353. The Oxidation of Hydrocarbons and Their Derivatives. Part III.* The Rôle of Intermediates.

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The products of oxidation by oxygen of methyl and ethyl formate and propane have been analysed chemically and polarographically. Formaldehyde, total aldehyde, and total acid analyses were made at six temperatures as the two regions of reactivity were traversed.

The polarograms of the oxidation mixtures showed two and sometimes three species present in the samples. The broad wave, characteristic of peroxide substances, was observed in all the analyses made. In the case of ethyl formate, as the temperature was increased, one species disappeared and was replaced by another. It was not possible to identify the two substances involved.

Changes during the actual passage of a cool flame could only be investigated with the propane–oxygen mixtures. Here a marked decrease in the concentration of peroxide occurred as the flame passed.

The more remarkable properties of hydrocarbon combustion include (*a*) the induction period followed by a rise in rate to a maximum, (*b*) the anomalous relation between rate and temperature, and (*c*) the occurrence in certain rather closely prescribed regions of concentration and temperature of cool flames, and sometimes of multiple bursts of cool flames.

These phenomena are closely interconnected. There is much to indicate that the active intermediates built up during the induction period are responsible for branching chains; and that the anomalous temperature effect is the result of alternative reactions of these intermediates or their precursors in side reactions, unfavourable to chain-branching. Severe changes in the concentrations of oxidation intermediates, principally peroxides, have been observed during the passage of a cool flame, and these same substances may well be responsible for the low-temperature explosion region.

The details of this general picture are, however, far from clear. Bardwell and Hinshelwood,[1] for example, found that during the passage of cool flames in butanone–oxygen mixtures there was a tremendous fall in the peroxide concentration. On the other hand, Eastwood and Hinshelwood [2] found that in the cool flames of ether the very much greater peroxide concentration suffered little proportional change (though some absolute decrease may have occurred).

The large amount of discussion that has appeared in recent years on the probable nature and structure of the more likely chain-branching agents tends to obscure the considerable degree of general agreement that has been attained. Mechanisms of combustion have been proposed by Ubbelohde,[3] Walsh,[4] Norrish,[5] Knox and Norrish,[6] Cullis and Hinshelwood,[7] and others. Several are of the general form in which the initial attack by an oxygen molecule leads to an oxygenated hydrocarbon derivative capable of decomposition at normal combustion temperatures into two or more free radicals (not necessarily similar) and the propagation of a chain-branching mechanism.

That differences in detail have arisen is not surprising. A hydrocarbon (or derivative) can give rise in the course of its oxidation to peroxide, hydroperoxide, aldehyde, alcohol, acid, and oxides of carbon. All except the oxides may show pyrolysis, and any radical thereby produced can interact with oxygen. Which of the vast array of possible intermediates are those most closely connected with the general physical chemistry of the

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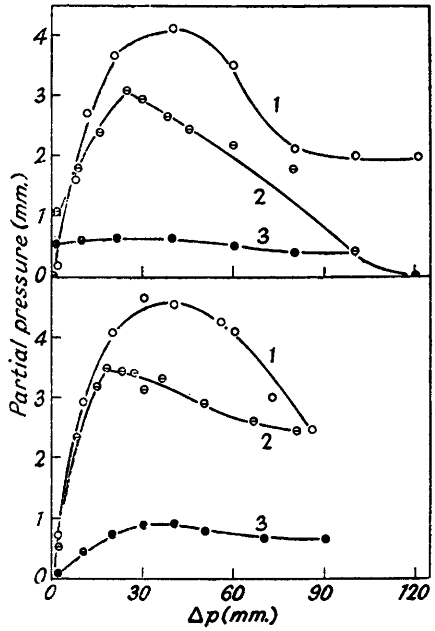
* Part II, preceding paper.

[1] Bardwell and Hinshelwood, *Proc. Roy. Soc.*, 1951, *A*, **205**, 375.
[2] Eastwood and Hinshelwood, *J.*, 1952, 733.
[3] Ubbelohde, *Proc. Roy. Soc.*, 1935, *A*, **152**, 354.
[4] Walsh, *Trans. Faraday Soc.*, 1947, **43**, 297, 305.
[5] Norrish, XVI International Colloquium, Centre National de Recherche scientifique, 1948, p. 16.
[6] Knox and Norrish, *Proc. Roy. Soc.*, 1954, *A*, **221**, 151.
[7] Cullis and Hinshelwood, *Discuss. Faraday Soc.*, 1947, **2**, 117.

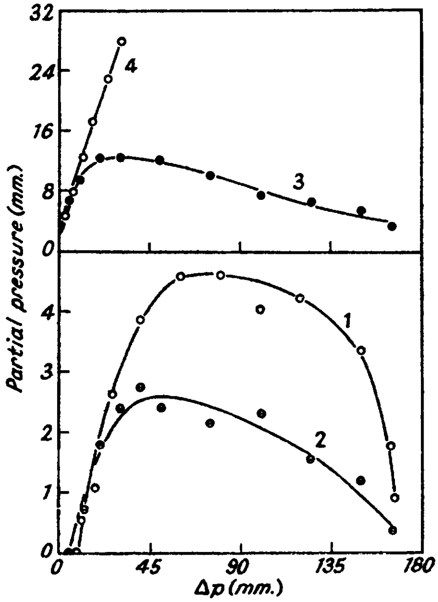
FIG. 1. *The formation of aldehyde and acid during the oxidation of ethyl formate.*



1. Formaldehyde. 2. Acetaldehyde.
3. Total acid.

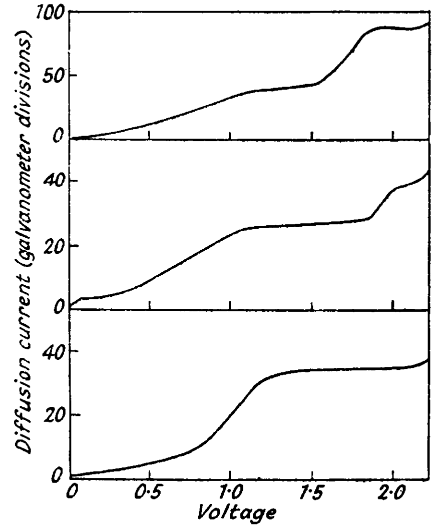
Top section of figure, 340°; bottom section, 280°.

FIG. 2. *The formation of aldehyde and acid during the oxidation and thermal decomposition of ethyl formate at* 425°.



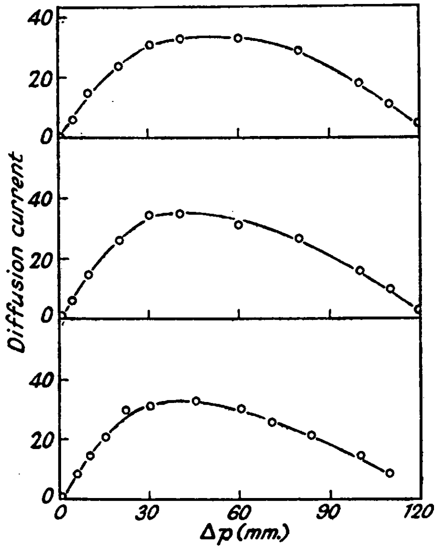
1. Formaldehyde.
2. Acetaldehyde.
3. Total acid (oxidation reaction).
4. Total acid (decomposition reaction).

FIG. 3. *Typical polarograms of the combustion mixtures of methyl and ethyl formate.*



Top: ethyl formate; Δp = 100 mm.; temperature = 425°.
Centre: ethyl formate; Δp = 20 mm.; temperature = 310°.
Bottom: methyl formate; Δp = 60 mm.; temperature = 390°.

FIG. 4. *The formation of peroxide (polarographic analyses) during the oxidation of methyl formate.*



Top: 450°. Centre: 415°. Bottom: 390°.

phenomena mentioned above is still largely to be decided, and experiments with new systems and as varied techniques as possible are therefore desirable.

In the present paper experiments are described on the chemical and polarographic examination of the intermediates formed in the oxidation of some esters and of propane. The main object has been to study the changes which occur in these as (*a*) the anomalous part of the temperature–rate curve is traversed and as (*b*) the cool-flame region is traversed at a given (initial) temperature.

EXPERIMENTAL

General.—The pressure–time curves of the oxidation of the esters, methyl and ethyl formate,[8] and propane were determined at various temperatures in both the low- and the high-temperature regions. The conditions of concentration selected for investigation were 100 mm. of ester or propane and 200 mm. of oxygen. For each series of analytical tests the reacting gases were admitted to the reaction vessel in the usual way, and at appropriate points along the pressure–time curve the combustion gases were shared with a gas pipette. The contents of the pipette were extracted with pure water or N/10-lithium chloride depending upon the constituents to be analysed. The reaction conditions were duplicated several times until a series of samples had been collected representing the whole range of pressure change.

Analytical Methods.—Formaldehyde was determined colorimetrically with chromotropic acid.[9] Total aldehyde was determined colorimetrically with benzenesulphohydroxamic acid.[10] Both methods for aldehyde were calibrated with pure samples of formaldehyde and acetaldehyde. The benzenesulphohydroxamic acid method was found to be less sensitive to formaldehyde than to acetaldehyde. The analyses for both formaldehyde and total aldehyde were accordingly carried out under exactly similar conditions; the contribution of formaldehyde to the total aldehyde was subtracted from the total aldehyde analyses and the remainder expressed as acetaldehyde. The results in each case were calculated back to the partial pressure of the component in the reaction vessel.

Total acid was determined by direct titration with 0·14N-sodium hydroxide at 0°, the indicator used being phenolphthalein. The solutions for titration were cooled in ice to prevent the rapid hydrolysis of the excess ester from obscuring the end-point.

For the polarographic analyses the method established by Shtern and Pollyak [11] was adopted. The contents of the gas pipette were extracted with N/10-lithium chloride. Two-ml. portions of the test solution were pipetted into the electrolytic cell, and the oxygen removed by passing hydrogen gas for 8·0 min. The voltage range investigated was zero to 2·2 v.

Results.—The esters selected for study were methyl and ethyl formate. The first was characteristic of those esters showing no anomalous temperature relationship, and the second showed two clearly defined temperature zones in the range 250—450°.

The results of the analyses for aldehyde and acid in the combustion mixtures of ethyl formate are shown in Figs. 1 and 2. In the high-temperature region (450°) a large increase in the partial pressure of acid was observed. A few experiments were made to examine the possibility that this increase resulted from the simple decomposition of the ester at elevated temperatures. The acid concentration does increase almost linearly with the increase in pressure accompanying decomposition, and the amounts formed are comparable with those observed towards the end of the induction period of the oxidation reaction.

Typical polarograms of the combustion samples of methyl and ethyl formate are illustrated in Fig. 3. Those for the combustion mixtures of ethyl formate usually showed two waves or steps. The first was a broad drawn-out wave at about 0·9 v characteristic of peroxidic substances. The second occurred at 1·9 v in the low-temperature region, and at 1·7 v in the high-temperature region. The polarograms of the methyl formate mixtures showed only the broad peroxide wave at 0·9 v. The general pattern shown by the propane combustion samples was very similar to that of ethyl formate, except that the steps observed above 1·5 v were small and relatively unaffected by changes in temperature. The height of the various waves and changes observed with the pressure changes in the reaction vessel and the temperature are shown in Figs. 4—8.

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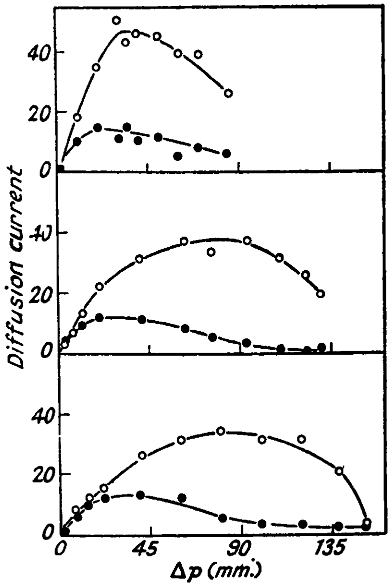
[8] Parts I and II, preceding papers.

[9] See Bricker and Johnson, *Ind. Eng. Chem. Anal.*, 1945, **17**, 400.

[10] See Damköhler and Eggerglüss, *Z. phys. Chem.*, 1942, *B*, **51**, 157.

[11] Shtern and Pollyak, *Acta Phys. Chem., U.R.S.S.*, 1939, **11**, 797.

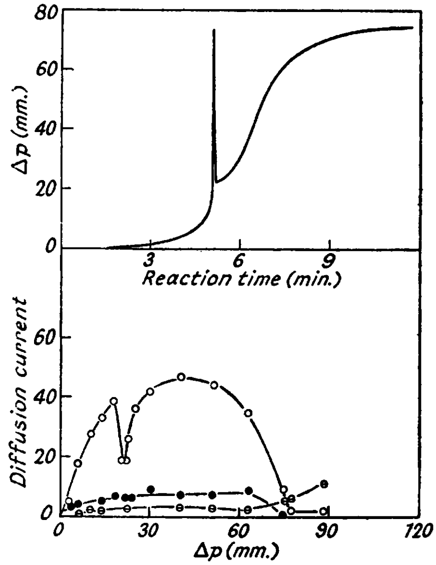
FIG. 5. *The variation in the height of the polarographic waves during the oxidation of ethyl formate.*



○ Wave at 0·9 v (characteristic of peroxide).
● Wave at 1·9 v (species unknown).

Top : 280°. Centre : 310°. Bottom : 340°.

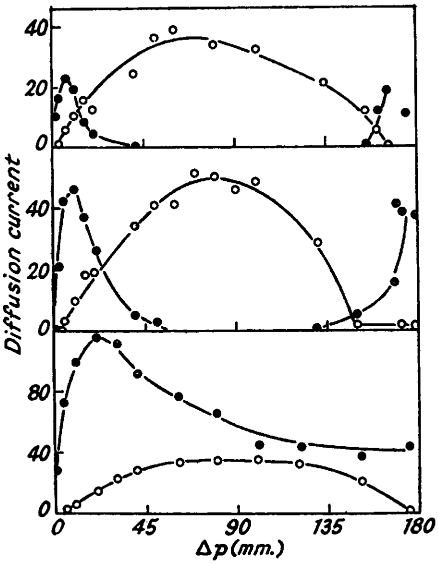
FIG. 7. *The variation in the height of the polarographic waves during the oxidation of propane at* 300°.



Top : typical pressure–time curve showing cool flame at Δp = 21 mm.
Bottom : Polarographic analyses :

○ Wave at 0·9 v (characteristic of peroxide).
⊖ Wave at 1·7 v (species unknown).
● Wave at 1·9 v (species unknown).

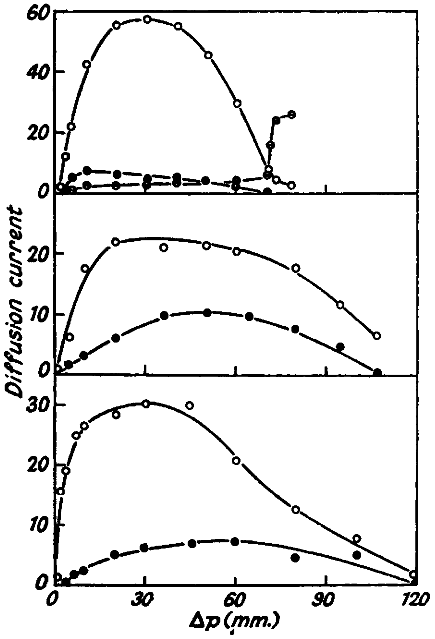
FIG. 6. *The variation in the height of the polarographic waves during the oxidation of ethyl formate.*



○ Wave at 0·9 v (characteristic of peroxide).
● Wave at 1·7 v (species unknown).

Top : 360°. Centre : 380°. Bottom : 425°.

FIG. 8. *The variation in the height of the polarographic waves during the oxidation of propane.*



○ Wave at 0·9 v (characteristic of peroxide).
⊖ Wave at 1·7 v (species unknown).
● Wave at 1·9 v (species unknown).

Top : 280°. Centre : 370°. Bottom : 400°.

DISCUSSION

In both the low- and the high-temperature regions of the oxidation of ethyl formate, the concentrations of higher aldehydes (C_2 upwards) and formaldehyde passed through a maximum as the reaction went to completion. The general trend of these results confirms the conclusions based on the mass-spectrometer analyses (Part I), *viz.*, that very little oxidation occurs during the induction period before the maximum rate of reaction is reached.

The theories of combustion proposed by Frank-Kamenetzki [12] and Walsh [4] predict a sine-wave dependence of the concentration of peroxide and aldehyde (and particularly of formaldehyde) on the extent of oxidation. The results of the present study, including the analyses for peroxide species during the cool-flame oxidation of propane, do not support the theory that reaction between the intermediates of the oxidation process is critical to the combustion mechanism in the way suggested by these schemes.

The changes observed in the polarograms of the combustion samples emphasise the differences between the low- and high-temperature regions of reactivity. As the temperature of the oxidation of ethyl formate was increased in the low-temperature region, the step at 1·9 v gradually decreased. In the transition region between the two temperature zones the wave at 1·9 v disappeared from the polarograms and a new step appeared at 1·7 v.

An attempt was made to identify the changes in the polarograms by comparisons with the polarograms of pure aldehydes and acids. Conclusive results were not obtained, though the wave at 1·7 v did resemble the polarograms of formic acid. This last observation is complicated by the fact that the relationship between the total acid concentration, as determined by direct titration, and the pressure change, Δp (Fig. 1), does not correspond to the changes observed in the height of the wave. There always exists the possibility of balancing reactions and separate laws governing the changes in the total acid and formic acid concentrations, but such changes would have to be quite complex. At the present stage in the investigation the best that can be inferred is that there is in fact the disappearance of one species and the appearance of a second during the traversing of the transition region between the low- and high-temperature regions of reactivity.

The only case in which it was practically feasible to investigate changes during the actual passage of a cool flame was with propane and oxygen.

The concentration of peroxide substances here showed a marked decrease with the passage of a cool flame through the reaction mixture, while the changes with time in the concentration of peroxide before and after the occurrence of the flame followed a more or less exponential law. Such behaviour would be expected according to the mechanism of cool-flame oxidation which depends upon the effect of temperature on the rate of decomposition of the peroxide intermediates and the self-heating of the reaction mixture.

Where the general form of the mechanism is

$$A + B \longrightarrow C \longrightarrow D + E$$

(compare Salnikov [13]) and the heat of reaction of the second step is considerably greater than that of the first, self-heating of the reaction mixture would result under the appropriate conditions of concentration and temperature. Any chain-branching mechanism similar to that described in the Introduction would be particularly sensitive to self-heating. The very greatly magnified effects of small changes in the initial concentrations of the reagents or the reaction temperature support some such scheme.

The outstanding feature of cool-flame combustion is the fact that the ignition does not spread through the primary reagents themselves. Analyses of the propane mixtures, similar to those described in Part I, indicate no significant changes in the concentration of propane, oxygen, carbon monoxide, or carbon dioxide with the passage of a cool flame. The low-temperature flames are clearly shown to be directly associated with the intermediate compounds of the oxidation process. Moreover, the position of the zone of cool-flame activity in the region of transition between the low- and high-temperature regions

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[12] Frank-Kamenetzki, *Compt. rend. Acad. Sci., U.R.S.S.*, 1939, **25**, 671.

[13] Salnikov, *ibid.*, 1948, **60**, 405.

suggests that the substances decomposing explosively are the chain-branching agents of low-temperature oxidation.

These results, therefore, throw further light upon the general character of the phenomena in question. The proof, or disproof, of more detailed schemes lies undoubtedly in an analytical method for the isolation and examination of the inferred chain-branching substances and for the recognition of their modes of decomposition and oxidation.

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