SPECIAL ARTICLES

PERFECTION AND AGGLOMERATION OF CRYSTALLINE PRECIPITATES ON AGING

IN extensive studies on the aging of freshly precipitated lead sulfate prepared from 0.1 molar lead nitrate and 0.1 molar potassium sulfate at room temperature we[1] arrived at the conclusion that the classical type of aging, the so-called Ostwald ripening, is of subordinate significance at room temperature. When dealing with a heterodisperse precipitate the Ostwald ripening involves the solution of the smaller particles and the growth of the larger particles at the expense of the small ones. Recent studies carried out in this laboratory on the aging at room temperature of barium sulfate[2] and of silver chloride,[3] details of which will be reported in the *Journal* of the American Chemical Society, have substantiated the above conclusion. The fresh precipitates, although crystalline, are highly imperfect, as indicated by the diffuseness of the x-ray lines. Especially during the early stages of aging in the mother liquor a very fast perfection process occurs as a result of recrystallization without *always* being accompanied by pronounced changes of the external surface (Ostwald ripening). It was found that all factors which decrease the solubility of the precipitate inhibit the speed of perfection, and hence of recrystallization; on the other hand, all factors which increase the solubility promote recrystallization and perfection. It was concluded that this recrystallization occurs in a liquid film around the primary particles. The surface of the latter is very irregular and contains spots of various activities. At these spots ions quickly enter into the liquid film, the solution being supersaturated with regard to the more normal surface, on which the ions redeposit. This process occurs so quickly that the lattice ions, in excess in the supersaturated film, hardly have an opportunity to enter the bulk of the solution and cause Ostwald ripening. The above recrystallization, therefore, results in a self-digestion and self-perfection of the primary particles. *The speed of perfection is not determined by the solubility of the precipitate in the bulk of the solution but by the solubility in the liquid film around the particle.* Thus, it was found by Noponen[2] that barium sulfate ages much faster in 0.005 m sulfate than in 0.005 m barium solution, although the solubility of the precipitate in both solutions is of the same order. The difference is attributed to the fact that barium ions are adsorbed much stronger on the fresh precipitate than sulfate ions. Consequently, the solubility of the barium sulfate in the liquid film around the particles is much smaller in 0.005 m barium than in 0.005 m sulfate. In studies by Yutzy[3] with freshly precipitated silver chloride it was found that the aging is much more pronounced in 0.001 m chloride than in 0.001 m silver. In interpreting this result it should be realized that silver halides have a pronounced tendency to adsorb their own ions, the halide ions being more strongly adsorbed than silver ions. Thus, the concentration of the adsorbed chloride ions in the solvated jacket around the particle may be much greater than in the bulk of the solution and may give rise to the formation of the complex $AgCl^-_2$ ions with the silver chloride. It is well known that the solubility of silver chloride in more concentrated chloride solutions is greater than in water, owing to formation of complex argento-chloride ions. If the concentration of the adsorbed chloride ions in the liquid film is great enough, the solubility of the silver chloride in the liquid jacket may be much greater than in the bulk of the solution, thus accounting for the more rapid aging of silver chloride in 0.001 m chloride than in 0.001 m silver or in pure water. So far, we have only considered the perfection of the individual particles. This process may be accompanied by an agglomeration. Various primary particles may share their water jackets and thus form loose agglomerates which can be easily peptized again. When the perfection process occurs in such an agglomerate, lattice ions may be deposited in the liquid canals between the particles, thus cementing them together by the formation of bridges consisting of lattice material. When the entire liquid space is filled up with lattice material, the crystalline aggregates will have a mosaic structure. The cementing process is irreversible and results in a decrease of the total surface of the precipitate as measured by the adsorption of a suitable dye. Factors which promote the perfection process will also promote the cementing process. It was found, for example, that no cementing occurred upon the slow aging of barium sulfate in a solution containing an excess of barium, but a very pronounced one upon the aging in excess of sulfate.[2] Also, the aging of silver chloride in an excess of chloride and even of silver is accompanied by a pronounced cementing process.

The above short review does not give a complete

[1] I. M. Kolthoff and Ch. Rosenblum, *J. Am. Chem. Soc.*, 56: 1264, 1658, 1934; 57: 597, 607, 2573, 2577, 1935; 58: 116, 121, 1936.

[2] G. E. Noponen, Thesis, 1936, University of Minnesota.

[3] H. Yutzy, Thesis, 1936, University of Minnesota.

insight into the complex mechanism of the aging, and more work is being done to investigate various phenomena and to experimentally test the interpretations presented.

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UTERINE RESPONSE TO DIHYDROTHEELIN[1]

IT has been observed for many years that the estrogenic hormones from any source caused a considerable thickening in the epithelium of the vagina and the development of a cornified layer of epithelium in experimental animals. Stockard and Papanicolaou[2] noted this while working with guinea pigs in 1917. Allen and Doisy[3] used this observation to develop a simple test for the estrus condition—namely, the vaginal smear method. Since then the method has been refined by various workers and is widely used. Fee, Mirian and Parkes,[4] Zondek[5, 6] and others have shown that estrogenic substances cause marked hypertrophy of the uterus and early vaginal introitus in immature females.

Dorfman, Gallagher and Koch[7] have suggested that quantitative observations on the hypertrophy of the uterus be used to distinguish between the estrogenic compounds. Twenty-five day-old rats were injected daily for five days with the assayed estrogenic substance. They were then sacrificed, and weights of both the uteri and the ovaries were determined. The ratio of uterine weight (mg) to animal body weight (gm) less the gut was plotted against the dosage in rat units. Theelin and theelol compared in the same way showed a marked difference in their effects upon uterine growth.

Ralls and Jordan,[8] D'Amour and Gustavson,[9] Thayer, Jordan and Doisy[10] and later MacCorquodale, Thayer and Doisy[11] have reported the presence of an estrogenic compound in the follicular fluid of the ovary. Using its properties as a basis of opinion the latter named authors suggested that the reported compound was dihydrotheelin.

As was stated above, Dorfman, Gallagher and Koch,[7] suggest that the uterine response is a good test method to distinguish between the various estrogenic compounds. It was decided to compare the standardized international theelin and dihydrotheelin in this respect. The technique used was that suggested by D'Amour and Gustavson,[12] theelin assayed 0.84 γ per rat unit; dihydrotheelin assayed 0.154 γ per rat unit. These preparations were incorporated in olive oil for injection. Olive oil was injected in controls. Litter mates were selected for each test. Dosages of .05, .1, .2, .3, .4, .5 and .6 rat units were used. The number of animals receiving dosage for each substance varied from three to ten.

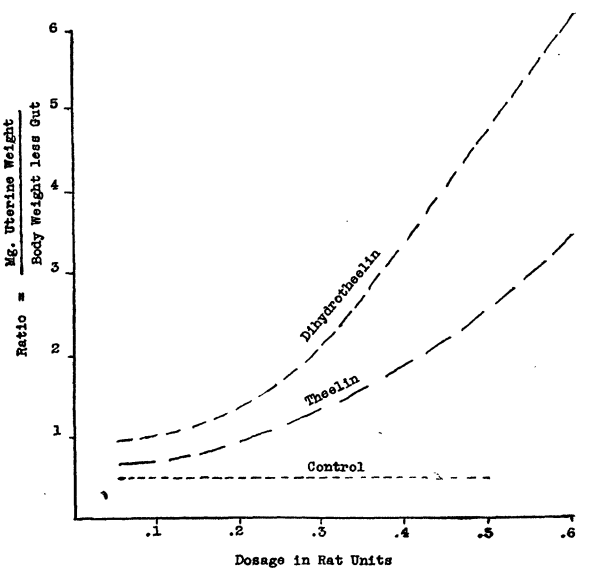

FIG. 1. Uterine response to theelin and dihydrotheelin.

By reference to Fig. 1, it can be seen that dihydrotheelin had a much greater effect upon hypertrophy of the uterus than theelin did. This is considered reasonable upon the basis of relative activity of the two as reported by several workers.

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THE VITAMIN C CONTENT OF THE HUMAN TONSIL[1]

THE tonsils of 54 persons, mostly children, were analyzed for vitamin C on the day of operation by the method used for foods by Birch, Harris and Ray.[2] Values ranged from 10.6 to 47.6 milligrams per 100

[1] Contribution No. 221, Department of Chemistry, Kansas State College.

[2] C. R. Stockard and G. N. Papanicolaou, *Am. Jour. Anat.*, 22: 225, 1917.

[3] E. Allen and E. A. Doisy, *Jour. Am. Med. Assoc.*, 81: 819, 1923.

[4] A. R. Fee, G. F. Mirrian and A. S. Parkes, *Jour. Physiol.*, 67: 377, 1929.

[5] B. Zondek, *Nature*, 133: 209, 1934.

[6] B. Zondek, *Nature*, 133: 494, 1934.

[7] R. I. Dorfman, T. F. Gallagher and F. C. Koch, *Endocrin.*, 19: 33, 1935.

[8] J. C. Ralls and C. N. Jordan, *Endocrin.*, 10: 273, 1926.

[9] F. E. D'Amour and R. G. Gustavson, *Jour. Pharm. and Exp. Therap.*, 49: 141, 1935.

[10] S. A. Thayer, C. N. Jordan and E. A. Doisy, *Jour. Biol. Chem.*, 79: 53, 1928.

[11] D. W. MacCorquodale, S. A. Thayer and E. A. Doisy, *Proc. Soc. Exp. Biol. and Med.*, 32: 1185, 1935.

[12] F. E. D'Amour and R. G. Gustavson, *Jour. Pharm. and Exp. Therap.*, 40: 473, 1930.

[1] Preliminary report.

[2] T. W. Birch, L. J. Harris and S. N. Ray, *Biochem. Jour.*, 27: 590, 1933.