[CONTRIBUTION FROM THE GOESSMANN CHEMISTRY LABORATORY, MASSACHUSETTS STATE COLLEGE]

Investigations of the Effects of Some Factors on Rhythmic Crystallization[1]

BY MAJEL M. MACMASTERS, JULIA E. ABBOTT AND CHARLES A. PETERS

In 1853, Sir David Brewster[2] reported the first recorded cases of rhythmic crystallization from aqueous solution. Since that time, numerous investigators have reported similar instances of periodic banding, although but little has been done to explain the cause of the phenomenon or the influence of factors affecting it.

The rhythmic crystallization of potassium dichromate from aqueous solution, first reported by Miers[3] in 1908, is typical of the phenomenon and is easily reproduced. This is described in detail by Hedges.[4]

Experimental

Ordinary non-corrosive white glass microscope slides were used as surfaces on which crystallization took place. Preliminary tests showed that the method of cleaning did not effect crystallization on the slide. Slides prepared at 23 or 25° were placed in a constant temperature room; slides prepared at 50°, or above, were kept at constant temperature in a Freas electric oven. All salts used were C. P. Baker's Analyzed.

Coarse Rhythm, Fine Rhythm and X-Rhythm.—Miers' method gives rows of dendritic crystals alternating with areas more or less devoid of crystalline material. This we shall call *coarse rhythm*. Occasionally there appear small areas of very narrow alternating bands of thickly crystalline area (crests) and thinly crystalline areas (troughs). A crest and a trough comprise a period. This we shall call *fine rhythm*. In fine rhythm the periods are very small, usually 0.005 to 0.01 mm. Fine rhythm is often overlooked unless polarized light is used for the examination of the slides. Coarse rhythm is often irregular, and in many instances occurs over only comparatively small areas, while fine rhythm is extremely regular and usually occurs over large areas. Forms simulating coarse rhythm are often caused by shocks affecting the slide during crystallization, but fine rhythm is never counterfeited by shocks. Areas of fine rhythm crossed by a second system of fine rhythm approximately at right angles to the first have been observed. We shall call this *x-rhythm*.

Influence of Temperature and of Concentration.—The influence of change of temperature and of concentration upon the rhythmic crystallization of potassium dichromate was first investigated by a modification of Miers' method. For this purpose 0.0017, 0.017 and 0.136 M solutions of potassium dichromate were used. Each solution was allowed to crystallize at constant temperatures of 25, 50 and 100°. Slide and solution were kept at constant temperature for some time before the solution was placed on the slide; this temperature was maintained until crystallization was complete. The solution was transferred to the slide by means of a pipet, also at the required temperature.

In the slides made with 0.0017 M potassium dichromate dendrites became less common as the temperature rose, and massive circular crests at the edge of the drop became more common. The amount of simple fine rhythm present was greatest in slides run at 100°, and did not much vary in those run at 50° from those run at 25°. All slides, at all three temperatures, showed good fine rhythm and well defined areas of x-rhythm. Temperature did not affect the period of fine rhythm; periods of 0.005 and 0.01 mm. were most common.

The slides made with 0.0170 M potassium dichromate solution showed an increasing tendency to form heavy crests with increase of temperature. Dendrites were more common at lower temperatures than at 100°. Coarse rhythm decreased in amount with increase of temperature. Fine rhythm was present at all temperatures and did not appear to vary in amount with change of temperature. Only one case of x-rhythm was noted, on a slide made at 23°.

All slides made with 0.136 M potassium dichromate solution were dendritic. At 50 and at 100° numerous small circular crystals were formed. Rhythm decreased with increase of temperature; at 100° there was no evidence of rhythm.

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(1) This paper includes portions of the work offered in partial fulfilment of the requirements for the degree of Master of Science by Julia E. Abbott, 1933, and for the degree of Doctor of Philosophy by Majel M. MacMasters, 1934, at the Massachusetts State College.

(2) Brewster, *Trans. Roy. Soc. Edin.*, **20**, 607–24 (1853).

(3) Miers, *Mineral. Mag.*, **15**, 39–41 (1908); *C. A.*, **2**, 1919 (1908).

(4) Hedges, "Liesegang Rings and Other Periodic Structures," Chapman and Hall, London, 1932.

The influence of concentration was obvious. Slides made with 0.0017 *M* potassium dichromate solution showed much fine rhythm and x-rhythm; those made with 0.017 *M* potassium dichromate solution showed much fine rhythm, but practically no x-rhythm; while slides made with 0.136 *M* potassium dichromate solution showed very little rhythm of any type. Within the limits studied, fine rhythm and x-rhythm occur most frequently in dilute solutions and at low temperatures; the heavy crests formed by concentrated solutions are too thick for observation of rhythm; similar crests are formed by dilute solutions allowed to crystallize at high temperatures.

If all the data are considered, it appears at once that coarse rhythm is often irregular and never constant enough to serve as the criterion of periodicity. It becomes plain, on the other hand, that temperature and concentration differences, within the wide limits studied, have no influence upon the production of fine rhythm, providing only that the solution is not too strong and the temperature not too high for the production of a film of crystals. With a concentrated solution run at a high temperature crystallization proceeds rapidly with the formation of heavy crests which, by their massiveness, prohibit the detection of rhythm which might be present. The periods most commonly observed were those of 0.005 and 0.01 mm.; these were constant over wide areas on slides made at varying temperatures, with different concentrations of the solution. The crest and trough were, in general, of equal width; where this was not the case, the crest was that of one period, while the trough was that of another period either one-half or double the width of the first. All commonly observed periods were either 0.005 mm. in width or some common multiple of this width. x-Rhythm appears to be a special case of fine rhythm, in which periods of fine rhythm have developed in two directions.

New Method.—The method of Miers seemed open to criticism, because it involves motion, strong convection currents and exposures to contaminated atmosphere; the following method, therefore, was developed.

The 0.5 *M* solution of potassium dichromate to be examined was brought to boiling temperature; the cleaned slide was drained from distilled water and dipped, without wiping, into the boiling solution. Of each set of five slides, two were allowed to crystallize while held above the hot solution, while the other three were placed, on edge, on a glass plate to crystallize. A temperature difference in the surrounding atmosphere was thus introduced. In no case did there appear to be any difference between the two slides and the three, and in most cases these films showed periodic banding. This method gives, consistently, large areas of fine rhythm.

Influence of Specific Impurities.—Preliminary tests showed that typical rhythm was formed in the presence of 12% ethyl alcohol, 4% sodium hydroxide or small quantities of various acids.

Sodium dichromate and ammonium dichromate were introduced, in turn, in order to study the effect of a single foreign ion upon rhythmic crystallization. Further investigation showed, however, that each of these salts exhibited rhythmic crystallization from aqueous solution. The banding shown by ammonium dichromate was very similar to that exhibited by potassium dichromate. Sodium dichromate gave finer but less continuous rhythm. The rhythmic crystallization of these salts has not hitherto been reported.

Specific Effect of Anions.—This part of the work was undertaken assuming that the cation was the most important factor in rhythmic crystallization. This assumption arose from the observation that potassium dichromate and ammonium dichromate, with similar cations, showed very similar rhythmic crystallization, while sodium dichromate, with a smaller cation, showed finer spacing of the periods, and finally, introduction of sufficient hydrogen ion, a very small cation, completely inhibited fine rhythm. The results obtained were surprising; apparently the foreign cation has little or no effect on the rhythm, while anion has a specific inhibitory effect.

A 0.5 *M* potassium chloride solution was mixed with the 0.5 *M* potassium dichromate solution to give molar ratios of chloride ion to dichromate ion varying from 10/2 to 10/7, increasing always by whole numbers. The tests showed that a 10/5 molar ratio of chloride ion to dichromate ion had a slight effect upon the rhythmic crystallization of potassium dichromate, while a 10/3 molar ratio completely inhibited the rhythmic crystallization of potassium dichromate. When the large amounts of the chloride ion were present, potassium dichromate built dendritically upon cubic crystals of potassium chloride, and no fine rhythm found when all of the dichromate was used in building such dendrites. Under the influence of the potassium chloride coarser dendrites of the potassium dichromate appeared coincident with the disappearance of fine rhythm. It seems probable, therefore, that potassium chloride inhibited fine rhythm by modifying the surface attractions of the potassium dichromate crystals. The period of fine rhythm when present was always that normally shown by pure potassium dichromate solutions.

The effect of the presence of 0.5 *M* sodium chloride upon the rhythmic crystallization of 0.5 *M* potassium dichromate was investigated in a similar way. Inspection of the various sets of slides in this series showed that the period of fine rhythm did not decrease, but remained constant at the normal value for potassium dichromate; it may be concluded from this that sodium dichromate did not form to any large extent, as preliminary tests had shown that sodium dichromate crystallizes rhythmically with a period smaller than that of the potassium salt. Fine rhythm persisted only slightly longer in this series than in that in which potassium chloride was used as impurity. A molar ratio of chloride ion (or sodium ion) to dichromate ion of 10/4 caused appreciable decrease in the amount of fine rhythm present, while a ratio of 10/2 caused complete absence of fine rhythm.

It appeared desirable to try the effect of the presence of a divalent cation; for this purpose a series of slides was made and examined, using a 0.25 *M* solution of calcium chloride as the specific impurity. When the molar ratio of chloride ion to dichromate ion was 10/4 fine rhythm was still present, but when the ratio was 10/3 fine rhythm was not typical, although a transitional type of rhythmic branching of dendrites was observed.

The transition from parallel branching of dendrites to typical fine rhythm is of especial interest, as it indicates more clearly the ultimate cause of fine rhythm. Fine rhythm is due to very regular branching of dendrites. The present writers have observed the crystals in crest and trough to be lying at right angles to each other; the branch lies at right angles to the parent stem.

The molar ratio of chloride ion to dichromate ion at disappearance of fine rhythm was 10/2, 10/3, 10/3, in the presence of sodium chloride, potassium chloride and calcium chloride, respectively. The charge on the cation cannot be an important factor, since the effect of the chloride ion is constant, no matter whether it is introduced with monovalent cation as sodium or potassium or with a divalent cation as calcium. There is also further substantiation of the view that the anion alone affects the inhibition of fine rhythm, in this case at least, since the ratio of chloride ion to dichromate ion is constant in the presence of sodium ion, calcium ion or excess potassium ion. These results were unexpected in view of the preliminary work.

Potassium nitrate, 0.5 *M*, was used with the 0.5 *M* potassium dichromate solution to introduce a monovalent anion other than the chloride ion. All fine rhythm of the series showed the usual period for potassium dichromate. Definite curtailment of fine rhythm did not appear until the molar ratio of nitrate ion to dichromate ion was 6/15; with a ratio of 7/15 fine rhythm was entirely suppressed. The corresponding ratio of chloride ion to dichromate ion was 10/3; the nitrate ion is, therefore, far more effective than the chloride ion in the inhibition of rhythmic crystallization of potassium dichromate from aqueous solution.

Potassium sulfate, 0.5 *M*, was used with 0.5 *M* potassium dichromate to determine the effect of the sulfate ion, a divalent anion, upon the periodic crystallization of potassium dichromate. The period of the fine rhythm was not affected. When the molar ratio of sulfate ion to dichromate ion was 1/1 the amount of fine rhythm formed began to decrease. When the ratio was 4/3 rhythm was almost completely inhibited. The sulfate ion is, therefore, more effective in inhibiting the formation of fine rhythm by potassium dichromate than is the chloride ion, but is less effective than the nitrate ion. From this evidence it would further appear that the charge on the anion is not a prime factor in the effect of the anion on rhythmic crystallization.

Spacing of Periods from the Center of Crystallization.—No data concerning the spacing of rings from the center of crystallization in cases of rhythmic crystallization from solution have been found in the literature. Such measurements are often difficult, as in some cases the center is surrounded by a large, irregular area of undifferentiated or dendritic precipitate; in other cases the arc of crystallization is so great

TABLE I

DATA ON SPACING OF PERIODS FROM CENTER OF CRYSTALLIZATION

No.	Soln. used	Dist. of period from center, mm.			Values of A $\frac{h_3 - h_2}{h_2 - h_1} = A$		Agreement with Jablczynski	Agreement with Hughes (see Fig. 1)
1	150 cc. 0.5 M $K_2Cr_2O_7$ with 100 cc. 0.5 M K_2SO_4	0.045	0.070	0.095	1.00	1.20	Partial	Fair
		.125	.155		1.00			
2	0.5 M $K_2Cr_2O_7$	.060	.075	.090	1.00	1.00	Perfect	Fair
		.105	.120	.135	1.00	1.00		
		.150			1.00			
3	50 cc. 0.5 M $K_2Cr_2O_7$ with 10 cc. 0.166 M $FeCl_3$	.010	.015	.020	1.00	1.00	Perfect	Almost perfect
		.025	.030	.035	1.00	1.00		
		.040	.045		1.00	1.00		
4	50 cc. 0.5 M $K_2Cr_2O_7$ with 20 cc. 0.25 M $CaCl_2$	.020	.040	.060	1.00	2.00	Partial	Good
		.100	.120	.140	0.50	1.00		
		.160			1.00			
5	50 cc. 0.5 M $K_2Cr_2O_7$ with 40 cc. 0.25 M $CaCl_2$	.015	.030	.045	1.00	1.00	Perfect	Excellent
		.060	.075	.090	1.00	1.00		
6	40 cc. 0.5 M $K_2Cr_2O_7$ with 100 cc. 0.25 M $CaCl_2$	.060	.095	.150	1.85	0.15	Negative	Fair
		.160	.200	.235	4.00	.88		

that the center would lie at a considerable distance off the slide. Measurements were undertaken, however, in an attempt to determine whether potassium dichromate, in the solutions under investigation, gave rhythmic bands similar in arrangement to those found by Jablczynski[5] in Liesegang rings, or by Hughes[6] and Dippy[7] in melts which crystallized rhythmically.

Jablczynski found the ratio between rings formed by metathesis of silver nitrate and potassium dichromate in gelatin gel to be constant, expressed by $(h_3 - h_2)/(h_2 - h_1) = A$, when h_n is the distance of the nth ring from the point of entrance of the diffusing silver nitrate solution.

Hughes and Dippy investigated cases of rhythmic crystallization from the melt, found that by plotting the logarithm of N, the number of rings counted from the center against the logarithm of r, the distance of the ring from the center, a straight line was obtained with the general equation

$$\log N = a \log r + \log K$$

when N and r are defined as above, a is the slope of the line to the axis of log r, and log K is the intercept on the axis of log N.

Slides were chosen at random, but only areas where the center of crystallization was clearly defined, and in which fine rhythm progressed evenly in all directions from the center of crystallization were used. Data and comparison with Jablczynski and with Hughes are given in Table I. The graph, Fig. 1, developed from Table I shows agreement with the work of Hughes.

Slides 2, 3 and 5, Table I, showed perfect agreement with the Liesegang ring relationship found by Jablczynski, while slides 1 and 4 showed partial agreement. Slide 6, however, showed negative agreement. The relationship apparently holds for many cases of rhythmic crystallization from solution, but may not be universally true.

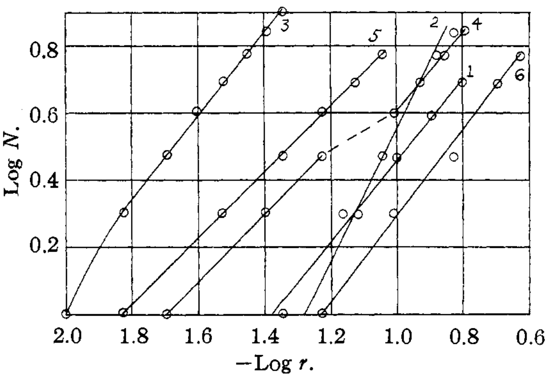

Fig. 1.—Log of number of period plotted against log of distance from center.

When the data from slides 1, 2 and 3, Fig. 1, are plotted as suggested by Hughes, they show a tendency to give a curve when the data are taken from near the centers of crystallization (curve 3), but the data as a whole give a statistically straight line. Only the statistically straight lines given by the data as a whole have been drawn in for slides 1 and 2. Many more cases would have to be investigated to prove that the tendency to give a curve from data near the center of crystallization is significant. Slide 4 shows two lines, both excellently straight, one from data near the center of crystallization, the other from data more re-

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[5] Jablczynski, *Kolloid-Z.*, **40**, 22–28 (1926).

[6] Hughes, *Nature*, **123**, 603–604 (1929).

[7] Dippy, *J. Phys. Chem.*, **36**, 2354–2361 (1932).

moved from the center. Slides 5 and 6 show statistically straight lines, in good agreement with the work of Hughes.

If slides had been taken exhibiting the usual fine rhythm of extremely constant spacing over wide areas in large arcs such that the theoretical center of crystallization would be situated off the slide, no distances from the center could have been measured. If the first period formed had been used as a center of crystallization, and measurements made from it, however, a regular series like those in slides 2, 3 and 5 would have been found in those numerous cases in which the periods are of equal width over large areas. These cases would give perfect agreement with the work of Jablczynski and good agreement with the work of Hughes and of Dippy.

For suggestion of the subject of research, acknowledgment and thanks are due to Professor Cecil H. Desch, George Fisher Baker lecturer in Chemistry at Cornell University, October, 1931, to January, 1932.

Summary

Distinction has been made between *coarse rhythm* and *fine rhythm* produced by crystallization of potassium dichromate from aqueous solutions. Fine rhythm has been shown to be the true criterion of periodicity. A method has been described by which very regular fine rhythm can be obtained over large areas.

It has been shown that differences in temperature and in concentration do not, within wide limits, materially affect the rhythmic crystallization of potassium dichromate from aqueous solution.

The rhythmic crystallization of ammonium dichromate and of sodium dichromate from their aqueous solutions has been reported.

The specific influence of a foreign anion in inhibiting the formation of fine rhythm of potassium dichromate has been shown. It has been determined that the nitrate ion is more effective than the sulfate ion, while the sulfate ion is more effective than the chloride ion. The molar ratio of each of these ions to dichromate ion necessary completely to inhibit formation of rhythm has been reported.

It has been shown that the spacing of periods from the center of crystallization, in rhythmic crystallization of potassium dichromate from aqueous solution, agrees, roughly, with the spacing of Liesegang rings reported by Jablczynski, and with the spacing of rhythmic banding resulting from crystallization from the melt, as reported by Hughes and substantiated by Dippy. This would indicate that there may be a common cause underlying the formation of Liesegang rings, rhythmic banding from the melt and rhythmic crystallization from solution.

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Additions to Conjugated Systems in the Anthracene Series. III. Factors Influencing the Mode and Extent of Reaction of the Grignard Reagent with Ketones

BY PERCY L. JULIAN, WAYNE COLE AND THOMAS F. WOOD[1]

When benzalanthrone (I) is treated with methylmagnesium iodide, the main product (II) isolated is the one formed by 1,2-addition. The reaction was puzzling for a long time, first of all because it is difficult to duplicate results unless the proper concentration of reactants is consistently maintained. Secondly, the behavior of our product (II) toward bromine, as well as behavior on attempted rearrangement into the isomer with the anthracene structure,[2] were not what we had expected. All these results appear, however, to find satisfactory explanation in the ease with which (II) loses water, possessing as it does a very reactive hydroxyl group.

The product secured on treatment of (II) with one mole of bromine in the cold indicates addition of two atoms of bromine and elimination of a molecule of water. It is highly fluorescent in solution, and both bromine atoms are very reactive, as is shown by the ease with which the dibromide is converted into a diacetate. We are suggesting structure (V) for it, and (III) and (IV) as logical intermediates. The diacetate would then have the structure (VI). On further treat-

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(1) Abstracted from the senior researches of Messrs. Cole and Wood at DePauw University, 1934–1935.

(2) *Cf.* Julian and Cole, THIS JOURNAL, **57**, 1607 (1935).