365. *The Gaseous Oxidation of Isopropyl Alcohol. Part I. The Influence of Temperature, Pressure, and Mixture Composition on the Formation of Hydrogen Peroxide and Other Products.*

By A. R. BURGESS, C. F. CULLIS, and E. J. NEWITT.

The gaseous oxidation of isopropyl alcohol can lead to high yields of acetone and hydrogen peroxide. The optimum temperature for the conversion is *ca.* 420° and the yields of the two major products are not substantially affected by pressure. Excess of oxygen has little effect on the yields of peroxides although it enhances the rate of disappearance of acetone. Added acetaldehyde, in contrast to other reaction products, markedly accelerates the reaction.

In the early stages of the oxidation, the only process in operation is a linear chain reaction giving acetone and hydrogen peroxide. However, a small proportion of the initial alcohol is converted into acetaldehyde, further reaction of which is responsible for the onset of autocatalysis; at this stage the yields of the major products start to decrease and considerable amounts of methyl alcohol, formaldehyde, glyoxal, and carbon monoxide are formed.

THE gaseous oxidation of organic compounds at high temperatures generally gives rise, *via* various partially oxidised compounds, to steam and oxides of carbon as final products. Under certain conditions, however, it is possible to isolate certain intermediate oxygenated products in high yield. One such intermediate which is produced during the gaseous oxidation of many aliphatic compounds is hydrogen peroxide, large yields of which are apparently formed from aliphatic alcohols.[1-6] The oxidation of isopropyl alcohol, for example, leads to the production of substantial amounts of hydrogen peroxide and acetone, and a detailed study has recently been made in these laboratories of the gaseous oxidation of this alcohol. In the present paper, the effects of reaction temperature, total pressure,

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[1] Harris, U.S.P. 2,479,111.

[2] Baccareda and Pedrazzini, *Riv. combustibili*, 1954, **8**, 417.

[3] Cullis and Newitt, *Proc. Roy. Soc.*, 1956, *A*, **237**, 530.

[4] Cullis and Newitt, *Proc. Roy. Soc.*, 1957, *A*, **242**, 516.

[5] Cullis and Newitt, Sixth Symposium on Combustion (London, Butterworth's Scientific Publications, 1957), p. 827.

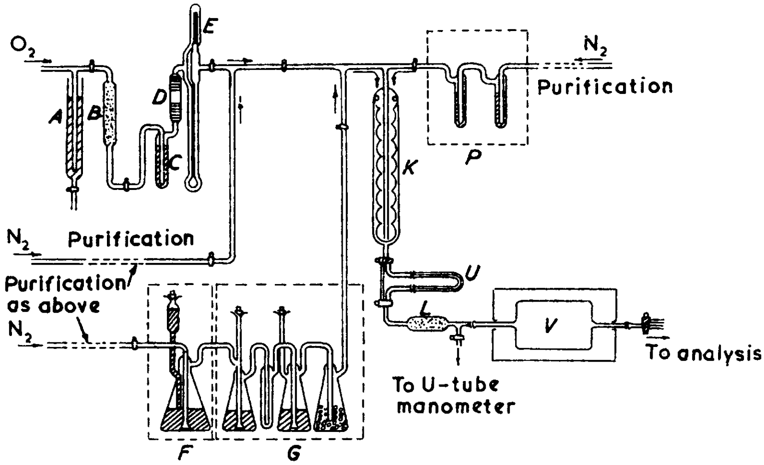
[6] Cullis and Newitt, *Proc. Roy. Soc.*, 1960, *A*, **257**, 402.

and mixture composition on the products are discussed, and the influence of the surface will be discussed in Part II.

EXPERIMENTAL

Apparatus.—The majority of measurements were made in the flow system, shown diagrammatically in Fig. 1. Oxygen and nitrogen, after being bubbled through a " blow-off " tube, A, were passed through a purification line (B,C,D) followed by a flow-meter, E. Part of the nitrogen stream then flowed through a series of flasks containing isopropyl alcohol at a known temperature. The first of these, F, was kept at a temperature 10° higher than the others, G, and was thus intended to act as a pre-saturator. Nevertheless, even with low gas-flow rates, less than the theoretical quantity of isopropyl alcohol was taken up and the amount passing had therefore to be determined for each set of flow conditions by chemical analysis (see p. 1886). Other additives (*e.g.*, acetone, water) could be introduced into the gas stream by bubbling another part of the nitrogen through the appropriate liquid contained in traps, P, which were kept at a constant temperature.

FIG. 1. *The flow apparatus.*



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

Most of the runs were at atmospheric pressure. Lower pressures could be maintained by a water-pump connected through a 5-litre reservoir to the outlets of the apparatus. The reactants were mixed and their flow-rates were measured at atmospheric pressure in the usual way. The gases then passed through a small heated capillary restriction, U, into the low-pressure part of the apparatus where the pressure was kept constant by a manostat which opened and closed a small capillary leak in the reservoir.

Some of the experiments on oxidation of acetone were carried out in a static apparatus. This consisted essentially of a cylindrical Pyrex reaction vessel, 8 cm. long and 6·4 cm. in diameter, kept at a constant temperature and connected both to a mercury manometer and to devices for admission of reactants and withdrawal of products. The course of the reaction could be followed both manometrically and by periodic chemical analysis.

Purification of Reactants.—*Oxygen and nitrogen.* Cylinder gases were purified from carbon dioxide by passage through Sofnolite (B), and dried by concentrated sulphuric acid (C) followed by magnesium perchlorate (D).

Isopropyl alcohol. The alcohol was heated under reflux with stannous chloride to destroy peroxides and with quicklime to remove moisture. It was then fractionally distilled, and the middle fraction was further purified by distillation from metallic calcium. It was poured into its storage vessel against a stream of pure dry nitrogen; it had b. p. 82·1° (lit., 82·3°).

Acetone. This was purified by the sodium iodide method [7] and then fractionally distilled; it had b. p. 56·2° (lit., 56·2°).

Acetaldehyde. This was freshly distilled in a current of nitrogen and then fractionated *in vacuo*; it had b. p. 21·1° (lit., 21·0°).

Formaldehyde. This was obtained by gentle heating of paraformaldehyde.

Analytical Procedure.—The gases leaving the reaction vessel passed immediately through a series of cold traps in which unchanged isopropyl alcohol and condensable products collected, a partial separation being achieved by having the traps surrounded by different coolants. Permanent gases were analysed qualitatively by an infrared spectrometer, and quantitatively by an Orsat apparatus.

Residual isopropyl alcohol and condensable products were extracted into water and the major constituents of the resulting solutions were determined as follows:

(i) *Alcohols.* The solution was passed through silver oxide to destroy peroxides and to oxidise aldehydes. It was then treated with an excess of standard potassium dichromate solution and sufficient sulphuric acid to give a final acidity of 3% w/v. The solution was heated at *ca.* 95° in a pressure bottle for 40 min., and under these conditions residual isopropyl alcohol and methyl alcohol, which were the only alcohols present, were completely oxidised to acetone and formic acid respectively.[8]

Methyl alcohol alone was estimated colorimetrically [9] and isopropyl alcohol could then be determined by difference, allowance being made for the fact that each molecule of the two alcohols consumes 4 and 2 equiv. of dichromate respectively.

(ii) *Aldehydes.* Total aldehydes were determined by the silver oxide method.[10] For the estimation of formaldehyde the solution was treated with powdered magnesium and hydrochloric acid in order to reduce any formaldehyde–peroxide complex.[11] The formaldehyde was then determined colorimetrically with chromotropic acid.[12] The reduction treatment also converts any formic acid into formaldehyde and an appropriate allowance must be made for this.

Acetaldehyde, which was the only other aldehyde found, was generally present in small quantities. It was estimated either by difference or independently by gas–liquid chromatography.

(iii) *Acetone.* This was determined, after treatment with silver oxide, by the iodoform method.[13]

(iv) *Acids.* These were estimated by titration under nitrogen with a solution of potassium hydroxide in methyl alcohol, phenolphthalein being used as indicator.

(v) *Peroxides.* Hydrogen peroxide, organic peroxides, and peroxy-acids were determined by a modification of the iodometric method.[3]

Minor condensable products (*e.g.*, glyoxal) were identified and estimated by gas–liquid chromatography, using a 12-ft. Embacel column impregnated with polyethylene glycol (M = 400) and a hydrogen flame detector.

RESULTS

(a) *Effect of Temperature.*—The consumption of isopropyl alcohol and the formation of reaction products were determined at temperatures from 350° to 450°. In general, the reaction is preceded by an induction period during which little or no consumption of reactants occurs and at the end of which acetone and peroxides are the first products to appear. The yields of peroxides invariably pass through a maximum with increasing contact time. Below 400°, the yields of acetone, methyl alcohol, and formaldehyde increase continuously with contact time, but above this temperature they also pass through a maximum although this is reached at a somewhat later stage than the peroxide maximum. Some of the analytical results are summarised in Table 1. These show that the optimum temperature for conversion of isopropyl

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[7] Shipsey and Werner, *J.*, 1913, **103**, 1255.

[8] Cf. Harris, *Analyst*, 1937, **62**, 729.

[9] Boos, *Analyt. Chem.*, 1948, **20**, 964.

[10] Bailey and Knox, *J.*, 1951, 2741.

[11] Newitt, unpublished results.

[12] Bricker and Johnson, *Analyt. Chem.*, 1945, **17**, 400.

[13] Morgan, Bardwell, and Cullis, *J.*, 1950, 3190.

alcohol into acetone and hydrogen peroxide is *ca.* 420°, and in Fig. 2 are presented the detailed analytical results obtained at this temperature, the yields shown here (and in all subsequent figures) being based on the total amount of isopropyl alcohol passed. Under these conditions 30% of the isopropyl alcohol can be converted more or less completely into acetone and hydrogen peroxide, but the yields of these primary products fall off rapidly if longer contact times are used. The only other products formed in appreciable quantities at this temperature are methyl alcohol, formaldehyde, and glyoxal.

(b) *Effect of Pressure.*—A detailed study of product formation in an equimolar reactant mixture was also carried out at 420° and at a total pressure of 300 mm. Consumption of isopropyl alcohol and acetone and formation of peroxide are shown in Fig. 3(*a*) alongside the values obtained at atmospheric pressure. Reaction is slower at the lower pressure but roughly the same proportion of isopropyl alcohol consumed is converted into the major products. The peroxide maximum occurs considerably later under reduced pressure conditions and this suggests that such compounds are better preserved at low pressures and that they normally disappear, at any rate, partly by a homogeneous process.

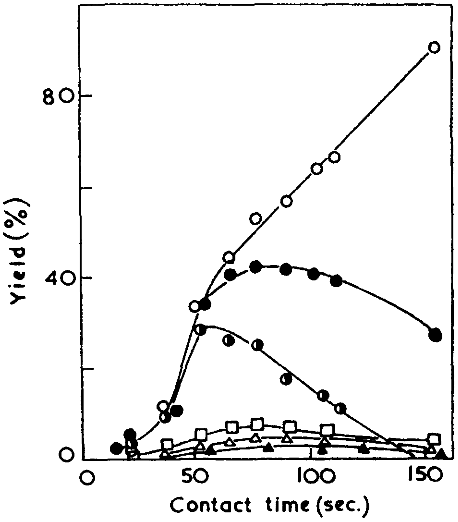


FIG. 2. *Reactant consumption and product formation at atmospheric pressure.*

Temp. 420°; isopropyl alcohol pressure 77·0 mm.; oxygen pressure 81·5 mm.; nitrogen pressure 601·5 mm.

○ Isopropyl alcohol consumed; ● acetone; ◑ total peroxides; □ formaldehyde; △ methyl alcohol; ▲ glyoxal.

TABLE 1. *Influence of temperature on products formed from reaction of equimolar isopropyl alcohol–oxygen mixtures.*

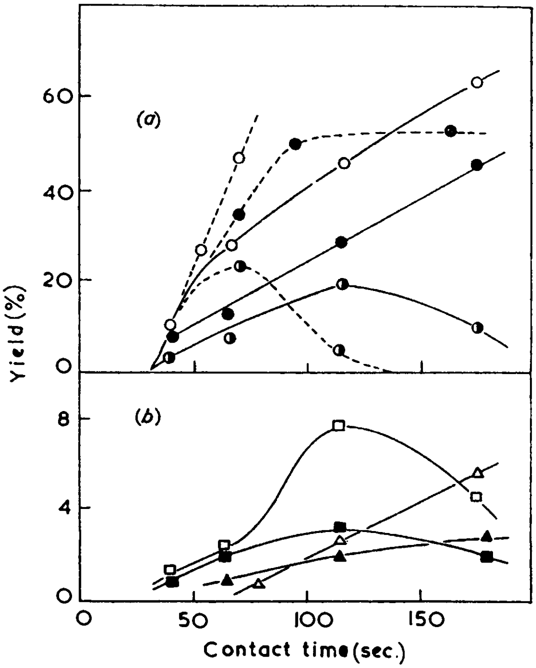
Temp. (°c)	Induction period (sec.)	Contact time for max. peroxide yield (sec.)	Max. peroxide yield (% of Pr^{i}OH passed)	Composition of peroxides (% of H_2O_2 in total peroxides)	Yields (% of Pr^{i}OH passed) of:			
					COMe$_2$	H·CHO	MeOH	Consumption of Pr^{i}OH
					at time of max. peroxide yield			
350	93	100	4·2	100	7·0	0·25	0·1	7·0
400	35	80	35	66	32	3·1	7·4	47
420	15	55	38	98	35	6·3	3·2	35
450	10	25	32	90	40	10	8·1	60

Formaldehyde, acetaldehyde, and glyoxal are formed in roughly equal amounts in the early stages of reaction [Fig. 3(*b*)] and the yields are similar to those obtained at atmospheric pressure; formaldehyde is, however, subsequently formed in somewhat greater amounts than acetaldehyde. Methyl alcohol first appears at a later stage in the experiments at 300 mm. total pressure but its yield eventually overtakes that found at atmospheric pressure.

The effect of total pressure on the yields of products at a particular stage of the reaction is shown in Fig. 4. The general pattern of formation of the major products remains largely unaffected by total pressure, and the yields are increased at higher pressures although the conversions are little changed. On the other hand, the yields of acetaldehyde remain substantially constant, while methyl alcohol is not formed at all below a pressure of *ca.* 500 mm.

(c) *Effect of Composition of Mixtures.*—Analysis of products was carried out for reactant mixtures containing the same amount of isopropyl alcohol and varying quantities of oxygen, with added nitrogen to make the total flow rate the same in each case. In general, the extents of consumption of isopropyl alcohol and of formation of acetone, peroxides, methyl alcohol, and formaldehyde increase rapidly with oxygen concentration until the oxygen : alcohol ratio reaches unity. Thereafter the influence of oxygen depends on the stage of the oxidation. Oxygen in excess of that required to give an equimolar mixture has little effect in the early stages of the reaction (Fig. 5). Thus the total isopropyl alcohol consumption remains substantially constant over a large range of oxygen pressures. Acetone and hydrogen peroxide are both formed in considerable yield, and the only difference in oxygen-rich mixtures is the formation of increasing amounts of methyl alcohol and formaldehyde. Oxygen has, however, a much more pronounced effect on the formation of C_1 compounds during the autocatalytic stages of reaction (Fig. 6). In particular, methyl alcohol and carbon oxides do not appear below an oxygen : alcohol ratio of 0·2. Above this value, the yield of carbon monoxide increases linearly with oxygen pressure, and carbon dioxide is not formed until the oxygen : alcohol ratio exceeds 1·3, and then probably only arises from further oxidation of carbon monoxide. Oxygen has little effect on the peroxide yields, which generally reach a maximum during this stage of the reaction. The later stages of oxidation are characterised

FIG. 3. *Reactant consumption and product formation at reduced pressure.*

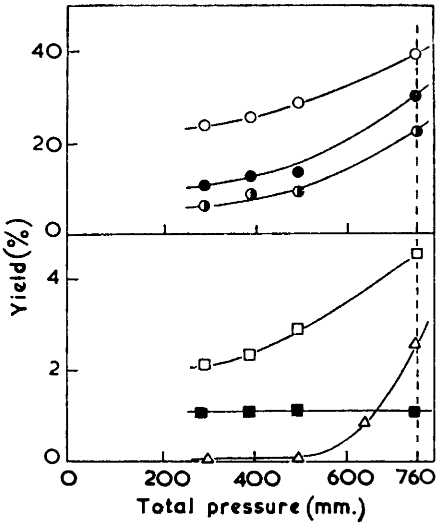


Temp. 420°; isopropyl alcohol pressure 30·0 mm.; oxygen pressure 36·0 mm.; nitrogen pressure 234·0 mm.

Continuous line: reduced pressure. Broken line: atmospheric pressure.

○ Isopropyl alcohol consumed; ● acetone; ◑ total peroxides; □ formaldehyde; ■ acetaldehyde; △ methyl alcohol; ▲ glyoxal.

FIG. 4. *Influence of total pressure on reactant consumption and product formation.*



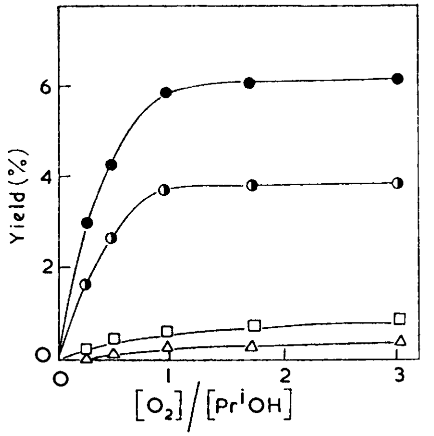
Temp. 420°; $Pr^iOH : O_2 : N_2 = 1 : 1 : 8$; contact time, 63·5 sec.

○ Isopropyl alcohol consumed; ● acetone; ◑ total peroxides; □ formaldehyde; ■ acetaldehyde; △ methyl alcohol.

by a strong decline in the overall rate of alcohol consumption, rapid decomposition of hydrogen peroxide, and a fall in the yields of acetone. Increase of oxygen pressure enhances the rate of disappearance of both isopropyl alcohol and acetone, but apparently has little effect on the decomposition of hydrogen peroxide or on the formation of aldehydes and methyl alcohol (Fig. 7).

(d) *Effect of Added Products.*—Acetone and formaldehyde have no appreciable effect on the course of the oxidation of isopropyl alcohol. On the other hand, even small additions of acetaldehyde markedly accelerate the reaction (Table 2).

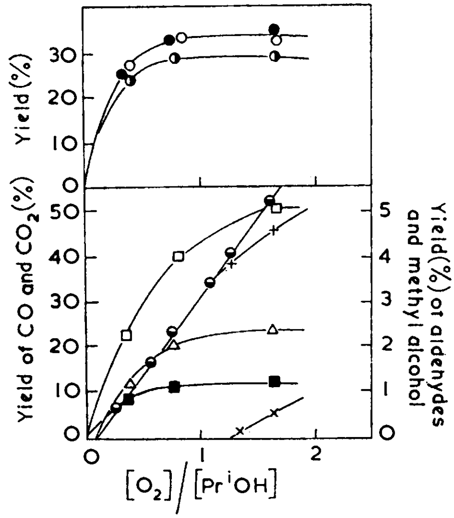
FIG. 5. *Influence of alcohol : oxygen ratio on product formation during early stages of reaction.*



Temp. 420°; total pressure 760 mm.; isopropyl alcohol pressure 46·1 mm.; contact time 21·5 sec.

● Acetone; ◑ total peroxides; □ formaldehyde; △ methyl alcohol.

FIG. 6. *Influence of alcohol : oxygen ratio on product formation during autocatalytic stages of reaction.*



Temp. 420°; total pressure 760 mm.; isopropyl alcohol pressure 65·0 mm.; contact time 51·7 sec.

○ Isopropyl alcohol consumed; ● acetone; ◑ total peroxides; □ formaldehyde; ■ acetaldehyde; △ methyl alcohol; ◒ total carbon oxides; -|- carbon monoxide; × carbon dioxide.

(e) *Oxidation of Acetone.*—Although acetone is by far the most abundant product of oxidation of isopropyl alcohol, the amounts formed are to some extent reduced by high temperatures and oxygen concentrations, particularly with long contact times. Some further reaction of acetone evidently occurs under these conditions, and some work was therefore carried out on the gaseous oxidation of acetone itself.

TABLE 2. *Influence of added acetaldehyde on the rate of oxidation of isopropyl alcohol.*

Temp. 375°; isopropyl alcohol pressure 50 mm.; oxygen pressure 200 mm.

Pressure (mm.) of added $CH_3 \cdot CHO$	0	0·5	1·0	2·5
Time (min.) for pressure increase of 5 mm.	7·8	5·0	3·9	1·9
Time (min.) for pressure increase of 200 mm.	11·1	9·6	8·4	5·7

The majority of measurements were made in a static system. Although acetone has been reported to be stable to oxidation below *ca.* 350°,[14] yet mixtures of acetone and oxygen were found to react at temperatures below 300°.[15] An equimolar mixture of acetone and oxygen is

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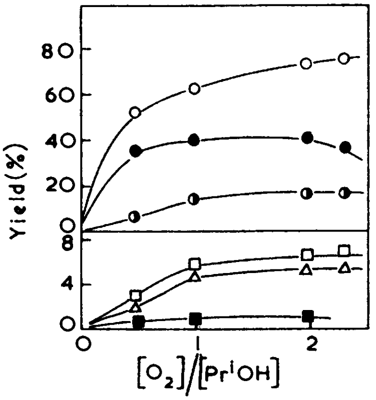
[14] Bardwell, *Proc. Roy. Soc.*, 1951, *A*, **207**, 470.

[15] Avramenko and Neumann, *Acta Physicochim. U.S.S.R.*, 1939, **10**, 601.

in fact considerably more reactive at 330° than a similar isopropyl alcohol + oxygen mixture (Table 3). The same conclusion emerges from a consideration of the pressure–time curves for oxygen-rich mixtures at 295° (Fig. 8). The initial rate of oxidation at the latter temperature is almost the same as at 375°, but after a pressure rise of *ca.* 10 mm. the rate decreases rapidly at the lower temperature and increases slightly at the higher temperature. Added acetaldehyde increases the initial rate, but after a pressure rise of about six times the initial aldehyde pressure the rate becomes similar to that for the oxidation of acetone alone. Isopropyl alcohol has no effect until after 6 min. (the induction period normally preceding the oxidation of this compound at 375°), whereupon the rate increases rapidly although it eventually becomes similar to that expected for the oxidation of acetone. However, the fact that the additional pressure rise is approximately double that accompanying oxidation of isopropyl alcohol alone indicates that the two organic compounds are not reacting completely independently of one another. Analysis of the products at 295° (Table 4) shows that formaldehyde, methyl alcohol,

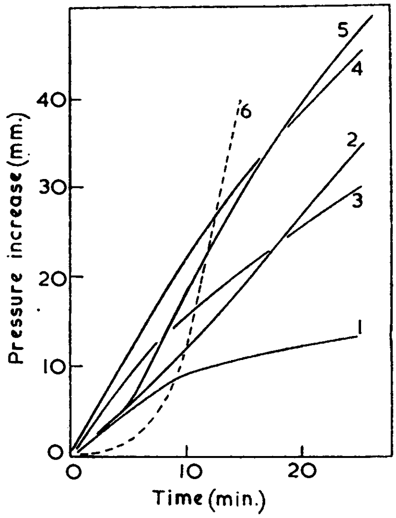
FIG. 7. *Influence of alcohol : oxygen ratio on product formation during late stages of reaction.*



Temp. 420°; total pressure 760 mm.; isopropyl alcohol pressure 76·5 mm.; contact time 106·0 sec.

○ Isopropyl alcohol consumed; ● acetone; ◑ total peroxides; □ formaldehyde; ■ acetaldehyde; △ methyl alcohol.

FIG. 8. *Influence of additives on the oxidation of acetone.*



Continuous lines: Acetone pressure 50 mm.; oxygen pressure 200 mm.

Curve 1, temp. 295°, no additive; curve 2, temp. 375°, no additive; curve 3, temp. 375°, 2·5 mm. of acetaldehyde added; curve 4, temp. 375°, 5·0 mm. of acetaldehyde added; curve 5, temp. 375°, 5·0 mm. of isopropyl alcohol added.

Broken line: Isopropyl alcohol pressure 50 mm.; oxygen pressure 200 mm.

Curve 6, temp. 375°, no additive.

TABLE 3. *Comparison of the oxidation of acetone and isopropyl alcohol.*

Temp. 330°; ketone or alcohol pressure, 100 mm.

Oxygen pressure (mm.)	Induction period (min.)		Max. rate of pressure increase (mm. min.$^{-1}$)		Total pressure increase (mm.)	
	$COMe_2$	Pr^iOH	$COMe_2$	Pr^iOH	$COMe_2$	Pr^iOH
33·5	6·0	—	1·2	—	13	—
49·5	—	15·5	—	1·0	—	38
57·0	2·0	—	4·3	—	28	—
100·0	1·0	13·5	12·2	2·2	55	75

and glyoxal are all formed although the extent of pressure rise is indicative of some further oxidation of these compounds (*e.g.*, to carbon monoxide).

More detailed analysis was carried out in a flow system at 420° and under these conditions, too, the main product was glyoxal together with methyl alcohol and formaldehyde, and no peroxides could be detected. When acetone was added to an isopropyl alcohol–oxygen mixture at the same temperature, appreciable oxidation of the ketone occurred. The consumption of isopropyl alcohol is unchanged in the presence of acetone (Table 5), although the pattern of the formation of products is different. One striking feature is that the decrease in the number of moles of carbon oxides formed is almost exactly equal to the increase in the number of moles of acetone consumed. This suggests that the ketone competes for oxygen with some other compound whose oxidation leads directly to the formation of carbon oxides. The increase in methyl alcohol is similar to that of glyoxal, showing that these products are probably formed together by the oxidation of acetone. There is also a substantial rise in the production of acetaldehyde, which is not normally found among the products of oxidation of acetone.

TABLE 4. *Products of the oxidation of acetone.*

Temp. 295°; acetone pressure 50 mm.; oxygen pressure 200 mm.

	Reaction time (min.)	
	7	43
Acetone consumed (mm.)	8·5	16·5
Glyoxal (mm.)	2·5	2·0
Methyl alcohol (mm.)	0·5	1·5
Formaldehyde (mm.)	0·5	0·5
Pressure increase (mm.)	7·5	17·5

TABLE 5. *The influence of addition of acetone on the products of oxidation of isopropyl alcohol.*

Temp. 420°; contact time 111 sec.; oxygen : isopropyl alcohol = 1·13; isopropyl alcohol 8·45 × 10^{-3} mole hr.$^{-1}$; additional acetone 3·14 × 10^{-3} mole hr.$^{-1}$.

	Flow rate (mole hr.$^{-1}$)			Flow rate (mole hr.$^{-1}$)	
	Acetone not added	Acetone added		Acetone not added	Acetone added
Alcohol consumed	7·28	7·28	Glyoxal	0·38	0·56
Acetone consumed	—	1·14	Peroxides	0·57	0·57
Acetaldehyde	0·04	0·08	Carbon monoxide	6·12	5·06
Formaldehyde	0·36	0·33	Carbon dioxide	0·46	0·40
Methyl alcohol	0·37	0·53			

DISCUSSION

Oxidation of Isopropyl Alcohol.—The first products to be formed during the oxidation of isopropyl alcohol are acetone and hydrogen peroxide. Under optimum conditions for the recovery of hydrogen peroxide about 30% of the initial alcohol is consumed and this appears to react almost entirely according to the overall equation:

$$\mathrm{CHMe_2{\cdot}OH + O_2 = COMe_2 + H_2O_2}$$

In general, however, when changes are made to the experimental conditions, the rate of consumption of isopropyl alcohol runs closely parallel with the amounts of acetone and hydrogen peroxide formed. This suggests that attack on the isopropyl alcohol is brought about mainly by HO_2 radicals and that the resulting radicals then react with oxygen to yield acetone, so that oxidation proceeds according to the chain reaction:

$$\mathrm{CHMe_2{\cdot}OH + HO_2 = \dot{C}Me_2{\cdot}OH + H_2O_2}$$

$$\mathrm{\dot{C}Me_2{\cdot}OH + O_2 = COMe_2 + HO_2}$$

Although this linear chain reaction is effectively the only process in operation during the early stages of the oxidation, other processes also occur in the later stages which do not result in the formation of these primary products. The other compounds first to appear are formaldehyde, acetaldehyde, and methyl alcohol, which are probably formed by the thermal decomposition of the radicals derived from isopropyl alcohol:

$$\dot{C}Me_2{\cdot}OH \longrightarrow CH_3{\cdot}CHO + CH_3$$

Acetaldehyde itself readily undergoes further oxidation, and the reaction of methyl radicals with oxygen would be expected to result in the formation of methyl alcohol and formaldehyde (and carbon monoxide).[16-19] In the present system, methyl alcohol is formed at a later stage than formaldehyde, suggesting that the predominant reactions are processes such as:

$$CH_3 + O_2 \longrightarrow H{\cdot}CHO + OH$$

Alternatively, if methoxy-radicals are formed as a result of the reactions [16]

$$CH_3 + O_2 \longrightarrow CH_3{\cdot}O_2{\cdot}$$
$$2CH_3{\cdot}O_2{\cdot} \longrightarrow 2CH_3{\cdot}O{\cdot} + O_2$$

they appear to be further oxidised rather than to stabilise themselves by abstraction of hydrogen. Since little or no carbon monoxide can be detected at this stage, alkoxy-radicals probably react with oxygen to yield an aldehyde and an HO_2 radical: [20]

$$CH_3{\cdot}O{\cdot} + O_2 \longrightarrow H{\cdot}CHO + HO_2{\cdot}$$

The products which are present at the beginning of the autocatalytic stage and might be responsible for chain-branching are acetone, hydrogen peroxide, formaldehyde, and acetaldehyde.

Now, when the surface conditions are unfavourable for the preservation of hydrogen peroxide, the overall rate of reaction decreases, but the time of onset of the autocatalytic stage is unaffected. Thus it seems unlikely that this compound is responsible for chain branching. Similarly experiments on addition of acetone and formaldehyde prove conclusively that neither of these compounds is capable of starting a branching reaction. On the other hand, introduction of small quantities of acetaldehyde decreases, or even eliminates, the induction period so it is probably this compound which is responsible for chain branching in the present system. If the formation (or further oxidation) of acetaldehyde could be prevented, the linear chain cycle would continue more or less unaffected, resulting in the exclusive formation of acetone and hydrogen peroxide.

Oxidation of Acetone.—Even below 400°, appreciable further oxidation of acetone evidently occurs. The main products are glyoxal, methyl alcohol, and formaldehyde. The appearance of these C_1 and C_2 products at such an early stage, and the absence of peroxides, makes it unlikely that initial attack involves simple abstraction of hydrogen from the ketone molecule. On the other hand, early C–C bond fission appears to be involved. The chain reaction occurring at much lower temperatures involves formation of formaldehyde, methyl alcohol, and possibly methylglyoxal,[21] but glyoxal itself has not previously been reported among the products of oxidation of acetone.

Since the only plausible mode of initial attack involving C–C bond fission and production of free radicals would be:

$$CH_3{\cdot}CO{\cdot}CH_3 + O_2 = CH_3{\cdot}CO + CH_3{\cdot}O_2{\cdot}$$

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[16] Raley, Porter, Rust, and Vaughan, *J. Amer. Chem. Soc.*, 1951, **73**, 15.
[17] Hentz, *J. Amer. Chem. Soc.*, 1953, **75**, 5810.
[18] Taylor and Blacet, *Ind. Eng. Chem.*, 1956, **48**, 1505.
[19] Ingold and Bryce, *J. Chem. Phys.*, 1956, **24**, 360.
[20] Jolley, *J. Amer. Chem. Soc.*, 1957, **79**, 1537.
[21] Christie, *J. Amer. Chem. Soc.*, 1954, **76**, 1979.

and since there is abundant evidence that the only fate of acetyl radicals at the temperatures concerned is decomposition according to the reaction: [22-24]

$$CH_3{\cdot}CO{\cdot} = CH_3{\cdot} + CO$$

it seems that the reaction occurring may be a molecular rather than a radical process. Such a conclusion would be consistent with the absence of any specific effect of added acetone on the rate of oxidation of isopropyl alcohol. On the other hand, the possibility of acetone's undergoing a radical-induced oxidation is shown by the enhanced consumption of ketone which is found in an isopropyl alcohol–oxygen mixture.

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CHEMISTRY DEPARTMENT, IMPERIAL COLLEGE, LONDON, S.W.7. [*Received, July 20th,* 1960.]

[22] Pitts and Blacet, *J. Amer. Chem. Soc.*, 1952, **74**, 455.

[23] Grumer, Fifth Symposium on Combustion (New York: Reinhold Publishing Corporation, 1955), p. 447.

[24] Blanchard, Farmer, and Ouellet, *Canad. J. Chem.*, 1957, **35**, 115.