

The Hydrogen-Oxygen Reaction on Lanthanide Oxides

IX. The Hydrogen-Oxygen Reaction on Holmium Oxide

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The stoichiometric hydrogen-oxygen reaction has been studied over holmium oxide at an approximately constant initial hydrogen pressure in the range 160 to 250 N m⁻² over the temperature range 449 to 768 K, and at different initial hydrogen pressures from 80 to 710 N m⁻² at 516, 567, and 626 K. In addition, stoichiometric reactions have been conducted at 487, 550, 551, 630, 690, and 744 K after pretreatment of the catalyst with hydrogen or oxygen. Non-stoichiometric reactions have been studied at 486, 548, 630, 690, and 748 K, at initial hydrogen pressures from 20 to 360 N m⁻² (740 N m⁻² at 548 K), and at hydrogen-oxygen ratios from 0.20 to 5. After detailed kinetic analysis it is shown that the results fit an equation of the form:

$$-\frac{dP_T}{dt} = \frac{k(b_{H_2}P_{H_2})^x b_{O_2}P_{O_2}}{(1 + b_{H_2}P_{H_2} + b_{O_2}P_{O_2})^{1+x}}$$

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, P_{H_2} and P_{O_2} are the partial pressures of hydrogen and oxygen, respectively, and $x = 1$ or 2 . The mechanism involves the competitive adsorption of molecular hydrogen and oxygen, with the rate-determining step involving the interaction between adsorbed hydrogen molecules and adsorbed oxygen or hydrogen peroxide (double hydroxide groups).

INTRODUCTION

Minachev (1) has summarized a great deal of the experimental work that has been conducted prior to 1973 using holmium oxide. This catalyst is a stable member of the yttrium group and often has properties very similar to erbium oxide (2). It has a relatively low activity toward oxidation reactions, but a relatively high activity toward dehydrogenation reactions [for example, (1, 3)]. The activation energy for oxygen exchange is very high, giving a value of 160 kJ mol⁻¹ in the temperature range 700 to 800 K on an oxygen pretreated sample (4). This value is considerably

lower, at 88 kJ mol⁻¹, over holmium oxide which has been heated in air and *in vacuo* (5). Sazonov *et al.* (6) calculated a value of 70 kJ mol⁻¹ in the temperature range 600 to 700 K, after alternating pretreatment *in vacuo* and in oxygen. The nitrous oxide decomposition is retarded by added oxygen, as is the reaction over most of the yttrium group oxides, indicating that the R₂ centers produced after adsorption of oxygen from the nitrous oxide are relatively stable (7).

The nonstoichiometric hydrogen-oxygen reaction has been studied for 1% oxygen in hydrogen and 2% hydrogen in oxygen

at a total initial pressure of $2.2 \times 10^3 \text{ N m}^{-2}$ in the temperature range 640 to 773 K (8). There is rapid deactivation, particularly in excess hydrogen. The original activity cannot be fully regained and the results are too irregular for an accurate activation energy to be determined. In excess oxygen, the activation energy is originally 180 kJ mol^{-1} which reduces to a value of 100 kJ mol^{-1} after several runs. The rate also decreases.

The adsorption of hydrogen on holmium oxide has been studied extensively from 100 to 1000 K at pressures from 0.1 to 70 N m^{-2} with various pretreatments (9). For a catalyst heated in oxygen and then *in vacuo* at 1000 K, fast, reversible, physical adsorption occurs at 100 K. The amount of adsorption decreases at temperatures up to 200 K. At this point a nondissociative, essentially neutral, partially reversible chemisorption commences, with the amount being adsorbed first increasing and then decreasing with temperature as the temperature is raised beyond 300 K. At 500 K adsorption is minimal but hydrogen absorption commences, as hydrogen interacts with lattice oxygen ions. This leads to an accumulation of hydroxyl groups and an increase in adsorption with temperature up to the pretreatment temperature of 1000 K. This dissociative reaction can produce oxygen vacancies which will adsorb oxygen without evolution of products. For a sample of holmium oxide which has been reduced in hydrogen at 1000 K, the adsorption pattern is similar except that adsorption in the range 300 to 500 K is slightly greater than before, whereas adsorption above 500 K is less, with a maximum at 800 K. At 1000 K the temperature is high enough for hydrogen pretreatment to cause loss of water from the surface. This produces more sites for adsorption in the range 300 to 500 K, and allows for dissociative adsorption of hydrogen in the range 800 to 1000 K, with the amount of adsorption decreasing as the temperature increases up

to 1000 K, at which point water is released from the surface. The effect of pretreatment is further illustrated by comparing the amount of hydrogen adsorbed at room temperature after various pretreatments. Reduction in hydrogen at 1000 K, with the removal of all carboxyl and hydroxyl groups and with the creation of vacancies, produces the most active catalyst. Heating in oxygen and *in vacuo* at 1000 K produces a slightly less active catalyst, which is further deactivated by heating in oxygen at room temperature. Cooling the hydrogen pretreated catalyst to 500 K in hydrogen further reduces the activity, due to hydride formation, and exposure to water or carbon dioxide at room temperature causes complete deactivation.

EXPERIMENTAL METHODS

The apparatus, experimental procedure, catalyst conditioning, method of analysis, and identification system for reactions are identical to those described in previous papers in this series [for example, (10)]. Specpure grade holmium oxide was used with a surface area of $1.01 \times 10^4 \text{ m}^2 \text{ kg}^{-1}$ and a total weight of $1.53 \times 10^{-4} \text{ kg}$.

Thirty groups of experiments were conducted. Groups 1 to 16 contain stoichiometric reactions at various temperatures in the range 449 to 768 K at an approximately constant initial hydrogen pressure in the range 160 to 250 N m^{-2} , three to five identical reactions being conducted in each group; groups 17, 18, and 19 contain stoichiometric reactions at 516, 567, and 626 K, respectively, each group comprising eight reactions at different initial hydrogen pressures in the range 80 to 710 N m^{-2} ; groups 20 to 24 contain nonstoichiometric and standard stoichiometric (with an initial hydrogen pressure of $210 \pm 20 \text{ N m}^{-2}$) reactions at 630, 690, 486, 748, and 548 K, respectively, and groups 25 to 30 contain standard stoichiometric reactions at 487, 550, 630, 690, 744, and 551 K,

TABLE 1
 Summary of the Experiments and Results for the Stoichiometric
 Hydrogen-Oxygen Reaction on Holmium Oxide

Group, sets, and runs	Average temperature (K)	Initial hydrogen pressure range (N m ⁻²)	Gas in stoichi- ometric excess immediately prior to reaction	Overall order with respect to time	Initial rate (N m ⁻² s ⁻¹)	Reaction type
0A1-3	510	200		0.4 ± 0.1	2.7 → 1.9	a
1A1-3	575	190 ± 20		0.7 ± 0.1	1.6 → 0.1	a → b
2A1-4	640	210 ± 10		0.6 ± 0.1	0.1 → 2.0	b → a
3A1-3	678	200 ± 10		0.6 ± 0.1	2.4 → 1.6	a
4A1-3	728	210		—	1.4	—
5A1-3	768	190 ± 10		0.8 ± 0.3	1.3 ± 0.2	a
6A1-3	746	200		0.2 ± 0.1	3.2 → 1.7	a
7A1-3	700	200 ± 10		0.2 ± 0.1	2.7 ± 0.3	a
8A1-3	621	180 ± 10		0.2 ± 0.1	2.6 → 3.4	a
9A1-5	602	200 ± 10		0.2 → 0.8	4.0 → 1.1	a
10A1-3	566	210		0.1	1.0	a
11A1-4	539	220 ± 20		0.6	0.8 → 2.0	a
12A1-3	484	240 ± 10		0.9	1.0	a
13A1-3	449	170 ± 20		0.2	0.8 ± 0.2	a
14A1-3	514	160 ± 30		0.2 ± 0.2	1.5 ± 0.4	a
15A1-3	568	160 ± 30		0.1	2.0 → 1.4	a
16A1-8	516	710 - 90		0 → 0.5	1.0 ± 0.4	b → a
17A1-8	567	660 - 80		0 → 0.6	1.0 ± 0.4	b → a
18A1-8	626	600 - 90		0 → 0.5	1.4 ± 0.6	b → a
19A1-2	630	230 ± 10		0.8	1.4	a
19C1-2		210 ± 5	H ₂	1.0	1.4	a
19E1-2		210 ± 10	O ₂	1.0	1.8, 1.5	a
19G1-2		210 ± 5	H ₂	0.9	1.6	a
19I1-2		200 ± 10	O ₂	0.1	2.1, 2.4	a
19K1-2		210 ± 5	H ₂	0.3	3.5, 1.7	a
19N1-2		210 ± 20	H ₂	0.3	2.3	a
19O1-2		205 ± 5		0.5	2.0, 1.7	a
19Q1-2		210	O ₂	0.5	2.1, 1.8	a
20A1-2	690	220 ± 20	H ₂	0.4	1.5, 2.6	a
20D1-2		210 ± 20	O ₂	0.4	2.3, 1.6	a
20E1-2		220 ± 20		0.5	1.4, 2.2	a
20H1-2		200	O ₂	0.5	1.5, 1.7	a
20I1-2		200 ± 5		0.5	2.4, 1.6	a
20L1-2		220 ± 5	O ₂	0.4	1.7, 2.1	a
20M1-2		230 ± 20		0.3	1.5, 3.3	a
20P1-2		200 ± 10	O ₂	0.6	1.7, 1.5	a
20Q1-5		220 → 70		0.9 ± 0.3	1.8 → 1.0	a
20S1-2		180	H ₂	0.5	1.9, 1.3	a
21A1-2	486	220 ± 20		0.6	1.2, 1.1	a
21D1-2		190	O ₂	0.7	1.0	a
21E1-2		200		0.5	1.6, 1.9	a
21H1-2		210 ± 10	O ₂	0.4	1.0, 1.7	a
21I1-2		180		0.4	1.2	a
21K1-2		190	H ₂	0.2	2.2	a
21N1-2		200 ± 10	H ₂	0.6	1.1, 1.0	a
21O1-2		200		0.5	1.4, 1.0	a
21Q1-5		250 → 90	O ₂	0.6 → 0.1	1.1 ± 0.3	a
22A1-2	748	210 ± 10		0.2	1.3, 1.4	a

TABLE 1—Continued

Group, sets, and runs	Average temperature (K)	Initial hydrogen pressure range (N m ⁻²)	Gas in stoichi- ometric excess immediately prior to reaction	Overall order with respect to time	Initial rate (N m ⁻² s ⁻¹)	Reaction type
22D1-2		200	O ₂	0.4	1.5	a
22E1-2		220 ± 20		0.5	1.5, 2.0	a
22H1-2		190	O ₂	0.4	1.2	a
22I1-2		510, 180		0.4	2.9, 1.9	a
22L1-2		250, 200	O ₂	0.5	1.3, 1.2	a
22M1-2		210		0.6	1.4, 1.6	a
22P1-2		220 ± 20	O ₂	0.5	1.3, 1.6	a
22Q1-5		180 ± 60		0.4 ± 0.1	1.3 ± 0.3	a
23A1-2	548	190		0.4	1.7, 1.5	a
23D1-2		190	O ₂	0.5	1.5, 2.2	a
23E1-2		210 ± 10		0.5	1.9, 1.3	a
23H1-2		190 ± 10	O ₂	0.4	1.2, 1.5	a
23I1-2		160		0.3	1.4, 1.2	a
23L1-2		210 ± 10	O ₂	0.4	1.4, 1.1	a
23M1-2		200		0.3	1.4, 1.3	a
23P1-2		220 ± 20	H ₂	0.5	2.7, 1.9	a
23Q1-5		160 ± 100		0.5 ± 0.1	1.7 ± 0.5	a

respectively, after pretreatment with hydrogen or oxygen. Within each pretreatment group, a standard set was first conducted. This was followed by evacuation for 1800 s, oxygen pretreatment at 500 N m⁻² for 600 s, evacuation for 180 s, and then another standard set. The system was then evacuated for 3 hr and subsequently the catalyst was pretreated with hydrogen in a manner identical to that used for oxygen. A third standard set was then conducted followed by evacuation for 1800 s and a final standard set with no immediate pretreatment. Each set comprised two identical reactions with 600 s evacuation time between them.

RESULTS

Structure of Holmium Oxide

At temperatures below about 2500 K, holmium oxide is reported to form only the stable cubic modification (C-type) with a space group Ia3 (T_h^7), for example (11). X-Ray and ir analysis confirmed this structure and indicated that the surface

was free of water and hydroxyl groups after normal conditioning.

Analysis of Data

The data were analyzed as before [e.g., (12)] and are summarized below and in the tables for the stoichiometric and nonstoichiometric reactions. The reaction types, "a," "b," and "c," referred to below, are illustrated in Fig. 1 in (12), and are described in the preceding paper in this series.

Summary of the Results for the Stoichiometric Reactions

Some of the results are summarized in Table 1. Missing letters within the groups indicate the presence of nonstoichiometric reactions.

Reaction type. Almost all of the reactions were type "a" and no type "c" were observed. Type "b" appears in groups 2 and 3 at 575 and 640 K at initial hydrogen pressures of about 200 N m⁻². No more type "b" appears until groups 17 and 19 at 516 and 630 K at initial hydrogen pres-

tures in the range 260 to 700 N m⁻². There is also a tendency toward type "b" in group 18 at 567 K in the initial hydrogen pressure range 300 to 700 N m⁻². The most well-defined type "b" plots occur in group 19 at 630 K and high initial pressures. Only type "a" plots are observed for the standard stoichiometric reactions in groups 20 to 30 inclusive.

Catalyst activity. The initial rates are directly correlated with reaction type, with type "b" giving low initial rates. Generally, initial rates are in the range 1 to 2.5 N m⁻² s⁻¹, with anomalously high rates in groups 8, 9, and 10 at 700, 621, and 602 K at initial hydrogen pressures of approximately 200 N m⁻². The change in initial rates between standard reactions with no pretreatment, and reactions conducted directly after nonstoichiometric reactions (groups 20 to 24) or after direct pretreatment (groups 25 to 30) is summarized in Table 2. Generally, it is seen that hydrogen decreases the initial rate, whereas oxygen decreases the initial rate below 630 K but increases it above this temperature.

The rate of the central, linear portion varies between 0.3 and 1.0 N m⁻² s⁻¹ with a tendency to increase with temperature and pressure. No consistent change is observed after pretreatment with hydrogen or oxygen.

The time taken for the reaction to go to completion is fairly constant, averaging about 700 to 850 s for 90% completion.

Orders with respect to time. These orders are calculated from the central, linear portion of each plot. The orders from groups 1 to 16 vary between 0 and 1.2 with no obvious temperature dependence. In groups 17, 18, and 19 the order decreases with increasing initial pressure, from a value of about 0.5 at an initial hydrogen pressure of 100 N m⁻² to a value of zero at 600 N m⁻². In groups 20 to 24 the orders range between 0.1 and 1.0 with no consistent effect of stoichiometric excess or temperature. Similarly, there does not

appear to be any effect with direct pretreatment in groups 25 to 30; most of the orders are in the range 0.4 ± 0.2 , with the highest orders being observed at 630 K and the lowest at 744 K.

Orders with respect to concentration. These orders are calculated from the three pressure dependent groups 17 to 19. The orders obtained are 1.2, 0.8, and 0.8 at 516, 567, and 626 K, respectively.

Temperature effects. Arrhenius plots, using typical reactions and assuming zero-order kinetics, give a low activation energy in the order of 6 kJ mol⁻¹.

Summary of the Results for the Nonstoichiometric reactions

Some of the results for nonstoichiometric reactions are summarized in Table 3. Missing letters within these groups indicate the presence of standard stoichiometric reactions.

Reaction type. Most reactions are of type "a," although type "c" does appear quite frequently. There are no type "b" reactions. Type "c" appears as the stoichiometry deviates significantly from 2, particularly outside the range 1.5 to 2.5, with a tendency towards more type "c" reactions as the stoichiometry becomes more extreme. Most sets start with type "a" at high pressures (the major exception being the sets with extreme stoichiometries), with type "c" often appearing later in the sets at lower pressures.

Catalyst activity. The initial rate generally decreases as the hydrogen-oxygen ratio increases, with the exception that the initial rate is usually very low at hydrogen-oxygen ratios less than unity.

The average rates for the major portion of the reactions at an initial hydrogen pressure of approximately 220 N m⁻² are summarized in Table 4. As the ratio deviates from stoichiometry in excess hydrogen the rate remains reasonably constant and then decreases as the ratio approaches the

TABLE 2
Initial Rate Change ($N m^{-2} s^{-1}$)

Groups	Temperatures (K)	Change in initial rates ($N m^{-2} s^{-1}$)			
		Hydrogen pretreatment		Oxygen pretreatment	
		Nonstoichiometric excess	Direct pretreatment	Nonstoichiometric excess	Direct pretreatment
22 and 25	486 and 487	0	-0.4	-0.2	-0.2
24 and 30	548 and 550	—	-0.4	-0.3	-0.3
20 and 27	630 and 630	-0.1	-0.5	+0.2	-0.1
21 and 28	690 and 690	-1.2	0	+0.2	+0.2
23 and 29	748 and 744	—	-0.2	—	+0.1

extreme value of 5.00. In excess oxygen the rate increases markedly as the ratio changes from stoichiometric to 1.75, and then to 1.50, with the rate in excess oxygen being about twice that in the equivalent amount of excess hydrogen. At more extreme stoichiometries the rate decreases, and at ratios of 0.20 and 5.00, the rate in excess oxygen is about half the rate in excess hydrogen.

Orders with respect to concentration. These orders vary between 0.2 and 1.6, with no obvious temperature effect, but with a tendency to give the highest orders at the lowest stoichiometric ratios, particularly at the lowest temperatures of 486, 548, and 630 K.

Orders with respect to time. These results are summarized in Table 3. When there is a change of order within a set this is shown with an arrow indicating the change in order from high to low initial pressure. Both the oxygen and the hydrogen orders follow the same pattern. They vary between zero and 1.2, show an increase as the initial pressure decreases, and show no obvious temperature dependence. The oxygen orders tend to increase as the hydrogen-oxygen ratio increases, and the hydrogen orders tend to increase as the hydrogen-oxygen ratio decreases. For sets 22P and 23O at the extreme ratio of 0.20 the hydrogen

orders are very high, in the vicinity of 3, but the accuracy is not great in these two cases.

Isobars. For all five nonstoichiometric groups the hydrogen and oxygen isobars exhibit maxima. The results are summarized in Table 5 and typical isobars are shown in Figs. 1 and 2.

The ratio at the maxima of the isobars decreases with increasing oxygen pressure and increases with increasing hydrogen pressure. The ratios for the oxygen isobars are higher than those for the hydrogen isobars, with a very slight tendency for both sets to decrease as the temperature increases. The average slopes on either side of the isobar are given in Table 5. The most consistent results are obtained from the low pressure side of the hydrogen isobars where an overall average value of 1.1 ± 0.1 is obtained. The oxygen isobars give less accurate results than the hydrogen isobars, with particularly high errors at 548 and 630 K. The average value, using absolute numbers, from the low pressure side of the hydrogen isobars and the high pressure side of the oxygen isobar is 1.1, and the average value of the opposite slopes is 1.4.

DISCUSSION

The overall results fit the general pattern described previously [for example, (12)]

TABLE 3
Summary of the Experiments and Results for the Nonstoichiometric
Hydrogen-Oxygen Reaction on Holmium Oxide

Group, sets, and runs	Average temperature (K)	Initial H ₂ pressure range (N m ⁻²)	Initial H ₂ -O ₂ ratio	Average order with respect to time		Reaction type	
				O ₂	H ₂		
20B1-5	630	250-200	2.30	0.4		a	
20D1-5		270-60	1.78		0 → 0.2	a	
20F1-5		280-80	2.53	0.3 → 0.6		a, a, a, c, c	
20H1-5		220-50	1.55		0 → 0.1	a	
20J1-5		290-60	2.99	0.6 → 0.9		a, a, c, c, c	
20L1-4		180-80	0.97		1.0 → 1.2	a, a, c, c	
20M1-5		360-90	4.92	0.6 → 0.7		a, a, a, c, c	
20P1-5		50-20	0.20		0.6 → 1.2	a, a, c, c	
20R1-5		270-50	2.23	0.3 → 0.8		a, a, a, c	
21B1-5		690	230-90	2.26	0.3 ± 0.2		a
21C1-5	270-70		1.80		0 → 0.2	a	
21F1-5	270-110		2.74	0.7		a, a, a, c, c	
21G1-5	250-60		1.50		0 → 0.2	a	
21J1-5	280-80		3.03	0.4 → 0.9		a, a, a, c, c	
21K1-5	210-100		1.02		0.9 ± 0.1	a, a, c, c, c	
21N1-5	320-130		5.08	0.9 ± 0.1		c, c, a, e, c	
21O1-5	50-20		0.20		1.0 ± 0.2	a, a, c	
21R1-5	340-100		2.40	0.4		a	
22B1-5	486		250-130	2.24	0.6 → 0.7		a
22C1-5		250-63	1.75		0	a	
22F1-5		270-70	2.47	0.3 → 0.6		a, a, a, a, c	
22G1-5		240-60	1.51		0	a	
22J1-5		260-90	2.96	0.6 ± 0.1			
22L1-5		170-40	0.99		1.0 → 1.2	c	
22M1-5		340-100	4.98	1.2		c	
22P1-5		80-25	0.20			c	
23B1-4		748	250-80	2.24	0.4 ± 0.1		a
23C1-5			280-60	1.75		0	a
23F1-5	260-80		2.50	0.3 → 0.6		a, a, a, c, c	
23G1-4	170-70		1.49		0	a	
23J1-5	280-60		3.04	0.6 → 0.8		c	
23K1-5	160-70		1.00		0.8	a, a, c, c, c	
23N1-5	310-120		5.05	1.0 ± 0.2		c	
23O1-5	300-80		0.20			c	
24B1-5	548		740-90	2.28	0.3 ± 0.1		a, a, a, a, c
24C1-5			250-70	1.75		0 → 0.2	a
24F1-4		270-80	2.49	0.5 → 0.6		a, a, a, c	
24G1-5		220-70	1.49		0	a	
24J1-5		280-85	2.99	0.5 → 0.7		a, a, c, c	
24K1-5		190-50	1.00		1.2	a, c, c, c, c	
24N1-5		320-100	4.95	1.0 ± 0.2		c	
24O1-5		300-100	0.20			c	

and so they will be discussed on the same basis as previous papers in this series.

It is interesting to note that holmium

oxide does not become active until about 450 K, which is much higher than samarium and gadolinium oxide but lower

TABLE 4
Summary of the Average Reaction Rates ($N \text{ m}^{-2} \text{ s}^{-1}$) for the
Nonstoichiometric Groups 20 to 24

Initial hydrogen- oxygen ratio	Group 22 (486)		Group 24 (548)		Group 20 (630)		Group 21 (690)		Group 23 (748)	
	Excess of H_2	Excess of O_2	Excess of H_2	Excess of O_2	Excess of H_2	Excess of O_2	Excess of H_2	Excess of O_2	Excess of H_2	excess of O_2
2.00	0.35		0.44		0.50		0.50		0.48	
2.25 or 1.75	0.35	0.70	0.48	0.77	0.50	0.80	0.52	0.80	0.48	0.87
		B ^a C		B C		B D		B C		B C
2.50 or 1.50	0.39	0.76	0.41	0.94	0.43	0.98	0.33	1.05	0.41	1.07
		F G		F G		F H		F G		F G
3.00 or 1.00	0.38	0.45	0.36	0.60	0.30	0.53	0.32	0.60	0.28	0.66
		J L		J K		J L		J K		J K
5.00 or 0.20	0.16	—	0.19	0.09	0.21	—	0.24	—	0.26	0.14
		M		N O		M		N		N O

^a Set from which the rates are taken.

than neodymium and erbium oxide. Therefore, a pattern is developing where the further out the oxide is from the middle of the series (gadolinium oxide) the less active it becomes.

General Characteristics

Reaction type. Most reactions are type "a" although type "b" does occur for some stoichiometric reactions and type "c" for some nonstoichiometric reactions. Type

"b" occurs at intermediate temperatures, generally $600 \pm 30 \text{ K}$, usually requiring a high initial pressure. Type "c" usually becomes more pronounced as the stoichiometry becomes more extreme and the pressure decreases. The standard reactions after the start of the nonstoichiometric reactions, and all the pretreatment reactions, show type "a" characteristics, indicating that the conditions are not sufficiently extreme to inhibit the initial fast

TABLE 5
Average Slopes and Maxima from the Isobars

Isobar	Group	Temperature (K)	$\text{H}_2\text{-O}_2$ ratio at max of isobar	Slope of isobar	
				Low pressure side of max	High pressure side of max
Hydrogen	20	630	1.1	1.1 ± 0.2	1.4 ± 0.3
Hydrogen	21	690	1.0 ± 0.1	1.0	1.4 ± 0.3
Hydrogen	22	486	1.2 ± 0.1	1.1 ± 0.1	1.1 ± 0.3
Hydrogen	23	748	1.0 ± 0.1	1.1 ± 0.1	1.2 ± 0.2
Hydrogen	24	548	1.1 ± 0.1	1.1 ± 0.1	1.8 ± 0.2
Oxygen	20	630	1.6 ± 0.3	1.3 ± 0.4	1.6 ± 0.9
Oxygen	21	690	1.1 ± 0.1	1.2 ± 0.3	0.9 ± 0.1
Oxygen	22	486	1.3 ± 0.1	1.2 ± 0.2	1.0 ± 0.2
Oxygen	23	748	1.1 ± 0.1	1.0 ± 0.1	0.9 ± 0.2
Oxygen	24	548	1.2 ± 0.1	2.0 ± 0.7	1.3 ± 0.3

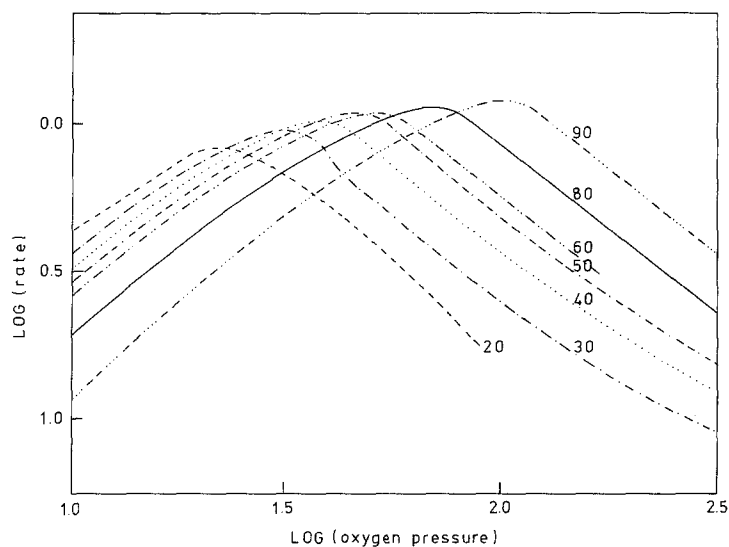


FIG. 1. Hydrogen isobars at 690 K from group 21. The constant hydrogen pressures are shown in N m^{-2} .

section of the reaction. It is assumed that either hydrogen or oxygen (or both) is causing deviation from type "a" by blocking some of the initially active surface sites under certain critical conditions.

Catalyst activity. There is little effect of temperature or pressure on the initial rate of reactions. However, as shown in Table 2, this rate decreases or remains constant for

standard stoichiometric reactions following hydrogen excess reactions or hydrogen pre-treatment, indicating that hydrogen deactivates some of the very active sites available at the start of the reaction. Above 630 K oxygen has the opposite effect, but below this temperature oxygen also deactivates these sites although to a lesser extent than hydrogen. For the non-

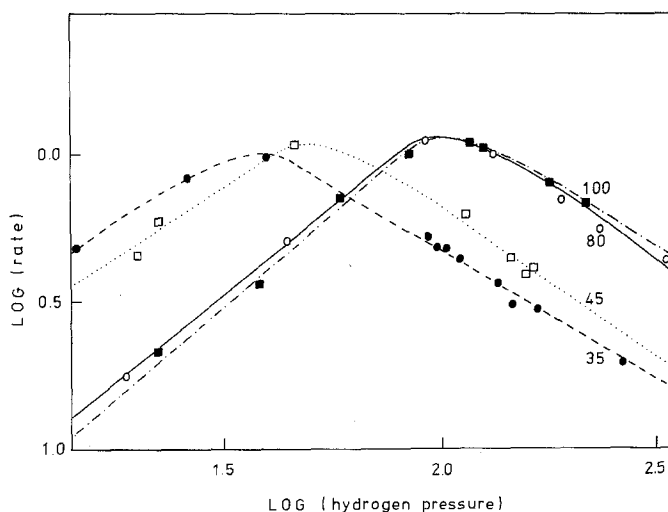


FIG. 2. Oxygen isobars at 690 K from group 21. The constant oxygen pressures are shown in N m^{-2} .

stoichiometric reactions, the initial rate decreases as the stoichiometric ratio increases, again showing a deactivating effect for hydrogen.

The rate of the central, linear, portion tends to increase with temperature and pressure but does not depend on pretreatment conditions. As is shown in Table 4, as the nonstoichiometric ratio deviates from 2 in excess hydrogen, there is little change in rate until the increasing scarcity of the alternate gas causes the rate to decrease. However, as the ratio deviates from 2 in excess oxygen, the rate increases dramatically, until the scarcity of the alternate gas causes this rate to decrease as well. At extreme ratios the rate in excess oxygen is less than that in excess hydrogen.

Active sites. As has been shown for similar oxides, and particularly for hydrogen adsorption on holmium oxide (9), there are many different interactions between gaseous molecules and the surface of lanthanide oxides. Specifically, Kreisberg *et al.* (9) identify four types of interaction between hydrogen and the surface of holmium oxide, dependent upon pretreatment conditions and adsorption temperature (see Introduction). The results in the present paper indicate that, as for other lanthanide oxides [for example, (13)], at least two different types of sites can be identified: a hyperactive set available at the start of the reactions which is affected by pretreatment conditions and to some extent by temperature, and a less active set on which most of the reaction occurs which is not affected by pretreatment conditions.

The hyperactive set is generally present but can be partially, or completely, reversibly deactivated under certain conditions. For stoichiometric reactions prior exposure to hydrogen usually causes a decrease in the number of these sites available, with a fairly drastic effect around 600 K at high pressure. This decrease in number of available sites is observed for the nonstoichiometric reactions, where the

initial rate consistently decreases as the hydrogen-oxygen ratio increases. From the introduction, from previous papers in this series, and from the present results, it is concluded that these sites result from the loss of hydroxyl groups during conditioning. Kreisberg *et al.* (9) noted that hydroxyl groups could be removed from the surface, especially by reduction in hydrogen at 1000 K, and that these groups could be reformed in the temperature range 570 to 870 K. The conditioning of the catalyst used in the present work was much more prolonged than that used by Kreisberg (6 days at 800 rather than 1 hr at 1000 K) and, therefore, the lack of any activation caused by additional removal of hydroxyl groups is as expected. The deactivating effect of hydrogen is therefore explained by the loss of active sites due to the reformation of hydroxyl groups. The activating effect of oxygen above 630 K (see Table 2) is consistent with this in that more sites for hydrogen adsorption are made available. The deactivating effect of oxygen below this temperature (and the appearance of type "b" plots at high pressures and temperatures around 600 K) parallels the observation by Kreisberg *et al.* (9) that below about 500 K hydrogen adsorption on an oxygen pretreated sample is lower than the adsorption on a nonoxygen-pretreated sample. They explain this by assuming that hydrogen adsorption is molecular below 500 K and dissociative above this temperature. Although the change in adsorption pattern is similar to that observed by Kreisberg *et al.*, there is little evidence from the present work to indicate a change from nondissociative to dissociative adsorption except for the slight decrease in order with respect to concentration, from 1.2 to 0.8, as the temperature increases from 516 to 567 K. It is difficult to estimate the number of sites but it appears as if there are at least 1×10^{20} sites m^{-2} on the surface. However, this

number can be greatly affected by pre-treatment conditions.

It is suggested that the second set of sites, responsible for the major portion of the reactions, are anion vacancies inherent in the crystal structure. Winter (7) has suggested that these sites are relatively stable and they appear to be the sites utilized for the oxygen exchange reaction (4). These sites are less numerous than the hyperactive set, with up to 1×10^{18} sites m^{-2} being available. The number of available sites is dependent on temperature, with surface oxygen mobility being an important factor. The high activation energies for oxygen exchange on an oxygen-pre-treated catalyst (4), and for the hydrogen-oxygen reaction in excess oxygen (100 kJ mol^{-1} , compared to 6 kJ mol^{-1} in the present work for stoichiometric reactions) (8) show that oxygen deactivation can occur, a fact which is illustrated by the lower rate in extreme oxygen excess than in extreme hydrogen excess observed in the present results. The increase in rate as the nonstoichiometric rate deviates slightly from stoichiometry in excess oxygen is attributed to differences in the adsorption properties of oxygen and hydrogen and is probably not due to the production of more active sites.

Kinetic Expression

The major part of the reaction can be considered as following the same kinetic expression as proposed for other oxides in this series [for example, samarium oxide (13)], namely,

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

where k is a proportionality constant, b_{H_2} and b_{O_2} are the adsorption coefficients for hydrogen and oxygen, respectively, and x and y are integers. The results will now be discussed in terms of this relationship.

Orders with respect to time. The orders for

the stoichiometric reactions vary between 0 and 1.2 with no consistent temperature effect but with a decrease as the initial pressure increases. At an initial hydrogen pressure of 600 N m^{-2} the overall order is zero, indicating that $[(2b_{\text{H}_2} + b_{\text{O}_2})/3] \times 900 \gg 1$, whereas, at 100 N m^{-2} the order is 0.5, indicating that $[(2b_{\text{H}_2} + b_{\text{O}_2})/3] \times 150 \approx 1$.

The individual orders obtained from the nonstoichiometric results are shown in Table 3. Both orders tend to increase up to about 1.2 as the accuracy increases by having a fairly large excess of the gas whose pressure is assumed to be constant, with very high orders in hydrogen being obtained at the extreme ratio of 0.20.

Isobars. The maximum in the isobars indicates that an expression of the form shown in Eq. (1) is valid. From the slopes of the isobars an accurate order for oxygen of unity is obtained. Although it is evident that the order for hydrogen is higher than that for oxygen, a definite value cannot be given to the hydrogen order. The overall average result is 1.4 with a tendency toward low values at extreme temperatures and a high value (approximately 2) at the intermediate temperature of 548 K.

The hydrogen-oxygen ratio at the maximum of the isobars changes with pressure in the same manner as for samarium oxide (13), showing that both adsorption coefficients decrease with increasing pressure. The increase in rate for nonstoichiometric reactions in slight oxygen excess indicates that the oxygen adsorption coefficient is more susceptible to pressure changes than is the hydrogen adsorption coefficient, whereas, the temperature effect indicates that the hydrogen adsorption coefficient increases with temperature slightly more than does the oxygen adsorption coefficient. Values for the adsorption coefficients can be calculated (though not with great accuracy) and the average values from the hydrogen isobars are shown in Table 6 using $y = 1$ and $x = 1$ or 2 in Eq. (1). In

all cases there is an increase in the value for the adsorption coefficient from 486 to 630 K but this is followed by a slight decrease at higher temperatures. The values for the hydrogen adsorption coefficients are identical using $x = 1$ or 2 but the value for the oxygen adsorption coefficient is reduced by a factor of two as x changes from 1 to 2. With $x = 2$, the oxygen adsorption coefficient is generally lower than the hydrogen adsorption coefficient, whereas, the converse is true when $x = 1$. On the assumption that the active sites are anion vacancies it might be expected that the heat of adsorption and, therefore, the adsorption coefficient, would be greater for oxygen than for hydrogen, lending some support to the value of x being unity, but the error in determining the adsorption coefficients is too large to place much stress on the absolute values. The values are approximately of the correct order of magnitude to give the observed changes in order with respect to time as the pressure varies, though they are a little higher than might be expected.

An approximate value for the proportionality constant, k , can be calculated and sample results are given in Table 7. There is a somewhat random effect of pressure,

TABLE 6

Average Values for the Adsorption Coefficients Calculated at a Constant Hydrogen Partial Pressure, with $y = 1$ and $x = 1$ or 2

Group number	Temperature (K)	x	$b_{O_2} \times 10^2$ ($N^{-1} m^2$)	$b_{H_2} \times 10^2$ ($N^{-1} m^2$)
22	486	1	6	3
		2	3	3
20	630	1	18	14
		2	9	14
21	690	1	15	12
		2	8	12
23	768	1	15	12
		2	8	12

TABLE 7

Sample Values for the Proportionality Constant, k

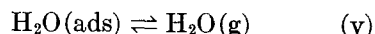
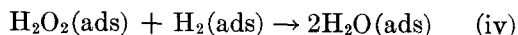
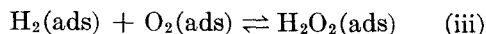
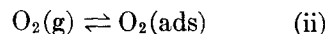
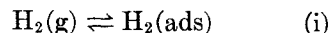
Run	Temperature (K)	Initial hydrogen pressure ($N m^{-2}$)	Proportionality constant ($N m^{-2} s^{-1}$)	
			$x = 1$	$x = 2$
1A1	500	200	4.3	7.1
17A2	516	596	3.7	5.1
17A8	516	87	3.9	7.8
19A4	626	452	3.1	4.4
19A7	626	178	6.6	7.3
19A8	626	94	4.6	6.6
4A3	678	202	9.6	10.3
6A3	768	214	8.7	11.8

and a tendency for the proportionality constant to increase slightly with temperature. Therefore, although these values show that Eq. (1) is generally obeyed, they do not help to distinguish between the possible values for x .

From a consideration of all the kinetic data, the evidence is conclusive that an expression of the form shown in Eq. (1) is obeyed and that the oxygen order is unity. The evidence for the order in hydrogen is not conclusive although it seems to be consistently higher than one, and in some extreme situations equals two.

Mechanism

In view of the general similarity between the present results for holmium oxide and previous results over similar oxides [e.g., erbium oxide (2)], the same general mechanism is proposed for the major portion of the reaction, namely,



This mechanism will give rise to the kinetic expression shown in Eq. (1), with

$x = 2$ and $y = 1$. However, in view of the uncertainty in the value of x , step (iii) may be the rate-determining step, or it may be a combination of steps (iii) and (iv). More experiments will need to be conducted to ascertain the order and the mechanism with more accuracy.

In conclusion, the kinetic results show that there are at least two sets of active sites on the surface of holmium oxide. The first set is a hyperactive set which is readily, reversibly, deactivated during the first part of most reactions, and is assumed to result from the loss of surface hydroxyl groups. The second set is more stable, is responsible for the major portion of the reaction, and is assumed to be anion vacancies. A kinetic expression has been obtained and a general mechanism has been proposed.

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REFERENCES

1. Minachev, Kh. M., *Int. Congr. Catal. 5th* 1, 219 (1973).
2. Read, J. F., and Crandlemire, A. L., *J. Catal.* **38**, 54 (1975).
3. Hattori, T., Inoko, J., and Murakami, Y., *J. Catal.* **42**, 60 (1976).
4. Winter, E. R. S., *J. Chem. Soc. A.*, 1832 (1969).
5. Minachev, Kh. M., and Antoshin, G. V., *Dokl. Akad. Nauk SSSR* **161**, 122 (1965).
6. Sazonov, L. A., Mitrofanova, G. N., Preobrazhenskaya, L. V., and Moskvina, Z. V., *Kinet. Katal.* **13**, 789 (1972).
7. Winter, E. R. S., *J. Catal.* **34**, 431 (1974).
8. Bakumenko, T. T., *Kinet. Katal.* **6**, 74 (1965).
9. Kreisberg, V. A., Topchieva, K. V., and Loginov, A. Yu., *Kinet. Katal.* **14**, 1065 (1973).
10. Read, J. F., Dunfield, L. G., Shreve, R. M., and Spinney, E. A., *J. Catal.* **33**, 335 (1974).
11. Bloor, D., and Dean, J. R., *J. Phys. C.* **5**, 1237 (1972).
12. Read, J. F., and Perkins, E. W., *J. Catal.* **42**, 443 (1976).
13. Read, J. F., Chan, Y. T., and Conrad, R. E., *J. Catal.* **55**, 166 (1978).