131. *The Comparative Ease of Oxidation of Various Ethers in the Gaseous Phase.*

By T. A. Eastwood and Sir Cyril Hinshelwood.

A comparative study has been made of the reactions of a series of ethers with gaseous oxygen. In the low-temperature region of slow reaction the kinetics are generally similar for the various members, which also resemble certain hydrocarbons in that the rate passes through a maximum with increasing oxygen concentration. This rate is linearly (or less) dependent on the ether concentration. In these respects the ethers can be regarded as substituted hydrocarbons and included in a general structural survey. Quantities of peroxides (much larger than with hydrocarbons) are formed and reach a maximum at the same time as the rate of pressure increase. Cool flames appear in certain regions of pressure and temperature. The general position of the areas of cool flame, ignition, and slow reaction has been mapped for the series of ethers. In sharp contrast with what occurs in the oxidation of butanone the peroxide concentration shows little change during the passage of a cool flame. The role and possibly the nature of the peroxides present in the two cases appear to be different.

The introduction of the ethereal oxygen leads to a very great enhancement of reactivity, and though the methyl group, as in hydrocarbons, remains resistant to attack, the response of the oxidation rate to increase in the length of the alkyl chain is subject to a marked saturation effect, there being no increase beyond diethyl ether—in contrast with what is observed in the normal paraffin series. The nature of the structural influence is discussed in terms of an electron attractive ($-I$) effect of OR groups.

Low-temperature reactions of gaseous oxygen with hydrocarbons and their derivatives present many features of interest, and this paper continues the study of the effect of structure and substitution on the various phenomena associated with the oxidation. It deals with the homologous series of the ethers. First, the general kinetic relations are examined for comparison with the hydrocarbon series. Then the role of peroxides in the slow reaction and in the cool flames is considered, and finally a comparison of reactivity throughout the series is made.

Experimental methods and results

Ether vapour and oxygen were admitted separately to a " Pyrex " reaction vessel of 250 ml. capacity and of diameter approximately 8 cm., kept at constant temperature, and the reaction was followed by observation of the pressure change and by peroxide analyses. The details were as previously described (Cullis and Hinshelwood, *Discuss. Faraday Soc.*, 1947, **2**, 117; Cullis and Smith, *Trans. Faraday Soc.*, 1950, **46**, 42). Peroxides were usually estimated by the ferrous thiocyanate method but auxiliary analyses were made with potassium iodide in neutral and acid solutions. An initial pressure decrease of some magnitude was observed during the slow combustion of the ethers but was eventually followed by the normal pressure increase. The maximum rate of pressure increase ($\rho_{max.}$) was taken as a measure of the rate of reaction.

Kinetic Characteristics of the Slow Reaction.—All the ethers studied were found to be generally similar in the kinetics of their slow oxidation, the results with diethyl ether, given below, being typical.

(1) *Oxygen pressure.* The dependence of the maximum rate on the oxygen pressure for a constant diethyl ether pressure of 150 mm. at several temperatures is shown in Fig. 1. It is seen that the rate first rises with increasing oxygen pressure but ultimately falls to low values. The curve for 173° is necessarily incomplete since ether-rich mixtures give rise to cool flames (characterised by a rapid increase in pressure and a final pressure increase of less than 50%) while oxygen-rich mixtures give more violent ignitions (rapid pressure increase and a final pressure increase of more than 50%) with the formation of carbon.

FIG. 1. *The effect of oxygen pressure on the maximum rate of oxidation of diethyl ether at* 150 *mm. pressure. Temperatures*; 173°, 168°, 167°, 162°, 157° *in descending order of curves.*

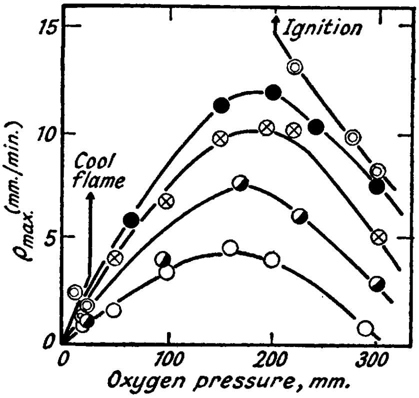

FIG. 2.

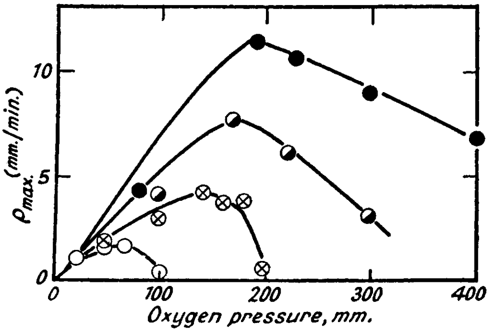

FIG. 3.

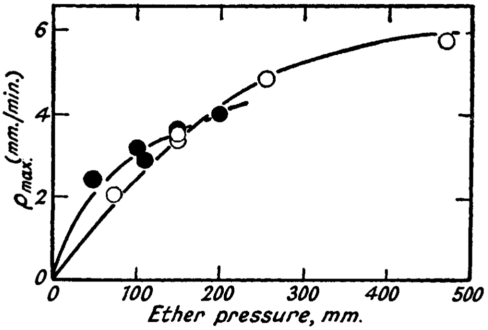

FIG. 2. *The variation of the maximum oxidation rate with initial oxygen pressure at* 162°. *Diethyl ether pressures*; 50, 100, 150, 200 *mm. in ascending order of curves.*

FIG. 3. *The variation of maximum oxidation rate with diethyl ether pressure at* 157°. *Oxygen pressures*: 50 *mm., open circles*; 100 *mm., filled-in circles.*

The $\rho_{max.}$–oxygen pressure relationship was found to be of the same form for various fixed ether concentrations ranging from 50 to 200 mm. at 162° (Fig. 2).

(2) *Ether pressure.* Fig. 3 shows how the rate increases with an increase in ether pressure, the apparent order of reaction being less than unity. Slightly lower ether-oxygen ratios were used with some of the other ethers, and the dependence was found to be linear. (The range of concentrations over which measurements can be made is restricted by the strong inhibiting influence of oxygen in oxygen-rich mixtures.)

(3) *Temperature.* With 50 mm. of diethyl ether and 50 mm. of oxygen the rate becomes appreciable at about 160° and increases steadily with increasing temperature (Fig. 4). Above 171° the reaction becomes explosive.

Ether combustion, in common with gas-phase oxidations generally, was found to be very sensitive to surface conditions and to deviations from the established experimental procedure. Nevertheless, the results of three groups of experiments with diethyl ether (Fig. 4) made at intervals in the course of over 600 experiments and involving explosions as well as slow reactions, show that reasonable reproducibility can be achieved by rigid standardization of the experimental technique.

To place the results in Fig. 4, and similar results with other ethers, in their proper perspective in the complete range of oxidation behaviour of the various ethers the temperatures at which slow reactions, cool flames, and ignitions occur in equimolar ether–oxygen mixtures were determined over a wide range of pressures. The resulting pressure–temperature explosion diagrams are compared in Fig. 5. Similar diagrams for some of the ethers have been published (Malherbe and Walsh, *Trans. Faraday Soc.*, 1950, **46**, 835, give a summary of the available results) but since they were obtained by different workers under different reaction conditions they are not immediately suitable for a comparative survey. In the region between the upright boundary lines in Fig. 5 (or in the completely enclosed area of the dimethyl ether diagram) combustion is accompanied by a cool flame. In the area beyond the right-hand boundary, that is at higher total pressures but in about the same temperature range, ignition occurs, while in the area beyond the left-hand boundary slow reaction is observed. As the temperature is lowered from the cool flame or ignition region a boundary is crossed below which slow reactions prevail. Di*iso*propyl ether was exceptional in that slow reactions and ignitions were not observed at all over a wide range where cool flames or negligible reaction occurred. A complete chart was made with dimethyl ether, and it was found that as the temperature is raised from the cool flame region slow reactions are encountered over a range of pressures, but that a further increase in temperature or an increase in pressure leads to conditions which favour ignition. With the other ethers it was not possible to extend the diagrams to high temperatures because the cool flame or ignition set in so rapidly that the products expanded into the connecting tubes before the oxygen could be completely added to the reaction mixture. Nevertheless, these diagrams demarcate the " low temperature " reaction regions, which are the areas of primary interest in the present survey, and show that the results in Fig. 4 and similar results for other ethers, to be considered in a later section, were obtained under comparable reaction conditions in the low-temperature region.

FIG. 4.

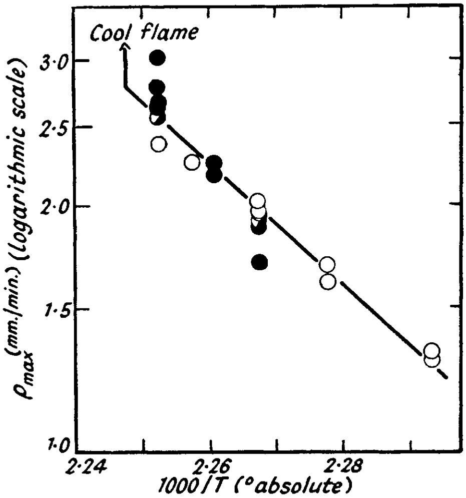

FIG. 5.

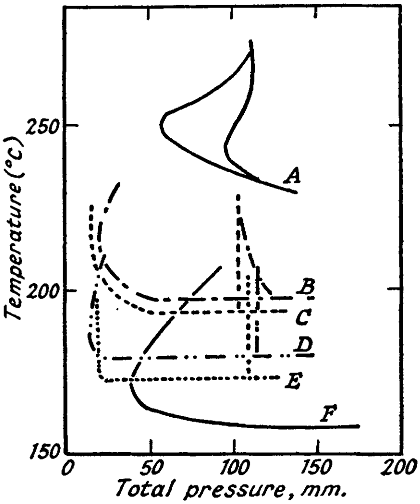

FIG. 4. *The effect of temperature on the maximum rate of oxidation of diethyl ether ; ether pressure* 50 *mm., oxygen pressure* 50 *mm. Experiments in Groups* 1, 2, *and* 3 *shown by different kinds of circle.*

FIG. 5. *The pressure–temperature explosion diagrams for equimolar ether–oxygen mixtures.*

A. Dimethyl ether. *B. Methyl* n-*propyl ether.* *C. Ethyl methyl ether.*
*D. Di-*n-*propyl ether.* *E. Diethyl ether.* *F. Di*iso*propyl ether.*

(4) *Inert gas.* Additions of nitrogen to various mixtures of diethyl ether and oxygen at 168° were found to have no significant influence on the oxidation.

(5) *Peroxide formation.* In the early stages of the reaction much larger quantities of peroxides were detected in the slow combustion of the ethers than with the hydrocarbons. In agreement, however, with observations on the paraffins, chloroparaffins, amines, and ketones, the *maximum* peroxide concentration is not reached until the pressure increase also reaches its maximum (Fig. 6). Corresponding to this large accumulation of peroxide there is initially a diminution of pressure, which is transformed into an increase only when the peroxide has reached its maximum so that its breakdown balances its formation.

In view of the general similarity of the ethers and the other organic compounds previously studied in the kinetics of their low-temperature, slow oxidation, the ethers can be regarded as substituted hydrocarbons and included in a general structural survey.

Role of Peroxides in the Cool-flame Reaction.—The variation in peroxide concentration during the cool-flame reaction of diethyl ether at 172° and 174° is compared with the formation of peroxides in the slow reaction at 170° in Fig. 7. In the cool-flame reaction the peroxide concentration is seen to increase rapidly until the cool flame appears, and thereafter to decrease very slowly.

FIG. 6.

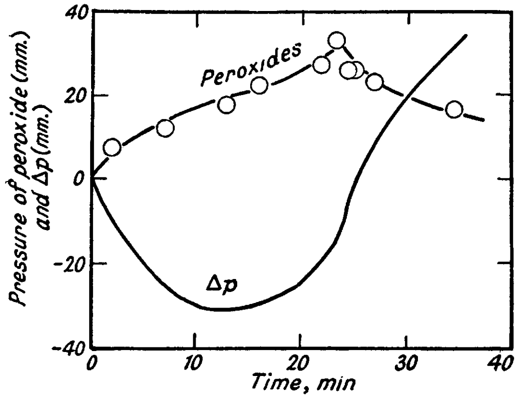

FIG. 7.

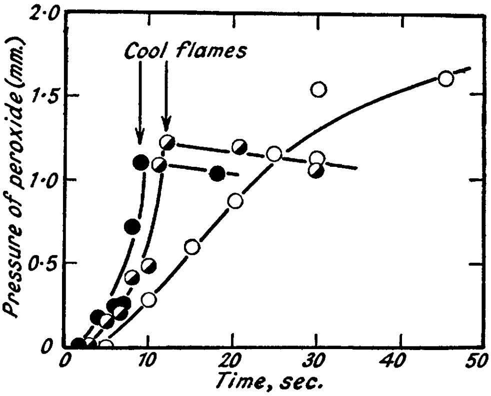

FIG. 6. *The variation of peroxide concentration during the slow reaction and the corresponding* Δp*-time curve. Ether pressure,* 150 *mm.* ; *oxygen pressure,* 250 *mm.*

FIG. 7. *Comparison of the formation of peroxides in the slow and cool-flame reactions, respectively, of diethyl ether. Ether pressure,* 30 *mm.* ; *oxygen pressure,* 30 *mm. Slow reaction at* 170°, *open circles* ; *cool-flame reaction at* 172°, *half-shaded circles* ; *at* 174° *filled-in circles.*

The stability of peroxides during the passage of the cool flame of diethyl ether contrasts strongly with the precipitous decline in the peroxide concentration during the butanone cool flame (Bardwell and Hinshelwood, *Proc. Roy. Soc.*, 1951, *A*, **205**, 375). The behaviour of peroxides in the diethyl ether cool-flame reaction was, therefore, investigated further. A large number of additional analyses of the reaction mixture in the last moment before the appearance of the cool flame confirm the results in Fig. 7 and show that it is unlikely that the concentration of peroxides ever exceeds the values recorded in the figure. It was found, moreover, that a mixture of 30 mm. of ether and 30 mm. of oxygen initially at 170° (*i.e.* in the region of slow reaction) could be heated to 198°, 27° above the lowest temperature at which cool flames appear, without the appearance of a cool flame even though the peroxide concentration was determined to be 2·9 mm. In a similar experiment more oxygen and ether were added separately to the reaction mixture after the temperature had been raised above the cool-flame temperature and again no cool flame appeared. The final temperature was 184° and the peroxide pressure was 3·5 mm. Since peroxides as a whole survive the passage of the cool flame of diethyl ether and, indeed, exist in concentrations above the maximum reached in a cool-flame reaction at temperatures higher than the minimum cool-flame temperature, it would appear that with diethyl ether they do not play the important role in the cool-flame reaction that they do with butanone. There still remains the possibility that a reactive type of peroxide, present in such small amounts relative to the total peroxide concentration that variations in its concentration are not detected, is responsible for the cool flame. Analyses by the methods involving acid or neutral potassium iodide reveal the same general picture of peroxide formation, so a decision on this matter is not at the moment possible.

Comparison of Reactivity.—In order to compare the reactivities of the ethers and the paraffins a link between the two was established by confirming the results of the slow oxidation of *n*-pentane (Cullis and Hinshelwood, *loc. cit.*) in the present apparatus. It was found that the difference between the reactivities of pentane and the ethers, and often between adjacent members of the ether series also, was so great that the rates could not be conveniently measured at the same temperature. It was usually necessary, therefore, to compare extrapolated values of the rate obtained from log $\rho_{\text{max.}}$–$1/T$ plots, similar to Fig. 4, for the appropriate compounds. The comparisons were made at the same pressure with equimolar mixtures of the organic reactant and oxygen, and the results are summarized in the table. With diethyl and di-*n*-propyl ethers, which can be compared directly at the same temperature, the relative rates depend on the ether–oxygen pressure ratio but the variation does not alter the position of these compounds in the table. Thus the order in which the compounds appear there probably applies over a fairly wide range of reaction conditions in the low-temperature region, although the actual figures may be subject to minor variations. The log $\rho_{\text{max.}}$–$1/T$ relation was not determined for di*iso*propyl ether since, as previously mentioned, the combustion of this compound is extremely slow in the slow-reaction region. A direct comparison, however, of the rates of reaction of 20 mm. of ether and 20 mm. of oxygen at 170° shows that di*iso*propyl ether oxidizes much less readily than diethyl ether.

Compound	Relative rate	
Pentane	1	—
Dimethyl ether	25	1
Ethyl methyl ether	175	7
Methyl *n*-propyl ether	175	7
Diethyl ether	2500	100
Di-*n*-propyl ether	1300	50

It is clear in the first place that the introduction of –O– into a carbon skeleton leads to a very great enhancement of the reactivity. In the second place it is of interest to observe that the influence of the ethereal oxygen is not reinforced by the lengthening of the carbon chain beyond diethyl ether, in contrast with the progressive increase in the rate of oxidation which occurs on ascent of the paraffin series. It would thus appear that the response of the oxidation rate to enhancement by substitutional influences is subject to a marked saturation effect. The stability of dimethyl and di*iso*propyl ethers emphasises once more the resistance of the methyl group to oxidative attack, a factor already prominent in the low-temperature oxidation of other series of organic compounds.

DISCUSSION OF STRUCTURAL INFLUENCES

The two major influences of structure on oxidation are (1) the great tendency for methyl groups to resist oxidation and (2) the influence of electron displacements on the chain-initiating and the chain-branching steps of the total sequence of reactions. This sequence is probably of the general form :

$$\begin{aligned} \mathrm{RH} + \mathrm{O_2} &\longrightarrow \mathrm{R{-}} + \mathrm{HOO{-}} \quad \text{(chain-initiating step)} \\ \mathrm{R{-}} + \mathrm{O_2} &\longrightarrow \mathrm{ROO{-}} \\ \mathrm{ROO{-}} + \mathrm{RH} &\longrightarrow \mathrm{ROOR} \\ \mathrm{ROOR} &\longrightarrow 2\ \mathrm{RO{-}} \quad \text{(chain-branching step)} \end{aligned}$$

While any step may respond to structural changes, the influence of electron displacements on the branching process is likely to be the most important since the effect on this step is magnified by the peculiar kinetics of the low-temperature oxidation reaction. In any case the effects of substitution are likely to be in the same direction in both the chain-initiating and chain-branching steps and so tend to reinforce one another (*Discuss. Faraday Soc.*, 1951, **10,** 266).

It appears in general that the influence of electron displacements on the branching step can be interpreted in terms of a stabilization of the –O–O– linkage in the peroxide by substituents which favour electron accession to the seat of reaction (*i.e.* by substituents with an inductive action represented by $+I$) and a weakening of the peroxide bond by $-I$ substituents. For example, methyl, which is electron-repelling, reduces the oxidation rate. The relative ease of ether oxidation compared with pentane suggests that the –O–O– linkage in peroxides derived from ethers must be comparatively weak, and thus, according to the rule mentioned, implies that the RO group (an ether being regarded as a hydrocarbon with an RO-substituent) is exerting a $-I$ inductive action. This implication is in agreement with the usual view about the inductive action of the CH_3O group.

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PHYSICAL CHEMISTRY LABORATORY, OXFORD UNIVERSITY. [*Received, September 29th,* 1951.]