A Model for Cool-flame Behaviour

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Summary A mathematical model is outlined which gives a realistic description of the complex behaviour observed for cool-flame oxidation systems and suggests that phenomenological complexity is not necessarily the result of chemical complexity.

WE report that a simple but realistic chemical model can describe the complex behaviour observed for cool-flame oxidation systems. This work treats a model for the non-isothermal chain-oxidation of acetaldehyde for which peracetic acid has been suggested[1] as the degenerate branching agent.

An understanding of the mechanism of the self-quenching, characteristic of cool flames, is essential to the explanation of their periodicity. The present model attributes self-quenching to a "thermal switch" in which the reaction

$$CH_3CO^\bullet + M \rightarrow CH_3^\bullet + CO + M \qquad (1)$$

of high activation energy competes with the low activation energy sequence responsible for the formation of the

$$CH_3CO^\bullet + O_2 \rightarrow CH_3CO_3^\bullet \qquad (2)$$

$$CH_3CO_3^\bullet + CH_3CHO \rightarrow CH_3CO_3H + CH_3CO^\bullet$$

branching agent. As the temperature rises during a cool flame, competition of reaction (1) with reaction (2) slows down the formation of peracetic acid and at the same time the decomposition by the branching reaction

$$CH_3CO_3H \rightarrow CH_3^\bullet + OH^\bullet + CO_2 \qquad (3)$$

accelerates until the concentration of branching agents falls, causing a rapid drop in reaction rates and temperature. The chemical model is completed by the reactions

$$\mathrm{CH_3^\bullet + O_2 + M \rightarrow CH_2O + OH^\bullet + M} \qquad (4)$$

$$\mathrm{OH^\bullet + CH_3CHO \rightarrow H_2O + CH_3CO^\bullet}$$

$$\mathrm{CH_3^\bullet + CH_3^\bullet} \rightarrow \text{termination}$$

$$\mathrm{CH_3^\bullet + CH_3CO_3^\bullet} \rightarrow \text{termination}$$

$$\mathrm{CH_3CO_3^\bullet + CH_3CO_3^\bullet} \rightarrow \text{termination}$$

The thermal model is that of Semenov[2] and, since the chemical mechanism is exclusively homogeneous, gives no account of the spatial propagation of cool flames.

The model takes account of reactant consumption and was treated as a set of nine non-linear stiff differential equations which were integrated numerically by means of a technique developed specifically for such problems.[3] This approach differs fundamentally from that recently developed by Gray[4] in an analytical examination of simple, linearized two-variable models which neglect reactant consumption.

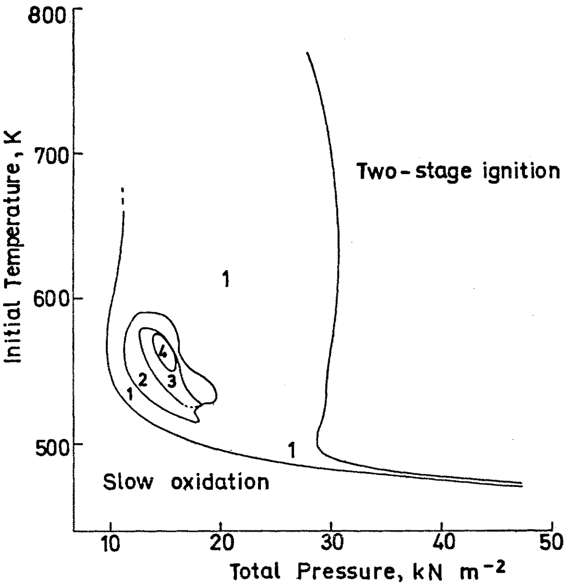

FIGURE 1. *Cool-flame and ignition diagram calculated for the model of acetaldehyde oxidation.* $\mathrm{CH_3CHO:O_2:Ar = 1:1:1}$. *Numbers indicate the number of cool flames observed in each bounded region.*

The coefficients in the differential equations were selected so that for an initial temperature of 530K and total concentration of 3×10^{-3} mole l^{-1} ($\mathrm{[CH_3CHO] = [O_2] = [Ar]}$) the computation produced a single cool flame with less than 25% conversion at the temperature maximum and an induction period between 10 and 15 seconds; to achieve this the rate constants of reactions (1), (2), (3), and (4) were varied about reasonable estimates of their likely values. The remaining coefficients were literature values or were estimates based on parameters for similar reactions.

The computer has been used in a conversational mode to map out a cool-flame diagram (Figure 1). On the Univac 1108 used for the work each integration took 10 to 20 seconds. Figure 2 shows the time-dependence of the gas temperature and branching agent concentration for conditions that give rise to four cool flames. The model also gives a satisfactory account of:—

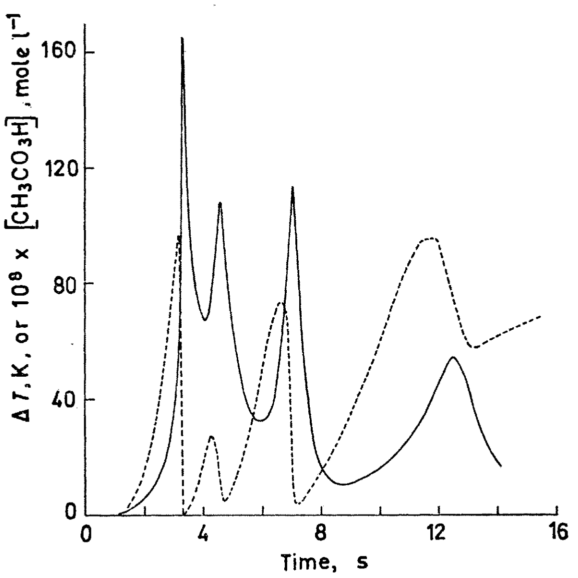

FIGURE 2. *Calculated course of reaction for the oxidation of acetaldehyde at* 561K *and a total pressure of* 15·0 kN m^{-2}. $\mathrm{CH_3CHO:O_2:Ar = 1:1:1}$. *Full line, excess of mean gas temperature over vessel temperature* (ΔT). *Broken line, peracetic acid concentration.*

(a) the sharp transition from slow oxidation to cool-flame behaviour,

(b) the dependence on initial conditions of the maximum temperature rise during the cool flame, and

(c) the negative temperature coefficient commonly observed in the slow-oxidation regime.

All the computations so far carried out suggest that phenomenological complexity is not necessarily the result of chemical complexity.

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[2] N. N. Semenov, "Chemical Kinetics and Chain Reactions," Pergamon Press, Oxford, 1953.

[3] A. Prothero, to be published.

[4] B. F. Gray, *Trans. Faraday Soc.*, 1969, **65**, 1603, 1614 and 2133.