Laboratory and found to be non-conductors.[21] This non-conductance is due in part to a high amount of covalent character in the lithium–carbon bond as shown by the much lower conductance of lithium ethyl in zinc diethyl than the corresponding sodium and potassium compounds.[22] It is probably due more to the inability of the lithium atom to serve as an acceptor atom for the unshared pair of the alkide ion in comparison with the high coördinating power of the zinc and magnesium atoms.

Summary

Transference studies of *n*-butylmagnesium bromide and ethylmagnesium bromide in ether are reported.

The conductances of magnesium diethyl and zinc diethyl in ether have been measured.

The exchange reaction between zinc chloride and ethylmagnesium bromide in ether has been found to be instantaneous.

From a consideration of all available data a theory is proposed for the ionization of the aliphatic Grignard reagents and for the electrode reactions in their electrolysis.

Both the halogen and the alkyl group can ionize. The cation is coördinated with ether and is small and slow. The anion is coördinated with RMgX, MgX_2 and R_2Mg and is large and mobile.

The importance of having both molecules with electron donor properties and molecules with electron acceptor properties to promote ionization in solvents of low dielectric strength is brought out.

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The Stability of β-Methylmaltoside toward Hot Alkali

BY THOMAS JOHN SCHOCH, E. JUSTIN WILSON, JR., AND C. S. HUDSON

In connection with studies on the decomposition of starch in alkaline medium, it was desirable to establish whether the 1,4-α-glucosidic linkage is susceptible to direct hydrolytic scission by hot aqueous alkali. Evans and Benoy[1] have shown that the action of hot alkali upon maltose results primarily in a rapid enediol splitting. If this reaction could be prevented by blocking the aldehyde group against enolization, as in β-methylmaltoside, then any acids developed during hot alkali digestion could be attributed to direct hydrolysis of the disaccharide linkage, and subsequent enolic splitting of the former glucosido portion of the maltoside molecule. β-Methylglucoside is known to be fully resistant to hot aqueous alkali.

β-Methylmaltoside and calcium maltobionate have been so tested, by dissolving 0.5 g. in 100 ml. of 0.1 *N* sodium hydroxide, heating at 100° for one, two and five hour periods, and then back-titrating the unconsumed alkali. Except for the use of longer heating periods, the technique is identical with that described by Schoch and Jensen[2] for alkali number evaluation of starches; in their method the time of heating is one hour. Production of acidity is similarly expressed, as the number of milliliters of 0.1 *N* sodium hydroxide consumed per gram of carbohydrate. Each value in Table I represents the average of three to five determinations; blank runs (without carbohydrate) showed negligible loss of alkali. As an additional check on the results obtained, beta-methylcellobioside was tested in the same manner.

TABLE I

ALKALI CONSUMPTION AT 100°

Digestion time, hr.	β-Methyl-maltoside	β-Methyl-cellobioside	Calcium maltobionate	Calcium gluconate
1[a]	0.32 ± 0.04	0.10 ± 0.05	0.72 ± 0.06	0.76 ± 0.03
2	.24 ± .04	.13 ± .05	.99 ± .06	.93 ± .08
5	.16 ± .04	.08 ± .05	1.60 ± .09	1.78 ± .11

[a] Starches give alkali numbers of about 4 (waxy maize), 7 (potato) and 11 (corn).

Since the alkaline decomposition of 1 g. of anhydrous glucose consumes 85.2 ml. of 0.1 *N* sodium hydroxide,[2] it may be calculated that β-methylmaltoside hydrate and calcium maltobionate would consume 41.0 ml. and 40.7 ml., respectively, if the disaccharide bond were completely hydrolyzed. The very slight consumption by the two glycosides is barely detectable and is not progressive, which leads us to believe that it is caused by traces of impurities which recrys-

(1) Evans and Benoy, THIS JOURNAL, **52**, 294 (1930).

(2) Schoch and Jensen, *Ind. Eng. Chem., Anal. Ed.*, **12**, 531 (1940).

tallization failed to remove. From the experimental data we conclude that β-methylmaltoside may be regarded as stable against hot alkali; a similar conclusion applies to β-methylcellobioside, containing the 1,4-β-glucosido linkage. While calcium maltobionate undergoes a slight progressive decomposition, this is of the same order of magnitude as for calcium gluconate, and therefore cannot be attributed to glycosidic hydrolysis. In all probability this decomposition follows the mechanism previously given by Upson and co-workers[3] as accounting for the action of 4 *N* barium hydroxide at 140° upon the aldonic acids. The results are in agreement with the theory of alkaline oxidation of carbohydrates, as developed by Evans and his co-workers.

We assume from the present data, in agreement with Evans' views, that alkali attacks starch only at a terminal aldehydo glucose, and this must undergo enolic splitting before the second glucose can in turn be attacked. Admittedly, this does not take into account the possibility of linkages other than 1,4-α-glucosidic bonds, which might be susceptible to direct alkaline hydrolysis since definite data to the contrary are not known.

It seems worthy of mention that what is commonly called the 1,4-α-glycosidic linkage that is present in maltose is not precisely the 1,4-linkage that is postulated as the main linkage in the starch structure or in the Schardinger dextrins. If the linkage in maltose be used as a definition of the true 1,4-α-linkage, the attachment of a substituent glucose molecule to carbon atom 4 changes the type of this linkage in chains made up of glucose units. The change may have great effect upon the character of enzyme actions on starch, and an alteration of the speed of acid hydrolysis is a possibility.

Experimental Part

Calcium Maltobionate.—The calcium maltobionate here employed was prepared by the method of Glattfeld and Hanke,[4] with subsequent purification through the basic lime compound.[5] The product contained 7.53% calcium oxide; theory 7.43%.

β-Methylcellobioside.—The heptaacetate of this substance was prepared according to the directions of Pacsu.[6] The β-methylcellobioside was obtained by deacetylation, using the method of Zemplén and Pacsu[7]; the substance melted at 190–193° (cor.) and rotated $[\alpha]^{20}D$ −19.7° in water (c = 3), in agreement with recorded values.[8]

Improved Preparation of β-Methylmaltoside.—Previously, β-methylmaltoside has been obtained in pure form only with considerable difficulty and in low yields.[9] The following procedure has been found to give readily excellent yields of the pure crystalline substance. Thirty grams of β-octaacetylmaltose (m. p. 157–159°) was converted to acetobromomaltose by the method of Brauns.[10] The resulting sirup was dissolved with gentle warming in 400 ml. of absolute methanol and the solution shaken with 20 g. of silver carbonate. It was then heated under reflux for one hour, filtered through Darco, and concentrated *in vacuo*. Fine needles separated on cooling; one recrystallization from absolute ethanol gave 20.6 g. of nearly pure heptaacetyl-β-methylmaltoside, melting at 126–128.5° as compared with the recorded value of 128–129° for the pure substance.[9] Deacetylation was effected by the procedure of Zemplén and Pacsu.[7] Twenty grams of the heptaacetate was dissolved in 120 ml. of absolute methanol, and the solution was boiled for one hour with 5 ml. of 0.2 *N* sodium methylate. The slight yellow color was removed by filtration with Darco, and the filtrate evaporated to dryness *in vacuo*. The resulting sirup was taken up in hot 95% ethanol, and the product crystallized as long needles on cooling. The yield was 10.8 g. (94%), melting at 111–113° (cor.), with $[\alpha]^{20}D$ +84.6° in water (c = 1.7) as compared with the recorded m. p. of 110–111° and $[\alpha]D$ of +83.9° in water (c = 1).[9] Recrystallization gave no further change in the constants. The product was isolated as the monohydrate.

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Summary

The 1,4-α-glucosidic linkages in β-methylmaltoside and calcium maltobionate do not undergo direct hydrolysis in hot alkali. The 1,4-β-glucosidic linkage in β-methylcellobioside is likewise stable to alkali.

It appears probable that alkali can attack starch only at the terminal aldehydo glucose, which must undergo enolic splitting before the second glucose can in turn be attacked. The present results agree with Evans' views on the degradation of starch by alkali.

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(3) Upson, Noyce and Albert, THIS JOURNAL, **61**, 779 (1939).
(4) Glattfeld and Hanke, *ibid.*, **40**, 989 (1918).
(5) Hudson and Isbell, *Bur. Standards J. Research*, **3**, 57 (1929).
(6) Pacsu, THIS JOURNAL, **52**, 2571 (1930).
(7) Zemplén and Pacsu, *Ber.*, **62**, 1613 (1929).
(8) Helferich, Löwa, Nippe and Riedel, *Z. physiol. Chem.*, **128**, 141 (1923).
(9) Irvine and Black, *J. Chem. Soc.*, 862 (1926).
(10) Brauns, THIS JOURNAL, **51**, 1820 (1929).