were compared with those of pure mannose phenylhydrazone by Dr. E. J. Roberts of this Laboratory and the two crystals were found to be identical. The results of the examination are stated by Dr. Roberts as follows. "Mannose phenylhydrazone crystallizes in the form of rhombic plates which are biaxial positive with $2V \doteqdot 75^\circ$; $\beta = 1.65$, $\alpha \doteqdot 1.60$, $\gamma \doteqdot 1.74$. Most of the plates show an *almost* perpendicular emergence of an optic axis, have an acute angle of 75° and an extinction angle of 23° in the acute angle. The trace of the axial plane passes through the acute angle of the rhomb. The crystals obtained from the phosphatide have identical properties."

Summary

One of the reducing sugars formed on hydrolyzing the phosphatide isolated from the human tubercle bacillus has been identified as mannose.

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[CONTRIBUTION NO. 24 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS AND COMPANY]

THE THERMAL DECOMPOSITION OF SODIUM AND POTASSIUM METHIDES

BY WALLACE H. CAROTHERS AND DONALD D. COFFMAN

RECEIVED NOVEMBER 22, 1929 PUBLISHED MARCH 6, 1930

In a previous paper[1] the results of a study of the thermal decomposition of sodium methide were reported.

The thermal decompositions of sodium and potassium methides have now been studied and found to proceed in accordance with Equation 1.

$$8MCH_3 \longrightarrow 6CH_4 + M_2C_2 + 6M \ (M{=}Na,\ K) \tag{1}$$

Pure methane is liberated in the calculated amount and, on treatment of the residue with water, the rest of the carbon is set free as acetylene mixed with ethylene and ethane.[2]

Sodium and potassium methides are primary salts of the very weak volatile polybasic acid, methane. When salts of this general class are heated the usual result is the liberation of free acid and the formation of a new salt in which all the available hydrogens of the residual acid have been replaced. This process consists in the displacement of a prototropic equilibrium[3] by the constant removal of one of the participating entities. In accordance with this general behavior is the liberation of methane from sodium or potassium methide

$$4CH_3^- \longrightarrow 3CH_4 + C^{----} \tag{2}$$

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[1] Carothers and Coffman, THIS JOURNAL, **51**, 588 (1929).

[2] The presence of ethylene and ethane may be ascribed to the fact that the acetylene is formed under powerfully reducing conditions (action of water on excess sodium or potassium).

[3] Lowry, *Institute International de Chemie Solvay*, **2**, 150 (1925).

Each of three methide ions captures a proton from a fourth ion, and the latter should, therefore, appear in the residue as the tetravalent methide anion. This, however, does not persist, for what is actually found in the residue is the acetylide ion. Electrons must, therefore, have been liberated (to sodium or potassium cations) and new covalent bonds established

$$2\mathrm{C}^{----} \longrightarrow \mathrm{C}\equiv\mathrm{C}^{--} + 6\,\ominus \qquad (3)$$

This union of the carbons must have occurred after they were completely stripped of their protons, since if it had occurred at any earlier stage, less than the calculated amount of methane would have been formed; moreover, hydrogen would then have appeared in the gas or sodium hydride in the residue.

The rather unusual reaction represented by Equation 3 may be regarded as an expression of carbon's very limited tolerance for a free electron pair, a property which is manifested in practically all the reactions of the alkali alkyls. The transformations of these extraordinarily reactive compounds almost invariably lead to the disappearance of the free electron pair either by sharing or by surrender. Thus, at 100° the ethide anion, $CH_3CH_2^-$, (in sodium ethide)[4] discards its free pair and, no more readily reducible substance than sodium ion being present to accept these electrons, a proton is lost with them, so that they appear as hydride ion. This permits the establishment of a new covalent bond between the two carbon atoms,[5] and ethylene[6] is formed. In the tetravalent methide ion this tendency to discard the free electron pairs is so great as to bring about the reduction of sodium and potassium ions to the free metals. The experiments here described do not prove that the tetravalent methide ion is incapable of existence; they merely indicate that at 250° its life must be very brief.

The thermal decomposition of magnesium methyl iodide has already been studied by Jolibois[7] with results in part similar to those recorded above. Four moles of CH_3MgI yielded three of methane. The residue, which appeared to be a mixture of $Mg_2C{\cdot}MgI_2$ and MgI_2 (from which the latter could be extracted with ether), reacted very violently with water at ordinary temperature with the liberation of gas composed of varying propor-

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[4] Carothers and Coffman, This Journal, **51**, 568 (1929).

[5] The analogy with the transformation $\overset{-}{\text{—CH}}\text{—}\overset{|}{\text{C}}\text{=O} \longrightarrow \text{—CH=}\overset{|}{\text{C}}\text{—}\overset{-}{\text{O}}\text{—}$ is obvious. Here the free electron pair is lost in effect to the oxygen atom, and a comparison of the probabilities of the first and second states may be found in the relative tendencies of hydrogen ion and oxygen atom to accept an electron pair.

[6] But to represent this (as is sometimes done) as permanently existing in the active form, CH_2^+—CH_2^-, which would be the immediate result of the steps indicated above, would be to ignore the forces responsible for its formation. There is no reason to suppose that the free pair would be more readily tolerated in such an active form than it is in the ethide ion, and this improbable situation can be corrected by the immediate establishment of the new covalent bond.

[7] Jolibois, *Compt. rend.*, **156**, 712 (1913).

tions of acetylene, ethylene and saturated hydrocarbons. When he carried out the reaction as slowly as possible by introducing moist ether at −80°, the evolved gas consisted of ethylene 3% and methane 97%. In view of these results we suspected that Na_4C and K_4C might actually be present in the residues from the thermolysis of the corresponding methides, and that the liberation of acetylene might be due to a catalytic transformation of Na_4C into Na_2C_2 under the influence of water. But when the water was introduced into the reaction tube at −80° and the action regulated by allowing the temperature to rise very slowly, the gas, as before, consisted of acetylene and ethylene together with a small amount of saturated hydrocarbon which may have been methane but which we assumed to be ethane.

Jolibois reports that the thermal decomposition of methylmagnesium iodide occurs at 240°. Under the conditions of our experiments the decompositions of sodium and potassium methides began very slowly at room temperature. The decomposition of sodium methide became quite rapid at about 200° and could be completed at a slightly higher temperature. The residual carbon present as sodium acetylide and representing 25% of the total was not liberated by heating to the softening point of pyrex glass. The thermal decomposition of potassium methide began at a much lower temperature—it was quite appreciable at 50° and rapid at 100°, but evolution of gas at this temperature ceased before decomposition was complete; on raising the temperature, gas was again evolved, but not until the temperature reached 240° did the evolution again become rapid. The gas consisted entirely of methane.

The compounds K_2CH_2 and K_3CH would naturally be intermediate in the passage from KCH_3 to K_4C, and the stepwise evolution of gas indicated that one of these intermediates has a higher thermal stability than KCH_3. In one experiment the amount of gas evolved below 203° was found to be about twice that evolved above 203°, as would be required if K_2CH_2 were an intermediate stable below that temperature.

$$8KCH_3 \longrightarrow 4CH_4 + 4K_2CH_2 \qquad (4)$$

$$4K_2CH_2 \longrightarrow 2CH_4 + K_2C_2 + 6K \qquad (5)$$

Attempts to prove the presence of K_2CH_2 by interrupting the thermolysis after the first stage and treating the residue with phenyl isocyanate or with carbon dioxide were unsuccessful. Moreover, the methane formed by treating this residue with water was contaminated with acetylene, and this indicated at least a partial overlapping of the steps. Nevertheless, we are still inclined to assume the intervention of K_2CH_2 and to ascribe some degree of stability to it, since it is otherwise difficult to explain the stepwise evolution of methane.

Experimental Part

The technique used in the preparation of sodium and potassium methides and in effecting their decomposition was the same as that previously described for sodium ethide.[1] Mercury methyl appears to react more rapidly with sodium than does mercury ethyl. The methides were not isolated as such; the decomposition was carried out directly on the mixture of metallic alkyl, alkali metal and mercury which resulted from the action of dimethyl mercury on the alkali metal.

Thermal Decomposition of Sodium Methide

Experiment 2.—Sodium methide was prepared from 1.052 g. of mercury methyl and 1 g. of sodium. The reaction between the mercury methyl and sodium appeared to be complete in three hours. After twenty-four hours the thermal decomposition was started. The rate of decomposition became appreciable at about 120° and rapid at 200°. The temperature of the heating bath was carried up to 268°; gas collected, 146.5 cc. (Fraction A). The residue was heated to the softening point of pyrex glass; gas collected, 15.0 cc. (Fraction B).

Analysis of Fraction A (by explosion): CH_4 (by contraction), 100.65; CH_4 (by absorption), 101.1; *C/A*, 1.99.[8]

Analysis of Fraction B (by explosion): CH_4 (by absorption), 60.9; H_2 (by contraction), 40.25; total, 101.1.

Thus from one mole of sodium methide there was evolved 0.715 mole of methane in Fraction A, and 0.0444 mole in Fraction B. The total (0.759 mole) is 101% of that required by Equation 3. The small amount of hydrogen (0.029 mole) formed at the higher temperatures was probably due to the liberation of water from the walls of the glass.

The action of absolute alcohol on the residue from the thermal decomposition led to the evolution of 51.6 cc. of gas which gave a positive qualitative test for acetylene.

Anal. (by explosion): C_2H_2 (by absorption), 56.43; H_2 (by contraction), 43.67; total, 100.1.

In this analysis all of the carbon is assumed to be present as acetylene, and calculation indicates 29.2 cc., while Equation 3 requires 25.6 cc.

Experiment 3.—Sodium methide prepared from 1.249 g. of mercury methyl and 0.5 g. of sodium was decomposed by heating slowly to 225°. One hundred and seventy-nine cubic centimeters of gas was evolved (Fraction A). Treatment of the residue with absolute ethyl alcohol at room temperature yielded 69.8 cc. of gas (Fraction B).

Analysis of Fraction A (by explosion): CH_4 (by contraction), 99.8; CH_4 (by absorption), 102.1; *C/A*, 1.95.

This fraction was, therefore, methane and its amount was 98% of that required by Equation 1.

Analysis of Fraction B (by explosion): C_2H_2, 46.32; (by absorption with ammoniacal silver nitrate solution and with potassium mercuri-iodide), C_2H_2, 33.13; C_2H_4 (by absorption with bromine water), 11.54; C_2H_6 (by explosion and absorption), 1.61; H_2 (by contraction), 35.64.

Thus Fraction B contained a total of 32.35 cc. of acetylene, ethylene and ethane, while the theoretical is 30.6 cc. The saturated gas calculated as ethane may have been methane, but it represented only a small fraction of the total.

Experiment 4.—From 1.057 g. of mercury methyl and 0.5 g. of sodium there was obtained by thermal decomposition 150 cc. of methane or 97% of the calculated amount.

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[8] $C/A = \frac{\text{Contraction due to combustion}}{\text{Contraction due to absorption}} = \frac{H_2O\text{ formed}}{CO_2\text{ formed}}$. Calcd. for methane 2.00.

The vessel containing the residue was cooled to −80°, and water was allowed to distil into it slowly, the whole system being completely evacuated. The temperature of the residue was allowed to rise very slowly to 25°. Two fractions of gas were collected. The first (Fraction A) had a volume of 97 cc.; the second (Fraction B) had a volume of 102 cc.

Analysis of Fraction A: C_2H_2 (by absorption with ammoniacal silver nitrate solution), 16.89; C_2H_4 (by absorption with bromine water), 3.04; C_2H_6 (by explosion and absorption), 1.64; H_2 (by contraction), 75.01.

Analysis of Fraction B: C_2H_2 (by absorption with ammoniacal silver solution), 2.17; C_2H_4 (by absorption with bromine water), 3.00; C_2H_6 (by explosion and absorption), 3.97; H_2 (by contraction), 84.77.

The total of the acetylene, ethylene and ethane in the two fractions amounts to 30.2 cc., while the theoretical is 25.7 cc. The saturated hydrocarbon amounting to 18.3% of this total is assumed to be ethane, and in accordance with this assumption its relative amount in Fraction A is much smaller than in Fraction B, while if it were methane originating from Na_4C, the reverse should be true.

Thermal Decomposition of Potassium Methide

Experiment 2.—Potassium methide formed by the action of 0.809 g. of mercury methyl on 0.5 g. of potassium was decomposed. The evolution of gas (collected in two fractions) commenced in the neighborhood of 50° and terminated at a temperature somewhat below 300°: Fraction A, 63 cc.; Fraction B, 55.8 cc.; total, 118.8 cc., or 100.8% of the calculated amount.

Analysis of Fraction A (by explosion): CH_4 (by contraction), 100.8; CH_4 (by absorption), 104.4; *C/A*, 1.93.

Analysis of Fraction B (by explosion): CH_4 (by contraction), 101.4; CH_4 (by absorption), 102.8; *C/A*, 1.97.

The residue on treatment with water yielded acetylene and hydrogen together with some ethylene and a saturated gas assumed to be ethane.

Experiment 3.—Potassium methide formed from 0.831 g. of mercury methyl and 0.5 g. of potassium was decomposed. The gas was collected in three fractions.

FRACTION A, 23.6 cc. This gas was pumped off before heating after the tube had stood at room temperature for twenty-four hours.

Anal. (by explosion): CH_4, 89.01; C_2H_6 or $Hg(CH_3)_2$, 10.99; *C/A*, 1.82.

The second gas was probably dimethyl mercury, since the characteristic odor of that substance was present; and, in the calculation of yield, correction was made for this loss.

FRACTION B, 52.7 cc. This fraction was evolved between 25 and 203°, most of it between 50 and 103° in one hour.

Anal. (by explosion): CH_4 (by contraction), 99.8; CH_4 (by absorption), 102.4; *C/A*, 1.94.

FRACTION C. Pumping was continued while the residue remained at 203° for one and one-half hours. Only a minute amount of gas was collected at this temperature. The temperature was then allowed to rise. Between 204 and 280°, 39 cc. of gas was collected in one hour.

Anal. (by explosion): CH_4 (by contraction), 100; CH_4 (by absorption), 103.2; *C/A*, 1.94.

The ratio of methane in Fractions A and B to that in C is 1.89:1, in fair agreement with the requirements of Equations 4 and 5.

Summary

On heating sodium or potassium methide, methane is evolved in accordance with the equation $4MCH_3 \longrightarrow 3CH_4 + M_4C$. Hydrolysis of the residue yields chiefly acetylene and hydrogen, together with some ethylene and ethane, indicating the transformation $2M_4C \longrightarrow M_2C_2 + 6M$. The thermolysis of sodium methide becomes rapid at about 200° and may be completed at a slightly higher temperature. The thermolysis of potassium methide first becomes rapid at 100° but is not completed below 250°. In this behavior evidence is found for the intervention of K_2CH_2 or K_3CH in the passage from KCH_3 to K_4C. The mechanisms of these reactions are discussed.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ILLINOIS]

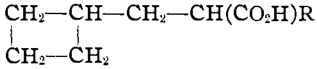
CYCLOBUTYLALKYL ALKYL ACETIC ACIDS AND THEIR BACTERICIDAL ACTION TOWARD B. LEPRAE. XVI[1]

BY S. G. FORD AND ROGER ADAMS

RECEIVED NOVEMBER 29, 1929 PUBLISHED MARCH 6, 1930

In a number of previous papers in this series[2] it was shown that certain ω-cyclohexylalkyl, ω-cyclopentylalkyl, ω-cyclopentenylalkyl and ω-cyclopropylalkyl alkyl acetic acids were bactericidal toward *B. Leprae.* The preparation of various cyclobutylmethyl alkyl acetic acids (I) was undertaken at the same time, but owing to experimental difficulties the compounds were not completed before the interesting discovery was made that no ring structure in the molecule was necessary for bactericidal action. The research on the cyclobutyl derivatives, however, was continued and results are described in this communication. Cyclobutylmethyl alkyl acetic acids (I) were prepared in which the alkyl group was *n*-octyl, *n*-nonyl, *n*-decyl, *n*-undecyl and *n*-dodecyl.

(I)



The bacteriological tests have shown that molecular weight is an important factor, as might have been anticipated from the study of the previous compounds which were prepared and tested. Those molecules which contained sixteen to eighteen carbon atoms were the most effective and gave results comparable to the other ring acids of the same molecular weight.

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[1] This communication is an abstract of a portion of a thesis submitted by S. G. Ford in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Illinois.

[2] For previous articles, see paper XV of this series, Stanley, Jay and Adams, THIS JOURNAL, **51**, 1261 (1929).