

THE INFLUENCE OF NITROGEN PEROXIDE ON THE LOW TEMPERATURE AUTO- IGNITION OF DIETHYL ETHER

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Summary

THE results indicate that the influence is similar to that previously recorded with *n*-butane-oxygen mixtures, in that the acceleration of the direct oxidation indicated by a decrease in the minimum pressures for ignition is observed simultaneously with the inhibition of the cool flame reaction, characterized by an increase in the induction lag.

Chemical analysis shows that the concentration of acetaldehyde in the products of the pre-cool flame reaction decreases with an increase in the nitrogen peroxide additions and provides additional support to the view that acetaldehyde is of primary importance in the formation of cool flames.

Introduction

Previous experiments on the spontaneous ignition of propane, *n*-butane or acetaldehyde-oxygen media have shown (*cf.* Kane, 1939) that at temperatures between 200-400° C., involving a two-stage ignition, NO₂ additions have a composite influence, consisting in a simultaneous inhibition of the reactions leading to cool flames and a promotion of the direct oxidation of the combustible. With propane, the inhibition was indicated by an increase, in the cool flame and total time lags, and the minimum pressures for the two-stage ignitions with NO₂ additions, up to a critical concentration of about 3·25 per cent. With greater NO₂ additions, an overall promoting influence was observed, since the cool flames were no longer observable and the mixtures ignited abruptly at greatly reduced minimum pressures and shorter time lags. With *n*-butane these abrupt ignitions were not observed, but lower minimum pressures for the two-stage ignitions even with small NO₂ additions indicated a greater promotion of the direct oxidation than with propane. The inhibition was again marked by a continuous increase of the time lags with NO₂ additions and elimination of cool flames with more than 5 per cent.

NO₂. Similar results were obtained with acetaldehyde, the inhibition being greater than either with propane or *n*-butane.

It was a matter of interest to investigate whether NO₂ additions would have a similar composite influence with other inflammable materials, such as di-ethyl ether. Ether resembles higher hydrocarbons very closely in that it exhibits well-developed cool flames and two-stage ignitions in the lower temperature region (200-400° C.) during spontaneous ignition (*cf.* Townend and Chamberlain, 1937), and also when ignition is induced artificially by means of a heated wire at room temperature and high enough pressure (Hshieh and Townend, 1939). Further, ether is known to peroxidise in air, even at room temperature and large amounts of higher aldehydes are found associated with the products obtained from a "stationary" cool flame, maintained in an ether-oxygen mixture (Maccormac and Townend, 1940).

The present paper records the results of experiments carried out with di-ethyl ether. Hitherto Kane had restricted his experiments to a study of the influence of NO₂ additions on two-stage ignitions only; now it has been possible to extend the observations to cool flames as well, since the time lags at the minimum pressures for the propagation of cool flames are not inconveniently long with ether-oxygen mixtures. In addition, a few analyses of the intermediate products formed prior to ignition have been carried-out to determine the variation in the aldehyde content due to NO₂ additions, in view of the suggestion of Kane that acetaldehyde is of primary importance in the formation of cool flames and two-stage ignitions.

Experimental

The minimum pressures for spontaneous ignition were determined by a static method, in which the prepared inflammable mixtures were admitted into an evacuated reaction vessel maintained at the requisite temperature. The apparatus and the procedure were similar to those previously described by Kane (*loc. cit.*). The inflammable mixtures with oxygen were prepared and stored at room temperature (28-30° C.), the di-ethyl ether employed being rendered free from peroxides by distillation over sodium.

At first, the limits of propagation of spontaneously ignited cool flames and two-stage ignitions were determined experimentally. Curves A and B (Fig. 1) were obtained by plotting the minimum pressures for cool flames at 20) and 206° C., respectively, against mixture composition expressed as per cent. ether in oxygen. Cool flames could be observed with mixtures containing between 23 and 70 per cent. of ether, within the area bounded

by the V-shaped curves. The time lags in seconds for the limit mixtures have been marked along the curves and it may be seen that both the minimum pressures and the time lags decrease with an increase in the experimental temperature.

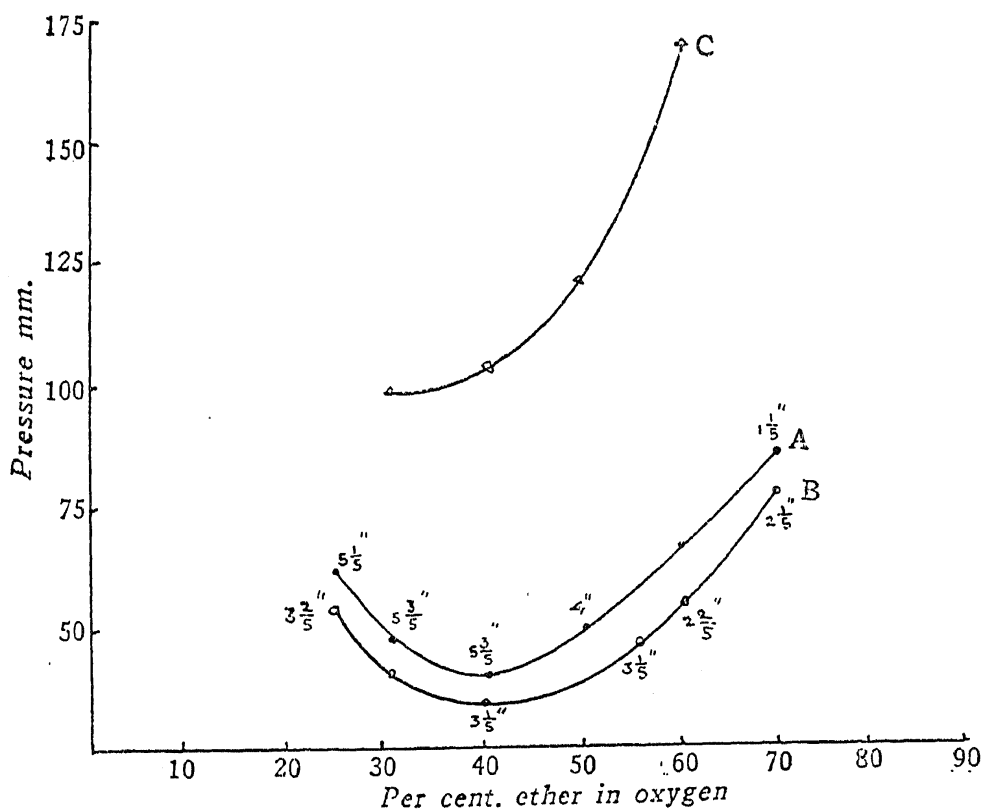


FIG. 1. Cool flame limits

Curves A and B refer to limits at 200° and 206° C.

With any particular mixture, at a critical pressure considerably above the minimum required for the propagation of cool flames, a rapidly moving yellow-flame appeared after a short interval, in the products left behind by the cool flame. Curve C (Fig. 1), refers to the variation in the minimum pressures for these two-stage ignitions, with a change in the mixture composition at a temperature of 200° C. The ignitions were accompanied by a sudden development of pressure, and increased in violence with an increase in the oxygen content of the mixtures. The curve was not extended, therefore to mixtures containing less than 30 per cent. ether.

In order to ensure that the available time-lag exceeded one second, all experiments were carried out at a temperature of 200° C., with NO_2 additions to mixtures containing 40, 50 and 60 per cent. ether.

Results

Two-stage ignitions—Minimum pressures.—Curve A (Fig. 2), indicates the variation in the minimum pressure for ignition (P = partial pressure of

combustible + oxygen, in mm.) for the 40 per cent. ether mixture, with increasing NO_2 additions. Small NO_2 additions decrease the minimum pressure considerably, the influence being at a maximum with about 3.25 per cent. of NO_2 . With further NO_2 additions, the minimum pressures again increase indicating an anti-catalytic influence probably due to the neutralization of active centres by mutual reaction. Curves B and C, which refer to mixtures containing 50 and 60 per cent. ether, respectively, show a similar behaviour and indicate in general that small NO_2 additions promote the normal ignition of ether, but an inhibiting influence becomes operative when the NO_2 addition exceeds 3.5 per cent. Cool flames preceding the ignitions became less intense as the NO_2 additions to the mixture increased and could not be observed at all, when the latter exceeded 5 per cent.

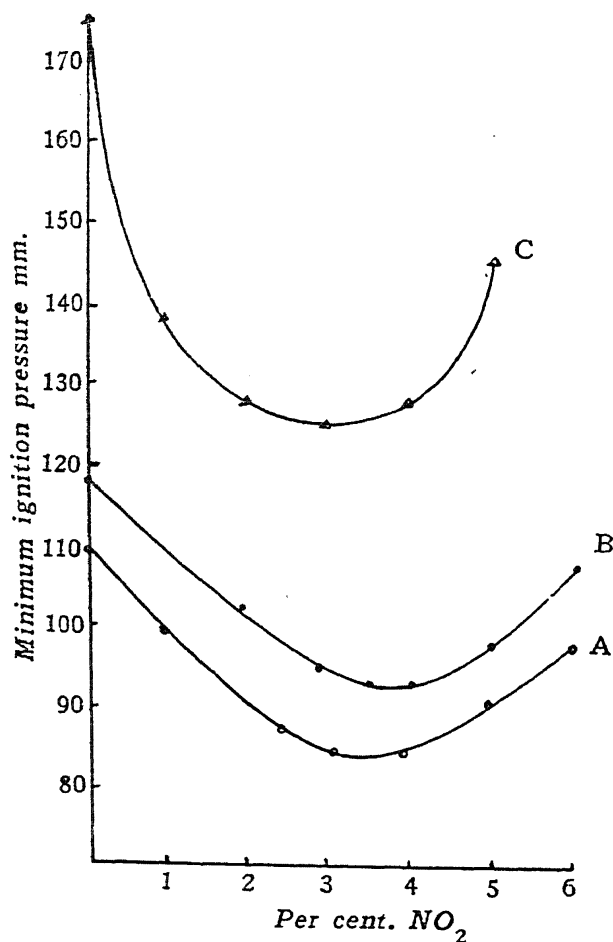


FIG. 2

Curves A, B and C denote the limits for the two-stage ignition for 40, 50 and 60 per cent. ether-oxygen mixtures respectively at 200°C .

Time lags.—Curves A, B and C (Fig. 3) illustrating the variation in time lag with NO_2 addition, at a constant initial pressure P (ether + oxygen), show

a definite inhibition of the two-stage ignitions. For instance, curve A shows that for the 40 per cent. ether mixture the time lag increases continuously from $1\frac{1}{5}$ seconds for the undiluted mixture to $9\frac{4}{5}$ seconds with 5 per cent. NO_2 . The 60 per cent. ether mixture behaved similarly (curve C), while the inhibiting influence was most marked with the 50 per cent. ether mixture,

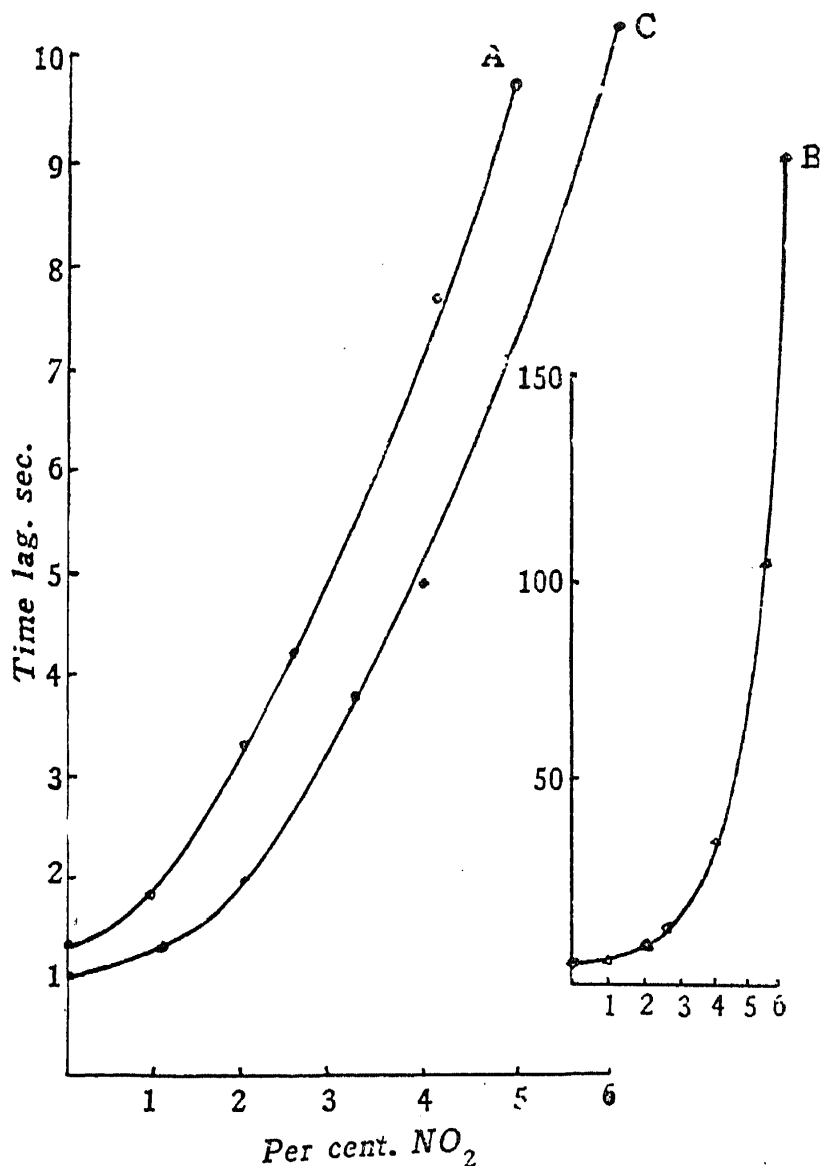


FIG. 3. Time lags for two-stage ignitions with NO_2 additions at constant ignition pressure. Curves A, B and C refer to 40, 50 and 60 per cent. ether mixtures, at $P = 109, 118$ and 170 mm. respectively at 200°C .

the time lag increasing from 2 to 204 seconds for 6 per cent. NO_2 addition. It may be mentioned that similar results have been obtained by Forsyth and Townend (in private communication) during experiments on ignitions initiated by a hot wire and therefore the observations recorded above are of general application so far as ether is concerned.

Cool flames—Minimum pressures.—The minimum pressures for cool flames with NO_2 additions, are given in Table I.

TABLE I

Per cent. NO ₂	0	1	2	2.5	3	4	5	6
<i>Minimum pressures in mm.</i>								
40 per cent. ether ..	40	39	39	38	37	44	44	44
50 " " ..	52	49	50	..	53	53

Since the accuracy of the minimum pressure determinations is of the order ± 1 mm. it may be inferred from Table I that NO₂ additions up to 3 per cent. hardly affect the minimum pressure, while with greater addition the pressures are raised slightly, indicating an inhibition of the reaction.

Time lags.—It may be seen from curves A, B and C (Fig. 4) that at constant ignition pressure, the time lags are distinctly longer with NO₂ additions, indicating an inhibition of the cool flame reaction. As with two-stage ignitions, the inhibition is most marked with the 50 per cent. ether mixture.

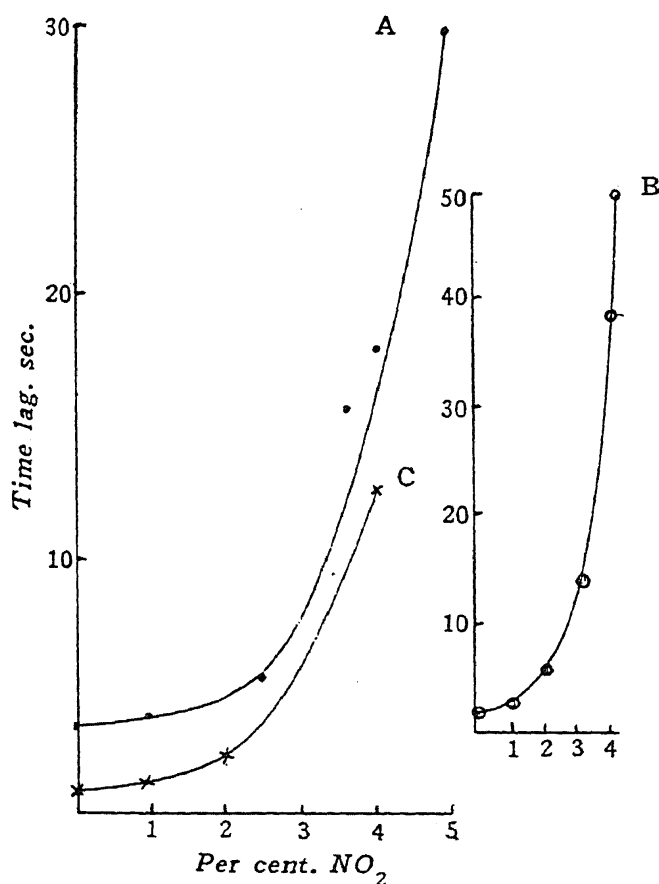


FIG. 4. Time lag at cool flame limits with NO₂ additions at constant ignition pressure
Curves A, B and C refer to 40, 50 and 60 per cent. ether mixtures,
at P = 60, 102 and 60 mm. respectively at 200° C.

Estimation of aldehydes.—In order to estimate the amount of aldehydes formed in the intermediate products prior to the propagation of cool flames, samples of gas were withdrawn at definite intervals of time by allowing the reaction mixture to expand into an evacuated bulb cooled with solid carbon dioxide. The sample was shaken with distilled water, and aldehydes determined colorimetrically with Schiff's reagent. Formaldehyde was found to be absent and it was assumed that with diethyl ether, the higher aldehydes would consist mainly of acetaldehyde.

Curves A A' and B B' (Fig. 5) at a time lag of 2 and 4 seconds and initial mixture pressures of 90 and 78 mm. respectively, indicate that in all the experiments there is a progressive diminution in the aldehyde content with NO_2 additions up to 6 per cent.

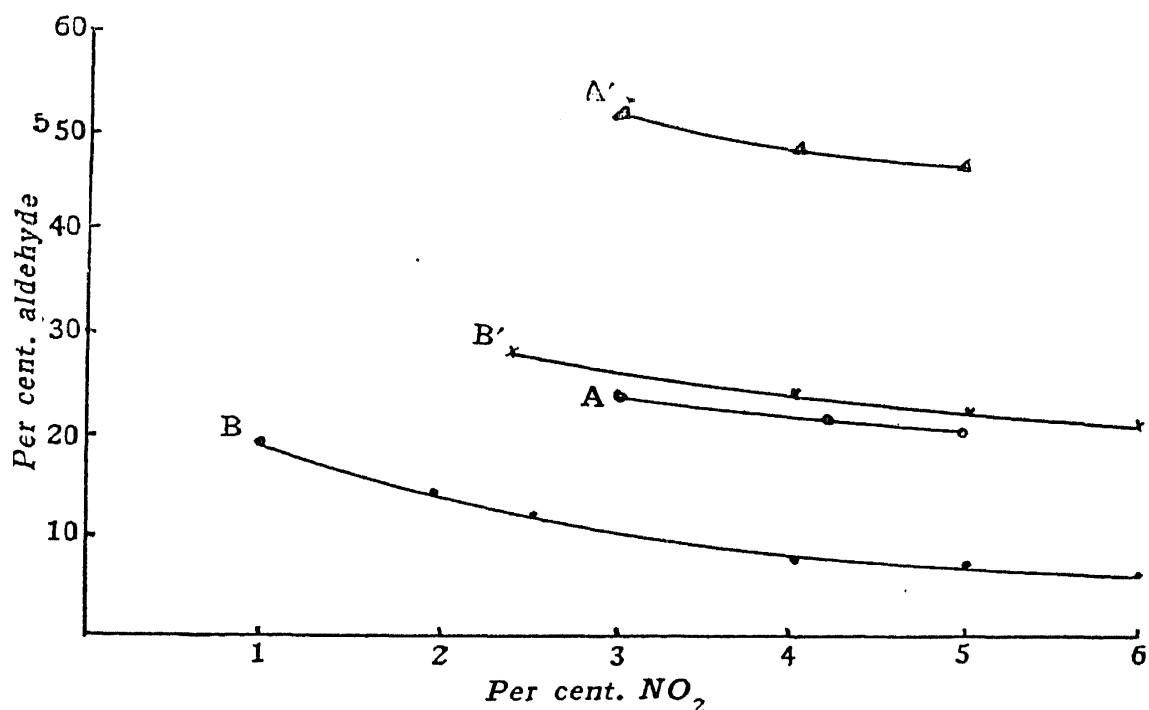


FIG. 5. 40 per cent. ether-oxygen mixtures at 200°C .

Curves A and A' refer to a mixture pressure (combustible + oxygen) at $P = 90$ mm. at 2 and 4 seconds respectively. Curves B and B' at $P = 78$ mm. at 2 and 4 seconds respectively

Discussion

The results obtained with di-ethyl ether correspond very closely with the previous observations with *n*-butane and acetaldehyde in that with small NO_2 additions, a promotion of the direct oxidation is denoted by lower minimum pressures for two-stage ignitions, and an inhibition of the cool flames by an increase in the time lags. A specific inhibition of the cool flames is further demonstrated since the minimum pressures for

cool flames are hardly affected, while the time lags are considerably increased with NO_2 additions.

The important rôle played by acetaldehyde as a promoter of the low temperature ignition of paraffinic hydrocarbons and allied fuels is well known. Since the inhibition of the cool flame reaction of acetaldehyde is greatest in the presence of NO_2 (*cf.* Kane), it may be expected that in the intermediate products the concentration of acetaldehyde would decrease with successive NO_2 additions to the combustible media. Such a result has been observed now with ether-oxygen mixtures and gives additional support to the view that acetaldehyde is primarily involved in the formation of cool flames.

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REFERENCES

1. Kane .. *Proc. Roy. Soc.*, 1939, 171 A, 251.
2. Hshieh and Townend .. *J.C.S.*, 1939, 337.
3. Maccormac and Townend .. *Ibid.*, 1940, 143.
4. Townend and Chamberlain .. *Proc. Roy. Soc.*, 1937, 158 A, 415.
5. Forsyth and Townend .. In private communication.