144. *Oxidation of Acetaldehyde and Benzaldehyde by Hydrogen Peroxide in Presence of Selenium Oxychloride.*

By J. B. Firth and H. H. Gething.

The oxidation of acetaldehyde and benzaldehyde to the corresponding acid by hydrogen peroxide takes place comparatively slowly under ordinary conditions. The addition of a little selenium oxychloride to the mixture substantially accelerates the reaction.

The rate of oxidation increases with rise of temperature. Hydrochloric acid would result from this decomposition of the selenium oxychloride, but experiments with this acid added instead of selenium oxychloride show that it does not itself materially catalyse the reaction.

With 0·5 g. of acetaldehyde, the maximum result is obtained with 0·1—0·2 c.c. of selenium oxychloride; the addition of a greater amount does not appear to affect the extent of oxidation of the aldehyde.

Experimental.

The amounts of acetic and benzoic acid produced were determined by direct titration with standard sodium hydroxide solution, phenolphthalein being used as indicator. Correction factors for the initial acidity of the aldehydes, of hydrogen peroxide, and of the products of hydrolysis of the selenium oxychloride were determined in each case. The conversion into acetic acid and benzoic acid was confirmed, and the latter acid crystallised out in the reaction vessel in the long-period experiments.

In all cases a parallel blank control was simultaneously carried out.

Typical results are given in the following tables, the results in columns 2 and 3 being the data after correction as indicated above.

Series I. Oxidation of Acetaldehyde.

0·5 G. of acetaldehyde, 25 c.c. of 20-vol. hydrogen peroxide, one drop of selenium oxychloride.

(i) Room temp., *ca.* 16°.			(ii) Temp. 20°.			(iii) Temp. 100°.			(iv) Temp. 5—6°.		
	Conversion, %.			Conversion, %.			Conversion, %.			Conversion, %.	
Time, days.	Control.	Actual.	Time, days.	Control.	Actual.	Time, hours.	Control.	Actual.	Time, days.	Control.	Actual.
2	1·3	6·2	42	11·0	77·0	1	12	71·0	50	4	23·0
6	1·5	15·0	50	12·0	80·0	2	19·5	79·5	100	5	41·0
12	3·5	26·0	63	18·5	88·5	3	28	86·0			
20	4·0	41·0									
35	7·0	56·0				H_2O_2 added in two equal proportions, the second being added after 1 hr. :					
56	11·5	64·0									
77	15·0	80·0				2	20·0	86·5			

Effect of varying the amount of selenium oxychloride added.

Duration of experiment, 15 days.

Selenium oxychloride, c.c.	0	0·05	0·1	0·2	0·3	0·5
Conversion, %	3·5	51·0	72·0	82·0	81·5	81·0

Effect of hydrochloric acid.

No selenium oxychloride. Duration of experiment, 15 days.

N/2-Hydrochloric acid, c.c.	0	0·5	0·7	1·25	1·5	2·0	5·0
Conversion, %	3·5	4·25	5·0	5·25	5·8	6·1	8·0

If 100-vol. hydrogen peroxide is used, after a slight lag, during which the mixture becomes warm, a very vigorous reaction sets in, and the mixture boils. The reaction may be kept under control by immersion in ice-water.

0·5 G. of acetaldehyde was added to 5 c.c. of 100-vol. hydrogen peroxide, then one drop of selenium oxychloride; the temperature of the mixture was kept between 5° and 7°.

Time, days	1	7	11	15
Conversion, %, in control	2	3	3	4
Conversion, %	7	16	32	35

Series II. Oxidation of Benzaldehyde.

Two sets of experiments were carried out, one at room temperature (about 16°) and the other at about 5°, the reaction vessel being shaken at intervals.

0·5 G. of benzaldehyde, 10 c.c. of 20-vol. hydrogen peroxide, and one drop of selenium oxychloride.

Room temp.			Temp. 5°.		
	Conversion, %.			Conversion, %.	
Time, days.	Control.	Actual.	Time, days.	Control.	Actual.
2	7·0	25·5	3	4·5	17·0
5	9·0	43·5	6	6·0	25·5
7	10·5	73·0	10	6·5	38·5
10	12·5	88·0	18	7·5	54·5

University College, Nottingham.

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