The Role of Hydroperoxides as Chain-branching Agents in the Cool-flame Oxidation of n-Heptane

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IN recent studies of the oxidation of n-heptane in the gas phase, some interesting results have been obtained about the chain-branching intermediate responsible for cool-flame formation. There has been much controversy about the most likely species causing cool flames in the gaseous oxidation of hydrocarbons, the two most likely candidates being aldehydes and organic hydroperoxides.[1–3] In the present work, measurement of the concentration of hydroperoxides during reactions in which cool flames occur, as well as the addition of 2-heptyl hydroperoxide to the system, suggest that the chain-branching intermediates in the cool-flame oxidation of n-heptane are hydroperoxides.

The apparatus used was a conventional static type, with a cylindrical acid-washed Pyrex reaction vessel. The reaction was followed using a sensitive pressure transducer and an ultraviolet recorder. Sampling was achieved rapidly using a glass electromagnetic valve.[4] Analysis of organic hydroperoxides was carried out using a modified form of the iodometric method of Clover and Houghton,[5] capable of distinguishing between hydrogen peroxide and organic hydroperoxides.

At 242°, with initial reactant pressures of 50 torr oxygen and 50 torr n-heptane, one cool flame occurs after an induction period of 45 sec. The concentration of organic hydroperoxides in the reaction vessel was measured over a range of reaction times from 0—90 sec. (see Figure 1). The partial pressure of the organic hydroperoxides (calculated as the monohydroperoxide, ROOH) builds up to a maximum of 3·4 torr immediately before the cool flame, during the passage of which they are completely destroyed.

2-Heptyl hydroperoxide was prepared by the method of Williams and Mosher,[6] and was introduced into the reaction mixture of n-heptane and oxygen at 242°. The total initial pressure was maintained at 100 torr by reducing the n-heptane and oxygen concentrations equally to compensate for the added hydroperoxide. The immediate effect of adding small quantities of hydroperoxide to the system was to reduce the induction period before the cool-flame (see Figure 2) without altering the pressure rise (ΔP) during the cool-flame. However, as shown in Figure 3, beyond a critical concentration of approximately 3·2 torr of 2-heptyl hydroperoxide, the pressure rise during the cool-flame increases. If more than 4·5 torr was added, the cool-flame induced ignition (*i.e.*, two-stage ignition) because the conditions used were quite close to the ignition limit for n-heptane oxidation.

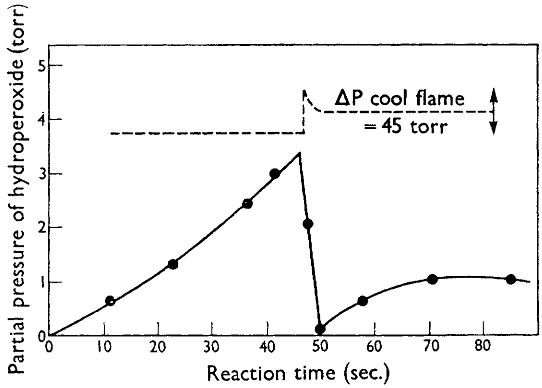

FIGURE 1. *Formation of organic hydroperoxides in the cool-flame oxidation of n-heptane at 242°.*
Initial pressure = 50 torr n-heptane + 50 torr oxygen
– – – shows the total pressure *vs.* time curve during the reaction.

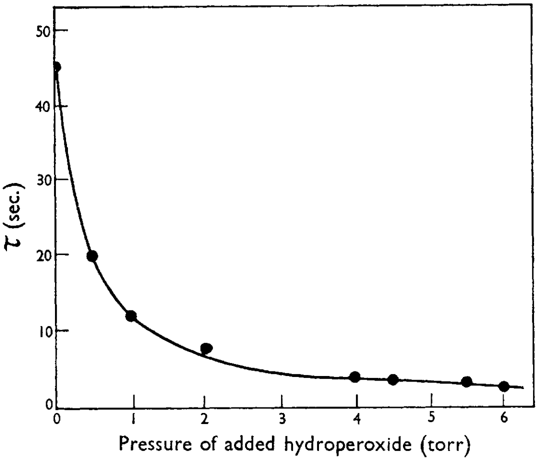

FIGURE 2. *The effect of added 2-heptyl hydroperoxide on the induction period* (τ) *before the cool flame.* $T_0 = 242°$; $p_0 = 100$ torr.

These results, particularly the good agreement

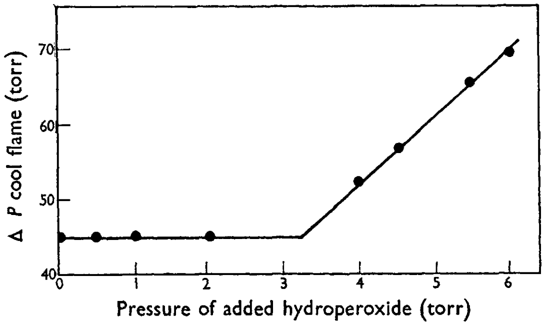

FIGURE 3. *The effect of added 2-heptyl hydroperoxide on the pressure rise during the cool flame.* $T_0 = 242°$; $p_0 = 100$ torr.

between the critical concentrations of the hydroperoxides in the two separate experiments, suggest very strongly that heptyl hydroperoxides are the degenerate chain-branching intermediates responsible for cool-flame formation in n-heptane oxidation. Initial oxygen attack on n-heptane forms the 2-,3-, and 4-heptyl hydroperoxides, but, since their decomposition rates will probably be very similar, the results of the addition of 2-heptyl hydroperoxide to the reaction mixture is good evidence of the role played by all three heptyl hydroperoxides in cool-flame formation.

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