Oxygen-Compound Formation with Acetaldehyde at Low Temperature.—A Note by D. LeB. Cooper, M. Sc., Chemistry Department, Dalhousie University. Halifax, N. S.

(Presented 19 March 1928)

Some evidence of the formation of a peroxide during the oxidation of acetaldehyde at low temperatures has been brought to my attention. The following experiment was designed with the object of gaining some information about the supposed reaction.

A small amount of acetaldehyde, together with finely powdered manganese acetate, was placed in the ordinary form of a bubbling tube which was kept immersed in a carbon dioxide-ether bath. Oxygen was circulated through this mixture by means of a Maass circulating pump. The oxygen was stored in a graduated cylinder, and admitted to the apparatus through a side arm on the bubbling tube, after having passed over phosphorus pentoxide, a tube of which was placed in series between the reservoir and the tube. During the circulation the storage system could be shut off by means of a series of stop cocks. An attempt was made to admit the oxygen directly into the pump, but this proved unsatisfactory owing to trappage of oxygen in the valve. Circulation with the tube empty and the apparatus arranged in the second manner showed that there was no trappage of oxygen.

Following are two typical experiments with acetaldehyde and the catalyst in the tube:

Time	Absorption	Time	Absorption
	cc.		cc.
5.30	0	9.45	0
3.40	12	1.00	10
4.30	19	5.30	19
5.00	25	9.15	21
6.00	22	11.25	21

After the absorption the solution was a dark pink colour.

An analysis of the material thus treated was made with sodium hydroxide (N-.187) with the following results.

1. A test of freshly prepared acetaldehyde showed no trace of acid.

2. A run in which the following absorption occurred.

Time	Absorption cc.
10.30	0
12.30	7

gave the following results when titrated for acetic acid.

Calculated amount of HAc from titration (.0043 and .0044) mean .004 gm. A calculation shows an absorption of 7 cc. of oxygen is required for the formation of this amount of acetic acid from acetaldehyde.

In view of the fact that the absorbed oxygen reached a maximum in all runs that were allowed to continue for a period of over four hours, it is not improbable that this represents the solubility of oxygen in the acetaldehyde mixture, the oxidation power of the catalyst being absent at the low temperature of the experiment. On warming the solution it is possible that an immediate oxidation of acetaldehyde to acetic acid occured, which would account for the value found above.

The pink colour of the solution may indicate the formation of some complex. If this be the case the formation must be very slow, and the product formed must rearrange to acetic acid on warming to room temperature.

The experiment indicates therefore, that no peroxide stable at room temperature is formed.

The author wishes to express his thanks to the National Research Council, a bursary from which enabled this work to be carried out.