

## How do diesel-fuel ignition improvers work?

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### Introduction

An important descriptor of diesel fuel is its Cetane Number: this is an indicator of the time delay between injection and spontaneous ignition of fuel in a standard diesel engine running under specified conditions; the shorter the ignition delay, the higher the cetane number. Thus, those groupings of atoms within a hydrocarbon molecule that are beneficial in conferring a resistance to spontaneous ignition in a gasoline, i.e. a high octane number, are undesirable when they occur in a diesel fuel, and *vice versa*.

The cetane number scale uses two standard compounds, cetane (*n*-hexadecane) defined as 100, and heptamethyl-nonane defined as 15, so that, assuming linear mixing, a 1:1 mixture would have a cetane number of 57.5, a 1:2 mixture would have one of 43.3, &c. Long-chain paraffins tend to have high cetane numbers, e.g. *n*-dodecane = 80, *n*-tridecane = 83, in addition to cetane itself = 100. On the other hand, hydrocarbons containing benzene rings tend to have very low cetane numbers,<sup>1</sup> e.g. diphenyl = 21, diphenylmethane = 11 and 1,2-diphenyl-ethane = 1. Extremely low cetane numbers are also found for hydrocarbons with a benzene ring carrying short-chain substituents, e.g. xylene = -10 and *m*-di-*iso*-propyl-benzene = -12, but as the side chain becomes longer, the cetane number rises, to 26 for *n*-hexyl-benzene and to 50 for *n*-nonyl-benzene. Substances containing fused rings also exhibit very low cetane numbers, e.g.  $\alpha$ -methyl-naphthalene = 0. A corollary is that the minimum spontaneous ignition temperatures for aromatic hydrocarbons are higher than for non-aromatics.<sup>2</sup>

Legislated National Standards usually require that the cetane number of commercial diesel fuel shall exceed a certain value, say 40. Most diesel engines do not perform well with fuels of cetane number below this: for

example, in cold weather, the difficulty of starting a cold engine increases as both the cetane number of the fuel and the temperature decrease. Diesel fuel is a distillate boiling between 150°C and 350°C, but this is not a unique description: other fractions boiling within this range, but meeting different secondary specifications comprise naphtha, jet fuel, kerosene, and so on; an approximate classification is shown in Table 1.

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**Table 1.** Classification of distillate fuels.

| classification          | approximate boiling range |
|-------------------------|---------------------------|
| gases                   | < 30°C                    |
| straight run gasoline   | 30–200°C                  |
| light naphtha           | 30–110°C                  |
| heavy naphtha           | 80–200°C                  |
| middle distillate fuels | 135–360°C                 |
| kerosene & jet fuel     | 145–280°C                 |
| diesel fuel             | 160–330°C                 |
| light fuel oil          | 215–360°C                 |
| heavy fuel oil          | 290–400°C                 |

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Within certain narrow limits, the relative amounts of gasoline, diesel and/or jet fuel, and of heavier (heating) oils, that can be obtained by simple fractional distillation, are fixed, and if there is a mismatch between this and what the market demands, then either shortages will ensue, or the legislated standards will not be met.<sup>3</sup> To compensate for this, refinery processes have been developed whereby heavier ‘gas oil’ fractions are subjected to catalytic cracking and hydrogenation to give more gasoline and distillate, but these cracked materials tend to be aromatic in nature; consequently, they make good gasolines, but poor diesel fuels. Mass-spectrometer analysis<sup>4</sup> shows that they are much richer in alkylbenzenes, as well as in 2- and 3-ring aromatic compounds; it requires much more severe hydrogenation conditions to saturate the aromatic rings. At the same time, some countries have undertaken massive projects to extract oils from shale and tar-sands deposits: typically, bitumen is separated from the rock or sand, and cracked at high temperature to form lighter materials; hydrogenation is then used to reduce both the nitrogen and sulphur content, and to help to stabilise the cracked products. Again, these materials possess much more aromatic character than

does diesel oil from conventional sources; typical assays are shown in Table 2.

**Table 2.** Comparison of composition (in wt%) of conventional diesel fuel with those of synthetic materials.

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|                  | conventional<br>diesel fuel | cracked<br>gas oil | synthetic<br>diesel fuel |
|------------------|-----------------------------|--------------------|--------------------------|
| Paraffins        | 39                          | 19                 | 17                       |
| Naphthenes       | 34                          | 16                 | 37                       |
| Alkylbenzenes    | 18                          | 34                 | 36                       |
| 2-Ring Aromatics | 8                           | 28                 | 8                        |
| 3-Ring Aromatics | 1                           | 3                  | 2                        |

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Furthermore,  $^1\text{H}$  and  $^{13}\text{C}$  NMR studies on the alkylbenzenes show that, for the same molecular weight, those found in conventional fuel have relatively few (1–3) longer aliphatic side chains, whereas those from synthetic sources have many (4–6) shorter side chains, several of them perhaps being methyl groups.<sup>4</sup> Thus, it is this preponderance of short side chains, rather than the increase in the aromatic content itself, that is the principal cause of the lower cetane numbers for synthetic diesel fuels; also, the high content of naphthalenic compounds in the cracked oil fractions makes them unsuitable for augmenting the diesel fuel and jet fuel supply.\*

A temporary palliative to the diesel fuel quality problem is the addition of ignition promoters, either organic nitrates or organic peroxides, but if the the cetane numbers of the available fuels were to continue to decline in the future, the cost of the additive would become significant: for example, to raise the cetane number of diesel fuel from 35 to 40 by addition of *iso*-octyl nitrate would add about 10% to the untaxed cost at present-day prices,<sup>3</sup> and release many unwanted tonnes per annum of  $\text{NO}_2$  into the atmosphere in major urban areas. Thus, a better understanding of how these additives work is becoming essential.

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\*We note in passing that high aromatic content is undesirable in jet fuels, principally because the higher luminosity of the flames and their greater propensity for soot formation adversely affect engine reliability and maintenance costs.

## Present knowledge of additive behaviour

A wartime study on the effect of 72 different additives (including 26 nitrates and 9 peroxides) on a selection of 10 different fuels found,<sup>5</sup> quite generally, that nitrates and peroxides caused substantial increases in cetane number, whereas for other types of additive, no clear patterns emerged: for example, a few amines accelerated ignitions weakly, others were slightly inhibiting. The general consensus from engine measurements is that a given additive is not equally effective in all fuels, that the lower the cetane number of the fuel, the more additive is needed to bring about the same increase in cetane number, and that the presence of an ignition improver may reduce the cycle-to-cycle variability in engine behaviour.<sup>3,5-9</sup> One of these studies,<sup>7</sup> using 4 additives and 3 different fuels, concluded that the improvement in cetane number correlated with the *number* of free radicals produced by the thermal decomposition of the additive during the pre-ignition period.

There are severe disadvantages inherent in trying to study chemical kinetic processes in a reciprocating engine: not only is it a dirty environment, with oil droplets, abraded metal, soot, and with combustion residues left from the preceding ignition stroke, but the temperature and pressure are changing all the time. A more controlled way is to use an instrumented steel bomb, held at a fixed temperature and charged with a known pressure of air, into which the fuel is injected as a spray; in this way, it is convenient to observe the variation of ignition delay with temperature, pressure and fuel formulation, and also to determine the minimum temperature at which each fuel will ignite.<sup>10</sup>

There are many examples where ignition of fuel droplets has been studied under controlled conditions in a shock tube,<sup>9b,11a</sup> including one in which the effects of additives were studied.<sup>11b</sup> The shock tube method is limited, however, because if one wants to simulate the low temperature conditions that occur in trying to start a cold engine, the costs for driver gases become prohibitive.

Another powerful method of determining ignition delay is the use of a rapid compression-ignition machine, but its use is limited to gases<sup>12</sup> and volatile fuels such as octanes.<sup>13</sup> Griffiths and coworkers have made an extensive study of the effect of *iso*-propyl nitrate and of di-*tert*-butyl peroxide on the spontaneous ignition of *n*-butane in the 700–900°K range, and of di-*tert*-butyl peroxide on the ignition of methanol.<sup>12a,14a</sup> They argue strongly that the most important factor is the heat released by the combustion of

the additive in the pre-ignition phase and, to some extent, the number and nature of the radicals formed; they estimate that a temperature rise of the order of 60°C would be necessary to cause the same acceleration in ignition rate as the presence of 1% of di-*tert*-butyl peroxide.<sup>14a,b</sup> In our engine (see below), with a cylinder capacity of 460 ml and an injection of 0.015 ml of liquid fuel per stroke, the complete combustion of di-*tert*-butyl peroxide present in 1% concentration, *if released homogeneously*, would raise the gas temperature by about 15°C;<sup>9b</sup> but di-*tert*-butyl peroxide is effective, even at 0.25% or below,<sup>7,14c</sup> corresponding to less than a 4°C rise, surely within the cycle-to-cycle variability, and therefore insignificant.

We have made engine measurements with several additives but at lower temperatures than usually found in a normally operating diesel engine.<sup>9</sup> Ignition delay fell monotonically with additive concentration (up to 10% additive), with no correlation between efficiency and the rate of thermal decomposition of the additive, nor with its normal heat of combustion, but this may not be a contradiction, since Griffiths and coworkers suggest that it is the heat of partial oxidation that is important.<sup>12a</sup>

Thus, the present state of our understanding is very spotty: there is general agreement that organic nitrates and organic peroxides stimulate ignition in a diesel engine, and that the more additive, the shorter the ignition delay. Other things being equal, the effect of a given additive is different for different fuel samples,<sup>6,10a</sup> and different for the same fuel under different engine conditions.<sup>6</sup> Several plausible correlations between efficacy and fundamental kinetic or thermal properties have been suggested, but none of them is without exception.

## Experimental details

Since our primary interest, originally, was in the cold-starting problem, there were only two previously tried choices, to use a bomb as discussed above,<sup>10</sup> or to use an electrically driven refrigerated diesel engine.<sup>15a</sup> We chose, instead, a simpler option of running one cylinder of a car engine in diesel mode, with the diesel injector replacing the spark plug: thus, with a compression ratio of 7.5 and a block temperature of 100°C, compression temperatures in the 350–400°C range, typical of those encountered when trying to start a cold high-compression diesel engine, could routinely be achieved.<sup>9a</sup> Our engine does not mimic the true conditions too closely: for although the peak temperatures are about right, the pressures are a factor of 2 or 3 too low, the

temperature gradients are different, because the cylinder walls are at 100°C instead of (say) -20°C, and, of course, hot rather than cold fuel is sprayed into the heated air. Nevertheless, probably because ignition delays follow rather similar patterns as a function of temperature at different pressures,<sup>10a</sup> we found a good correlation between ignition delay and cetane number

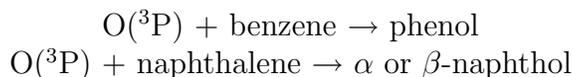
$$\text{CN} = 91 - 6.4\tau_{\text{ign}}$$

in the region  $3 \leq \tau_{\text{ign}} \leq 8$  msec; ignition delays of between 1 and 2 msec would be observed for these same fuels in a proper diesel engine. In our engine, the ignition delay is quite sensitive to the diameter of the air intake to the instrumented cylinder, and this was chosen to make the ignition delay for ordinary diesel fuel about 7.5 msec. Figure 1 shows pressure traces for diesel fuel and for fuel with 1% of *iso*-octyl nitrate (2-ethyl-hexyl nitrate).

Three different types of fuels were studied: regular diesel fuel, cetane number 42–45; low-sulphur low-nitrogen kerosene, cetane number 35–40; and HT-CLHO (Hydro-Treated-Catalytic-Light-Heating-Oil), cetane number 12–15. The former was purchased locally, but the two latter were supplied by Esso Petroleum Canada; each material was aquired in substantial quantity but, as to be expected from the experience of others, each batch exhibited a different ignition delay and sensitivity of that delay to the presence of various additives. This variability in stock fuels, although undesirable, could not be avoided since each engine run required a minimum of 300 ml of fuel to wash out the fuel pump and connecting lines, and to record data from 15–20 ignition strokes. In the case of the kerosene and heating oil samples, they were blended with cetane in order to bring the ignition delays into our accessible range.

### Which manifestation of aromatic character is important?

There are two properties possessed by aromatic hydrocarbons which could render them more difficult to ignite than paraffins. The first is the ability of the benzene ring to add oxygen atoms to form a phenol, e.g.



thereby interfering with the growing chains in the pre-ignition phase;<sup>16</sup> the rates of many such reactions have now been studied, and they have rather

small activation energies.<sup>17</sup> The other is that the benzylic hydrogen atom, adjacent to the benzene ring, is readily abstractable, and since the resulting benzyl radical is very unreactive, we have an alternative mechanism for breaking the chains necessary to initiate the ignition.

It is relatively easy to distinguish between these two. In our earlier study,<sup>9a</sup> we found that diethyl ether, admitted to the air intake, would stimulate the ignition of diesel fuel, but that this stimulation was less strong if the fuel contained toluene; ethyl-benzene behaves similarly, but benzene and naphthalene do not exhibit any interference with these ether-assisted ignitions. Thus, suspicion falls more heavily on the benzyl groups than on the mere presence of the aromatic rings.

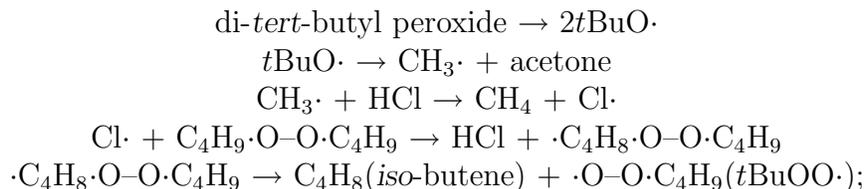
### Does the important additive chemistry occur in the liquid or the gas phase?

It is widely accepted that the important kinetic processes which lead to spontaneous ignition in a diesel engine take place in the gas phase;<sup>15</sup> reduction of the fuel spray velocity below a critical value, and evaporation, occur on a shorter time scale.<sup>18</sup> However, the additives are unstable substances, and it is possible that their oxidation or other reaction in the liquid droplets could generate sufficient heat<sup>9b</sup> to cause a micro-explosion, a common occurrence in higher-temperature sprays;<sup>19</sup> alternatively, reactive species initially formed in the higher-density liquid phase, could survive through the evaporation process.

First, we present some additional circumstantial evidence in support of the conventional view that, without additives, the important spontaneous ignition processes occur in the gas phase. We observed extreme sensitivity of the ignition delay to the presence of very small amounts of other gases introduced into the air-intake stream: entrainment of 20 ml/min of either Cl<sub>2</sub> or of NO in the air stream to the instrumented cylinder reduced the ignition delay for diesel fuel from 7.4 msec to 5.2 msec. Since the air flow, per cylinder, at 800 rpm in a 6-cylinder 2.75 litre engine is approximately 180 l/min, these additives amount to just over 100 ppm. Likewise, ozone present in a concentration of about 10 ppm reduces the ignition delay from 7.4 to 6.5 msec; a similar effect with ozone has also been reported independently by others recently.<sup>20</sup> It seems very unlikely that these minute traces of reactive gas could affect any chemistry that was occurring in the liquid phase.

Convincing evidence that the additives also function in the gaseous phase

was obtained from the following experiments. In trying to synthesise peroxy radicals *in situ*, we made use of the sequence of reactions:



HCl was produced by thermal elimination from *tert*-butyl chloride. The results were as follows: ignition delay for the fuel was 7.4 msec, falling to 5.9 msec with 1% of di-*tert*-butyl peroxide added, and to 5.1 msec when both di-*tert*-butyl peroxide and *tert*-butyl chloride were present; however, if the peroxide was present in the fuel, and 20 ml/min of either gaseous *tert*-butyl chloride, or of HCl, was included in the air stream, the ignition delay fell to 4.5 msec. The same amount of *tert*-butyl chloride on its own, either in the fuel or in the air stream, gives a smaller improvement in ignition delay, to the 6.3–6.5 msec range.

A similar conclusion can be reached by considering the effect of *iso*-octyl nitrate on the ignition delay. The thermal decomposition of *iso*-octyl nitrate leads to the formation of NO<sub>2</sub>, some formaldehyde, and some rather inert radicals.<sup>9b</sup> The equivalent amount of formaldehyde, produced by the thermal decomposition of *s*-trioxane present in the fuel, only improves the ignition delay to about 6.4 msec, whereas 1% of *iso*-octyl nitrate in the fuel causes the ignition delay to fall to 4.9 msec. With untreated fuel, and the same volumetric flow in the air stream of either NO or of NO<sub>2</sub> as would have been produced by the complete decomposition of 1% of *iso*-octyl nitrate, the ignition delays were within 0.1 msec of that found for *iso*-octyl nitrate. This suggests, not only that *iso*-octyl nitrate works primarily in the gas phase, but that the principal function<sup>†</sup> of the *iso*-octyl nitrate is to generate NO<sub>2</sub>.

## One mechanism or many?

As our investigation proceeded, we began to unearth hints that the additives worked in different ways, whereas the previous focus has always been to find

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<sup>†</sup>If one conjectures that the peroxide labelled P5 in Table 3 were to decompose thermally into CO<sub>2</sub> and a *t*BuO· radical, then the third fragment would be the same octoxy radical as is initially produced in the thermal decomposition of *iso*-octyl nitrate: since this peroxide is very much less effective than is *iso*-octyl nitrate, this supports the notion that it is the NO<sub>2</sub> that is important.

THE mechanism by which additives stimulate ignition. Figure 2 shows the results of ignition measurements on untreated diesel fuel, on fuel containing 1% of di-*tert*-butyl peroxide, 1% of *iso*-octyl nitrate, and 0.5% of each. The trace for the neat fuel exhibits considerable cycle-to-cycle variability, as, to a lesser extent, do those with 1% of additive; however, with the mixed additives, the cyclic variation is considerably reduced. Hence, there must be at least two factors leading to variability in ignition delay, one affected by *iso*-octyl nitrate, the other by di-*tert*-butyl peroxide.

In our survey of the effects of additives, we found one commercial sample of low-sulphur kerosene (lamp fuel) for which di-*tert*-butyl peroxide gave *absolutely no improvement* in speed of ignition, whereas *iso*-octyl nitrate did; also, if di-*tert*-butyl peroxide was added to the fuel containing *iso*-octyl nitrate, there was no change in ignition delay, confirming that these two additives act independently of each other. Eventually, we were able to reproduce this behaviour by treating our sample of low-sulphur low-nitrogen kerosene with silica gel to reduce further its aromatic sulphur and nitrogen content.<sup>21</sup> Thus, it appears that di-*tert*-butyl peroxide is not involved at all in the hydrocarbon ignition chemistry at our low temperatures, but that it counteracts some sulphur or nitrogen compounds present in the fuel.

A third useful piece of evidence comes from chemical treatment of the fuels, which will be discussed in more detail below. When HT-CLHO is treated with ozone, its cetane number is raised from 12 to about 15; likewise, if it is treated with lead tetra-acetate, the cetane number also rises to near 15. However, if the fuel is treated successively with both reagents, in either order, the cetane number goes to about 18. It is clear that there must be two kinds of inhibiting material present, one affected by ozone, and the other by lead tetra-acetate.

## Other evidence from the use of mixed additives

Figure 2 appears to show that the effect on the ignition delay of using a half-and-half mixture of *iso*-octyl nitrate and di-*tert*-butyl peroxide is midway between that of using either additive on its own. On the other hand, it has been reported recently that a mixture of *iso*-propyl nitrate and di-*tert*-butyl peroxide is more effective than either additive by itself, implying some synergy between the actions of the additives.<sup>14c</sup> We found several striking counter-examples, as shown in Table 3: apart from the last entry, there appears to be *strong* interference between the actions of the various pairs of

peroxides; the interference between di-*tert*-butyl peroxide and the peroxide P4 was also reported, without comment, by Griffiths and coworkers.<sup>14c</sup>

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**Table 3.** Ignition delays for peroxide additives, alone or mixed with di-*tert*-butyl peroxide. The ignition delay for the untreated fuel is 7.4 msec.

| peroxide | 1% DTBP  | 1% P <i>n</i> | 0.5% of each |
|----------|----------|---------------|--------------|
| P1       | 5.9 msec | 5.2 msec      | 6.6 msec     |
| P2       | 5.9 msec | 5.4 msec      | 6.4 msec     |
| P3       | 5.9 msec | 5.8 msec      | 6.4 msec     |
| P4       | 5.9 msec | 6.1 msec      | 6.9 msec     |
| P5       | 5.9 msec | 6.1 msec      | 5.8 msec     |

Key to peroxides:

DTBP = di-*tert*-butyl peroxide

P1 = *tert*-butyl perbenzoate\*

P2 = 1,1-di-(*tert*-butylperoxy)-3,3,5-trimethyl cyclohexane\*

P3 = *n*-butyl-4,4-bis(*tert*-butylperoxy)-valerate

P4 = 2,5-dimethyl-2,5-di-(*tert*-butylperoxy)-hexane

P5 = OO-*tert*-butyl-O-(2-ethylhexyl)-monoperoxy-carbonate

Notice that the two peroxides marked with an asterisk were included in our previous study,<sup>9a</sup> but with that fuel sample, they were somewhat less effective than was di-*tert*-butyl peroxide, whereas now they are quite superior.

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This interference between pairs of peroxides essentially destroys the thesis that the heat of combustion of the additive, partial or otherwise, is an important contributor to the ignition process; the mixture will not have a lower heat of combustion than if the two substances were burned separately.

## Modelling calculations

The modelling of the combustion of simple hydrocarbons is now an active area of research, with much emphasis on the differences between branched and unbranched hydrocarbons in relation to engine knock.<sup>22</sup> Less well advanced are the topics of aromatic hydrocarbon oxidation,<sup>23</sup> and of ignition of hydrocarbons at the low temperatures of interest to us here. In order to

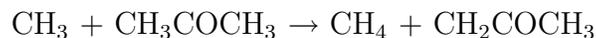
investigate what might be the mechanisms by which alkyl nitrates and peroxides stimulate ignition in the very-low temperature régime, we undertook to study their possible effects on the ignition of methane at 400°C. Bone and Gardner<sup>24</sup> found that at 1 atm and 400°C, the induction time for ignition of a 2:1 mixture of CH<sub>4</sub>:O<sub>2</sub> was about 20 minutes, but in the presence of NO<sub>2</sub>, it was reduced to a few seconds. We used the 35-step mechanism of Seshadri and Peters,<sup>25</sup> which appears to work well over a wide temperature range down to 1300°K, and computed an ignition delay of 9300 seconds at 1 atm and 900°K, but no ignition at 800°K. Since Bone and Gardner admit that their gases contained impurities, and since the calculated ignition delays will be *extremely* sensitive to small uncertainties in the assumed rates under these conditions, we regarded this as a satisfactory result upon which to base an exploratory study of the effect of additives on low-temperature ignition.

Extending the mechanism<sup>26</sup> to allow for the addition of 0.1 mole % of NO<sub>2</sub>, the ignition delay at 900°K fell to 36 seconds; in fact, ignition would now occur down as far as 700°K. The principal mechanism by which NO<sub>2</sub> does this is the abstraction of an H atom from CH<sub>4</sub> to give HNO<sub>2</sub>, which then dissociates into OH + NO: the NO is recycled to NO<sub>2</sub> and the OH takes part in the ignition process; whether the initial additive is NO<sub>2</sub>, HNO<sub>2</sub>, or NO does not make a great deal of difference, and they can probably be regarded as equivalent. HNO<sub>2</sub> is also readily formed in a rapid sequence whereby NO<sub>2</sub> successively strips H atoms from any intermediate CH<sub>2</sub>O, first to give CHO and then CO; since formaldehyde is formed in the thermal decomposition of *iso*-octyl nitrate,<sup>9b</sup> this probably contributes to its superiority as an ignition improver.

We next modelled the effect of di-*tert*-butyl peroxide on these ignitions, using the set of reaction rates given by Griffiths and Phillips.<sup>27</sup> The ignition delays with 0.1 mole % of additive were 11,000, 140, 27, and 8 seconds at 600, 700, 800, and 900°K respectively; these are to be compared with a delay of nearly 10,000 seconds at 900°K in the absence of additive. In all cases, there is an instantaneous rise of about 20°C, caused by the oxidation of the di-*tert*-butyl peroxide, followed by a two-stage ignition, most clearly separated near 800°K: here, there is an additional rise of 100°C during the first 2 seconds, with ignition occurring 25 seconds later. We conclude that although the oxidation of di-*tert*-butyl peroxide is highly exothermic, and causes an initial temperature rise, most of the effectiveness of di-*tert*-butyl peroxide stems from chemical origins; varying the rate of decomposition of di-*tert*-butyl peroxide had no effect, which is sensible, since all of the peroxide

is decomposed in less than a millisecond at any of these temperatures.

The ignition delay is by far the most sensitive to the rate assumed for the reaction



the latter radical being a source of ketene,  $\text{CH}_2$  and  $\text{HO}_2$ , but only above  $800^\circ\text{K}$ .<sup>12a</sup> In fact, a methane–oxygen mixture containing 0.2 mole % of acetone, starting at  $830^\circ\text{K}$ , follows virtually the same track as the  $800^\circ\text{K}$  0.1 mole % di-*tert*-butyl peroxide case: thus, the  $100^\circ\text{C}$  rise, which is a major cause of the acceleration, comes from the reactions of acetone.<sup>‡</sup>

These superficial studies of the effect of additives on the very-low temperature ignition of methane and oxygen, which were carried out by using the CHEMKIN routines,<sup>28</sup> provide some pointers as to how  $\text{NO}$  and  $\text{NO}_2$  (and indirectly, alkyl nitrites and nitrates) accelerate ignition; they also tend to support our observation that di-*tert*-butyl peroxide does not, by itself, accelerate hydrocarbon ignition in our low temperature régime. Moreover, they demonstrate conclusively that the acceleration that results from the simultaneous presence of di-*tert*-butyl peroxide and  $\text{HCl}$  has nothing to do with the possible formation of  $t\text{BuOO}\cdot$  radicals, but is caused by the presence of  $\text{Cl}$  atoms.

## Chemical treatments of the fuel

There are several reagents that are specific for benzylic hydrogen atoms.<sup>29</sup> We chose lead tetra-acetate, and found that stirring 300 ml of diesel fuel with 3 gm of lead tetra-acetate at  $55^\circ\text{C}$  for 3 hours reduced its ignition delay from 7.4 to 6.3 msec, corresponding to an increase in cetane number from about 44 to about 50. The unused lead tetra-acetate was treated with formic acid, and from the volume of  $\text{CO}_2$  recovered, it was estimated that about 0.2–0.3 mole % of the fuel had been reacted, on the assumption that its average molecular weight is about 250. Analysis of the fuel showed that there was no change in sulphur content, but that the lead content increased from undetectable to about 6 ppm, even up to 40 ppm when the lead tetra-acetate was synthesised *in situ* from red lead and glacial acetic acid.

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<sup>‡</sup>This suggests that acetone itself should accelerate the ignitions: it does, both in our engine, and also under normal diesel operating conditions,<sup>5</sup> but it is about an order of magnitude less efficient than di-*tert*-butyl peroxide.

We examined the reactions of several aromatic hydrocarbons under the same conditions, among them, phenyl-cyclohexane, *m*-di-*iso*-propyl-benzene, 9-methyl-anthracene, 9-ethyl-fluorene. In general, very little occurred: for example, with 1-phenyl-hexane, about 1% was oxidised to 1-phenyl-1-hexanone, and about 0.1% to 1-phenyl-1-hexanol, neither of which would be sufficient to cause the improvement in ignition quality that was observed.<sup>§</sup> We will return to the question of what lead tetra-acetate does to the fuel later, but it is clear that it neutralises, in some way, some very powerful ignition inhibitor that is present in 0.2–0.3 mole % concentration.

It is known that passing ozone through diesel fuel will improve its cetane number by some 5–10 units with, at the same time, a moderate reduction in sulphur content.<sup>30</sup> With our samples of diesel fuel and heating oil, ozone is *completely* absorbed initially until about 5 gms of ozone per litre of fuel has been consumed. They turn dark in colour, and deposit black resinous and odorous materials, which are soluble in acetone or glacial acetic acid, but not in hydrocarbons; ozonised heating oil even yields a copious precipitate when mixed with cetane for the engine tests! On analysis, the deposits were found to contain 3–4 times as much sulphur as did the original fuel; we also confirmed the reduction in sulphur content of the fuel itself, as shown in Table 4. Conversely, low-sulphur low-nitrogen kerosene absorbs very little ozone, it remains clear, and gives pale brown transparent deposits.

Kittrel *et. al.* used a complicated recovery process,<sup>30</sup> but we simply ozonised the fuel, filtered off the precipitated material, and made the ignition delay measurements. This procedure has its disadvantages, as the ozonised fuel continues to put down sticky residues upon standing over long periods (months); thus, without careful filtration immediately before use, and diligent cleaning of the injector pump immediately after use, blockages in the pump or the pintle injector can occur. We presume that this is mainly due to the formation of peroxides, as both diesel fuel and heating oil still contained 15 ppm of peroxide 4 months after ozonisation.

The ignition delay is unaffected at low levels of ozonisation, but at about 4 gm O<sub>3</sub>/litre, the improvement in ignition delay corresponds to an improvement in cetane number from about 44 to about 54; further ozonisation causes a lengthening of the ignition delay to some 6.2–6.4 msec, representing an apparent reduction in cetane number. Also, unlike the heating oil case, the

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<sup>§</sup>Note also that any significant degree of oxidation of the fuel itself would have the undesirable result of reducing its heat of combustion.

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**Table 4.** Effect of ozone on ignition delay and sulphur content of diesel fuel.

| function       | base fuel | 0.25 gm O <sub>3</sub> /litre | 4 gm O <sub>3</sub> /litre |
|----------------|-----------|-------------------------------|----------------------------|
| total sulphur  | 0.21%     | 0.21%                         | 0.12%                      |
| thiol          | 12 ppm    | 6 ppm                         | 4 ppm                      |
| ignition delay | 7.4 msec  | 7.4 msec                      | 5.7 msec                   |

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effects of ozone and lead tetra-acetate are not cumulative: treatment with both reagents, in either order, gives intermediate ignition delays of about 6.0 msec; it is clear that several conflicting effects must be at work.

Another useful observation is that the treatment of diesel fuel with DDQ (2,3-dichloro-5,6-dicyano-*p*-benzoquinone) at *room temperature* reduces the ignition delay by about 1 msec, about the same as does lead tetra-acetate. At room temperature, this reaction can only be a de-hydrogenation, and suggests that, perhaps, the principal result of treatment with lead tetra-acetate, which we have found has little effect on a selection of alkylbenzenes, could a de-hydrogenation too. Treatment with both lead tetra-acetate and DDQ, in either order, is no better than either treatment on its own.

Whilst not exactly a “chemical” treatment, it has been known for a very long time that adsorbents like silica gel and alumina will remove polar materials from diesel fuel.<sup>21</sup> Filtration of our diesel fuel through silica gel yields an almost colourless liquid having the same ignition delay as that which had been treated with lead tetra-acetate or with DDQ. Treatment of this filtered material with either lead tetra-acetate or DDQ did not produce any further reduction in ignition delay, showing that the silica gel had removed all of the inhibiting materials with which they would react. The adsorbed materials could be completely recovered by Soxhlet extraction with boiling acetone, to give a dark odorous liquid; addition back to the filtered fuel restored it to its original appearance, odour, and ignition delay. Similar results were obtained with alumina as the adsorbent.

## A search for possible inhibitors

The results of Table 4 clearly indicate that sulphur compounds should be screened for potential ignition inhibitors; also, we should not overlook the possibility of finding a hydrocarbon inhibitor.

a) *hydrocarbons*: The least readily ignitable of the aromatic hydrocarbons

we mentioned earlier had slightly negative cetane numbers; such numbers are usually deduced by blending the substance with cetane, measuring the cetane number of the mixture, and calculating the unknown cetane number by a linear mixture rule formula. Since our inhibitor is present in only 0.2–0.3% concentration, this would mean that we are looking for a hydrocarbon with a blending cetane number of (say)  $-400$ , which is quite unheard of. We considered dibenzosuberane to be a possible candidate: this molecule has 3 benzyl groups, and could easily be de-hydrogenated to form a conjugated bridge between the two benzene rings. Addition of 1% of dibenzosuberane to diesel fuel increased the ignition delay by less than 0.1 msec, well within the repeatability of our measurements. This means that dibenzosuberane cannot have a blending cetane number much worse than that of *m*-di-*iso*-propylbenzene, somewhere in the  $-10$  to  $-20$  range, and we conclude, tentatively, that no hydrocarbon exists that could be sufficiently inhibiting to match our requirements.

*b) sulphur compounds:* We screened a series of readily available sulphur-containing compounds (all present in 0.4% concentration), and found that, generally, various thiols and sulphides were beneficial: e.g. benzyl mercaptan, *p*-thiocresol, thiophenol, diphenyl sulphide and thianthrene, with accelerations of 0.2, 0.5, 0.4, 0.3 and 0.5 msec respectively. On the other hand, available benzothiophenes were found to be quite strong inhibitors, e.g. benzothiophene (thianaphthene) and dibenzothiophene, 0.8 and 0.6 msec longer delay times respectively. More interestingly, dibenzothiophene sulphone had no effect on the ignition delay.

The question then arises as to whether dibenzothiophene-like molecules are affected, either by the additives in the fuel, or by the treatments which we have found to be beneficial? Some experiments designed to provide answers to these questions are described in the next three sections.

## Additives *versus* inhibitors

The experiments described here were performed with one of the fuels, as described above, which was unaffected by the presence of 1% of di-*tert*-butyl peroxide. The addition of 1% of *iso*-octyl nitrate to this fuel shortened the ignition delay by 0.9 msec, and addition of 0.4% of dibenzothiophene to the fuel lengthened it by 0.4 msec. Then, addition of this amount of dibenzothiophene to the fuel containing *iso*-octyl nitrate also increased its ignition delay by 0.4 msec, whereas it did not change *at all* that of the fuel containing

di-*tert*-butyl peroxide. Thus, it is clear that di-*tert*-butyl peroxide is able to cancel completely the inhibiting effect of dibenzothiophene, whereas *iso*-octyl nitrate cannot; this is further clear evidence that these two additives work in different ways and, at the same time, provides a clue as to what di-*tert*-butyl peroxide does.

## Chemical treatments *versus* inhibitors

It is known that ozone reacts quantitatively with dibenzothiophene to form, first the sulphoxide, and then the sulphone,<sup>31</sup>



which we have found not to be an inhibitor. We found that fuel containing dibenzothiophene, when treated with just sufficient ozone to complete this reaction exhibited the same ignition delay as did the untreated fuel; thus, ozone can remove dibenzothiophenes from the fuel. However, treatment with either lead tetra-acetate or DDQ does not counteract the inhibition by dibenzothiophene.

As a result of the interactions between dibenzothiophene and di-*tert*-butyl peroxide, described above, another form of chemical treatment suggests itself: that of pre-heating the fuel with di-*tert*-butyl peroxide. Diesel fuel containing 1% of di-*tert*-butyl peroxide was heated, under reflux, at 150°C for a sufficient length of time to have decomposed all of the peroxide. A small amount of brown residue was produced, which contained about 4 times as much sulphur as did the original fuel; correspondingly, the sulphur content of the fuel fell to about 95% of its original value and its cetane number was increased to about 60! The amount of peroxide used in the pre-treatment had to be reduced to 0.1% before the ignition delay of the treated fuel equalled that of the fuel containing 1% of di-*tert*-butyl peroxide as an additive; in fact, a noticeable improvement (0.3 msec) in ignition delay was measured when only 0.01% of di-*tert*-butyl peroxide was used in the pre-treatment. These results suggest that the fuel contains a small fraction of sulphur-containing material which is very strongly inhibiting, but that the preponderance of the sulphur compounds present are benign, at least as far as ignition delay is concerned.

## How does di-*tert*-butyl peroxide interact with dibenzothiophene?

Little is known about the reactions of dibenzothiophene with free radicals in the gas phase. However, phenyl radicals, produced by thermal decomposition of benzoyl peroxide in molten dibenzothiophene at 110°C, yield mono-phenyl-substituted dibenzothiophenes, and a small amount of the sulphone.<sup>32</sup> With the sulphur atom numbered as 5, and the substituent positions in the benzene ring numbered 4, 3, 2, 1 with increasing distance from the S atom, phenyl substitutions were 28%, 21%, 12%, 31%, respectively.

We heated a 2.5:1 molar ratio mixture of di-*tert*-butyl peroxide and dibenzothiophene, dissolved benzene, in a stainless steel bomb at 150°C until all of the peroxide had decomposed. After reaction, the product was found to contain a large amount of unreacted dibenzothiophene, a small amount of the sulphone, and a mixture of mono-methyl-substituted dibenzothiophenes. We were not able to resolve the 2- and 3-isomers,<sup>33</sup> but they amounted only to about 18% of the product, with the 1- and 4-isomers dominating at about 38 and 44% respectively; the proportions are different from those of phenyl case. In view of the small yields, it does not seem that these reactions can account for the effects of di-*tert*-butyl peroxide, as described in the two preceding sections.

## Conclusions

It should be remembered that the results proved here obtain in a rather low-temperature régime, roughly equivalent to that found when starting a cold diesel engine at temperatures below 0°C and, in the absence of direct experimental confirmation, they should only be assumed to be transferable to the normal diesel régime with some caution.

We have found, quite conclusively, that the important chemistry contributed to the spontaneous ignition process by the ignition-improver additives takes place exclusively in the gas phase. We have also found, equally conclusively, that there is no single generic mechanism by which these additives reduce the ignition delay: for whereas both *iso*-octyl nitrate and di-*tert*-butyl peroxide may accelerate the ignition of ordinary diesel fuel about equally,<sup>9</sup> we have found certain low-nitrogen low-sulphur fuels for which *iso*-octyl nitrate causes the anticipated improvement, but for which di-*tert*-butyl peroxide has no effect. We infer, in fact, that *iso*-octyl nitrate acts, *via* the formation of NO<sub>2</sub>, mainly on the hydrocarbon itself, whereas di-*tert*-butyl

peroxide acts on some inhibitors present in the fuel, most likely sulphur-containing inhibitors; however, only a small fraction of the total sulphur content resides in inhibiting molecules. Here, our primitive modelling studies were of help in showing how  $\text{NO}_2$ , which is formed in the thermal decomposition of *iso*-octyl nitrate, can accelerate ignition by abstracting hydrogen from the hydrocarbon to form  $\text{HNO}_2$ : presumably, this is true for all aliphatic nitrates and nitrites, with differences in efficiency among them stemming from variety in behaviour of the alkyl radicals formed alongside the  $\text{NO}_2$ . Likewise, with di-*tert*-butyl peroxide, as already noted by Griffiths and coworkers,<sup>12a</sup> our calculations reveal an almost instantaneous temperature rise caused by combustion of the peroxide, but below about 800°K, until reactions involving acetone become important, it is insufficient to stimulate rapid ignition. Thus, it is not surprising that one can find certain fuels for which the ignition delay in our low-temperature régime is unaffected by the presence of di-*tert*-butyl peroxide. However, for lack of knowledge of the products and/or mechanisms of decomposition of other peroxides, we cannot speculate on what causes the observed differences in behaviour between them.

We have located one general type of sulphur-containing inhibitor: the benzothiophenes. Much of the sulphur content of our diesel fuels resides in dibenzothiophenes which have survived the catalytic hydrogenation used to reduce the sulphur content: this is because they have bulky alkyl groups in the 4,4'-positions, which interfere with the action of the catalyst. It seems probable, therefore, that dibenzothiophenes, in general, are ignition inhibitors: just as they pick up oxygen atoms from ozone, they readily pick up O atoms in the pre-ignition phase, thereby killing the chains required to cause the ignition. However, hydrocarbon fuels contain an enormous range of types of sulphur compounds, some of them also containing nitrogen or oxygen too,<sup>34</sup> and inhibition is by no means restricted to the one type that we have identified. In fact, we have not yet made a positive identification of any substance that is present in the fuel that is a potent inhibitor, and intriguing amongst the inhibitors present are those that are so readily deactivated by lead tetra-acetate or by DDQ, possibly by de-hydrogenation.

## Future requirements

On an industrial scale, ozonisation is not a practical proposition because of the huge quantities that would be required, the low yield of ozone per kilowatt-hour of electrical input, and because of the unstable state in which it

leaves the fuel; the stability requirements for long-term storage under a wide range of conditions of heat and cold are very demanding.<sup>5</sup> Nor is treatment with lead tetra-acetate (or, equivalently, red lead and acetic acid) because it introduces lead into the fuel: for example, recent Canadian legislation requires that the lead content of a fuel shall not *knowingly* be increased. Nor would the simple device of generating Cl atoms in the pre-ignition phase be acceptable: it is now known that the presence of chlorine compounds in fuels leads to the formation of dioxins,<sup>35</sup> and their formation would be especially likely with highly aromatic fuels. Thus, at the present time, there seems to be no alternative but to seek a yet better understanding of the problem.

An important task is to identify some of the inhibitors that actually exist in the fuel: we need to be able to identify, say by GC/MS, some substances that are destroyed on treatment with lead tetra-acetate, or with DDQ, and possibly some new substances formed as a result. This is not an easy task: the gas-phase chromatogram of diesel fuel comprises some 300–350 peaks,<sup>14b</sup> and we are searching for inhibitors that make up some 0.2–0.3% of the total; however, we are almost certainly not looking for just one or two substances, but for series of similar substances, perhaps even hundreds, each present in concentrations of tens of ppm. The silica-gel extracts offer a better chance, but here again, the chromatogram also gives more than 300 peaks: the number of peaks observed is determined more by instrumental factors, such as the threshold sensitivity of the integrator and the column resolution, and by the boiling range of the sample than by the number of distinct substances present.

It would be useful to study the kinetics of the reactions of atoms and free radicals with dibenzothiophene, carbazole, and their homologues, and to perform parallel molecular orbital calculations on structure and reactivity in these systems. Also to elucidate the mechanisms for the thermal decomposition, in the gas phase, of some of the more esoteric peroxides shown in Table 3, with a view to explaining the interferences demonstrated there between pairs of additives.

We have not described here any results for nitrogen-containing compounds because the situation is not clear cut, as was also the case in the initial study of ignition improvers,<sup>5</sup> cited earlier. Simple amines (*n*-decylamine, tri-*n*-butylamine, pyridine, indole) appear to be mildly inhibiting – perhaps not unexpected in view of the known anti-knock properties of amines; also, our simple modelling calculations show that NH<sub>3</sub> inhibits the ignition of methane and oxygen at low temperatures. Carbazoles, which are known to be present

in these fuels, seem to be ignition promoters, some of them quite strong, and amides and imides have no effect. We are continuing to try to unravel these contradictory results.

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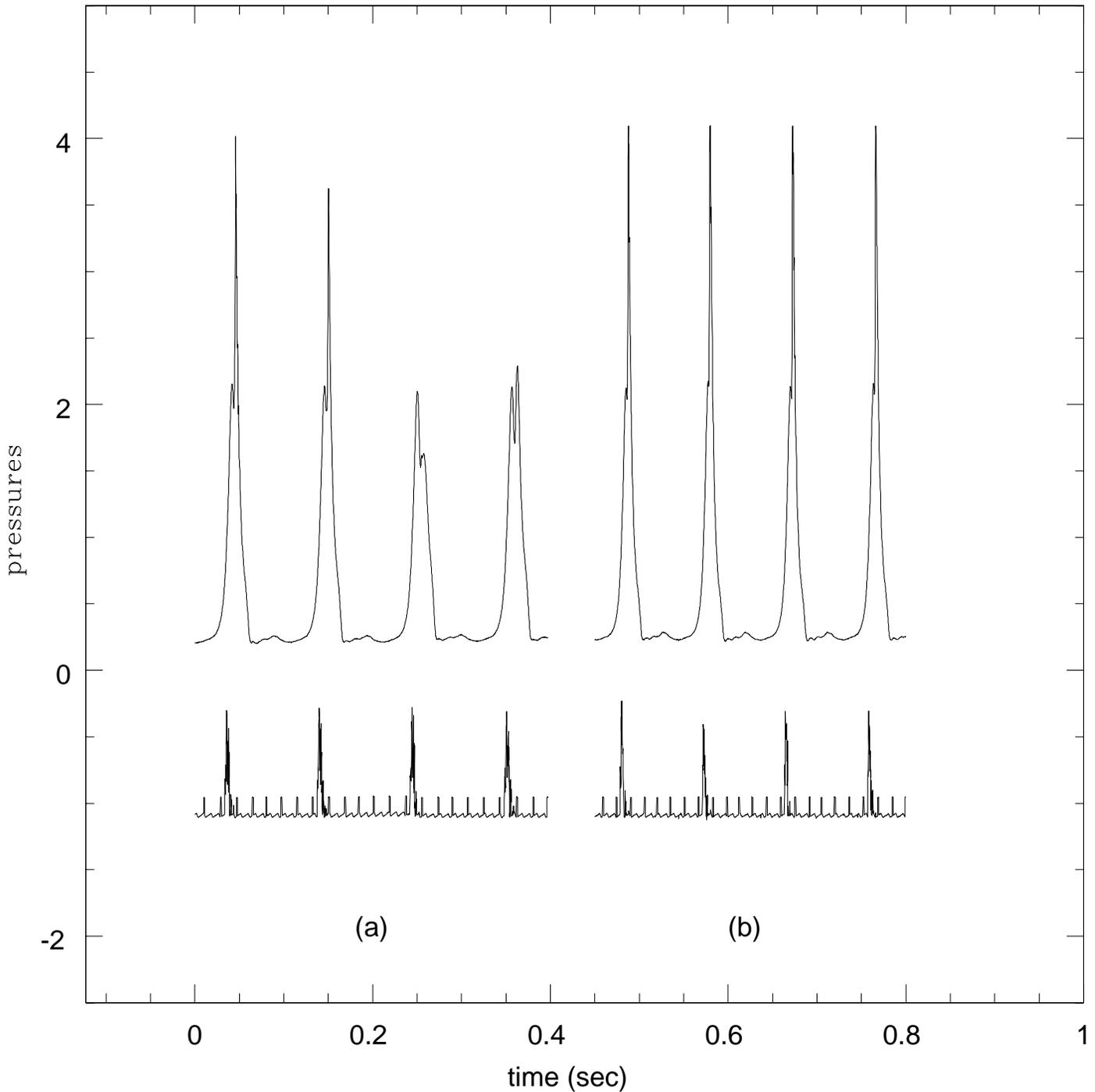


Figure 1: Ignition traces for a) neat diesel fuel; b) diesel fuel containing 1% of *iso*-octyl nitrate. Upper traces: cylinder pressures; at top-dead-centre (first peak of each doublet), the excess pressure above baseline is  $\sim 12.5$ – $13$  atm (180–190 psi). Lower traces: composite of timing markers generated from spark signals and pressure at diesel injector; pressure peaks are  $\sim 240$  atm (3500 psi). Ignition delay is taken to be the time interval between the initial downslope of the injector pressure trace and the beginning of the steep pressure rise of the cylinder pressure trace.

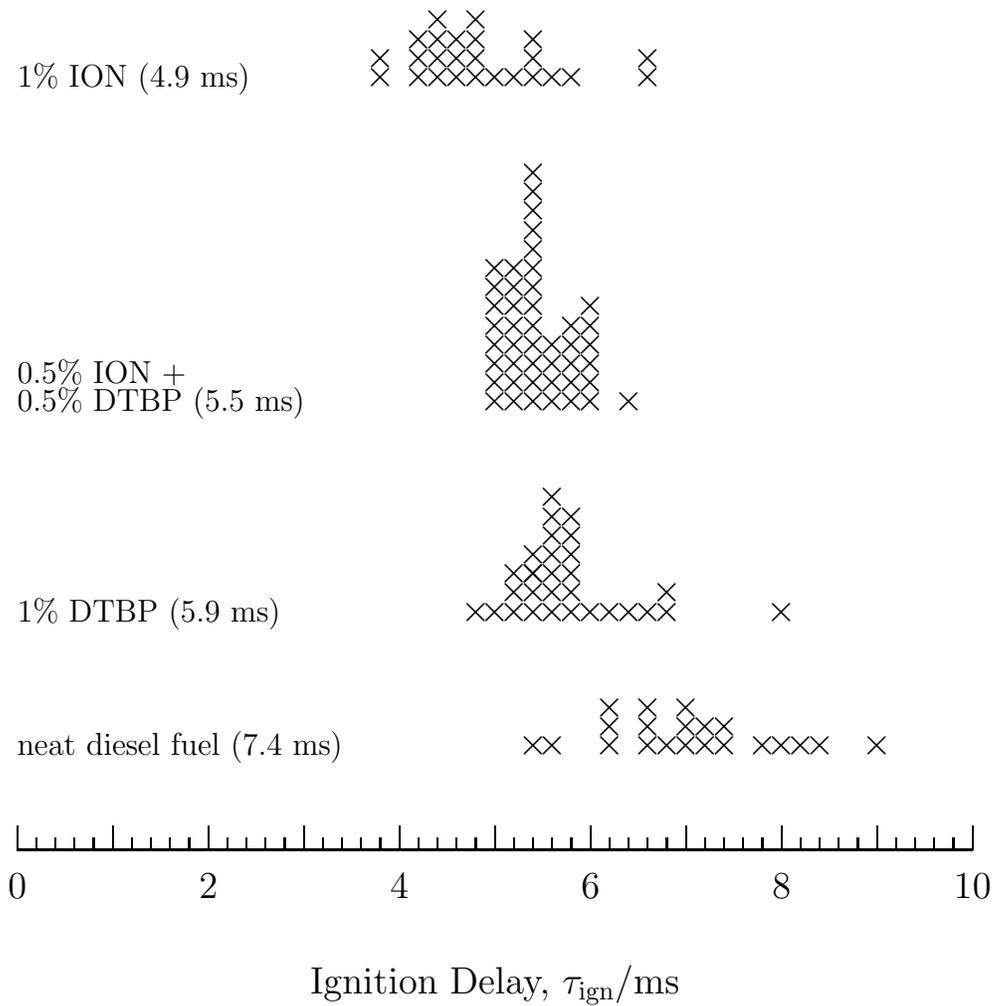


Figure 2: Distribution of ignition delays for neat diesel fuel, diesel fuel containing 1% di-*tert*-butyl peroxide, 0.5% each of *iso*-octyl nitrate and of di-*tert*-butyl peroxide, and 1% of *iso*-octyl nitrate; each cross represents one ignition. Notice the smaller spread in the times for the fuel containing both additives.

## Contents Page

### How do diesel-fuel ignition improvers work?

*By P. Q. E. Clothier, B. D. Aguda, A. Moise and H. O. Pritchard*

A wide-ranging study of the effect of free-radical initiators, especially *iso*-octyl nitrate and di-*tert*-butyl peroxide, on the spontaneous ignition of diesel fuel is reported. The important kinetic processes induced by these additives occur in the gas phase, and not in the liquid droplets. *Iso*-octyl nitrate and di-*tert*-butyl peroxide work in quite different ways: the nitrate is involved in the ignition process itself, whereas the peroxide competes for sulphur-containing inhibitors in the fuel.

## Biographical Notes

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