

Taylor and his co-workers did not assume all the fatty acid was present as an ester with the carbohydrate substance, contrary to the author's statement [Sherman, Columbia Dissertation (1932)]. If such was the case then the treatment with alkali would liberate *all* the fatty acid. That such is not the case has been shown.<sup>2</sup> It seems rather unusual, if the fatty acids are only present extraneously as an impurity in the granules, that different samples of the same starch have the same amount of fat. Furthermore, other starches have different amounts of fat, while potato hasn't any at all.<sup>3</sup> In the original work<sup>4</sup> the starch granules were destroyed by gelatinization with ammonium thiocyanate and ethyl alcohol, the starch precipitated with acetone and then extracted with acetone, ethyl alcohol and ether. It was then shown that most of the fatty acid was still in the starch. Taylor concluded from this that the fatty acid "cannot be attributed to retention of fat between the layers in the granules." This important fact was further demonstrated from different approaches to the problem by Taylor and several of his co-workers.<sup>5</sup>

In the light of the above it is hard to believe, because of the extraction of fatty acid by fat solvents having hydrophilic groups, that the fat is distributed extraneously as an impurity in the starch granules. It is conceivable that the fatty acid might be present as an adsorption complex with the carbohydrate. This could account for the selective solution by the solvents Schoch used. It might also explain some of the results Taylor and his co-workers obtained, such as the polarity of the fat-bearing carbohydrate component. As a matter of fact it has been shown by the work of Taylor and Werntz that the fatty acid present accounts for the electrical charge on  $\alpha$ -amylose.

(2) Taylor and Werntz, *THIS JOURNAL*, **49**, 1584 (1927).

(3) Lehrman and Kabat, *ibid.*, **55**, 850 (1933).

(4) Taylor and Nelson, *ibid.*, **42**, 1726 (1920).

(5) Taylor and Iddles, *Ind. Eng. Chem.*, **18**, 713 (1926); Taylor and Beckman, *THIS JOURNAL*, **51**, 294 (1929); Taylor and Sherman, *ibid.*, **55**, 258 (1933); Taylor and Morris, *ibid.*, **57**, 1070 (1935).

THE COLLEGE OF THE CITY OF NEW YORK  
NEW YORK CITY, N. Y. RECEIVED NOVEMBER 21, 1938

### Attempts to Prepare the Methylene Radical by the Thermal Decomposition of Hydrocarbons

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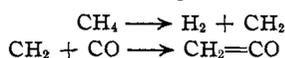
The question as to whether the methylene radical is produced in the thermal decomposition of methane and other hydrocarbons, and whether

it should be regarded as a molecule or a free radical has been discussed in a number of papers.<sup>1</sup> In view of Pearson and co-workers' recent paper supporting the work of Belchetz and Rideal, it seems desirable to give a supplementary report of work in this field that has been in progress in the author's laboratory for a number of years.<sup>2</sup>

We have attempted to obtain methylene from methane and other hydrocarbons by passage over heated filaments in an apparatus similar to that used by Belchetz and Rideal. Under their conditions for detecting methylene<sup>1b</sup> (Fig. 1), we succeeded in removing tellurium mirrors, but were unable to obtain enough tellurium compound to identify: we found that even after runs of several days, the amount of tellurium removed could not be weighed on an ordinary analytical balance.

On the other hand, by using much longer wires<sup>1b</sup> (Fig. 2) and larger mirrors, our results agreed with those reported by Belchetz and Rideal, and were similar to those obtained by passing methane through a quartz furnace;<sup>2d</sup> dimethyl ditelluride was obtained and identified by its melting point at  $-19.5^\circ$ .

Another series of experiments was then undertaken in which methane and other hydrocarbons were mixed with carbon monoxide and passed over the heated filament in the hope that ketene would be formed according to the equations



No ketene was ever detected, although a great many experiments under different conditions were performed.<sup>3</sup> These negative results, in conjunction with the positive results of other experiments,<sup>4</sup> indicate that trivalent carbon radicals are the primary products of organic dissociations, and even in the few cases (such as diazomethane and ketene) in which methylene is the primary product, it passes readily into the trivalent state.

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RECEIVED NOVEMBER 14, 1938

(1) (a) Belchetz, *Trans. Faraday Soc.*, **30**, 170 (1934); (b) Belchetz and Rideal, *THIS JOURNAL*, **57**, 1168 (1935); (c) **57**, 2466 (1935); (d) Pearson, Purcell and Saigh, *J. Chem. Soc.*, 409 (1938).

(2) (a) Rice and Glasebrook, *THIS JOURNAL*, **55**, 4329 (1933); (b) Rice, *Trans. Faraday Soc.*, **30**, 169 (1934); (c) Rice and Glasebrook, *THIS JOURNAL*, **56**, 2381 (1934); (d) Rice and Dooley, *ibid.*, **56**, 2747 (1934).

(3) We may also note that if such reactions do occur, carbon monoxide would appear to act as an inhibitor of decompositions studied in a static manometric system.

(4) Rice, Johnston and Evering, *THIS JOURNAL*, **54**, 3259 (1932); Rice and Evering, *ibid.*, **56**, 2105 (1934).