paper, with a few further results based upon it. The equation of condition for appearance of an inflection may be written, with the same symbols as previously except that H replaces (H^+) as follows:

$$(1 - K_W/K_BH)(cK_A/(K_A + H)^2 + K_W/H^2 + 1) - (K_W/K_BH^2)(cK_A/(K_A + H) + K_W/H - H) - 2(K_W/K_BH + 1)(cK_AH/(K_A + H)^3 + K_W/H^2) = 0$$

Using this equation for several cases not previously considered in which acid and base are both weak, I find that if K_A or $K_B = 10^{-3}$ the inflection occurs if the ionization constant of the titrating base or acid is as large as 10^{-9} but not if it is $= 10^{-10}$. Similarly, if K_A or K_B is taken as 10^{-9} the inflection occurs if the ionization constant of the titrating agent is 10^{-3}, but not if it is 10^{-4}.

Indefinite elaboration of such calculations is possible. I believe, however, that all that is ordinarily required for correct orientation is provided in the following summary.

If acid and base are both strong (ionization constant infinite) the inflection appears at all concentrations and always coincides with the endpoint.

If the acid is weak and the added base strong the inflection appears if $cK_A > 2.7 \times 10^{-13}$, as shown by Roller. The inflection precedes the end-point by about 3% in titer if $cK_A = 10^{-12}$. This last value decreases approximately 10-fold for each 10-fold increase in cK_A.

With acid and base both weak, and with c between 0.001 M and 1 M, the numerical results above may be generalized by the approximation that the inflection will appear if $K_AK_B \geqq 10^{-12}$, but not if $K_AK_B \leqq 10^{-13}$. The inflection in these cases does not coincide with the end-point. The deviation in titer is nearly independent of concentration in the indicated range. It is of the order of 5% if $K_AK_B = 10^{-12}$ and again decreases about 10-fold for each 10-fold increase in K_AK_B. It will be observed that the generalization above limits the critical value of K_AK_B for the disappearance of the inflection only within one power of 10, and that it is based on examples in which neither constant exceeded 10^{-3}. It can no doubt be applied somewhat beyond this point, but must fail eventually if K_A or K_B is indefinitely increased. Further refinement of the criterion, within more restricted limits of K, is possible, but of little additional value.

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An Investigation of the Benzoate Method for the Separation of Iron, Aluminum and Chromium and Some Suggested Changes for its Application to Qualitative Analysis

BY LEO LEHRMAN AND JACOB KRAMER

Recently a method of separating aluminum, chromic and ferric ions, using ammonium benzoate as a precipitant, from the other ions of the third and fourth groups and magnesium was offered.[1] While the procedure was devised essentially for quantitative work the authors say it can be used in a qualitative scheme. However, certain features of the method seem not to be clearly developed for the qualitative analysis of the common metals and others may not be readily adaptable. These points in question, which we thoroughly investigated are: (A) the application of the procedure for 500 mg. total metallic ion content, the usual amount for qualitative work, especially when it is mostly trivalent; (B) diminution of the lengthy period of boiling required to precipitate the Cr^{+++}; (C) the possible difficulty of filtering the precipitate representing 500 mg. of trivalent metallic ion; (D) reduction of the number of washings and possible change of the wash solution. Our investigation, the results of which are given below, showed that with certain changes the method can be used for the qualitative analysis of the common metals.

With 500 mg. separately of each of the divalent ions of Groups 3 and 4 and Mg^{++}, no precipitation is obtained with 10% ammonium benzoate reagent in acetic acid solution. For separate solutions of 500 mg. each of Al^{+++}, Cr^{+++} and Fe^{+++}, 90 ml., 60 ml. and 40 ml., respectively, of the precipitant are needed to cause complete precipitation after one minute of boiling. Mixtures of 250 mg. of each of the trivalent metallic ions, Fe^{+++} and Cr^{+++}, Al^{+++} and Cr^{+++}, and Fe^{+++} and Al^{+++}, required 40 ml., 50 ml. and 60 ml., respectively, to give the same result. In all cases if not enough precipitant is originally added for complete precipitation, prolonged boiling has no effect. Thus it is possible to precipitate completely 500 mg. of Cr^{+++} in a short period of boiling (one minute). The size of the precipitate obtained with 500 mg. of the trivalent metallic ions is rather large but can be contained in an 11 cm. filter paper if filtered with suction. Under these conditions two or three washings with 10

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[1] Kolthoff, Stenger and Moskowitz, THIS JOURNAL, 56, 812 (1934).

ml. of 5% ammonium nitrate solution removes practically all of the divalent metallic ions. Finally 1 mg. of the divalent metallic ions can be detected in the filtrate after precipitation of 500 mg. of any one of the trivalent or combination of them. Before testing the filtrate for the divalent ions the benzoic acid present is removed by evaporating until crystallization just begins, cooling and filtering with suction.

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[CONTRIBUTION FROM THE DIVISION OF PLANT BIOLOGY, CARNEGIE INSTITUTION OF WASHINGTON, AND THE DIVISION OF PLANT NUTRITION, UNIVERSITY OF CALIFORNIA]

Polymerization of Dihydroxyacetone

BY HAROLD H. STRAIN AND W. H. DORE

x-Ray diffraction measurements demonstrate the polymerization of crystalline monomolecular dihydroxyacetone to dimolecular dihydroxyacetone. These measurements also indicate that the polymerization begins shortly after the preparation of the monomolecular form and that it is complete in twenty-five to thirty days. At the end of this period, higher polymers and condensation products were not detectable by x-ray, cryoscopic or solubility methods.

Experimental

Dimolecular dihydroxyacetone, prepared by crystallization (from ethanol) of dihydroxyacetone which had stood for several months[1] and shown to be dimolecular by cryoscopic measurements of freshly prepared aqueous solutions, exhibited (when powdered) a clear and characteristic x-ray diffraction pattern (Column B, Table I). Monomolecular dihydroxyacetone, prepared by distillation of the dimolecular form[2] and shown to be monomolecular by cryoscopic measurements of freshly prepared aqueous solutions, likewise exhibited a clear and characteristic x-ray diffraction pattern (Column A, Table I). After crystals of the monomolecular dihydroxyacetone had stood for several days it was observed that the diffraction pattern resembled that obtained from the dimolecular form even though molecular weight determinations demonstrated that the crystals were composed of the monomolecular form. This indicated that the monomolecular form was slowly polymerizing to the dimolecular form and, in order to determine the rate of the polymerization, x-ray diffraction patterns of monomolecular dihydroxyacetone were obtained at intervals over a period of thirty days. The results indicated that, at room temperature and within the experimental error, polymerization to the dimolecular form was complete in twenty-five to thirty days and was independent of radiation with x-rays. The average molecular weight of the polymerized product determined by cryoscopic methods corresponds to that of dimolecular dihydroxyacetone.[3]

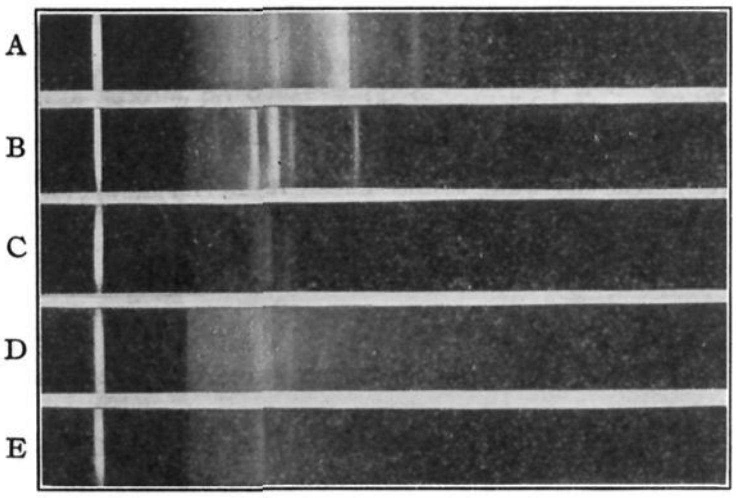

Fig. 1.—x-Ray patterns of some forms of dihydroxyacetone: A, monomolecular dihydroxyacetone, m. p. 72°; B, dimolecular dihydroxyacetone, m. p. 78–81°; C, polymolecular dihydroxyacetone, m. p. 130–133°; D, polymolecular dihydroxyacetone, m. p. 230–260° with dec.; E, polymolecular dihydroxyacetone, m. p. 230–250° with dec.

Attempts were made to determine whether or not higher polymers and condensation were

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[1] Bertrand, *Compt. rend.*, **126**, 842, 984 (1898); *Ann. chim. phys.*, [8] **3**, 215, 246 (1904).

[2] Fischer and Mildbrand, *Ber.*, **57**, 707 (1924); Reeves and Renbom, *Biochem. J.*, **25**, 412 (1931).

[3] Single crystals of dimolecular dihydroxyacetone of sufficient size for optical, goniometric and Laue diffraction measurements were obtained by crystallizing the sugar from ethanol. Optical examination revealed that the crystals were monoclinic but that they were twinned in some complex fashion and clear Laue diffraction patterns could not be obtained. The results indicated a unit cell composed of two molecules of dimolecular dihydroxyacetone. Single crystals of monomolecular dihydroxyacetone could not be obtained by crystallization because of the rapid polymerization to the dimolecular form described in this paper.