2. The use of rapid agitation during the addition of water greatly aids solution. This is a factor favoring the individual evacuated ampuls as when water is injected into them extremely vigorous agitation results.

3. Compression of the porous material does not alter its solubility but retards the rate somewhat due to a decrease in surface area exposed to the solvent.

4. Exposure to air was found to reduce the ease with which a given sample could be dissolved.

5. The lyophile process does not apparently alter the jelly strength of the gelatin so treated. When 5 per cent gels of the initial gelatins were prepared and compared with 5 per cent gels made with the lyophile product no difference in jelly strength could be detected.

6. Although samples prepared in "vacuoles" were, in general, easier to dissolve than identical bulk samples, in some few cases small films of insoluble material were observed which would not dissolve even upon heating. The significance of these is being investigated.

With ordinary gelatins, after a solution is made some considerable reduction in temperature is required in order for gelation to take place. However, by the use of a soluble lyophile gelatin a phenomenon of considerable interest to the colloid chemist may be accomplished, namely, what is in effect an isothermic sol→gel transformation. Five grams of a lyophile gelatin (sample F) are slowly dissolved in water at 25° C. in such a manner as to avoid any appreciable rise in temperature. The resulting solution when allowed to stand at the same temperature will slowly set to form a firm jelly. One might go even a step further and prepare a sol at a given temperature, then raise the temperature a few degrees and have a gel form. Obviously, the temperature at which the solution is allowed to stand must not approach too closely 35° C., the temperature at which gelatin can exist only in the sol state.

CONCLUSIONS.

1. The properties of lyophile gelatin have been investigated and in particular its solubility behavior.

2. Some explanations are advanced for the effect of several variables on the solubility of lyophile gelatin.

3. The change of gelatin from the dry solid state→sol→gel with the temperature being maintained constant is described.

ACKNOWLEDGMENT.

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DEGRADATION STUDIES ON DIBENZOYL DISULFIDE.*

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The use of dibenzoyl disulfide as an antipuritic (1) has led to the recent study of satisfactory methods of synthesis (2), (3). We were further interested in studying the degradation of dibenzoyl disulfide by various methods in order to obtain quantitative conversion to a simple derivative which might supplement the routine Parr bomb sulfur analysis. Several procedures were tried before a successful quantitative degradation to benzoic acid was accomplished. This degradation was mentioned briefly in the paper of Shelton and Rider (2) but it seems worth while to pre-

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sent it in more detail. At the same time the other degradation studies will be summarized briefly since they are revealing as to the stability of dibenzoyl disulfide and the reactions in which it will take part.

(1) *Conversion to Benzanilide.*—Dibenzoyl disulfide is readily converted to benzanilide by refluxing in benzene (4) or in alcohol (benzanilide is soluble in hot alcohol but very slightly soluble in benzene):

$$C_6H_5COSSCOC_6H_5 + 2C_6H_5NH_2 \rightarrow 2C_6H_5CONHC_6H_5 + H_2S + S$$
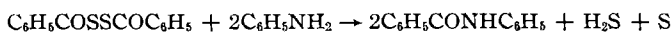
This reaction, although apparently quantitative, did not lend itself to practical use because it was impossible completely to free the benzanilide from sulfur. Hence, attempts were made to hydrolyze the benzanilide to benzoic acid. This could not be accomplished quantitatively by aqueous or alcoholic alkali or by 50% (w/v) sulfuric acid. Five hours' refluxing with 75% (w/v) sulfuric acid brought about the hydrolysis but it was impossible to obtain consistent results. This resistance to hydrolysis is in accord with the recently published observation of Asinger (5) that benzanilide is only 50% hydrolyzed on 16 hours' boiling with methyl alcoholic potassium hydroxide.

The preparation of the more easily hydrolyzed benzamide by reaction of dibenzoyl disulfide with ammonia is complicated by the formation of ammonium thiobenzoate (4b) together, in our experience, with other by-products, and was not further investigated:

$$C_6H_5COSSCOC_6H_5 + 2NH_3 \rightarrow C_6H_5CONH_2 + C_6H_5COSNH_4 + S$$

(2) *Oxidation with Potassium Permanganate.*—It was thought that the use of a reagent which would convert all of the sulfur into a non-interfering form, such as sulfate, might be of value. Alkaline permanganate is recommended as a reagent which will oxidize sulfur completely to sulfate in organic sulfur compounds where sulfur is not attached to oxygen (6), (7). However, an excessive amount of permanganate ($9^1/_2$ moles) was necessary to react all of the dibenzoyl disulfide and this undoubtedly led to too extensive degradation and only about 35% of the theoretical amount of benzoic acid was obtained. Of course, sulfur could be determined after this treatment by the usual barium sulfate procedure but the simpler Parr bomb method is to be preferred.

(3) *Direct Hydrolysis to Benzoic Acid.*—Dibenzoyl disulfide may be hydrolyzed to a mixture of benzoic and thiobenzoic acids (2a):

$$C_6H_5COSSCOC_6H_5 + 2KOH \rightarrow C_6H_5COOK + C_6H_5COSK + S + H_2O$$

The thiobenzoic acid can then be converted to benzoic acid by further hydrolytic treatment giving a total of two molecules from one molecule of dibenzoyl disulfide. Saturated alcoholic potassium hydroxide did not complete the conversion to benzoic acid after boiling for 30 hours. Sodium ethylate, as might be expected, was likewise ineffective and gave a mixture of by-products. Dibenzoyl disulfide is remarkably resistant to acid hydrolysis, complete breakdown not occurring after 24 hours' boiling with 75% (w/v) sulfuric acid; benzaldehyde was detected among the products of reaction. Five and 25 per cent aqueous potassium hydroxide do not give quantitative yields of benzoic acid after 30 and 6 hours' boiling, respectively. Forty per cent aqueous potassium hydroxide, however, is entirely satisfactory in 3 hours and was the reagent chosen. Typical results are shown in Table I. The use of stronger alkali is disadvantageous since the solubility of potassium benzoate is so decreased that the reaction mixture does not remain fluid.

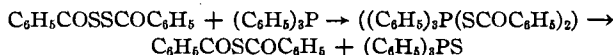TABLE I.—BENZOIC ACID FROM DIBENZOYL DISULFIDE BY HYDROLYSIS WITH 40% AQUEOUS POTASSIUM HYDROXIDE.

Wt. Disulfide Gm.	Wt. Benzoic Acid Obtained Gm. (Theory = 0.890 Gm.)	Per Cent of Theory Obtained.
1	0.871	98.0
1	0.883	99.2
1	0.875	98.3

PROCEDURE FOR CONVERSION OF DIBENZOYL DISULFIDE TO BENZOIC ACID.

Reflux 1 Gm. of dibenzoyl disulfide and 30 cc. of 40% w/v potassium hydroxide solution in a 100-cc. round bottom flask for three hours. Cool, transfer to a Squibb separatory funnel (rinsing out flask with water), acidify with concentrated hydrochloric acid, and allow to cool again. Shake the benzoic acid into ether, using five portions (total of 120 cc.) and collect the ether extracts in another separatory funnel. Wash the ether with 25 cc. of approximately $0.1 N$ hydrochloric acid, and then wash this aqueous portion with 15 cc. of ether. Combine the ether extracts and filter through cotton into a beaker, washing the cotton with fresh ether. Evaporate the ether with the aid of a stream of air. (Evaporation may be hastened by placing the beaker in a water-bath at not over 40° C. until 30 cc. remains; then remove from water-bath and complete removal with air.) Treat the residue with a solution of 1.5 Gm. of sodium bicarbonate in 50 cc. of water. Warm the mixture and allow it to stand until all the benzoic acid has dissolved; the sulfur will be practically insoluble. Filter the liquid through a coarse filter paper into a Squibb separatory funnel and wash the paper thoroughly with water. Acidify the sodium benzoate solution with 10% hydrochloric acid, allow it to cool, and shake out the benzoic acid with chloroform, using five portions (total of 100 cc.). Collect the chloroform extracts in another separatory funnel. Wash the chloroform with 20 cc. of approximately $0.1 N$ hydrochloric acid, and then wash this aqueous portion with 10 cc. of chloroform. Filter the combined chloroform extracts through cotton into a tared beaker and evaporate the chloroform with the aid of a stream of air, placing the beaker in a water-bath at a temperature of not over 40° C. as before. Dry the benzoic acid over night in a vacuum over sulfuric acid and weigh.

In the above procedure ether is used for the first extraction since sulfur is much less soluble in it than in chloroform. The benzoic acid can be identified by melting point and the usual tests. The method in our hands has given consistent results of from 98% to 99.2% of the theoretical yield of benzoic acid which is within the limits of error of the shake-out.

One other method of degradation of dibenzoyl disulfide has recently appeared in the literature (8). This is the reaction with triphenyl phosphine and does not lend itself to practical quantitative use:

$$C_6H_5COSSCOC_6H_5 + (C_6H_5)_3P \rightarrow ((C_6H_5)_3P(SCOC_6H_5)_2) \rightarrow$$
$$C_6H_5COSCOC_6H_5 + (C_6H_5)_3PS$$

SUMMARY.

A method is described for the quantitative conversion of dibenzoyl disulfide to benzoic acid by hydrolysis with 40% aqueous potassium hydroxide. Several ineffectual procedures for the quantitative degradation of dibenzoyl disulfide are summarized.

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