

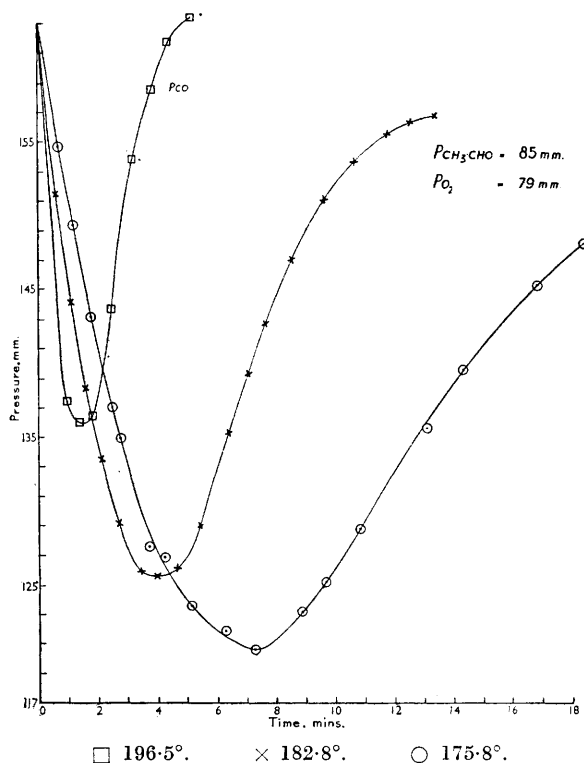
#### 474. *Oxidation of Aldehydes in the Gaseous Phase. Part II. Oxidation of Acetaldehyde in the Pre-explosion Region: Thermal Stability of the Acetyl Radical.*

By C. A. McDOWELL and J. H. THOMAS.

The oxidation of acetaldehyde has been studied in the pre-explosion region at temperatures from 170° to 200°. It has been found that there is an initial decrease in pressure which coincides with the formation of peracetic acid, and then an increase of pressure which is due to the decomposition of the per-acid. In view of the fact that the acetyl radical plays an important part in the oxidation of acetaldehyde (see preceding paper), these results can only be interpreted as showing that this radical is more stable than has hitherto been supposed.

In this paper we describe further experiments on the oxidation of acetaldehyde carried out at temperatures just below the cool-flame ignition temperatures for the mixtures studied. The method of investigation was the same as that described in the previous paper.

FIG. 1.



The pressure-time curves for the reaction at 120° showed an upward trend after the minimum, which seemed to be due to peracetic acid or the peracetyl radical decomposing to yield carbon dioxide and a carboxylic acid. Experiments at higher temperatures with acetaldehyde and oxygen concentrations chosen so as to be just outside the explosion limits show that this upward trend in the pressure-time curves is now greatly accentuated. Fig. 1 shows a series of curves for a given acetaldehyde-oxygen mixture at temperatures from 170° to 196.5°.

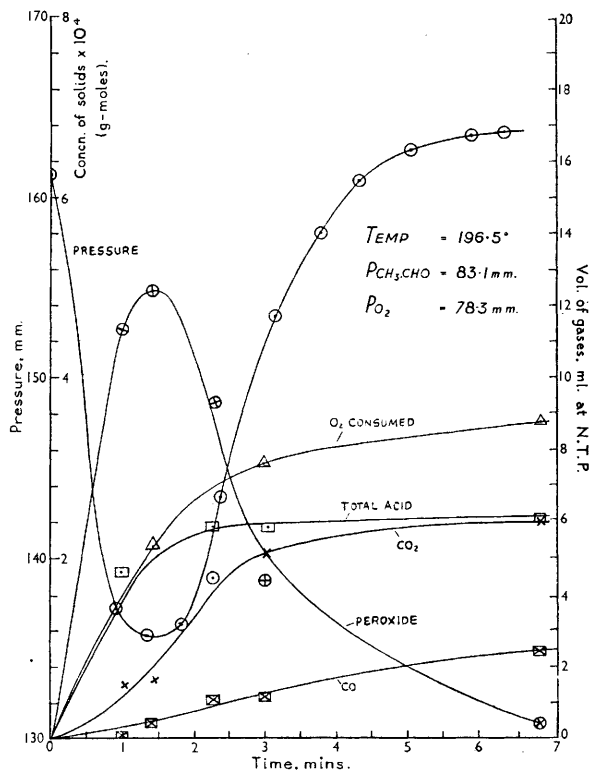
The course of the reaction has been investigated by allowing a chosen mixture to react for a certain time, and then pumping off the contents of the vessel and analysing the products. Analytical methods identical with those described in the preceding paper were employed, and the results for a particular mixture at 196.5° are shown in Fig. 2.

Examination of the curves in this figure shows beyond doubt that the upward trend in the

pressure is due to the decomposition of peracetic acid or the peracetyl radical into a carboxylic acid and carbon dioxide.

In connection with Fig. 2 it is again interesting to examine the curves showing the yield of peroxides and carboxylic acids. As in the previous paper, we see that the yield of peroxide increases as the pressure falls to a minimum and then the amount of peroxide begins to fall off; but the amount of carboxylic acid rises gradually and then remains stationary. Shortly after the minimum in the pressure-time curve, the yield of peroxide falls below that of the carboxylic acids, and by the time the pressure reaches its maximum and remains fairly stationary, the amount of peroxide in the system has fallen to practically zero. Since in the early stages of the

FIG. 2.  
Course of the reaction.

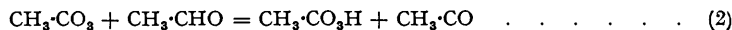


reaction more peroxide than carboxylic acid is produced, we are led to the view that, besides peracetic acid, hydrogen peroxide is also produced. The facts leading to this view have been discussed in the preceding paper.

We have investigated the effect of varying the initial concentrations of the reactants in this high-temperature region and find that variation of the oxygen concentration has little effect on the rate either of decrease or of increase of pressure in the pressure-time curves. Variation of the acetaldehyde concentration affects both the rate of decrease and the rate of increase of pressure during the course of the reaction. This is only to be expected, for it was shown in the previous paper that the rate of formation of peracetic acid was proportional to the square of the acetaldehyde concentration. Similarly, for a fixed amount of oxygen, increasing the acetaldehyde increases the amount of peracetic acid formed and so will, in turn, cause an increase in the rate of decomposition of this acid (or its radical).

Another interesting fact emerges from the experimental results presented above. In the previous paper we discussed the various mechanisms proposed for the oxidation of acetaldehyde, and though there are disagreements about the exact mechanism, it is generally agreed (Bäckström, *Z. physikal. Chem.*, 1934, B, 25, 115; Lewis and von Elbe, "Combustion, Flames, and Explosions in Gases," Cambridge, 1938; Bodenstein, *Rec. Trav. chim.*, 1940, 59, 48) that

the acetyl radical plays an important part in the reaction, and that the propagation reactions are :



There has, however, been considerable controversy regarding the thermal stability of the acetyl radical. Most of the evidence for its existence and its stability has been obtained in photo-chemical experiments, and the facts have recently been collated and discussed by Steacie ("Atomic and Free Radical Reactions," Reinhold, New York, 1946). Briefly, early evidence (Glazebrook and Pearson, *J.*, 1937, 576; Spence and Wild, *ibid.*, p. 352) appeared to show that acetyl was unstable above 60°. Later, Gorin (*Acta Physicochim.*, U.S.S.R., 1938, 8, 513; *J. Chem. Physics*, 1939, 7, 256), from a study of the photolysis of acetone in the presence of iodine vapour, showed that some acetyl iodide was produced at a temperature as high as 140°, and from his results he estimated a minimum value of 17 kcal. for the activation energy of the decomposition  $\text{CH}_3\cdot\text{CO} = \text{CH}_3 + \text{CO}$ , which is in excellent agreement with the value of 16 kcal. estimated by Bawn (*Trans. Faraday Soc.*, 1938, 34, 598) by transition-state theory, and with more recent experimental values (Herr and Noyes, *J. Amer. Chem. Soc.*, 1940, 62, 2052). Later work by Benson and Forbes (*J. Amer. Chem. Soc.*, 1943, 65, 1399) threw some doubt on the reliability of some of Gorin's analytical methods, though they do find evidence that the acetyl radical is capable of existence at 100° and above. Gorin's views are, however, supported by the work of Anderson and Rollefson (*ibid.*, 1941, 63, 816).

Because of the belief that acetyl is unable to exist above 60°, Rice and Schildknecht (*ibid.*, 1938, 69, 3044) and Walsh (*Trans. Faraday Soc.*, 1946, 42, 269) have rejected oxidation mechanism involving this radical. Rice and Schildknecht worked on the photo-oxidation of acetone at 80—100°; but though they reject the acetyl radical from consideration, they do not present any compelling experimental evidence for doing so. In any case, their mechanism for the oxidation of acetone can hardly be taken seriously, for it fails to account for the occurrence of carbon dioxide which makes up about 45% of the reaction products.

Consideration of the results presented in Fig. 2, and the general agreement that the peracetic acid is formed in this oxidation by reactions (1) and (2), lead us to the view that the acetyl radical must be sufficiently stable to exist at about 200° long enough to react with oxygen to form the peracetyl radical.

Experiments were carried out by one of us (C. A. McD.), using the sodium-flame technique developed by Bawn and his co-workers (*Trans. Faraday Soc.*, 1938, 34, 608; 1939, 35, 185, 889), in an attempt to detect and study the properties of the acetyl radical. Using the reaction  $\text{CH}_3\cdot\text{COCl} + \text{Na} = \text{NaCl} + \text{CH}_3\cdot\text{CO}$  at 300°, we were unable to detect any diacetyl and so concluded that the acetyl radical does not long survive its own collisions at this temperature.

One of us (J. H. T.) thanks the University of Liverpool for a Campbell Brown Fellowship.

UNIVERSITY OF LIVERPOOL.

[Received, September 21st, 1948.]