesium oxalate in the solution is not altered. When crystallization starts, the slope decreases.

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[1] Department of Chemistry, Columbia University. This work was carried out while a senior student at the City College.

[2] Z. Karaglanov, *Z. anorg. Chem.*, **124**, 92 (1942); E. Pozner and K. A. Samov, *J. Phys. Chem., U.S.S.R.*, **13**, 889 (1939); W. M. Fischer, *Z. anorg. allgem. Chem.*, **153**, 62 (1926).

[3] K. Pedersen, *Trans. Faraday Soc.*, **35**, 277 (1939).

[4] H. Reiss, *Trans. N. Y. Acad. of Sci.*, [II] **11**, 236 (1949); H. Reiss and V. K. LaMer, *J. Chem. Phys.*, **18**, 1 (1950); H. Reiss, *ibid.*, **18**, 840 (1950).

[5] G. Walden, L. Hammett and R. Chapman, THIS JOURNAL, **55**, 2649 (1933).

From the slope of the line, the velocity constant for the crystallization reaction is obtained. Extrapolation of the line corresponding to the crystallization reaction, to the line corresponding to the nuclei formation reactions gives the time lag. The time lag so determined was checked visually with the aid of a Tyndall beam. The determination of the time lag from the plot is however more precise than the visual method only when the initial concentration of magnesium oxalate is 0.17 molar or greater. At greater dilutions, the crystallization rate is slow and therefore during the initial stages of crystallization some of the fine particles pass through the filter medium.

Typical Kinetic Run.—20.0 ml. of 0.836 *M* potassium oxalate, 6.10 g. of Na_2SO_4, 25.0 ml. of 0.820 *M* magnesium chloride and 5.00 ml. of buffer solution were diluted to 205 ml., yielding a magnesium oxalate solution of initial concentration 0.0815 *M* with 0.0185 *M* excess magnesium ion over oxalate ion. The normality of ceric solution was 0.1065 meq. per ml. and for this run, the ceric–ferrous titer was 0.956 ml. per ml. ferrous. The kinetic data are summarized in Table I. The first column gives the time in minutes, the second and third columns give, respectively, total ml. of ceric and ferrous solutions for titration of 10.00 ml. filtered aliquot portions, and the fourth column gives the concentration of magnesium oxalate present in terms of ml. ceric solution. A plot of log ml. Ce^{4+} *vs.* time yields, after precipitation starts, the straight line from which $k = 3.24 \times 10^{-3}$ per min. is calculated. The intersection of the line through the points representing constant concentration of magnesium oxalate with the line representing the decrease in concentration yields a time lag of 115 minutes. For the runs in which an excess of oxalate over magnesium ion was initially present, the quantity of ceric solution equivalent to this excess was also subtracted from the total ml. of ceric solution.

Solubility Data. Degree of Supersaturation.—The solubility data were obtained by allowing solutions, similar to the solutions used for the kinetic experiments, to remain in the thermostat for periods of several weeks at the end of which the magnesium oxalate concentration was determined, as above, in terms of ml. Ce^{4+}. The titration on a second aliquot portion was repeated several weeks later and when both determinations agreed, equilibrium was assumed to exist between the solid magnesium oxalate and the solution. The ratio of the initial ml. Ce^{4+} to the final gives the degree of supersaturation, S_2/S_1.

TABLE I

SUMMARY OF DATA FOR A TYPICAL KINETIC RUN

Time, min.	Total ml. Ce^{4+}	Fe^{2+}, ml.	Cor. ml. Ce^{4+}
0	20.25	5.27	15.20
88	17.24	2.11	15.20
133	16.70	2.42	14.38
183	13.52	2.01	11.60
238	13.43	3.41	10.17
328	11.55	4.04	7.69
388	9.70	2.85	6.97

Results and Discussion

If the steps involving the removal of ions were rate determining, then the conductivity of the solution should decrease during precipitation and, since oxalate ion is a base, the *p*H of the solution should also decrease during precipitation. However, these properties of the solution remain sensibly constant during the formation of embryos and during precipitation. The *p*H of unbuffered solutions of sodium oxalate and magnesium sulfate, possessing an initial *p*H of 6.48 ± 0.02, remained at 6.50 ± 0.02 during the precipitation of magnesium oxalate. Resistance measurements made during the precipitation of magnesium oxalate, from solutions of sodium oxalate and excess magnesium sulfate having an initial resistance of 65 ohms, yielded values of 71, 60 and 66 ohms. The resistance of a solution of composition equivalent to the solution obtained after complete precipitation of the magnesium oxalate was 62 ohms. Also, the step involving the association of magnesium oxalate must be practically complete thereby driving the combination of magnesium and oxalate ions to practical completion. Hence, the addition of single molecules to form the nuclei is the rate determining step.

An estimate of the value of *n*, the order of the successive reactions leading to the formation of nuclei minus one, is obtainable, in accord with the Christiansen–Neilsen equation,[6] from the slope of the plot of the negative log of the product of the original molar ionic concentration, for approximately equivalent amounts of reactants, against the log of the time lag, column 6, Table II. The value of *n* so obtained is 2.08; the nuclei formation reaction is thus third order.

TABLE II

Temp. = 25.0°, ionic strength = 0.94, *p*H 5.70

Initial Molarities Mg^{2+}	$C_2O_4^{2-}$	MgC_2O_4	$k \times 10^3$ min.$^{-1}$	S_2/S_1	Time log, min.
0.1000	0.1224	0.1000	3.35	100	50
.1125	.0900	.0900	3.60		88
.1000	.0815	.0815	3.24	29.5	115
.0800	.0815	.0800	3.52	8.87	189
.0691	.0707	.0691	3.40		
		.8350		175	1

Av. 3.42, R.M.D. 3.3%

Our results (column 4, table II) also indicate that the precipitation of magnesium oxalate is first order with respect to the concentration of magnesium oxalate.

The mechanism for the precipitation of magnesium oxalate may thus be summarized as

$$Mg^{2+} + C_2O_4^{2-} = MgC_2O_4 \quad \text{rapid} \qquad (1)$$

$$MgC_2O_4 + MgC_2O_4 = (MgC_2O_4)_2 \quad \text{rapid and complete} \qquad (2)$$

$$(MgC_2O_4)_2 + MgC_2O_4 \longrightarrow (MgC_2O_4)_3 \quad \text{slow} \qquad (3)$$

$$(MgC_2O_4)_3 + MgC_2O_4 = \text{individual crystals} \qquad (4)$$

Individual crystals so formed should be homogeneous in size. Microscopic examination of the suspension of magnesium oxalate reveals that the crystals are rhombic. The lengths of the sides of the individual crystals for a given experiment are the same within a relative average deviation of 4%.

The time lag data may also be used to calculate the critical point—the magnesium oxalate concentration leading to spontaneous precipitation—at which the critical particle size may be estimated from the Thomson equation[7]

$$2.3RT \log \frac{S_2}{S_1} = \frac{2\gamma M}{dr}$$

S_2/S_1 represents the ratio of the concentration of magnesium oxalate in solution to the concentration of a saturated magnesium oxalate solution at the same temperature, column 5, Table II. *M* is expressed in grams per mole, *d* in grams per cm.^{3}, and *R* in ergs per mole per degree.

The surface tension, γ, is estimated to be 3 ×

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(6) J. A. Christiansen and A. E. Neilsen, *Acta Chem. Scand.*, **5**, 673 (1951).

(7) W. Thomson, *Phil. Mag.*, **42**, 448 (1871); J. J. Thomson, "Applications of Dynamics to Physics and Chemistry," Chapters X and XI; W. Ostwald, *Z. physik. Chem.*, **34**, 493 (1900).

10^3 dynes per cm. from the crude relationship[8] that the surface tension of a solid is directly proportional to the hardness of the solid. It is, of course, widely acknowledged that any single value for the surface tension of a solid is an almost meaningless quantity. Also, the surface tension of a solid in bulk, even if it were known, does not correspond to the surface tension of a particle of the same solid of the size involved at the critical point.

The value of S_2/S_1 at the critical point is 180 obtained by extrapolation of the plot of log S_2/S_1 *vs.* time lag. The corresponding critical radius, 2.9×10^{-6} cm., is larger than the radius found[9] for sulfur, silver chloride and tetraphenylarsonium perchlorate but is of the same order of magnitude found for barium sulfate. The reasonableness of this value is nevertheless difficult to evaluate since the crystal structure of magnesium oxalate has not been determined but it is undoubtedly larger than the $(MgC_2O_4)_2$ suggested by the proposed mechanism. However, because of the uncertainties associated with the calculations based on the Thomson equation, the size of $(MgC_2O_4)_2$ is probably a more accurate value than 2.9×10^{-6} cm.

From the proposed mechanism, it is probable that the structure of the activated complex is similar to the product of the reaction and, therefore, the entropy of activation should be about the same as the ΔS for the over-all reaction. Measurements of the temperature dependence of the rate constant for the precipitation of magnesium oxalate, from which the entropy of activation may be calculated, are in progress.

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[8] M. L. Dundon and E. Mack, Jr., THIS JOURNAL, **45**, 2479, 2658 (1923); G. E. Boyd, "Surface Chemistry," A.A.A.S. 1941 Symposium, p. 128, 1943.

[9] V. K. LaMer and R. H. Dinegar, THIS JOURNAL, **73**, 380 (1951); F. R. Duke and L. M. Brown, Abstracts Division of Phys. and Inorg. Chem., A.C.S. March '53 Meeting, page 46P.

[CONTRIBUTION FROM HOUDRY PROCESS CO.]

The Catalytic Activity of Barium and Calcium Hydrides. III. Hydrogen Exchange with Some C_4 Hydrocarbons

BY LEON WRIGHT AND SOL WELLER

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A study has been made of the exchange of hydrogen between the C_4 hydrocarbons (*n*-butane, isobutane and isobutylene) and barium and calcium hydrides. Exchange proceeds much more slowly with the paraffins than with the olefin. Normal butane exchanges with the hydrides as readily as does isobutane, and all hydrogen atoms in the hydrocarbons are exchangeable. The primary hydrogen atoms in isobutane exchange more rapidly than the tertiary atom; this may be a steric effect. The exchange is interpreted in terms of a homolytic split of a carbon–hydrogen bond in the hydrocarbon, with the intermediate formation of a kind of metal alkyl and metal hydride.

Introduction

In recent years, considerable attention has been directed to the mechanism of interaction of hydrocarbons with both acidic and metallic catalysts. Of the many approaches to this problem, hydrogen exchange reactions have been particularly useful in supplying information on the nature of the catalyst–hydrocarbon complex.

Hydrogen exchange with butanes over oxide catalysts has been reported by Hansford, Waldo, Drake and Honig[1] and Hindin, Mills and Oblad[2]; over metal catalysts by Thompson, Turkevich and Irsa[3]; and in sulfuric acid by Otvos, Stevenson, Wagner and Beeck.[4] Hansford, *et al.*, and Hindin, *et al.*, found that isobutane exchanges with deuterated silica–alumina cracking catalyst at 60–150°, whereas *n*-butane does not exchange under these conditions. Similar results are obtained with sulfuric acid at 25°.[4] Thompson, *et al.*, studied the exchange of normal and isobutane with deuterium over a Fischer–Tropsch catalyst (Co–ThO_2–MgO–SiO_2) at 183°. In contrast to the results with acid catalysts, they found that both butanes exchanged to about the same extent. In unpublished work at the Houdry Laboratories, Mills[5] has found that both normal and isobutane exchange over a deuterated supported platinum catalyst at 28–100°.

In view of the difference existing in the exchange behavior of normal and isobutane over acid and metal catalysts, a study was undertaken of the exchange of butanes with barium and calcium hydrides in order to gain information as to the mode of interaction of these catalysts with hydrocarbons.

Experimental

Materials.—Calcium metal was obtained as a dark gray powder (100–200 mesh) from the Ethyl Corporation.

Deuterium of >99% purity was obtained from the Stuart Oxygen Company and used without further purification.

Calcium deuteride was prepared from the reaction of calcium metal and deuterium at 200–300°.

Barium deuteride was prepared from barium hydride (Metal Hydrides, Inc.) by exhaustive exchange with deuterium at 200–300°.

Normal butane, isobutane and isobutylene of research grade (>99.5%) were obtained from the Phillips Petroleum Company and were used after drying over anhydrous calcium sulfate at 25°.

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[1] R. C. Hansford, P. G. Waldo, L. C. Drake and R. E. Honig, *Ind. Eng. Chem.*, **44**, 1108 (1952).

[2] S. G. Hindin, G. A. Mills and A. G. Oblad, THIS JOURNAL, **73**, 278 (1951).

[3] S. O. Thompson, J. Turkevich and A. P. Irsa, *ibid.*, **73**, 5213 (1951).

[4] J. W. Otvos, D. P. Stevenson, C. D. Wagner and O. Beeck, *ibid.*, **73**, 5741 (1951).

[5] G. A. Mills, private communication.