

The hydrolysis of the sucrose was brought about by heating a 10% solution of the sugar at 80–85° in a thermostat for several hours. The increase in the rate of hydrolysis of the sucrose was studied originally by the quantitative determination of the ratio between the amount of reducing sugar formed in the control solution (containing no cellulose) and the amount formed in the solution containing cellulose. In later experiments the effect was studied by comparison of the specific rotation of the unhydrolyzed (unheated) sugar solution with that of the control solution, and that of the solution containing cellulose, respectively.

In a typical determination of the relative amounts of reducing sugar formed in the catalyzed and uncatalyzed hydrolysis of sucrose, the controls showed less than 0.01% of reducing sugar, whereas the cellulose catalyzed solutions showed  $0.1 \approx 0.02\%$  of reducing sugar. This corresponds to a ten-fold difference. A one hundred and thirty-fold difference was observed in an hydrolysis carried out at 96–98°.

The writers are at present investigating the catalytic properties of dried cellulose fiber for the purpose of determining: (1) the conditions best suited to the activation of cellulose fiber; (2) the relationship (if any) between the structure of disaccharides and the effectiveness of dried cellulose fiber in promoting their hydrolysis; (3) the nature of the effect herein described.

A full account of this investigation will be submitted shortly to THIS JOURNAL.

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RECEIVED MARCH 10, 1932  
PUBLISHED MAY 7, 1932

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#### THEBAINONE

*Sir:*

The investigations of Clemens Schöpf have shown that the ketone originally called thebainone, resulting from reduction of thebaine with stannous chloride in concentrated hydrochloric acid, contains a new structural skeleton, differing from that present in the starting material. The ketone has been renamed metathebainone. In a recent publication [Schöpf and Hirsch, *Ann.*, **489**, 224 (1931)] the isolation of the true thebainone from the mother liquors of metathebainone preparation is described. In a footnote the statement is made that the true thebainone is undoubtedly different from the "sulfur-free ketone" obtained by Pschorr in 1910 by hydrolysis of  $\beta$ -ethylthiocodide.

In the course of studies which we have been conducting in the thiocodide series we have prepared a quantity of the "sulfur-free ketone" and find it to

be identical in every respect with Schöpf's true thebainone. A sample of the latter, generously supplied by Professor Schöpf, showed no depression in melting point with the "sulfur-free ketone." Schöpf's base shows  $[\alpha]_D^{26} -45.7^\circ$ , while Pschorr's shows  $[\alpha]_D^{28} -46.4^\circ$ ,  $-46.9^\circ$  in 95% alcohol. Schöpf bases his statement that the two ketones are different upon discrepancies in the melting points of the methiodide and hydriodide, and the fact that Pschorr's hydriodide is hydrated. The methiodide which we obtain from Schöpf's thebainone sample melts at  $250-251^\circ$ . that from the "sulfur-free ketone" at  $251^\circ$ . When the hydriodide of Schöpf's thebainone is crystallized from a large amount of water, it separates hydrated, and shows two melting points,  $163-165^\circ$  and  $257-260^\circ$ , like the "sulfur-free ketone" hydriodide, whose melting point it does not depress.

The structure of Pschorr's "sulfur-free ketone" is thus settled, and another case of supposed isomerism in the thebainone series eliminated. The true thebainone is obtained in nearly quantitative yield by the hydrolysis of  $\beta$ -ethylthiocodide, which constitutes a very convenient preparative method.

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RECEIVED MARCH 17, 1932  
PUBLISHED MAY 7, 1932

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#### THE HEAT OF DISSOCIATION OF THE SODIUM MOLECULE

Sir:

The original determination of the heat of dissociation of  $\text{Na}_2$  from the band spectrum indicated a value of about 1 volt (= 23,000 cal.). If this were the case saturated sodium vapor should show an abnormal density at all pressures. Rodebush and Walters [THIS JOURNAL, 52, 2654 (1930)] found this to be true but the abnormality is small and the value of the heat of dissociation calculated from their best results is 0.79 volt (= 18,200 cal.).

Lewis [*Z. Physik*, 69, 786 (1931)] calculated the heat of dissociation from a vapor density determination by a molecular ray method and obtained the value 0.73 volt (= 16,900 cal.). Recently Nusbaum and Loomis [*Phys. Rev.*, 39, 179 (1932)] have carried out an accurate analysis of the vibrational bands and find the heat of dissociation to be 0.76 volt (= 17,500 cal.) with an uncertainty of 0.02 volt. It seems quite certain that 0.76 volt is the lower limit and that the true value is in the interval of 0.76-0.78 volt.

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RECEIVED MARCH 28, 1932  
PUBLISHED MAY 7, 1932

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