Effects of Surfaces on Products Formed in the Oxidation of Propane

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THE COURSE of oxidation reactions can be profoundly affected by the nature of surfaces present and their extent. The present paper summarizes a series of studies made under comparable conditions with one specific reaction—the oxidation of propane—on a variety of surfaces. The focus of attention was the effect of the kind of surface and the surface-volume ratio on the nature and distribution of products.

Studies of the partial oxidation of propane (*17, 20*) have usually been carried out in borosilicate, silica, or other glass reactors. In the temperature range between 300° and 500° C., with a propane-rich system, the products consist of a gas mixture containing primarily CO_2, CO, C_3H_6, C_2H_4, H_2, and a liquid mixture primarily of CH_2O, CH_3CHO, CH_3OH, H_2O_2, and H_2O. Traces of C_2H_2 and C_2H_6 may also appear. If the reactor is coated with potassium chloride or sodium chloride, it has been reported (*8, 10, 12-14*) that the reaction rates are lower but that the product distribution is not greatly changed, except that peroxides are essentially eliminated.

EXPERIMENTAL

Oxidations were carried out in one of several continuous flow reactors at atmospheric pressure and temperatures between 375° and 475° C. with inlet propane-oxygen mole ratios of 5.5 to 6.5. Analytical methods have been described (*20, 21*). All the reactors but one were 1 inch in inside diameter and about 3 feet long.

Borosilicate glass tube, coated inside with a thin film of KCl (*16*)
Borosilicate glass tube, coated inside with a thin film of B_2O_3 (*16*)
300 series stainless steel tube (*15*)
Alundum tube (*16*)
Spherical borosilicate glass reactor of the same volume as the above reactors but with a tangential feed inlet and a center tube take-off line (*23*)

In all experiments the propane and oxygen were first metered and then preheated separately. They were mixed just before entering the reactor. The products were passed through an ice-water condenser and a cold trap, and the residual gases were then metered in a wet-test meter. The product gases were not analyzed for CH_4, H_2, and C_2H_6 in every run, but when complete analyses were made, material balances on C, H_2, and O_2 closed within 10%.

The KCl-coated borosilicate glass, stainless steel, and Alundum reactors were expected to be active wall surfaces for the decomposition of peroxides. The B_2O_3-coated tube was originally expected to be relatively inert to H_2O_2 decomposition on the basis of a patent by Cook (*4*). However, a later study (*18*) showed that although the activities of such surfaces vary with method of preparation, they are not less than that of clean borosilicate glass. The spherical reactor was expected to show the least surface effects, particularly since the feed gases were introduced tangentially at the outside wall in order to minimize mass transport of active species from the main body of reacting gas to the wall surface.

RESULTS AND DISCUSSION

Since the phenomena here are so complex, one of the most illuminating methods of comparing surfaces is by matching pairs of runs carried out at the same temperature, inlet feed ratio, and per cent oxygen reacted. Table I shows the product distribution for one typical run in each type of reactor, matched against our standard, a run carried out in a clean borosilicate glass reactor (*17*) under comparable conditions. The comparison is made on the basis of equal per cent conversions of oxygen rather than equal residence times, since the length of the induction period in hydrocarbon oxidations is profoundly affected by slight variations of the surface. (This variation in induction period caused the wide variations in residence time shown in Table I.)

Studies of the oxidation kinetics of other hydrocarbons and other organic compounds in the presence of various surfaces have led to suggestions that their effect on the reaction may be closely correlated to their activity in decomposing H_2O_2 (*3, 11*). Here, propylene, one of the main products, is probably formed from oxygen by attack on the propyl radical (*17*):

$$C_3H_7 + O_2 \rightarrow C_3H_6 + HO_2 \quad (1)$$

In a fuel-rich system H_2O_2 is then presumably formed primarily by reaction of the HO_2 radical with propane.

$$HO_2 + C_3H_8 \rightarrow H_2O_2 + \dot{C}_3H_7 \quad (2)$$

Propylene is resistant to further oxidation (*17*) and essentially all that is formed here should persist and be found in the product. Homogeneous decomposition of H_2O_2 under these conditions is negligible (*9, 19*). Wall reactions, however, may reduce the amount of H_2O_2 isolated in the product. Hydrogen peroxide may also be formed to a slight degree by oxidation of methanol (*2*) or acetaldehyde (*22*). The latter, however, is believed to be relatively unimportant at these temperatures and in any event the amount of H_2O_2 isolated should be related to the character of the wall.

A parameter, Φ, defined as moles of H_2O_2 isolated per mole of C_3H_6 isolated, is introduced here as a measure of the extent of participation of the wall in the reaction. Figure 1 shows that at 375° C. Φ does not vary substantially with residence time in a clean 1-inch-diameter borosilicate glass reactor (6 seconds' residence time corresponds to about 95% completion of reaction). This is consistent with the known rates of decomposition of H_2O_2 vapor on clean borosilicate glass (*18, 19*). For example, one would estimate that for the surface-volume ratio and H_2O_2 partial pressures existing here, approximately 2 to 10% of the H_2O_2 present would decompose on the wall per second at 375° C. Figure 2 shows that at 475° C., however, Φ drops rapidly with contact time, because of the wall decomposition. At each temperature level, Φ is lower in an aged borosilicate glass reactor than in a clean one. Figure 2 also shows that Φ does not vary significantly with the feed ratio of C_3H_8 to O_2 in highly fuel-rich systems. Table I shows that all the 1-inch tubular reactors have Φ values lower than that of clean borosilicate glass under comparable conditions, thus indicating their surfaces were more reactive. The spherical

Table I. Effect of Surfaces on Nature of Products Formed in Oxidation of Propane

	Borosilicate Glass						Clean Borosilicate Glass	Stainless Steel	Clean Borosilicate Glass	
	Clean	KCL coated	Clean	B_2O_3 coated	Clean tubular	Clean spherical				Al_2O_3
Av. reactor temp., ° C.	375	375	375	375	375	375	425	425	475	475
C_3H_8–O_2 feed ratio	5.5	5.5	5.5	5.5	5.5	6.5	5.5	5.5	5.5	5.5
Res. time, sec.	2	3	3	3	5.5	7.5	12	5.3	2.3	...
% O_2 reacted	13	13	50	50	90	85	95	95	60	61
	Product Distribution, Moles[a]/Mole of O_2 Reacted									
CO_2	0.05	0.05	0.01	0.08	0.04	0.06	0.03	0.41	0	0.13
CO	0.05	0.15	0.20	0.25	0.31	0.47	0.22	0.33	0.12	...
C_3H_6	0.70	0.50	0.48	0.42	0.30	0.41	0.78	0.63	0.85	0.54
C_2H_4	0.05	0.05	0.06	0.09	0.07	0.06	0.30	0.64	0.20	0.34
CH_2O	0.25	0.30	0.25	0.27	0.24	0.12	0.06	0.01	0.06	0.03
CH_3CHO	0.09	0.01	0.14	0.09	0.05	0.17	0.11	0.01	0.07	0.01
CH_3OH	0.30	0.35	0.26	0.35	0.33	0.33	0.07	0.01	0.09	0.02
H_2O_2	0.25	0.06	0.19	0.10	0.11	0.27	0.23	0	0.22	0.08
H_2O	0.85	0.85	0.80	0.86	0.77	0.25	1.00	0.87	1.21	1.24
Φ (H_2O_2/C_3H_6)	0.36	0.12	0.40	0.24	0.37	0.66	0.30	0	0.26	0.15

[a] Analyses for CH_4, C_2H_6, and H_2 not available.

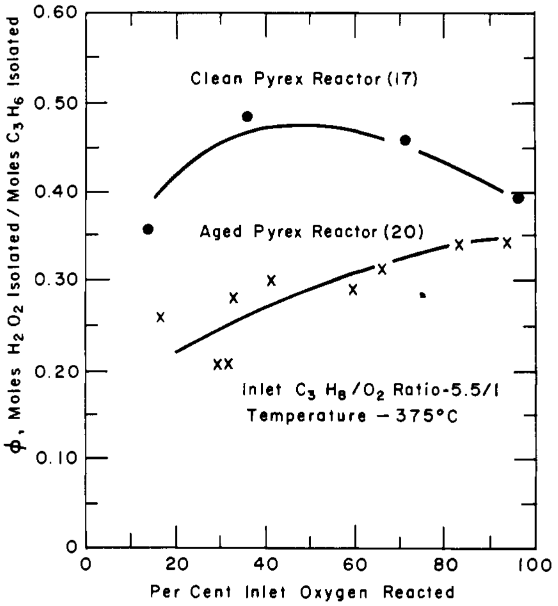

Figure 1. Effect of extent of reaction on Φ at 375° C.

borosilicate glass reactor, however, showed a Φ value of about 0.66, indicating less significant wall effects than in the tubular uncoated vessel (Φ = 0.35 to 0.40).

If only Reactions 1 and 2 were of significance in determining the amounts of C_3H_6 and H_2O_2 formed, one would expect Φ to equal approximately unity in the absence of wall decomposition of H_2O_2. The fact that Φ never exceeds about 0.45 in the clean 1-inch-diameter borosilicate glass tube at 375° C. is, therefore, surprising, as this discrepancy cannot be attributed to H_2O_2 decomposition. The most plausible explanation is that a portion of the HO_2 radicals formed by Reaction 1 react or decompose on the wall to yield some product(s) other than H_2O_2 (Reaction 4). The fact that Φ increases as the surface-volume ratio is decreased also supports this conclusion. No alternative explanation seems very likely. There is good evidence that the C_3H_6 is formed predominantly by Reaction 1 in this kind of system (*7, 17, 20*).

There have been much discussion and difference of opinion in the literature concerning which of the two competitive reactions (3 and 4) occurs under various circumstances in different oxidations, particularly the hydrogen-oxygen reaction. Only indirect evidence is available.

$$2HO_2 \xrightarrow{\text{wall}} H_2O_2 + O_2 \tag{3}$$

$$HO_2 \xrightarrow{\text{wall}} \text{destruction} \tag{4}$$

Reaction 3 implies release to the vapor space of H_2O_2 after formation on the wall. Reaction 4 implies that if H_2O_2 is formed, it is destroyed before leaving the wall. Reaction 3 has been postulated to explain certain characteristics of the hydrogen-oxygen reaction (*6, 24*). On the other hand, in a recent study of this reaction in boric acid-coated vessels Baldwin and Mayer (*1*) concluded that HO_2 radicals formed H_2O_2 in the gas phase rather than by surface recombination —i.e., that Reaction 3 did not occur. Conditions under which 3 or 4 might occur have also been hypothesized by Walsh and others (*3*). Our opinion is that it is difficult to visualize the occurrence of Reaction 3, at least at temperatures substantially above ambient, in view of the fact that even clean borosilicate glass shows a substantial activity in decomposing H_2O_2.

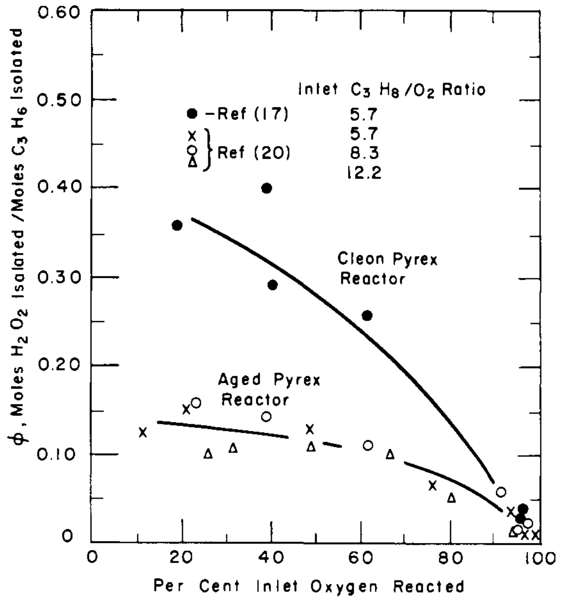

Figure 2. Effect of extent of reaction on Φ at 475° C.

The previous discussion suggests that a semiempirical way of characterizing the extent of participation of a surface in the reaction would be by the ratio of Φ for the surface under study to Φ for clean borosilicate glass, under comparable conditions.

Figure 3 shows this Φ ratio plotted against the ratio of a product quantity for the surface under study to the same product quantity obtained in the clean 1-inch borosilicate glass reactor—for the same experimental conditions and the same extent of reaction as measured by per cent of inlet oxygen consumed. This assumes that activity in decomposing H_2O_2 (and HO_2) parallels the extent to which the surface participates in other wall reactions. Our knowledge of the effects of surfaces on the products formed is almost completely empirical, so this assumption is unquestionably imprecise, but it does provide a method of correlating and analyzing information on effects of surfaces. If the experimental data for a particular product approximate a horizontal line in this type of correlation, the formation or subsequent reactions of the product are hypothesized to be largely homogeneous in nature. Propylene and CH_3OH are examples of such products. If, however, the ordinate decreases in the Φ ratio, it indicates that the product is formed by a heterogeneous reaction on an active surface. Ethylene appears to be an example of such a product; it may then be surmised that the formation of C_2H_4 from C_3H_7 proceeds here as follows:

$$C_3H_7 \xrightarrow{\text{wall}} C_2H_4 + CH_3 \qquad (5)$$

Since much of the CH_3 appears finally in the product as CH_4, if data were available on CH_4 yields, the same trend for CH_4 as for C_2H_4 might be expected. Yields of H_2O_2 and CH_3CHO, on the other hand, increase with the inertness of the surface. The data on CH_2O are not conclusive. Apparently in very active wall reactors it is readily decomposed; however, in inert wall reactors it is also reduced in yield. To a large degree CH_2O results from further reaction of the CH_3CHO molecule, and inert wall reactors appear to reduce such reactions. The stainless steel reactor used here was found later to have a considerable amount of oxide on its inside surface, probably as the result of condensation of partial oxidation products in preliminary runs. Therefore, the data in Table I and Figure 3 for a Φ ratio of zero represent a surface somewhat more active than a stainless steel which has been in contact with vapors only.

Several other qualitative observations fit into the above framework. It has been realized for some years that the results of oxidation studies change as the reactor "ages," at least until the reaction has been carried out in the vessel for some time. Kooijman (*10*) cleaned his reactor with hydrofluoric acid before each run in order to obtain consistent results. The reactor originally used by Wilson (*20*) after several hundred hours of operation had apparently aged to such a degree that when propane oxidation experiments were performed by Ebeling and Belknap (*5*) in the aged reactor, results were different from those noted in Wilson's first work—e.g., significantly higher formaldehyde-acetaldehyde ratios and a decreased H_2O_2 yield. Inspection of the internal surface of the aged reactor showed a brownish red film deposited on the initial section of the reactor as well as on the propane preheater. (This film may have been present over the entire reactor, but was visible to the eye only on the inlet section.) The film dissolved in nitric acid. Runs carried out in the reactor after cleaning showed an increase in the reaction rate and a decrease in the formaldehyde-acetaldehyde ratio. The film was combustible in oxygen and it is now believed that it was a substance of high molecular weight resulting from polymerization of propylene and possibly ethylene. The aging process may not be due, in all cases, to this polymer coating, but it evidently plays an important part. In present nomenclature, the aging process would seem to be a lowering of the Φ ratio. Harris and Egerton (*8*) also reported earlier a decrease in the formaldehyde-acetaldehyde ratio on going from a sodium chloride–coated reactor to a clean silica surface, on studying an equimolal propane-oxygen mixture at 320° C. This is consistent with the generalized curves of Figure 3.

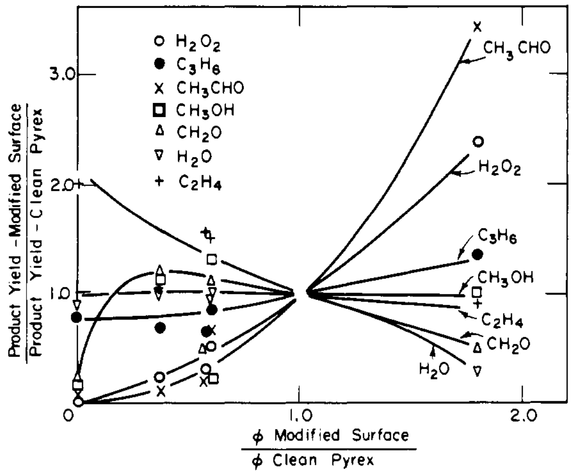

Figure 3. Effect of wall surface on product distribution

The role of the wall in partial oxidation studies is still only poorly understood; however, the data discussed above shed additional light on the mechanisms and the method of analysis may apply to other partial oxidation reactions.

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