153. *The Gaseous Oxidation of Aliphatic Esters. Part II.*[1] *Comparative Studies and General Mechanism.*

By A. Fish and A. Waris.

The effects of temperature on the rates and products of oxidation of ethyl formate, methyl acetate, n- and iso-propyl acetate, and ethyl propionate have been studied. The major products of these reactions are aldehydes and carboxylic acids, except with isopropyl acetate which produces acetone. Peroxidic products are also formed in small quantities. Each reaction exhibits at least two temperature regions, and determination of the pattern of product formation in each of these has shown to what extent the mechanism postulated for the slow combustion of ethyl acetate (Part I) may be regarded as a general mechanism for the gaseous oxidation of aliphatic esters. The results are consistent with the general occurrence of such a mechanism and enable the effects of differences in structure within the ester series to be elucidated.

In Part I,[1] a mechanism for the slow combustion of ethyl acetate was postulated which accounted qualitatively for the nature of the oxidation products and the variations with temperature of the amounts formed. This mechanism involved formation of hydroperoxide by a free-radical chain cycle and its breakdown by one of several routes, the predominant mode being dependent on the temperature. The effects of temperature on the rates and products of oxidation of ethyl formate, methyl acetate, n-propyl acetate, isopropyl acetate, and ethyl propionate have been studied in order to discover to what extent this mechanism is generally applicable to the oxidation of aliphatic esters and to elucidate the influence of structural changes in the molecule.

Experimental

Apparatus.—The apparatus has been described in Part I.[1] The only modification was adjustment of the saturator temperature so that, in each case, a convenient vapour pressure was attained.

Purification of Reactants.—Oxygen and nitrogen were purified as described in Part I. Each ester was purified by distillation from phosphorus pentoxide, dried over anhydrous sodium sulphate, and redistilled; ethyl formate had b. p. 53—55° (lit., 54·5°), n_D^{20} 1·360 (lit., 1·3597); methyl acetate had b. p. 56—58° (lit., 57·1°), n_D^{20} 1·359 (lit., 1·3593); n-propyl acetate had b. p. 100—102° (lit., 101·7°), n_D^{20} 1·384 (lit., 1·3842); isopropyl acetate had b. p. 87—88° (lit., 88°), n_D^{20} 1·377 (lit., 1·377); ethyl propionate had b. p. 98—100° (lit., 99·1°), n_D^{20} 1·384 (lit., 1·3838).

Analytical Procedure.—The analytical procedure adopted was similar to that described in Part I.

(i) *Acids.* The separation and estimation of individual carboxylic acids by liquid chromatography (as described in Part I) gave quantitative results for mixtures containing propionic as well as acetic and formic acid.

(ii) *Aldehydes.* Oxidation of ethyl propionate and of n-propyl acetate produced mixtures containing propionaldehyde and acetaldehyde. The presence of these individual aldehydes was confirmed by spot tests with ninhydrin[2] and sodium nitroprusside–piperidine,[3] respectively, and the ratio of their concentrations was determined by gas–liquid chromatography.

Formaldehyde and total aldehydes were estimated as described in Part I. Ethyl formate was appreciably hydrolysed on the silver oxide column; control analyses for total aldehydes were therefore carried out on this ester.

(iii) *Acetone.* Acetone was estimated after removal of aldehydes by addition of an excess of neutralised hydroxylamine hydrochloride and titration of the hydrochloric acid liberated.[4]

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[1] Part I, Fish and Waris, *J.*, 1962, 4513.

[2] Jones and Riddick, *Analyt. Chem.*, 1954, **26**, 1035.

[3] Feigl and Anger, *Mikrochim. Acta*, 1937, **1**, 138.

[4] Bryant and Smith, *J. Amer. Chem. Soc.*, 1935, **57**, 57.

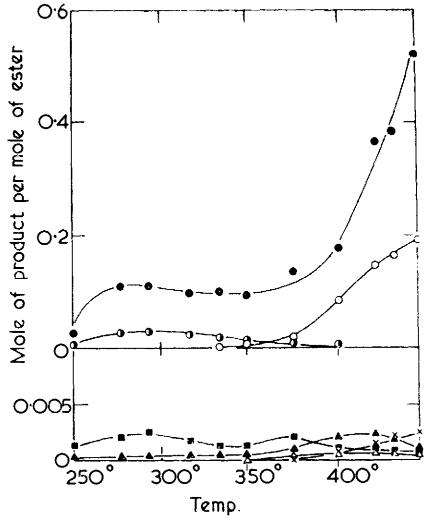


FIG. 1.

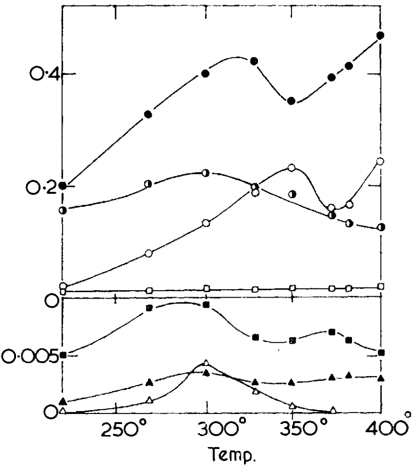


FIG. 2.

FIG. 1. Oxidation of methyl acetate: product formation. Oxygen : methyl acetate = 1 : 1; contact time = 134 sec.

● Methyl acetate consumed; ○ total carboxylic acids; ◑ acetaldehyde; ■ organic peroxides; ▲ peroxyacids; △ hydrogen peroxide; × acid anhydrides.

FIG. 2. Oxidation of n-propyl acetate: product formation. Oxygen : n-propyl acetate = 1 : 1; contact time = 134 sec.

● n-Propyl acetate consumed; ○ total carboxylic acids; ◑ acetaldehyde + propionaldehyde; □ formaldehyde; ■ organic peroxides; ▲ peroxyacids; △ hydrogen peroxide.

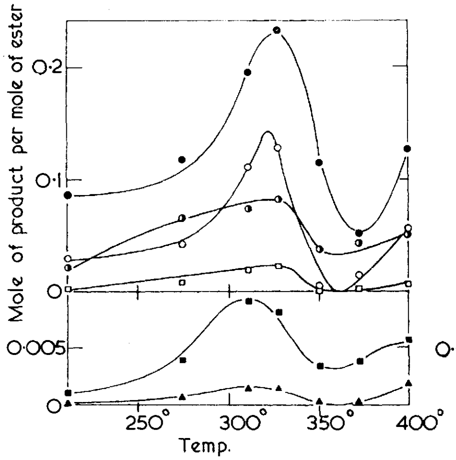


FIG. 3.

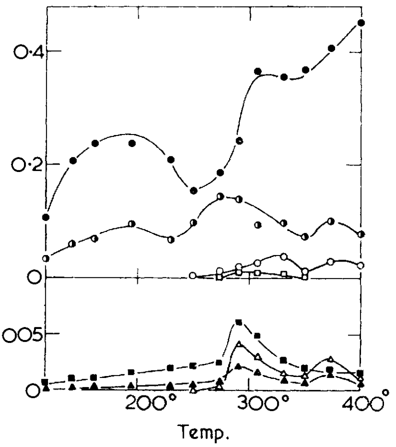


FIG. 4.

FIG. 3. Oxidation of ethyl propionate: product formation. Oxygen : ethyl propionate = 1 : 1; contact time = 134 sec.

● Ethyl propionate consumed; ○ total carboxylic acids; ◑ acetaldehyde + propionaldehyde; □ formaldehyde; ■ organic peroxides; ▲ peroxyacids.

FIG. 4. Oxidation of ethyl formate: product formation. Oxygen : ethyl formate = 1 : 1; contact time = 134 sec.

● Ethyl formate consumed; ○ formic acid; ◑ acetaldehyde; □ formaldehyde; ■ organic peroxides; ▲ peroxyacids; △ hydrogen peroxide.

Results

Determinations were made for each ester of the effect of temperature on the consumption of ester and formation of products during the reaction of an equimolar oxygen–ester mixture with a contact time of 134 sec. The results are shown in Figs. 1—5, and the consumptions of esters are compared in Fig. 6.

Methyl Acetate (Fig. 1).—The oxidation has two temperature regions, 250—340° and 340—450°, although the boundary between them is not so well marked as in the oxidations of other esters. At a given temperature, the consumption of this ester is less than that of any other ester studied (Fig. 6). The only major product in the lower-temperature region is acetaldehyde; acetic acid and formic acid are formed in the higher region, the former predominating by a factor greater than ten. Organic peroxides are formed in both regions and the other minor products, which appear in the upper region, are peroxyacids, acid anhydrides, and hydrogen peroxide.

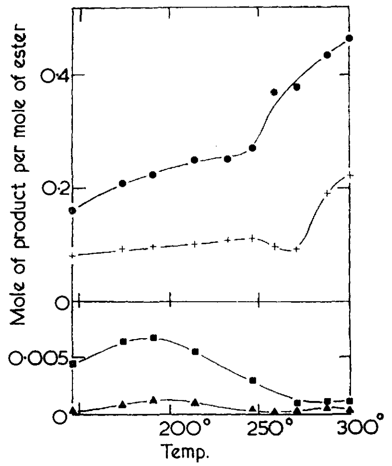


Fig. 5. Oxidation of isopropyl acetate: product formation. Oxygen : isopropyl acetate = 1 : 1; contact time = 134 sec.

● Isopropyl acetate consumed; + acetone; ■ organic peroxides; ▲ peroxyacids.

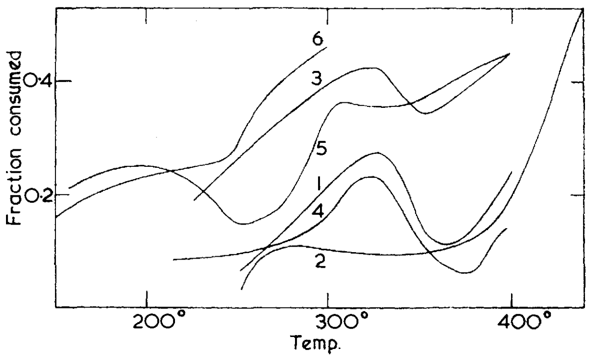


Fig. 6. Comparison of consumption of esters at various temperatures in 134 sec.

(1) Ethyl acetate; (2) methyl acetate; (3) n-propyl acetate; (4) ethyl propionate; (5) ethyl formate; (6) isopropyl acetate.

n-Propyl Acetate (Fig. 2).—There are two clearly defined temperature regions, the limits of which are almost identical with those found for ethyl acetate. (Part I). Aldehydes and carboxylic acids are the major products. Aldehydes predominate at low temperatures, and gas chromatography has shown that acetaldehyde is formed in far larger concentrations than propionaldehyde. In the upper-temperature region propionic acid and propionaldehyde predominate. A fairly constant small amount of formaldehyde is formed throughout the temperature region studied. In the lower region, a quantity of hydrogen peroxide is formed which is large compared with those produced from the other esters. Organic peroxides and peroxyacids are produced in both regions.

Ethyl Propionate (Fig. 3).—Again there are two clearly defined temperature regions; the major products are acids and aldehydes and the minor products are peroxyacids and organic peroxides. In the lower-temperature region, acetic, propionic, and formic acid were detected and separated, of which the first predominates; gas-chromatography showed that the ratio of propionaldehyde : acetaldehyde present was *ca.* 4 : 1. In the higher region, however, more acetaldehyde than propionaldehyde, and more propionic than acetic acid, is produced. The effect of temperature on the formation of organic peroxides and peroxyacids (the minor products) shows an increase–decrease–increase trend paralleling that in ester consumption.

Ethyl Formate (Fig. 4).—Oxidation occurs at a very low temperature (120°) compared with the lower-temperature limits for the other esters studied. Three temperature ranges (120—260°, 260—340°, and 340—400°) were found; this is one of the first recorded cases of the rate of a slow and apparently isothermal oxidation displaying two well-defined maxima as the temperature is altered.

Acetaldehyde is the major product in all these regions, formic acid is found in the two higher regions, and formaldehyde between 260° and 340°. Organic peroxides are formed in the two lower regions, and peroxyacids and hydrogen peroxide in the two upper regions.

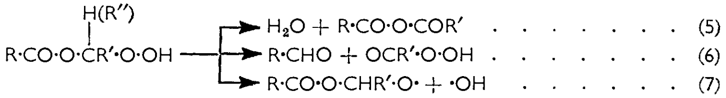
Isopropyl Acetate (Fig. 5).—Oxidation occurs below 140° and studies have been carried out between this temperature and 300°, above which pyrolysis ensues. The only products in each of the two temperature regions are acetone, organic peroxides, and peroxyacids. No carboxylic acid or aldehyde was detected. Acetone, the major product, is formed at a much greater rate in the higher- than in the lower-temperature region, and the production of organic peroxides at high temperatures is small.

DISCUSSION

The similar effects of temperature on the oxidation of this range of esters suggest that a common mechanism of oxidation operates in comparable temperature regions. For ethyl acetate (Part I), methyl acetate, n-propyl acetate, and ethyl propionate, the limits of these regions are similar (Fig. 6), and ethyl formate is comparable with these esters provided that, of the three temperature regions of this oxidation, the lowest is the " anomalous " one, *i.e.*, that which is not exhibited by the oxidations of the other esters studied. The oxidation of the sixth ester, isopropyl acetate, again takes place in two regions, but this ester is oxidised at generally lower temperatures than the other acetates and ethyl propionate. This is to be expected from the order of C–H bond strengths.[5] Abstraction of hydrogen from the tertiary centre of isopropyl acetate is easier than from any of the other esters, which contain secondary and primary centres only. Similarly, methyl acetate contains primary centres only, suggesting that its rate of oxidation at a given low temperature will be less than those of the other five esters; this expectation is borne out by the experimental results (Fig. 6).

The effects of temperature on the consumption of each ester are therefore consistent with the general occurrence of a chain reaction which is propagated by abstraction of hydrogen from the carbon atom adjacent to the ethereal group, as discussed for ethyl acetate (Part I).

The product of this reaction is the hydroperoxide R·CO·O·CR′R″·O·OH which may break down by several routes (reactions 5, 6, and 7 followed by 7a, b, or c; numbering from Part I). These routes are written in the scheme annexed in terms of a general ester molecule.

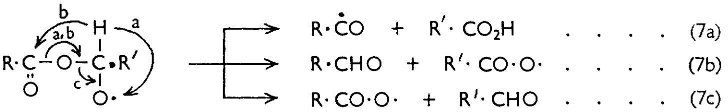


$$\mathrm{R{\cdot}CO{\cdot}O{\cdot}\overset{H(R'')}{C}R'{\cdot}O{\cdot}OH} \longrightarrow \mathrm{H_2O + R{\cdot}CO{\cdot}O{\cdot}COR'} \tag{5}$$

$$\longrightarrow \mathrm{R{\cdot}CHO + OCR'{\cdot}O{\cdot}OH} \tag{6}$$

$$\longrightarrow \mathrm{R{\cdot}CO{\cdot}O{\cdot}CHR'{\cdot}O{\cdot} + {\cdot}OH} \tag{7}$$

Reaction (7) is followed by:



$$\longrightarrow \mathrm{R{\cdot}\dot{C}O + R'{\cdot}CO_2H} \tag{7a}$$

$$\longrightarrow \mathrm{R{\cdot}CHO + R'{\cdot}CO{\cdot}O{\cdot}} \tag{7b}$$

$$\longrightarrow \mathrm{R{\cdot}CO{\cdot}O{\cdot} + R'{\cdot}CHO} \tag{7c}$$

Comparison of the products formed in a given temperature region with those which would be produced by each of these modes of peroxide decomposition indicates under which conditions each reaction occurs.

Methyl Acetate, R = Me, R′ = R″ = H.—Reaction (7) followed by (7b) appears to be the predominant mode of peroxide breakdown at low temperatures, producing acetaldehyde directly. In the higher-temperature region, (7a and 7c) may be responsible for

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

the production of formic acid and acetic acid, respectively, the latter predominating. Reaction (7c) produces also formaldehyde, which has not been detected in the products, but it is likely that in this temperature range (>350°) it would suffer rapid oxidation. The small quantities of anhydrides formed at high temperatures are produced by reaction (5). Reaction (6) is unimportant as acetaldehyde and peroxyacids are not produced in the same region.

n-Propyl Acetate, R = Me, R′ = Et, R″ = H.—The predominant mode of low-temperature breakdown is (7) followed by (7b), producing acetaldehyde, the major product, although reactions (7a), producing propionic acid, and (6), producing peroxyacids, may occur to a small extent. The production of comparatively large quantities of hydrogen

$$\mathrm{CH_3{\cdot}CO{\cdot}O{\cdot}CHEt{\cdot} + O_2 \longrightarrow HO_2{\cdot} + CH_3{\cdot}CO{\cdot}O{\cdot}CH{=}CHMe} \quad . \; . \; . \; . \; . \; . \quad (8)$$

peroxide in the lower-temperature region is probably due to reaction (8) as an additional propagation step, followed by further abstraction of hydrogen from ester molecules by the $HO_2{\cdot}$ (cf. ref. 6). This reaction will occur more readily with n-propyl acetate than with the other esters, as hydrogen abstraction from a methyl group is not involved.

At higher temperatures, the production of carboxylic acids and propionaldehyde overtakes that of acetaldehyde, suggesting that reactions (7a) and (7c) have become more important.

A further possibility in oxidation of n-propyl acetate is the initiation step

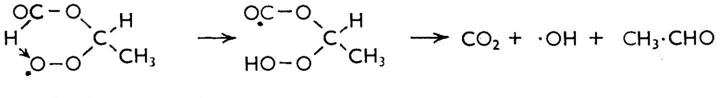
$$\mathrm{CH_3{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 + O_2 \longrightarrow HO_2{\cdot} + CH_3{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}CHMe{\cdot}} \quad . \; . \; . \; . \quad (9)$$

but the resulting hydroperoxide, $CH_3{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}CHMe{\cdot}O{\cdot}OH$, would break down giving acetone (cf. 7c) and a hydroxy-compound (cf. 7a), neither of which is formed. α-Hydroperoxylation followed by secondary attack at the β-methylene group would, however, produce eventually a biradical $CH_3{\cdot}CO{\cdot}O{\cdot}CH(O{\cdot}){\cdot}CHMe{\cdot}O{\cdot}$, which would decompose giving high yields of acetaldehyde, as found experimentally at low temperatures. It is indeed in this temperature region, where the breakdown of hydroperoxides is relatively slow, that secondary attack may occur.

Ethyl Propionate, R = Et, R′ = Me, R″ = H.—In the low-temperature region, the predominant mode of peroxide breakdown is again (7) followed by (7b), producing propionaldehyde and a radical precursor of acetic acid. Reaction (7a) produces acetic acid directly and may also be important in this region. At higher temperatures, reaction (7c), producing acetaldehyde and a radical precursor of propionic acid, operates. Reaction (6) may also occur to a small extent but the absence of anhydrides shows that (5) is not operative.

In the case of ethyl propionate, the group R (Et) contains a secondary centre and the possibility of initial attack here should also be considered. As conventional breakdown of the resulting hydroperoxide would produce ethoxy-radicals, the absence of ethyl alcohol suggests that this series of reactions is unlikely to be important.

Ethyl Formate, R = R″ = H, R′ = Me.—The peroxy-radical produced by the primary oxidation chain in the case of the above esters is $R{\cdot}CO{\cdot}O{\cdot}CRR'{\cdot}O{\cdot}O{\cdot}$. In the case of ethyl formate, in which R = H, intramolecular hydrogen transfer around a six-membered ring is possible:[7]



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producing acetaldehyde as the major product. This mechanism is therefore consistent with the pattern of product formation in the "anomalous" low-temperature region of

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[6] Burgess, Cullis, and Newitt, *J.*, **1961**, 1884.

[7] Kossiakoff and Rice, *J. Amer. Chem. Soc.*, 1943, **65**, 590; Rust and Collamer, *ibid.*, 1954, **76**, 1055.

the oxidation of ethyl formate. With other esters, this intramolecular mechanism is far less likely to operate as a seven-membered ring would be involved, so oxidations of these esters do not exhibit this third temperature region.

In the middle-temperature region, there is little doubt that hydroperoxide is produced as usual by intermolecular hydrogen abstraction, and the analytical results suggest that reactions (6), (7b), and (7c) occur. Acetic acid is not formed so that reaction (7a) is evidently unimportant.

In the high-temperature region, little hydroperoxide is formed, suggesting the occurrence of alternative propagation steps such as

$$H{\cdot}CO{\cdot}O{\cdot}CHMe{\cdot} \longrightarrow H{\cdot} + CO + OCHMe \quad . \; . \; . \; . \; . \; . \; . \quad (11)$$

$$H{\cdot} + O_2 \longrightarrow HO_2{\cdot};\; HO_2{\cdot} + H{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}CH_3 \longrightarrow H_2O_2 + H{\cdot}CO{\cdot}O{\cdot}CHMe{\cdot}$$

consistently with the formation of acetaldehyde and hydrogen peroxide, although the production of acids and peroxyacids shows that other mechanisms also operate.

Isopropyl Acetate, $R = R' = R'' = Me$.—The hydroperoxide produced by the primary chain reaction has no hydrogen atom attached directly to the peroxidised carbon atom ($R'' \neq H$). Reactions (6), (7a), and (7b), which involve such hydrogen migration, and (5), which involves its removal, cannot take place. The analogous migration of a methyl group does not occur as it would produce methyl acetate which is not detected among the products. Reaction (7c) must be largely responsible for hydroperoxide breakdown in this case, producing acetone, the observed major product. If this were the sole mechanism in operation, however, there would be only one temperature region. A second mechanism must operate and it is evident that this cannot involve the hydroperoxide $CH_3{\cdot}CO{\cdot}O{\cdot}CMe_2{\cdot}O{\cdot}OH$. It is possible that, in the higher region, breakdown of the alkyl radical formed by initiation takes place in preference to combination with oxygen, producing acetone directly:

$$CH_3{\cdot}CO{-}\vdots{-}O{\cdot}CMe_2{\cdot}O{\cdot} \longrightarrow CH_3{\cdot} + CO + OCMe_2 \quad . \; . \; . \; . \; . \; . \; . \quad (11)$$

This is consistent with the large amounts of acetone formed and the negligible production of hydroperoxides. Such a mechanism might be expected to be the precursor of oxygen-catalysed pyrolysis (as oxygen is involved only in an initiation step), and this indeed occurs at slightly higher temperatures.

General.—It is thus possible to account qualitatively for the broad features of the oxidations of all six esters studied, by a common mechanism involving initiation by hydrogen abstraction from the alkyl group adjacent to ethereal oxygen, propagation steps producing hydroperoxides, and various modes of decomposition of these compounds [reactions (5), (6), and (7) followed by (7a, b, or c), as postulated for ethyl acetate (Part I)]. Structural influences can be consistently explained by the occurrence of additional reactions (8), (10), and (11). The reactions occurring in each temperature region are summarised in the Table, consideration of which shows that reaction (7), fission of the peroxidic O–O bond, is the most frequent rupture leading to hydroperoxide decomposition. In general, reactions (7b) and (7a) (in that order of importance) are the modes of breakdown of the resulting alkoxy-radicals between 250° and 350°, but (7c) becomes

Reactions occurring during the oxidation of esters.
The more important reactions in each temperature region are italicised.

Ester Temp.	<250°	*ca.* 250—350°	>350°
Ethyl acetate	Nil	*7a*	5, 6, *7b*,* *7c**
Methyl acetate	Nil	*7b*	5, 7a, *7c*
n-Propyl acetate	Nil	6, *7b*, 7a, 8	*7a*, *7c*
Ethyl propionate	Nil	*7b*, 7a	6, *7c*
Ethyl formate	*10*	6, 7a, *7c*	*11*
Isopropyl acetate	*7c*	*11*	Pyrolysis

* Indistinguishable here, except by isotopic techniques.

more important at higher temperatures. A general mechanism of the gaseous oxidation of aliphatic esters by molecular oxygen can thus be derived. Before any quantitative statements concerning the relative importance of the reactions involved is justified it will, however, be necessary to undertake a wider survey than has been attempted in the present studies

The authors thank the Colombo Plan authorities for the provision of a Fellowship (for A. W.), Laporte Chemicals Ltd. for financial assistance in the purchase of apparatus, and Dr. C. F. Cullis for his interest and encouragement.

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[*Received, July* 30*th*, 1962.]