CONDITIONS FOR THE IGNITION OF GAS MIXTURES

COMMUNICATION 22. EFFECT OF ADDITIONS OF DIETHYL PEROXIDE AND ACETALDEHYDE ON THE KINETICS OF COOL-FLAME OXIDATION OF BUTANE

A. A. Dobrinskaya and M. B. Neiman

In a series of investigations, Neiman, Tutakin, Blat, and Gerber [1, 2] have studied the effect of the addition of diethyl peroxide on the period of induction of the butane cool flame. It was shown that the induction period for the butane cool flame depends on the amount \( x \) of added peroxide, the relationship being expressed by the following equation:

\[
K_1 \tau = a - \ln x.
\]

Neiman and coworkers [3, 4] have shown that this equation is applicable to the oxidation of propane and of dimethyl ether. Similar results were obtained by Egerton and Harris [5] in an investigation of the effect of diethyl peroxide on the induction period for the propane cool flame.

In the present investigation we have set ourselves the task of studying in greater detail the effect of diethyl peroxide on the process of cool-flame oxidation of butane and also of the effect on this process of acetaldehyde, the kinetics of the formation of active products during the induction period being investigated in each case. Studies of the kinetics, in absence of additives, of the build-up of active intermediate products during the period of induction of the butane cool flame have also been made previously [6, 7].

EXPERIMENTAL

Experimental Procedure

a) Description of apparatus. Apart from some minor modifications, the procedure followed was the same as that described in detail in previous papers [6, 7]. The cool flame was obtained by admitting a mixture of butane and oxygen into a previously evacuated quartz vessel heated to a definite temperature; the formation of flame was observed visually. Induction periods were determined with the aid of a stop watch. Analytical tests on the gaseous reaction mixture were made as follows. At a definite time the gaseous mixture was allowed to pass from the reaction vessel to an intermediate flask, and was slowly pumped off through a U-tube cooled by liquid oxygen. The condensed reaction products were then warmed and blown out with a stream of hydrogen into a train of two absorption vessels. The solutions were then analyzed polarographically for their content of organic peroxides and aldehydes [8-13].

b) Preparation and purification of the starting materials. Butane was prepared by the hydrogenation of 2-butene; it was purified from unsaturated hydrocarbons and tested for organic peroxides and aldehydes in the manner described in the literature [8]. Diethyl peroxide was prepared from diethyl sulfate and 12% hydrogen peroxide [14]. Diethyl sulfate (105 parts) and hydrogen peroxide (125 parts) were carefully mixed together in a flask at 15°. A 5% solution of KOH (180 parts) was added dropwise to the mixture. Reaction proceeded under careful cooling for six hours, and the reaction products were then fractionated on an oil bath. The fraction boiling between 55° and 76° was collected and was washed with a 30% solution of NaOH and with water in order to remove alcohol and ether. The diethyl peroxide obtained was repeatedly distilled; the fraction boiling between 63.5° and 65° was used in the experiments. The refractive index \( n_\rho \) of diethyl peroxide was found to be 1.37014, a value in good agreement with that found by Neiman, Blat, and Gerber, namely \( n_\rho = 1.37009 \) [2].

Measurements were made also of the vapor pressure of diethyl peroxide at various temperatures. The latent heat of vaporization of diethyl peroxide calculated from these results was \( \lambda = 7400 \) cal/mole, in good agreement with the value of \( \lambda = 7300 \) cal/mole obtained by Blat [2]. Acetaldehyde \( \text{CH}_2\text{CHO} \) was prepared by the depolymerization of pure paraaldehyde, and was carefully fractionated. The fraction boiling at 20° was used in the experiments. In order
to avoid the formation of peroxides, the acetaldehyde was kept in sealed ampoules in absence of oxygen. Before an experiment, qualitative tests for peroxides were made, and the results were always negative. Oxygen and hydrogen were prepared by the electrolysis of a 15% solution of NaOH, and they were then purified as indicated in previous papers [6, 7].

EXPERIMENTAL RESULTS

1. Effect of Addition of Diethyl Peroxide on the Kinetics of Cool-Flame Oxidation of Butane

   a) Shortening of the induction period due to addition of diethyl peroxide. We investigated the shortening of the induction period resulting from addition of diethyl peroxide at 310° and 333 mm. As will be seen from the curve (Fig. 1), as the addition of diethyl peroxide was increased, the period of induction was reduced in a regular manner.

   In order to verify Equation 1, we plotted the experimental results with log x and t as coordinates (Fig. 2), and, within the limits of experimental error, the experimental points fall on a straight line, as required by Equation 1. From the slope of this line we find \( K = 0.008 \).

   b) Build-up of peroxides and aldehydes. We investigated the build-up of peroxides and aldehydes during the induction period, the reaction being carried out in presence of diethyl peroxide. In this series of experiments, carried out at 310° and 333 mm, an addition of 0.54 mm of diethyl peroxide was made to the butane-oxygen mixture. The amounts of peroxides and aldehydes were determined by a polarographic method, as described above. The results of our analyses are represented in Fig. 3.

   It will be seen from Fig. 3 that the concentration of diethyl peroxide rapidly fell immediately after the admission of the mixture into the heated vessel. Simultaneously peroxides, which were reduced at -0.2 and -0.1V, (Curves 2 and 3) and aldehydes (Curve 4) began to accumulate in the mixture. The decomposition of diethyl peroxide resulted in the appearance of appreciable amounts of aldehydes, and many initiating centers were evidently formed. As a result, the oxidation reaction was accelerated.

2. Effect of Addition of Acetaldehyde on the Kinetics of Cool-Flame Oxidation of Butane

   a) Shortening of the induction period due to addition of acetaldehyde. It has been shown by the work of Alivazov and Nelman [15] that addition of acetaldehyde leads to a shortening of the period of induction of the pentane cool flame. We have investigated the effect of addition of acetaldehyde on the period of induction of the cool flame of butane at 333 mm and 310°. As the addition of \( \text{CH}_3\text{CHO} \) was increased, the induction period for the cool flame was reduced in a regular manner (Fig. 4). Addition of \( \text{CH}_3\text{CHO} \) in amounts appreciably in excess of that which, according to our analyses, builds up by the end of the induction period, although shortening the induction period, did not eliminate it completely. Newitt and Thornes's hypothesis [16], according to which the cool flame arises as a result of the building up of a critical concentration of aldehydes, is therefore evidently incorrect.