577°K., is represented to within an average deviation of 0.3% by the equation

$$H_T - H_{298.16} = 29.56T + 6.11 \times 10^5 T^{-1} - 10,863$$

In Table III also are values for the liquid at the melting and boiling points, 577 and 592°K., respectively, and for the gas (in terms of 0.5 mole Fe_2Cl_6) at the boiling point. These values were obtained by supplementing the present data with the heat of fusion and vaporization values from the N. B. S. Tables.[4]

[4] National Bureau of Standards, Tables of Selected Values of Chemical Thermodynamic Properties, Ser. II, Table 47-2 (Sept. 30, 1949).

BERKELEY 4, CALIFORNIA RECEIVED MARCH 14, 1951

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, GENERAL MILLS, INC.]

Periodate Oxidation of the Formyl Esters of Starch[1]

BY OWEN A. MOE, SIDNEY E. MILLER AND MARJORIE IWEN BUCKLEY

The formyl esters and the 2-cyanoethyl ethers of diverse starches have been subjected to periodate oxidations and it has been found that the consumption of oxidant is dependent on a number of variants. The results of the current study show that the selectivity of the periodate is dependent on the concentration of the oxidant and the *p*H of the media.

In connection with some of the periodate oxidation studies[2] underway in this Laboratory, it became of interest to investigate the oxidation of the formyl esters of starch by periodate. Previous investigators[3] observed that the periodate oxidation of the formyl esters of corn starch (essentially a monoformate, degree of substitution approximately 1.1) proceeded in the same general course as that observed with the original starch although the reaction was slower for the formate ester. They found that approximately 1 mole of periodate had been consumed per mole (substituted anhydropyranose unit) of derivative after a reaction period of one hundred twenty hours. The results of the periodate oxidation studies indicated that the formyl group was located primarily in the C_6-position.

In view of our previous observations[2a] relative to the importance of the *p*H of the oxidation medium and the temperature at which the oxidation was carried out, it was considered possible that considerable hydrolysis accompanied oxidations of this type when the proper conditions were not imposed. This assumption was verified by the experimental evidence presented in this paper.

In agreement with Gottlieb, Caldwell and Hixon,[3] it was found that formyl esters of starch were slightly in excess of monoformates. The formyl content of the esters was usually within the range 16.3–16.8%.

When the oxidations involving the starch formates were carried out in buffered (0.05 *M*)[2a] media (*p*H 4.2–4.3) approximately 0.6–0.7 mole of oxidant had been consumed per mole of derivative after a 96-hour period as shown in Table I. This proved to be so with the formates of either cereal or tuber starches.

TABLE I

PERIODATE OXIDATIONS OF STARCH FORMATES IN BUFFERED (0.05 *M*) MEDIA, 19°

Source	Formyl, %	Degree of substitution	Reaction time in hours	Mole periodate consumed/mole derivative
Wheat	16.8	1.13	24	0.58
			48	.60
			96	.61
Potato	16.5	1.10	24	.60
			48	.62
			96	.66
Corn	16.8	1.13	24	.60
			48	.66
			96	.69

However, when the oxidations with periodate were carried out in unbuffered media, completely different results were obtained, and the final values were in all cases at least twice as high as those obtained when the oxidations were carried out in buffered media. The results of the oxidations in unbuffered media are presented in Table II.

TABLE II

PERIODATE OXIDATIONS OF STARCH FORMATES IN UNBUFFERED MEDIA, 23°

Source	Degree substitution	Molar concentration of HIO_4	Reaction time in hours	Moles periodate consumed/mole derivative
Wheat	1.15	0.5	24	1.08
			96	1.64
		.05	24	0.99
			48	1.19
			96	1.32
Potato	1.10	.5	24	1.19
			96	1.77
		.05	24	1.09
			48	1.21
			96	1.34

The molar concentration of the aqueous periodic acid employed appeared to have an appreciable effect and substantially higher values were obtained as the molar concentration was increased. From the tables, it becomes apparent that the oxidations carried out in buffered media were substantially complete after 24 hours and an increase of only 0.06 ± 0.03 mole of periodate per mole of derivative occurred during the next 72-hour period. However, when the oxidations were carried out in unbuffered media, the increase

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[1] Paper No. 99, Journal Series, General Mills, Inc., Research Dept.

[2] (a) O. A. Moe, S. E. Miller and Marjorie H. Iwen, THIS JOURNAL, **69**, 2621 (1947); (b) H. Wittcoff, O. A. Moe and M. H. Iwen, *ibid.*, **70**, 742 (1948).

[3] D. Gottlieb, C. G. Caldwell and R. M. Hixon, *ibid.*, **62**, 3342 (1940).

in periodate consumption during the next 72-hour period ranged from approximately 0.3 mole to approximately 0.6 mole per mole of derivative depending on the molar concentration of aqueous periodic acid employed.

In view of the above results, it was desirable to study the periodate oxidation of a different water insoluble starch derivative, preferably a derivative which would not be so prone to undergo hydrolytic cleavage under the conditions employed for the oxidation studies. The 2-cyanoethyl ether of starch was considered suitable for this purpose. It was prepared by the reaction between wheat starch and acrylonitrile in the presence of an alkaline catalyst essentially as described by Bock and Houk.[4] The nitrogen analysis indicated that the 2-cyanoethyl ether derivative possessed a degree of substitution of approximately 1.1. Hence, it was comparable to the starch formates which were studied.

Accordingly this 2-cyanoethyl ether of wheat starch was subjected to oxidation by periodate in both buffered and unbuffered media and the results obtained are given in Table III.

TABLE III

PERIODATE OXIDATIONS OF THE 2-CYANOETHYL ETHER OF WHEAT STARCH

Periodate used	Reaction time in hours	Moles periodate consumed/ mole derivative	% N of oxidized product
Buffered	48	0.56	7.03
(0.05 *M*)	96	.58	
Unbuffered	48	.59	6.41
(0.5 *M*)	96	.66	

The oxidations were essentially complete after 48 hours. A greater "drift" in the consumption of the oxidant was observed when the oxidation was carried out in 0.5 molar unbuffered periodic acid. However, it is readily apparent that the 2-cyanoethyl ethers are much more resistant to hydrolysis than are the formyl esters under similar oxidation conditions. The final values (approximately 0.6 mole of oxidant consumed per mole of derivative) are indeed comparable to the values obtained by the periodate oxidations of the formyl esters of starch in buffered media.

Hence it appears that the formyl groups and the 2-cyanoethyl groups are distributed in a similar manner in the starch molecule and it appears that the formyl groups are substituted predominantly at the C_6-position[3] although not exclusively so.

The results of the present investigation clearly indicate that the concentration of the oxidant and the *p*H of the media (as well as the temperature[2]) are very important factors to consider in the periodate oxidations of complex molecules. The selectivity of periodic acid oxidations is dependent on these considerations.

Experimental

Preparation of Starch Formates.—The formyl esters of starch were prepared essentially as described by Gottlieb, Caldwell and Hixon[3] except that the products were precipitated in acetone, mixed thoroughly with acetone in a Waring blendor, collected, washed with acetone and dried extensively *in vacuo*. The formyl esters were obtained as white powdery products.

Anal. Calcd. for starch monoformate: $C_{17}H_{10}O_6$, 15.26. Found: for wheat, 16.8; for potato, 16.5; for corn, 16.8.

Periodate Oxidation of the Formyl Esters of Starch. A. Buffered Media.—The buffered oxidation reactions were carried out using 0.5 g. (dry basis) of the formyl esters and 350 cc. of an 0.05 *M* solution of periodate.[2a] The reaction temperature was maintained at 10° and the formyl esters were kept in a finely divided state. The titrations of aliquot portions of the periodate solution were carried out at various time intervals according to the method of Fleury and Lange[5] as modified by Grangaard, Gladding and Purves.[6] The results obtained from the buffered oxidations at 19° are summarized in Table I.

B. **Unbuffered Media.**—The unbuffered oxidations were carried out using 0.5 g. (dry basis) of the formates and either 350 cc. of 0.05 *M* or 60 cc. of 0.5 *M* aqueous periodic acid. When the unbuffered oxidations were carried out in 0.5 *M* aqueous periodic acid, it was observed that the formyl esters of starch had gelatinized to an appreciable extent. The titrations were carried out as previously noted and the results from the experiments using 0.05 and 0.5 *M* aqueous periodic acid are summarized in Table II.

Preparation of the 2-Cyanoethyl Ether of Wheat Starch.—It was desirable to prepare a cyanoethyl ether of wheat starch possessing approximately 1.1 cyanoethyl groups per anhydropyranose unit. This was achieved in the following manner: Wheat starch (33 g.) was dispersed in 300 cc. of water. Aqueous sodium hydroxide (10 g. of a 20% solution) was added and the resulting reaction was stirred vigorously until a uniform dispersion was achieved. Acrylonitrile (31.8 g.) was added and the resulting reaction mixture was stirred for a three-hour period at room temperature. After standing at room temperature for an additional three-hour period, the product was precipitated as a gummy mass by pouring into an excess of methanol. This gummy mass was mixed vigorously with fresh methanol in a Waring blendor and it gradually hardened. Finally, the 2-cyanoethyl ether derivative was ground under methanol to yield a fine powder, collected, washed with methanol and dried *in vacuo*.

Anal. Calcd. for the mono-2-cyanoethyl ether ($C_9H_8O_5N$): N, 6.67. Found: N, 6.94.

Periodate Oxidation of the 2-Cyanoethyl Ether Derivative of the Wheat Starch.—The buffered and unbuffered oxidations were carried out essentially as described for the corresponding oxidations of the formyl esters of starch. The insoluble oxidation products were collected, washed extensively with water and methanol and dried *in vacuo*. These insoluble cleavage products were analyzed.

Anal. Found: for buffered oxidation product: N, 7.03. Found: for unbuffered oxidation product: N, 6.41.

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RECEIVED MARCH 29, 1951

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[4] Bock and Houk, U. S. Patent 2,316,129.

[5] P. Fleury and J. Lange, *J. pharm. Chem.*, [8] **17**, 107, 196 (1933).

[6] D. H. Grangaard, E. K. Gladding and C. B. Purves, *Paper Trade J.*, **115**, 41 (1942).