

SLOW COMBUSTION OF METHYL VINYL KETONE

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(Received January 22, 1972)

Abstract. In the slow combustion of methyl vinyl ketone, the variation of maximum reaction with temperature was studied for equimolar mixtures of methyl vinyl ketone and oxygen at a fixed total initial pressure. The temperature range covered was 250–450°C. The results of these experiments are presented as $\log_{10} P$ against $1/T$ °K. The variation of the induction period and the acceleration constant was also studied. In the high and low temperature zones the overall activation energies were obtained.

The slow combustion of acetone,^{1,2} methyl ethyl ketone^{3,4} and diethyl ketone⁶ have been studied in detail. It has been found that those reactions possess many of the features of hydrocarbon oxidation. The high and low temperature regions are well differentiated. In case of methyl vinyl ketone no detailed study of the various products of reaction in the two temperature regions were studied, except the general kinetics, e.g. the effect of temperature on the maximum rate of reaction, on the net branching factor and on the induction period. These general characteristics resemble the slow combustion of organic compounds and can be further studied in order to justify this prediction.

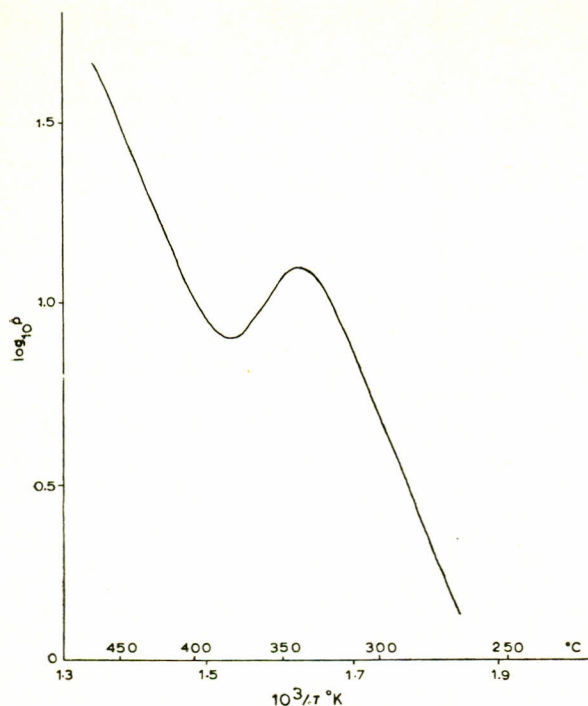


Fig. 1. Effect of temperature on the maximum rate of reaction (pmvk, 40 mm; p_{O_2} , 40 mm)

Experimental

Apparatus. The apparatus was of the usual static type, and the reaction was followed by pressure change using a glass spiral monometer. Particular care was taken to avoid mercury vapour from the reacting mixture, although Kirchner reported² that presence of mercury vapour from the reacting mixture had no effect on the slow combustion of acetone. A cylindrical silica reactor having approximately 300 cm³ volume was used. The normal preparation involved washing with concentrated nitric acid and then rinsing several times with water.

Materials. Methyl vinyl ketone (G.R.P. grade, Koch-Light Laboratories) was used without purification. Gas chromatography showed no impurities. Oxygen was taken from cylinder and passed through soda-lime, silica gel and a trap cooled to -80°C, before being stored in a 2-litre container. Mass spectrometric analysis showed no impurities except a trace of moisture.

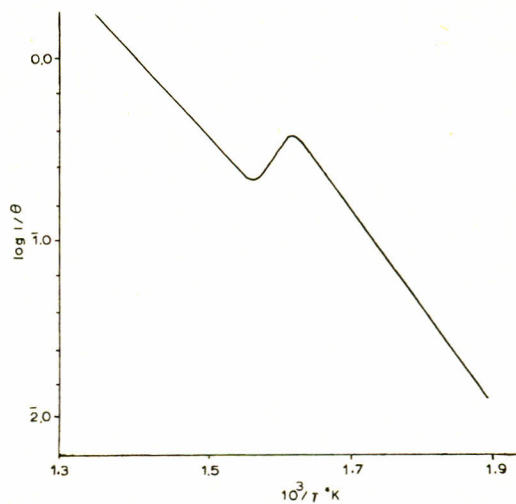


Fig. 2. Variation of the induction period with temperature (pmvk, 40 mm; p_{O_2} , 30 mm).

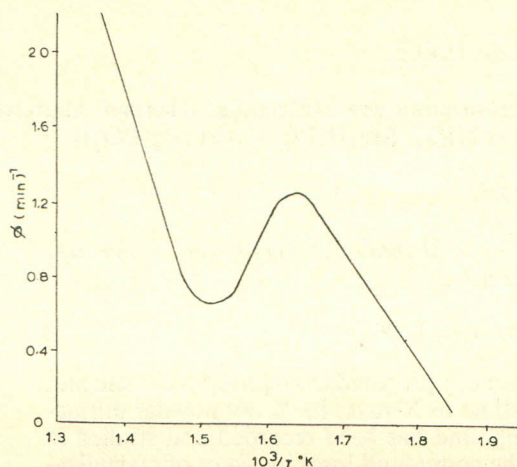


Fig. 3. Effect of temperature on the net branching factor (pmvk, 40 mm; P_O , 40 mm).

Results and Discussion

It was observed that the aging of reactor require only one to two runs in order to obtain reproducible results. The reaction was studied between 250–450°C. The pressure time curves were sigmoidal, the induction period varying from 0.5 to 3 sec at the higher temperature, to 5–50 sec at the lower temperature. The variation of the maximum rate of reaction (as given by the maximum rate of pressure change) with temperature for an equimolar fuel+oxygen shown in Fig. 1 indicates that the slow combustion of methyl vinyl ketone can proceed by two different mechanisms, one operating below 325–330°C and the other above 375–400°C.

This statement is supported by the induction period as shown in Fig. 2 and was also reported by other combustion systems,^{7,8} (θ induction period defined as the intercept on the time axis of the tangent to the pressure time curve at the maximum rate) and the acceleration constant as shown in Fig. 3.

There is no doubt that in both regions, the combustion involves degenerate chain-branching. The pressure time curves are sigmoidal and the plots of $\log \Delta P$ against time show that the acceleration is exponential as required by the theory.⁹ The overall activation energies obtained in the high temperature zone was 23 kcal/mole whereas in the low temperature zone it was 17–18 kcal/mole.

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