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AUTO-IGNITION TEMPERATURES OF BINARY MIXTURES OF ALKANES IN A CLOSED VESSEL: COMPARISONS BETWEEN EXPERIMENTAL MEASUREMENTS AND NUMERICAL PREDICTIONS

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Abstract

Autoignition temperatures of the binary mixtures methane + ethane and methane + butane in air were measured at atmospheric pressure in a 0.56 dm^3 spherical reaction vessel. The method used followed that for standard ASTM and BS tests for gaseous fuels. Fixed proportions by volume of the total fuel in air were studied, which corresponded at the extreme of each composition range to the equivalence ratios for methane, ethane and butane of $\phi = 0.93$, 1.63 and 3.04 respectively. Supplementary experiments were carried out on butane alone under the same conditions, in which its proportion was varied in the equivalence range $0 < \phi < 3.04$.

The autoignition of methane was sensitized by ethane most strongly when the ethane was present at up to 10% of the total fuel. The autoignition temperature ($T_{a,cr}$) was reduced by 40 K with respect to that for pure methane ($T_{a,cr} = 900$ K). There was an even stronger sensitization by similar proportions of butane added to methane, such that $T_{a,cr}$ decreased to 810 K. In neither case were the effects linearly dependent on the proportion of additive.

There was an additional sensitive region when butane was present in the proportion 0.5 - 0.7 of the methane/butane mixture, at which $T_{a,cr}$ fell sharply by 50 K over this limited composition range. Remarkably, except at the leanest mixtures($\phi_{butane} < 0.5$), the autoignition temperatures of compositions containing butane alone matched very closely the autoignition temperatures of the equivalent methane/ butane mixtures. We believe that this is a new and very important observation in relation to the understanding and interpretation of combustion hazards involving mixtures of fuels.

Numerical simulations of spontaneous ignition based on a comprehensive kinetic model, which included reactions that are important in hydrocarbon oxidation at temperatures below 850 K (such as RO_2 isomerisations), yielded predicted autoignition temperatures that were in very satisfactory agreement with the measured values throughout all ranges of composition. More importantly, the same regions of sensitivity were distinguished. We discuss the kinetic interactions that were revealed by these numerical studies to be important in controlling the autoignition temperature. The origins of the limited reactivity of methane when it undergoes co-oxidation with butane are identitied.

Introduction

Closed vessel measurements under specified conditions at atmospheric pressure are commonly used to characterise the autoignition temperature of different fuels in air (*e.g.* BS 4056 and IEC standard 79-4 (1975), or ASTM-E 659-78). The purpose is to define the lowest possible temperature at which spontaneous ignition may take place in that particular vessel. Such data serve as a basis for comparing reactivities of different fuels. The spontaneous ignition temperature will not be exactly the same under different conditions (*e.g.* vessel size or shape, and reactant pressure or composition).

The definitive texts, up to *ca* 1960, on the spontaneous ignition of gaseous and liquid fuels are probably the books by Mullins [1], by Mullins and Penner [2] and by Sokolik [3]. Whilst these publications give considerable background and empirical assessment of data, they seem not to address how to interpret the effects of scale or of changes of other parameters on the autoignition temperature. Morever, despite the emergence of rigorous theoretical foundations for the interpretation of spontaneous ignition of hydrocarbon and related substances [4,5] and the increasing quantitative knowledge of the kinetic repurcussions of different isomeric structures of fuels [6], there does not seem to have been a concerted effort to develop fundamental, thermokinetic methods for the quantitative application of the data from standard tests, such as is required for ensuring industrial safety. Although serving the primary purpose of interpretation of the experimental results obtained in the present work, the numerical analysis described in this paper constitutes a contribution towards the quantitative prediction of spontaneous ignition hazards of organic gases and vapours in different circumstances.

The autoignition temperatures of mixtures of hydrocarbons and related materials cannot be interpreted directly from the autoignition temperatures of pure components on the basis of *e.g.*

proportionate mass, partial pressure, overall exothermicity for complete combustion, or any other simple physicochemical basis. The "sensitizing" of a fuel (such as methane) by one or more of greater reactivity than it (such as the higher alkanes) originates predominantly in kinetic interactions [7]. Experimental measurements are a prerequisite for reliable quantitative data appropriate to complex mixtures, and for developing predictive models.

The experiments reported here are concerned with the variation of autoignition temperatures of the binary alkane mixtures methane + ethane and methane + butane. These compositions focus on the important distinctions in spontaneous ignition behaviour that emerge when elementary reactions involving the isomerisation of alkylperoxy radicals become possible. Additional experiments were also carried out on varying compositions involving butane alone, which provided some very important and interesting comparisons and contrasts with the behaviour of the binary methane + butane mixtures. The procedures adopted to measure autoignition temperatures were very similar to those specified for gaseous samples in BS 4056 and IEC Standard 79-4 (1975). A numerical analysis based on a comprehensive kinetic model was used to interpret the experimental results, and the most important conclusions are discussed here.

Apparatus, Experimental Procedures and Materials

Auto-ignition temperatures were determined in a spherical reaction vessel (Pyrex glass, 0.56 dm^3). The reaction vessel was located in the cavity (8 dm^3, cube) of a recirculating air oven. Thermal insulation was achieved by firebrick walls (10 cm thick) and a layer of Rockwool above the lid. The vessel was suspended from the oven lid so that it was accessible for gaseous fuel injection. A glass wool plug was inserted in the neck of the vessel to minimise reactant diffusion and heat loss by convection from the vessel. The chamber was heated by an element that was located on the sides of the void. The temperature was controlled from a proportional power supply, by reference to a platinum resistance sensor located in the air-space. The external surface temperature of the vessel was measured at four points by use of chromel-alumel thermocouples referred to a junction maintained at 273 K in an ice/water bath. The output from each thermocouple pair was measured by a digital voltmeter (± 0.01 mV). The variation of the surface temperature was minimized (± 3 K) by surrounding the vessel with aluminium foil. Temperatures of up to *ca.* 900 K were accessible in this apparatus.

Pure components or their mixtures were injected into the vessel from a filled hypodermic syringe (50 cm^3). Experiments involving varying amounts of butane alone were carried out in a similar manner, the syringe being filled with an appropriate mixture of butane and air. A long, fine-bore needle was used in order to cause a high velocity of injection of the fuel and so ensure as good mixing throughout the vessel as could be achieved by rapid, manual operation of the syringe. The compositions achieved in the vessel were assumed to correspond to the mixture that would have been obtained by displacement of 50 cm^3 of air from the vessel on admission of the reactants. The reaction vessel was purged with air after each experiment, and the temperature was allowed to stabilize after the purging process, or whenever a temperature change was made, before a subsequent experiment was carried out. All experiments were carried out at atmospheric pressure. Gaseous reactants (99.9%) were taken directly from cylinders without further purification.

The events taking place were monitored by a fine Chromel/Alumel thermocouple (0.1 mm dia.) located within the reactant volume. Its reference junction was located on the external surface of the vessel so that the temperature rise that occurred during reaction was measured. The signal was recorded on a chart recorder. At all reactant compositions studied there was a clear discontinuity between "slow oxidation" and ignition as the vessel temperature was raised, and from which the critical vessel temperature, or autoignition temperature, of a given composition was established. Ignition was identified from the temperature record as a sharp peak following a brief delay. The temperature traces obtained during an ignition were not a fully quantitative record because the combined response of the thermocouple and recorder was slow relative to the rate of temperature change in ignition.

Numerical Analysis and Kinetic models

The numerical modelling calculations were carried out using the HCT program [8], which solves the coupled non-linear differential equations for conservation of mass, momentum, energy and each chemical species in finite difference form. The reaction mechanism included more than 700 elementary chemical reactions with their reverse steps. Owing to space limitations, the entire mechanism cannot be reproduced here, but it is included in a recent publication that is conveniently available [9]. This reaction mechanism includes submechanisms for oxidation of C_1 - C_4 hydrocarbon species, validated against a variety of experimental data for ignition and combustion environments [10-12]. These mechanisms not only relate to temperature ranges appropriate for flames and shock tubes ($T \geq 1000$ K), but also they include the mechanisms governed by formation and consumption of alkylperoxy radical species that are appropriate to lower temperature conditions.

Essential features of the low temperature kinetic mechanisms for n-butane include distinctions between rates of abstraction of H atoms from primary and secondary sites in n-butane, and individual values of the equilibrium constants for addition of molecular oxygen to each isomeric structure of the butyl radical. The two distinct butylperoxy radicals so formed may react with other species to produce butyl hydroperoxide (which can then decompose to butoxyl and hydroxyl radicals) or they may isomerize *via* internal H atom abstraction. The rates of internal H atom abstraction depend primarily on the type of C-H bond broken and the ring strain energy of the intermediate transition state [13-15]. There are, therefore, six distinct isomeric forms of the C_4H_8OOH radical, each of which can decompose thermally and produce hydroxyl radicals and a cyclic ether compound. The C_4H_8OOH radicals in which the free radical site is adjacent to the carbon atom at which peroxy linkage is located may also decompose *via* fission of a C-O bond to produce butene and a hydroperoxy radical. Rates and equilibrium constants for these reaction paths have been assembled from recent work [13-17]. Supplementary steps are also taken into account in which a further oxygen molecule may add to the C_4H_8OOH radicals to produce dihydroperoxy species. It seems not to be generally recognized that the formation of dihydroperoxides species was first identified in 1961, by Cartlidge and Tipper [18].

Spatial uniformity of temperature and concentration of the reactants and products were assumed. The overall rate of heat release was summed from the products of reaction rate and exothermicity of each elementary step. The heat loss rate was calculated on the basis of a Newtonian cooling time of 0.5 - 0.7 s over the range of conditions studied. This parameter characterises the timescale of heat transer from the reacting gas to the vessel walls; its magnitude is comparable with values measure recently in unstirred gases at atmospheric pressure [19], and is equivalent to a heat transfer coefficient (χ) under well-stirred conditions of 14 W m^{-2} K^{-1}. No experimental values were available for the heat transfer coefficient from the present experiments; the magnitude adopted was obtained by matching the calculated ignition temperature for the composition $0.5\ CH_4 + 0.5\ C_2H_6 + 2.14\ O_2 + 8.05\ N_2$ to that measured experimentally.

Experimental Results and Their Numerical Simulation

The volume of 50 cm^3 fuel injected into the reaction vessel gave rise to the overall composition 1 RH + 2.14 O_2 + 8.05 N_2. For methane, this corresponded to a mixture (equivalence ratio $\phi = 0.93$) that was lean with respect to the stoichiometric mixture, for which $\phi = 1$. When 50 cm^3 of ethane was injected the richer mixture, $\phi = 1.63$, was obtained. The corresponding mixture containing butane was equivalent to $\phi = 3.04$.

The experimental results were obtained from very many individual experiments to locate the critical transition from "slow combustion" to ignition in each mixture studied (± 3 K). A typical pair of temperature-time records for marginally subcritical and supercritical experiments are shown in Fig. 1. The numerical distinctions between subcritical reaction and ignition throughout all composition ranges are also very clear and are extremely sensitive to the vessel temperature and reactant composition (Fig. 2). In general the calculated ignition delay times close to criticality were comparable with the experimental values, but we cannot expect quantitative agreement because the supplementary experimental artifacts of reactant injection, mixing and heating to the vessel temperature were not taken into account in the simulations.

The variation of minimum ignition temperature at atmospheric pressure in the spherical vessel for the pure components and their binary mixtures are shown in Fig. 3. The minimum vessel temperature for ignition of pure methane was found experimentally to be 900 K, with a corresponding numerical model value of 883 K. For pure ethane, the experimental minimum autoignition temperature was found to be 810 K, corresponding to a model value of 787 K, and the experimental value for n-butane was 660 K, with a model value of 637 K. A calculated value for the autoignition temperature of propane (757 K) may also be compared with the isolated experimental result $T_{a,cr}$ = 775 ±3 K, at $\phi = 2.34$, under the present experimental conditions.

In binary mixtures of methane and ethane, the greatest sensitivity of the autoignition temperature to variations in composition was observed for mixtures in which the fuel fraction of ethane was less than about 0.1 (by volume). The binary mixture of methane and n-butane also showed a marked sensitivity when the percentage of n-butane was less than 10% of the fuel. In the case of binary methane/n-butane mixtures, another region of extreme ignition sensitivity was measured in mixtures containing between 0.50 and 0.70 n-butane in the fuel (Fig. 3, curve B). A very similar transition was predicted numerically in the butane fraction range 0.60-0.75, over which range the calculated critical ignition temperature fell rapidly by about 100 K (Fig. 3, curve B'). In both the experimental and numerical results, when the butane proportion exceeded 0.75 of the methane + butane mixture, the ignition temperature was already found to be close to that for butane alone. The kinetic interpretation of this complex behaviour is discussed below.

The limiting composition for n-butane added to methane consists of a fuel mixture with 100% n-butane and 0% methane. This is equivalent to a mixture of n-butane and air with a very rich equivalence of $\phi = 3.04$ in the present experimental conditions. We carried out an additional series of ignition studies, both experimentally and computationally, in which the initial n-butane concentration was systematically reduced from this limiting value. These n-butane/air mixtures may be compared with the binary methane/n-butane mixtures by considering only the ratio of n-butane to oxygen in both cases (for example, $0.5\ CH_4 + 0.5\ n\text{-}C_4H_{10} + 2.14\ O_2 + 8.05\ N_2$ and $0.5\ n\text{-}C_4H_{10} + 2.14\ O_2 + 8.05\ N_2$). The results are also summarized as curves C and C' in Fig. 3.

Overall, we found both experimentally and numerically that the critical ignition temperature for comparable compositions were nearly identical over much of the range of initial n-butane concentration (Fig. 3). In the richest butane mixtures, down to the fraction 0.70 (ϕ = 2.13), the critical ignition temperature was relatively constant. In the range of butane concentrations corresponding to the fractions 0.70 - 0.50 (ϕ = 2.13- 1.52) there was an increase in the measured autoignition temperatures, and a still more marked change in the calculated critical vessel temperatures. For n-butane fractions below this range, and down to *ca.* about 0.2 (corresponding to ϕ = 0.61), the critical ignition temperature increased only gradually. However, at still lower fractions of n-butane (ϕ < 0.61), the binary mixtures exhibited the lower values of the critical ignition temperature, owing primarily to the fact that the very lean n-butane/air mixtures could no longer sustain as readily as the binary methane/n-butane mixtures a sufficient heat release rate to cause thermal runaway. This transition also occurred in the experimental results but at a weaker butane/air mixture. Nevertheless, over much of the range, both the experimental and model results revealed that the incorporation of methane with n-butane/air mixtures had very little influence on the overall rate of heat release under the present conditions.

There are important supplementary features of the temperature-time record preceding ignition. Thus, for 0.5 CH_4 + 0.5 n-C_4H_{10} at a vessel temperature of 768 K, which is above the critical ignition temperature by about 2 K, ignition is predicted to take place after 1.19 sec, but preceded by a marked initial rise and decay in reactant temperature(Fig. 4, curve A). Curve B in Fig. 4 represents the results at the same temperature of 768 K for the related mixture containing only n-C_4H_{10}. The features are qualitatively identical but the computed ignition time of 0.97 sec shows that the inclusion of methane actually retards the overall reaction rate during the ignition delay period at these conditions. Subcritical reaction is predicted for the n-butane/air mixture at an initial temperature of 765 K (Fig. 4, curve C). We note, in parenthesis, that the predicted supercritical temperature-time profiles represent a cool flame preceding the ignition, characteristic of the "delayed ignitions" that were reported by Bardwell [20] in the combustion of butane/oxygen mixtures of similar equivalence ratio to the present mixtures. The phenomenon belongs to the general classification of multiple-stage ignition phenomena [21].

Discussion

Although the present experiments were directed to a furthering of knowledge of autoignition temperatures as measured by prescribed test procedures, the results and their interpretation have a much wider significance in the context of the general understanding of interactions between hydrocarbon fuels leading to spontaneous ignition. Certainly, the only viable route forward for the quantitative interpretation of hazards in different conditions, in single component or mixed fuels, is the establishment of numerical methods in which thermokinetic models (either in reduced form [9,22-24] or very detailed, as here) are used to explore the appropriate interactions between the physics and the chemistry in given circumstances. Empirical relationships, as presented in earlier work [1-3], are untenable insofar that their application cannot be justifiably extended beyond the bounds of the data used for their derivation.

Hitherto, virtually all numerical predictions of spontaneous ignition based on complex chemical models assume spatial uniformity of temperature and concentration (*i.e.* zero dimensional models). There are very few experimental tests that attempt to reproduce such conditions by forced mixing [5,25,26]. A well-mixed condition may be approached if sufficiently high Reynolds numbers prevail within the reactants [19,25]. Part of the discrepancy between the experimental and numerical results presented here no doubt arises from the non-idealities of the experimental study, and their existence underlines the need for as much attention to be paid to the interpretation of heat and mass transfer as is currently being paid to detailed kinetics if general applications to the prediction of combustion hazards are to be successful. Validation against as much and as varied experimental data as possible is essential in these early stages of development.

Reid et al[19] showed that the minimum autoignition temperature of 99% methane (885 K) is achieved at $\phi = 0.7$. The value (900 K) for the autoignition temperature at $\phi = 0.94$ in our spherical vessel (S/V = 0.58 cm^{-1}) is consistent with their value (890 K) for that composition obtained under unstirred conditions in a spherical vessel (800 cm^3, S/V = 0.52 cm^{-1}). Our minimum autoignition temperature for butane (660 K) corresponds quite well with that (681 K) given by Scott *et al*[27] who used the smaller vessel size as specified in the ASTM method (conical vessel, 125 cm^3). The difference may be attributed principally to the difference in vessel size and shape, and shows just how limited is the application of these data when not supported by interpretations based on fundamental principles.

Although there is some discrepancy between the experimental and numerical interpretations of autoignition temperatures of methane + ethane mixtures, there is common accord that the variation through a range of compositions is not linear. Moreover, an approximation to linearity between the auto-ignition temperatures for each of the reactants alone would yield an overestimate of the autoignition temperature of a given mixture of the two components. Such a procedure cannot, therefore, be supported as a basis for hazard assessment in, for example, natural gas compositions in which ethane may be a significant component. The same remarks apply to the autoignition temperature of methane containing small proportions of n-butane (<10% by volume).

From the kinetic modelling analysis, it is clear that the size and structure of the various fuel molecules influence the autoignition process in several interconnected ways. The concept of the "ceiling temperature" [6,28], at which the alkyl and alkylperoxy radicals in

$$R + O_2 = RO_2$$

have equal concentrations is central to the understanding of the distinctions between ignition of methane, ethane, and n-butane.

At temperatures above the ceiling temperature, which for these experimental conditions is between 800 and 850 K, the equilibrium above lies to the left side for the methyl, ethyl, and primary and secondary butyl radicals. Above 800 K, these radicals react predominantly with HO_2 and other radical species,and are also directly oxidized. Furthermore, except for the methyl radicals, the alkyl radicals decompose thermally, producing small radical species (such as H atoms) which accelerate the overall rate of ignition [11]. This additional route for radical production is the cause of the sensitization observed in Fig. 3 for mixtures in which small fractions of either ethane or n-butane are present in methane. The same phenomenon has been shown [7] to cause similar sensitization of methane by ethane or propane in shock tube ignition experiments.

The kinetic model also shows how n-butane can be more effective than ethane as a sensitizer of methane ignition. At the temperatures encountered in the present experiments, abstraction of H atoms from secondary sites in hydrocarbon fuels is considerably faster than abstraction from primary sites. Inclusion of n-butane provides access to secondary sites, so the radical pool required for a sufficiently rapid oxidation and heat release rate for ignition to occur can be supplied by n-butane at a temperature somewhat lower than is necessary in either methane or ethane oxidation. Experiments being planned for the future, in which autoignition of methane-propane mixtures will be examined, should lie between the current methane-ethane and methane-butane cases, since propane provides H atoms at secondary sites, but only half the number available in n-butane.

Below about 800 K, the concentrations of CH_3O_2, $C_2H_5O_2$, $pC_4H_9O_2$ and $sC_4H_9O_2$ become significantly larger than the concentrations of CH_3, C_2H_5, pC_4H_9 and sC_4H_9, respectively. For all of these RO_2 species, reactions of the type

$$R'H + RO_2 = R' + ROOH$$

followed by

$$ROOH = RO + OH$$

become important sources of OH radicals. However, only in the case of n-butane and the butylperoxy radicals does the additional reaction path of alkylperoxy radical isomerization become rapid. In the case of CH_3O_2, no internal H atom transfer is possible. For ethane, this process is very slow, since the ring-like transition state involves a considerable strain energy barrier, and the internal H atom transfer involves breaking a primary C-H bond. In distinct contrast, relatively strain-free internal H atom transfers, many involving abstraction of H atoms from secondary sites, are possible in the case of butylperoxy radicals. It is the emergence of these paths, and the associated enhancement of the heat release rate, that is found to be responsible for the precipitous decrease in autoignition temperature for curves B' and C' in Fig. 3 at n-butane fractions of 0.6 - 0.8. Computationally, when the alkylperoxy radical isomerization reactions were eliminated artificially from the reaction mechanism, this sudden decrease in ignition temperature was suppressed entirely.

Furthermore, the location of this transitional region was found to depend on the values chosen for the equilibrium constants for the addition reactions of O_2 to the two possible butyl radicals. The equilibrium constants for O_2 addition at primary and secondary sites have different temperature dependences, and we have employed recent experimental results of Slagle *et al* [16, 17] for the present model. When the equilibrium constants were changed by a factor of five towards dissociation, the sharp decrease in ignition temperature was not observed computationally. A similar variation by a factor of two results in a movement of the transition region to an n-butane fraction of about 0.8 - 0.9. Based on these computational results, a similar feature would be expected for any fuel in which rates of alkylperoxy radical isomerisation was significant. However, there appears not to be any special importance to be attached to the formation and decomposition of dihydroperoxides in the systems investigated here.

The present computational results demonstrate that the size of the fuel molecule plays an important part in determining the rate of heat release by controlling the extent to which RO_2 isomerization is significant. Fuel structure plays an important part by its role in the rates of RO_2 isomerization (through the strain energy barriers, which are greater in more compact molecules) and by the mixture of primary, secondary and, by implication, tertiary C-H bonds.

It is clear from the numerical predictions of the autoignition temperatures that the remarkable correspondence between the minimum temperatures for the spontaneous ignition of methane/butane mixtures and the analogous butane compositions arises from a domination of butyl/butylperoxy radical chemistry also in the binary fuel mixtures. As is shown in Fig. 4, methane plays only a small part in the onset of ignition, since throughout the induction period leading to ignition of $0.5\ CH_4 + 0.5\ C_4H_{10} + 2.14\ O_2 + 8.05\ N_2$, the extent of consumption of methane is extremely small(< 2.5%), whereas that of butane is very high (> 75%). The principal effect of methane is to compete for OH radicals, and thus induce inhibitory characteristics which not only increase the ignition delay relative to that of butane alone, but also cause the region of high sensitivity of the autoignition temperature to the proportion of butane present to be displaced to slightly higher concentrations of butane.

When ignition itself takes place, however, the combustion of methane/butane remains extremely vigorous throughout the range of compositions. By contrast, ignition of the butane alone occurs with a decreasing vigour as the proportion of butane is reduced, and although criticality is still observed, the ignition itself becomes very feeble in lean compositions.

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Legends to Figures

Figure 1. Experimental ΔT-time profiles in a butane/air mixture at $\phi = 3.03$ showing the distinction between ignition (at $T_a = 675$ K) and exothermic subcritical reaction (at $T_a = 670$ K). The initial fall in temperature is associated with the injection of cold reactants to the hot vessel.

Figure 2. Computed temperature -time profiles in $0.2\ CH_4 + 0.8\ C_4H_{10} + 2.14\ O_2 + 8.05\ N_2$ showing the distinction between ignition (at $T_a = 868$ K) and exothermic subcritical reaction (at $T_a = 866$ K).

Figure 3. The minimum vessel temperatures ($T_{a,cr}$) for spontaneous ignition of various compositions plotted as a function of the fraction of ethane or butane injected into the reaction vessel from a 50 cm^3 syringe. The experimental and numerically computed results are shown for each composition, as follows. A (I), methane/butane (experimental); A' (o), methane/butane (computed); B (I), methane/butane (experimental); B' (▵), methane/butane (computed); C (•), butane (experimental); C' (∇), butane (computed).

Figure 4. Computed temperature and composition profiles in butane + air and in methane/butane + air mixtures, as follows. Temperature change: A, $0.5\ CH_4 + 0.5\ C_4H_{10} + 2.14\ O_2 + 8.05\ N_2$ at $T_a = 768$ K; B, $0.5\ C_4H_{10} + 2.14\ O_2 + 8.05\ N_2$ at $T_a = 768$ K; C, $0.5\ C_4H_{10} + 2.14\ O_2 + 8.05\ N_2$ at $T_a = 765$ K. Partial pressures: D, CH_4 at conditions corresponding to A; E, C_4H_{10} at conditions corresponding to A.

FIG 1

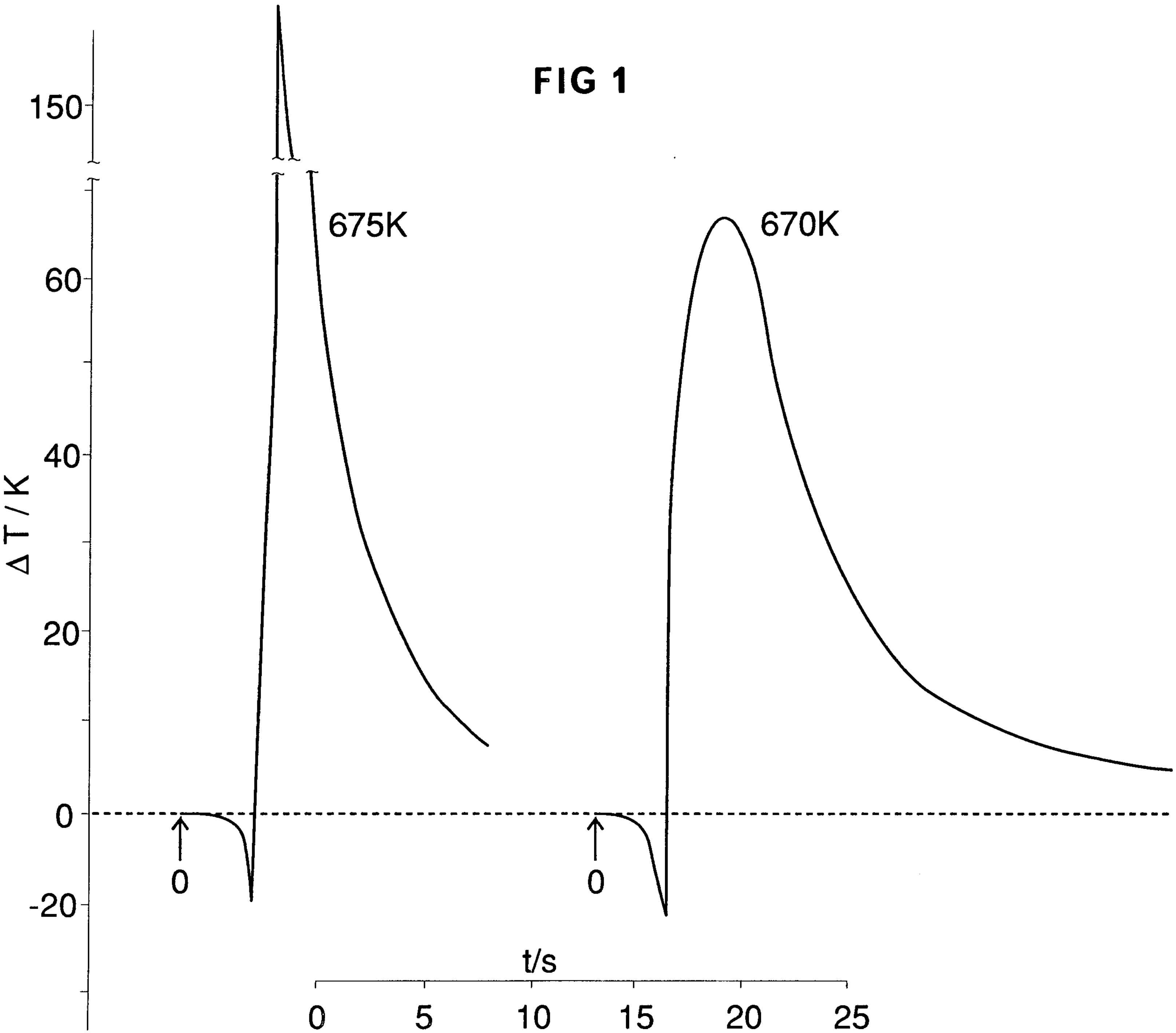


FIG 2

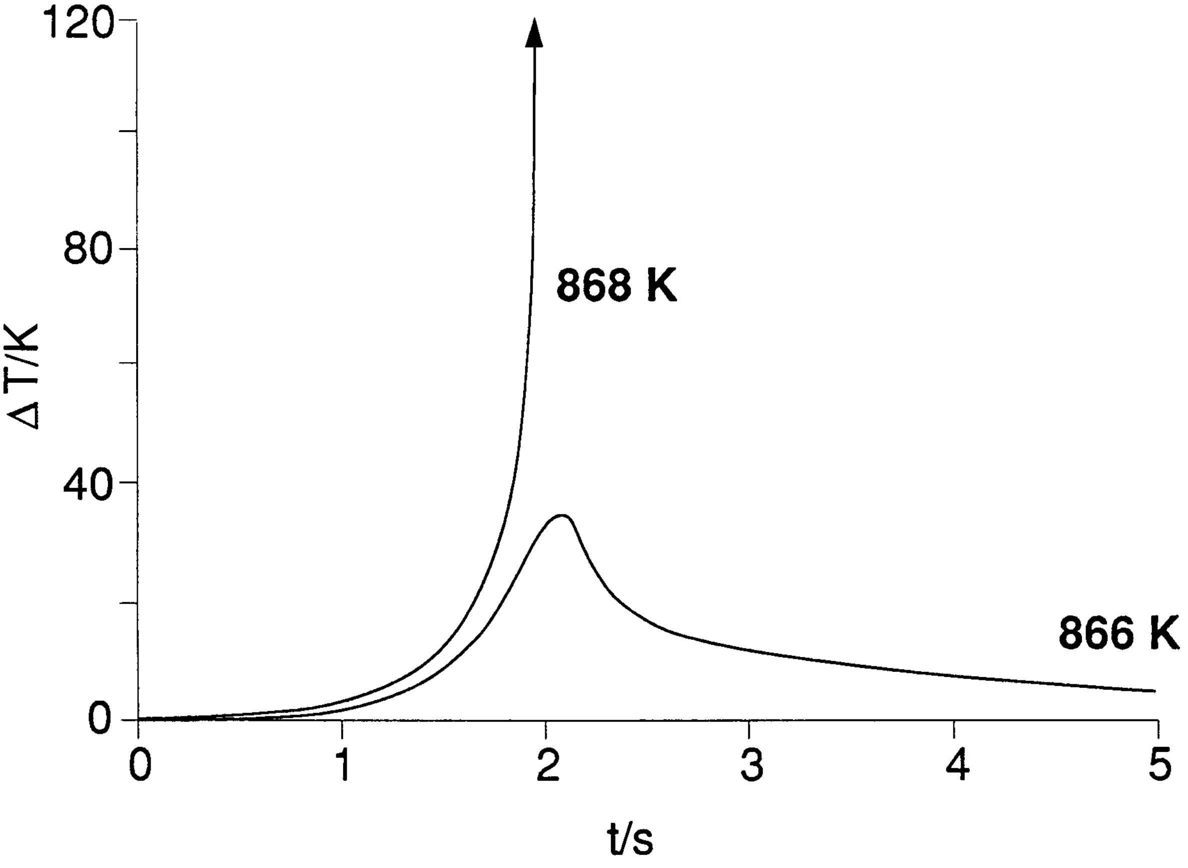
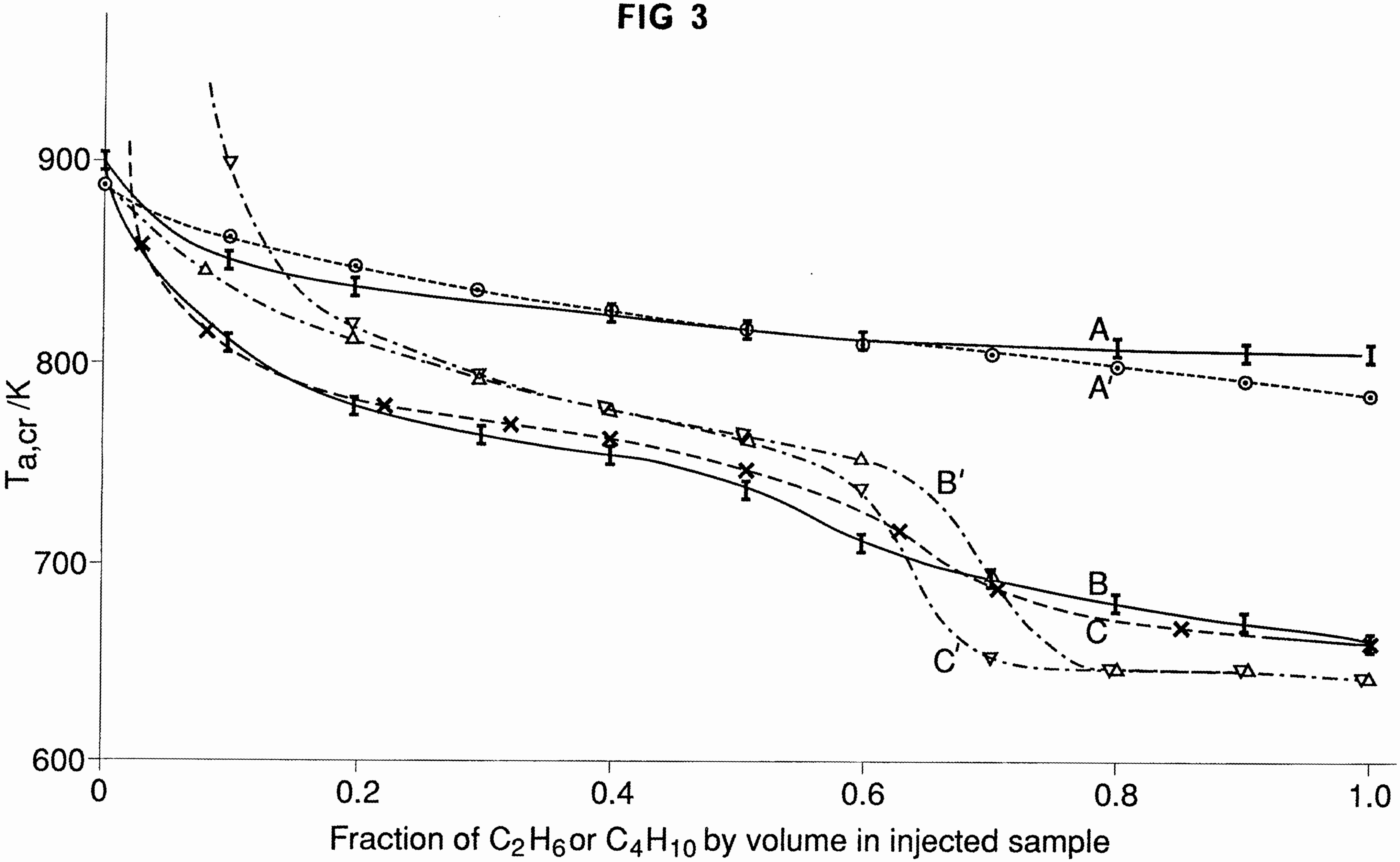
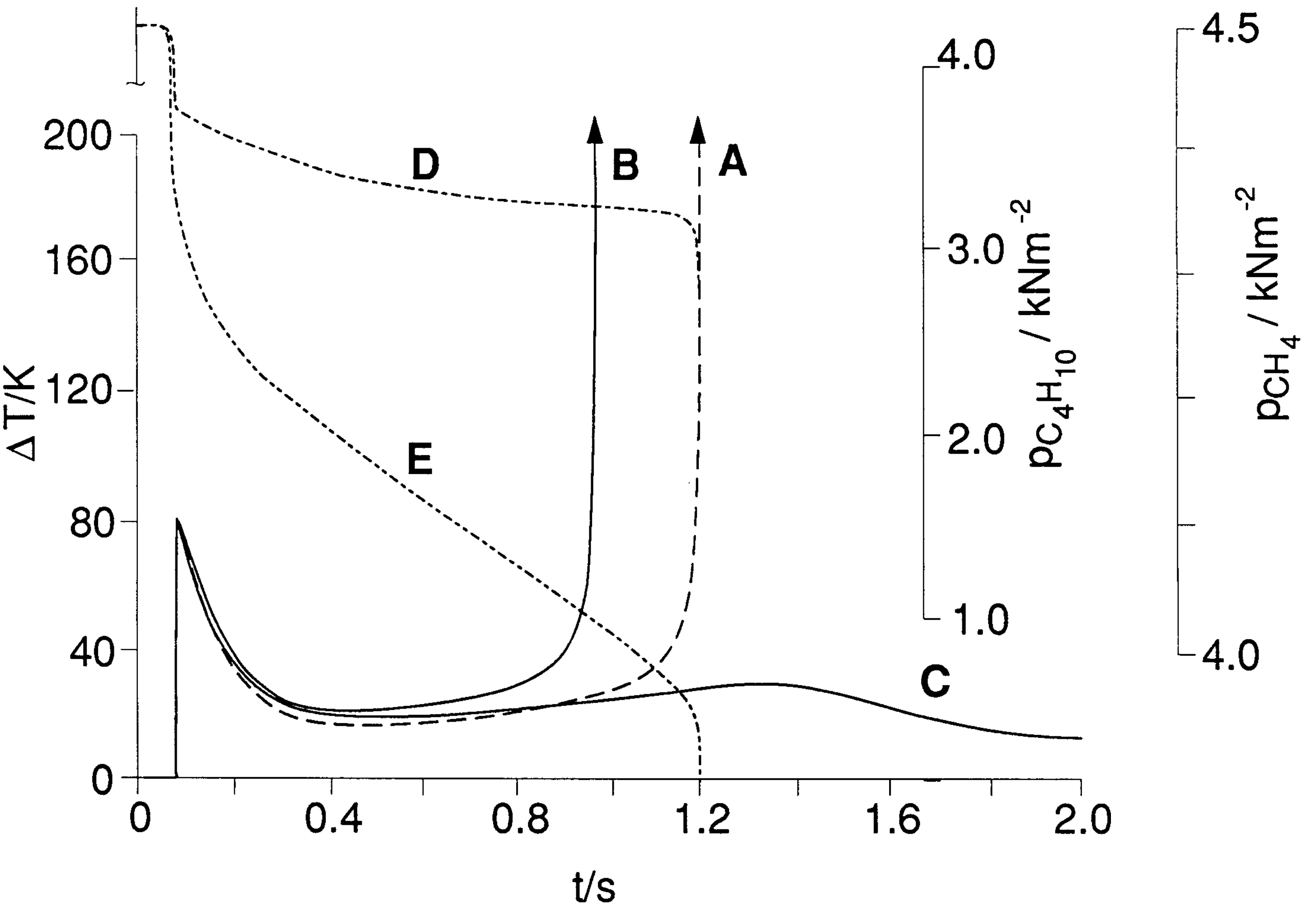


FIG 3



900
800
700
600
Ta,cr /K
0
0.2
0.4
0.6
0.8
1.0
Fraction of C2H6 or C4H10 by volume in injected sample
A
A'
B
B'
C
C'

FIG 4



ΔT/K
200
160
120
80
40
0
0
0.4
0.8
1.2
1.6
2.0
t/s
D
B
A
E
C
4.0
3.0
2.0
1.0
$p_{C_4H_{10}}$ / kNm^{-2}
4.5
4.0
p_{CH_4} / kNm^{-2}

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