The Low-temperature Oxidation of iso*Butane. The Progressive Accumulation of Products and Consumption of Reagents.*

By J. J. Batten, H. J. Gardner, and M. J. Ridge.

[Reprint Order No. 6271.]

The progressive accumulation of products and consumption of reagents during the oxidation of *iso*butane at 291° have been studied. During the induction period (12·5—60 min. depending upon conditions) small but appreciable quantities of reactants are converted into products. There is a significant difference in the distribution of products during and after the induction period, indicating a difference in mechanism. It is suggested that the reaction during the induction period is surface-inhibited and probably proceeds by straight chains. The amounts of higher aldehydes, total peroxides, and to a smaller extent of formaldehyde, reach pronounced maxima at the maximum rate of pressure rise. The evidence does not exclude the participation of alkyl peroxides or peroxy-radicals in the reaction. The formation of acetone indicates tertiary attack on *iso*butane.

THE reaction between hydrocarbon vapours and oxygen is autocatalytic. There is an induction period of little or no change in pressure, which may extend for hours, followed by a period of accelerating increase in pressure. Hydrocarbons containing three or more carbon atoms show different mechanisms at high and at low temperatures. It is generally accepted that both modes of oxidation are degenerate branching-chain reactions (Semenov, " Chemical Kinetics and Chain Reactions," Oxford Univ. Press, 1935), *i.e.*, chain reactions in which branching takes place through a relatively stable intermediate. There is, however, little agreement regarding details of mechanisms proposed for hydrocarbon–oxygen reactions and in particular the identity of the intermediate responsible for degenerate branching is still under discussion. For the low-temperature reaction two classes of compound have been suggested, *viz.*, organic peroxides, particularly hydroperoxides (Ubbelohde, *Proc. Roy. Soc.*, 1935, *A*, **152**, 354; Hinshelwood, *Discuss. Faraday Soc.*, 1947, **2**, 111; Walsh, *Trans. Faraday Soc.*, 1946, **42**, 269) and aldehydes (Norrish, XVI Internat. Colloquium, Centre National de la Recherche Scientifique, Paris, p. 16; Knox and Norrish, *Proc. Roy. Soc.*, 1954, *A*, **221** 151). At present it is difficult to decide which of these theories of degenerate branching is to be accepted, and additional definite information is needed regarding the progressive formation of products and consumption of reagents during hydrocarbon–oxygen reactions.

Results for the oxidation of *iso*butane are now presented. Particular attention has been directed to the earlier stages of the reaction, where the process may be expected to be less complicated by the reactions of products, and unambiguous information should be more readily obtained than from the region of the maximum rate of pressure change.

For a study of the mechanism of its oxidation, *iso*butane has several attractive features. For instance, its molecule contains nine primary and one, weaker, tertiary C–H bond. Consequently, the predominant point of attack on the hydrocarbon during oxidation is probably known. Also, the hydroperoxide (*tert.*-butyl) derived directly from *iso*butane is comparatively stable to heat and should be readily determined.

The autoxidation of *iso*butane has been studied by Pease (*J. Amer. Chem. Soc.*, 1929, **51**, 1839) who by a flow method found methane, hydrogen, carbon monoxide, carbon dioxide, and unsaturated substances among the products. Analyses were made for gaseous products only, and the lowest temperature studied was 350°. The ignition diagram of *iso*butane has been determined by Townend (*Chem. Rev.*, 1937, **21**, 268).

EXPERIMENTAL

The apparatus and procedure were those described by Mulcahy and Ridge (*Trans. Faraday Soc.*, 1953, **49**, 906). The induction period was defined as the time required for the rate of pressure increase to reach 0·5 mm./min.

*Materials.—iso*Butane (Phillips Petroleum Company, Pure Grade, 99%) was passed through soda–asbestos and condensed in liquid air. After being degassed it was subjected to two trap-to-trap distillations, generous first and last portions being rejected. The fraction retained was passed through phosphoric oxide before storage. Commercial (medical grade) oxygen was used after passage through phosphoric oxide and liquid-air traps.

The formaldehyde solution used in the polarographic work was prepared by heating paraformaldehyde and dissolving the evolved gas in water. Formaldehyde peroxide (m. p. 57—59°) was prepared according to Wieland and Wingler (*Annalen*, 1923, **431**, 301). *tert.*-Butyl hydroperoxide was prepared by extracting a commercial material with aqueous sodium hydroxide and regenerating the peroxide with hydrochloric acid. Reagent-grade hydrogen peroxide was used.

Analysis.—The mixture formed was analysed quantitatively for *iso*butane, oxygen, methane, C_2 hydrocarbons, carbon monoxide, carbon dioxide, total peroxide, acetone, formaldehyde, total aldehydes, higher aldehydes (by difference), and acids.

Samples were taken by connecting the reaction vessel to an evacuated sampling vessel (450 ml.) at −80° (acetone–carbon dioxide). The volatile components were then admitted to an analysis system which included a LeRoy–Ward still (LeRoy, *Canad. J. Res.*, 1950, *B*, **28**, 492), McLeod gauge, Töpler pump, and gas burette. When it was desired to determine condensable products, the samples were taken with 10—15 ml. of a suitable solvent in the sampling vessel.

Volatile components were determined by cutting the sample into three fractions by pumping off with the Ward still at (1) −196° (liquid nitrogen), (2) −170°, and (3) *ca.* −110°.

Oxygen, carbon monoxide, and methane were determined by combustion of fraction (1) in a Cu–CuO furnace fitted with a liquid-air trap (Marcotte and Noyes, *Discuss. Faraday Soc.*, 1951, **10**, 236). In this furnace carbon monoxide was oxidized to carbon dioxide, hydrogen to water, and oxygen was removed as copper oxide. Methane was measured as an uncondensable residue. On replacement of the liquid-air trap by an acetone–carbon dioxide trap, carbon dioxide was evaporated, pumped off, and measured. When the trap was warmed to room temperature any water (never more than a trace) could be detected. Oxygen was determined by difference. Ethane and ethylene occur in fraction (2), which was negligible in all cases. *iso*Butane and carbon dioxide constitute fraction (3). Carbon dioxide was absorbed in a soda–asbestos thimble and determined by difference. The residue was taken as *iso*butane.

The methods for the determination of total peroxide, total aldehyde, formaldehyde, and acid have already been described (Mulcahy and Ridge, *loc. cit.*). Acetone was determined by the hydroxylamine hydrochloride method on a sample which had been passed through a silver oxide column to destroy aldehydes.

To gain information regarding the components of the " total peroxides," the reaction products were subjected to polarographic examination.

Polarographic procedure. Samples were taken with distilled water or a solution of the supporting electrolyte in the cold sampling vessel. Current–voltage curves were obtained by using Lingane and Kolthoff's three-electrode circuit (*J. Amer. Chem. Soc.*, 1939, **61**, 825) with a device for reproducible liquid junctions (Gardner and Diamantis, *Austral. J. Sci.*, 1951, **14**, 23). The saturated calomel electrode was prepared, the precautions mentioned by Hills and Ives (*J.* 1951, 301) being observed, and was 0·244 v *versus* the hydrogen electrode of unit activity at 25°. The rate of mercury flow was 1·42 mg. $sec.^{-1}$; the drop time had the following values for the given potentials: −0·5 v, 3·75 sec.; −1·0 v, 3·5 sec.; −2·0 v, 2·8 sec.

Reaction Conditions.—The reaction was studied in oxygen-rich (A) and hydrocarbon-rich (B) mixtures. Owing to fluctuations in the activity of the reaction vessel, slight modifications had to be made from time to time in the compositions of the actual mixtures used, which were:

Mixture	*iso*Butane (mm.)	Oxygen (mm.)	Nitrogen (mm.)	Mixture	*iso*Butane (mm.)	Oxygen (mm.)	Nitrogen (mm.)
A 1	80	350	—	B 1	200	100	—
2	70	350	—	2	150	100	350

All experiments were carried out at 291°.

RESULTS.

The decline in the concentrations of the reagents, the pressure rise, and the accumulation of products for mixtures A and B are shown in Figs. 1—6. The quantities are expressed in mm. of partial pressure in the reaction vessel at the reaction temperature. The reaction vessel used to obtain the results shown in Figs. 3 and 6 was destroyed by an explosion. A second, similar vessel was used for all other results. The shapes of the pressure curves indicate that the change in reaction vessel has not altered the type of the reaction.

There is an interesting difference in the shapes of the curve of pressure increase for mixtures A and B. In hydrocarbon-rich mixtures (type B) the rate of pressure change does not pass through a smooth maximum and tail off, as it does with oxygen-rich mixtures (type A), but abruptly falls to zero after a period of vigorous acceleration. In the first reaction vessel this halt occurred so sharply that no transition could be detected between a state of accelerating pressure increase and that of constant pressure (see Fig. 6). In the second vessel there was a short period (0·5 min.) of slackening reaction rate (see arrow in Fig. 5).

FIG. 1. iso*Butane, oxygen, carbon dioxide, carbon monoxide, and methane concentrations, and pressure rise* v. *time, for* 80 *mm. of* iso*butane* + 350 *mm. of oxygen* (A, 1).

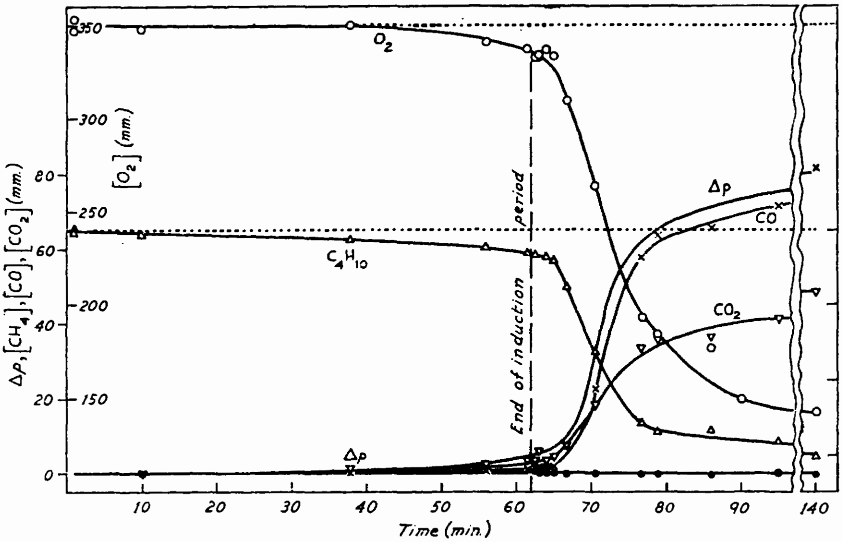
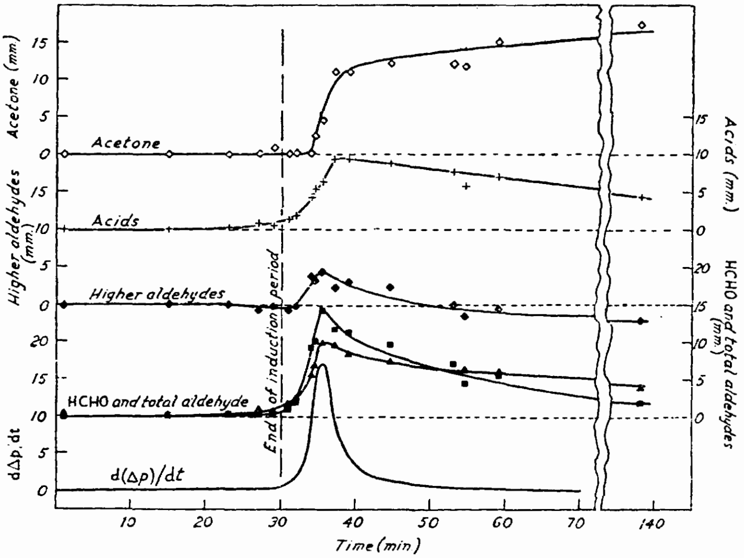


FIG. 2. *Acetone, acid, higher aldehyde, total aldehyde, and formaldehyde concentrations, and rate of pressure rise* v. *time for* 80 *mm. of* iso*butane* + 350 *mm. of oxygen* (A, 1).



Figs. 4, 5, and 6 show that the halt in pressure increase reflects a general cessation of reaction when the oxygen concentration has been reduced to a low figure. This discontinuous change in direction of the upward-curving Δp *versus* time curve indicates that chain branching is independent of oxygen concentration down to very low partial pressures.

Table 1 gives pressures of products and the decreases in the reactants, (*a*) at the end of the induction period (θ) for both reaction mixtures, (*b*) at the maximum rate of pressure change ($\rho_{\max.}$) for mixture A, and at the halt in pressure increase for mixtures B, and (*c*) near the completion of reaction for mixture A.

Consumption of Reagents.—By the end of the induction period the amounts of reagents consumed indicate that appreciable reaction has occurred (see Table 1). For both mixtures A and B the ratios of the quantities consumed are approximately the same ($-\Delta O_2/-\Delta RH = 2{\cdot}2$ and 1·6, respectively) despite the difference in initial reagent concentrations. This is similar to behaviour in the propene–oxygen system (Mulcahy and Ridge, *loc. cit.*). However, the absolute amounts of each reagent consumed appear to vary more with initial concentration of the reagents than was the case with propene. In both systems the absolute amounts of reagents consumed by the end of the induction period are approximately the same.

FIG. 3. *Total peroxides and rate of pressure rise* v. *time for* 70 *mm. of* iso*butane* + 350 *mm. of oxygen* (A, 2).

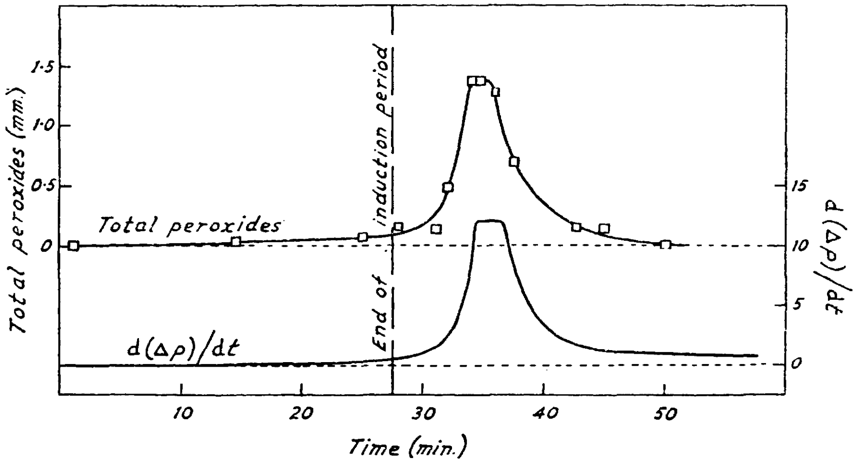
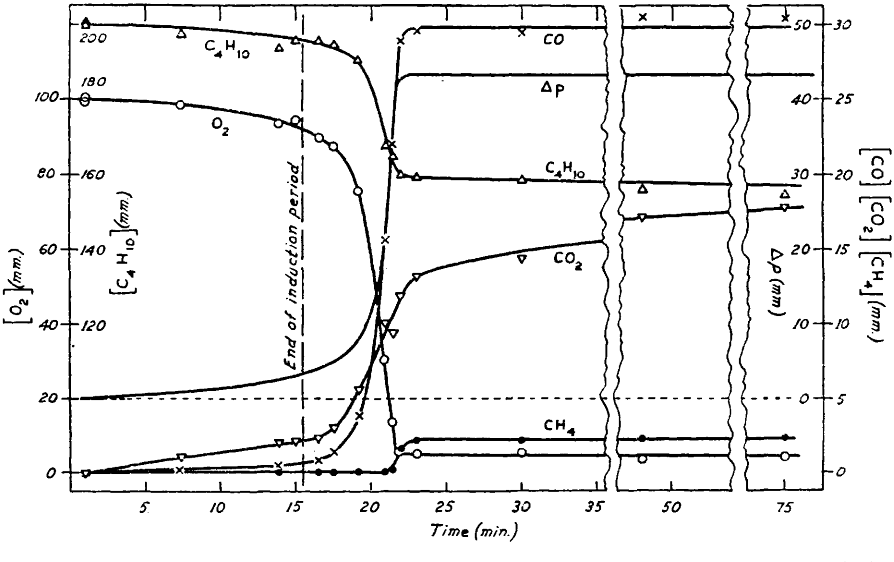


FIG. 4. iso*Butane, oxygen, carbon monoxide, carbon dioxide, and methane concentrations and pressure rise* v. *time for* 200 *mm. of* iso*butane* + 100 *mm. of oxygen* (B, 1).



After the induction period the ratio $-\Delta O_2/-\Delta RH$ for mixtures A increases somewhat until at the maximum rate it is about 2·6. Near the completion of the reaction it reaches 3·4. In mixture B the ratio has reached 2·3 when the pressure becomes constant. The increase in this ratio is due to the increasing importance of the oxidation of products as the reaction progresses.

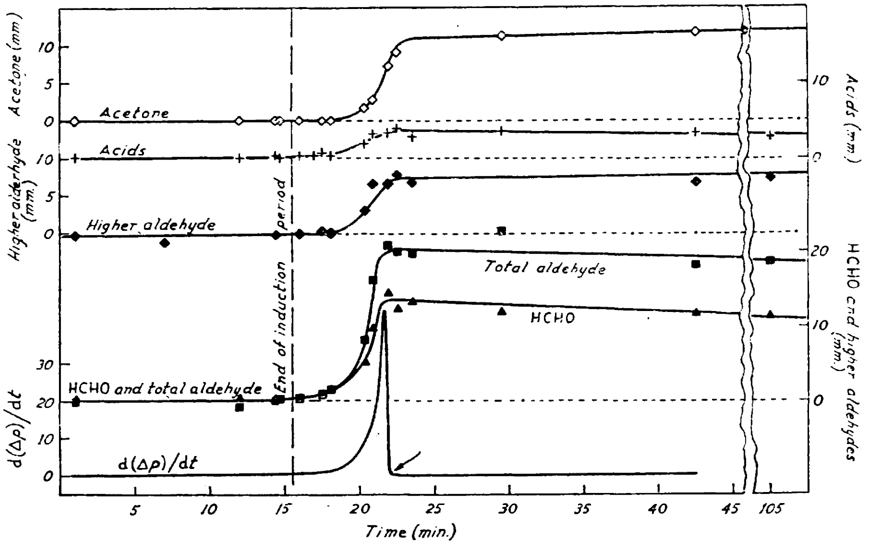
Formation of Products.—The products fall into two classes: (*a*) Compounds such as carbon monoxide and dioxide, acetone, acids, etc., which gradually accumulate as the reaction proceeds and represent the debris of the reaction chains. (*b*) Transient products such as peroxide, higher aldehyde, and formaldehyde whose concentrations build up to a maximum at the maximum rate, and which readily undergo reaction in the environment in which they are produced. These are vital intermediates in the reaction chains and one of them is probably responsible for degenerate branching.

TABLE 1. *Consumption of reagents, yields of products, and total pressure increase during reaction.*

Mixture	Stage of reaction	Pressure (mm.) Δp	$-\Delta O_2$	$-\Delta RH$	ΔCH_2O	ΔR·CHO	Total perox.	$\Delta COMe_2$	ΔCO	ΔCO_2	ΔCH_4	ΔAcid
A 1	at θ *	4·8	14	6·2	1·0	−0·5	0·1 ‡	0·0	1·0	3·0	0·0	1
	at $p_{max.}$	34·0	90	34·5	10·0	4	1·4	6·0	25·0	19·5	0·0	6
	at t_∞	80·5	207	60·5	3·8	−2·0	0·0	*ca.* 16	81·5	49·0	0·0	4
B 1	at θ	3·0	8	5	0·3	0·0	0·1 †	0·0	0·6	2·2	0·0	0·1
	at halt	43·1	*ca.* 95	41	13·5	7·2	4·2	7·5	29·8	13·2	2·2	3

* θ means end of induction period; $p_{max.}$, maximum rate; and t_∞ end of reaction.
† Reaction mixture A 2. ‡ Reaction mixture B 2.

FIG. 5. *Acetone, acid, higher aldehyde, total aldehyde, and formaldehyde concentrations, and rate of pressure rise* v. *time for* 200 *mm. of* isobutane + 100 *mm. of oxygen* (B, 1).



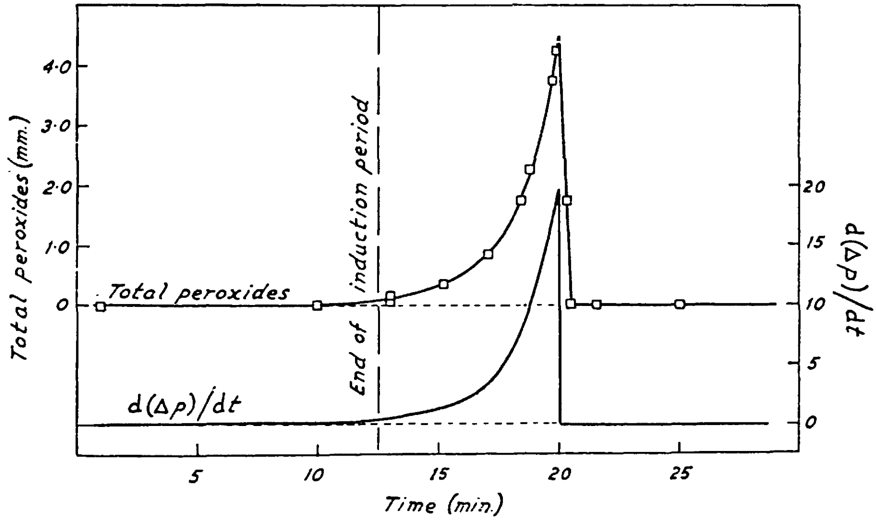
The close association between total peroxide content and the rate of reaction is shown in Fig. 3. The dΔp/dt curve has a plateau at the maximum rate, indicating the attainment of a steady state. This is reflected in the peroxide curve. In the hydrocarbon-rich mixture the total peroxide content falls sharply to zero when the reaction stops, emphasizing the short-lived nature of peroxide in the reaction system.

During the induction period the distribution of products is radically different from that in the region of the maximum rate. The earliest products detected are carbon dioxide and formaldehyde and these represent a considerable degradation of the original *iso*butane molecule. The shapes of the carbon dioxide *versus* time curves suggest that this gas is produced at a constant rate during the induction period (cf. propene; Mulcahy and Ridge, *loc. cit.*). After the induction period the yield of carbon monoxide increases sharply and rapidly out-strips the yield of dioxide. Higher aldehydes likewise become important after the end of the induction period. Fig. 1 demonstrates that a close connection exists between the rate of carbon monoxide production and the rate of pressure rise.

A polarographic study shows that the peroxidic products consist of hydrogen peroxide and aldehyde peroxides, and strongly suggests the presence of *tert.*-butyl hydroperoxide and other alkyl peroxides.

Polarographic Examination of Reaction Products.—Current-voltage curves for the reaction products of 200 mm. of *iso*butane and 100 mm. of oxygen, recorded for various supporting electrolytes, are shown in Fig. 7 (the reaction was taken to 6 min. past the induction period, and the products were made up to 25 ml.). The waves which extend from 0·0 to −1·2 v *versus* the standard calomel electrode, cover the potential region where peroxides are expected to yield waves (Shtern and Polyak, *Acta Physicochim., U.R.S.S.*, 1939, **11**, 797; Knox and Norrish, *loc. cit.*). The lowered height in lithium hydroxide solution is probably due to ionization (see Everett and Minkoff, *Trans. Faraday Soc.*, 1953, **49**, 410). The waves with half-wave potentials at −1·5 to −1·6 v in the various solutions correspond in height and position to that expected for formaldehyde (Kolthoff and Lingane, "Polarography," Interscience Publ. Inc., New York, 2nd Ed., 1952). The wave at −1·88 v in 0·01 and 0·1M-LiOH (curves *e* and *f*) is probably due to acetaldehyde, and that at −1·83 v in 0·1M-LiCl (curve *a*) to acetaldehyde plus formic acid (see Kolthoff and Lingane, *op. cit.*). By comparison with the curve for a standard solution of formaldehyde (Fig. 8) and by reference to the published data for acetaldehyde and formic acid, it was estimated that the reacting mixture contained *ca.* 10 mm. of formaldehyde, *ca.* 0·5 mm. of acetaldehyde, and *ca.* 1·2 mm. of formic acid. The partial pressure of total peroxide was *ca.* 1·7 mm. These figures are in qualitative agreement with those obtained by chemical methods, the figures for acetaldehyde being the most divergent. Quantitative agreement was not expected because the small sample size did not permit the use of gas bubblers.

FIG. 6. *Total peroxide and rate of pressure rise* v. *time for* 150 *mm. of* isobutane + 350 *mm. of nitrogen* + 100 *mm. of oxygen* (B, 2).



Current–voltage curves for formaldehyde peroxide, hydrogen peroxide, formaldehyde, *tert.*-butyl hydroperoxide, and the reaction mixture are shown in Fig. 8.

The fresh solution of formaldehyde peroxide (0·44 mM) yielded two waves with half-wave potentials at −0·3 v and −0·9 v respectively (curve *b*). Merely upon letting the solution stand for a few hours (curve *c*), or alternatively by shaking it with mercury (curve *d*), the current–voltage curve changed in character, the wave at −0·3 v disappearing. By comparing curve *d* with *e* and *f* the decomposed solution was estimated to contain *ca.* 0·45 mM-hydrogen peroxide and *ca.* 0·5 mM-formaldehyde. Removal of the hydrogen peroxide by titanium chloride and ammonia (MacNevin and Urone, *Analyt. Chem.*, 1953, **24**, 1760) yielded wave *h*, which is similar in shape to the curve *g* obtained for commercial "AnalaR" formaldehyde.*

---

* The decomposition of formaldehyde peroxide solution was investigated by using the colour reaction of hydrogen peroxide with titanium chloride. Hydrogen peroxide was detected within an hour of preparation. However, any handling, particularly where mercury was involved, as was the case with the polarographic cell, resulted immediately in the solutions' yielding the colour typical of hydrogen peroxide, when treated with titanium chloride. A colorimetric estimation gave *ca.* 0·5 mM-hydrogen peroxide (originally 0·44 with formaldehyde peroxide). From these experiments it is concluded that the curves obtained by Shtern and Polyak (*loc. cit.*) and Knox and Norrish (*loc. cit.*) for formaldehyde peroxide and probably other aldehyde peroxides are largely due to hydrogen peroxide and free aldehyde. The decomposition of formaldehyde peroxide to give hydrogen peroxide and formaldehyde has already been observed (Wieland and Wingler, *loc. cit.*). Our results indicate that metallic mercury catalyses this reaction, which is the reverse of that producing the peroxide from formaldehyde and hydrogen peroxide.

Advantage was taken of the effect of mercury on formaldehyde peroxide (and probably other aldehyde peroxides) in an attempt to determine alkyl hydroperoxides in the reaction mixture. The solution of products was shaken with mercury, and hydrogen peroxide then removed by treatment with titanium chloride and ammonia (see curves *k* and *j*, Fig. 8). The difference in height between curves *k* and *j* should correspond to the total hydrogen peroxide present (0·7 mm. in the reaction vessel).

Curve *j* probably represents those peroxides which are stable for a few hours in contact with mercury. Its shape suggests that at least two peroxides are present, and comparison with curve *i* shows that the wave between 0·0 and −0·55 v is probably due to *tert.*-butyl hydroperoxide (0·7 mm. in the reaction vessel). The remainder of the wave should then be due to other alkyl peroxides.

FIG. 7.

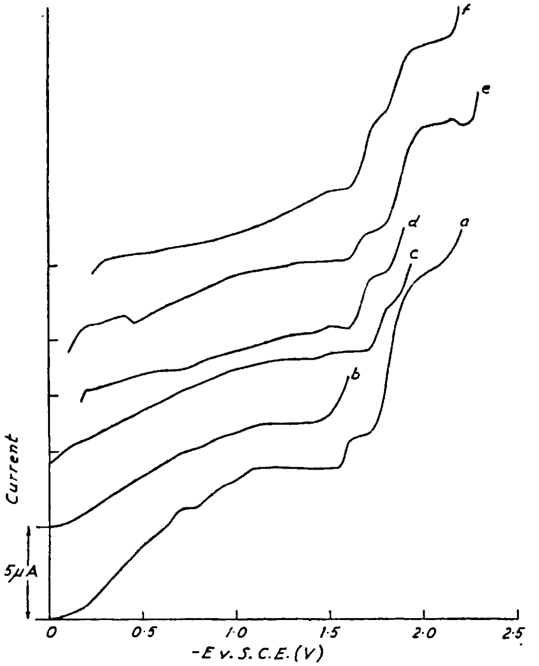


FIG. 8.

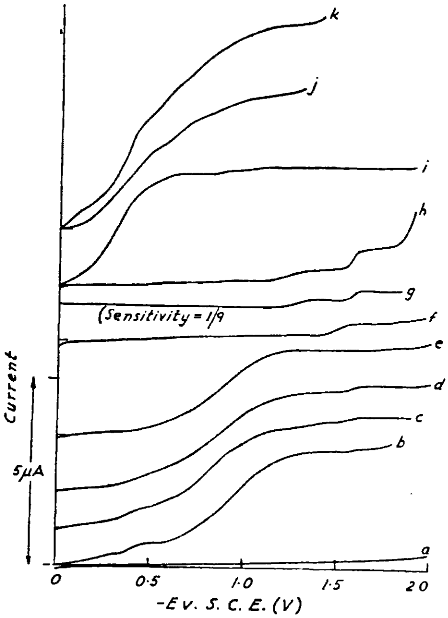


FIG. 7. *Current–voltage curves for the oxidation products of* iso*butane dissolved in* 25 *ml. of aqueous solution. The supporting electrolytes are :* (*a*) 0·1M-LiCl; (*b*) 0·1M(*each*) *acetic, phosphoric, and boric acid, and* NaOH *to make* pH 4·5; (*c*) *as for* (*b*), pH 7·7; (*d*) *as for* (*b*), pH 11·5; (*e*) 0·01M-LiOH; (*f*) 0·1M-LiOH. *Zero current for each curve is indicated.*

FIG. 8. *Polarograms for various peroxides in* 0·1M-LiCl *:* (*a*) *residual current;* (*b*)—(*d*) 0·44mM-*formaldehyde peroxide ;* (*b*) *fresh solution ;* (*c*) *after* 10 *min. in cell ;* (*d*) *after shaking with mercury ;* (*e*) 0·39mM-*hydrogen peroxide;* (*f*) 1·15mM-*formaldehyde prepared as described;* (*g*) 0·45mM-*commercial* " *AnalaR* " *formaldehyde ;* (*h*) *formaldehyde peroxide treated with* $TiCl_4$ *and aq.* NH_3 *;* (*i*) 0·5mM-tert.-*butyl hydroperoxide;* (*j*)—(*k*) *oxidation products of* iso*butane dissolved in* 25 *ml. and shaken with mercury,* (*k*) *before further treatment,* (*j*) *after addition of* $TiCl_4$ *and* NH_3. *Zero current for each curve is indicated.*

From these results it is seen that hydrogen peroxide and its derivatives, although important constituents, may not amount to 50% of the total peroxides.* This is contrary to the findings by Knox and Norrish (*loc. cit.*) for the low-temperature oxidation of propane.

DISCUSSION

Under hydrocarbon-rich conditions methane makes a sudden appearance as a product when the consumption of oxygen is almost complete (see Fig. 4). In no case was methane

---

* A study of the rates of decomposition of the residual peroxide after treatment with mercury and titanium chloride, and of *tert.*-butyl hydroperoxide added to the treated solution of reaction products, as measured by the current at —0·6 v, supported the conclusion that *tert.*-butyl hydroperoxide occurs in the oxidation products.

detected when the system contained substantial quantities of oxygen (see Fig. 1). This suggests the presence of methyl radicals in the reacting mixture. The formation of acetone in conjunction with methyl radicals suggests the occurrence of *tert.*-butoxy-radicals, which are known to decompose thus: $(CH_3)_3C{\cdot}O{\cdot} \longrightarrow (CH_3)_2C{:}O + CH_3{\cdot}$. This evidence for *tert.*-butoxy-radical strengthens the case for the presence of *tert.*-butyl hydroperoxide, as it is likely that *tert.*-butoxy-radicals arise from the decomposition of a related peroxide or peroxy-radical.

The acetone found is evidence for tertiary attack on the hydrocarbon molecule. This is to be expected from the known reactions of *iso*butane. At the completion of the reaction the ratio $\Delta COMe_2/-\Delta RH$ is *ca.* 0·2 for both conditions of concentrations studied.

At the maximum rate of pressure change, *i.e.*, when the concentration of higher aldehyde is a maximum, the ratio Δ R·CHO$/-\Delta$RH is *ca.* 0·12. At the completion of the reaction the procedure for the estimation of higher aldehydes gave negative results which were undoubtedly due to effects arising from the polymerisation of formaldehyde. The higher aldehyde is probably acetaldehyde, formed as a result of primary attack on the *iso*butane molecule.

The difference, already noted in the distribution of products during and after the induction period, suggests that the reactions taking place in these two regions proceed by different mechanisms. Other factors than the time required for the development of slowly branching chains are operative during the induction period. This is supported by the fact that effects of inert gases (Ridge, unpublished results) suggest that the reaction during the induction period is surface-inhibited, and that the length of the induction period depends on the rate of destruction of an active intermediate at the walls. The relative importance of carbon dioxide among the products during the induction period suggests heterogeneous reaction. Carbon monoxide, which is obviously associated with the reaction producing the pressure increase, probably results largely from the decomposition of the radical R·CO· arising from oxidation of aldehydes. (As noted previously, aldehydes are also associated with the reaction which produces the pressure increase.) Hence, the fall in the ratio $\Delta CO_2/\Delta CO$ after the end of the induction period suggests that the onset of pressure increase marks a transition from a surface-dominated reaction to a reaction in which effects resulting from chain branching predominate. This is confirmed by Ridge's observation (unpublished) that, whereas the induction period is sensitive to the concentration of inert gas, the maximum rate of pressure change in both the propene–oxygen and the *iso*butane–oxygen system is unaffected by inert gas. Somewhat similar behaviour regarding distribution of products was encountered in the propene–oxygen system where comparatively large quantities of carbon dioxide were found during the induction period by Mulcahy and Ridge (*loc. cit.*): these authors, however, did not determine carbon monoxide.

The results show to a first approximation that the partial pressure of carbon dioxide increases linearly during the induction period. Whether or not carbon dioxide is in fact produced largely by a heterogeneous reaction during the early stages of the reaction, its constant rate of accumulation during the induction period implies that the reaction during the induction period proceeds by unbranched chains. This reaction also produces the active intermediate responsible for initiating the eventual autocatalytic reaction which produces the main pressure increase and the conversion of the bulk of the reactants.

From the available evidence it is not possible to determine the identity of this active intermediate. Higher aldehydes are present in significant quantities from the end of the induction period onwards, and the reaction evidently involves peroxides, although the quantities of hydroperoxide present are comparatively small. Experiments in which the reaction was interrupted by the withdrawal of the reactants and the treated reaction mixture subsequently fed back into the reaction vessel, indicate that peroxides in their normal state are not the substances responsible for the termination of the induction period in the low-temperature oxidation of hydrocarbons (Batten and Ridge, *Austral. J. Chem.*, in the press).

CHEMISTRY DEPARTMENT, UNIVERSITY OF MELBOURNE.
DIVISION OF TRIBOPHYSICS, C.S.I.R.O.

[*Received, March* 28*th*, 1955.]