874. *Gaseous Oxidation of Aliphatic Esters. Part I. Slow Combustion of Ethyl Acetate.*

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Slow combustion of ethyl acetate takes place in two temperature regions. In the lower region, acetic acid and formaldehyde are the major products, but in the higher acetaldehyde predominates. Formic acid, acid anhydrides, organic peroxides, peroxyacids, and hydrogen peroxide are formed in smaller quantities, but no alcohol has been detected. Determination of the effects of composition and contact time has shown which of these products are stable and which are susceptible to decomposition or further oxidation.

A mechanism has been postulated which is consistent with this pattern of products and with the relative strengths of C–H bonds in hydrocarbons and their derivatives. The existence of two temperature regions is considered to be due to more than one mode of breakdown of hydroperoxides.

GASEOUS oxidations of hydrocarbons and their derivatives are free-radical chain reactions whose kinetics are sensitive to the structure of the fuel as well as to temperature, pressure, mixture composition, and homogeneous and heterogeneous catalysts. Introduction of a functional group into a hydrocarbon changes considerably the rate and course of oxidation [1] and, even within a given homologous series, slight alterations in the nature of the alkyl groups present have a marked effect.[2] Studies of the slow combustion of ketones [3] have shown that the replacement of a methylene by a carbonyl group slightly reduces the rate of oxidation, while similar work with ethers [4] has demonstrated that the ethereal oxygen greatly activates attack at the α-C–H bonds. These results suggest that the site of initial oxidative attack on an ester will be more specific than on the corresponding hydrocarbon, being the C–H bond adjacent to the "ethereal" linkage. Parsons, Danby, and Hinshelwood [5] applied these principles to studies of the oxidation of several esters. Anomalous rate–temperature dependences characterised some of these reactions and it was considered that variations, with temperature, of the rate of peroxide fission and the fate of the products thereof explained the existence of the regions of negative temperature coefficient, although no specific mechanism was suggested.

The studies to be described in the present series of papers were designed to elucidate the oxidation mechanism, with particular reference to the modes of decomposition of peroxide in the various temperature regions. In this paper, an account is given of detailed kinetic and analytical studies of the intermediate products of the gaseous oxidation of ethyl acetate, and of the probable mechanism of oxidation.

EXPERIMENTAL

Apparatus.—The reaction was studied in a flow system. Oxygen and nitrogen from cylinders were passed through a purification line, the rates of flow being controlled by needle-valves and metered by passage through calibrated capillaries. One of the nitrogen streams then flowed through a 500-ml. flask containing liquid ethyl acetate, at 50·0° ± 0·1°. As only *ca.* 95% of the theoretical quantity of ethyl acetate was taken up, the amount passing was determined for each set of flow conditions by chemical analysis. The use of presaturators at higher temperatures than the final saturator caused the flow rates to become irreproducible.

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[1] Cullis, *Chem. and Ind.*, 1962, 23.

[2] Small and Ubbelohde, *J. Appl. Chem.*, 1953, **3**, 193.

[3] Bardwell and Hinshelwood, *Proc. Roy. Soc.*, 1950, *A*, **201**, 26; Bardwell and Hinshelwood, *ibid.*, 1951, *A*, **205**, 375; Bardwell, *ibid.*, **207**, 461.

[4] Chamberlain and Walsh, Third Symposium on Combustion, Williams & Wilkins, Baltimore, 1949, pp. 368, 373.

[5] Parsons and Danby, *J.*, 1956, 1795; Parsons and Hinshelwood, *J.*, 1956, 1799; Parsons, *J.*, 1956, 1802.

To prevent condensation of organic vapours, those parts of the apparatus between the saturator and the analytical traps were electrically heated to *ca.* 80°.

The separate streams all entered a gas mixer consisting of three concentric tubes joined at alternate ends and electrically heated to *ca.* 90°, and the mixed gases next passed, through a flame trap containing glass chips and glass wool, into a cylindrical Pyrex reaction vessel, 12 × 4·5 cm., enclosed in an electric furnace, the temperature of which was automatically controlled to within ±0·25°.

When steady conditions had been attained, the products and unchanged ester emerging from the reaction vessel after a suitable residence time were condensed from the gas stream in a " cold-finger " trap at 0° and a system of traps at −195°. These traps were fitted with 20-ml. funnels from which solvents could be added. A U-tube and by-pass trapping device [6] was incorporated to collect samples for gas–liquid chromatography.

All the runs were carried out at atmospheric pressure.

Purification of Reactants.—Oxygen and nitrogen (from cylinders) were freed from carbon dioxide by passage through Sofnolite and dried with concentrated sulphuric acid followed by magnesium perchlorate.

" AnalaR " ethyl acetate was purified by distillation from phosphorus pentoxide, dried over anhydrous sodium sulphate, and redistilled; it had b. p. 76—78° (lit., 77·15°) and n_D^{20} 1·3723 (lit., 1·3721).

Analytical Procedure.—*Acids and anhydrides.* An aliquot part of an aqueous solution of the products was titrated under nitrogen with 0·01N-sodium hydroxide (phenolphthalein). After titration the pink quinonoid form of phenolphthalein slowly disappeared, owing to the slow hydrolysis of anhydrides. By successive titration and extrapolation of the amount of alkali added to zero time (*i.e.*, to the time of dissolution of the products in water) and infinite time, the true concentrations of " total acids " and " total anhydrides " were obtained.

Individual carboxylic acids were separated by chromatography with 1% of butan-1-ol in chloroform as eluent on a silica gel column buffered with 2 : 1 potassium hydrogen phosphate–potassium dihydrogen phosphate.[7] Successive portions of eluent were titrated with 0·01N-sodium hydroxide (Cresol Red). The method allowed formic and acetic acid to be separately estimated. It also gave a semiquantitative estimation of the concentrations of peroxyacids present.

Unchanged ester. After titration of acids and anhydrides, an excess of 0·01N-sodium hydroxide was added and the solution was kept at 40° for 30 min., calibration having shown that complete hydrolysis of ethyl acetate takes place under these conditions. The unchanged alkali was back-titrated with 0·01N-hydrochloric acid.

Aldehydes. Formaldehyde was determined colorimetrically by the chromotropic acid method.[8] Before this estimation it was necessary to reduce formaldehyde–peroxide complexes with magnesium and concentrated hydrochloric acid. The method therefore estimates formaldehyde *plus* formic acid. Ethyl acetate, when treated with concentrated sulphuric acid, reacted slightly with chromotropic acid to give a positive test for formaldehyde. Therefore, for each determination, a control was carred out with an amount of ester equal to that in the reaction products.

Total aldehydes were determined by the silver oxide method [9] which was found to give reliable results even in the presence of peroxides and ethyl acetate.

Alcohols. After destruction of aldehydes and peroxides by passage through silver oxide, attempts were made to estimate total alcohols by oxidation with acid dichromate and to determine methyl alcohol spectrophotometrically by oxidation to formaldehyde. These methods showed that alcohols were not present in the combustion products.

Peroxides. A modified iodometric method [10] of analysis which enables distinction to be made between peroxyacids, hydrogen peroxide, and other organic peroxides was used. Interaction of such peroxides (particularly hydrogen peroxide) with aldehydes and acids, however, renders the distinction somewhat artificial.

Gas-chromatography.—A 12-ft. gas–liquid chromatographic column [6] containing 10% by

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[6] Cullis, Fish, Hardy, and Warwicker, *Chem. and Ind.*, 1961, 1158.
[7] Moyle, Baldwin, and Scarisbrick, *Biochem. J.*, 1948, **43**, 308.
[8] Bricker and Johnson, *Ind. Eng. Chem.*, 1945, **17**, 400.
[9] Bailey and Knox, *J.*, 1951, 2741.
[10] Cullis and Newitt, *Proc. Roy. Soc.*, 1956, *A*, **237**, 530.

weight of polyethylene glycol (*M*, 400) on 40—60 mesh Embacel at 56·2° was used to confirm the absence of alcohols and to check the concentrations of ethyl acetate and of individual aldehydes found by the above chemical methods.

RESULTS

The Effect of Temperature.—The consumption of ethyl acetate and the amounts of the products were determined in the range 250—450°. Below 250° no oxidation occurs, and above 450° pyrolysis of the ester ensues. For an equimolar mixture of oxygen and ethyl acetate, reacting with a contact time of 134 sec., the variations with temperature of the amounts of products formed are shown in Fig. 1. The reaction takes place in two temperature regions, below 320° and above 350°, with a region of " negative temperature coefficient " between them. In the lower region, acetic acid and formaldehyde are the major products and smaller quantities of organic peroxides, peroxyacids, and formic acid are formed. Acetaldehyde is almost absent in this region but becomes the principal product at temperatures between 350° and 380°. Anhydrides and very small quantities of hydrogen peroxide are also formed in the higher-temperature region, together with the low-temperature products. A striking feature is that no alcohols were produced under any of the conditions used.

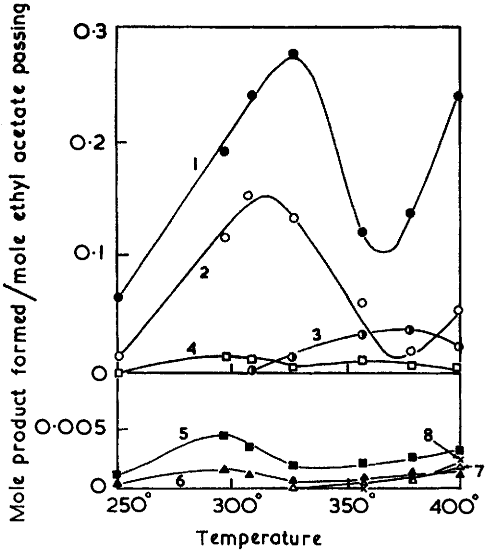

FIG. 1.

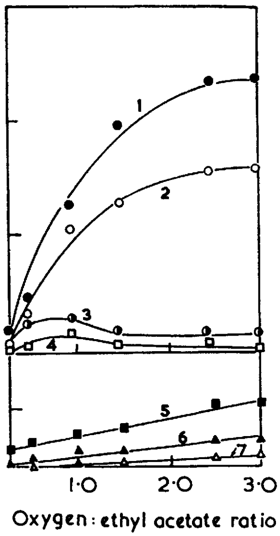

FIG. 2.

FIG. 1. The effect of temperature on the oxidation of ethyl acetate. Oxygen : ethyl acetate = 1 : 1; contact time = 134 seconds.

FIG. 2. The effect of reactant ratio on the oxidation of ethyl acetate at 358°; contact time = 134 seconds.

1, Ethyl acetate consumed; 2, total carboxylic acids; 3, acetaldehyde; 4, formaldehyde; 5, organic peroxides; 6, peroxyacids; 7, hydrogen peroxide; 8, anhydrides.

The Effect of Composition of the Reacting Mixture.—At each of a series of temperatures, ester–oxygen mixtures of various compositions were allowed to react, nitrogen being added to maintain a constant flow rate. The results of such studies at 358° (where the " low-temperature " mechanism is dying out and the " high-temperature " mechanism is beginning to appear) and with a contact time of 134 sec. are shown in Fig. 2, and illustrate the following general conclusions. The consumption of ester increases as the oxygen : ethyl acetate ratio is increased from zero to 1·5, but further increase in the proportion of oxygen has little effect. At low oxygen : ester ratios production of acetaldehyde closely parallels that of total acids, suggesting that these products have a common precursor; at higher ratios the production of acids increases considerably whereas that of acetaldehyde falls. Carboxylic acids, then, are stable products of oxidation at this temperature whereas acetaldehyde is susceptible to further oxidation, as is formaldehyde. The concentration of each of the peroxidic species increases with oxygen concentration, suggesting that these products are not further attacked *by oxygen.*

The Effect of Contact Time.—Such series of measurements were repeated for several contact times in the range 30—280 sec. Ester consumption increased with contact time, as did the formation of all the products for low values (<1·0) of the oxygen : ethyl acetate ratio. At higher values of this ratio, sufficient oxygen is available to produce considerable concentrations of products even with fairly low contact times (<150 sec.). Raising the contact time to 200—280 sec., therefore, demonstrates which of these products will eventually decompose in the hot reaction vessel. These results show that hydrogen peroxide, peroxyacids, and organic peroxides decompose in this way and confirm the above conclusion that formaldehyde and acetaldehyde are further oxidised but carboxylic acids are not.

Carbon Balance for the Reaction.—Carbon balances, expressed as (carbon estimated in products/carbon in ester consumed), have been calculated for reaction at 358° and vary from 1·00 at low values of contact time and oxygen : ester ratio to 0·41 at higher values. The effect of reactant ratio is much more marked than that of contact time. Carbon oxides were not systematically analysed and these trends show that the carbon " lost " is very probably converted into such products. The good balances obtained at low oxygen : ester ratios ensure that no important intermediate oxidation products have been neglected.

DISCUSSION

The gaseous oxidation of ethyl acetate takes place in two temperature regions, and the pattern of formation of certain products (*e.g.*, acetaldehyde) confirms the operation of different mechanisms in each of these. The phenomenon of a dual mechanism is not new in ester oxidation, having been reported for ethyl formate, methyl n-butyrate, and n-propyl formate.[5]

The C–H bonds of alkyl groups have strengths in the order primary > secondary > tertiary,[2,11] and the directive influences of the functional groups in an ester molecule have been discussed above. These show that the initial oxidative attack on ethyl acetate is very probably at the methylene group:

$$\underset{\text{(RH)}}{\mathrm{CH_3{\cdot}CO{\cdot}OEt}} + \mathrm{O_2} \longrightarrow \underset{\text{(R·)}}{\mathrm{CH_3{\cdot}CO{\cdot}O{\cdot}\dot{C}HMe}} + \mathrm{HO_2{\cdot}} \quad \ldots\ldots \quad (1)$$

The radical R· so formed readily participates in the chain cycle:

$$\mathrm{R{\cdot}} + \mathrm{O_2} \longrightarrow \mathrm{RO_2{\cdot}} \quad \ldots\ldots \quad (2)$$

$$\mathrm{RO_2{\cdot}} + \mathrm{RH} \longrightarrow \mathrm{ROOH} + \mathrm{R{\cdot}} \quad \ldots\ldots \quad (3)$$

accounting for the production of organic peroxides. The probable primary chain is thus similar to that generally postulated for hydrocarbon oxidation. The chain may also be continued by the reaction

$$\mathrm{HO_2{\cdot}} + \mathrm{RH} \longrightarrow \mathrm{R{\cdot}} + \mathrm{H_2O_2} \quad \ldots\ldots \quad (4)$$

The concentrations of hydrogen peroxide found experimentally are very low. The above reaction scheme is consistent with this fact as reaction (4) is unlikely to be of primary importance, HO_2· radicals being produced during the initiating step only.

The results show that the organic peroxide formed decomposes, and the concentration–temperature dependence (Fig. 1) suggests that several modes of such breakdown operate. Possible modes are:

$$\mathrm{CH_3{\cdot}CO{\cdot}O{\cdot}CHMe{\cdot}OOH} \longrightarrow \begin{cases} \longrightarrow \mathrm{H_2O} + \mathrm{CH_3{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CH_3} \quad \ldots\ldots \quad (5) \\ \longrightarrow \mathrm{CH_3{\cdot}CHO} + \mathrm{CH_3{\cdot}CO{\cdot}OOH} \quad \ldots\ldots \quad (6) \\ \longrightarrow \mathrm{CH_3{\cdot}CO{\cdot}O{\cdot}CHMe{\cdot}O{\cdot}} + \mathrm{{\cdot}OH} \quad \ldots\ldots \quad (7) \end{cases}$$

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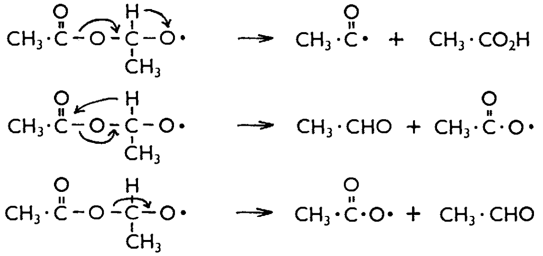
[11] Walsh, *Discuss. Faraday Soc.*, 1951, **10**, 320; Cullis and Hinshelwood, *ibid.*, 1947, **2**, 111.

As acetaldehyde and anhydrides are not formed in the lower-temperature region, mechanisms (5) and (6) do not operate here. Mechanism (5) is generally regarded as a high-temperature mechanism[12] and is no doubt responsible for the production of anhydrides in this region.

Fission of the weak O–O bond [reaction (7)] is the most usual mode of breakdown of hydroperoxide, particularly at low temperatures. The reaction produces two radicals per molecule of hydroperoxide and is probably largely responsible for chain branching during oxidation, the ·OH radicals abstracting hydrogen from further ester molecules. Reaction (7) will therefore have a much more profound effect on the observed kinetics than molecular reactions such as (5). The absence of alcohols in the products shows that ·OH radicals do not recombine with alkyl radicals to an appreciable extent.

The ether-oxy-radical formed by decomposition (7) may break down further by several routes:



$$CH_3\cdot\overset{O}{\overset{\|}{C}}-O-\underset{CH_3}{\overset{H}{C}}-O\cdot \longrightarrow CH_3\cdot\overset{O}{\overset{\|}{C}}\cdot + CH_3\cdot CO_2H \qquad \cdots\cdot (7a)$$

$$CH_3\cdot\overset{O}{\overset{\|}{C}}-O-\underset{CH_3}{\overset{H}{C}}-O\cdot \longrightarrow CH_3\cdot CHO + CH_3\cdot\overset{O}{\overset{\|}{C}}\cdot O\cdot \qquad \cdots\cdot (7b)$$

$$CH_3\cdot\overset{O}{\overset{\|}{C}}-O-\underset{CH_3}{\overset{H}{C}}-O\cdot \longrightarrow CH_3\cdot\overset{O}{\overset{\|}{C}}\cdot O\cdot + CH_3\cdot CHO \qquad \cdots\cdot (7c)$$

Routes (7b and c) produce acetaldehyde, and so they can operate only in the high-temperature region. The mechanism of hydroperoxide breakdown at low temperatures therefore involves reaction (7), followed by (7a), which accounts for the production of acetic acid. The acetyl radicals produced will react in two ways. Addition of further oxygen followed by hydrogen abstraction gives peracetic acid, while decomposition produces carbon monoxide and methyl radicals.[13] These radicals do not produce methyl alcohol. It is therefore likely that their further reaction involves the sequence: [14]

$$CH_3\cdot + O_2 \longrightarrow CH_3\cdot O\cdot O\cdot \longrightarrow CH_2O\cdot OH$$

This reaction scheme, then, explains qualitatively the formation of acetic acid, formaldehyde, organic peroxides, and peroxyacids, and the absence of acetaldehyde at low temperatures.

In the higher temperature region, reactions (5), (6), (7b), and (7c) may operate, producing anhydrides, peroxacids, and acetaldehyde, as found experimentally. The acetate radicals formed in (7b and c) may abstract hydrogen, to give acetic acid, or decompose to methyl radicals (hence formaldehyde). The acetaldehyde will be further oxidised, *via* acetyl radicals, to carbon monoxide and methyl radicals.

If, then, reaction (7) followed by (7a) is the major mode of peroxide breakdown at low temperatures and the other modes operate in the high-temperature region, the existence of these separate regions and the experimentally found pattern of product formation are explained.

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[12] Chernyak, Antonovskii, Bevzin, and Shtern, *Zhur. fiz. Khim.*, 1954, 240; Antonovskii and Shtern, *Doklady Akad. Nauk S.S.S.R.*, 1951, **78**, 303.

[13] McDowell and Farmer, Fifth Symposium on Combustion, Reinhold Publ. Corpn., New York, 1955, p. 453; Blundell and Skirrow, *Proc. Roy. Soc.*, 1958, *A*, **244**, 331.

[14] Byrko, Kryuglakova, and Lukovnikov, *Doklady Akad. Nauk S.S.S.R.*, 1956, **108**, 1093.