than spherical. The ratio between the two values for the particle radius given by the two laws (r_E/r_S) is 1.43. This compares well with similar ratios already obtained in the cases of hemoglobin, serum albumin, serum globulin and phycocyan. This probably means that the departure of the particle from a spherical shape is about the same amount for all of these proteins.

Summary

1. Casein prepared by the Hammarsten method has been examined at *P*H 6.8 in phosphate buffer solution by the centrifugal sedimentation velocity method and found to consist of a mixture of protein molecules of different weight.

2. Hammarsten casein was extracted with hot acidified 70% alcohol and the soluble protein precipitated out with dilute sodium hydroxide. This protein after washing was dissolved in phosphate buffer solution of *P*H 6.8. Various concentrations were examined by both the sedimentation velocity and sedimentation equilibrium methods.

3. It was found that within the limits of experimental error the acid-alcohol soluble protein was homogeneous with regard to molecular weight and that it therefore probably was a pure chemical individual.

4. The molecular weight was found to be 375,000 ± 11,000.

5. The molecule was not spherical and deviated from the spherical shape by about the same amount that has been found for several other proteins.

UPSALA, SWEDEN
GENEVA, NEW YORK

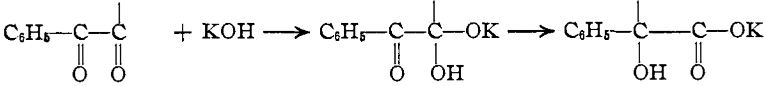
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON]

THE BENZILIC ACID REARRANGEMENT

BY THEODORE W. EVANS AND WILLIAM M. DEHN

RECEIVED JULY 1, 1929 PUBLISHED JANUARY 8, 1930

It seems probable that the benzilic acid rearrangement is best formulated as follows



$$C_6H_5-\underset{O}{\underset{\|}{C}}-\underset{O}{\underset{\|}{\overset{C_6H_5}{\overset{|}{C}}}} + KOH \longrightarrow C_6H_5-\underset{O}{\underset{\|}{C}}-\underset{OH}{\underset{|}{\overset{C_6H_5}{\overset{|}{C}}}}-OK \longrightarrow C_6H_5-\underset{OH}{\underset{|}{\overset{C_6H_5}{\overset{|}{C}}}}-\underset{O}{\underset{\|}{C}}-OK$$

The addition of one molecule of potash was postulated by Hoogewerff and van Dorp;[1] the migration of both C_6H_5 and H, by Michael;[2] ex-

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[1] Hoogewerff and van Dorp, *Rec. trav. chim.*, **9**, 225 (1890). These authors assumed that Ph and OK migrate from one carbon atom to the other.

[2] Michael, THIS JOURNAL, **42**, 814 (1920). Michael assumes the addition of one mole of potassium hydroxide, and this forms a system which "may now completely convert itself, by the transmigration of phenyl and hydrogen, into a salt of the relatively strong benzilic acid."

perimental indication of $C_{14}H_{10}O_2 \cdot KOH$ was given by Scheuing.[3] It has been assumed that benzil adds to H_2O,[4] to $2H_2O$,[5] to 2KOH,[6] or to KOH.[7] Since it is possible to avoid water[8] and to limit the alkali to one molecule, it is possible to obtain definite proof not only that water is not necessary but that the intermediate additive[9] compound is formed.

All experiments directed toward increasing the yield of the acid have involved large excesses[10] of alkali. Experiments of only theoretical interest have always involved either water alone, or alkali alcoholate alone, or alcoholic potash, or mixtures of these. In no case has only one molecule of benzil, one molecule of potash and an indifferent solvent such as ether, benzene, etc., been employed. We have treated equivalents of benzil, furil and diacetyl with potash in anhydrous ether and have found that only one molecule of potash is necessary for the transformation.

A single lump of potassium hydroxide weighing 1.4 g., placed in absolute ether with 5.4 g. of benzil and shaken occasionally during four days, was replaced by 5.6 g. of a powdery, light yellow solid; the ether yielded 1 g. of unchanged benzil, melting at 95°. The solid was analyzed.

Anal. Calcd. for $C_{14}H_{10}O_2 \cdot KOH$: K, 14.68. Found: K, 15.04.

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[3] Scheuing, *Ber.*, **56**, 252 (1923); **57**, 1963 (1924). Schönberg, *ibid.*, **58**, 235 (1925), criticizes Scheuing's product as affording no proof of an intermediate compound, "da das Anlagerungsproduct weder analysiert noch sein molekular gewicht bestimmt worden ist."

[4] Nef, *Ann.*, **298**, 372 (1897). For a criticism of Nef's interpretation see Michael, THIS JOURNAL, **42**, 812 (1920).

[5] Lachman first assumed the addition of two molecules of water but later assumed only one molecule of water. *Cf.* THIS JOURNAL, **44**, 330 (1922), and **45**, 1509, 1522, 1529 (1923); **46**, 779 (1924). His contention that a mobile hydroxyl group shifts, that water is necessary for the benzilic acid rearrangement and his use of the word "metakliny," involving intramolecular oxidation and reduction, seem unjustified.

[6] Tiffeneau, *Rev. gen. sci.*, 585 (1907). Staudinger and Binkert, *Helv. Chim. Acta*, **5**, 703 (1922).

[7] Schroeter, *Ber.*, **42**, 2336 (1909), also assumed initial addition of one mole of potassium hydroxide, but his theory of rearrangement, involving the intermediate formation of diphenylketene was disproved by Nicolet and Pelc, THIS JOURNAL, **43**, 935 (1921); see also Schönberg and Keller, *Ber.*, **56**, 1638 (1923).

[8] Lachman states unequivocally that water is necessary for the benzilic acid rearrangement; see especially THIS JOURNAL, **46**, 781 (1924). Others who have observed the effects of water are Jena, *Ann.*, **155**, 78 (1870); Klinger, *Ber.*, **19**, 1868 (1886).

[9] Scheuing used equivalents of alcoholic potash and benzil in ether solution and obtained a light yellow solid which he claimed was changed gradually at 0° and rapidly at 80° to potassium benzilate.

[10] From 3 to 8 equivalents of potassium hydroxide have been used. Liebig, *Ann.*, **25**, 27 (1838); Zinin, *ibid.*, **31**, 329 (1839); Limpricht and Schwandert, *Ber*, **2**, 134 (1869); Jena, *Ann.*, **155**, 79 (1870); Fischer, *Ber.*, **14**, 326 (1881); Klinger, *ibid.*, **22**, 1212 (1889); H. v. Liebig, *ibid.*, **41**, 1644 (1908); Staudinger, *Ann.*, **356**, 71 (1907); "Organic Syntheses," Vol. I, **1921**, p. 29; Scheuing, *Ber.*, **56**, 255 (1923); Schönberg and Keller, *ibid.*, **56**, 1640 (1923).

Some of this salt, treated with concentrated sulfuric acid, gave the characteristic red color which benzilic acid does.[11] Upon acidifying 4.64 g. of this potassium benzilate, 3.71 g. (94%) of white needles of benzilic acid melting at 150° were obtained. Since no benzaldehyde or benzoic acid was detected, the precipitate represented an 81% transformation to potassium benzilate. The transformation was effected in the absence of water and while the additive compound was in the solid state. In another experiment equivalents of materials were ground up in a mortar under dry ether, but owing to rise of temperature or unavoidable contact with atmospheric moisture and oxygen, the yield was poor and contained benzaldehyde and benzoic acid.

From anhydrous ammonia, benzil and toluene was obtained a white solid, which proved to be benzilam,[12] melting point at 110°. With anhydrous ammonia, benzil and ether a white solid melting at 158° was obtained. With potash, it yielded ammonia and a white solid, insoluble in water, and melting at 203°. It will be further investigated.

When 5 g. of furil and 1 g. of sodium hydroxide in dry ether were shaken during twenty-four hours, 5.33 g. (88%) of a dark brown powdery mass was obtained.

Anal. Calcd. for $C_{10}H_6O_4 \cdot NaOH$: Na, 10.00. Found: Na, 10.27.

Acidification of the salt and extraction with ether yielded white needles of furilic acid agreeing in all properties with Fischer's product.[13]

With 10 g. of diacetyl and 6.5 g. of potassium hydroxide in dry ether, an immediate blackening of the potash resulted; the final sticky mass was brown-black, and though it contained acetaldehyde, resin, acetic acid and other products, it could not be made to yield dimethylglycolic acid.

Summary

One molecule of potash transforms benzil to benzilic acid; water is not necessary for this reaction. An additive compound is first formed which undergoes molecular rearrangement while in the solid phase.

SEATTLE, WASHINGTON

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[11] We have observed that 60% perchloric acid and 85% phosphoric acid also give red colorations with benzilic acid.

[12] Laurent, *J. prakt. Chem.*, [1] **35,** 461 (1846).

[13] Fischer, *Ann.*, **211,** 222 (1884).