

CATALYTIC OXIDATION OF THE CARBOHYDRATES AND RELATED COMPOUNDS BY OXYGEN IN THE PRESENCE OF IRON PYROPHOSPHATES

IV. Methyl Alcohol, Formaldehyde, Formic Acid, Sodium Formate, Ethyl Alcohol, Acetaldehyde, Acetic Acid, Sodium Acetate, Glycol, Glycollic Acid, Sodium Glycollate, Oxalic Acid, and Sodium Oxalate

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In any study on oxidative mechanism, one must always establish, under identical conditions, the effect of the oxidative reagents upon all of the probable intermediates that may be formed during the degradational process. Information relative to the stability or instability of the probable intermediates is equally important whether it be positive or negative. Hence it seems pertinent to the study of the oxidation of the simple sugars in the presence of iron pyrophosphates, to include similar experiments on the probable simple intermediates.

The results of the experiments with methyl alcohol, formaldehyde, formic acid, sodium formate, ethyl alcohol, acetaldehyde, acetic acid, and sodium acetate at a temperature of 50° C. have been reported in previous papers.¹ But for convenience in a study of these results, some of these data from the previous reports have been combined with the data from the present study. Furthermore, all of these substances have been studied under the same conditions other than temperature at both 50° C. and 75° C. The results from the study of the three-carbon probable intermediates will be presented later.

The procedure employed in the study of these probable intermediates was identical with that presented in a previous report.² A tenth of a mol of the compound was used for each determination, and the experiments were carried out at 50° C. and at 75° C., the results appearing below in tabular form. Carbon dioxide is reported in grams for the total period concerned. Titrations of the resulting solutions for acid production were in agreement with the results obtained for the production of carbon dioxide.

In each set of experiments four control tubes were used, and the average change in weight of the control tubes was used as a correction factor. Hence the values given in the tables represent the average net change in weight in the experimental tubes.

¹ J. Biol. Chem. 95, 409. 1932.

Proc. Ind. Acad. Sci., 43, 105. 1933.

² J. Biol. Chem. 94, 423. 1931; 95, 409. 1932.

Carbon Dioxide Formed in the Presence of Iron Pyrophosphates at 50° C. by

Time in days	1	2	5	8	12	16	% C as CO ₂	Runs
CH ₃ .OH	.0000	-.0008	-.0023	-.0039	-.0059	-.0050	-0.11	3
H.CO.H	.0000	.0006	.0027	.0036	.0049	.0046	0.10	4
H.CO.OH	.0028	.0034	.0044	.0055	.0057	.0058	0.11	3
H.CO.ONa	.0008	.0018	.0013	.0008	.0019	.0025	0.06	4
CH ₃ CH ₂ .OH	-.0004	-.0004	-.0007	-.0011	-.0021	-.0022	-0.02	3
CH ₃ CHO	-.0006	-.0009	.0025	.0232	.0603	.1366	1.55	3
CH ₃ .CO.OH	-.0044	-.0080	-.0087	-.0096	-.0034	-.0019	0.02	3
CH ₃ .CO.ONa	.0000	.0000	-.0014	-.0008	-.0013	.0018	-0.02	3
CH ₂ OH.CH ₂ OH	-.0002	-.0002	-.0008	-.0015	-.0041	-.0064	-0.07	4
CH ₂ OH.CO.OH	-.0003	-.0003	-.0007	-.0026	-.0007	-.0048	-0.05	4
COOH.COOH	.0001	-.0002	.0012	.0014	.0032	.0077	0.09	4

Carbon Dioxide Formed in the Presence of Iron Pyrophosphates at 75° C. by

Time in days	1	2	5	8	12	16	% C as CO ₂	Runs
CH ₃ .OH	.0001	-.0008	-.0023	-.0040	-.0060	-.0025	-0.03	6
H.CO.H	.0000	-.0002	-.0011	-.0015	-.0029	+.0034	-0.04	6
H.CO.OH	.0015	.0047	.0064	.0071	.0056	.0103	0.11	6
H.CO.ONa	-.0023	-.0024	-.0026	-.0038	-.0054	-.0054	-0.05	6
CH ₃ CH ₂ .OH	-.0023	-.0026	-.0022	-.0036	-.0053	-.0062	-0.06	6
CH ₃ CHO	.0232	.2954	.3661	.4553	.6074	.6756	7.67	6
CH ₃ .CO.OH	.0000	.0022	.0029	.0033	.0042	.0035	0.04	6
CH ₃ .CO.ONa	-.0015	-.0012	-.0013	-.0021	-.0035	-.0060	-0.06	6
CH ₂ OH.CH ₂ OH	-.0028	-.0028	-.0035	-.0049	-.0060	-.0056	-0.05	6
CH ₂ OH.CO.OH	-.0003	.0018	.0030	.0038	.0052	.0050	0.05	6
CH ₂ OH.CO.ONa	-.0003	.0002	.0004	.0005	.0018	.0033	-0.04	6
COOH.COOH	.0038	.0074	.0400	.0757	.1171	.1751	1.99	6
COONa.COONa	-.0001	.0004	-.0003	-.0006	-.0016	-.0032	-0.04	6

From a study of the data given in the above tables, it is apparent that methyl alcohol, formaldehyde, formic acid, sodium formate, ethyl alcohol, acetic acid, sodium acetate, glycol, glycollic acid, sodium glycolate, and sodium oxalate do not yield carbon dioxide under the conditions of these experiments. Titrations for total acid production, and for volatile acid constituents, likewise indicated the absence of oxidation. This is in agreement with the general behavior of the most of these compounds, and also agrees with the results previously reported.³

The experiments on acetaldehyde and oxalic acid showed production of carbon dioxide, which definitely indicates oxidation. Titrations for total acid production in the case of acetaldehyde, led to the same conclusion. But the formation of carbon dioxide in the case of acetaldehyde and the lack of carbon dioxide formation in the case of acetic acid, indicate that the oxidation of the acetaldehyde to yield carbon dioxide under the conditions of these experiments is somewhat complex. Hence the study of the other end products of this oxidation and the mechanism involved is reserved for a later paper.

³ See the first three articles of this series.

In the work by Spoehr and Smith⁴ at about 38° C., they report that "sodium acetate is oxidized very slowly: 0.0063 g. of carbon dioxide was produced during the first 24 hours; thereafter, it practically ceases. Potassium glycolate, sodium oxalate . . . showed the same behavior." While this may seem to be in disagreement with the above data, the author is inclined to believe that the values reported by Spoehr and Smith were well within the range of experimental error for the method they employed. The present work showed an actual loss of weight by the ascarite tubes over and above that of the control tubes, as tabulated for sodium acetate at both 50° C. and at 75° C. When making a 24-hour determination, in which a continuous passage of gas is involved, it is obvious that there must be an appreciable source of experimental error; and one of the main purposes of the above tabulation is to indicate the extent of this error for the period of the determinations. In every case the carbon returned as carbon dioxide at the end of the sixteen-day period is about one tenth of one per cent or less, except in the case of acetaldehyde at both temperatures and oxalic acid at the higher temperature. Otherwise the author is inclined to interpret the results as negative.

In conclusion, then, it appears from the data obtained in this series of experiments that (1) methyl alcohol, formaldehyde, formic acid, sodium formate, ethyl alcohol, acetic acid, sodium acetate, glycol, glycolic acid, sodium glycolate, and sodium oxalate are not oxidized to give carbon dioxide and could, therefore, be identified as *end products* in the oxidation of the simple sugars under the conditions of these experiments; (2) acetaldehyde is oxidized to give carbon dioxide, but acetic acid cannot be an intermediate step in the oxidation of acetaldehyde to carbon dioxide; (3) oxalic acid yields carbon dioxide under the conditions of these experiments at 75° C., but little, if any, at 50° C.; and (4) acetaldehyde and oxalic acid are the only products, which, if formed in the subsequent studies on the oxidation of the simple sugars, would be expected to be oxidized, in part at least, to carbon dioxide.

⁴ J. Amer. Chem. Soc. 48, 241. 1926.