

**620.** *The Effect of Some Additives on the Oxidation Rate of Cyclopentane.*

By R. C. HORSCROFT.

A study is made of the relative efficiencies of various heterogeneous additives, mainly salts, in the inhibition of cyclopentane oxidation. Inhibition occurs by destruction of peroxy-radicals, or more probably peroxide molecules.

THE principal object of the present work was to investigate means of inhibiting or controlling gaseous combustion reactions. Unpublished work in this laboratory has shown that the characteristic slow start and accelerating development of these reactions depends upon the gradual accumulation of active intermediates. These are susceptible, in principle, to destruction, both by homogeneous additives and by surface reaction, whereby combustion might be suspended for a long time or even indefinitely. Homogeneous additions of an effective kind in the oxidation of cyclopentane have proved difficult to find. Small amounts of formaldehyde, acetaldehyde, propionaldehyde, benzaldehyde, or chlorine all reduce the induction period in some degree: di-*t*-butyl peroxide and bromine, even in amounts of less than 0.1%, completely eliminate it. Isopropyl halides, aniline, carbon tetrachloride, and carbon tetrafluoride have little or no effect on induction period or rate. The effect of nitrogen and carbon dioxide, even in large amounts, is negligible. The substances which accelerate the reaction are believed to do so by the production of free radicals through either oxidation or decomposition.

Since satisfactory homogeneous additions have been difficult to find, the action of various salt and metal surfaces which are known in principle to have inhibitory effects has been investigated in more detail. Many of these markedly prolong the induction period, sometimes almost indefinitely.

Pease and his co-workers,<sup>1</sup> oxidising propane in a flow system at temperatures between 325° and 400°, found that coating the reaction tube with potassium chloride reduced the yield of peroxides almost to zero, without other effect on the reaction. Static experiments, on the other hand, at 270–280° with a Pyrex reaction vessel coated with potassium chloride showed a greatly lengthened induction period. Similar results have been obtained more recently by Egerton, Minkoff, and Solooja<sup>2</sup> and by Walsh<sup>3</sup> who have studied the effect of surfaces on the oxidation of methane at about 500°. Walsh divides the surfaces into three types according to their effect on the rate of oxidation, namely, (i) acidic—silicic acid, boric acid, phosphoric acid, germanium dioxide, (ii) salts in general and metallic oxides, and (iii) metals. The rates in vessels having the above types of surfaces fell in the order (i) > (ii) > (iii), the third type (metals) giving the slowest rate.

The object of the present work has been to extend knowledge of the influence of these heterogeneous additions, to ascertain which were most effective in suppressing the oxidation of cyclopentane, to find their influence on the intermediates responsible for the development of the reactions, and to obtain clues to the mechanism of their action.

## EXPERIMENTAL

The apparatus and methods, and the criteria of maximum rate and induction period, were as in the preceding paper. Cyclopentane was used as the oxidisable gas throughout. In some experiments reaction vessels of Pyrex glass were coated on the inside with a thick layer of a salt, deposited from a concentrated aqueous solution by heating and pumping. All vessels, whether to be used with or without a salt coating, were washed with boiling, fuming nitric acid and then with distilled water. Peroxides were estimated iodometrically, ferrous and molybdate

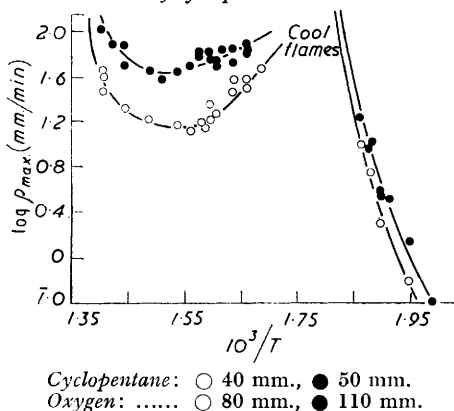
<sup>1</sup> Pease, *Chem. Rev.*, 1937, **21**, 279; *J. Amer. Chem. Soc.*, 1929, **51**, 1839; Pease and Munro, *ibid.*, 1934, **56**, 2034; Pease, *ibid.*, 1935, **57**, 2296.

<sup>2</sup> Egerton, Minkoff, and Solooja, *Combustion and Flame*, 1957, **1**, 25.

<sup>3</sup> Walsh, 7th Internat. Symposium on Combustion, 1958, p. 183.

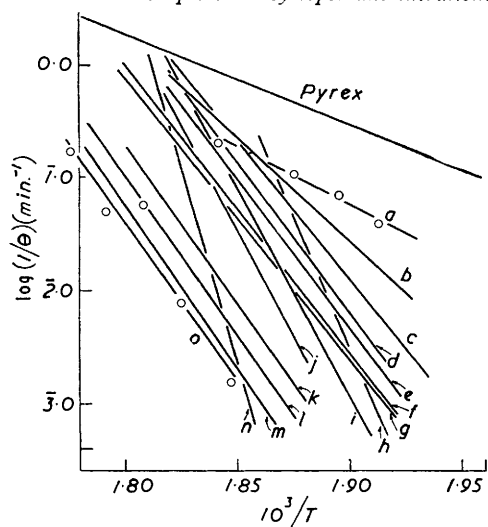
ions being added to help the decomposition of dialkyl and alkyl hydrogen peroxides.<sup>4</sup> No attempt was made to discriminate between different types.

FIG. 1. Influence of temperature on oxidation rate of cyclopentane.



The points refer randomly to experiments with silica or Pyrex vessels, and with or without the addition of peroxide initiator. Neither factor made any systematic difference to the rate.

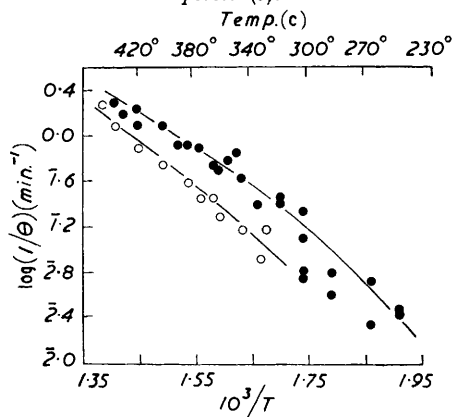
FIG. 3. Comparison of the effects of various salts on the induction period in cyclopentane oxidation.



Cyclopentane, 350 mm.; oxygen, 110 mm.

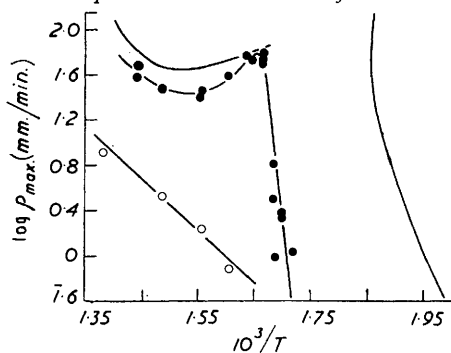
a, KF; b, Au foil; c, KI; d, MgSO<sub>4</sub>; e, LiCl; f, KBr; g, KCl; h, K<sub>2</sub>SO<sub>4</sub>; i, Ag wire; j, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>; k, LiBr; l, LiI; m, MgCl<sub>2</sub>; n, CsCl; o, Pt wire.

FIG. 2. Influence of temperature on induction period (θ).



Points marked as in Fig. 1.

FIG. 4. Effect of lithium bromide and of magnesium sulphate on maximum rate of oxidation.



Cyclopentane, 50 mm.; oxygen, 110 mm.

○ MgSO<sub>4</sub>. ● LiBr. Line without points = uncoated silica vessel.

## RESULTS

*Comparison of Different Additives.*—The relative efficiencies of salts are very different and vary with temperature. The temperature coefficient of the cyclopentane oxidation rate in an uncoated silica vessel is of the form shown in Fig. 1. The reciprocal induction period, however, plotted in a similar way to the maximum rate, shows no anomalous behaviour (Fig. 2).

The effect of temperature on the length of the induction period in vessels coated with

<sup>4</sup> Ubbelohde and Egerton, *Phil. Trans. Roy. Soc.*, 1935, A, 234, 487.

different salts is shown in Fig. 3. To include all the experimental points would cause confusion, so that two typical sets only are given.

It was found that for at least two salts, lithium bromide and lithium chloride, a few grams lying in the bottom of a Pyrex vessel had the same inhibiting effect as a coating over the whole

FIG. 5. *Effect of lithium bromide and of magnesium sulphate on the induction period.*

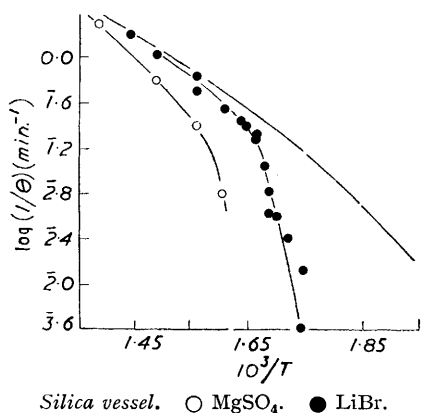
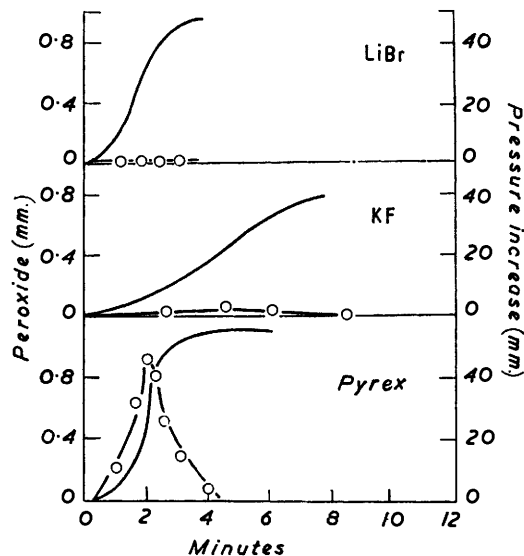


FIG. 6. *Effect of different salt coatings on peroxide formation at 400°.*



*Cyclopentane, 50 mm.; oxygen, 110 mm. Curves without points =  $\Delta p$ .*

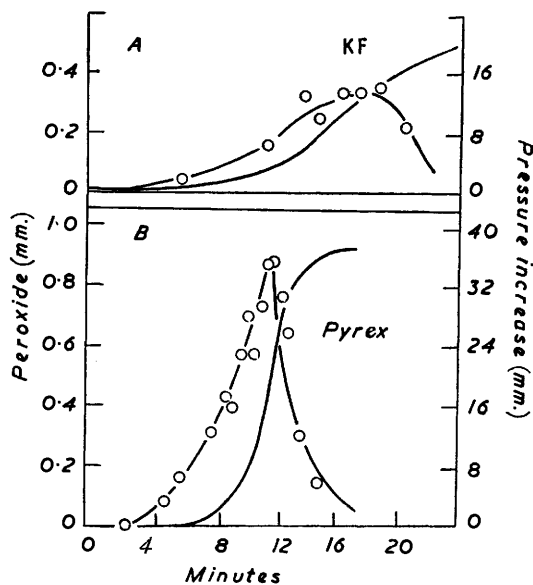


FIG. 7. *Effect of potassium fluoride coatings on peroxide formation at 250°.*

*A, KF coating: cyclopentane, 350 mm.; oxygen, 110 mm.*

*B, Clean Pyrex glass: cyclopentane, 150 mm.; oxygen 110 mm.*

interior. This, however, does not apply only to salts, since silver wire, platinum wire, and gold foil also showed inhibitory actions. The surface areas of the salts were unknown, but the silver wire had an area of 89 cm.<sup>2</sup>, the platinum wire 65 cm.<sup>2</sup>, and the gold foil 90 cm.<sup>2</sup>.

Attempts were made to measure the rate in salt-coated vessels at 250°, with di-*t*-butyl peroxide added as an initiator. Only a few of the less efficient salts gave rates which could be

measured at all, and with these the rates generally fell as the salt became more effective in lengthening the induction period, though there was no exact relation.

Despite their great effect on rate and induction period, the salts do not seem to affect greatly the general form of the kinetics, where this can be determined at all.

The complexity of the temperature effect is illustrated in Figs. 4 and 5, for lithium bromide and magnesium sulphate. The former has a very marked influence on the rate in the cool flame region and a much smaller one at higher temperatures. Magnesium sulphate, on the other hand, exerts its effect over the whole accessible range. Evidently no measurable reaction could be expected at 250° with either of these salts, and none is found.

*Peroxide Formation.*—Peroxides are formed during the oxidation, the maximum concentration occurring at the time of maximum rate, and some results are shown in Figs. 6 and 7. At the lower temperature only the less efficient salts can be used, since others would permit no measurable reaction. Potassium fluoride, however, proved suitable for use at both temperatures.

Figs. 6 and 7 show that the salt coatings considerably reduce the peroxide concentrations. At 400°, however, the effect on the rate of reaction,  $\rho_{\max}$ , is not reduced in anything like the same proportion. This fact suggests strongly that in the high-temperature region the peroxides do not play an essential part in the propagation of the reaction.

At the lower temperature the peroxide concentration is also appreciably reduced by the salt, but, in contrast with the higher temperature, the rate is now reduced correspondingly.

In a Pyrex vessel at 250° the maximum peroxide pressure reached with 110 mm. of oxygen was about 0.8 whether the hydrocarbon pressure was 350, 250, or 150 mm. Thus the reduction in peroxide content shown in Fig. 7 is due to the potassium fluoride coating and not to the difference in cyclopentane pressure.

#### DISCUSSION

According to Walsh<sup>3</sup> the activity of an inhibitor at higher temperatures is due to the destruction of  $\text{HO}_2\cdot$  radicals and  $\text{H}_2\text{O}_2$  molecules on the surface, and is supposed to be associated with the ability of the surfaces to donate electrons to the adsorbed radical.

If this is the correct interpretation of such effects at higher temperatures, there is clearly a possible analogy in the low-temperature region involving the removal of  $\text{RO}_2\cdot$  and  $\text{RO}\cdot\text{OH}$  (or  $\text{RO}\cdot\text{OR}$ ) whereby chain-branching is prevented so that the reaction cannot accelerate in the normal way.

The above results show that very varied salts may greatly lengthen the induction period of cyclopentane oxidation. Since there is no need to coat the whole inside of the reaction vessel but only to introduce loose salt (lithium bromide and chloride), and since gold, platinum, and silver are active in the form of wire or foil, the effect is more probably due to the destruction of a branching intermediate than to the suppression of a surface initiation reaction. Moreover, since the diffusion time must be appreciable, the destruction of a peroxide intermediate is perhaps more likely than that of a much more transient peroxy-radical.

The rate at higher temperatures is hardly affected by a coating of lithium bromide, but at 250° where the "low-temperature" peroxide branching mechanism probably operates, a very marked fall is observed. Magnesium sulphate, on the other hand, lowers the rate over the whole accessible temperature range. The actions, therefore, seem to be quite complex, and we must conclude that for some reason magnesium sulphate is more efficient than lithium bromide itself in destroying the chain carriers of the high-temperature reaction.

The differences in the efficiencies of the various salts may be the result of a number of conflicting factors. If Walsh's explanation of  $\text{HO}_2\cdot$  and  $\text{H}_2\text{O}_2$  destruction, and the analogous explanation in terms of  $\text{RO}_2\cdot$  and  $\text{RO}\cdot\text{OH}$  is correct, then the efficiency of the salts might indeed lie in the order of their ability to donate electrons. Some such order is observable, and although other factors must play a part, this effect may well be the most important single one.

There is, incidentally, no discernible relation of efficiencies to crystal structure.

Some surfaces lose their activity with use. With silver wire the lost activity could be

restored by wiping the wire clean with cotton wool. Platinum required more drastic treatment to restore its activity, but it seems likely that the covering of the surface layer with carbonaceous matter is the cause of the loss of efficiency.

The results for lithium bromide at 400° suggest that peroxides are not essential for the development of the chains in the high-temperature region since the rate is little affected despite the almost complete destruction of peroxide. At 250° lithium bromide could not be used, since it suppressed the reaction entirely, so that at this temperature presumably the destruction of peroxide has become important. That destruction of peroxide occurs at 250° is shown by the results with the less efficient salt, potassium fluoride, which causes the peroxide concentration to be halved. The complexity of the factors at work is, however, shown by the fact that with potassium fluoride, not only is the peroxide destroyed, as it is with lithium bromide, but the rate is also lowered. In spite of the complications it seems clear that the most marked effect is the greater dependence upon peroxide at lower temperatures, and the fact that in general the salts which destroy the peroxide become relatively less efficient inhibitors as the temperature is raised.

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PHYSICAL CHEMISTRY LABORATORY, OXFORD UNIVERSITY.

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