352. *The Oxidation of Hydrocarbons and Their Derivatives. Part II.* Structural Effects in the Ester Series.*

By B. I. PARSONS and SIR CYRIL HINSHELWOOD.

A comparison is made, under standardised conditions, of the relative oxidation rates of a series of esters: methyl formate, methyl acetate, methyl butyrate, ethyl formate, methyl propionate, and propyl formate. Oxidation rates have been determined as a function of the concentrations of ester and of oxygen, and at a series of temperatures.

In one group the rate–temperature relation follows the Arrhenius law; in another the rate passes through a maximum and then a minimum as the temperature is raised.

The ease of oxidation is considered in relation to structure, and the results are found to be generally explicable in terms of the principles which have emerged from the study of other series of compounds.

THE oxidation of hydrocarbons and their derivatives is profoundly influenced by structural changes. In particular, the substitution of methyl groups has a great stabilizing influence, and the point of attack in the molecule which leads to the most rapid oxidation seems to be one as remote as possible from such groups. Chlorine atoms and alkoxy-groups (in ethers) facilitate oxidation and the replacement of a methylene by a carbonyl group retards it.[1]

Esters contain both carbonyl and alkoxy-groups, and in the aliphatic esters, R·CO·OR′, the number of methylene groups in either R or R′, or in both, can be varied. It is, therefore, of interest to see how far the structural principles mentioned above work out in this series.

The conditions of comparison are important. In the first place, oxidation rates are not simple functions of the reactant pressures, and these functions must first be examined. With the esters there is the usual relative insensitivity to oxygen pressure and the much more marked dependence on the ester pressure. In the second place, the rate may depend in a complex way upon temperature, rising, falling, and then rising again as the temperature increases. Where this abnormal dependence on temperature occurs it is convenient to distinguish the "low-temperature" region and the "high-temperature" region, there being good reason to believe that in the two the mechanisms of reaction are different.

The form of the rate–temperature curve, the structural effect, and the reaction mechanism are related in an important way. Peroxides are widely held to play an essential part in the mechanism, their fission into radicals giving rise, in the low-temperature region, to branching chains. The equations for the kinetics of such a branching-chain reaction show that a relatively small change in the ease of fission of the peroxide can produce a greatly magnified effect on the reaction rate. In this way, the exceptional sensitiveness of the oxidation to structural influences can be partly accounted for.[2] The abnormal temperature dependence is explained by the increasing loss of peroxide, as the temperature rises, in decompositions which do not help the chain branching (or as the result of the decomposition of precursors to the peroxide). Either process would lead to a fall in the rate of oxidation. The resumed rise at still higher temperatures is ascribed to the intervention of a new kind of mechanism, no longer directly associated with peroxide fission. If these considerations are valid, the great sensitiveness to structure evident in the low-temperature region should largely disappear in the high-temperature region.

EXPERIMENTAL

The reacting gases and vapours were placed in a heated silica vessel and the pressure changes accompanying oxidation were followed on a manometer. The validity of following the reaction

---

* Part I, preceding paper.

[1] (*a*) Cullis, Hinshelwood, and Mulcahy, *Proc. Roy. Soc.*, 1949, *A*, **196**, 160; (*b*) Bardwell, *ibid.*, 1951, *A*, **207**, 470; Hinshelwood, *Discuss. Faraday Soc.*, 1951, **10**, 266; (*c*) Eastwood and Hinshelwood, *J.*, 1952, 733.

[2] Cullis, Hinshelwood, Mulcahy, and Partington, *Discuss. Faraday Soc.*, 1947, **2**, 111.

by observation of pressure changes has been examined in Part I.[3] The reaction, in general, shows an induction period during which the rate rises to a maximum. Typical pressure–time curves for the six esters investigated have been given in Part I. The laws governing the influence of concentrations on the maximum rate and the induction period are not expressible by any simple formula, and for the present at least the dependence of each must be recorded separately. The important relations are shown in Figs. 1, 2, and 3.

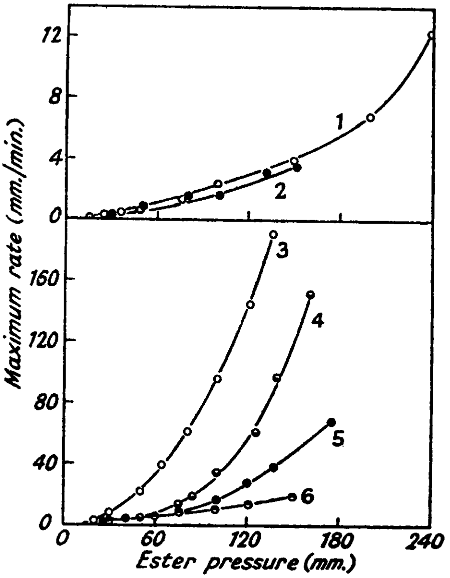
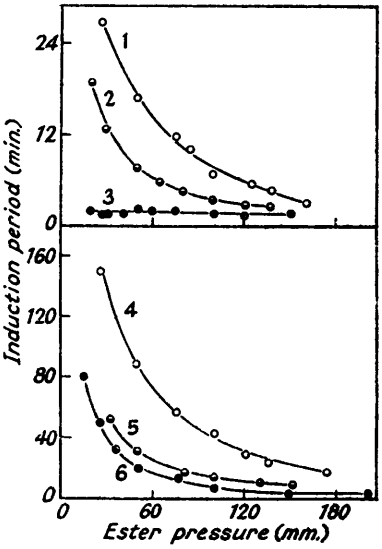


FIG. 1. *The effect of ester concentration on the maximum rate of oxidation.*

1. Methyl formate. 2. Methyl acetate.
3. Methyl butyrate. 4. Ethyl formate.
5. Methyl propionate. 6. Propyl formate.

Temperature : curves 1—5, 380°; curve 6, 260°. Oxygen pressure : 200 mm.

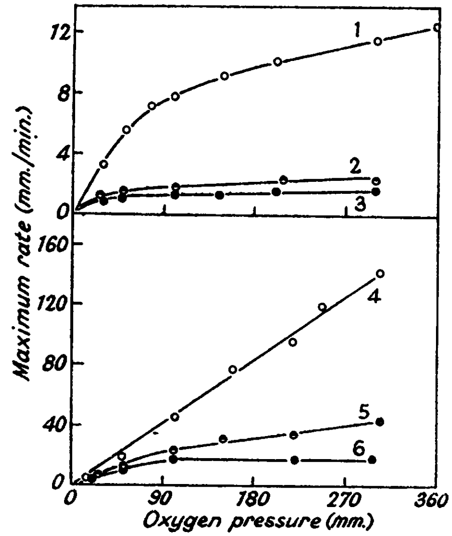
FIG. 2. *The effect of ester concentration on the induction period.*



1. Ethyl formate. 2. Methyl butyrate.
3. Propyl formate. 4. Methyl propionate.
5. Methyl acetate. 6. Methyl formate.

Temperature : curves 1, 2, 4, 5, 6, 380°; curve 3, 260°. Oxygen pressure : 200 mm.

FIG. 3. *The effect of oxygen concentration on the maximum rate of oxidation.*



1. Propyl formate. 2. Methyl formate.
3. Methyl acetate. 4. Methyl butyrate.
5. Ethyl formate. 6. Methyl propionate.

Temperature : curves 2 to 6, 380°; curve 1, 260° Ester pressure : 100 mm.

---

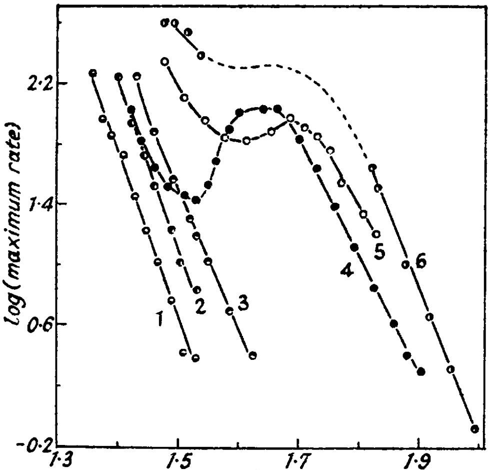
[3] Preceding paper.

The influence of initial concentrations on the maximum rate and induction period of the oxidation of the esters was very similar to that observed during the oxidation of the paraffins. In general, the rate is much more sensitive to the pressure of the organic vapour than to that of the oxygen. The induction period was equally dependent on the initial pressure of the combustible material. Except at very low oxygen pressures the induction period was independent of the initial oxygen concentration.

It is necessary to bear in mind the somewhat varying relations between rate and the pressures of oxygen or ester when comparisons between the different esters are made. The partial pressures chosen for most of the comparisons were 100 mm. of ester and 200 mm. of oxygen.

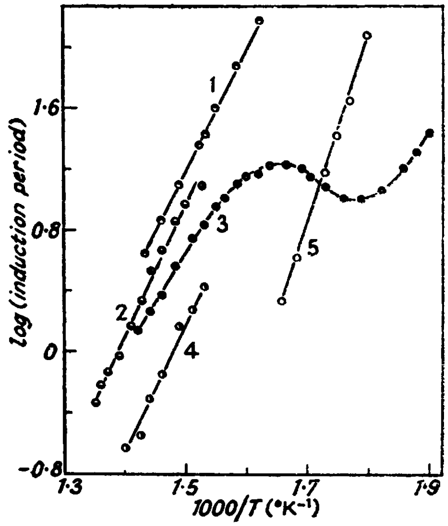
In order to construct a table of relative oxidation rates applicable at one given temperature, extrapolations are sometimes necessary, and for this purpose, as well as for the information the results give about the nature of the reaction mechanism, the temperature effect was determined in each example. The maximum rates are plotted in the conventional way in Fig. 4 as a function of temperature, and analogous results for the induction period are shown in Fig. 5. Since the rates for methyl formate and methyl acetate are nearly the same, the results selected for illustration in the case of methyl formate refer to 200 mm. initial ester pressure instead of the conventional 100 mm., this choice being made so that the curves for the two esters may be displaced relatively to one another and not interfere on the diagram.

FIG. 4. *The effect of temperature on the maximum rate of oxidation.*



1. Methyl acetate.
2. Methyl formate.
3. Methyl propionate.
4. Ethyl formate.
5. Methyl butyrate.
6. Propyl formate.

FIG. 5. *The effect of temperature on the induction period.*



1. Methyl propionate.
2. Methyl acetate.
3. Ethyl formate.
4. Methyl formate.
5. Methyl butyrate.

It is clear from Fig. 4 that in the temperature range studied the esters fall into two very clearly defined groups : one in which the Arrhenius equation is followed, and the other in which the low- and high-temperature regions are distinguished, and separated by a region where the rate actually decreases with increasing temperature. Whether the characteristics of the second group would be shown by the first in another range of temperature cannot be said with certainty. What can be said, however, is that the factors responsible for the anomalous temperature effect in the esters of the second group are not operative in the other esters in any of the experiments carried out.

Structural Influences.—The relative values of the maximum rate of oxidation of the esters are shown in the Table. The experimental techniques used during the present study were very similar to those used in previous studies in this laboratory, and several approximate values of the corresponding rates of oxidation of normal hydrocarbons, ketones, and ethers are included in the list. Where the reactivities of the compound are very different the relative rates were determined by the extrapolation of the log rate–$1/T$ plots until the temperature regions overlapped.

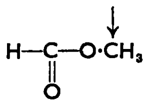
In an attempt to understand the influence of structure on the rate of oxidation it is necessary to consider also at which point in the molecule the initial attack occurs. The two problems are interconnected, since, although oxidation may begin in more than one place, it is only that attack which initiates a rapid and effective chain reaction which can lead to an important total contribution to the oxidation. The significant point of attack, therefore, is one which can lead to the formation of the most highly active chain-branching agents, or, in accordance with our own present working hypothesis, to the most active peroxides.

	Maximum rate relative to methyl formate			Maximum rate relative to methyl formate	
Compound	(low-temperature region)	(high temperature-region)	Compound	(low-temperature region)	(high temperature-region)
Methyl formate	1	1	*n*-Pentane	750	—
Methyl acetate	1	1	Pentan-2-one	750	—
Methyl propionate ...	6	6	Pentan-3-one	3500	—
Methyl butyrate ...	350	24	Dimethyl ether	20×10^3	—
Ethyl formate	350	3·6	Ethyl methyl ether	130×10^3	—
Propyl formate	2000	47			

Previous work has given several definite rules indicating which kinds of structure are susceptible to this kind of fruitful attack. If the oxidation has to begin within a methyl group the resulting rate is usually low: methyl groups adjacent to the site of initiation are unfavourable. Methylene groups, on the other hand, as remote as possible from methyl groups constitute vulnerable points. Carbonyl groups in themselves tend to favour oxidation unless they replace an attackable methylene group, and thereby force the attack into a methyl group as in acetone. An ethereal oxygen atom has a very great activating influence.

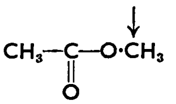
If these principles are applied to the ester series, a good idea can be formed of the place where in a given molecule the oxidation will begin, and an approximate idea can be formed of the relative speed of the total reaction which will ensue. In this way a general understanding of the results in the Table can be arrived at.

The formulæ of the esters used are as follows :



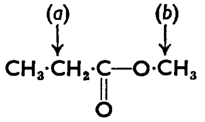
$\mathrm{H{-}\underset{\underset{O}{\|}}{C}{-}O{\cdot}\overset{\downarrow}{CH_3}}$

(I)



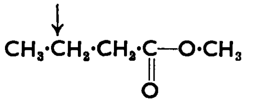
$\mathrm{CH_3{-}\underset{\underset{O}{\|}}{C}{-}O{\cdot}\overset{\downarrow}{CH_3}}$

(II)



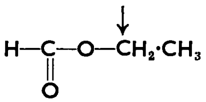
$\mathrm{CH_3{\cdot}\overset{(a)\downarrow}{CH_2}{\cdot}\underset{\underset{O}{\|}}{C}{-}O{\cdot}\overset{(b)\downarrow}{CH_3}}$

(III)



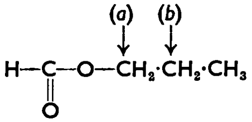
$\mathrm{CH_3{\cdot}\overset{\downarrow}{CH_2}{\cdot}CH_2{\cdot}\underset{\underset{O}{\|}}{C}{-}O{\cdot}CH_3}$

(IV)



$\mathrm{H{-}\underset{\underset{O}{\|}}{C}{-}O{-}\overset{\downarrow}{CH_2}{\cdot}CH_3}$

(V)



$\mathrm{H{-}\underset{\underset{O}{\|}}{C}{-}O{-}\overset{(a)\downarrow}{CH_2}{\cdot}\overset{(b)\downarrow}{CH_2}{\cdot}CH_3}$

(VI)

In view of the great activating influence of the ethereal oxygen it seems not unreasonable to assume that the effective attack on the esters (I) and (II) will be in the methyl group attached to this oxygen. But no methyl group is in itself a really advantageous point, so that esters (I) and (II) show relatively low rates. Methyl propionate (III) has a methylene group which could be attacked, but this is still adjacent to a methyl group. At which of the two points indicated by the arrows the attack by oxygen will lead to a more successful chain reaction is hard to say. If it is (*a*) this point is at least not in a methyl group itself, while if it is (*b*) a stabilising methyl group is one step further removed than in methyl acetate (II). Ester (III) thus shows a small but not important increase in rate. In esters (IV), (V), and (VI) the point of attack can move out of methyl groups, without becoming too remote from the ethereal oxygen. With these compounds the increase in rate, in the low-temperature region, is very marked. Since propyl formate (VI) has the greatest oxidation rate of the series it seems that the provision of a point of attack, (*a*) as remote as possible from the methyl group is the important factor.

Reference to the Table shows that in the high-temperature region the structural effects are considerably less pronounced than they are in the low-temperature region. It is also evident that with the esters (I), (II), and (III) there is one region only, and that the structural influence is small. The result is thus as though the single region of temperature dependence covered by the experiments has the characteristics of a " high-temperature " region. In these three esters it seems at least quite likely that the initial attack is in the methoxy-group itself. This may be the reason why anomalous temperature dependence, structure sensitivity, and also cool-flame production are all absent.

With esters (IV), (V), and (VI) attack is probably in a methylene group. In the low-temperature region the rate is enormously enhanced compared with that of the other esters. The usual effect of a lengthening of the carbon chain is evident in the comparison of esters (VI) and (V); propyl formate (VI) is considerably more easily oxidised than methyl butyrate (IV). The reason would seem to be that in the latter the propyl group is immediately adjacent to a carbonyl group, whereas in ester (VI) it is adjacent to the ethereal oxygen, which assists more powerfully.

On the whole, therefore, the ester series seems to offer a further general confirmation of the structural principles already illustrated by other groups of compounds.

The comparison of the esters with the ethers is of interest. For this purpose, a considerable degree of extrapolation is necessary, but this, while rendering numerical values open to some doubt, leaves none about the qualitative differences.

Ethyl formate (V) is oxidised something like 10^3 times more slowly than ethyl methyl ether. This fact seems hard to understand except by the supposition that the conversion of H CH_2 into H C:O has in some way partly neutralised the effect which the adjacent ethereal oxygen has on the ethyl group. The same consideration applies to a comparison between propyl formate (VI) and methyl propyl ether.

The nature of this action of the carbonyl group does not seem explicable simply in terms of the normal inductive effects of the substituent groups. The question indeed arises whether some special circumstance may not be involved in the great oxidisability of the ethers, possibly the formation of peroxides involving the ethereal oxygen itself, which act as powerful initiators of combustion. It has already been found [1c] that the concentration of some kind of peroxidised body is much higher than usual in ether oxidations, and that this concentration does not show the large relative decrease which occurs in other examples when a cool flame passes.[4] There are thus indications that the ethers may constitute a special problem.

Apart from this, the study of the esters seems to bear out the general principles which have emerged from the study of other groups of compounds.

The expectation expressed in the Introduction that the structure sensitiveness would be much smaller in the high-temperature region is fully borne out. It also appears that the only three of the six esters which, in the low-temperature region, are oxidised very many times faster than methyl formate are those which show anomalous rate–temperature relations. Thus the idea is further confirmed that the great influence of structure is upon something which as the temperature rises eventually ceases to be important, that is, according to the peroxide theory, the peroxide itself, or according to another theory a precursor of the peroxide.

PHYSICAL CHEMISTRY LABORATORY,
OXFORD UNIVERSITY.

[*Received, October 24th,* 1955.]

---

[4] Bardwell and Hinshelwood, *Proc. Roy. Soc.*, 1951, *A*, **205**, 375.