A Thermokinetic Foundation for Oscillatory Phenomena in Gaseous Organic Oxidations under Well Stirred Flowing Conditions

BY JOHN F. GRIFFITHS,* STEPHEN M. HASKO, NIGEL K. SHAW⁺ AND TOMAS TORREZ-MUJICA

Department of Physical Chemistry, The University, Leeds LS2 9JT

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An experimental and theoretical attack on the fundamentals of thermokinetic phenomena associated with the gaseous, non-isothermal oxidation of hydrocarbons and other organic substrates is described. Quantitative comparisons are made between numerical modelling and experimental measurements under well stirred flowing conditions.

Two chemical systems are considered, involving reactions of methyl radicals. These are: (i) di-t-butyl peroxide decomposition in nitrogen and (ii) di-t-butyl peroxide decomposition in an excess of oxygen. Simplified kinetic mechanisms for each of these systems are described and numerical computations for non-isothermal reactions are discussed. Stationary states and two different types of oscillatory modes are predicted to exist within limited ranges of p, T_a and composition, and these match experimental measurements quite satisfactorily. The integral role played by self-heating in thermokinetic oscillations is demonstrated and relationships to cool-flame phenomena are outlined.

This paper is part of an experimental and theoretical programme concerned with the thermokinetic interpretation of non-isothermal oscillatory phenomena and multiple-stage ignitions associated with gaseous organic oxidations. It deals with reactions of methyl radicals in non-degenerately branched modes and aims to bridge the gap between thermal ignition on the one hand, for which exothermic reaction and a positive, Arrhenius-like temperature dependence of rate are the only chemical pre-requisites, and, on the other, thermokinetic 'cool-flame' phenomena, in which kinetics involving realms of negative temperature dependence of the overall rate of reaction are strongly coupled to self-heating.

The data presented here are drawn from experimental and numerical studies of two chemical reactions under well stirred flowing conditions [*i.e.* in a continuous, stirred-tank reactor (c.s.t.r.)]. Non-isothermal, but non-adiabatic, reactions in a c.s.t.r. may lead to stationary or oscillatory states, and even a multiplicity of them. They are equally amenable to straightforward experimental or numerical study: there is neither spatial variation within the reactor (as occurs in unstirred vessels) nor the total consumption of reactants (as occurs in closed systems).

The systems considered are (i) the decomposition of di-t-butyl peroxide (DTBP) in nitrogen and (ii) the decomposition of DTBP in a substantial excess of oxygen. Each is very reactive from *ca.* 460 K up, at total pressures down to 50 Torr, and both stationary and oscillatory states are predicted and observed. The effects of changes in concentration of DTBP, the (p, T_a) conditions at which different reaction modes

[†] Present address: Geometric Modelling Project, Department of Mechanical Engineering, The University, Leeds LS2 9JT.

occur and the frequencies and amplitudes associated with oscillatory reactions are studied. DTBP is an efficient source of methyl radicals within the temperature range of interest (475-600 K).

Studies of DTBP decomposition span many decades; they have yielded precise kinetic^{1, 2} and thermochemical data,^{3, 4} and they have also been used to validate aspects of thermal-explosion theory.^{5, 6} In addition, the decomposition has been used⁷ to test the performance of a Longwell type of c.s.t.r. The decomposition of DTBP in the presence of oxygen is less well characterised. It has been investigated in closed vessels⁸⁻¹⁰ and studied recently in the context of thermal explosions.¹¹ It has been used a source of methylperoxy radicals in kinetic studies.¹² In laminar flow, Williams *et al.*¹³ have utilised this oxidation to study the origins of cool-flame chemiluminescence (CH₂O^{*}), and Ballinger and Ryason¹⁴ investigated the stabilised 'cool flame' on a flat-flame burner. The mechanism for the *isothermal* decomposition of DTBP in the presence of oxygen has been subjected to a numerical study.¹⁵

The apparatus and experimental procedures adopted have been described in detail previously.¹⁶ Adaption of the existing stirred-flow apparatus to admit DTBP vapour is to be described fully in a subsequent paper. Briefly, the principal need is for its very carefully controlled generation and its 'cold' admission to the c.s.t.r. in order to prevent excessive preliminary decomposition. The experimental results discussed here have been obtained in a mechanically stirred, spherical, flow-through vessel (Pyrex glass, 0.5 dm³) under a mean residence time for the reactants of 3 s. Measurements have been confined so far to temperature changes within the reacting mixture using a very fine, silica-coated, Pt–Pt/13% Rh thermocouple. Signals were recorded using either a chart or oscilloscope.

THERMOKINETIC FOUNDATION TO NUMERICAL MODELS

Numerical and analytical interpretations of behaviour in a c.s.t.r. are founded on a set of time-dependent, differential expressions representing the reactant temperature and concentration of each species. Stationary-state analysis and the application of theorems for stability-of-motion are very powerful techniques for qualitative identification and location of the singularities for the thermokinetic system in parameter phase-space.^{17, 18} Quantitative predictions require numerical integration of the set of differential expressions. The terms in each equation are determined by the mechanistic basis that is invoked and pre-ordained characteristics for heat and mass transport. One underlying premise in this work is to adopt the simplest kinetic schemes consistent with recognised features of low-temperature 'hydrocarbon' oxidation. Even by using simplified schemes there is very satisfactory agreement between theory and experiment, but there are obvious areas for detailed improvement; the price that may be paid is the loss of the generality that is conveyed by simplicity.

THE ENERGY-CONSERVATION EQUATION

The rate of temperature change is expressed in each case in the form

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{1}{c} \sum_{j} h_{j} k_{j} F_{j} - \left(\frac{f}{V} + \frac{\chi S}{cV}\right) (T - T_{\mathrm{a}}) \tag{I}$$

where $c/J \,\mathrm{m}^{-3} \,\mathrm{K}^{-1}$ is the volumetric heat capacity for reactor contents, T/K is the reactant temperature, T_a/K is the vessel temperature, $h_i/J \,\mathrm{mol}^{-1}$ is the exothermicity of the *j*th elementary reaction (= $-\Delta H_{298}^{\odot}$), k_j/s^{-1} is the rate constant for the *j*th elementary reaction, $F_j/\mathrm{mol} \,\mathrm{m}^{-3}$ is the concentration term for the *j*th elementary reaction given by, e.g., [A]^a[B]^b ... where *a* and *b* are orders with respect to species

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A and B, $f/m^3 s^{-1}$ is the volumetric flow rate, $\chi/W m^{-2} K^{-1}$ is the Newtonian heattransfer coefficient between the gas and the vessel walls and $(S/V)/m^{-1}$ is the surface-to-volume ratio.

The first term on the right-hand side represents the summation of the heat-release rates from all of the elementary steps involved. We have taken constant enthalpies (ΔH_{298}^{\odot}) in the present study. The second term is the heat-loss rate from the system and is controlled by combined effects of (i) transport from the system by hot products and (ii) Newtonian heat loss via the walls of the vessel. The second part is overwhelmingly dominant when the mean residence time exceeds 1 s. Pre-heating of all reactants to the vessel temperature is assumed. The reference temperature T_* may be used¹⁹ to allow for entry of gases at a different temperature from that of the vessel, T_a . T_* is the temperature at the outflow to which non-reactive gases, entering a vessel at T_a , would be raised when their inflow temperature is T_0 and is a weighted mean. Thus

$$T_* = (T_0 f c + T_a \chi S) / (f c + \chi S). \tag{II}$$

 T_* can be measured experimentally and its simultaneous measurement with T_0 and T_a at known flow rates and compositions is an established route to evaluation of the heat-transfer coefficient.²⁰

Since the present work constitutes a pilot study, corrections for the variation of heat capacity with temperature or reactor contents, and of the heat-transfer coefficient χ with pressure, have been omitted to avoid disproportionate consumption of c.p.u. time. The heat-transfer coefficient (χ) is known to vary with pressure, temperature and composition, and allowance for its change is possible.^{21, 22} We have chosen to fix it at $\chi = 15.8$ W m⁻¹ K⁻¹, consistent with measurements made both previously^{21, 22} and during the course of this work. Nevertheless, there is an in-built correction for different rates of heat loss at different conditions because the volumetric heat capacity also plays a part [eqn (I)].

KINETIC AND THERMOCHEMISTRY FOR THE THERMAL DECOMPOSITION OF DTBP

The mechanism, and kinetic and thermochemical data, for the thermal decomposition of DTBP are unequivocal,^{2,6} To be consistent with later requirements we represent it as a two-step process, as shown in scheme A.

Scheme 4	4
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	m	A/s^{-1} or nol ⁻¹ m ³ s ⁻¹	<i>E</i> /kJ mol ⁻¹	ΔH^{\ominus}_{298} /kJ mol ⁻¹	
$(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_2CO + 2CH_3$ $CH_3 + CH_3 \rightarrow C_2H_6$	(1) (2)	6.3×10^{15} 2.5×10^{7}	158 0	191 - 371	

For reasons connected with the present computational method we regard the methyl radical recombination (2) to be at the high-pressure limit. This is also the case for reactions (3), (4) and (8) below. This kinetic foundation for DTBP decomposition leads to five, time-dependent, differential equations representing the rate of temperature change and the rate of concentration change for the four species DTBP, acetone, methyl and ethane. The initial concentration is solely that for DTBP, but allowance is made numerically for the flow-through and heat capacity of the inert carrier (N_2) that is necessary experimentally.

KINETICS AND THERMOCHEMISTRY FOR THE DECOMPOSITION OF DTBP IN OXYGEN

The minimum viable scheme consistent with present understanding of the lowtemperature oxidation of methyl radicals involves 17 species in 14 reactions, as shown in scheme **B**.

Scheme B

		1/c=1 cm	E	ΔH_{298}^{\ominus} /kJ mol ⁻¹
	:	$mol^{-1} m^3 s^{-1}$	$/kJ \text{ mol}^{-1}$	
$DTBP \rightarrow 2(CH_3)_2CO + 2CH_3$	(1)	6.3 × 10 ¹⁵	158	191
$CH_3 + CH_3 \rightarrow C_2H_6$	(2)	2.5×10^{7}	0	-371
$CH_3 + O_2 \rightarrow CH_3O_2$	(3)	1×10^{6}	0	-115
$CH_3O_2 \rightarrow CH_3 + O_2$	(4)	1×10^{14}	115	115
$CH_3O_2 + CH_3O_2 \rightarrow 2CH_3O + O_2$	(5)	1×10^{6}	0	-26
$CH_3O + CH_3O \rightarrow CH_3OH + CH_2O$	(6)	1×10^{5}	0	-338
$CH_3O_2 + CH_2O \rightarrow CH_3OOH + CHO$	(7)	1×10^{6}	43	-12
$CH_3OOH \rightarrow CH_3O + OH$	(8)	2×10^{15}	170	184
$CH_2O + OH \rightarrow CHO + H_2O$	(9)	6×10^{6}	0	-135
$CH_3OH + OH \rightarrow CH_2OH + H_2O$	(10)	2×10^{7}	7	-106
$CHO + O_2 \rightarrow CO + HO_2$	(11)	5×10^{7}	8	-128
$CH_3O + O_2 \rightarrow CH_2O + HO_2$	(12)	7×10^{7}	11	-102
$CH_2OH + O_2 \rightarrow CH_2O + HO_2$	(13)	1×10^{6}	7	-60
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	(14)	$1.8 imes 10^6$	0	-177

Rate data are drawn from several sources²³⁻²⁶ without substantial amendment and enthalpies are calculated from heats of formation of the components in each elementary step.

The most important features of this mechanism are (i) the secondary initiation mode (8) *via* methyl hydroperoxide and (ii) the 'thermokinetic switch' *via* the equilibrium

$$CH_3 + O_2 \stackrel{(3)}{\underset{(4)}{\rightleftharpoons}} CH_3O_2$$

that diverts the main course of reaction away from the oxidation route as the temperature increases. To maintain simplicity we have purposely suppressed processes subsidiary to the fundamental kinetic framework; the main effect is to yield an overall stoichiometry and heat output that do not exactly match experiment.

DEVELOPMENT AND TESTS OF THE NKSCHEM NUMERICAL PROGRAM

The program in this study, NKSCHEM, has been developed for application to c.s.t.r. studies consistent with the principles set out above. The main numerical routine used is the NAG Library routine DØ2QBF exploiting Gear's method²⁷ for numerical integration of first-order differential equations exhibiting considerable stiffness. In c.s.t.r. simulations the concentration of a particular species may become negative over a single step of the solver. An appropriate back-step is taken if this occurs and the size of the time step is reduced. In extremely stiff cases it is possible to proceed by setting the negative concentration to zero, corresponding to total depletion of the species concerned.

Reactant pressures, flow rates and vessel temperatures, and the thermal, kinetic and stoichiometric parameters are specified in a single data file. The procedure is simple and maintains generality, enabling factors not explicit in a stoichiometric matrix to

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be included, e.g. the presence of inert gases, which is sometimes necessary experimentally. If the reactants are set to zero initially and the internal temperature set at T_a , the simulated evolution is equivalent to starting up an experiment at a vessel temperature T_a by displacement of an inert gas of the same volume heat capacity and pressure as those of the incoming reactants. Simulations of > 30 s experimental time from start-up to steady-state in the c.s.t.r. (10 residence times) rarely take > 10 s c.p.u. time. Simulations of oscillations for the same duration of experiment can take up to 150 s c.p.u. time, but are often completed more quickly.

TEST OF NKSCHEM AND AN IMPORTANT CONSEQUENCE OF SELF-HEATING

The same rates, extents of reaction and overall exothermicity will be observed in a stationary state under non-isothermal conditions at temperature T as under isothermal conditions where the vessel temperature is given by $T_a = T$. The well characterised KINPAK isothermal program has thus been used to test the validity of results from the NKSCHEM non-isothermal program at the same reactant temperatures. KINPAK²⁸ is a program developed to predict isothermal reaction rates, extents and stoichiometries of chemical processes. In the present study KINPAK has been used to compute the extents of reaction achieved in the c.s.t.r. over the temperature range 450–600 K during isothermal reaction of DTBP in oxygen consistent with kinetic scheme B.

Representative results displayed in fig. 1 refer to the composition DTBP $(7.5 \text{ mol } \%) + O_2$ at a total pressure of 80 Torr and a mean residence time of 3 s. For KINPAK the abscissa T/K signifies the vessel temperature T_a/K . For NKSCHEM the abscissa $T/K = T_a + \Delta T$, and the temperature excesses predicted using this program under non-isothermal conditions are also displayed in fig. 1.

Over the initial part of the reactant temperature range, 450-490 K, the predicted extents of conversion (up to 30%) and product formation are exactly matched. Insofar that KINPAK is a well established program that does not have to cope with the non-linearities and stiffness associated with temperature change, the predictions using NKSCHEM are to be regarded as giving a reliable account of the input data. In the reactant temperature range 490-545 K no stationary state exists under the present non-isothermal conditions: oscillatory behaviour is predicted. Stationary states are established again beyond 545 K; here the conversion of DTBP is virtually complete. Stationary states exist throughout the entire range of temperatures under isothermal conditions.

COMPARISONS BETWEEN NUMERICAL AND EXPERIMENTAL RESULTS

Although the present emphasis is directed principally to an experimental validation of numerical interpretations, from the thermokinetic point of view it also concerns the similarities and differences between DTBP decomposing in the presence or absence of oxygen. We consider numerical predictions and experimental measurements of stationary and oscillatory reactions for the compositions DTBP (10.0 and 16.5 mol%) in N₂ and DTBP (5.0 mol%) in O₂, each at a total pressure of 80 mmHg* and mean residence time (t_{res}) of 3 s in the vessel temperature range 460–540 K.

NUMERICAL COMPUTATION OF TEMPERATURE EXCESS AND OSCILLATORY WAVEFORMS

Fig. 2 shows the stationary-state temperature excesses that are predicted for DTBP decomposing in nitrogen. At the lowest concentration considered (10 mol % DTBP)

* 1 mmHg = $13.5951 \times 980.665 \times 10^{-2}$ Pa.



Fig. 1. Numerically computed fraction of reactant and extent of self-heating as a function of gas temperature for 7.5 mol % DTBP in an excess of oxygen. p = 80 torr, $t_{res} = 3$ s. (----) Fraction of reactant remaining predicted by NKSCHEM and (----) that predicted by KINPAK for isothermal conditions; (-·--) extent of stationary-state self-heating from NKSCHEM. The open segments of (----) and (-·--) mark a region of oscillatory behaviour in non-isothermal circumstances.



Fig. 2. Variations of the extent of self-heating with gas temperature for the exothermic decomposition of 16.5 mol % DTBP in nitrogen (a), and 10 mol % DTBP in nitrogen (b). p = 80 Torr, $t_{res} = 3$ s. Solid lines (----) show computer-predicted values of ΔT , broken lines (----) and points (\bigcirc , 16.5 mol %; \triangle , 10 mol %) mark experimentally measured values. For 16.5 mol % the open section [lines (a)] mark a realm of oscillatory behaviour. No oscillations are observed or predicted at 10 mol % DTBP.

 $\Delta T_{\rm ss}$ rises smoothly and continuously throughout the range $480 < T_{\rm a}/{\rm K} < 540$, reaching 14 K at 540 K. When the proportion of DTBP is increased to 16.5 mol % there is a smooth transition to oscillatory reaction at 501 K (T = 517 K). A stationary state is restored beyond 509 K (T = 528 K), $\Delta T_{\rm ss}$ rising slightly to 22.5 K by $T_{\rm a} = 540$ K. The oscillations occupy a very narrow realm, their amplitudes are small (see fig. 4 later) and their birth and death occur by a finite growth and decay, respectively, of amplitude as $T_{\rm a}$ is raised. The threshold concentration of DTBP at which such oscillations are predicted is 13 mol %.



Fig. 3. Variations of the extent of self-heating with gas temperature for a mixture of 5 mol % DTBP in oxygen. p = 80 Torr, $t_{res} = 3$ s. The solid line (----) shows the computed prediction; the broken line (----) and points (\bullet) show experimentally measured values. The breaks in both curves mark the range of temperatures over which oscillatory behaviour is predicted or measured experimentally.

When 5.0 mol % DTBP reacts in an excess of oxygen the overall pattern is different from either of those described for decomposition in nitrogen (fig. 3). Stationary states exist at the lowest vessel temperatures and ΔT_{ss} rises as T_a is increased. There is then a marked discontinuity in the temperature excess and it heralds the birth of large-amplitude oscillations which exist over a range of vessel temperatures of *ca*. 35 K. There is a gradual diminution in the amplitude and increase in the frequency when T_a is raised (fig. 4); oscillations cease by convergence to a stationary state. The stationary temperature excess is close to its maximum at the upper limit for oscillations and it does not vary much when T_a is increased further. There is no oscillatory realm when the initial concentration of DTBP in oxygen is reduced to below 2.5 mol %.

EXPERIMENTALLY MEASURED STATIONARY TEMPERATURE EXCESSES AND OSCILLATORY REACTION MODES

Measured stationary-state temperature excesses and their variation with vessel temperature during the decomposition of DTBP in nitrogen and in oxygen are given in fig. 2 and 3, respectively. There is excellent agreement in kind with the predicted modes of behaviour at each of the conditions investigated, the quantitative stationary temperature excesses match satisfactorily, and the temperature ranges within which oscillations are predicted are close to those measured experimentally. The distinctions of the two types of oscillatory behaviour are to be seen in the temperature-time records displayed in fig. 5. Measured amplitudes of the oscillations are smaller than those predicted numerically. Oscillatory reaction is not found experimentally when the proportion of DTBP is reduced to below 13 mol % in nitrogen and below 3 mol % in an excess of oxygen.



Fig. 4. Computed oscillatory temperature excesses for (a) 16.5 mol % DTBP in nitrogen and (b) 5 mol % DTBP in oxygen at selected values of T_a . p = 80 Torr, $r_{res} = 3$ s. This comparison shows the contrasting entry to oscillatory behaviour by the presence of oxygen; the system enters the oscillatory realm *via* thermal criticality and a hard excitation. The decomposition in nitrogen (even at 16.5 mol % DTBP) shows a soft excitation into the oscillatory realm.

DISCUSSION

The purpose of this paper is to lay the foundation for thermokinetic phenomena in organic oxidations. There are fundamental links to theories for stationary states, criticality and oscillatory instability in a gaseous, exothermic, first-order reaction under well stirred flowing conditions. We have not aimed at a definitive interpretation of methyl-radical oxidation at low temperatures; nevertheless, it is pertinent to make





Fig. 5. Experimental records of oscillatory modes of reaction for (a) 16.5 mol % DTBP in nitrogen and (b) 5 mol % DTBP in oxygen. p = 80 Torr, $t_{res} = 3$ s. Vessel temperatures are indicated.

some comparisons between theory and experiment and to highlight some of the significant features. Associations to degenerately chain-branched reactions and cool flames are also noted.

TEMPERATURE CHANGE IN A NON-ADIABATIC C.S.T.R.

The agreement between the computed and experimentally measured compositions and vessel temperatures within which oscillations occur is very satisfactory. The discrepancies that exist between the magnitudes of the measured and calculated oscillatory-temperature excursions is attributed principally to our initial premise that

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heat capacities do not change with temperature. The heat-transfer coefficient does not have a very significant effect on the amplitudes of oscillations; in them the rates of heat release are high and adiabatic temperature rises (ΔT_{ad}) may be reached.

During stationary-state reaction heat transfer through the wall is the predominant heat-loss process and the ratio of the mean residence time to the Newtonian cooling time is important. (This ratio is expressed conveniently as $\chi S/fc$.) The highest possible stationary temperature excess that can be achieved is given by^{19, 29}

$$\Delta T_{\rm ss}(\rm max) = \Delta T(\rm ad)/(1 + \chi S/fc) \tag{III}$$

and is 0.05 $\Delta T(ad)$ in the present experimental conditions. The adiabatic temperature excess [$\Delta T(ad)$] is obtained from the quotient

(overall exothermicity per mole DTBP) (inlet concentration of DTBP) volumetric heat capacity

Since for the decomposition of DTBP diluted 10-fold by nitrogen $\Delta T(ad) = 310$ K, $\Delta T_{ss}(max)$ cannot exceed 15 K in our c.s.t.r. at a mean residence time of 3 s. Both experimental and numerical values are in good agreement with this. For decomposition of DTBP (5 mol %) in oxygen the overall, simplified stoichiometry¹¹ derived from that measured by Williams *et al.*¹³ at 550 K is

$$DTBP + 9O_2 \rightarrow 2(CH_3)_2CO + 1.45CH_3OH + 0.55CO + 0.1H_2 + 8O_2$$

$$\Delta H_{298}^{\ominus} = -438 \text{ kJ mol}^{-1}$$
(14)

from which $\Delta T(ad) = 806$ K and so $\Delta T_{ss}(max) = 40$ K. The numerical value for $\Delta T_{ss}(max)$ is roughly in accord with this but the experimental value is higher, probably because of different stoichiometry and exothermicity at higher temperatures than that specified in reaction (14). There are no other experimental data available to offer a more satisfactory comparison.

OSCILLATORY REACTION MODES AND THE NATURE OF TRANSITIONS INTO THEM

Sustained oscillatory reaction in a first-order, exothermic reaction under nonadiabatic conditions is possible when the criterion

$$B = \frac{\Delta T(\text{ad}) E}{RT_{\text{a}}^2} > (t_{\text{ch}} + t_{\text{res}}) \left(\frac{2}{t_{\text{res}}} + \frac{1}{t_{\text{ch}}} + \frac{1}{t_{\text{N}}}\right)$$
(IV)

is satisfied.³⁰ The term on the left-hand side, the dimensionless adiabatic temperature excess (*B*), may be established experimentally from the minimum proportion of DTBP and the reactant temperature at which oscillations are found. For 13 mol % DTBP decomposing in nitrogen at 510 K, B = 26. *B* also equals 26 for 2.5 mol % DTBP decomposing in an excess of oxygen, in accord with the simplified stoichiometry of reaction (14). Each of these values corresponds to the limiting compositions found in the present study. The term on the right-hand side of eqn (IV) incorporates each of the characteristic time responses for the system: these are the residence time (t_{res}), the Newtonian cooling time ($t_N = cV/\chi S$) and chemical time [$t_{ch} = 1/k(T)$]. For DTBP reacting at 510 K under a mean residence time of 3 s in our vessel they combine to yield the numerical value in broad agreement with the present results.

Whether or not thermal criticality, and hence 'hard excitation' into the oscillatory reaction, occurs is determined by the condition

$$B^* = \Delta T_{\rm ss}(\max) E/RT_{\rm a}^2 > 4 + (RT/E). \tag{V}$$

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Since, from eqn (III)

$$B^* = B/(1 + fc/\chi S)$$

oscillations [guaranteed by eqn (IV)] may be entered continuously or discontinuously (see for example fig. 5) according to the ratio of the Newtonian cooling time to the mean residence time (= $fc/\chi S$). Changes of flow rate have been found to give these alternative transitions.²⁹ In the present study the different responses of 16.5 mol % DTBP in N₂ and 5 mol % DTBP in O₂ are brought about by a change of exothermicity. Thus $B^* < 3$ for 16.5 mol % DTBP in nitrogen at 510 K. The augmentation of heat output due to the presence of oxygen is sufficient to give $B^* > 4$ even when the concentration of DTBP is much reduced.

REACTION MECHANISMS AND THERMOKINETIC IMPLICATIONS

The quantitative distinctions between the decomposition of DTBP in the presence of oxygen or nitrogen that are reported here may be accounted for solely on the basis of an enhanced exothermicity of reaction when oxygen is present. Chain branching does not have to be invoked.

Although secondary initiation via methyl hydroperoxide decomposition is included, it does not lead to degenerate branching. A degenerately branched reaction would be brought about only if we admit generation of methyl hydroperoxide via H-atom abstraction by CH_3O_2 from DTBP itself. We do not include this step because its activation energy is high ($E > 60 \text{ kJ mol}^{-1}$) and test insertions show no measurable effect. In fact the predicted behaviour is the same qualitatively and not much modified quantitatively if kinetic scheme B is reduced to steps (1)–(6). Further paring-down of the scheme by suppression of the dissociation step (4), $CH_3O_2 \rightarrow CH_3+O_2$, enhances temperature changes when T_a is > ca. 530 K. This is, of course, a matter of degree and is due to enhancement of the overall exothermicity by forcing reaction in the presence of oxygen to the oxidation products $[CH_2O+CH_3OH]$ in the simplest scheme, reactions (1)–(6)]. When the equilibrium

$$CH_3 + O_2 \stackrel{(3)}{\underset{(4)}{\Longrightarrow}} CH_3O_2$$

is established, C_2H_6 may become a final product even in the presence of oxygen and the route to its formation releases less heat. The shift of equilibrium explains the slight fall in ΔT_{ss} at $T_a > 530$ K (fig. 2).

Ballinger and Ryason¹⁴ reported the existence of a stabilised 'cool flame' of DTBP on a flat-flame burner. It is our belief that they stabilised a normal near-adiabatic combustion wave, not a 'cool flame' in the sense associated with hydrocarbon oxidation. The temperature was not reported, but with modest exothermicity $(\Delta H_{800}^{\odot} = -480 \text{ kJ mol}^{-1})$ and quite high product heat capacities it may remain sufficiently low that the only light emissions are those commonly associated with 'cool flames' of hydrocarbons (CH₂O^{*}); Williams *et al.*¹³ have established DTBP+O₂ as an excellent source of CH₂O^{*}.

Fig. 1 demonstrates unequivocally that the existence of non-isothermal oscillatory phenomena in a c.s.t.r. is due to a subtle balance between the rates of heat release and heat loss *via* the vessel walls. We may take a step, in principle, to the realm of oscillatory cool flames. When reactions of the kind

$$RH + CH_3O_2 \rightarrow CH_3O_2H + R$$
 ($E < 50 \text{ kJ mol}^{-1}$)

$$RH + X \rightarrow R + HX$$

and

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where RH is deemed to be an additional fuel with a labile hydrogen atom and, for mechanistic simplicity leading to $R = CH_{3}$, are added to reactions (1)-(8) in kinetic scheme B, the predicted behaviour is significantly modified. Not only does a region of substantial negative temperature coefficient evolve in the overall dependence of reaction rate on temperature in isothermal reactions, but also, in non-isothermal circumstances, oscillatory 'cool flame' phenomena are now predicted. Their major distinction from the oscillatory modes reported here is that not all of the fuel (RH) is consumed during the course of each cycle.¹⁶ Neither of these features is found if reaction (4) is suppressed.

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