The Action of Weak Alkalies upon Glucose. II.

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The formation of acetol from glucose by the action of various alkaline reagents has been often reported. Concerning the mechanism of the formation, there have been two different views. Nef⑴ postulated that the acetol is a reduction product of methylglyoxal which is formed from glucose through glyceric aldehyde. Pinkus⑵, on the contrary, assumed it to be a primary decomposition product of the sugar. The former view has been supported by several investigators among whom Neuberg⑶ put forward an opinion that methylglyoxal transforms disproportionately into acetol and pyruvic acid.

In the previous work⑷, it was confirmed chemically and spectrographically that when a mixture of glucose and 1/25 mol solution of sodium carbonate (alone or with sodium sulphite) was distilled, acetol appeared along with diacetyl in the distillate. In the present work, aqueous solutions of glucose, glyceric aldehyde, methylglyoxal, and acetol were respectively distilled with sodium carbonate and the distillates analyzed (as semicarbazones), by methods similar to those described in the previous paper. In Table 1 the experimental results are tabulated.

Table 1.

No.	Sample		Na_2CO_3 $\frac{1}{25}$ mol sol. c c.	Na_2SO_3 g.	Distillate c.c.	Iodine consuming substance as acetol g.	Semicarbazones g.	
	Name	g.					Diacetyl m.p. 278–80°	Acetol m.p. 196–7°
1	Glucose	5	250	15	1200	0.146	0.021	0.084
2	,,	5	250	0	1400	0.159	0.020	0.092
3	Methylglyoxal	3	250	15	1500	0.072	0.043	0
4	,,	3	250	0	1500	0.055	0.031	0
5	Glyceric-aldehyde	2	250	15	1500	0.075	0.014	0
6	,,	3	250	15	1000	0.117	0.023	Trace
7	,,	2	250	0	1500	0.068	0.011	0
8	,,	3	250	0	1000	0.093	0.020	0.010
9	Acetol	1	250	15	1500	0.382	0.001	0.411
10	,,	1	250	0	1500	0.343	0.002	0.400

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(1) J. U. Nef, *Ann.*, **335** (1904), 247; **357** (1907), 214.
(2) G. Pinkus, *Ber.*, **31** (1898 , 31.
(3) C. Neuberg, *Biochem. Z.*, **49** (1913), 502.
(4) R. Nodzu and R. Goto, this Bulletin, **11** (1936), 381.

As will be seen from the table, methylglyoxal gave not even a trace, glyceric aldehyde only a trace of acetol, and glucose an abundance of acetol. It was also found that the yield of acetol from glucose (Table 1. No. 1, 2.) was not increased by the addition of methylglyoxal in similar distillation experiments (Table 2.). Moreover, the origin of acetol from glyceric aldehyde (Table 1. No. 6, 8.) should rather be attributed to a hexose⁽⁵⁾ which may be derived from the latter during the experiment in an alkaline medium.

Table 2.

No.	Sample		Na_2CO_3 $\frac{1}{25}$ mol sol. c.c.	Na_3SO_3 g.	Distillate c.c.	Iodine consuming substance as acetol g.	Semicarbazones g.	
	Name	g.					Diacetyl m.p. 278–80°	Acetol m.p. 196-7°
1	Glucose Methylglyoxal	5 1	250	15	1500	0.213	0.055	0.060
2	Glucose Methylglyoxal	5 1	250	0	1500	0.193	0.045	0.045

The acetol, therefore, is formed from glucose neither through glyceric aldehyde nor through methylglyoxal, showing that at least here, the postulations of Nef and others are untenable.

It is noteworthy that methylglyoxal distilled over from the weak alkaline solution as diacetyl, but not as itself, contradicting the assumption often made. It is very likely that under such conditions nearly all the methylglyoxal transforms easily into lactic acid and diacetyl (or acetoin).

Experimental Part. *Materials.* Methylglyoxal (b.p. 35°–38°/10 mm) was obtained by oxidation of acetone by means selenium dioxide⁽⁶⁾; and glyceric aldehyde (m.p. 130°) was prepared by way of acrolein acetal from glycerin following the Witzemann's method.⁽⁷⁾ Acetol (b.p. 53°–54°/18 mm.) was synthesized from monobromoacetone by the method of Levene and Walti⁽⁸⁾.

Distillation and Analysis. The distillation⁽⁹⁾, the estimation of iodine consuming substances in the distillate, and the analysis of distillate were done in the same ways as described in the previous papers. The experimental results are tabulated in Tables 1 and 2. The distillation residue from methylglyoxal was evaporated to syrup under reduced pressure and the syrup was made strongly acidic by sulphuric acid. Then it was extracted with ether for about 30 hours, following⁽¹⁰⁾ Evans' method.

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(5) E. Schmitz, *Ber.*, **46** (1913), 2327; H. O. L. Fischer, *Helv. Chim. Acta*, **19** (1936), 519.

(6) H. L. Riley, J. F. Morley and N. A. C. Friend, *J. Chem. Soc.*, **1932**, 1875.

(7) E. J. Witzemann, *J. Am. Chem. Soc.*, **36** (1914), 1908.

(8) "Organic Syntheses." Vol. X, p. 1, (1930).

(9) During the distillation of methylglyoxal (alone or with glucose), 1/25 mol solution of Na_2CO_3 was supplied from time to time in order to keep a weak alkalinity of the distilling flask content.

(10) W. L. Evans and co-workers, *J. Am. Chem. Soc.*, **48** (1926), 2665.

From the ether extract, lactic acid was isolated in the form of its zinc salt (found: H_2O, 18.2; Zn 21.6; Calc. for $ZnC_6H_{10}O_6 + 3H_2O$: H_2O, 18.18; Zn 21.89%). Also, the acid was quantitatively titrated following Tanaka and Endo(11). The analytical results are cited in Table 3.

Table 3.

No.	Methylglyoxal g.	Na_2CO_3 $\frac{1}{25}$ mol sol. c.c.	Na_2SO_3 g.	Distillate c.c.	Lactic acid in residue g.	%
1	3	250	15	1500	0.654	21.8
2	3	250	0	1500	1.013	34.4

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(11) S. Tanaka and M. Endo, *Biochem. Z.*, **210** (1929), 120.