# Negative Temperature-coefficient of Reaction Rate during Hydrocarbon Oxidation

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*Summary* A new region of negative temperature-coefficient of rate is observed at the low-temperature limit for cool flame formation.

STUDIES of hydrocarbon oxidations in both flowing[1] and static[2–4a] systems have shown that the maximum rate of reaction for the autocatalytic process does not increase steadily with increased initial temperature ($T_0$) but exhibits both a maximum and a minimum (curve a, Figure 1). In addition, multiple cool flames propagate successively through static vessels at rather similar initial temperatures to those in the region of negative temperature-coefficient (the flames usually first appear at lower values of $T_0$). The negative coefficient is thought to play a part in the self-quenching mechanism of each cool flame as the attendant heat release increases the reaction temperature.[4,5]

Recently, a unified theory[6,7] for cool flames and ignitions has predicted that periodic oscillations (multiple cool flames) and a negative temperature-coefficient in the maximum rate of heat release are inseparable, the oscillatory cool flame first occurring at bath temperatures in the negative temperature-coefficient zone. Experimental evidence testing the above hypothesis is presented here.

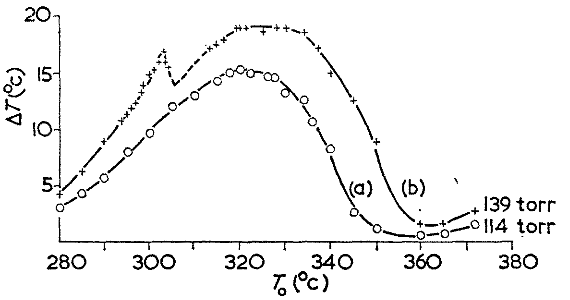

FIGURE 1. *Plot of* $\Delta T_{max}$ *against* $T_0$. (*a*) P = 114 *torr*; (b) P = 139 *torr.*

An equimolar mixture of propane and oxygen was allowed to react in a spherical vessel (1 l.). Acetaldehyde (1%) was added to reduce the otherwise considerable induction period preceding reaction. The difference ($\Delta T$) between the temperature at the centre ($T$) and that at the wall ($T_0$) of the reaction vessel was monitored by a very fine platinum alloy thermocouple (0·001 in. diam.) for various initial temperatures at two values of initial pressure. One pressure isobar (139 torr; AB on Figure 2) intersected the cool flame zone, while the other (114 torr; CD on Figure 2) lay just below it.

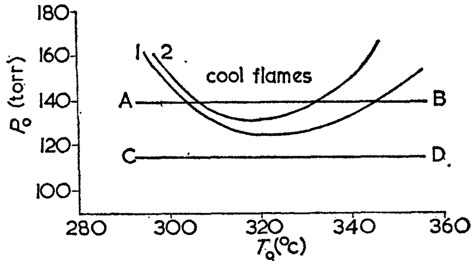

FIGURE 2. *Cool flame limits for an equimolar mixture of* $C_3H_8$ *and* $O_2$ + 1% $CH_3CHO$ *in* 1 *l. spherical vessel.*

At the steady state, the temperature rise in a system is proportional to the rate of heat release.[8] In hydrocarbon oxidation, the system attains only a quasi-steady state as a result of fuel consumption. Nevertheless, the maximum temperature rise is a measure of the maximum rate of heat release during reaction.[9] In this work $\Delta T_{max}$ has been measured as a function of $T_0$.

Both at 139 torr and 114 torr the maximum rate of heat release (strictly $\Delta T_{max}$) exhibits a negative temperature-coefficient for initial temperatures in excess of 330° (Figure 1), which is in accord with that detected in the maximum rate of reaction for other systems.[3,4a] However, for the higher pressure (through the cool flame zone), an additional region of negative temperature-coefficient is observed (curve b, Figure 1), and the initial temperature at which this new region occurs coincides with that for the onset of cool flames. This additional negative coefficient zone is not found at the lower pressure. Thus, a negative temperature-coefficient of rate, independent of that observed above 330°, is now established as a condition associated with the occurrence of periodic oscillations.

Although these results are confined to the region of two cool flames the oscillatory nature of the reaction is clearly seen (Figure 3). At higher pressures, as many as six temperature oscillations are observed. The existence of multiple cool flames signifies that the approach to the steady-state temperature is not monotonic but occurs in an oscillatory manner.[6] Hence, the temperature rise that is important when cool flames occur is the rise to the steady state about which the system is oscillating and not that determined from the maximum of the temperature spike (Figure 3). It is not always easy to locate the temperature at this steady state owing to the effect of fuel consumption, and in such cases a value of $\Delta T$ was not determined, leaving the $\Delta T$ against $T_0$ curve incomplete.

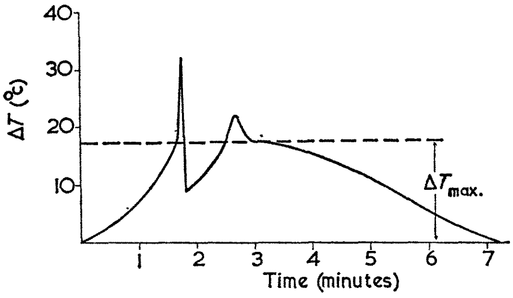

FIGURE 3. *A typical* $\Delta T$ *against time profile for two cool flames.* P = 139 *torr,* $T_0$ = 320°.

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