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The Hydrogen–Oxygen Reaction on Lanthanide Oxides

IV. The Hydrogen–Oxygen Reaction on Erbium Oxide

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The hydrogen–oxygen reaction has been studied over three erbium oxide catalysts at hydrogen:oxygen ratios from 0.2 to 10, at pressures of hydrogen up to approximately 300 N m^{-2} and oxygen up to approximately 400 N m^{-2}, and at temperatures in the range 543 to 723 K. The activity is increased by pretreatment with either hydrogen or oxygen, the effect being greater with oxygen. The kinetic results fit an equation of the form

$$\frac{-dP_T}{dt} = \frac{k b_{H_2}{}^2 P_{H_2}{}^2 b_{O_2} P_{O_2}}{(1 + b_{H_2} P_{H_2} + b_{O_2} P_{O_2})^3}$$

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. A probable 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 $H_{2(ads)}$.

INTRODUCTION

Erbium oxide is an effective catalyst for many redox reactions. Minachev (*1*), and others (e.g., *2–6*) have compared the activity of erbium oxide with the other lanthanide oxides towards many organic reactions including the dehydrogenation of cyclohexane, the dehydrocyclization of heptane, the cracking of butane, the hydrogenation and isomerization of olefins, the dehydrogenation, dehydration and ketonization of alcohols, the ketonization of acids, the exchange between deuterium and hydrocarbons, and the oxidation of propylene. In general, the oxides in the yttrium group (this includes erbium oxide) have a fairly uniform activity which is lower than that for the cerium group, although erbium oxide is particularly active towards heptane dehydrocyclization and acid ketonization (*1,6*). For many of the reactions, the change in activity across the lanthanide oxides parallels the change in magnetic moment.

Several other reactions which are catalyzed by erbium oxide have been investigated in some detail. Winter (*7*) and Read (*8*) noted that the desorption of oxygen is an important rate-controlling step in the decomposition of nitrous oxide. Read also observed an increase in activity after exposure to added oxygen (attributed to the creation of *F* centers), and a decrease in activity during the course of reactions (attributed to the formation of a stable surface oxygen species, possibly $O^{2-} | \square_s{}^-$). Sazonov and others (*1,9–12*) studied the oxidation of carbon monoxide and the oxygen exchange reaction, and found parallel changes across the lanthanide oxides for the activation energy of carbon dioxide desorption, the rate of oxygen exchange, the surface oxygen mobility and the mag-

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netic moment. The order was assumed to be first in carbon monoxide and zero in oxygen for carbon monoxide oxidation (with the oxygen dissociatively adsorbed), and first in oxygen for the exchange reaction. Winter (*13*) found that the desorption of molecular oxygen was rate determining in the oxygen exchange reaction, but he did not observe a dependence of activity on magnetic moment. Ashmead *et al.* (*14*) and Selwood (*15*) studied the parahydrogen conversion. At low temperatures, Ashmead *et al.* observed a dependence of rate upon magnetic properties. Selwood changed the magnetic field surrounding erbium oxide and noticed an increase in activity in a strong field but no change in activity in a weak field.

Preliminary studies have been made of the hydrogen–oxygen reaction over erbium oxide. Bakumenko and Chashechnikova (*16*) used temperatures in the range 620–740 K and oxygen pressures of about 700 N m^{-2} to investigate the stoichiometric reaction in excess argon and the nonstoichiometric reaction with excess hydrogen. They found that erbium oxide was less active than cerium, praseodymium, neodymium, or terbium oxide. Minachev (*1*) reported that the change in activity towards the hydrogen–oxygen reaction across the lanthanide oxides parallels the change in activity towards the oxygen exchange reaction and concluded that the rate-determining step is probably the surface interaction of nondissociatively adsorbed hydrogen and dissociatively adsorbed oxygen. Read and Conrad (*17*) used temperatures in the range 380–460 K and total pressures of the stoichiometric mixture in the range 30–1200 N m^{-2} and explained their results in terms of a general kinetic expression based on the Langmuir isotherm, namely

$$-\frac{dP_T}{dt}=\frac{(A_mP_T)^m}{(1+BP_T)^m}, \qquad (1)$$

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 present contribution extends the work of Read and Conrad (*17*) to include nonstoichiometric reactions and the effect of catalyst pretreatment.

EXPERIMENTAL METHODS

The apparatus and experimental procedure were identical to that described in the previous paper in this series (*18*). The catalyst was "Specpure" grade erbium oxide (Johnson Matthey) with a surface area of 1.6 × 10^3 m^2 kg^{-1}. The structure was determined by X-ray powder diffraction and by ir analysis.

As before, each reaction is identified by two numbers and one letter. The first number indicates the group of experiments conducted at an approximately constant temperature with a specified pretreatment (called the initial pretreatment); the central letter indicates the set of experiments within the group, each set having a common initial hydrogen:oxygen ratio and a common immediate pretreatment; and the final number indicates the run within the set, the total initial pressure usually changing for each separate run.

The detailed experimental conditions are given in Table 1. Twenty-five groups of experiments were conducted using three different catalyst samples from the same batch, each weighing 1.77 × 10^{-4} kg. Unless otherwise stated in Table 1, immediate pretreatment before each reaction was evacuation of the reaction manifold for 10 min. After initial pretreatment with oxygen or hydrogen, the gas was evacuated for 10 min, and after immediate pretreatment, the gas was evacuated for 3–5 min.

Groups 1–6 (using catalyst sample 1) serve to illustrate the effects of oxygen pretreatment on the stoichiometric hydrogen–oxygen reaction at various pressures and temperatures. The pressure of

TABLE 1

Summary of the Experimental Conditions for the Hydrogen–Oxygen Reaction on Erbium Oxide

Initial pretreatment before each group	Immediate pretreatment before each reaction	Group	Set and run	Temp (K)	Initial hydrogen:oxygen ratio	Initial hydrogen pressure (N m^{-2})	Initial rate (N m^{-2} s^{-1})
6 days at 773 K and $<10^{-4}$ N m^{-2} + 12 hr at 603 K and $<10^{-4}$ N m^{-2}	7.5 min (Set C) and 15 min (Set D) with oxygen at 460 N m^{-2}	1	A 1–3[a]	602	Stoichiometric group	198, 197, 199	0.49, 1.98, 2.31
			B 1–5	604		258, 215, 169, 130, 79	2.35, 2.31, 1.91, 0.54, 0.48
			C 1–5	605		256, 213, 152, 127, 52	0.71, 0.68, 0.64, 1.59, 0.56
			D 1–5	605		239, 166, 131, 114, 85	1.85, 1.82, 0.58, 0.58, 0.60
4 hr at 603 K and $<10^{-4}$ N m^{-2} + 10 hr at 603 K with oxygen at 520 N m^{-2}	7.5 min (Set B) and 15 min (Set C) with oxygen at 460 N m^{-2}	2	A 1–4	603	Stoichiometric group	195, 195, 193, 186	2.30, 2.07, 1.94, 1.64
			B 1–5	603		248, 197, 146, 123, 66	1.93, —, 1.76, 0.57, 0.53
			C 1–5	604		213, 60, 192, 156, 76	1.88, 0.51, 1.85, 1.78, 1.34
5 hr at 603 K and $<10^{-4}$ N m^{-2} + 10 hr at 603 K with oxygen at 300 N m^{-2}	7.5 min (Set B) and 15 min (Set C) with oxygen at 280 N m^{-2}	3	A 1–3	603	Stoichiometric group	174, 164, 172	2.51, 1.70, 2.02
			B 1–5	603		254, 207, 154, 125, 68	1.85, 2.21, 1.61, 1.58, 1.15
			C 1–5	603		252, 211, 164, 81, 122	1.97, 1.85, 1.80, 0.54, 0.57
5 hr at 603 K and $<10^{-4}$ N m^{-2} + 10 hr at 603 K with oxygen at 90 N m^{-2}	7.5 min (Set B) and 15 min (Set C) with oxygen at 90 N m^{-2}	4	A 1–3	603	Stoichiometric group	195, 192, 191	2.18, 2.12, 1.70
			B 1–5	603		248, 210, 166, 127, 80	2.21, 2.19, 1.76, 0.52, 0.52
			C 1–6	603		247, 213, 165, 118, 86, 34	1.89, 1.89, 1.94, 0.52, 1.05, 0.43

5 hr at 663 K and $<10^{-4}$ N m^{-2} + 10 hr at 663 K with oxygen at 290 N m^{-2}	7.5 min (Set B) and 15 min (Set C) with oxygen at 280 N m^{-2}	5	A 1–3	663	Stoichiometric group	198, 193, 194	2.86, 2.78, 2.20
			B 1–5	663		255, 234, 124, 76, 167	2.87, 2.45, 1.86, 1.16, 1.84
			C 1–6	663		253, 169, 212, 127, 81, 36	2.43, 2.16, 2.21, 1.49, 1.08, 0.47
5 hr at 723 K and $<10^{-4}$ N m^{-2} + 10 hr at 723 K with oxygen at 290 N m^{-2}	7.5 min (Set B) and 15 min (Set C) with oxygen at 280 N m^{-2}	6	A 1–3	723	Stoichiometric group	199, 197, 193	2.37, 2.28, 2.56
			B 1–5	722		258, 212, 172, 131, 91	2.98, 2.36, 1.92, 1.44, 0.95
			C 1–6	723		253, 211, 170, 124, 82, 42	2.54, 2.13, 1.64, 1.25, 0.96, 0.37
6 days at 773 K and $<10^{-4}$ N m^{-2} + 14 hr at 603 K and $<10^{-4}$ N m^{-2}	6 min (Set C) and 15 min (Set D) with hydrogen at 450 N m^{-2}	7	A 1–3	604	Stoichiometric group	182, 182, 187	1.81, —, 2.22
			B 1–5	603		252, 206, 158, 123, 83	2.43, 1.99, 1.75, 1.60, 1.35
			C 1–5	603		255, 205, 160, 121, 81	2.52, 2.06, 1.71, 1.19, 0.76
			D 1–5	603		243, 205, 166, 128, 78	2.03, 1.86, 1.58, 1.19, 0.78
3.5 hr at 603 K and $<10^{-4}$ N m^{-2} + 10 hr at 603 K with hydrogen at 470 N m^{-2}	6 min (Set B) and 15 min (Set C) with hydrogen at 450 N m^{-2}	8	A 1–3	604	Stoichiometric group	186, 185, 181	1.84, 2.30, 1.68
			B 1–6	603		240, 206, 158, 121, 82, 40	2.27, 2.10, 0.50, 1.36, 1.07, 0.42
			C 1–6	604		247, 204, 159, 121, 81, 40	2.21, 2.02, 1.56, 1.29, 0.92, 0.44
6 hr at 603 K and $<10^{-4}$ N m^{-2} + 10 hr at 603 K with hydrogen at 290 N m^{-2}	6 min (Set B) and 15 min (Set C) with hydrogen at 290 N m^{-2}	9	A 1–3	604	Stoichiometric group	190, 188, 187	2.09, 2.02, 1.54
			B 1–6	604		216, 243, 162, 123, 87, 38	1.38, 1.90, 1.51, 1.40, 1.12, 0.46
			C 1–6	603		251, 206, 161, 124, 80, 40	1.94, 1.91, 1.53, 1.20, 1.00, 0.46

TABLE 1 (*Continued*)

Initial pretreatment before each group	Immediate pretreatment before each reaction	*Group*	Set and *run*	Temp (K)	Initial hydrogen : oxygen ratio	Initial hydrogen pressure (N m^{-2})	Initial rate (N m^{-2} s^{-1})
5 hr at 603 K and $<10^{-4}$ N m^{-2} + 10 hr at 603 K with hydrogen at 70 N m^{-2}	6 min (Set B) and 15 min (Set C) with hydrogen at 70 N m^{-2}	10	A 1–3	603	Stoichiometric group	190, 188, 182	1.98, 2.02, 1.61
			B 1–6	603		250, 201, 158, 124, 83, 40	1.87, 1.48, 1.88, 1.56, 1.07, 0.45
			C 1–6	603		245, 203, 161, 125, 84, 39	2.45, 1.74, 1.71, 1.27, 1.14, 0.47
5 hr at 663 K and $<10^{-4}$ N m^{-2} + 10 hr at 663 K with hydrogen at 290 N m^{-2}	6 min (Set B) and 15 min (Set C) with hydrogen at 300 N m^{-2}	11	A 1–3	664	Stoichiometric group	191, 184, 185	1.60, 2.29, 2.03
			B 1–6	664		246, 197, 164, 125, 78, 41	2.38, 2.00, 1.88, 1.26, 1.00, 0.46
			C 1–6	663		250, 205, 165, 125, 82, 40	2.96, 1.82, 1.85, 1.45, 0.92, 0.39
5 hr at 723 K and $<10^{-4}$ N m^{-2} + 10 hr at 723 K with hydrogen at 290 N m^{-2}	6 min (Set B) and 15 min (Set C) with hydrogen at 300 N m^{-2}	12	A 1–3	723	Stoichiometric group	189, 183, 184	1.98, 1.81, 2.06
			B 1–6	723		248, 206, 161, 124, 79, 44	2.86, 2.12, 1.86, 1.35, 0.98, 0.41
			C 1–6	723		254, 206, 162, 125, 81, 36	2.21, 1.96, 1.59, 1.08, 0.80, —
6 days at 773 K and $<10^{-4}$ N m^{-2} + 12 hr at 603 K and $<10^{-4}$ N m^{-2}		13	A 1–3	605	2.0	206, 199, 203	1.72, 1.42, 1.51
			B 1–5	603	2.0	289, 207, 144, 104, 74	1.96, 1.51, 1.57, 1.03, 0.72
			C 1–5	603	1.8	260, 185, 129, 90, 69	1.72, 0.67, 0.53, 0.50, 0.21
			D 1–5	603	2.2	244, 185, 109, 103, 68	1.79, 0.88, 0.51, 0.51, 0.38

15.5 hr at 603 K and $<10^{-4}$ N m^{-2}	14	A 1–3	603	2.0	206, 203, 205	1.46, 1.71, 1.46
		B 1–5	603	2.5	306, 218, 225, 88, 62	1.80, 0.88, —, 0.22, 0.24
		C 1–5	603	1.5	252, 178, 123, 90, 63	2.65, 1.48, 1.29, 1.00, 0.73
		D 1–5	604	2.9	305, 216, 152, 110, 78	1.86, 0.24, 0.20, 0.18, 0.15
		E 1–6	605	1.0	212, 149, 106, 77, 55, 32	2.62, 1.79, 1.82, 1.58, 1.17, 0.51
12.5 hr at 603 K and $<10^{-4}$ N m^{-2}	15	A 1–3	603	2.0	206, 200, 203	1.72, 1.51, 1.46
		B 1–5	603	5.0	300, 199, 152, 109, 77	0.66, 0.33, 0.12, 0.11, 0.10
		C 1–5	603	0.20	61, 42, 29, 22, 15	0.66, 0.08, 0.07, 0.07, 0.08
		D 1–5	603	10.0	313, 221, 157, 113, 80	0.12, 0.06, 0.05, 0.04, 0.04
24 hr at 773 K and $<10^{-4}$ N m^{-2} + 15 hr at 663 K and $<10^{-4}$ N m^{-2}	16	A 1–3	665	2.0	206, 206, 201	1.08, 1.31, 1.05
		B 1–5	663	2.0	294, 216, 153, 110, 77	1.72, 1.13, 0.81, 0.64, 0.47
		C 1–5	663	1.7	226, 159, 114, 79, 55	1.45, 0.94, 0.68, 0.47, 0.26
		D 1–5	663	2.3	298, 211, 147, 106, 75	1.43, 0.32, 0.25, 0.22, 0.19
		E 1–5	663	1.5	224, 157, 111, 78, 57	1.78, 0.98, 0.78, 0.54, 0.42
		F 1–6	663	2.5	286, 203, 144, 103, 68, 61	1.14, 0.28, 0.25, 0.20, 0.16, 0.16
7.5 hr at 663 K and $<10^{-4}$ N m^{-2}	17	A 1–3	666	2.0	203, 203, 200	1.06, 1.10, 1.11
		B 1–5	663	3.0	283, 197, 203, 124, 59	0.76, 0.23, —, 0.19, 0.15
		C 1–5	663	1.0	202, 141, 98, 71, 51	2.74, 1.74, 1.34, 0.97, 0.73
		D 1–5	663	5.1	299, 210, 167, 107, 77	0.22, 0.11, 0.85, 0.08, 0.07
		E 1–5	663	0.20	61, 43, 30, 21, 14	0.58, 0.14, 0.37, 0.25, 0.23
		F 1–5	664	9.9	302, 214, 153, 110, 77	0.08, 0.06, 0.05, 0.04, 0.04

TABLE 1 (*Continued*)

Initial pretreatment before each group	Immediate pretreatment before each reaction	Group	Set and run	Temp (K)	Initial hydrogen : oxygen ratio	Initial hydrogen pressure ($N\ m^{-2}$)	Initial rate ($N\ m^{-2}\ s^{-1}$)
24 hr at 773 K and $<10^{-4}\ N\ m^{-2}$ + 12 hr at 543 K and $<10^{-4}\ N\ m^{-2}$		18	A 1-3	546	2.0	204, 204, 207	0.30, 0.21, 0.22
			B 1-5	543	2.0	285, 203, 142, 103, 72	0.54, 0.20, 0.15, 0.16, 0.14
			C 1-5	543	1.7	262, 186, 131, 94, 69	0.78, 0.18, 0.33, 0.16, 0.14
			D 1-5	543	2.3	315, 222, 240, 89, 63	0.50, 0.15, 0.17, 0.10, 0.10
			E 1-5	543	1.5	252, 179, 125, 90, 63	0.62, 0.22, 0.17, 0.16, 0.16
			F 1-5	544	2.5	309, 221, 155, 110, 79	0.21, 0.13, 0.10, 0.09, 0.08
8 hr at 543 K and $<10^{-4}\ N\ m^{-2}$		19	A 1-3	544	2.0	201, 201, 199	0.21, 0.18, 0.18
			B 1-5	543	3.0	306, 222, 156, 113, 79	0.14, 0.11, 0.08, 0.07, 0.07
			C 1-5	543	1.0	204, 144, 101, 70, 52	0.81, 0.65, 0.45, 0.37, 0.31
			D 1-5	543	5.1	307, 220, 155, 112, 77	0.09, 0.06, 0.04, 0.04, 0.03
			E 1-5	543	0.20	83, 33, 24, 16, 10	0.37, 0.14, 0.14, 0.03, 0.03
			F 1-5	543	9.4	308, 220, 156, 111, 77	0.04, 0.04, 0.02 0.02, 0.02
24 hr at 773 K and $<10^{-4}\ N\ m^{-2}$ + 12 hr at 723 K and $<10^{-4}\ N\ m^{-2}$		20	A 1-3	726	2.0	205, 203, 198	0.55, 0.72, 0.62
			B 1-5	723	2.0	304, 218, 155, 108, 78	0.89, 0.64, 0.27, 0.41, 0.30
			C 1-5	723	1.8	301, 213, 152, 108, 77	1.13, 0.67, 0.49, 0.36, 0.27
			D 1-5	723	2.3	285, 201, 140, 102, 73	0.66, 0.18, 0.33, 0.25, 0.12
			E 1-5	723	1.5	292, 207, 148, 102, 75	1.29, 0.76, 0.56, 0.40, 0.31
			F 1-5	723	2.5	298, 213, 149, 106, 74	0.58, 0.20, 0.16, 0.16, 0.11

9 hr at 723 K and $<10^{-4}$ N m^{-2}	21	A 1–3	723	2.0	201, 196, 194	0.72, —, 0.68
		B 1–5	722	3.0	283, 200, 142, 103, 73	0.20, 0.16, 0.12, 0.11, 0.10
		C 1–5	723	1.0	211, 149, 103, 73, 53	1.94, 1.04, 0.65, 0.54, 0.37
		D 1–5	723	5.1	281, 201, 141, 100, 71	0.16, 0.10, 0.07, 0.08, 0.07
		E 1–5	723	0.20	59, 41, 29, 20, 14	0.70, 0.40, 0.41, 0.29, 0.24
		F 1–5	723	10.0	309, 218, 153, 113, 79	0.07, 0.04, 0.03, 0.05, 0.04
10 hr at 663 K and $<10^{-4}$ N m^{-2}	22	A 1–3	635	2.0	199, 196, 199	1.15, 1.11, 1.13
		B 1–3	633	2.0	267, 135, 75	1.40, 0.76, 0.49
		C 1–3	633	1.7	227, 109, 57	1.19, 0.67, 0.35
		D 1–3	632	2.0	285, 144, 73	1.28, 0.66, 0.39
		E 1–3	632	2.2	288, 121, 82	0.85, —, 0.41
15 hr at 573 K and $<10^{-4}$ N m^{-2}	23	A 1–3	575	2.0	196, 197, 195	0.95, 0.78, 0.77
		B 1–3	573	2.0	283, 134, 67	0.98, 0.56, 0.37
		C 1–3	573	1.7	270, 133, 63	1.18, 0.54, 0.36
		D 1–3	573	2.0	293, 135, 71	0.92, 0.47, 0.30
		E 1–3	574	2.3	283, 139, 72	0.74, 0.35, 0.28
16 hr at 603 K and $<10^{-4}$ N m^{-2}	24	A 1–3	605	2.0	199, 194, 196	1.10, 0.93, 0.71
		B 1–3	604	2.0	292, 140, 76	1.43, 0.58, 0.41
		C 1–3	603	1.7	267, 132, 66	1.42, 0.63, 0.44
		D 1–3	602	2.0	245, 144, 70	—, 0.60, 0.26
		E 1–3	603	2.3	276, 137, 67	0.59, 0.43, 0.28
15 hr at 603 K and $<10^{-4}$ N m^{-2}	25	A 1–3	605	2.0	204, 202, 196	1.25, 1.02, 0.82
		B 1–3	604	2.0	271 + 41(N_2), 126 + 19(N_2), 62 + 9(N_2)	0.98, 0.57, 0.35
		C 1–3	604	2.0	210 + 157(N_2), 132 + 89(N_2), 56 + 42(N_2)	0.80, 0.49, 0.32
		D 1–4	603	2.0	139 + 206(N_2), 68 + 100(N_2), 33 + 49(N_2), 17 + 25(N_2)	0.38, 0.27, 0.19, 0.12

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[a] 1 A 1–3 signifies the three reactions 1 A1, 1 A2 and 1 A3.

the pretreating gas is decreased consecutively for groups 2–4 at constant temperature, and then the temperature is increased at constant pretreatment pressure for groups 5 and 6. Similarly, groups 7–12 (using catalyst sample 2) illustrate the effects of hydrogen pretreatment.

Groups 13–24 (using catalyst sample 3) are experiments conducted at various pressures, temperatures and stoichiometries with no initial or immediate pretreatment with hydrogen or oxygen. Group 25 (using catalyst sample 3) is a special group showing the effect of an inert gas.

The first three reactions in every group (reactions A1–3) are stoichiometric at an approximately constant initial hydrogen pressure of 200 N m^{-2}.

An IBM 1130 computer was used in the analysis of the data, the reaction rates being determined by cubic spline interpolation (*19*).

RESULTS

Structure of Erbium Oxide

Although most of the lanthanide oxides can exist in three different crystalline modifications, erbium oxide only forms the stable cubic modification (*C*-type) with a space group $Ia3(T_h{}^7)$. X-Ray and ir analysis confirmed the structure for erbium oxide and indicated that the surface was free of water and hydroxyl groups after the normal pretreatment procedures.

Analysis of the Data

The data were initially analyzed using the general equation

$$-\frac{dP_T}{dt} = k_1 P_{H_2}{}^x P_{O_2}{}^y, \qquad (2)$$

where P_{H_2} and P_{O_2} are the partial pressures of hydrogen and oxygen, respectively, and k_1 is the pseudo-rate constant. For stoichiometric reactions, plots of log(rate) versus log(total pressure) gave the overall order, and for nonstoichiometric reactions, plots of log(rate) versus log(pressure minor component) gave an approximation to the order for the gas present in less than the stoichiometric amount. Typical plots are shown for stoichiometric reactions in Fig. 1, and for nonstoichiometric reactions in Figs. 2 and 3. The data are presented in Tables 1, 2 and 3. Table 1 gives the initial rate data for all reactions, and Tables 2 and 3 summarize the experimental conditions and give the average orders with respect to time for the stoichiometric and nonstoichiometric reactions, respectively. The orders with respect to time are taken from the linear section of the log plots, after the initial high slope. These orders,

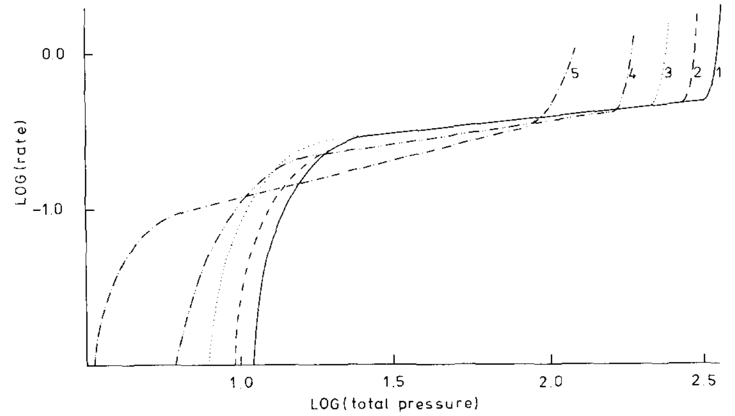

Fig. 1. Log(rate) versus log(total pressure) plot for stoichiometric group 7 at 603 K. The numbers refer to the runs in set D.

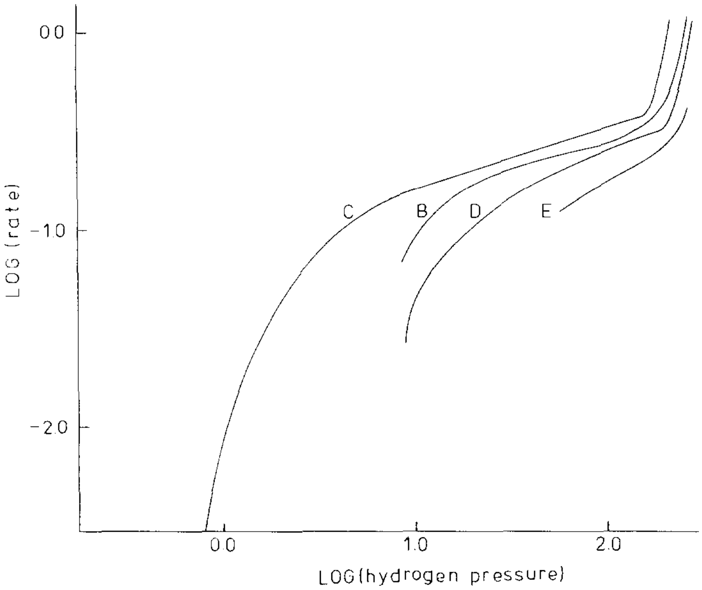

FIG. 2. Log(rate) versus log(hydrogen pressure) plot for nonstoichiometric group 22 at 633 K. The letters refer to the sets, the first run being plotted in each case.

shown in Table 3, are average values calculated for hydrogen : oxygen ratios greater than 3 : 1 (oxygen order), and less than 1 : 1 (hydrogen order).

The data were also analyzed by drawing isobaric curves through nonstoichiometric reactions, at a constant temperature. Typical isobars are shown in Figs. 4 (hydrogen isobar) and 5 (oxygen isobar). The results from the isobars are summarized in Tables 4, 5 and 6.

Summary of Results

Shape of the Log Plots

Most of the plots of log(rate) versus log(pressure) show three distinct regions: an initial section with a large slope, lasting for about 1 min; a second, linear section, lasting for most of the reaction; and a third section with a rapidly increasing slope. The initial section is less pronounced in

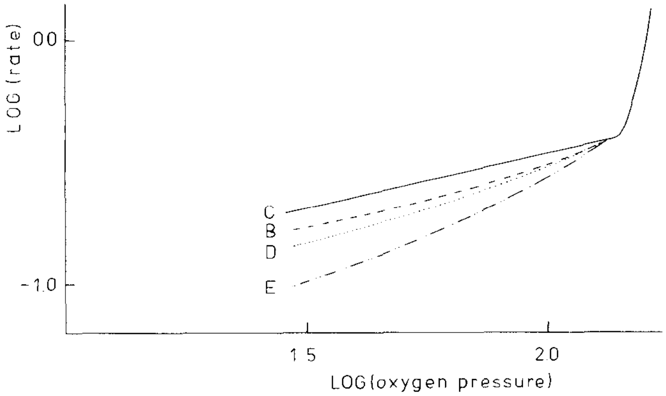

FIG. 3. Log(rate) versus log(oxygen pressure) plot for nonstoichiometric group 23 at 574 K. The letters refer to the sets, the first run being plotted in each case.

TABLE 2

SUMMARY OF THE RESULTS FROM THE STOICHIOMETRIC HYDROGEN–OXYGEN REACTION ON ERBIUM OXIDE

Group	Pretreating gas	Av temp (K)	Initial hydrogen pressure range (N m^{-2})	Overall order with respect to time
1	Oxygen	604	50–100	0.3
			100–130	0.2
			130–170	0.1
			170–260	0
2	Oxygen	603	60	0.3
			60–130	0.2
			130–170	0.1
			170–250	0
3	Oxygen	603	60–120	0.3
			120–130	0.2
			130–190	0.1
			190–250	0
4	Oxygen	603	40	0.7
			80–140	0.2
			140–250	0.1
5	Oxygen	663	40	0.7
			80–120	0.4
			120–250	0.3
			260	0.2
6	Oxygen	723	40	0.8
			80–110	0.6
			110–120	0.5
			120–170	0.4
			170–260	0.3
7	Hydrogen	603	80	0.5
			120	0.4
			130–140	0.3
			140–200	0.2
8	Hydrogen	604	40	0.6
			70–120	0.3
			120–250	0.2
			180–250	0.1
9	Hydrogen	604	40	0.6
			80–120	0.3
			120–250	0.2
10	Hydrogen	603	40	0.6
			80	0.2
			90–250	0.1
11	Hydrogen	663	40	0.7
			80	0.5
			120–200	0.3
			200–250	0.2
12	Hydrogen	723	40	0.7
			70	0.5
			90	0.4
			100–200	0.3
			200–260	0.2
13	None	604	80–120	0.5
			120–200	0.4
			200–280	0.3
			290	0.2
14	None	603	200	0.3
15	None	603	200	0.3
16	None	665	70–170	0.6
			170–240	0.5
			290	0.4
17	None	666	200	0.5
18	None	545	70–110	0.5
			110–200	0.4
			200	0.3
19	None	544	200	0.6–0.7
20	None	724	80–310	0.7–0.6
21	None	723	200	0.6
22	None	634	80	0.6
			130	0.5
			200–270	0.4
23	None	574	70–170	0.5
			170–290	0.4
24	None	605	80	0.6
			130–200	0.5
			200–290	0.4
25	None	604	10–200	0.7–0.4

TABLE 3
SUMMARY OF THE RESULTS FROM THE NONSTOICHIOMETRIC HYDROGEN–OXYGEN REACTION ON ERBIUM OXIDE

Reaction	Av temp (K)	Initial hydrogen: oxygen ratio	Av order with respect to time	
			Oxygen	Hydrogen
14 D	604	2.9	1.6	
14 E	605	1.0		1.1
15 B	603	5.0	1.6	
15 C	603	0.2		2.9
15 D	603	10.0	2.2	
17 B	663	3.0	1.0	
17 C	663	1.0		0.8
17 D	663	5.1	1.8	
17 E	663	0.20		2.1
17 F	664	9.9	1.6	
19 B	543	3.0	1.1	
19 C	543	1.0		1.8
19 D	543	5.1	1.4	
19 E	543	0.2		3.3
19 F	543	9.4	1.3	
21 B	722	3.0	0.9	
21 C	723	1.0		0.2
21 D	723	5.1	1.5	
21 E	723	0.20		1.7
21 F	723	10.0	2.2	

the log(rate) versus log(oxygen pressure) plots than in the other types of log plots.

Catalyst Activity and the Effect of Pretreatment

1. *Initial pretreatment.* The effect of initial pretreatment, that is, the pretreatment before a group of reactions, can be obtained by observing the activity of the standard A set in each group. For the fresh catalysts (groups 1, 7 and 13), the activity increases during the first few reactions. With oxygen pretreatment (groups 1–6), the activity decreases as the pressure of the pretreating gas is decreased at constant temperature, and as the pretreatment temperature is increased at constant pressure. These effects are shown in Fig. 6. With hydrogen pretreatment (groups 7–12), the effects are less pronounced, though there is a slight increase in activity as the pressure of the pretreating gas is decreased at constant temperature. In addition, the activity increases for successive runs within the standard sets. With no pretreating gas (groups 13–25), the activity remains fairly constant for groups evacuated at the reaction temperature, whereas, for groups evacuated at 773 K, there is an irregular change in activity within the first set. It should be noted that many of the reactions in groups 13–25 are nonstoichiometric, having the effect of pretreating the catalyst for subsequent reactions with the gas in stoichiometric excess.

2. *Immediate pretreatment.* The effect of immediate pretreatment, that is, the pretreatment before each reaction, is the same as that for initial pretreatment except that as the pretreatment temperature is in-

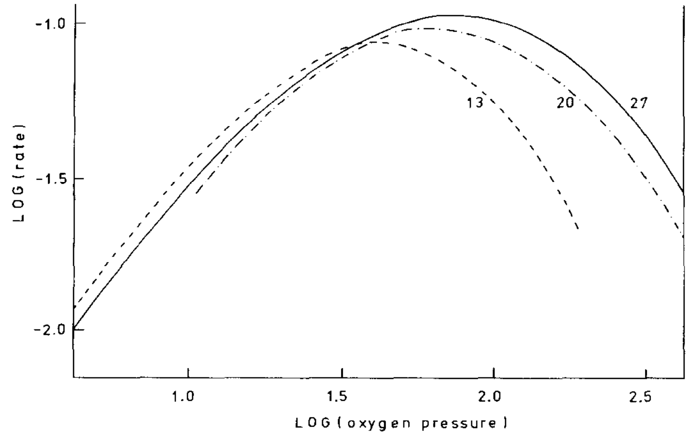

FIG. 4. Hydrogen isobars from groups 20 and 21 at 723 K. The constant hydrogen pressures are shown in N m^{-2}.

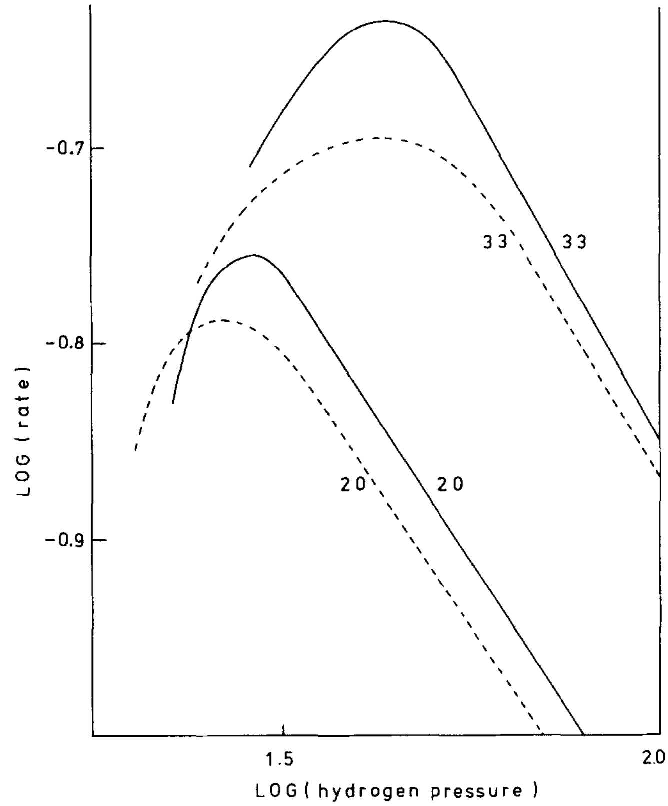

FIG. 5. Oxygen isobars from group 22 at 633 K (—) and group 24 at 603 K (---). The constant oxygen pressures are shown in N m^{-2}.

creased at constant hydrogen pressure the activity decreases slightly. Also, for hydrogen pretreatment at 723 K the activity decreases as the length of pretreatment time increases.

A comparison of the activity of the catalyst after various pretreatments shows that at all temperatures the catalyst is more active after pretreatment by either hydrogen or oxygen than it is when no pretreating gas is used; the first reactions in groups 13–25 being particularly slow. Also, the change in activity with temperature for the standard reactions in groups 13–25, shows that the activity is highest in the temperature range 603–633 K, the activity being lower both above and below these temperatures.

The catalyst can be regenerated so that it will yield reproducible results under similar conditions, and there is no decrease in activity with time.

The effect of pretreatment on the kinetic orders and isobars are described below.

Kinetic Orders

For stoichiometric reactions, the overall orders with respect to time are summarized in Table 2. The orders range from zero at high pressures for groups 1–3, to about 0.8 at low pressures and high temperatures. The effects of pressure and temperature follow a similar pattern for the different pretreatments; the orders decreasing with increasing initial pressure or decreasing reaction temperature. The pressure effect is most pronounced after hydrogen pretreatment and least pronounced after oxygen pretreatment, whereas, the converse is true for the temperature effect.

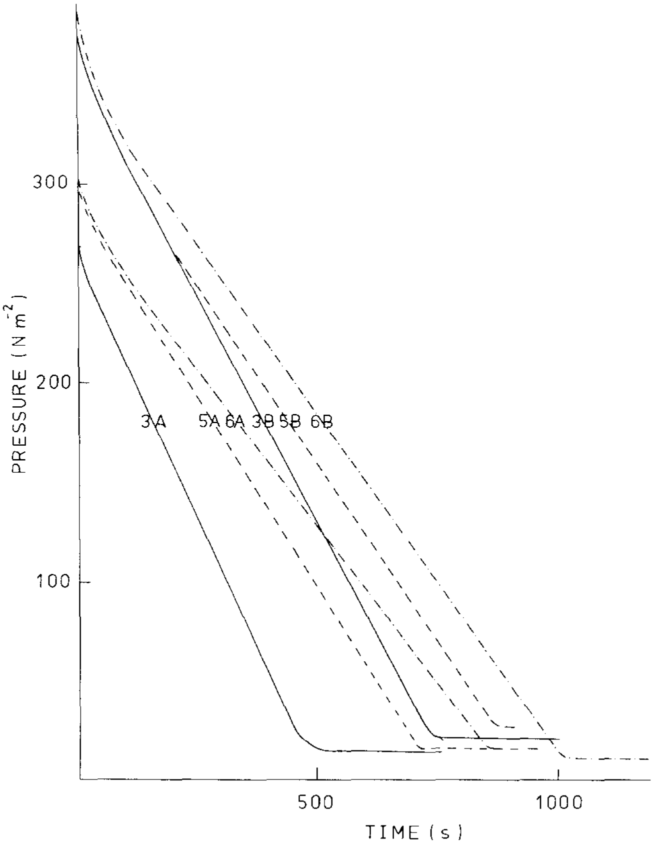

FIG. 6. Total pressure versus time plots for the first runs in sets 3A (603 K), 5A (663 K) and 6A (723 K) all with initial oxygen pretreatment, and 3B (603 K), 5B (663 K) and 6B (722 K) all with initial plus immediate oxygen pretreatment.

The orders are highest when no pretreating gas is used and lowest after oxygen pretreatment. And, the orders decrease as the hydrogen pretreatment pressure decreases, whereas, the orders increase as the oxygen pretreatment pressure decreases. There is a tendency for the first reactions of any group to have irregular orders.

The orders with respect to concentration could not be obtained accurately because of the inherent difficulty in measuring initial rates and the problems associated with the initial large decrease in total pressure. However, orders were obtained whenever possible, most of them falling in the range 0.8–1.0. The lowest orders are about 0.4 and the limiting value at the highest temperatures studied is about 1.0.

For nonstoichiometric reactions, the calculated average orders with respect to time are shown in Table 3. No overall pattern emerges from this method of analysis except an indication that the order lies between 1 and 2 for oxygen, and 1 and 3 for hydrogen.

Isobars

At all temperatures, the hydrogen and oxygen isobars have maxima, and the results from these isobars, drawn at approximately regular intervals, are given in Table 4. The average slopes and ratios at the maxima are shown in Table 5, and also the rise in values with increasing pressure of the appropriate isobar in cases where a trend is perceptible. The hydrogen isobars

TABLE 4
SUMMARY OF THE RESULTS FROM THE ISOBARIC PLOTS AT CONSTANT HYDROGEN OR OXYGEN PRESSURE

		Isobar at constant hydrogen pressure			Isobar at constant oxygen pressure		
			At maximum of isobar			At maximum of isobar	
Group	Av temp (K)	Constant hydrogen pressure (N m^{-2})	Oxygen pressure (N m^{-2})	Hydrogen: oxygen ratio	Constant oxygen pressure (N m^{-2})	Hydrogen pressure (N m^{-2})	Hydrogen: oxygen ratio
18, 19	543	80	107	0.8	80	47	0.6
		53	80	0.7	53	33	0.6
		27	47	0.6	27	27	1.0
		20	40	0.5	20	17	0.9
		13	31	0.4			
23	574	260	137	1.9	113	181	1.6
		247	145	1.7	107	171	1.6
		233	166	1.4	100	150	1.5
		220	169	1.3	93	140	1.5
		207	159	1.3	87	131	1.5
		193	161	1.2	80	120	1.5
		180	164	1.1	73	102	1.4
		167	152	1.1	27	35	1.3
		153	153	1.0	20	26	1.3
		140	140	1.0	13	16	1.2
		87	79	1.1			
		73	61	1.2			
		47	59	0.8			
		33	83	0.4			
		20	40	0.5			
13, 14 15, 24	603	133	133	1.0	107	139	1.3
		107	119	0.9	53	48	0.9
		93	93	1.0	40	36	0.9
		80	100	0.8	27	30	1.1
		53	88	0.6	13	14	1.1
		40	67	0.6			
		27	45	0.6			
		13	26	0.5			
22	633	200	181	1.1	113	113	1.0
		87	73	1.2	107	118	1.1
		80	73	1.1	100	100	1.0
		73	81	0.9	93	84	0.9
		67	84	0.8	87	70	0.8
		40	57	0.7	80	64	0.8
		27	39	0.7	73	58	0.8
		13	26	0.5	27	30	1.1
					20	22	1.1
					13	13	1.0
16, 17	663	80	80	1.0	53	53	1.0
		53	67	0.8	27	27	1.0
		27	45	0.6	20	20	1.0
		20	36	0.6			
		13	33	0.4			

TABLE 4 (*Continued*)

		Isobar at constant hydrogen pressure			Isobar at constant oxygen pressure		
			At maximum of isobar			At maximum of isobar	
Group	Av temp (K)	Constant hydrogen pressure ($N\ m^{-2}$)	Oxygen pressure ($N\ m^{-2}$)	Hydrogen: oxygen ratio	Constant oxygen pressure ($N\ m^{-2}$)	Hydrogen pressure ($N\ m^{-2}$)	Hydrogen: oxygen ratio
20, 21	723	80	100	0.8	27	24	0.9
		27	54	0.5	13	12	0.9
		20	50	0.4			
		13	43	0.3			

at 723 K and 13, 20 and 27 $N\ m^{-2}$ are shown in Fig. 4. The oxygen isobars at 603 and 633 K, and 20 and 33 $N\ m^{-2}$ are shown in Fig. 5.

The hydrogen isobars exhibit ratios at the maxima which rise with increasing pressure, whereas these ratios tend to remain constant for the oxygen isobars. For any particular temperature, the maxima in the hydrogen and oxygen isobars are similar, and there is no obvious trend with temperature. There is an upward displacement of these maxima for isobars drawn through the initial section of the log(rate) versus log(pressure) plots.

Accurate slopes on either side of the isobaric maxima are difficult to measure. A consistent value of 1.0 ± 0.2 is obtained for the positive slope of the hydrogen isobars, and a trend towards absolute values of 1 and 2 are noted for the negative slopes of the oxygen and hydrogen isobars, respectively, as the pressure of the corresponding isobar increases.

DISCUSSION

Kinetic Expression

It has been shown previously (*17*) that the stoichiometric hydrogen–oxygen reaction obeys a kinetic expression of the form given in Eq. (1). Assuming that the rate is dependent on the fraction of active surface covered competitively by molecular hy-

TABLE 5
AVERAGE SLOPES AND MAXIMA FROM THE ISOBARS

				Slope of isobar	
Isobar	Group	Av temp (K)	Hydrogen: oxygen ratio at maxima of isobar	Low pressure side of maxima	High pressure side of maxima
Hydrogen	18, 19	543	0.4 to 0.8	1.1 ± 0.1	−1.7 ± 0.1
	23	574	0.4 to 1.9	0.9 ± 0.1	
	13, 14, 15, 24	603	0.5 to 1.0	1.0 ± 0.1	
	22	633	0.5 to 1.2	0.9 ± 0.1	−1.5 to −2.0
	16, 17	663	0.4 to 1.0	1.1 ± 0.3	
	20, 21	723	0.3 to 0.8	0.9 ± 0.2	
Oxygen	18, 19	543	0.8 ± 0.2	1.8	−0.4 to −0.6
	23	574	1.4 ± 0.2		−0.3 to −0.9
	13, 14, 15, 24	603	1.1 ± 0.2		−0.3 to −1.2
	22	633	1.0 ± 0.2		−0.5 to −0.9
	16, 17	663	1.0		−0.3 to −0.9
	20, 21	723	0.9		0 to −0.5

TABLE 6
CALCULATED VALUES FOR THE ADSORPTION COEFFICIENTS

Temp (K)	From Eq. (4) b_{H_2} ($N^{-1}m^2$)	b_{O_2} ($N^{-1}m^2$)	From Eq. (4a) b_{H_2} ($N^{-1}m^2$)	b_{O_2} ($N^{-1}m^2$)
543	0.06	0.06	0.06	0.03
574	0.04	0.05	0.05	0.03
603	0.05	0.05	0.05	0.03
663	0.04	0.05	0.04	0.03
723	0.04	0.04	0.04	0.02

drogen and oxygen, and that adsorption obeys the Langmuir isotherm, Eq. (1) could be considered a reduced form of

$$-\frac{dP_T}{dt}=\frac{k(b_{H_2}P_{H_2})^x(b_{O_2}P_{O_2})^y}{(1+b_{H_2}P_{H_2}+b_{O_2}P_{O_2})^{x+y}}, \quad (3)$$

where k is a proportionality constant, b_{H_2} and b_{O_2} are the adsorption coefficients for hydrogen and oxygen, respectively, and $x+y=m$ in Eq. (1).

The results, after the initial fast rate of reaction, will now be discussed in relation to Eq. (3) to determine the validity of this kinetic expression.

Kinetic Orders

According to Eq. (3) the overall order with respect to time for a stoichiometric mixture can vary from zero when $b_{H_2}P_{H_2} + b_{O_2}P_{O_2} >> 1$ (high pressures and low temperatures), to $x+y$ when $b_{H_2}P_{H_2} + b_{O_2}P_{O_2} << 1$ (low pressures and high temperatures). The stoichiometric results in this paper (Table 2) and a previous paper (*17*) show this trend, with a maximum observed order of about 0.8 at the highest temperatures (723 K) and lowest pressures (about 40 N m^{-2}). Zero-order kinetics were only observed after oxygen pretreatment at the lowest temperatures studied (603 K) and the highest pressures (200–250 N m^{-2}). These results would indicate that $b_{H_2}P_{H_2} + b_{O_2}P_{O_2} \approx 1$ at the lowest pressures used and in the temperature range 545–724 K. In the previous paper (*17*), where the reaction was studied at lower temperatures, zero-order kinetics were obeyed for 50% of the reaction at temperatures below 423 K with total initial pressures of about 400 N m^{-2}.

For nonstoichiometric reactions, an approximation to the order with respect to time is obtained by the method described previously, provided that Eq. (2) is a valid reduction of Eq. (3). From the results shown in Table 3 it is obvious that this method is not suitable in this case, particularly with regard to calculating the order in hydrogen. To obtain the order in hydrogen, the pressure of oxygen must be sufficiently high so that log P_{O_2} can be considered effectively constant, and so that $1 + b_{H_2}P_{H_2}$ can be neglected with respect to $b_{O_2}P_{O_2}$, but not so high that preferential adsorption of oxygen affects the kinetics. If the oxygen adsorption coefficient is relatively low, it may be impossible to obtain an appropriate pressure of oxygen to meet both the above-mentioned criteria.

The fact that pretreatment by either hydrogen or oxygen lowers the orders shows that both these species are adsorbed. The decrease in order and hence increase in the adsorption coefficients, may be due to the creation of more active sites or simply to the fact that one or other of the reactants is already present on the surface. If the latter is the case, the smaller effect of hydrogen pretreatment may indicate that hydrogen is readily adsorbed during the reaction, that is, that $b_{H_2} > b_{O_2}$. This observation is paralleled by the effects of pretreatment on activity. There is an increase in activity after pretreatment by either hydrogen or oxygen, with oxygen having the greater effect. Prolonged exposure to high pressures of hydrogen causes a decrease in activity due to saturation of the surface with hydrogen.

Isobars

In order to obtain maxima in the isobars, there must be competitive adsorption as reflected in Eq. (3). Information can be obtained about the values for x and y from an analysis of the slopes on either side of the maxima and from the relative positions of the maxima on the hydrogen and oxygen isobars at a specific temperature. From a reduction of Eq. (3), x can be equated to the positive slope of the oxygen isobar, and y can be equated to the positive slope of the hydrogen isobar. Similarly, but with less accuracy, x can be equated to the absolute value of the negative slope of the hydrogen isobar (with accuracy increasing as the hydrogen pressure increases), and y can be equated to the absolute value of the negative slope of the oxygen isobar (with accuracy increasing as the oxygen pressure increases). Hence, from the results summarized in Table 5, it can be stated that $y = 1.0 \pm 0.2$ and x tends towards 2. These values are consistent with the ranges shown in Tables 2 and 3.

Differentiation of Eq. (3), using $x = 1$ or 2 and $y = 1$, gives the following relationships for the positions of the maxima in the hydrogen and oxygen isobars.

For $x = y = 1$, hydrogen isobar,

$$\frac{P_{H_2}}{P_{O_2}} = \frac{b_{O_2}P_{O_2} - 1}{b_{H_2}P_{O_2}}, \tag{4}$$

for $x = y = 1$, oxygen isobar,

$$\frac{P_{H_2}}{P_{O_2}} = \frac{b_{O_2}P_{O_2} + 1}{b_{H_2}P_{O_2}}, \tag{5}$$

for $x = 2$, $y = 1$, hydrogen isobar,

$$\frac{P_{H_2}}{P_{O_2}} = \frac{2b_{O_2}P_{O_2} - 1}{b_{H_2}P_{O_2}}, \text{ and,} \tag{4a}$$

for $x = 2$, $y = 1$, oxygen isobar,

$$\frac{P_{H_2}}{P_{O_2}} = \frac{2b_{O_2}P_{O_2} + 2}{b_{H_2}P_{O_2}}. \tag{5a}$$

From the variation in ratio at the maxima with oxygen pressure, average values for b_{H_2} and b_{O_2} can be calculated from Eqs. (4) and (4a), and these are shown in Table 6 at five different temperatures. The order of magnitude for the adsorption coefficients is realistic and would make $(b_{H_2}P_{H_2} + b_{O_2}P_{O_2})$ close to unity, giving the low overall orders. In addition, the slight decrease in the adsorption coefficients with increasing temperature is paralleled by the slight change in activity and order with temperature. There is an indication that the adsorption coefficients at 633 K are slightly higher than those at lower and higher temperatures, but the erratic nature of the results precludes an accurate determination. This effect is also observed by the maximum catalyst activity in the temperature range 603–633 K. It is likely that there is a change in the type of adsorption occurring in this temperature range, an effect which has already been noted for neodymium oxide (*18*) and confirmed by adsorption studies.

It is impossible to distinguish between the two likely values for x on the basis of an analysis of the relative values for the adsorption coefficients except to note that previous discussion predicts that b_{H_2} may be greater than b_{O_2} and hence, $x = 2$ would be the more appropriate value.

Attempts were made to fit the results from the stoichiometric reactions to the integrated form of Eq. (1). This analysis is inconclusive, with slightly better fits obtained with $m = 1$ or 3 than with $m = 2$.

In summary, after the initial fast section, the reaction data fit a kinetic expression of the form shown in Eq. (3). The most likely values for x and y are 2 and 1, respectively, although the value for x cannot be obtained with great certainty.

Mechanism

Information about possible mechanisms can be obtained from the effects of pretreatment and from the characteristics of the kinetic expression.

The presence of anion vacancies in erbium oxide makes this catalyst particularly sensitive to pretreatment. From the results of the decomposition of nitrous oxide (*8*), it has been shown that activity is increased by exposure of the catalyst to oxygen, with the creation of F centers. Activity is also increased by heating *in vacuo* to very high temperatures. Minachev (*1*) shows that double bond migration in olefins only occurs above 613 K when erbium oxide is evacuated at 773 K, whereas migration occurs at room temperature after evacuation at 1000 K. The effect of hydrogen is generally less pronounced. For example, the activation energy for the hydrogen–oxygen reaction changes from 37 kJ mol^{-1} for a stoichiometric mixture (*17*) to 33 kJ mol^{-1} in hydrogen excess (*16*). Similar effects are observed in the present work, showing that both adsorbed hydrogen and adsorbed oxygen are participating in the overall mechanism. Both the activity and the adsorption coefficients are increased by pretreatment with either gas.

The initial section of the log plots is still apparent after pretreatment. This result, coupled with the fact that isobars (displaced upwards) can be drawn through these initial sections, indicates that reaction first occurs on a small number of hyperactive sites, with a mechanism similar to that followed later in the reaction. Evidence for the presence of sites with differing activities is presented by the anomalous activity of fresh catalyst surfaces. However, deactivation of these sites soon occurs and the activity becomes constant, as can be seen from the similar activities of groups 13–15 and 24.

Several mechanisms can give rise to Eq. (3) with $x = 2$ and $y = 1$, and still be compatable with all the evidence. A probable mechanism would be based on the following steps.

$$\begin{aligned} H_{2(g)} &\rightleftarrows H_{2(ads)}, \\ O_{2(g)} &\rightleftarrows O_{2(ads)}, \\ H_{2(ads)} + O_{2(ads)} &\rightleftarrows H_2O_{2(ads)}, \\ H_2O_{2(ads)} + H_{2(ads)} &\rightarrow 2H_2O_{(ads)}, \\ H_2O_{(ads)} &\rightleftarrows H_2O_{(g)}. \end{aligned}$$

The adsorbed species formed in the third step is probably best represented as H_2O_2 rather than 2OH, and this can then react with additional adsorbed hydrogen by a concerted mechanism to form water. Although Minachev (*1*) concluded that the rate-determining step involved dissociatively adsorbed oxygen, there is no evidence for this in the present study.

In conclusion, the results obtained in this work, together with a previous investigation (*17*), show that the hydrogen–oxygen reaction is catalyzed by erbium oxide. Hydrogen and oxygen are competitively, nondissociatively, adsorbed on the surface and the rate-determining step involves the interaction between $H_{2(ads)}$ and $H_2O_{2(ads)}$. Hydrogen or oxygen pretreatment increases the activity of the catalyst.

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