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The Catalytic Activity of the Rare Earth Oxides for Parahydrogen Conversion and Hydrogen–Deuterium Equilibration

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Parahydrogen conversion and hydrogen–deuterium equilibration have been investigated on neodymium, gadolinium, dysprosium, and erbium oxides over the temperature range 77° to 657°K. At low temperatures, where the equilibration reaction is absent, the conversion proceeds by a paramagnetic mechanism in which the rate is dependent upon the 4*f* electronic structure of the oxides. There is evidence for a similar mechanism for conversion at intermediate temperatures (140–400°K). At high temperatures both the conversion and equilibration reaction proceed with comparable rates on all four oxides studied. Both reactions are considered to proceed by the same chemical mechanism, in which the similar outer electronic states, 5*s* and 5*p*, control catalytic activity.

INTRODUCTION

Few investigations have been made of the influence of 4*f* electronic structure on the catalytic properties of the rare earth oxides. Studies of ethyl alcohol decomposition (*1*) and of cyclohexane dehydrogenation (*2*) have shown little variation in activity over the series of oxides, and it has been suggested that the similar outer electronic states, 5*s* and 5*p*, control catalytic activity. The oxides have been found to be catalysts for carbon monoxide oxidation, but no comparison of activities was considered possible (*3*). This arose from the observation that the activities were dependent on oxygen and temperature pretreatments, and on unknown deviations from stoichiometry in cases where the rare earth ion can possess different valency states.

In a previous publication (*4*) it has been shown that neodymium oxide is a catalyst for the parahydrogen conversion over the temperature range 77° to 642°K. It was established that the conversion proceeded by a physical, paramagnetic mechanism at low temperatures and by a chemical mechanism at high temperatures. Comparison of experimental rates with those calculated from theoretical models showed that only a small fraction of the surface was catalytically active at all temperatures. One reason for this small active fraction may be that only cations situated at macro defects or next to surface anion vacancies are active. Alternatively, the surface may be almost saturated with irreversibly adsorbed water, in the form of hydroxyl ions, which block access to the neodymium ions. The present contribution reports experiments which were made to ascertain which, if either, of these explanations is correct. A full study of parahydrogen conversion and hydrogen–deuterium equilibration on gadolinium, dysprosium, and erbium oxides is also reported. The results of this study are discussed in conjunction with those of the earlier work on neodymium oxide.

EXPERIMENTAL

The apparatus, procedure, and method of calculating both experimental rate constants k_e and absolute rates k_m have previously been described (*4, 5*). The samples of oxide used were of "Specpure" grade supplied by Johnson, Matthey & Co., and had been prepared by heating the corresponding oxalates to ~1073°K. Surface areas were determined by the BET method using krypton at 77°K ($\sigma_{Kr} = 21$ Å^2), and were found to be independent of the time of evacuation at 673°K. The following specific surface areas, the mean of three determinations, were obtained: Nd_2O_3, 11.9 m^2/g; Sm_2O_3, 4.14 m^2/g; Gd_2O_3, 2.27 m^2/g; Dy_2O_3, 2.96 m^2/g; Er_2O_3, 2.77 m^2/g.

RESULTS

General

In the previous work on Nd_2O_3 (*4*) it was found that evacuation for 150 hr at 673°K gave a surface of reproducible activity. In an effort to determine why only a small fraction of the surface was responsible for this activity, an investigation of the effect of evacuation at higher temperatures has now been made. Three separate samples of Nd_2O_3 and one of Dy_2O_3 were first evacuated for 150 hr at 673°K, and then evacuated at a series of progressively higher temperatures. The catalytic activity for parahydrogen conversion at 77°K was determined after each evacuation. Table 1 shows the thermal history and rates of conversion at a hydrogen pressure of 4 mm Hg that were obtained for Dy_2O_3 and one representative sample of Nd_2O_3. It can be seen that the temperature of evacuation has no significant influence on the subsequent catalytic activity. Furthermore, it was observed that the pressure dependency (see below) also remained effectively unaltered after each thermal treatment.

TABLE 1
THE EFFECT OF HIGH-TEMPERATURE EVACUATION ON CATALYTIC ACTIVITY AT 77°K

Nd_2O_3		Dy_2O_3	
Evacuation	k_m (molecules/cm^2 sec)	Evacuation	k_m (molecules/cm^2 sec)
150 hr at 673°K	2.19×10^{13}	150 hr at 673°K	2.20×10^{14}
plus 14 hr at 793°K	2.50×10^{13}	plus 16 hr at 825°K	2.34×10^{14}
plus 16 hr at 950°K	3.03×10^{13}	plus 22 hr at 994°K	2.28×10^{14}
plus 16 hr at 1085°K	2.19×10^{13}	plus 16 hr at 1175°K	1.91×10^{14}

The effect of pretreating the oxide surface with hydrogen at high temperatures was investigated with Nd_2O_3. Such treatment could give rise to partial surface reduction and may also assist the removal of surface hydroxide ions. The hydrogen pretreatments and subsequent rates of conversion at 77°K and a hydrogen pressure of 4 mm Hg on a single sample of Nd_2O_3 are given below:

1. Evacuation for 150 hr at 673°K
   $k_m = 2.84 \times 10^{13}$ molecules/cm^2 sec
2. Heat for 64 hr in 2.2 mm of H_2 at 881°K, followed by 2 hr evacuation at 881°K
   $k_m = 3.15 \times 10^{13}$ molecules/cm^2 sec
3. Heat for 16 hr in 2.2 mm of H_2 at 1028°K, followed by 2 hr evacuation at 1028°K
   $k_m = 3.01 \times 10^{13}$ molecules/cm^2 sec

The rates, although higher than those previously observed for Nd_2O_3, show little variation on hydrogen pretreatment, and it is concluded that negligible surface reduction has taken place. Once again, the pressure dependency of conversion remained effectively unaltered.

If water is irreversibly adsorbed on rare earth oxides as surface hydroxyl ions it may be expected to undergo hydrogen isotope exchange with deuterium gas; this is known to occur with silica and alumina (*6, 7*). To test this, a sample of Nd_2O_3 was evacuated for 150 hr at 673°K and then exposed to deuterium for 72 hr at the same temperature. Analysis of the gas phase was then attempted using a micro-Pirani gauge, but the sensitivity was insufficient to determine if exchange had occurred. This experiment awaits repeating using a more sensitive method of gas analysis.

The above observations show that high-temperature evacuation and hydrogen pretreatment do not increase the catalytic activity to any marked extent. This suggests that evacuation for 150 hr at 673°K is sufficient to give a reproducibly clean surface, and this procedure was adopted for all oxides used in the present study.

The Effect of Temperature

The effect of temperature on the rate of conversion, at a constant hydrogen pressure of 4 mm, has been studied on Gd_2O_3, Dy_2O_3, and Er_2O_3. Two series of experiments were made on each oxide, one at increasing temperatures and one at decreasing temperatures. The results, plotted as log k_m against $1/T$°K, are shown in Figs. 1–3. Apart from small numerical differences, the plots show the same features for both series. The numerical differences probably arise from the presence of chemisorbed hydrogen atoms in the series at *decreasing temperatures*, which are absent

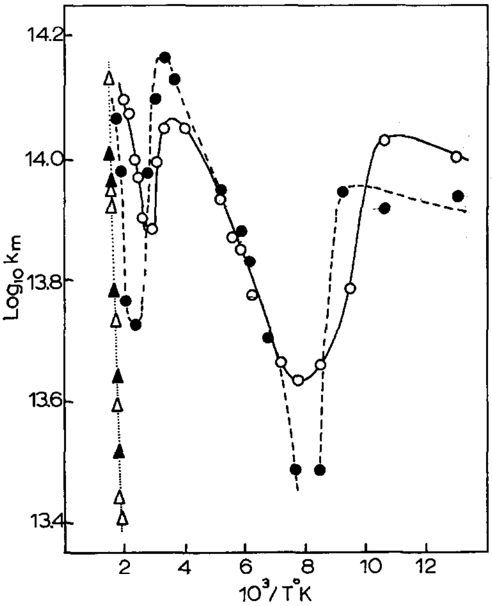

FIG. 1. Plots of $\log_{10}k_m$ against $1/T$°K for Gd_2O_3; -○-, parahydrogen conversion at increasing temperatures; --●--, parahydrogen conversion at decreasing temperatures; ···▲···, and ···△···, hydrogen–deuterium equilibration.

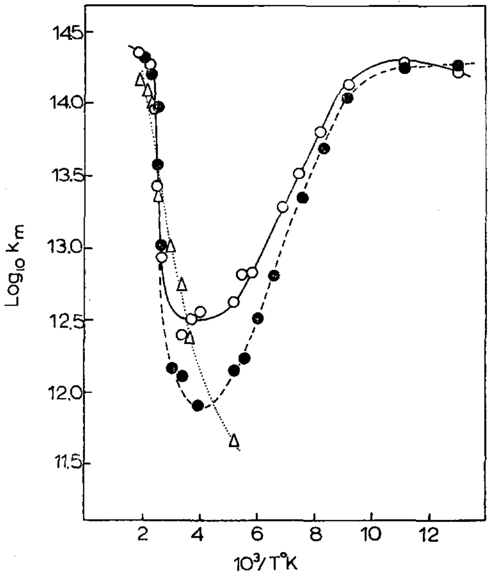

FIG. 2. Plots of $\log_{10}k_m$ against $1/T$°K for Dy_2O_3; -○-, parahydrogen conversion at increasing temperatures; --●--, parahydrogen conversion at decreasing temperatures; ··· △ ···, hydrogen-deuterium equilibration.

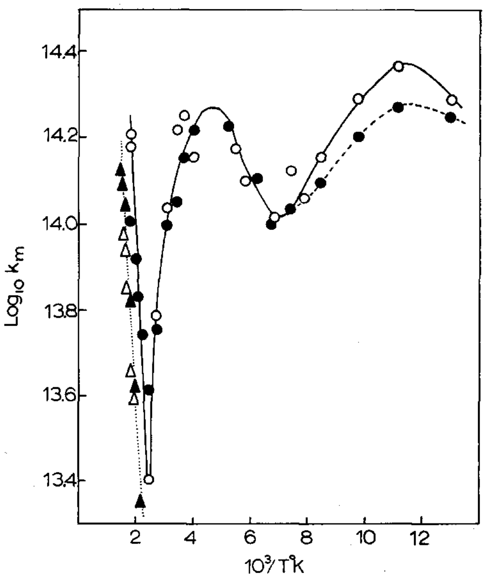

FIG. 3. Plots of $\log_{10}k_m$ against $1/T$°K for Er_2O_3; -○-, parahydrogen conversion at increasing temperatures; --●--, parahydrogen conversion at decreasing temperatures; ···▲···, and ···△···, hydrogen-deuterium equilibration.

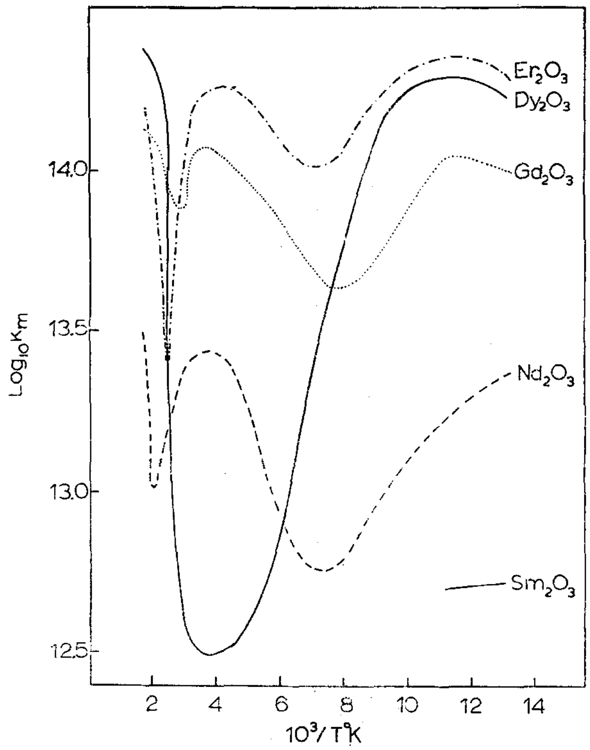

FIG. 4. Collected plots of $\log_{10}k_m$ against $1/T°K$ for parahydrogen conversion at increasing temperatures.

at increasing temperatures. Figure 4 shows collected data, together with that for Nd_2O_3 (*4*), at increasing temperatures only. The curves for Nd_2O_3, Gd_2O_3, and Er_2O_3 have the same general form, but with Dy_2O_3 the activity peak at intermediate temperatures (140–400°K) is absent.

The low-temperature conversion proceeds by a physical mechanism, and is of particular interest since it can be used to investigate surface paramagnetism. This may arise either from the presence of free surface valencies or from paramagnetic surface ions. Table 2 gives the rates of conversion observed at 77° and 90°K on five rare earth oxide surfaces which were free from chemisorbed hydrogen. In a separate study of the adsorptive properties of rare

TABLE 2

LOW-TEMPERATURE PARAHYDROGEN CONVERSION AND ADSORPTION OF HYDROGEN

Oxide	Ionic radius of Me^{3+} ion (Å)	Magnetic moment of Me^{3+} ion (Bohr magnetons)	k_m at hydrogen pressure of 4 mm (molecules/cm sec) 77°K	90°K	Hydrogen uptake at pressure of 4 mm (molecules/cm²) 77°K	90°K	Heat of adsorption (kcal/mole)
Nd_2O_3	1.15	3.68	2.29×10^{13}	1.67×10^{13}	4.15×10^{13}	1.14×10^{13}	1.85
Sm_2O_3	1.13	1.65	5.16×10^{12}	4.94×10^{12}	4.87×10^{13}	1.56×10^{13}	2.06
Gd_2O_3	1.11	7.94	1.01×10^{14}	1.07×10^{14}	5.37×10^{13}	1.81×10^{13}	2.13
Dy_2O_3	1.07	10.60	1.72×10^{14}	1.98×10^{14}	6.55×10^{13}	3.03×10^{13}	2.26
Er_2O_3	1.04	9.60	1.94×10^{14}	2.31×10^{14}	—	—	—

earth oxides (*8*), information has been obtained on low-temperature hydrogen adsorption. This is summarized in Table 2 as, (*i*) the adsorption uptake at 77° and 90°K at an equilibrium pressure of 4 mm, and (*ii*) the isosteric heat of adsorption. The values for Nd_2O_3 differ from those previously obtained (*4*), but they are regarded as the more reliable. It can be seen that although the hydrogen uptake and heat of adsorption increase with the lanthanide contraction, this is not so for the rate of conversion. The rate of conversion and its major dependence on surface paramagnetism is discussed below.

The Effect of Pressure

The effect of pressure on the rate of conversion has been measured over a range of pressures at a number of different temperatures. If hydrogen adsorption obeys the Freundlich isotherm, then $k_m = k_1 p^n$ or $k_e = k_2 p^{(n-1)}$, where p is the pressure, n is the kinetic order of reaction, k_1 and k_2 are constants; n is given by the expression $n = (\partial \log k_m / \partial \log p)_T$, or $n = 1 + (\partial \log k_e / \partial \log p)_T$. The values of n determined by this method, together with the applicable pressure ranges, are given in Table 3. No change in the value of n at 77°K was observed after high-temperature evacuation of Nd_2O_3 and Dy_2O_3, or after hydrogen pretreatment of Nd_2O_3.

At low temperatures, and with the oxides showing the greatest hydrogen adsorption, negative reaction orders were obtained. These negative orders were shown to be a reproducible effect by changing the geometry of the reaction system, and they are indicative of catalyst poisoning by adsorbed hydrogen molecules.

Hydrogen–Deuterium Equilibration

Hydrogen–deuterium equilibration on Gd_2O_3, Dy_2O_3, and Er_2O_3 has been studied over the temperature range 193–650°K, using a mixture of 50% normal hydrogen and 50% deuterium, at a constant pressure of 4 mm. The samples of oxide were not the same as those used for the conversion experiments, but were from the same preparation and were evacuated in identical fashion.

The rates of equilibration at 193° and 294°K are shown in Table 4, together with the results previously obtained for Nd_2O_3 (*4*). The figures in brackets against the rates of equilibration are the ratios of the rate of equilibration to that of parahydrogen conversion at the same temperature and pressure. The magnitude of the ratios are such that, with the exception of Dy_2O_3,

TABLE 3
VARIATION OF REACTION ORDER

	T(°K)	65°		77°		90°		193°	273°	373°	461°	588°
Nd_2O_3	Pressure (mm)	1–3	4–12	1–3	4–18	2–10		2–8	2–5	2–5	2–9	2–10
	n	0.20	−0.30	0.54	0.10	0.06		0.11	0.00	0.42	0.42	0.13
	T(°K)	—		77°		90°		—	—	—	—	—
Sm_2O_3	Pressure (mm)	—		2–4	5–21	1–4	5–19	—	—	—	—	—
	n	—		0.54	0.00	0.30	0.00	—	—	—	—	—
	T(°K)	—		77°		90°		158°	273°	—	—	543°
Gd_2O_3	Pressure (mm)	—		1–10		1–10		2–7	3–9	—	—	2–9
	n	—		0.00		0.12		0.09	0.21	—	—	0.00
	T(°K)	—		77°		90°		193°	273°	377°	—	544°
Dy_2O_3	Pressure (mm)	—		1–9		2–10		2–8	2–8	2–8	—	2–8
	n	—		−0.07		0.00		0.10	0.00	0.29	—	0.45
	T(°K)	—		77°		90°		193°	—	327°	—	524°
Er_2O_3	Pressure (mm)	—		2–4	5–11	3–9		2–8	—	2–7	—	2–7
	n	—		−0.06	−0.47	−0.13		0.16	—	0.35	—	0.49

TABLE 4

CATALYTIC ACTIVITY FOR HYDROGEN-DEUTERIUM EQUILIBRATION

Oxide	k_m at 193°K[a] (molecules/cm² sec)	k_m at 294°K[a] (molecules/cm² sec)	Rate expression for k_m (molecules/cm² sec) and applicable temperature range
Nd_2O_3	$<3 \times 10^{10}$ $(<2 \times 10^{-3})$	$<3 \times 10^{10}$ $(<1 \times 10^{-3})$	$k_m = 1.72 \times 10^{15} \exp(-5160/RT)$ 472–635°K
Gd_2O_3	6.25×10^{9} (7.4×10^{-5})	1.52×10^{10} (1.4×10^{-4})	$k_m = 1.49 \times 10^{16} \exp(-6410/RT)$ 389–653°K
Dy_2O_3	4.55×10^{11} (1.1×10^{-1})	5.47×10^{12} (2.2)	$k_m = 4.03 \times 10^{16} \exp(-5470/RT)$ 273–475°K
Er_2O_3	1.67×10^{11} (1.4×10^{-3})	4.32×10^{11} (2.6×10^{-3})	$k_m = 1.50 \times 10^{16} \exp(-6010/RT)$ 389–657°K

[a] The values in parentheses are the ratios of the rate of H_2–D_2 equilibration to the rate of p–o H_2 conversion at the same temperature and pressure.

the parahydrogen conversion at these temperatures is predominantly proceeding by a physical mechanism. Alternatively, it may be proceeding by a chemical mechanism on isolated double sites. Equilibration could not be studied below 193°K owing to the limitations of the micro-Pirani method, but there is nothing to suggest that the rate is anything but less than that at 193°K.

At higher temperatures, where the rates are higher, they can be expressed by the relationship $k_m = A\exp(-E/RT)$. The relationships for the four oxides, together with the applicable temperature ranges, are given in Table 4. The rate data are also plotted in Figs. 1–3.

DISCUSSION

The parahydrogen conversion at low temperatures is considered to take place by a physical mechanism, which arises from the interaction of the nuclear spin of the hydrogen molecule with the inhomogeneous magnetic field at the surface of the catalyst. Several possible mechanisms have been developed from the original theory of paramagnetic conversion proposed by Wigner (*9*). Harrison and McDowell (*10*) have considered a mechanism where the conversion takes place during the translational motion of physically adsorbed hydrogen molecules across a paramagnetic surface. A mechanism proposed by Sandler (*11*) and developed by ourselves (*4*) considers conversion taking place when an adsorbed molecule vibrates perpendicularly to the plane of the surface on an individual adsorption site. Under these conditions, each vibration is equivalent to a simple collision.

In considering the low-temperature conversion on Nd_2O_3 (*4*), calculation showed that conversion during elastic collisions without adsorption was insufficient to account for the observed rate by a factor of $\sim 10^4$. This also applies to the additional oxides now studied. For the translational mechanism of Harrison and McDowell to give the kinetic orders that have been observed in the present work (Table 3), a complete or almost complete monolayer of physically adsorbed molecules would be required. With the oxides studied the maximum hydrogen uptakes that were observed are only 0.01 to 0.04 of a calculated monolayer, and it is concluded that the translational mechanism is not applicable.

The kinetic orders and hydrogen uptakes are, however, in accord with the vibrational mechanism taking place on a small saturated fraction of the total surface. On the basis of the vibrational mechanism the absolute rate is given by the expression $k_m = \phi n \nu$, where ϕ is the collisional efficiency, n the number of molecules adsorbed per cm², and ν their frequency of vibration perpendicular to the surface. The collisional efficiency is given by $\phi = K\mu^2 r_s^{-6}$ where μ is the effective magnetic moment of the adsorption site, r_s the distance of the hydrogen molecule from the adsorption site during interaction, and K is a constant which varies with temperature. Calculations of the rate of conversion on the oxides at 90°K and 4 mm pressure have been made putting μ equal to the magnetic moment of the trivalent rare earth ion, $r_s = 2$ Å, ν as Dewing and Robertson's value of 4.5×10^{11}/sec (*12*) and $n = 10^{13}$ molecules/cm². For all oxides the calculated rates are ~0.01 of the observed rates.

The numerical discrepancy between observed and calculated rates of conversion would be reduced considerably if r_s were less than 2 Å and if a higher value of ν were obtainable. Consideration of the reason why only a small fraction of the oxide surface is catalytically active leads to a further possible source of the discrepancy. The experiments on high-temperature evacuation and hydrogen pretreatment indicate a clean catalyst surface which would be expected to be uniformally active. However, if the surface is polarized and rearranged in the Verwey-Weyl sense, with the oxygen ions outermost, close access to the paramagnetic metal ions might be prevented. Surface anion vacancies would then give rise to a number of isolated sites at which hydrogen molecules could approach the metal ions. At such sites more than one ion would be accessible and a number of vibrational modes could contribute to conversion, resulting in an absolute rate higher than that calculated on the basis of a single perpendicular vibration. Furthermore, if more than one hydrogen molecule could "enter" the vacancy, a condition favored by increasing the surface concentration of hydrogen, a number of the vibrations would be restricted and the rate of conversion would fall. This may be the reason for the negative kinetic orders observed with Dy_2O_3 and Er_2O_3, and with Nd_2O_3 at 65°K.

The oxides used in the present study were prepared at ~1073°K and they can be expected to have the cubic type C structure (*13*). It was possible that the Nd_2O_3 was an exception to this, since it has the hexagonal type A structure if prepared at 1123°K or above. X-ray powder photography of the Nd_2O_3, following 150 hr evacuation at 673°K, confirmed that it was of the type C structure. The type C structure is closely related to the face-centered cubic fluorite structure, and is derived from it by the ordered absence of oxygen ions from one-quarter of the lattice positions, thus giving rise to a high concentration of anion vacancies. Anderson and Gallagher (*14*), in considering possible oxygen adsorption sites on Pr_2O_3, have shown that the undistorted surface of a type C rare earth oxide has one in four anion sites vacant. Following Anderson and Gallagher, we calculate the number of anion vacancies in a Nd_2O_3 surface, containing equal areas of (100), (110), and (111) planes, to be 2.49×10^{14}/cm². This number increases slightly throughout the series of oxides used to 2.74×10^{14}/cm² for Er_2O_3, owing to the size of the unit cell decreasing with the lanthanide contraction. Consideration of the kinetic and adsorption data at 90°K indicates that the concentration of catalytically active sites is ~10^{13}/cm², and clearly these cannot be identified with the concentration of surface vacancies. However, if association of these vacancies to give vacancy clusters can occur, the concentration of these would be lower than that of single vacancies and may form the active sites. Such an argument is based on the assumption that cations exposed in the surface have insufficient adsorption potential to contribute any significant conversion.

In Fig. 5 the rate of conversion at 90°K and 4 mm pressure is plotted against μ^2.

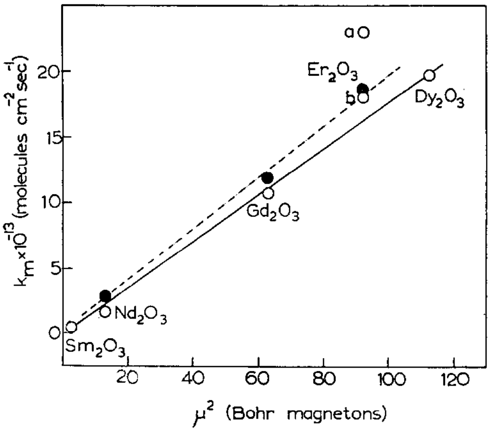

FIG. 5. Plots of k_m at 4 mm pressure against μ^2; -○-, 90°K (Er_2O_3—a from Table 2, b other experiments); ···●···, the maximum rate at intermediate temperatures (140–400°K).

The data is from Table 2, with the exception of point *b* for Er_2O_3, which is from further experiments. The plot shows the fundamental dependence of the rate of conversion upon μ^2, and the intercept is such that a surface containing no paramagnetic ions can be expected to show vanishingly small catalytic activity. However, unpublished data for the rate of conversion on Al_2O_3 at 90°K and 5 mm pressure shows that $k_m = 6.45 \times 10^{13}$ molecules/cm^2 sec (*15*). On Al_2O_3 the conversion is not caused by paramagnetic ions, but by free valencies arising from surface distortion following the removal of adsorbed water. It follows that free valencies do not play a part in the conversion on rare earth oxides, with the possible exception of Er_2O_3, where the rate lies above the line in Fig. 5.

At intermediate temperatures (140–400°K) Nd_2O_3, Gd_2O_3, and Er_2O_3 show similar behavior, with the activity for conversion rising with temperature to a maximum at 240–270°K and then falling as the temperature is further increased. For these oxides the rate of hydrogen–deuterium equilibration is only a very small fraction of that for parahydrogen conversion at the same temperature (Table 4). Dy_2O_3 is an exception to this and shows no maximum for conversion; the rates of hydrogen–deuterium equilibration and parahydrogen conversion being closely similar. It is possible that for Nd_2O_3, Gd_2O_3, and Er_2O_3 the conversion is proceeding by a chemical mechanism on isolated double sites with no surface migration of adsorbed atoms or interaction with other hydrogen molecules. There is, however, no evidence for such a mechanism on other surfaces. It is considered that, with the exception of Dy_2O_3, the conversion occurs by the vibrational physical mechanism on sites that are associated with an energy of accessibility. This energy is sufficient to prevent the sites functioning at low temperatures, but does not slow down the rate at intermediate temperatures since the hydrogen molecule, having reached the active site, will undergo an increased number of vibrations before being desorbed. As the temperature is increased above that corresponding to the maximum rate, desorption of the hydrogen is favored and the rate of conversion falls. It is unlikely that the sites responsible for conversion can be the anion vacancies or vacancy clusters which are considered to be active at low temperatures. Possible alternative sites include anion vacancies in the subsurface layer and the octahedral interstices (*14*) which are inherent in the type C structure. The lower activity of Dy_2O_3 is obscure, but it is unlikely to arise from a difference in crystal structure, since no alternative to type C is known to have been reported. Figure 5 shows a plot of the maximum rate of conversion against μ^2 for Nd_2O_3, Gd_2O_3, and Er_2O_3. The dependence of the rate upon magnetic properties is again emphasized.

At high temperatures ($T > 400$°K) the rate of parahydrogen conversion is only slightly greater than that of hydrogen–deuterium equilibration for each of the oxides studied. This indicates that both reactions proceed by the same chemical mechanism, although the parahydrogen conversion may still contain a small contribution from a paramagnetic mechanism. If the dissociative adsorption of hydrogen is the rate-controlling step in the chemical mechanism, calculation (*4*) shows that the catalytic activity is associated with only a small fraction of the available surface. This is in keeping with the findings at low temperatures, and supports the concept of a polarized and rearranged surface.

From the present investigation it can be seen that low-temperature activity is controlled by the magnetic properties of the oxides, which result from the 4*f* electronic structure of the rare earth ions. At high temperatures the activities for parahydrogen conversion and for hydrogen–deuterium equilibration are closely similar for each oxide, suggesting that the outer electronic states, 5*s* and 5*p* control activity. It appears that in reactions where hydrogen is present—alcohol decomposition (*1*), cyclohexane dehydrogenation (*2*), hydrogen–deuterium equilibration and parahydrogen conversion—the rare earth oxides show similar or regularly changing activities. This is in contradistinction to reactions where oxygen is present—carbon monoxide oxidation (*3*) and nitrous oxide decomposition (*8*)—where deviations from oxygen stoichiometry give rise to irregular and irreproducible activities.

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