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The Metal/Metal-Oxide–Catalyzed Decomposition of *t*-Butyl Hydroperoxide Vapor

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The catalytic decomposition on metal/metal oxides of *t*-butyl hydroperoxide vapor in concentrations up to 1 mm has been examined in a flow system from 110–175°. Metal oxides were supported on a fine-mesh gauze of the metal held normal to the gas stream. The kinetics of the decomposition to *t*-butyl alcohol and oxygen on silver, cobalt, and cuprous oxides was first order with respect to *t*-butyl hydroperoxide, with experimental activation energies, 4.6, 8.7, and 13.0 kcal/mole and frequency factors 2.2×10^4, 8.6×10^5, and 4.9×10^8 sec^{-1}, respectively.

The results are discussed in terms of a decomposition scheme favored by electron transfer from the supported oxide to chemisorbed hydroperoxide, and compared with those obtained in the heterogeneous decomposition of hydrogen peroxide vapor.

INTRODUCTION

A comprehensive flow-system study of heterogeneous decomposition of hydrogen peroxide vapor by a wide range of oxides (*1*) and mixed oxides (*2*) has indicated that the catalyst activity is most probably related to its properties as a defect solid. It seemed relevant to extend these studies to include other gases containing the hydroperoxide group as a step towards a more general scheme.

At the same time the present study could be of value as a link with investigations on low temperature ignition of hydrocarbons in which the inhibitive effect of certain additives, such as lead tetraethyl, is partly due to the destruction of peroxide intermediates probably at a surface (*3*).

In the present experiments decomposition studies have been made on surfaces of copper, nickel, silver, cobalt, and aluminum. These are considered to be covered with coherent oxide films, as shown by Allen (*4*), Rhodin (*5*), and others, and this oxide surface is presented to the gas stream.

EXPERIMENTAL

Materials

t-Butyl hydroperoxide was prepared as outlined by Milas and Surgenor (*6*). The crude yield of 63–65% hydroperoxide was concentrated by repeated vacuum fractionation in a 4-ft column packed with glass beads. The final product was found by refractive index and chemical analysis to be 98–99% pure. Further supplies of crude peroxide were kindly supplied by Messrs. Laporte, Luton.

Silver and copper gauzes, 30-mesh, were cut into discs of 2.2 cm diameter to fit the reaction tube. Before use, copper gauzes were degreased in benzene and left to stand overnight in a desiccator. Silver gauzes were treated with dilute nitric acid, to remove the sulfide skin, and washed in turn with ethanol and water and finally stored overnight in a desiccator. Nickel gauzes were prepared in the same manner.

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The cobalt catalyst was prepared by thoroughly cleaning 30-mesh Monel gauze (70% Ni; 29% Cu; 1% Mn) with a mixture of equal parts sulfuric and hydrochloric acids. It was washed with water, dried, and then electroplated with cobalt to a thickness of 16 μ. Aluminum was used in the form of a fine, pliable mass of foil which was closely packed into the whole of the interior space of the reaction tube.

Apparatus and Method

The flow system was a slightly simplified version of that used in the hydrogen peroxide work (*1*). High purity nitrogen ($>$99.9%) was streamed from a cylinder into a 5 liter stock bottle. This acted as a gas reservoir at a constant pressure-head and served to minimize pressure fluctuations in changing the absorbers. The nitrogen was then passed through a drying tower, needle valves, differential pressure flow meter, splash trap, saturator, reaction tube, and finally to atmosphere via the gas absorbers. An alternative metered stream was provided up to the reaction tube and bypassing the saturator.

Vapor from the saturator was passed into the horizontal reaction tube held in an aluminum tubular furnace. The reaction tube was 45 cm long and gauzes were placed at a constant 40 cm distance from the entrance. The temperature was recorded by a thermistor connected to a Wheatstone bridge circuit. The effluent gases from the reaction tube were bubbled into two absorbers, in series, each containing 15 ml of 33% acetic acid. In blank test runs of 10 min duration, it was shown that approximately 97% of the delivered peroxide vapor was retained by the first absorber with the balance in the second unit. The solution from the absorbers was diluted to 150 ml and 2 g of sodium bicarbonate and 1.5 g potassium iodide added. This was allowed to stand in the dark overnight and finally titrated with 0.01 *M* sodium thiosulfate. This method as first proposed by Skellon and Wills (*7*) was found to be most satisfactory.

Three or four blank-test runs were carried out at each temperature before inserting the catalyst.

RESULTS

Figures 1a and 1b illustrate the course of decomposition changes on first exposure of catalysts to a partial pressure of 0.99 mm Hg *t*-butyl hydroperoxide vapor at a flow rate of 300 ml/min. Copper, silver, and cobalt gauze surfaces exhibited a similar rise in activity for the first 20–30 min exposure and then settled to a steady value which depended on temperature. Nickel gauzes gave only brief decompositions and poisoned rapidly at all temperatures after about 40 min exposure to the peroxide stream, and eventually gave no catalysis. When the reaction tube was packed with aluminum foil (giving superficial areas some 20 times that of a single gauze) no decomposition was detected until 170° when values of 8–9% were recorded.

The reproducibility of these results was good for repeat runs with the same gauze but variations were found in steady decomposition values when different gauzes of the same material were examined. The extent of these variations is shown for copper/copper oxide catalysts at 141° and 122° in Fig. 1b. They arise, most probably, from differences in the absorption area and oxide film thicknesses of different gauzes and were minimized as far as possible by standardization of the preparation procedure.

In separate experiments, the reaction product from decompositions over copper/copper oxide was examined by refractive index. The n_D^{20} values obtained were identical to those of synthetic mixtures of *t*-butyl alcohol and *t*-butyl hydroperoxide. Thus, for example, 80% decomposed fractions gave $n_D^{20} = 1.3904$. In addition, the products from catalysis on copper/copper oxide and nickel/nickel oxide gave negative chemical tests for carbonyl groups, while infrared analysis (liquid film method) gave spectra wholly attributable to *t*-butyl alcohol and *t*-butyl hydroperoxide. In particular, no carbonyl stretching vibrations were detected.

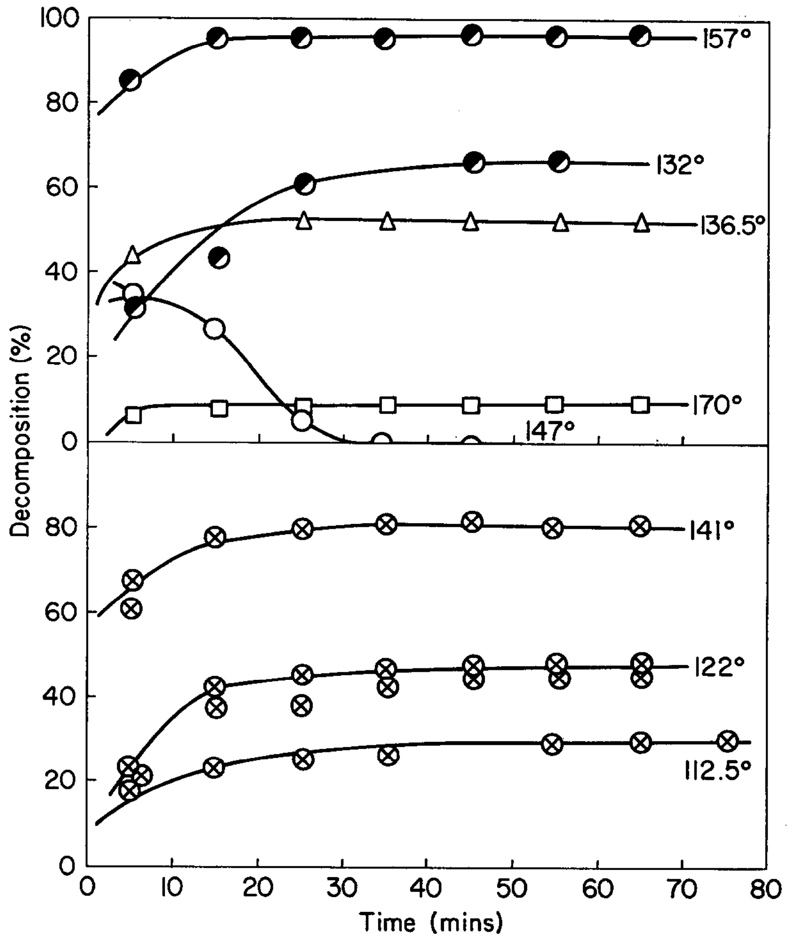

FIG. 1. Initial decomposition patterns. a. (upper) ◐, Silver/silver oxide (gauze); △, cobalt/cobalt oxide (gauze); ⊙, nickel/nickel oxide (gauze); ⊡, aluminum/aluminum oxide (foil). b. (lower) ⊗ Copper/copper oxide (gauze).

The reaction order was determined by varying the partial pressure of hydroperoxide vapor entering the reaction tube (C_0), while keeping the total flow rate constant at 300 ml/min. This was effected by adding diluent nitrogen from the alternative stream to give additional hydroperoxide partial pressures of 0.75 mm and 0.50 mm Hg. Thus, at a constant temperature and steady flow rate throughout the saturator six analytical determinations were made in 1 hour. In this time a steady decomposition value was always achieved. Then 75 ml/min of the total nitrogen flow was diverted through the alternative circuit and two 10 min determinations completed. Following this, the entire nitrogen stream was again directed through the saturator and two further 10 min determinations made. In a similar fashion concentration changes were then carried out from 0.99 mm Hg to 0.50 mm Hg and finally in the reverse sequence.

In Fig. 2, the concentration of hydroperoxide vapor (C_F) leaving the catalyst is plotted against C_0 and the points are numbered in experimental sequence, starting from the initial steady decomposition value obtained after one hour's exposure of a catalyst to 0.99 mm Hg partial pressure *t*-butyl hydroperoxide vapor. Each point represents a run of 10 min duration. These results indicate that the decomposition reaction is first order with respect to *t*-butyl hydroperoxide concentration on the metal/metal oxide surfaces of copper, cobalt, and silver.

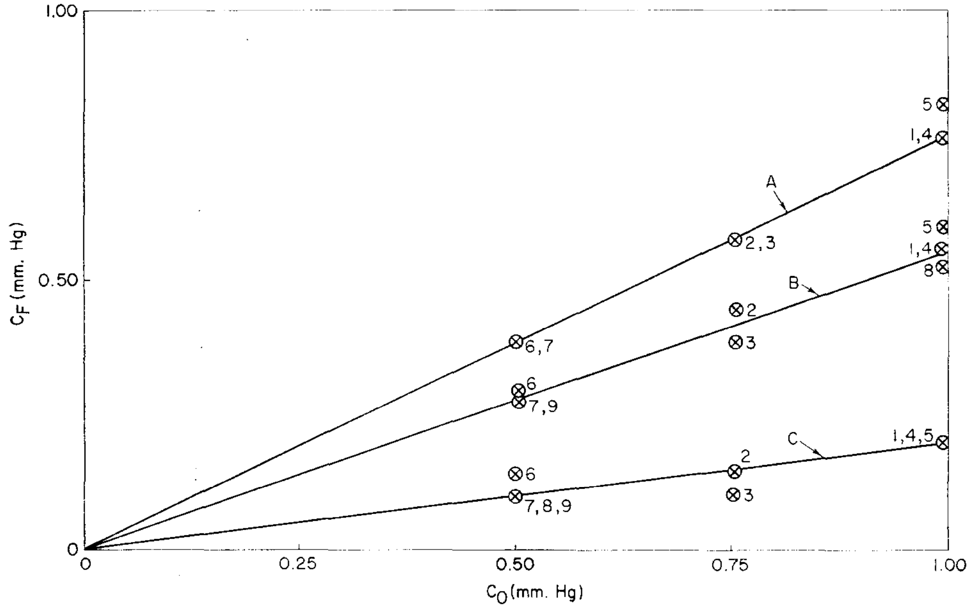

FIG. 2. First order kinetic plots of concentration of peroxide leaving reactor (C_F) against concentration entering (C_0). Points numbered in experimental sequence. Curve A, copper/copper oxide at 132°; curve B, cobalt/cobalt oxide at 165°; curve C, silver/silver oxide at 130°.

In the work on H_2O_2 decomposition (*1, 2*) energies of activation were computed on a basis of fast temperature changes which are considered to preclude subsequent slow changes of the catalyst surface. However, in the present experiments the furnace could not be adequately adjusted to give an accurate fast change and so energies of activation were calculated from steady decomposition values at a given temperature. Five or six determinations were made at steady temperature, as before, then keeping the nitrogen flow constant and diverting it through the alternative circuit, the furnace control was adjusted to give a rise or fall in temperature of about 10–20°. When the thermistor was recording a steady temperature the nitrogen stream was redirected through the saturator and catalyzed runs carried out until three consecutive steady values were obtained. From the slopes of the conventional Arrhenius plots the experimental E_A was determined. Figure 3 records the results obtained with a silver gauze and Table 1 summarizes the experimental activation energies and frequency factors for the metal/metal oxides studied.

TABLE 1
EXPERIMENTAL ACTIVATION ENERGIES (E_A) AND FREQUENCY FACTORS (A)

Catalyst	E_A (kcal/mole)	A (sec^{-1})
Ag/Ag_2O	4.6	2.2×10^4
Co/CoO	8.7	8.6×10^5
Cu/Cu_2O	13.0	4.9×10^8

DISCUSSION

The reproducibility of steady decomposition results obtained in this study was not as good as that found with H_2O_2 (*1, 2*). The results for different gauzes of the same material, similarly prepared, gave repro-

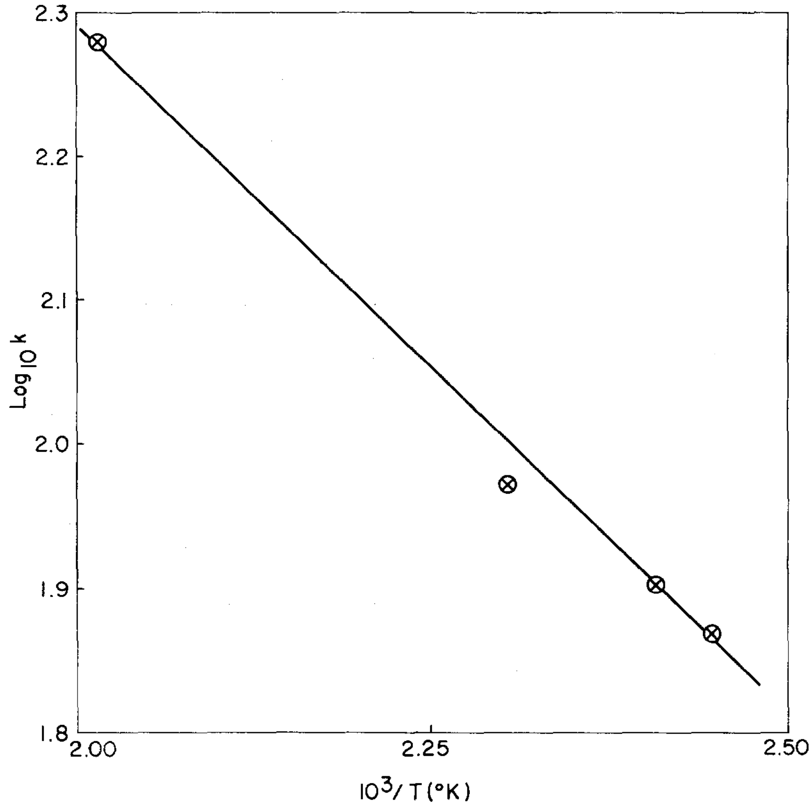

FIG. 3. Arrhenius plot, silver/silver oxide.

ducibilities which generally were no better than 5%. However the experimental activation energies for each metal/metal oxide were accurately reproducible and differences in steady decompositions may be related to variations in certain surface parameters such as surface area. The oxide film thickness on the silver and copper catalysts before exposure to the hydroperoxide vapor lay between 60 and 200 Å as shown by a coulometric reduction technique (*8*).

The effective decomposition reaction may be represented simply as:

$$t\text{-BuOOH(g)} + \text{S(s)} \rightleftharpoons [t\text{-BuOOH-S}]^*\text{(ads)} \rightleftharpoons t\text{-BuOH(g)} + \tfrac{1}{2}\text{O}_2\text{(g)} + \text{S(s)} \quad (1)$$

where S is an active surface species which may be a single or dual adsorption site. Since the effect of oxygen and *t*-butyl alcohol on the decomposition kinetics was not studied, it is not possible to suggest a more formal mechanistic scheme. However, it may be noted that the experimental activation energies of 4.6 and 13.0 kcal/mole on silver/silver oxide and copper/copper oxide, respectively, are very similar to the values obtained with these surfaces for H_2O_2 decomposition; as also is the low activity of the aluminum foil. These factors, together with the kinetic order results for *t*-BuOOH, suggest that similar mechanisms may operate in both cases. Thus the initiation step would be that of electron transfer from the catalyst surface to chemisorbed hydroperoxide:

$$\text{-BuOOH(ads)} + e \rightarrow t\text{-BuO}\cdot\text{(ads)} + \text{OH}^-\text{(ads)} \quad (2)$$

The source of the electron could be an O^- or O_2^- species which are recognized to be present on the oxide surface (*9*). Such species could conceivably act as loci for a subsequent catalytic cycle based on *t*-BuOOH.

On all active surfaces studied, equivalent decompositions of the organic peroxide were found at temperatures 40–50° higher than with H_2O_2. However, a more striking difference in this comparison is the susceptibility of nickel catalysts to poison rapidly on exposure to *t*-BuOOH. This feature was entirely absent in H_2O_2 studies where nickel catalysts were examined as the bulk oxide and as the oxide on metal gauze or flashed metal film. Nickel has been shown to form a stable methoxide (*10*) and also complex alkoxides (*11*), but there is insufficient experimental evidence to allow an explanation of the activity loss on this basis.

Finally, it may be noted that the results in Table 1 show a "Compensation Effect" between E_A and A. Of the two sources of variation in the A factor (*12*), the concentration of active sites (C_s) and the entropy term (ΔS), it is fairly certain that C_s is the main one since, for an adsorption process ΔS varies only slightly according to whether the adsorbed species is held firmly or in a mobile surface state.

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