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(11) This inequality applies whether the first, the second, or both routes are considered.
(12) It is assumed that *y* being much smaller than *x* can be neglected.

Reaction of Diacyl Peroxides with Alumina

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Abstract: Several diacyl peroxides, as well as perbenzoic acid and hydrogen peroxide, react rapidly with alumina surfaces to give a nonextractable oxidant of equivalent oxidizing power. This surface oxidant decomposes to O_2. The only organic product is the carboxylic acid corresponding to the peroxide used. The decay kinetics of the surface oxidant are interpreted in terms of Al_sOOH groups at nonequivalent sites.

When a solution of a diacyl peroxide is placed in contact with alumina, diacyl peroxide disappears from the solution and an equivalent amount of a titratable oxidant appears on the alumina. In most cases the process is complete within a few minutes at 26 °C. The amount of oxidizing power that can be transferred to the alumina depends on the activity of the alumina as an adsorbent. Chromatographic alumina, reacting with benzoyl peroxide, will acquire about 3×10^{-4} equiv of oxidizing power per gram of alumina. This corresponds roughly to N (Avogadro's number) times 100 Å^2 per equivalent. For comparison, the area of a benzoic acid molecule lying flat is about 60 Å^2.

Even though the amount of oxidant that can be formed on the alumina parallels its adsorptive capacity, the surface oxidant is not adsorbed benzoyl peroxide, contrary to what might be supposed from an earlier report on the removal of peroxidic impurities from solvents by means of alumina.[1] There are several compelling reasons for this conclusion. First, the benzoyl peroxide is not extractable from the alumina by means of ether, unlike compounds such as adsorbed phenyl benzoate. Secondly, the rate of decay of the surface oxidant titer at 26 °C is several orders of magnitude greater than the rate of decomposition of benzoyl peroxide in ordinary solvents. The rate is also nearly independent of the diacyl peroxide used to form the surface oxidant (Figures 1 and 2) and of the nature or continued presence or absence of the solvent with which the peroxide is put on the surface (Figure 3).

Lastly, the products of the reaction are O_2 and benzoic acid with none of the usual CO_2, biphenyl, or phenyl benzoate characteristic of the decomposition of benzoyl peroxide. The oxygen yield is somewhat less than the theoretical 0.5 mol per mole of peroxide because of losses during the removal of the solvent with which the benzoyl peroxide is applied to the surface. Benzoic acid, which can be extracted with considerable difficulty by treating with HCl and ether, was isolated in 86% of the theoretical 2 mol. This is also the amount of benzoic acid recoverable from adsorption on alumina in a control experiment.

Isobutyryl Peroxide. Isobutyryl peroxide reacts with alumina in the same way as benzoyl peroxide, giving a nonextractable surface oxidant with approximately the same oxidant decay kinetics (Figure 1), and isobutyric acid. It is worth noting, however, that isobutyryl peroxide is very much unlike benzoyl peroxide in its behavior in solution. In polar media the decomposition of isobutyryl peroxide is fast even at 40 °C,[2] while the products are mostly carboxyinversion[3] or other ionic products involving the decarboxylation of one of the isobutyroxy moieties. Since carboxyinversion reactions are acid catalyzed,[3-6] the decomposition of isobutyryl peroxide on the surface of acidic alumina should be quite fast. Nevertheless, the decomposition reaction is unable to compete with the reaction that produces surface oxidant unless excess peroxide is used. Thus with 5.7×10^{-4} mol of this peroxide per gram of Merck acidic alumina, not all of the peroxide is removed from the solution. If this same amount of peroxide is forced onto the surface by distilling off the solvent, the ionic products isopropyl isobutyrate and isopropyl alcohol are isolated in 20 and 41% yields, respectively. About half of the peroxide has reacted with the surface in the usual way to give surface oxidant and isobutyric acid. The isobutyric acid blocks the alumina surface and is not mobile enough to permit access of the remaining peroxide before the latter undergoes the ionic decomposition reaction.

The Effect of Benzoic Acid. Benzoyl peroxide is much less subject to Bronsted acid-catalyzed[4] ionic decomposition than is isobutyryl peroxide, although the reaction is catalyzed by $AlCl_3$.[6] We find that if acidic alumina is first covered with benzoic acid, loss of peroxide from the solution is prevented almost entirely. If less benzoic acid is used, so that the total of the benzoic acid and the benzoyl peroxide does not exceed the adsorptive capacity of the alumina, all of the peroxide reacts in the usual way. It is significant that the decay kinetics of the surface oxidant (Figure 4) are indistinguishable from those of an ordinary run at about the same initial concentration of peroxide.

The Use of Different Aluminas. The behavior of benzoyl peroxide on Merck acidic alumina has been illustrated in Figures 1–3. This alumina is of adsorption activity grade II[7] and has 3.0×10^{-4} equiv of acid per gram as titrated with NaOH to a phenolphthalein end point. A different lot from the same source gave the same surface oxidant decay behavior.

Baker acidic alumina, activity grade I and 0.73×10^{-4} equiv of titratable acid per gram, behaves as shown in Figure 4. The major difference from the Merck alumina is that the surface oxidant decay rate is more uniform, i.e., somewhat slower at the beginning of the run but decreasing much less rapidly.

Allied neutral alumina, of low adsorptive capacity (less than grade II), adsorbs only a little benzoyl peroxide, but the small amount of surface oxidant formed still decays rapidly as in the case of the acidic aluminas. If 1.2×10^{-4} mol per gram of

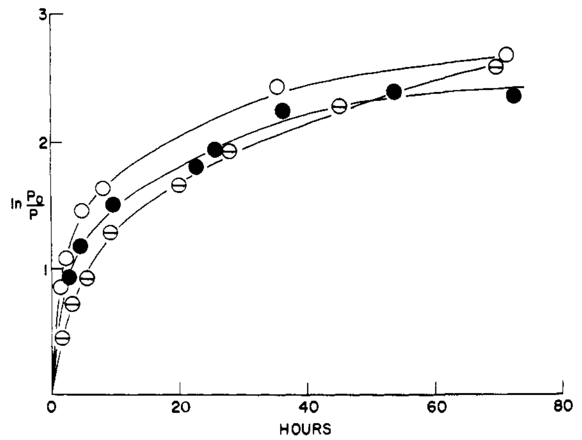


Figure 1. Decomposition of the surface oxidant on Merck acidic alumina at 26 °C: ● prepared from benzoyl peroxide, $P_0 = 1.6 \times 10^{-4}$ mol of peroxide per gram of alumina; ○ prepared from perbenzoic acid, $P_0 = 2.46 \times 10^{-4}$ mol/g; ⊖ prepared from isobutyryl peroxide, $P_0 = 2.47 \times 10^{-4}$ mol/g.

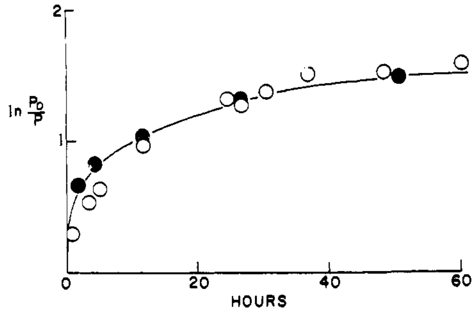


Figure 2. Decomposition of the surface oxidant on Merck acidic alumina at 26 °C: ○ prepared from δ-phenylvaleryl peroxide, $P_0 = 0.92 \times 10^{-4}$ mol/g; ● prepared from benzoyl peroxide, $P_0 = 0.70 \times 10^{-4}$ mol/g.

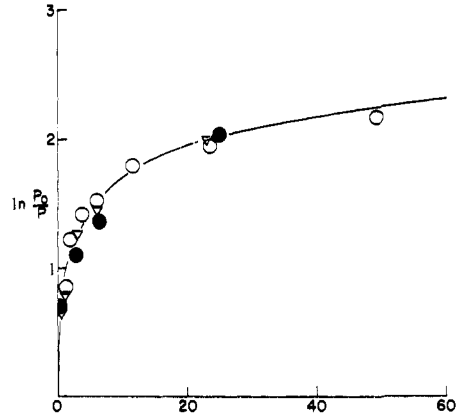


Figure 3. Decomposition of the surface oxidant on Merck acidic alumina at 26 °C: ○ prepared from benzoyl peroxide, $P_0 = 1.33 \times 10^{-4}$ mol/g, put on the surface with $CHCl_3$-hexane, which was then removed by filtration followed by pumping in vacuo; ▽ prepared from benzoyl peroxide, $P_0 = 1.32 \times 10^{-4}$ mol/g, put on the surface with CCl_4, which was allowed to remain in contact during the run; ● prepared from benzoyl peroxide, $P_0 = 1.28 \times 10^{-4}$ mol/g, put on with benzene, which was also left in contact.

peroxide is forced onto this alumina by distilling off the solvent, about one-third of the titer is lost in a few hours at 26 °C. The remainder, which is stable indefinitely, is unchanged benzoyl peroxide which can easily be recovered by extraction.

Alcoa F-20 chromatographic alumina, activity grade between I and II, easily adsorbed 1.2×10^{-4} mol of benzoyl peroxide per gram. The decay kinetics of the resulting surface oxidant were indistinguishable from those of a similar run on Merck acidic alumina even though the pH of the Alcoa alumina is 9.

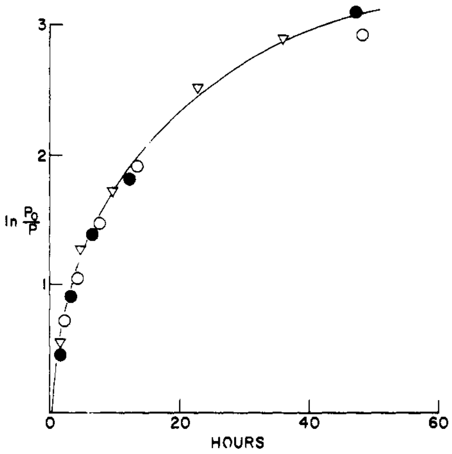


Figure 4. Decomposition of the surface oxidant on Baker acidic alumina at 26 °C: ○ prepared from benzoyl peroxide, $P_0 = 0.63 \times 10^{-4}$ mol/g; ● prepared from benzoyl peroxide, $P_0 = 0.75 \times 10^{-4}$ mol/g; ▽ prepared from benzoyl peroxide, $P_0 = 0.65 \times 10^{-4}$ mol/g, but on alumina that had first been covered with 0.84×10^{-4} mol of benzoic acid per gram.

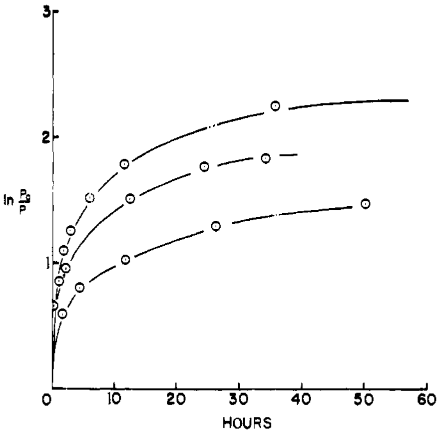
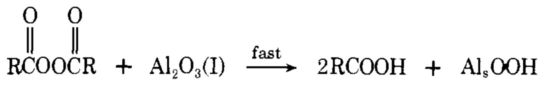


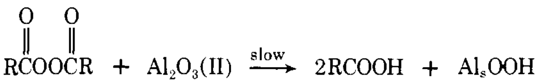
Figure 5. Decomposition of the surface oxidant on Merck acidic alumina at 26 °C. Effect of decreasing P_0. From the top to bottom, 1.6×10^{-4}, 1.2×10^{-4}, and 0.70×10^{-4} mol/g.

Concentration Dependence of the Decay. The decrease in the titratable oxidant on the surface of Merck acidic alumina (Figure 5) falls off rapidly in rate both within a run and as a function of the initial titer. For a heterogeneous reaction, a high apparent kinetic order within a run does not necessarily mean that the individual surface groups react other than unimolecularly, since nonequivalent surface sites usually cause the rates to vary in any case, just as do different surfaces.[8] On γ-alumina there are at least three different kinds of surface hydroxyl groups[8,9] and several different kinds of Lewis acid sites.[8,10,11]

The apparent high order with respect to *initial* concentration can also be explained in terms of surface sites with different properties. To simplify the discussion we will divide the sites into two categories, I and II, and anticipate our conclusion that the titratable oxidant groups are surface hydroperoxides, Al_s-OOH. The category I sites, if this explanation is the correct one, must adsorb or react with the diacyl peroxide more rapidly than do the type II sites (eq 1 and 2). The model also requires that the oxidant at the type I sites ($Al_sOOH(I)$) decompose *more slowly* than the oxidant at the type II sites ($Al_sOOH(II)$) (eq 3 and 4). At high initial peroxide loadings, requiring the



$$\mathrm{R\overset{\overset{O}{\|}}{C}O\overset{\overset{O}{\|}}{C}R + Al_2O_3(I) \xrightarrow{fast} 2RCOOH + Al_sOOH(I)} \quad (1)$$



$$\mathrm{R\overset{\overset{O}{\|}}{C}O\overset{\overset{O}{\|}}{C}R + Al_2O_3(II) \xrightarrow{slow} 2RCOOH + Al_sOOH(II)} \quad (2)$$

$$\mathrm{Al_sOOH(I) \xrightarrow{slow} Al_sOH + \tfrac{1}{2}O_2} \quad (3)$$

$$\mathrm{Al_sOOH(II) \xrightarrow{fast} Al_sOH + \tfrac{1}{2}O_2} \quad (4)$$

utilization of almost all of the surface sites of both types, Al_s-OOH(I) and Al_sOOH(II) are formed in proportion to the relative numbers of the corresponding type I and type II sites on the particular kind of alumina used. At lower initial peroxide loadings, the higher reactivity of the type I sites toward the limited amount of peroxide causes a preponderance of Al_sOOH(I) in the surface oxidant. The less abundant but more reactive Al_sOOH(II) will be exhausted earlier in the run, thus accounting for the earlier decrease in rate in the runs at low initial peroxide concentrations. As the initial peroxide concentration approaches the value needed to saturate the surface, the ratio of Al_sOOH(II) to Al_sOOH(I) approaches the ratio of type II to type I sites, and the kinetic behavior becomes nearly independent of the initial peroxide concentration. For benzoyl peroxide on Merck acidic alumina this condition obtains in the 1.3×10^{-4} to 1.6×10^{-4} range.

Besides the characteristics already mentioned, only a few additional ones are suggested for the hypothetical type I and type II sites by our experiments. From the fact that Allied neutral alumina, and also Alcoa chromatographic alumina (F-20, pH 9), still gave a rapidly decomposing surface oxidant, we can deduce that the type II sites do not require the presence of titratable acid. We also note that the effect of heating Merck acidic alumina to 525–550 °C for 1.5 h, and then loading the benzoyl peroxide under argon, was to give a surface oxide whose decay kinetics resembled those of a much more dilute run. The actual P_0 was 1.62×10^{-4} mol/g, but the decay curve looked like that for a run with a P_0 of only 1.0×10^{-4} mol/g. This suggests that type I sites are more dehydrated than type II sites. The fact that pretreating Baker acidic alumina with benzoic acid (Figure 4) failed to change the shape of the decay curve, suggests that benzoic acid does not discriminate between the two types of site. It should be noted, however, that there seems to be less difference between the type I and type II sites in Baker alumina than in Merck alumina, at least in respect to the oxidant decay rate.

The choice of Al_sOOH groups as structures for the surface oxidant is prompted by the fact that the decay reaction releases molecular oxygen. The decomposition of tertiary alkyl hydroperoxides is a chain reaction involving intermediate trioxides and tetroxides,[12] with hydroxyl radicals as one of the chain-carrying species. Unless peroxide molecules always react with the surface at adjacent sites, which seems unlikely, the formation of O_2 requires the participation of at least one intermediate that is able to diffuse on the surface. We suggest that this intermediate may be hydroxyl radical, formed either by homolysis of the Al_s-OOH groups or by reactions at Fe impurities.[13]

$$\mathrm{Al_sOOH + HO\cdot \rightarrow H_2O + Al_sOO\cdot} \quad (5)$$

$$\mathrm{Al_sOO\cdot + HO\cdot \rightarrow Al_s\text{-}OOOH \rightarrow Al_sOH + O_2} \quad (6)$$

Hydrogen peroxide, $P_0 = 1.9 \times 10^{-4}$ mol/g, placed on Merck acidic alumina from ether solution also gives a titratable surface oxidant. The decay curve resembled that for a low concentration of a diacyl peroxide. However, since this reaction gives no carboxylic acid to block sites, the comparable loading with a diacyl peroxide should be only one-third of 1.9×10^{-4} mol/g. The result with hydrogen peroxide then requires only that this peroxide also react more rapidly with the type I sites than with the type II sites.

Experimental Section

The Reaction with the Alumina. Three methods were used to bring about the reaction of the peroxide with the alumina.

(a) **The Filter Method.** A solution of the peroxide in $CHCl_3$ is added to a stirred suspension of the alumina in $CHCl_3$-hexane. After removing the liquid by suction filtration the alumina is dried by tumbling in vacuo in a rotating flask with indented sides. The filtrate is examined for any excess peroxide or reaction products, but for moderate initial peroxide concentration these substances are usually absent. When $CHCl_3$-hexane was used as the solvent the ratio of total $CHCl_3$ to hexane, by volume, ranged from 0.17 to 0.66. Other solvents used were benzene, CCl_4, and ether. The ratio of solvent to alumina ranged from 4 to 5 ml/g.

(b) **The Slurry Method.** This procedure is the same as (a) except that the solvent is not removed and entire ampules of solid plus liquid phase are titrated. Method a is used to establish that all of the oxidant is in fact on the solid.

(c) **The Evaporative Method.** This method is used when more than one monolayer is desired. The slurry is rotated, without filtering, in an evacuated round-bottom flask with indented sides to promote a tumbling motion. This is continued until the alumina is dry and free-flowing. In some cases it is advantageous to add a few glass beads.

Titrations. Glacial acetic acid (10 ml), 1 ml of fresh, saturated aqueous KI solution, and a dry ice (CO_2) pellet are added to a flask containing the sample. After stirring under CO_2 for 10 min to promote good contact between the solid and the solution, 50 ml of carbonated water is added and the liberated iodine titrated with 0.05 N sodium thiosulfate to a starch iodine end point.

Alumina. The Merck acidic alumina used in most of the experiments came from a single lot (no. 61 789), but a sample from a different lot from the same manufacturer gave the same results. Titration with sodium hydroxide to a phenolphthalein end point indicated 3.04×10^{-4} equiv of acid per gram. The activity as determined by dye adsorption[7] was grade II.

Baker acidic alumina (lot no. 526 053) had 0.734×10^{-4} equiv of acid per gram and was of activity grade I.

Allied neutral alumina (code no. 1236, lot D257) was already basic to phenolphthalein. The activity was less than grade II.

Alcoa F-20 chromatographic alumina is reported to have a pH of 9.0, a surface area of 210 m^2/g, and to contain 0.08% Fe_2O_3 and 0.09% SiO_2. Its activity is between I and II.[7]

Extraction of Acid. The alumina sample (40–50 g) is placed in a 500-ml round-bottom flask fitted with a liquid-liquid extraction device and covered with 150 ml of H_2O, 40 ml of concentrated HCl, and enough ether to fill the extraction apparatus. Extraction is continued for 20–36 h, and the benzoic acid recovered by evaporation of the ether. An additional 3% can be recovered by making the aqueous layer basic with KOH, stirring for 24 h, reacidifying, and extracting with three 200-ml portions of ether in a separatory funnel. The extent of recovery is 84–88% both for a sample made by reaction of benzoyl peroxide with alumina and for a sample made with benzoic acid. The alumina used in these experiments was Merck acidic alumina.

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Oxyfunctionalization of Hydrocarbons. 4.[1] FSO_3H–SbF_5, FSO_3H, H_2SO_4, and HF Induced Electrophilic Oxygenation of Alkanes with Hydrogen Peroxide

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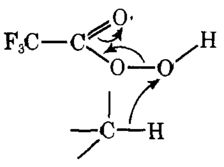
Abstract: The oxygenation of alkanes with hydrogen peroxide in the presence of FSO_3H-SbF_5, FSO_3H, H_2SO_4, and HF was studied under typical electrophilic conditions. From the results obtained, it is concluded that the reactions proceed in strong acids via initial electrophilic hydroxylation of the appropriate σ bonds of the alkanes by the incipient hydroxyl cation, formed through protolytic cleavage of H_2O_2 through the hydroperoxonium ion $H_3O_2^+$.

In the preceding paper,[1] we reported the study of electrophilic oxygenation of alkanes with ozone in superacidic media. The reactions proceed via electrophilic oxygen insertion into the single σ bonds of the alkanes, effected by protonated ozone, i.e., O_3H^+, similar to such electrophilic reactions as hydrogen–deuterium exchange, protolysis,[2] chlorination (chlorolysis),[3] and nitration (nitrolysis)[4] of alkanes.

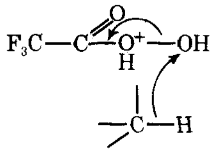
In a continuation of our studies on oxyfunctionalization of hydrocarbons, we extended our investigations to electrophilic hydroxylation of alkanes using hydrogen peroxide in strongly acidic media.

The acid-catalyzed reaction of hydrogen peroxide with alkanes was studied by Alder and Whiting.[5] They found 85% hydrogen peroxide with hydrogen fluoride-boron trifluoride to be an exceptionally powerful but unselective oxidant. For example, it reacted with cyclohexane at room temperature to cause extensive or even total oxidative decomposition of the substrate.

Frommer and Ullrich[6a] reported the hydroxylation of 2-methylbutane, methylcyclohexane, and *n*-pentane with 85% hydrogen peroxide in the presence of trifluoroacetic acid at 20 °C, giving 2-methyl-2-butanol, 1-methylcyclohexanol, and 2- and 3-pentanol, respectively, as major products. They suggested a nonionic transition state to be involved in the course of the reactions, such as



However, an ionic reaction path is also compatible with the results.



Hamilton has also observed that the CF_3CO_3H oxidation of cyclohexane and 1,2-dimethylcyclohexane to the corresponding alcohols occurs with retention of configuration.[6b]

We now wish to report the results of the reactions of alkanes with hydrogen peroxide (98%) in excess strong acid at various temperatures.

Results and Discussion

Reactions of Branched Chain Alkanes. The reactions of branched chain alkanes with hydrogen peroxide in magic acid (the equimolar mixture of FSO_3H and SbF_5)-SO_2ClF solution were studied (by ^1H NMR spectroscopy) with various ratios of alkane and hydrogen peroxide, and at different temperatures. The results are summarized in Table I.

As neither hydrogen peroxide nor magic acid-SO_2ClF alone, under the reaction conditions employed, led to any reaction products, it is considered that the reactions proceed via electrophilic hydroxylation of the C–H bond of alkanes with protonated hydrogen peroxide (**2**), yielding the hydroxycarbenium ion (**3**), which cleaves to give either alcohol (**4**) or carbenium ion (**5**). Since 1 mol of isobutane required 2 mol of hydrogen peroxide to complete the reaction to oxonium ion **3**, **4** or **5** seem to react with excess hydrogen peroxide, giving *tert*-butyl hydroperoxide (**6**). The strong acid induced rearrangement and cleavage of **6** results in very rapid formation of the dimethylmethoxy carbenium ion (**7**). A similar rearrangement of tertiary alkyl hydroperoxides in strong sulfuric acid was previously shown to occur by Deno and co-workers.[7] The path of the reaction is depicted in Scheme I.

Under the reaction conditions employed the intermediacy of *tert*-butyl alcohol (**4**), *tert*-butyl cation (**5**), and/or hydroperoxide (**6**) could not be directly observed because of high reactivity of all these species with acidic hydrogen peroxide. Indeed, when a solution of *tert*-butyl alcohol was treated with hydrogen peroxide in magic acid-SO_2ClF at −78 °C, immediate quantitative formation of **7** was observed.

When the reaction was carried out at room temperature by means of passing isobutane into magic acid (excess)-hydrogen peroxide solution, the formation of methyl alcohol (**9**), methyl acetate (**11**), and some dimethylmethoxy carbenium ion (**7**), together with dimeric acetone peroxide (1,1,4,4-tetramethyl-2,3,4,5-tetraoxacyclohexane, **10**) was observed. Formation of **10** was confirmed by a comparison of spectra in