leaves the first term, corresponding to an order of 1.5, predominating over the remainder of the reaction.

This is the first of a series of papers on the characteristics of n-butane decomposition.

NOTES

The Preparation of Methyleneaminoacetonitrile

BY LAWRENCE H. AMUNDSEN AND RUTH VELITZKIN

After repeated experimentation the method of preparing methyleneaminoacetonitrile as described in "Organic Syntheses"[1] has been improved. The following modifications have been made: (1) time of reaction decreased; (2) higher temperatures; (3) internal cooling with solid carbon dioxide;[2] (4) acetic acid added in one portion before the addition of sodium cyanide.

Experimental

A mixture of 150 cc. (1.9 moles) of 35% formaldehyde, 54 g. (1 mole) of ammonium chloride and 38 cc. (0.66 mole) of glacial acetic acid was cooled to below 15° by the addition of crushed ice. When as much as 10% more formaldehyde was used, no significant difference in yield or purity of the product was observed but 50% more formaldehyde appeared to decrease the yield. It has been found possible to add small pieces of solid carbon dioxide instead of crushed ice. When one works with ten times the quantities stated here, the necessity for handling such a large volume of solution is thus avoided. There is probably no advantage in making this substitution if sufficiently large vessels are available. The mixture was stirred vigorously and a solution of 49.5 g. (0.98 mole) of 96–98% sodium cyanide in approximately 100 cc. of water was added from a dropping funnel over a period of fifteen to twenty minutes. The temperature was kept at 15–20° by the addition of crushed ice. When the temperature was permitted to go as low as 0°, no difference was noted in the results. Also momentary increases in temperature above 20° caused no significant change but when the temperature was maintained throughout at 35–40° an oily product was formed. After the addition was completed, the stirring was continued for fifteen minutes while the same temperature was maintained. Somewhat longer periods of stirring gave identical results, but if the solution was filtered at once, a small additional

quantity of the compound was deposited from the filtrate. The precipitate was filtered off and washed well with water. It seemed to be best to filter off the product the same day for the product was less pure, as indicated by the melting point, when the reaction mixture was allowed to stand for several days. This may be due to the formation of the lower melting isomer.[3] When the product was not thoroughly washed, the melting point was low and suspended solid material seemed to be present in the melt. This may have been ammonium chloride. The yields with few exceptions have been from 45–55% of the theoretical and the melting points have been between 124 and 129° (uncorr.) with a 2 or 3° range. Although these yields are somewhat lower than those reported by Adams and Langley,[1] they are equal to those obtained in this Laboratory by following their directions. This method has given equally satisfactory results with batches ten times the size of the one described, i. e., the same size batch used by Adams and Langley.[1] When solid carbon dioxide was used for cooling these larger batches, 3–4 kg. was sufficient to keep the temperature at 15–20°.

(3) Johnson and Rinehart, THIS JOURNAL, **46**, 772 (1924).

DEPARTMENT OF CHEMISTRY
CONNECTICUT STATE COLLEGE
STORRS, CONNECTICUT   RECEIVED NOVEMBER 10, 1938

Comment on "Absence of Combined Fatty Acid in Cereal Starches"

BY LEO LEHRMAN

No doubt all the workers in the field of starches will note with a great deal of interest the above entitled communication of Schoch.[1] The author reports the complete removal of the fatty acids in three cereal starches by extraction with water-miscible fat solvents, particularly methanol, the cellosolves and 80% dioxane. He gives two other results, viz., (1) the de-fatted starch retains the usual properties of starch; (2) fatty acid can be reintroduced into the defatted starch by treatment with alcoholic oleic acid, and then concludes that "the fatty acid is distributed throughout the starch granule as an extraneous impurity."

It is with the interpretation of the experimental work that I think exception must be taken.

(1) Schoch, THIS JOURNAL, **60**, 2824 (1938).

(1) Adams and Langley, "Organic Syntheses," edited by Gilman, John Wiley and Sons, Inc., New York, N. Y., 1932, Coll. Vol. I, p. 347. This method in a more or less modified form has been described or mentioned several times in the literature. A complete bibliography is given in "Organic Syntheses." As far as the authors have been able to determine, no more recent information has appeared.

(2) The authors are indebted to Raymond I. Longley, Jr., for proposing temperature control by adding solid carbon dioxide directly to the mixture.

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.[2] 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.[3] In the original work[4] 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.[5]

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 α-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

BY F. O. RICE

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.[1] 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.[2]

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[1b] (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[1b] (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;[2d] dimethyl ditelluride was obtained and identified by its melting point at $-19.5°$.

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

$$CH_4 \longrightarrow H_2 + CH_2$$
$$CH_2 + CO \longrightarrow CH_2{=}CO$$
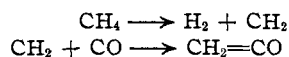
No ketene was ever detected, although a great many experiments under different conditions were performed.[3] These negative results, in conjunction with the positive results of other experiments,[4] indicate that trivalent carbon radicals are the primary products of organic dissociations, and even in 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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(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).