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# The Hydrogen–Oxygen Reaction on Lanthanide Oxides

## V. The Hydrogen–Oxygen Reaction on Dysprosium Oxide

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The hydrogen–oxygen reaction has been studied over three dysprosium oxide catalysts at hydrogen:oxygen ratios from 0.2 to 10, at pressures of hydrogen up to approximately 600 N $m^{-2}$, and at temperatures in the range 368 to 553 K. The kinetic results can best be explained in terms of an equation of the form: $-dP_T/dt = (kb_{H_2}^2P_{H_2}^2b_{O_2}P_{O_2})/(1 + b_{H_2}P_{H_2} + b_{O_2}P_{O_2})^3$, where $k$ is a proportionality constant, $b_{H_2}$ and $b_{O_2}$ are the adsorption coefficients for hydrogen and oxygen, respectively, $P_T$ is the total pressure of hydrogen plus oxygen, and $P_{H_2}$ and $P_{O_2}$ are the partial pressures for hydrogen and oxygen, respectively. The most likely mechanism is one involving the competitive adsorption of molecular hydrogen and oxygen, with the rate-determining step involving the interaction between $H_2O_{2(ads)}$ and $H_{2(ads)}$. There is a change in the availability of sites at approximately 430 K, with the effects of excess gas and the activation energy changing at this temperature.

### INTRODUCTION

Minachev (*1*) has recently summarized many of the catalytic properties of dysprosium oxide with particular reference to organic reactions. The activity of dysprosium oxide is very similar to that of erbium oxide [which has been described recently (*2*)], with dysprosium oxide being especially active towards *n*-butane cracking, and double bond migration in 1-butene.

Many studies have been made of reactions involving hydrogen or oxygen on dysprosium oxide. Adsorption results (*3*) show that the amount of adsorption depends on temperature, with a maximum adsorption at about 600 K. Hydrogen is probably adsorbed nondissociatively, but oxygen may be dissociatively adsorbed above 600 K. The hydrogen–deuterium exchange reaction occurs above 250 K (*4*) and shows a temperature dependence similar to the parahydrogen conversion reaction, leading to the conclusion that both these reactions involve equivalent dissociative mechanisms at these temperatures. Selwood (*5*) studied the nondissociative mechanism in a magnetic field and observed an increase in activity towards parahydrogen conversion in a strong field but no change in activity in a weak field. Oxygen exchange reactions indicate that activity increases with a rise in mobility of surface oxygen, with dysprosium oxide becoming active at about 600 K. Oxygen desorption is the rate-determining step (*1, 6*). Sazonov and others (*7–9*) also noticed the importance of surface oxygen mobility in the oxidation of carbon monoxide, with the rate of carbon monoxide oxidation increasing and the rate of carbon dioxide desorption decreasing as the oxygen became more mobile. Winter (*10*) and Read (*11*) reported that the desorption of oxygen is an important rate-controlling step in the decomposition of nitrous oxide.

Preliminary studies have been made of the hydrogen–oxygen reaction on dysprosium oxide. Bakumenko (*12*) used temperatures in the range 600 to 800 K and total pressures of $7 \times 10^3$ N $m^{-2}$ for the nonstoichiometric reactions of 1% oxygen in hydrogen and 2% hydrogen in oxygen. He calculated activation energies of 55 kJ $mol^{-1}$ in excess hydrogen and 197 kJ $mol^{-1}$ in excess oxygen. Minachev (*1*) suggests that the rate-determining step is the interaction between adsorbed molecular hydrogen and surface oxygen. A correlation between catalytic activity and oxygen mobility is again observed, the mobility being particularly significant above 600 K. Read and Conrad (*13*) studied the stoichiometric reaction in the temperature range 350 to 420 K at total pressures from 270 to 430 N $m^{-2}$ and fitted their results to the general kinetic expression

$$-dP_T/dt = (A_m P_T)^m/(1 + BP_T)^m, \quad (1)$$

where $A_m$ and $B$ are temperature-dependent constants, $P_T$ is the total pressure of hydrogen plus oxygen, and $m$ is an integer of value 1 to 3. The overall order is zero below 380 K and as high as three at low pressures and high temperatures. The activation energy, assuming $m = 1$ in the above equation, is calculated as approximately 45 kJ $mol^{-1}$.

The present contribution extends the work of Read and Conrad (*13*) to include nonstoichiometric reactions, and the following paper in this series relates the effects of catalyst pretreatment on the stoichiometric reaction.

## EXPERIMENTAL METHODS

The apparatus and experimental procedure were identical to that described in a previous paper in this series (*14*), with the same precautions and extra experimental work carried out to ensure that there were no mass or heat transfer limitations. The catalyst was Specpure grade dysprosium oxide (Johnson, Matthey) with a surface area of $2.0 \times 10^3$ $m^2$ $kg^{-1}$. The structure, composition, and surface species were investigated using X-ray fluorescence and powder diffraction and ir analysis.

Each reaction is identified by two numbers and a letter. The first number indicates the group of experiments conducted at an approximately constant temperature; the central letter indicates the set of experiments within the group, each set having a common initial hydrogen : oxygen ratio; and the final number indicates the run within the set, the total initial pressure usually changing for each separate run. For example, 1 A 1–3 represents the three reactions 1 A 1, 1 A 2, and 1 A 3, all in group 1 and set A. The groups are numbered in the order in which the experiments were performed; missing numbers indicate that experiments were also conducted on the catalyst after hydrogen or oxygen pretreatment, and these groups are included in the following paper in this series.

Nineteen groups of experiments were conducted using three different catalyst samples, each weighing $3.54 \times 10^{-4}$ kg. All conditioning and pretreatment involved evacuation at $<10^{-4}$ N $m^{-2}$. Fresh catalysts were heated for 6 days at 773 K, and, prior to each group and most sets of reactions, the catalyst was heated at the reaction temperature for several hours. There was a 10-min evacuation time before each run.

The experiments are summarized in Table 1 for stoichiometric mixtures and Table 2 for nonstoichiometric mixtures. Missing letters in Table 1 indicate that nonstoichiometric sets have been conducted between the stoichiometric sets. Groups 1 to 13 (catalyst sample #1) contain stoichiometric reactions at various temperatures in the range 368 to 553 K, and group 14 (catalyst sample #1) contains reactions with various stoichiometries, all at 473 K. Groups 18 (catalyst sample #2) and 23 (catalyst sample #3) contain stoichiometric reactions on fresh catalyst surfaces. Groups 31 and 32 (catalyst sample #3) contain reactions with various stoichiometries, at

473 and 398 K, respectively, on surfaces which have previously been pretreated with hydrogen and oxygen (see following paper). Group 33 (catalyst sample # 3) is a stoichiometric group at 473 K.

The first set in every group (the "A" set) contains standard stoichiometric runs at an approximately constant total initial pressure of 300–350 N $m^{-2}$. Standard stoichiometric sets are also included within the nonstoichiometric groups 14, 31, and 32.

An IBM 1130 computer was used in the analysis of the data, the reaction rates being determined by cubic spline interpolation (*15*).

## RESULTS

### *Structure of Dysprosium Oxide*

At temperatures below about 2000 K, dysprosium oxide is reported to form only the stable cubic modification (C-type) with a space group Ia3 [e.g., (*16*) and (*17*)]. X-ray and ir analyses confirmed this structure and indicated that the surface was free of water and hydroxyl groups after normal pretreatment.

### *Analysis of the Data*

The data were analyzed as before (*14*) including calculations of the initial rate of reaction, evaluated as the rate of decrease of total pressure. In Table 1 the results are summarized for the stoichiometric reactions, showing the overall order with respect to time obtained from the linear section of the log (rate) versus log (total pressure) plots and the dependence of this order on pressure and temperature. The nonstoichiometric results are summarized in Table 2, with the orders with respect to time obtained from the log (rate) versus log (minor component) plots with the orders for the minor component being quoted. The orders with respect to concentration are obtained from initial rate data.

The data were also analyzed by drawing isobaric curves through the log (rate) versus log (partial pressure) plots for nonstoichiometric reactions. These results are presented in Tables 3 and 4.

### *Summary of the Results for the Stoichiometric Reactions*

*Shape of the log plots.* Three different types of log (rate) versus log (pressure) plots can be characterized as illustrated in Fig. 1. Types "a" and "b" show three distinct regions: an initial section of short duration with a slope which is either greater than the second section (type "a") or less than the second section (type "b"); a second linear section lasting for most of the reaction (the quoted orders with respect to time are calculated from this slope); and a third section with rapidly increasing slope. Type "c" does not show the "initial" section. The type of plot is listed in Table 1. Where there is a change of type within a set, the type is shown for each individual run.

From the results shown in Table 1 it can be seen that, as the temperature increases for sets 1A to 14E inclusive, there is a change from type "c" (368 to 398 K) to type "b" (398 to 425 K) to type "a"

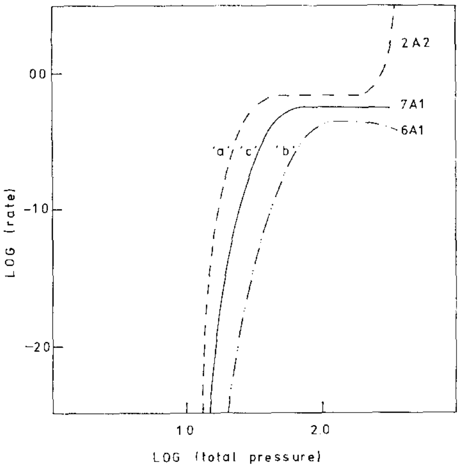

FIG. 1. Typical features of the three types of log (rate) versus log (pressure) plots. Reaction 2A2 is type "a", reaction 6A1 is type "b", and reaction 7A1 is type "c."

(443 to 553 K). After exposure to non-stoichiometric reactions or after the pretreatment experiments, both types "a" and "c" appear in the temperature range 398 to 473 K, but only one type "b" plot is observed. At 473 K there is an indication that it is exposure to hydrogen which is causing the change from type "a" to type "c".

*Catalyst activity.* The initial activity (as recorded by the initial rates) and the overall activity (obtained by comparing the time taken for similar reactions to go to completion) can be evaluated throughout the series of experiments from the rates of the standard stoichiometric sets at initial total pressures of approximately 330 N $m^{-2}$. Both the initial and the overall activities are abnormally high on fresh catalysts or after prolonged evacuation, but a consistent, lower, activity is soon attained. The highest initial rate of 3.6 N $m^{-2}$ $s^{-1}$ is observed at 472 K on a fresh catalyst.

The effects of stoichiometric excess on the subsequent set depends on the temperature. In groups 14 and 31 (473 K), excess of either gas reduces the initial activity, with hydrogen excess having the greater

TABLE 1

Summary of the Experiments and Results for the Stoichiometric Hydrogen–Oxygen Reaction on Dysprosium Oxide

| Group, set, and runs | Gas in stoichiometric excess in set immediately preceding the set indicated | Average temperature (K) | Initial hydrogen pressure range (N $m^{-2}$) | Overall order with respect to time | Reaction type |
|---|---|---|---|---|---|
| 1 A 1–3 | [Catalyst #1] | 372 | 205 ± 5 | 0.9 → 0.3 | a c c |
| 2 A 1–5 | | 553 | 200 ± 70 | 0 | a |
| 3 A 1–5 | | 490 | 230–130 | 0 | a |
| 4 A 1–5 | | 443 | 210 | 0 | a |
| 5 A 1–4 | | 398 | 200 | 0.3 ± 0.1 | b |
| 6 A 1–4 | | 418 | 270–130 | 0.1 ± 0.1 | b |
| 7 A 1–5 | | 464 | 200 ± 70 | 0 | c a a a a |
| 8 A 1–5 | | 513 | 200 ± 70 | 0 | a |
| 9 A 1–4 | | 368 | 200 | 0.3 ± 0.2 | c |
| 10 A 1–3 | | 384 | 200 | 0.1 ± 0.1 | c |
| 11 A 1–3 | | 393 | 200 | 0.4 ± 0.3 | c |
| 12 A 1–4 | | 425 | 200 | 0 | b b c c |
| 13 A 1–4 | | 398 | 190 ± 70 | 0.1 ± 0.1 | c |
| 14 A 1–3 | | 473 | 200 | 0 | a |
| B 1–5 | | | 300– 70 | 0 | a |
| E 1–3 | Hydrogen | | 200 | 0 | a |
| J 1–3 | Hydrogen | | 200 | 0 | c |
| 18 A 1–5 | [Catalyst #2] | 472 | 230– 80 | 2.2 → 0.8 | a a c a c |
| 23 A 1–4 | [Catalyst #3] | 418 | 400 ± 190 | 0.3 | a a c c |
| 31 A 1–3 | | 473 | 220 | 0.2 → 0 | c a c |
| B 1–5 | | | 250–110<br>80 | 0<br>0.5 | a c c a b |
| C 1 | | | 220 | 0.1 | a |
| E 1 | Hydrogen | | 220 | 0 | c |
| G 1 | Oxygen | | 220 | 0.1 | c |
| H 1–3 | | | 220 ± 10 | 0.1 | c c a |
| J 1 | Hydrogen | | 220 | 0 | c |
| L 1 | Oxygen | | 230 | 0.1 | a |

TABLE 1 (*Continued*)

| Group, set, and runs | Gas in stoichiometric excess in set immediately preceding the set indicated | Average temperature (K) | Initial hydrogen pressure range (N m$^{-2}$) | Overall order with respect to time | Reaction type |
|---|---|---|---|---|---|
| 31 N 1 | Hydrogen | | 220 | 0.2 | c |
| P 1 | Oxygen | | 220 | 0 | a |
| Q 1-3 | | | 220 ± 10 | 0.1 | a a c |
| S 1 | Hydrogen | | 220 | 0.1 | a |
| U 1 | Oxygen | | 220 | 0.1 | a |
| W 1 | Hydrogen | | 220 | 0.1 | a |
| 32 A 1-3 | | 398 | 225 ± 5 | 0.2 | a |
| B 1-6 | | | 250- 80 | 0.1 | a |
| | | | 60 | 0.6 | |
| C 1 | | | 230 | 0.3 | a |
| E 1 | Hydrogen | | 230 | 0.2 | a |
| G 1 | Oxygen | | 210 | 0.3 | c |
| H 1-3 | | | 215 ± 5 | 0.3 | a c a |
| J 1 | Hydrogen | | 220 | 0.3 | a |
| L 1 | Oxygen | | 220 | 0.4 | a |
| N 1 | Hydrogen | | 210 | 0.3 | c |
| P 1 | Hydrogen | | 220 | 0.2 | c a a |
| Q 1-3 | | | 220 ± 10 | 0.1 → 0.5 | c |
| S 1 | Oxygen | | 220 | — | c |
| U 1 | Hydrogen | | 210 | 0.5 | c |
| W 1 | Hydrogen | | 200 | 0.6 | c |
| X 1-6 | | | 140 ± 90 | 0.5 | a a a a c a |
| 33 A 1-7 | | 473 | 230- 80 | 0.1-0.2 | a a a a a c a |
| | | | 50 | 0.6 | |

effect. In general, the initial activity in group 31 is lower than in group 14. Excess gas has very little effect on the overall activity, with perhaps a slight decrease in some cases.

In group 32 (398 K), hydrogen excess has very little effect on the initial activity but there is a drastic reduction in initial activity after oxygen excess. The overall activity is increased slightly after hydrogen excess and decreased after oxygen excess.

*Orders with respect to time.* As shown in Table 1, all the orders (except for the high order on fresh catalyst #2) are in the range zero to one. The orders decrease for successive reactions in set 1A (fresh catalyst #1), set 18A (fresh catalyst #2), and set 31A (after the oxygen pretreatment set) whereas the orders increase for successive reactions in set 32 Q (after nonstoichiometric set 32 O with hydrogen excess). These trends are indicated by the arrows in Table 1.

The orders decrease as the initial pressure increases (indicated by a dash in Table 1). From groups 1–14, the overall order at approximately 200 N m$^{-2}$ initial hydrogen pressure is zero above 418 K and 0.1 to 0.4 below this temperature. The orders in groups 31 and 32 are about 0.1 higher than the corresponding orders in groups 1–14, and there is a slight tendency for the orders to increase for successive sets within group 32.

It is difficult to determine the orders accurately with respect to concentration but these fall in the range 0.2 to 0.9.

*Temperature effects.* In general, the initial and overall reaction rates increase with temperature, although the change is not regular. From the results of groups 1–13 the initial rates increase with temperature from 0.1 to 2.2 N $m^{-2}$ $s^{-1}$, and the change in overall rates is shown by the Arrhenius plot in Fig. 2. Zero-order kinetics are assumed, with a similar plot being obtained for first-order kinetics. The error is fairly large, particularly below about 400 K. From this plot, it can be seen that the activation energy is changing with temperature from a value of about 40 kJ $mol^{-1}$ below about 430 K to a value of about 3 kJ $mol^{-1}$ above this temperature.

### *Summary of Results for the Nonstoichiometric Reactions*

*Shape of the log plots.* The shapes are similar to those described for stoichiometric reactions and they are listed in Table 2. Within the sets of group 14 (473 K) there is a tendency for type "a" plots to occur for the first runs at high ratios and later runs at low ratios. Type "b" plots appear at low initial pressures and high ratios. For group 31 (473 K, after hydrogen pretreatment reactions) there is a tendency towards type "c" and only one type "b" plot occurs, and for group 32 (398 K) there is a mixture of types "a" and "c".

Reactions with excess oxygen are slower than reactions with excess hydrogen, particularly in group 32.

*Orders with respect to time.* From the results presented in Table 2, it can be seen that it is impossible to determine accurate orders from the log (rate) versus log (minor component pressure) graphs. However, certain trends are apparent.

For oxygen orders, the values vary from 0.3 to 1.2 with an increase in order (with the exception of 32 V) as the initial ratio increases and with a decrease in order for successive groups. The hydrogen orders are more erratic, varying from zero to two. There is a fairly marked pressure dependence in many cases (indicated by an arrow in Table 2) with a tendency towards high orders at low initial pressures.

*Orders with respect to concentration.* The orders with respect to concentration are particularly difficult to determine because of the variety of reaction types within many of the sets. However, most of the orders are in the region 0.5 ± 0.3 except for sets 14 G, 31 K, 32 F, 32 K, and 32 R where the orders are in the region 1.5 to 2.7, with the highest orders being in group 32. All these sets contain type "c" plots

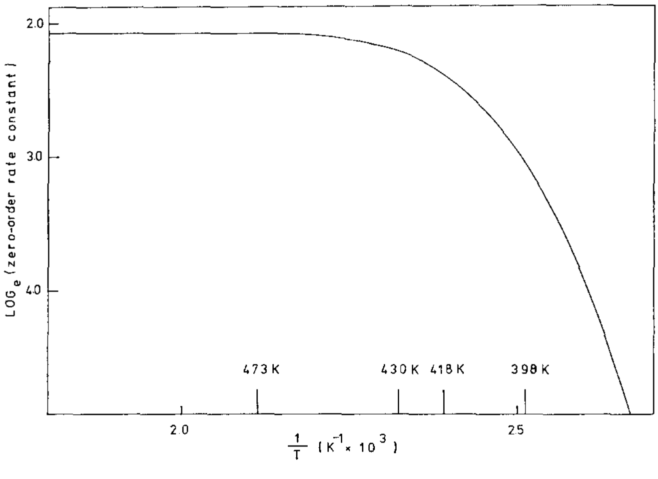

FIG. 2. Arrhenius plot from the results of groups 1 to 13.

TABLE 2

Summary of the Experiments and Results for the Nonstoichiometric Hydrogen–Oxygen Reaction on Dysprosium Oxide

| Group, set, and runs | Average temperature (K) | Initial hydrogen pressure range ($N\ m^{-2}$) | Initial hydrogen: oxygen ratio | Average order with respect to time | | Order with respect to concentration | Reaction type |
|---|---|---|---|---|---|---|---|
| | | | | Oxygen | Hydrogen | | |
| 14 C 1–5 | 473 | 260– 60 | 1.8 | | 0 → 0.2 | 0.4 | a |
| D 1–5 | | 370– 50 | 2.2 | 0.3 | | 0.7 | c c a b b |
| F 1–5 | | 250– 60 | 1.5 | | 0 → 0.2 | 0.5 | c c a a a |
| G 1–5 | | 300– 70 | 2.5 | 0.6 | | 1.7 | c a a a a |
| H 1–5 | | 200– 50 | 1.0 | | 0.2 ± 0.2 | 0.2 | c a a a a |
| I 1–5 | | 300– 70 | 3.0 | 0.9 | | 0.5 | a b b b b |
| K 1–5 | | 310– 70 | 5.0 | 1.0 ± 0.1 | | 0.3 | a b b b b |
| L 1–5 | | 60– 10 | 0.2 | | 1.0 → 0 | — | c |
| M 1–5 | | 310– 70 | 9.6 | 1.1 ± 0.1 | | 0.5 | b |
| 31 D 1–5 | 473 | 250– 80 | 2.3 | 0.3 ± 0.1 | | 0.3 | a a a a c |
| F 1–6 | | 240– 80 | 1.7 | | 0 | 0.1 | a a c a a c |
| I 1–5 | | 250– 80 | 2.5 | 0.5 ± 0.2 | | 0.4 | a |
| K 1–5 | | 220– 70 | 1.5 | | 0 | 1.5 | a a c a b |
| M 1–5 | | 280–120 | 3.0 | 0.7 | | 0.6 | a |
| O 1–5 | | 160– 50 | 1.0 | | 0.5 → 2.5 | 0.3 | c a a c c |
| R 1–5 | | 300–100 | 5.0 | 0.5 ± 0.2 | | 0.6 | a c c a c |
| T 1–5 | | 60– 20 | 0.2 | | 0.1 → 1.2 | 0.6 | a c a c a |
| V 1–5 | | 340–110 | 10.0 | 0.7 ± 0.4 | | 0.4 | c |
| 32 D 1–6 | 398 | 250– 60 | 2.3 | 0.5 ± 0.2 | | 0.6 | a |
| F 1–6 | | 240– 60 | 1.8 | | 0 → 0.8 | 2.7 | a c c a a a |
| I 1–6 | | 260– 60 | 2.5 | 0.5 ± 0.1 | | 0.5 | a |
| K 1–5 | | 220– 70 | 1.5 | | 2.0 → 0 | 2.5 | a a c a a |
| M 1–5 | | 270– 90 | 3.0 | 0.6 ± 0.1 | | — | b c a a a |
| O 1–3 | | 250– 90 | 2.3 | 0.5 ± 0.1 | | 0.7 | a c c |
| R 1–3 | | 160– 90 | 1.0 | | 0 | 2.2 | c |
| T 1–5 | | 300–100 | 5.0 | 0.8 ± 0.1 | | 0.9 | c c a a c |
| V 1–6 | | 340– 80 | 10.0 | 0.6 ± 0.2 | | — | c |

and, hence, the orders can be associated with the second, linear, section of the log plots. At 473 K, the orders appear to be slightly greater in sets with hydrogen excess, whereas the opposite is true at 398 K.

*Isobars.* For all three nonstoichiometric groups the hydrogen and oxygen isobars exhibit maxima. The results are given in Tables 3 and 4 and typical isobars are shown in Figs. 3 and 4.

In general, the ratio at the maxima of the isobars decreases with increasing pressure of oxygen and increases with increasing pressure of hydrogen, with oxygen pressure having the greater effect. Also, the ratios in groups 14 and 31 (473 K) are comparable, but the equivalent ratios in group 32 (398 K) are higher. All the hydrogen isobars and the oxygen isobar at 398 K show anomalously low ratios at low pressures. The ratios from the oxygen isobars are higher than the equivalent ratios from the hydrogen isobars.

Accurate slopes on either side of the iso-

TABLE 3

Summary of the Results from the Isobaric Plots at Constant Hydrogen or Oxygen Pressure

| Group | Average temperature (K) | Isobar at constant hydrogen pressure | | | Isobar at constant oxygen pressure | | |
|---|---|---|---|---|---|---|---|
| | | Constant hydrogen pressure (N m$^{-2}$) | At maximum of isobar | | Constant oxygen pressure (N m$^{-2}$) | At maximum of isobar | |
| | | | Oxygen pressure (N m$^{-2}$) | Hydrogen: oxygen ratio | | Hydrogen pressure (N m$^{-2}$) | Hydrogen: oxygen ratio |
| 14 | 473 | 13 | 8 | 1.7 | 3 | 10 | 3.4 |
| | | 27 | 13 | 2.1 | 4 | 13 | 3.3 |
| | | 40 | 21 | 1.9 | 13 | 39 | 3.0 |
| | | 67 | 39 | 1.7 | 23 | 25 | 1.1 |
| | | 80 | 44 | 1.8 | 40 | 76 | 1.9 |
| | | 107 | 76 | 1.4 | 53 | 69 | 1.3 |
| | | 133 | 166 | 0.8 | 67 | 100 | 1.5 |
| | | 167 | 209 | 0.8 | 81 | 113 | 1.4 |
| | | | | | 96 | 144 | 1.5 |
| | | | | | 99 | 158 | 1.6 |
| 31 | 473 | 7 | 6 | 1.1 | 13 | 40 | 3.1 |
| | | 27 | 17 | 1.6 | 27 | 68 | 2.5 |
| | | 40 | 31 | 1.3 | 40 | 76 | 1.9 |
| | | 60 | 33 | 1.9 | 67 | 114 | 1.7 |
| | | 80 | 73 | 1.1 | 80 | 136 | 1.7 |
| | | 107 | 63 | 1.7 | 93 | 140 | 1.5 |
| | | 133 | 166 | 0.8 | | | |
| | | 167 | 134 | 1.3 | | | |
| | | 173 | 216 | 0.8 | | | |
| 32 | 398 | 13 | 16 | 0.8 | 7 | 17 | 2.5 |
| | | 27 | 11 | 2.5 | 13 | 27 | 2.1 |
| | | 40 | 20 | 2.0 | 27 | 95 | 3.5 |
| | | 53 | 19 | 2.8 | 36 | 94 | 2.6 |
| | | 67 | 25 | 2.7 | 47 | 122 | 2.6 |
| | | 96 | 48 | 2.0 | 53 | 138 | 2.6 |
| | | 107 | 45 | 2.4 | 67 | 161 | 2.4 |
| | | 133 | 67 | 2.0 | 81 | 113 | 1.4 |
| | | 173 | 67 | 2.6 | 93 | 177 | 1.9 |

TABLE 4

Average Slopes and Maxima from the Isobars

| Isobar | Group | Temperature (K) | Hydrogen:oxygen ratio at maximum of isobar | Slope of isobar | |
|---|---|---|---|---|---|
| | | | | Low pressure side of maximum | High pressure side of maximum |
| Hydrogen | 14 | 473 | 2.1–0.8 | 1.2 ± 0.2 | −2.0 |
| Hydrogen | 31 | 473 | 1.2 ± 0.4 | 1.5 ± 0.5 | −2.3 ± 0.3 |
| Hydrogen | 32 | 398 | 2.4 ± 0.4 | 1.5 ± 0.5 | −2.6 ± 0.4 |
| Oxygen | 14 | 473 | 3.4–1.4 | 2.3 ± 0.5 | −1.2 ± 0.3 |
| Oxygen | 31 | 473 | 3.1–1.5 | 2.3 ± 0.5 | −1.5 ± 0.3 |
| Oxygen | 32 | 398 | 3.5–1.9 | 2.3 ± 0.4 | −1.2 ± 0.2 |

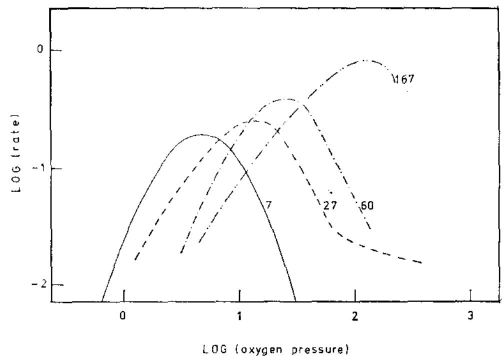

FIG. 3. Hydrogen isobars at 473 K from group 31. The constant hydrogen pressures are shown in newtons per square meter.

baric maxima are difficult to measure but fairly consistent values are obtained from the results of the three nonstoichiometric groups as shown in Table 4. The absolute value of the overall average for the low pressure side of the hydrogen isobar and the high pressure side of the oxygen isobar is 1.3 ± 0.3 and for the remaining slopes is 2.3 ± 0.4.

## DISCUSSION

The lanthanide oxides are particularly susceptible to conditioning, making the "history" of the catalyst very important. For this reason, the results have been separated into those without any specific pretreatment and those with specific pretreatment by hydrogen or oxygen, the latter being presented and discussed in the next paper. However, any reaction, particularly one with a large excess of one of the gases, pretreats the catalyst to some extent.

The results are now discussed in terms of general characteristics, with particular reference to the first section of the log (rate) versus log (pressure) plots; kinetic expressions, applied mainly to the second section of the log plots; and possible mechanisms.

### *General Characteristics of the Kinetic Results*

There appears to be a distinct temperature effect, giving rise to qualitatively different results at different temperatures. From Fig. 2, it can be seen that the change in the Arrhenius plot occurs at about 430 K. For this reason experiments were conducted in the region of low activation energy (groups 14 and 31 at 473 K) and high activation energy (group 32 at 398 K). The higher value for the activation energy (40 kJ mol$^{-1}$) agrees favorably with the value of 45 kJ mol$^{-1}$ obtained by Read and Conrad (*13*) in the temperature range 350 to 420 K.

*Shape of log plots.* The majority of the plots are type "c" with no initial fast (type "a") or slow (type "b") portion. However, type "a" is fairly common, particularly for reactions on fresh catalysts and on the untreated catalyst at high tem-

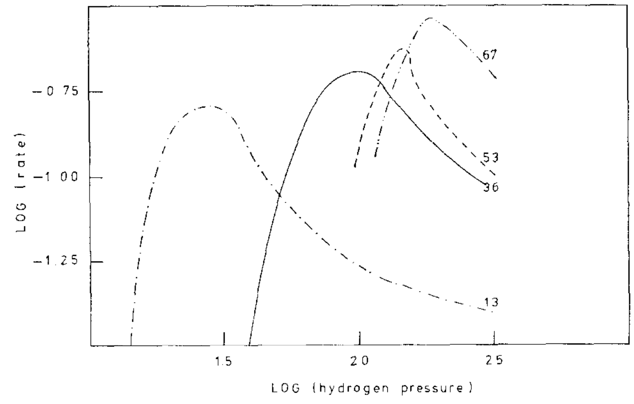

FIG. 4. Oxygen isobars at 398 K from group 32. The constant oxygen pressures are shown in newtons per square meter.

peratures. Type "b" occurs at intermediate temperatures for stoichiometric reactions and at high temperatures and low pressures for nonstoichiometric reactions with excess hydrogen. Catalysts which have been used for pretreatment experiments, or which have been exposed to excess of either gas, produce a combination of types "a" and "c," with a tendency towards type "c" after hydrogen exposure.

The large slope of the initial section of the type "a" plots could be related to adsorption of reactants or to reaction on a hyperactive, readily deactivated set of sites. From adsorption studies (*3*), from the fast overall rate of reaction for type "a" reactions, and from the isobars discussed later, it appears that the initial section is the result of reaction on a hyperactive set of sites. These sites are present on the fresh catalyst and can be partially regenerated at high temperatures or by excess of either gas. The greater preponderance of type "a" in group 31 over group 14 is presumably due to the hydrogen pretreatment reactions of groups 24 to 29.

Type "b" plots are characterized by a low initial activity and their appearance for stoichiometric reactions around the temperature at which the Arrhenius plot changes may be associated with a change in mechanism or a change in availability of sites at this temperature. There is no kinetic evidence for a change in mechanism and so the latter explanation is more probable. Type "b" plots also occur for nonstoichiometric reactions, particularly at 473 K with hydrogen excess.

*Catalyst activity.* As expected from the appearance of type "a" plots for fresh catalysts, the initial activity is also high. Excess of either gas generally decreases the initial activity of the subsequent set, presumably due to deactivation of the active sites. The most drastic reduction occurs after oxygen excess at 398 K. At 473 K, hydrogen excess reduces the initial activity more than oxygen excess, a result which parallels the appearance of type "b" plots for nonstoichiometric reactions with hydrogen excess. Thus, oxygen has a greater effect on the initial activity at 398 K whereas hydrogen has the greater effect at 473 K. Again, for the overall activity, the effects are smaller (and almost negligible) at 473 K, and oxygen decreases the activity at 398 K.

*Order with respect to concentration.* For all the stoichiometric reactions and most of the nonstoichiometric reactions, the orders are in the range 0.2 to 0.9. However, certain sets with type "c" plots show orders as high as 2.7, with the orders at 398 K tending to be higher than those at 473 K. These orders can be compared with the overall orders with respect to time obtained from the second section of the log plots. At 398 K, the orders with respect to concentration are slightly greater in excess oxygen, and, at 473 K, the reverse applies. Therefore, at 398 K, the initial activity is reduced by oxygen, decreasing the number of available active sites and increasing the order for the reaction on the remaining sites. At 473 K, the initial activity is reduced by hydrogen, with the order again increasing.

### *Kinetic Expression*

From a previous analysis (*13*) and from the results over erbium oxide (*2*), a general kinetic expression can be proposed, namely,

$$-\frac{dP_{\mathrm{T}}}{dt} = \frac{k(b_{\mathrm{H}_2}P_{\mathrm{H}_2})^x(b_{\mathrm{O}_2}P_{\mathrm{O}_2})^y}{(1 + b_{\mathrm{H}_2}P_{\mathrm{H}_2} + b_{\mathrm{O}_2}P_{\mathrm{O}_2})^{x+y}}, \quad (2)$$

where $k$ is a proportionality constant, $b_{\mathrm{H}_2}$ and $b_{\mathrm{O}_2}$ are the adsorption coefficients for hydrogen and oxygen, respectively, and $x + y = m$ in Eq. (1). The results will now be discussed in terms of this relationship.

*Orders with respect to time.* Although previous results (*13*) for the stoichiometric reaction show a tendency towards high orders as the temperature increases to 420 K, this trend is not continued at higher temperatures, with overall orders of zero being obtained above 430 K in groups 1–14. In Eq. (2), $b_{H_2}$ and $b_{O_2}$ would be expected to decrease with increasing temperature and, therefore, if this expression is valid, $b_{H_2}$ and/or $b_{O_2}$ are higher at temperatures above 430 K than at lower temperatures due to a change in available sites. The higher orders in groups 31 and 32 show that pretreatment experiments have decreased $b_{H_2}$ and/or $b_{O_2}$. The change in order with initial pressure is as expected from Eq. (2).

For nonstoichiometric reactions, values for $x$ and $y$ can be obtained with particular accuracy for relatively low pressures of the gas for which the order is being determined. From Table 2 it is seen that the value for $x$ lies in the range 0.3 to 1.2 and for $y$ in the range 0 to 2. This evidence, together with the orders with respect to concentration, and the fact that zero-order kinetics will be obtained only if the powers of $P_{H_2}$ and $P_{O_2}$ in the denominator are the same suggest that $x = 2$ and $y = 1$, although the evidence for $x = 2$ is largely based on the results at 398 K.

*Isobars.* In order to obtain maxima in the isobars, there must be competitive adsorption as shown in Eq. (2). The positive slope of the hydrogen isobar and, to a lesser extent, the negative slope of the oxygen isobar give a value for $y$ and vice versa for $x$. From Table 4, therefore, $x = 2.3 \pm 0.4$ and $y = 1.3 \pm 0.3$. Again, it appears as though the best fit for Eq. (2) is $x = 2$ and $y = 1$. The variations in the maxima with pressure are as expected, and the ratio at the maxima of the oxygen isobars should be higher than the ratio for the hydrogen isobars. It is possible to calculate values for $b_{O_2}$ and $b_{H_2}$ from the oxygen isobars. Assuming that $x = 2$ and $y = 1$, $b_{O_2} = 0.05$ $N^{-1}$ $m^2$ and $b_{H_2} = 0.11$ $N^{-1}$ $m^2$ at 473 K, and $b_{O_2} = 0.01$ $N^{-1}$ $m^2$ and $b_{H_2} = 0.03$ $N^{-1}$ $m^2$ at 398 K. These values are realistic, giving the low overall orders that have been obtained experimentally and showing the anomalous increase in value with increasing temperature. Also, the change in relative values for $b_{O_2}$ and $b_{H_2}$ with temperature, parallels the change in the relative effects of oxygen and hydrogen on reaction type and activity. (With $x = y = 1$, $b_{O_2} = 0.05$ $N^{-1}$ $m^2$ and $b_{H_2} = 0.06$ $N^{-1}$ $m^2$ at 473 K, and $b_{O_2} = 0.01$ $N^{-1}$ $m^2$ and $b_{H_2} = 0.02$ $N^{-1}$ $m^2$ at 398 K). The small values of the maxima at low pressures (particularly at 398 K) indicate that $b_{O_2}$ is low and that adsorption is not appreciable at these pressures.

There is no indication of a change in the slopes of the isobaric plots or in overall orders with temperature, and, therefore, it is assumed that the same kinetic expression can be applied over the entire temperature range. Similarly, identical isobars but with higher values for the adsorption coefficients can be drawn through the initial section of the type "a" plots, showing that the kinetic expression is valid for the whole reaction.

### *Mechanism*

From the kinetic results, it appears that a similar mechanism, but with different types of adsorption, is operating over the complete reaction at all temperatures. Although adsorption results (*3*) and the oxygen exchange reaction (*1, 6*) indicate that oxygen is dissociatively adsorbed above 600 K, the kinetic results show that at lower temperatures the rate-determining step in the hydrogen–oxygen reaction involves nondissociated oxygen. Some of the orders with respect to time (particularly at 398 K) are low but this is because of the method of analysis and the orders increase as the relative pressure of the gas whose order is being determined decreases. Adsorption results show that hydrogen adsorbs nondissociatively, although the hydrogen–deuterium exchange reaction and the parahydrogen conversion reaction (*4*) proceed by dissociative mechanisms at temperatures from about 300 to 450 K.

Several general mechanisms may give rise to Eq. (2) with $x = 2$, $y = 1$ but the most likely would appear to be:

$$H_{2(g)} \rightleftarrows H_{2(ads)} \qquad (i)$$

$$O_{2(g)} \rightleftarrows O_{2(ads)} \qquad (ii)$$

$$H_{2(ads)} + O_{2(ads)} \rightleftarrows H_2O_{2(ads)} \qquad (iii)$$

$$H_2O_{2(ads)} + H_{2(ads)} \rightarrow 2H_2O_{(ads)} \qquad (iv)$$

$$H_2O_{(ads)} \rightleftarrows H_2O_{(g)} \qquad (v)$$

The change in the values of the adsorption coefficients are associated with adsorption onto different types of sites, probably producing different forms of the adsorbed species. This will be discussed in the next paper after the pretreatment results have been presented.

In conclusion, the results obtained in this work, together with a previous investigation (*13*), show that the hydrogen–oxygen reaction is catalysed by dysprosium oxide. Hydrogen and oxygen are competitively, nondissociatively adsorbed on the surface and the rate-determining step involves the interaction between $H_{2(ads)}$ and $H_2O_{2(ads)}$, with the latter species being considered as equivalent to two adjacent hydroxyl groups. Temperature is critical, with changes in activation energy and effects of excess gas occurring at about 430 K. The next paper in this series will deal in more detail with the mechanism and the effects of pretreatment.

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