582. *The Gaseous Oxidation of Isopropyl Alcohol. Part II.*[1] *Influence of the Surface on the Formation of Hydrogen Peroxide and Other Products.*

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Studies of the gaseous oxidation of isopropyl alcohol have been carried out in Pyrex vessels treated with hydrofluoric acid and in a boric acid-coated vessel. Improved mixing of the reactants and an increased surface area of glass enhance the recovery of acetone but have little effect on the formation of peroxides. In a boric acid-coated vessel, the maximum yields of peroxides are lower than in Pyrex vessels but once such compounds are formed they are better preserved after long contact times. In order to account for these results it is necessary to distinguish between the effects of the different surfaces on HO_2 radicals and on hydrogen peroxide itself. The rate of reaction and the yields of peroxides increase as both types of surface are allowed to " age," and it has been shown that this effect is at any rate partly due to adsorption of water vapour.

IN Part I,[1] it was shown that the only products formed during the early stages of the gaseous oxidation of isopropyl alcohol are acetone and hydrogen peroxide. As reaction proceeds, however, the yield of hydrogen peroxide falls off sharply. Although some homogeneous decomposition of the peroxide takes place at the temperatures used,[2-6] the decrease in yield of peroxide is probably also partly due to breakdown of this compound at the surface of the vessel. The influence of the surface on the yields of hydrogen peroxide and other products formed during the reaction has therefore been studied.

EXPERIMENTAL

The flow apparatus and the experimental procedures have already been described in Part I. Three cylindrical Pyrex reaction vessels were used in this work; they were all 12 cm. long and 4·5 cm. in diameter. Vessel 1 was an open cylinder and had a surface : volume ratio of 1·07 cm.$^{-1}$. Vessel 2 was designed to improve mixing of the reactants and had six baffles placed at equal distances along its length; each of these contained one small hole, 1 mm. in diameter, which was placed near the circumference and at positions diametrically opposite in alternate baffles. The resulting surface : volume ratio of vessel 2 was 2·01 cm.$^{-1}$. Both vessels 1 and 2 were rinsed with hydrofluoric acid and washed three times with water before use. Vessel 3 was similar to vessel 1 but its surface was coated with a thick layer of boric acid.

RESULTS

(a) *The Effect of Re-mixing the Reacting Gases.*—In experiments with vessel 1, it was found that even after long reaction times the initial isopropyl alcohol was never completely used up.

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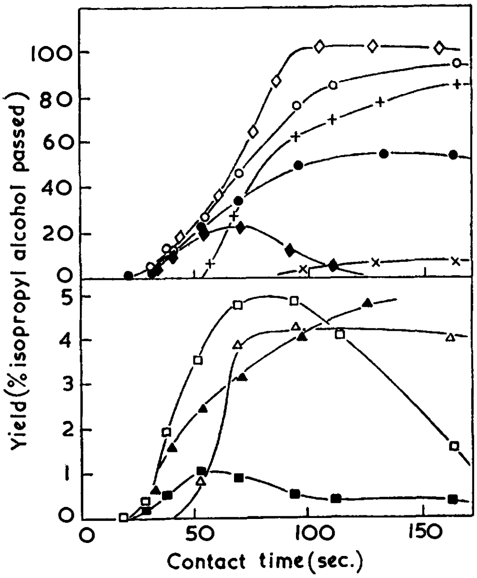
[1] Part I, Burgess, Cullis, and Newitt, *J.*, 1961, 1884.
[2] McLane, *J. Chem. Phys.*, 1949, **17**, 379.
[3] Satterfield and Stein, *J. Phys. Chem.*, 1957, **61**, 538.
[4] Satterfield and Stein, *Ind. Eng. Chem.*, 1957, **49**, 1173.
[5] Giguère and Liu, *Canad. J. Chem.*, 1957, **35**, 283.
[6] Hoare, Protheroe, and Walsh, *Trans. Faraday Soc.*, 1959, **55**, 548.

This is probably due to the fact that, in a flow system and with an open vessel, a small proportion of the reactants flows rapidly straight through the centre of the vessel before it has a chance to react. In vessel 2, in which the reactants and products were effectively re-mixed six times, a greater proportion of the alcohol was used up after long contact times, and the results obtained were much more reproducible. This vessel was therefore used for a detailed study of the reaction at 420° C.

Some typical results are given in Fig. 1 which shows the consumption of reactants and the formation of products for an equimolar isopropyl alcohol + oxygen mixture. The two reactants are used up at equal rates until about half the alcohol has reacted. Thereafter the oxygen is used up rather more rapidly, no doubt owing to secondary oxidation of intermediate products.

During the initial stages of reaction, acetone and peroxides (shown to be nearly exclusively hydrogen peroxide at 420°) are formed in almost 100% yield. Although these compounds remain major products throughout, the efficiency of their formation starts to fall after about 20% of the reactants have been consumed, the yield of peroxide soon passing through a maximum and then decreasing again. Both formaldehyde and acetaldehyde appear quite early in the reaction, and the yields rise rapidly during the initial part of the autocatalytic stage, reaching a maximum at about the same time as the peroxide yield. Glyoxal too is formed quite early and its concentration rises steadily.

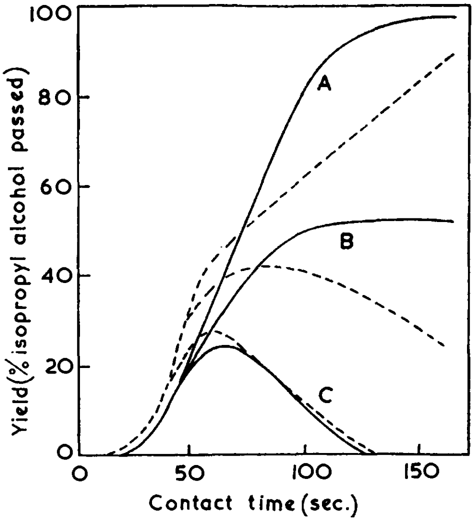
Fig. 1. *Consumption of reactants and formation of products in vessel 2.*



Temp. 420° c; pressure of isopropyl alcohol 75·3 mm.; of oxygen 78·8 mm.; of nitrogen 605·9 mm.

○ Isopropyl alcohol consumed; ◇ oxygen consumed; ● acetone; ◆ total peroxides; □ formaldehyde; ■ acetaldehyde; △ methyl alcohol; ▲ glyoxal; + carbon monoxide; × carbon dioxide.

Fig. 2. *Comparison of consumption of isopropyl alcohol* (A) *and of formation of acetone* (B) *and peroxides* (C) *in vessels* 1 *and* 2.



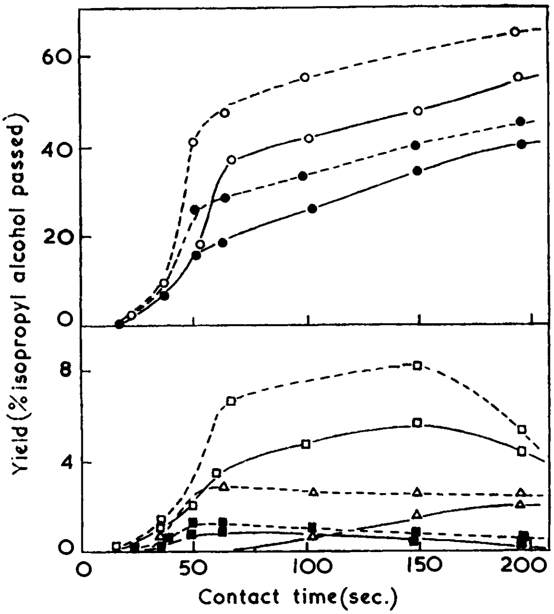
Temp. 420° c; pressure of isopropyl alcohol *ca.* 76 mm.; of oxygen *ca.* 76 mm.; of nitrogen *ca.* 608 mm.

Broken line: vessel 1. Continuous line: vessel 2.

Methyl alcohol is not detectable until the middle of the autocatalytic stage, and it is then formed rapidly, the yield soon reaching a steady value of about 4%. Carbon monoxide starts to appear at about the same time, and by the end of reaction large amounts are present in the products; carbon dioxide is produced in much smaller quantities, probably arising from further oxidation of carbon monoxide.

Fig. 2 compares the extents of alcohol consumption and of the yields of the two main products (acetone and hydrogen peroxide) in vessels 1 and 2. The induction period is the same but the maximum rate of oxidation is smaller in vessel 2. After *ca.* 70 sec., however, the alcohol

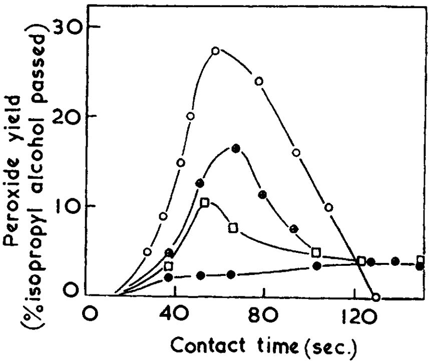
FIG. 3. *Comparison of consumption of reactant and of formation of products in " new " aud " aged " boric acid-coated vessel.*



Temp. 420° c; pressure of isopropyl alcohol *ca.* 76 mm.; of oxygen *ca.* 76 mm.; of nitrogen *ca.* 608 mm. Continuous line: " new " vessel 3. Broken line: " aged " vessel 3 (3—4 weeks).

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

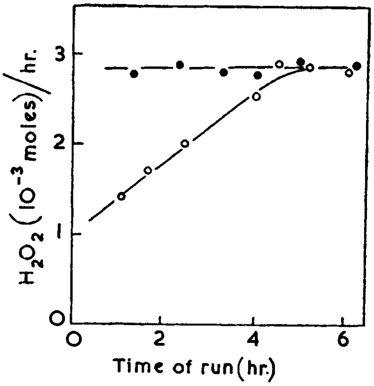
FIG. 4. *Comparison of formation of peroxide in uncoated and boric acid-coated vessels.*



Temp. 420° c; pressure of isopropyl alcohol *ca.* 76 mm.; of oxygen *ca.* 76 mm.; of nitrogen *ca.* 608 mm.

○ " Aged " vessel 2; ● " new " vessel 3; □ " aged " vessel 3; ⊕ " aged " vessel 3 (samples taken after 5—6 hr.).

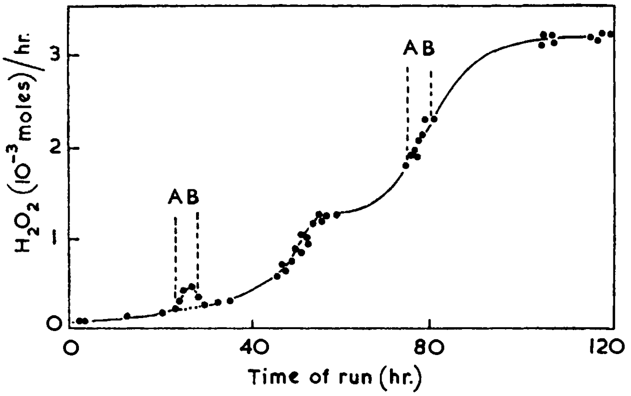
FIG. 5. *The influence of sampling time on the formation of peroxides in an " aged " boric acid-coated vessel.*



Temp. 420° c; pressure of isopropyl alcohol *ca.* 76 mm.; of oxygen *ca.* 76 mm.; of nitrogen *ca.* 608 mm.

○ Dry reaction mixture; ● reaction mixture containing 5·2 moles % of water vapour.

FIG. 6. *The influence of " ageing " of Pyrex glass surface on the formation of peroxides.*



Temp. 420° c; pressure of isopropyl alcohol *ca.* 76 mm.; of oxygen *ca.* 76 mm.; of nitrogen *ca.* 608 mm.; vessel 2. A, water on; B, water off.

consumption is higher in this vessel and remains so until reaction is complete. The yield of acetone too is higher in vessel 2, and this compound appears to be better preserved under conditions of improved mixing. Despite the increased surface : volume ratio, the yield of peroxide is only slightly lower in vessel 2 and this suggests that in both the Pyrex vessels decomposition of hydrogen peroxide occurs mainly as a homogeneous process under the experimental conditions used.

(b) *The Effect of a Boric Acid Surface.*—In spite of the above conclusion, it was thought that it might be possible to minimise further the decomposition of hydrogen peroxide by use of a boric acid-coated vessel (vessel 3). Although it was expected that this would preserve peroxides more effectively, it was found that in a freshly-coated vessel, oxidation was much slower and yields of acetone, aldehydes, methyl alcohol, and peroxides were considerably lower (Figs. 3 and 4). Nevertheless, as the surface " aged " during 3—4 weeks, both the rate of oxidation of isopropyl alcohol and the amounts of the above products steadily increased. In the fully " aged " boric acid-coated vessel, the reaction rate was almost the same as in vessel 1, but the maximum yields of peroxide always remained somewhat lower (Fig. 4). The amount of peroxide remaining after long contact times was however greater in vessel 3 than in vessel 1, and this suggests that boric acid does in fact preserve hydrogen peroxide even though it is not conducive to its formation.

It was also noticed that when vessel 3 was fully " aged," yields of peroxides tended to be higher if the products were sampled after 5—6 hr. instead of after 1—2 hr. (Figs. 4 and 5). It was thought that this might be due to adsorption on the surface of the vessel of water vapour from the mixture of products and indeed when yields of hydrogen peroxide were measured as a function of the duration of the run, it was found that these increased up to *ca.* 6 hr. If, however, water vapour was artificially added to the mixture, after the surface had been allowed to attain its original condition, the maximum yield of peroxide was obtained immediately and no progressive increase occurred during a long run (Fig. 5). The vessel returned to its original condition after being evacuated for several hours at the reaction temperature so that the effect of water vapour is evidently not permanent.

(c) *The Effect of " Ageing " of Pyrex Glass.*—The effects noticed with vessel 3 prompted further study of the ageing of a Pyrex-glass surface. For this purpose an equimolar mixture of isopropyl alcohol and oxygen was passed continuously for several days through vessel 2 which had previously been washed with hydrofluoric acid; samples of products were collected every hour or so and analysed for peroxides. Some typical results are shown in Fig. 6. These suggest that " ageing " is a two-stage process and this belief is strengthened by observations of the effect of added water vapour during the two different stages. During the first stage, when water vapour was introduced into the reactant mixture, the yield of peroxide increased rapidly; when the water flow stopped, the yield immediately decreased again. On the other hand, addition of water vapour to the reactant mixture during the second stage of " ageing " did not exert any appreciable influence on the yields of hydrogen peroxide obtained.

DISCUSSION

Much of the information at present available concerning the influence of the surface on gaseous oxidations is derived from detailed studies of the hydrogen + oxygen [7-9] and methane + oxygen [10-12] reactions. In the former, recent kinetic investigations [13-15] suggest that an aged boric acid surface is one of the most inert toward destruction of HO_2 radicals and of hydrogen peroxide. It has, too, been reported [2,16] that the use of boric acid-coated surfaces reduces to a minimum the heterogeneous decomposition of hydrogen peroxide.

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[7] Willbourn and Hinshelwood, *Proc. Roy. Soc.*, 1945, *A*, **185**, 376.

[8] Egerton and Warren, *Proc. Roy. Soc.*, 1951, *A*, **204**, 465.

[9] Warren, *Proc. Roy. Soc.*, 1952, *A*, **211**, 86, 96.

[10] Hoare, *Trans. Faraday Soc.*, 1953, **49**, 628.

[11] Hoare and Walsh, Fifth Symp. Combustion, Reinhold Publ. Corp., New York, 1955, pp. 467, 474.

[12] Egerton, Minkoff, and Salooja, *Combustion and Flame*, 1957, **1**, 25.

[13] Baldwin and Mayor, *Rev. l'Inst. français Petrole*, 1958, **13**, 397.

[14] Baldwin and Mayor, Seventh Symp. Combustion, Butterworths, London, 1959, p. 8.

[15] Baldwin and Mayor, *Trans. Faraday Soc.*, 1960, **56**, 80, 93, 103.

[16] Cook, U.S.P. 2,368,640, 2,368,806.

On the other hand, other workers [3-6] have found that clean vitreous surfaces are in certain cases possibly even more suitable for the preservation of hydrogen peroxide and it has been suggested [17] that all acidic surfaces (including acid-treated vitreous materials which can be regarded as having a silicic acid coating [18]) should favour the formation of this compound since they facilitate conversion of HO_2 radicals into it.

In the present system, the largest amounts of peroxides are formed in acid-washed Pyrex vessels, and the extent of such a surface has relatively little effect on peroxide yields.[5] The results also indicate, however, that although boric acid helps to preserve hydrogen peroxide once it is formed, such a surface does not favour its production.[12] This suggests that, although the use of boric acid minimises decomposition of hydrogen peroxide, it is not as effective as an acid-treated vitreous surface in promoting the reaction: [17]

$$HO_2 + H^+ \longrightarrow \tfrac{1}{2}H_2O_2 + \tfrac{1}{2}O_2 + H^+$$

It is of interest that Broida,[19] from experiments on the second limit of the hydrogen + oxygen reaction, concluded that while a boric acid surface was the most inert toward the destruction of hydrogen atoms, Pyrex glass was the most effective material for the preservation of HO_2 radicals. Since probably only the latter species play a part in the gaseous oxidation of isopropyl alcohol, this may account for the greater yields of hydrogen peroxide formed in vessels 1 and 2 in the present system.

Surface " ageing " in oxidations generally leads to increased rates of reaction and to improved yields of peroxides. Such effects have frequently been ascribed to the adsorption of water vapour,[20] and Badin [21] has shown that in the $H + O_2$ reaction the yield of hydrogen peroxide varies with the " wetness " of the surface used. Voevodsky [22] suggested that adsorbed water vapour promotes the reaction:

$$HO_2 + H_2O \longrightarrow H_2O_2 + OH$$

although other workers [13-15] can find no support for such a process. There is certainly evidence that water vapour is strongly adsorbed by fused boric acid [5,12] and this probably accuents for the results now obtained with such a surface.

The experimental results show, however, that a similar hydration of a glass (silicic acid) surface is one of the causes of " ageing " effects shown in a Pyrex vessel. Nevertheless, even after full hydration has occurred, the " ageing " process can evidently continue so that it is clear that other factors are also involved. It is important to stress how difficult it is to draw general conclusions from results obtained for a particular system, for other workers [23,24] have shown that, in the propane + oxygen reaction, " ageing " of a Pyrex vessel leads to a steady decrease in rate of reaction and in peroxide yields.

The authors thank Laporte Chemicals Ltd. for the provision of a Research Studentship for one of them (A. R. B.) and for financial assistance in the purchase of apparatus.

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[17] Cheaney, Davies, Davis, Hoare, Protheroe, and Walsh, Seventh Symp. Combustion, Butterworths, London, 1959, p. 183.
[18] Cheaney and Walsh, *Fuel*, 1956, **35**, 258.
[19] Broida, *J. Chem. Phys.*, 1951, **19**, 790.
[20] Lewis and von Elbe, " Combustion Flames and Explosion of Gases," Academic Press, New York, 1951.
[21] Badin, *J. Amer. Chem. Soc.*, 1948, **70**, 3651.
[22] Voevodsky, *Zhur. fiz. Khim.*, 1946, **20**, 1285.
[23] Satterfield and Wilson, *Ind. Eng. Chem.*, 1954, **46**, 1001.
[24] Satterfield and Reid, Fifth Symp. Combustion, Reinhold Publ. Corp., New York, 1955, p. 511.