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# Extrinsic Field Conversion of Parahydrogen Over the Rare Earths

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Parahydrogen conversion rates have been measured at room temperature over most of the rare earths as catalysts. With the catalyst in zero extrinsic magnetic field the conversion rates are, within experimental error, proportional to the square of the magnetic moment of the paramagnetic species. With the catalyst in an extrinsic field of 18 kOe, large increases in conversion rates are observed for all rare earths. These increases bear no relation to the number of *f* electrons, or to the presence of even or odd numbers of unpaired electrons in the paramagnetic ions. It appears, therefore, that the electron-spin relaxation time cannot be rate-determining for either the zero field effect or the extrinsic field acceleration, over these catalysts.

## INTRODUCTION

Catalysis of the ortho–parahydrogen conversion by paramagnetic solids has been known for over 40 years. More recently (*1*) it has been shown that the rate of the reaction may be further increased if the catalyst is placed in a magnetic field. The purpose of the present work was to gain a more nearly complete understanding of the nature and cause of this effect.

The field produced by the paramagnetic species in the catalyst is referred to as the intrinsic field, that coming from the outside as the extrinsic field. Whatever may be the reason for the extrinsic field effect, it must be related to the intrinsic field effect. Diamagnetic solids lacking dissociative activity give no appreciable catalysis in zero extrinsic field and none in a field of 20 kOe. The intrinsic field effect was first treated theoretically by Wigner (*2*), and later refined by Kalckar and Teller (*3*). The concept is that of a hydrogen molecule approaching a paramagnetic ion and interacting with the electronic spin so as to decouple the proton spins, thus allowing recoupling in the equilibrium ratio appropriate to the temperature. The rate of conversion was found to be proportional to $\mu^2/a^6$ where $\mu$ is the magnetic moment of the paramagnetic species and $a$ the distance of nearest approach. There is substantial evidence that the rate is indeed proportional to the square of the magnetic moment, but there is very little evidence of any kind concerning the distance of nearest approach (*4*), although mechanisms based on the Wigner theory have been developed by Harrison and McDowell (*5*), Sandler (*6*), Ashmead *et al.* (*7*), Nielsen and Dahler (*8*), and Golovin and Buyanov (*9*).

A paper by Leffler (*10*) explores an alternative possibility that the rate-determining step may be found in the vibration–rotation transition suffered by an adsorbed molecule undergoing conversion. If this is the case, then the conversion rate should depend upon the electron-spin relaxation time of the paramagnetic ion; those ions with long relaxation times being the better catalysts. On the basis of accessible theoretical work we are, therefore, compelled to conclude that the extrinsic field effect is caused by some hitherto unsuspected increase of magnetic moment brought about by the applied field or, alternatively, that the electron-spin relaxation time is changed by the applied field. In view of the magnitude of the effects the first seems too improbable to be considered seriously; the second forms the basis for the work described below.

Comparison of specific reaction rates over different catalytic solids is at best treacherous. For the magnetic parahydrogen conversion the rare earths offer some advantages. For the most part these oxides are isostructural, or may be made so. The lanthanide contraction, possibly affecting the distance of nearest approach, is accurately known, and small. Stability of the oxides toward chemical change is much the same, with a few well-known exceptions. The range of magnetic moments is large. Gadolinium has a long spin-lattice relaxation time and should, therefore, be a good magnetic catalyst. The other rare earths have short relaxation times. Furthermore, the sequence of even and odd numbers of unpaired electrons in the rare earth series gives an opportunity to take advantage of the Kramer's doublets splitting that occurs in a magnetic field for those ions possessing an odd number of unpaired electrons. Such splitting, if it occurs, would change the spin-lattice relaxation time. Comparison of parahydrogen conversion rates over the rare earths appears, therefore, to offer as good an opportunity as may be hoped for to test the possible effect of relaxation time on the rates, both with and without an extrinsic field. On the other hand, no way has been found to avoid the uncertainties always present concerning the precise structural configuration to be expected at the surface of any solid.

Previous studies on comparative parahydrogen conversion rates over carefully characterized sesquioxides of the rare earths are few in the literature. The most careful, and most nearly complete, survey appears to be that of Ashmead *et al.* (*11*), who found good constancy of the rate constants divided by $\mu^2$ in the room temperature, and lower, range over $Nd_2O_3$, $Sm_2O_3$, $Gd_2O_3$, $Dy_2O_3$, and $Er_2O_3$. Unfortunately, all of the rare earth ions in these compounds have an odd number of unpaired electrons. All previous studies appear to have been made in the earth's extrinsic field, which is too small to have a measurable influence on the conversion rate, except possibly as described below.

## EXPERIMENTAL METHODS

All rare earths were obtained from American Potash and Chemical Corporation, and were stated to be of 99.9% purity, or better, with respect to actual or potential paramagnetic species. They were at least 99.99% pure with respect to species reducible to form catalysts capable of dissociating molecular hydrogen at or near room temperature. From the 14 rare earths, lanthana and lutetia were excluded because they are diamagnetic, ceria (3+) because of its instability, and promethia for obvious reasons. To eliminate water and carbon dioxide all samples were heated in air at 800° for 18 hr, except as indicated below. In view of the well-known difficulties in the preparation of $Pr_2O_3$ this sample was heated in hydrogen at 1 atm for 12 hr at 1100°. The $Nd_2O_3$ was converted to the *C* form by prolonged ignition of the oxalate at 630° for better comparison with the rare earths of higher atomic number, although Errett (*12*) reports no difference in activity of *C* and *A* forms. Supported $Tb_2O_3$ on high-area $\gamma$-$Al_2O_3$ was prepared as previously described (*19*, *20*). All samples were kept sealed except for momentary exposure to air for removal of small portions for X-ray diffraction, specific surface (BET, $N_2$), or catalytic measurements.

All samples, after being placed in the reactor, were heated in hydrogen at 550° for 1 hr, after which they were rapidly cooled in hydrogen to 25°. This procedure was adopted so as to insure, so far as possible, that all surfaces were in a comparable state at the start of the activity measurements. The terbium oxide became almost, but not quite, white after this treatment. The praseodymium oxide was a bright green. The above procedure probably does not remove all chemisorbed hydrogen but, on the other hand, it is not sufficiently severe as to create surface defects capable of dissociating molecular hydrogen and thus of greatly complicating interpretation of the results.

The catalytic reactor for the flow method used, the purification of hydrogen, and the source of the extrinsic field have all been described before as have the following observations (*1, 13*): there was no zero field conversion and no extrinsic field effect for the empty reactor, and no magnetic conversion over diamagnetic solids such as $Al_2O_3$. The extrinsic field caused no shift of the ortho–para equilibrium, the effect occurs for both para to ortho and ortho to para conversion, and application of the extrinsic field causes no measurable change of hydrogen flow rate (no nuclear magnetic "wind") whether the catalyst was present or not.

Samples weighing from 15 to 250 mg were used in various runs at hydrogen flow rates of either 30 or 50 ml/min, at 1 atm. All measurements were made at 25° except as otherwise stated. Experimental specific rates were calculated by the method used by Buyanov (*14*) except that the quantity of catalyst present was expressed in terms of surface rather than of volume. Thus

$$k = \frac{f}{s} \ln \left[ \frac{C_{eq} - C_0}{C_{eq} - C_x} \right] \qquad (1)$$

where $f$ is the hydrogen flow rate in moles $sec^{-1}$, $s$ is the catalyst specific surface multiplied by the catalyst mass and expressed in $cm^2$, $C_{eq}$ is the fractional equilibrium concentration of orthohydrogen at 25°, $C_0$ is the fractional initial concentration of orthohydrogen, and $C_x$ is the fractional concentration of orthohydrogen emerging from the reactor. In all cases $C_{eq} = 0.25$ and $C_0 = 0.50$. A plot of $s$ vs $\ln[(C_{eq} - C_0)/(C_{eq} - C_x)]$ was found, as reported by Errett (*12*), to give a straight line passing through the origin for all but the most active samples. For these samples moderate mechanical dilution of the oxide with pure $\alpha$-$Al_2O_3$ corrected the situation, as also shown by Errett. Serious poisoning of the catalysts by hydrogen, as previously reported for $Cr_2O_3$ (*19*), was not a serious problem except for terbia, and to some degree for praseodymia.

## RESULTS

Table 1 shows the specific surfaces and rates $k_0$ for all rare earths studied in zero extrinsic field. The rates, $k_{18}$, with the catalysts in an extrinsic field of 18 kOe are also shown.

Figure 1 shows rates as a function of extrinsic field for erbium sesquioxide. The field strength dependence found for $Er_2O_3$ proved to be characteristic for all the rare earths. However, several rare earths showed a negative conversion rate change at quite low fields. Thus at 100 Oe a diminution in rate of about 10% was observed over $Pr_2O_3$, $Sm_2O_3$, and $Yb_2O_3$. A somewhat smaller change was found over $Nd_2O_3$. None of the other rare earths showed any such low field effect except that supported $Tb_2O_3$ on high-area alumina showed a 20% negative change at 100 Oe. This low field effect is quite different from, and apparently not related to, the high field effect. A more complete report will follow in due course.

TABLE 1
SURFACE AREAS AND CONVERSION RATES IN 0 AND 18 kOe EXTRINSIC FIELD

| $R_2O_3$ | Surface ($m^2$ $g^{-1}$) | $k_0 \times 10^9$ (mole $sec^{-1}$ $cm^{-2}$) | $k_{18} \times 10^9$ (mole $sec^{-1}$ $cm^{-2}$) |
|---|---|---|---|
| Pr | 5.4 | 2.0 | 4.0 |
| Nd(*c*) | 1.8 | 2.2 | 5.7 |
| Sm | 4.4 | 0.26 | 0.39 |
| Eu | 5.6 | 1.6 | 2.8 |
| Gd | 2.2 | 3.5 | 4.8 |
| Tb | 1.3 | 11.2 | 24.6 |
| Dy | 2.1 | 11.1 | 18.9 |
| Ho | 2.0 | 10.9 | 18.5 |
| Er | 2.1 | 7.1 | 11.4 |
| Tm | 1.1 | 7.0 | 17.5 |
| Yb | 5.6 | 0.94 | 2.9 |

The one final result to be recorded is that for $Tb_2O_3$ supported on high-area $Al_2O_3$ at 18 kOe. All samples of alumina tend to show dissociative catalytic activity after treatment in hydrogen at 550°, and this is complicated by magnetic conversion unless the sample is scrupulously purified. Thus a sample of reasonably pure commercial

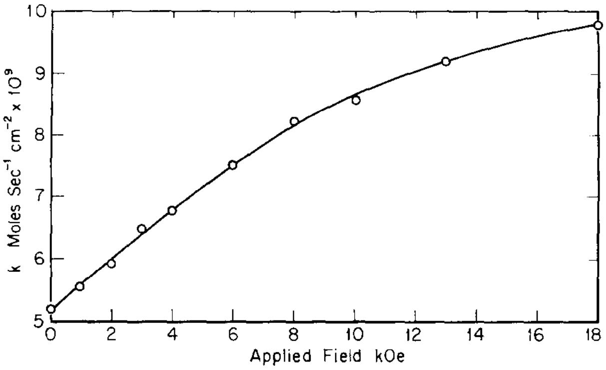

FIG. 1. Specific parahydrogen conversion rates at 25°C, over erbium sesquioxide, as a function of applied extrinsic magnetic field to the catalyst. The effect is reversible.

alumina catalyst of specific surface 84 m$^2$ showed both magnetic and dissociative activity at 25°, but no measurable acceleration in 18 kOe. A sample of high-area alumina prepared by hydrolysis of triple distilled aluminum isopropoxylate and of specific surface 120 m$^2$ showed strong dissociative activity but no change in either high or low fields.

The sample of supported 0.14 atom % $Tb_2O_3$ on high area alumina of specific surface 160 m$^2$ showed only moderate dissociative activity, but strong magnetic activity. The calculation of $k_0$ involved an estimate of the surface of the terbia. This was found as follows: In a 100-mg sample, $s = 0.100\ g \times 1.4 \times 10^{-3} \times 1.6 \times 10^{6}$ cm$^2$ g$^{-1}$ $= 2.2 \times 10^2$ cm$^2$. The zero field rate, $k_0$, was then found to be $14 \times 10^{-9}$ mole sec$^{-1}$ cm$^{-2}$, in satisfactory agreement with the specific rate over the pure terbia. As stated above, this sample showed a strong negative rate change in 100 Oe but the rate change was almost exactly zero in 18 kOe. There is thus little difference between $k_0$ for pure versus supported terbia, but a great change for $k_{18}$.

## DISCUSSION

Table 2 shows the effective magnetic moments, $\mu$, for the rare earth ions at 25°. These data are from Schieber (*13a*) corrected for what appear to be typographical errors for $Dy_2O_3$, $Er_2O_3$, $Tm_2O_3$, and $Yb_2O_3$. Table 2 also gives the ratio $k_0/\mu^2$ for all samples, and the fractional increase $(k_{18} - k_0)/k_0$. For convenience the number of $f$ electrons in each ion and the number of unpaired electrons are also shown.

TABLE 2
CORRELATION WITH MAGNETIC MOMENTS AND $f$ ELECTRONS

| $R_2O_3$ | $\mu$(Bohr) magnetons | $k_0/\mu^2 \times 10^{10}$ | $(k_{18} - k_0)/k_0$ | $f$ Electrons | Unpaired electrons |
|---|---|---|---|---|---|
| Pr | 3.59 | 1.5 | 1.0 | 2 | 2 |
| Nd | 3.66 | 1.7 | 1.6 | 3 | 3 |
| Sm | 1.50 | 1.2 | 0.5 | 5 | 5 |
| Eu | 3.64 | 1.2 | 0.8 | 6 | 6 |
| Gd | 7.85 | 0.58 | 0.4 | 7 | 7 |
| Tb | 9.67 | 1.2 | 1.2 | 8 | 6 |
| Dy | 10.6 | 0.99 | 0.7 | 9 | 5 |
| Ho | 10.4 | 1.0 | 0.7 | 10 | 4 |
| Er | 9.4 | 0.80 | 0.6 | 11 | 3 |
| Tm | 7.5 | 1.2 | 1.5 | 12 | 2 |
| Yb | 4.5 | 0.47 | 2.1 | 13 | 1 |

The data for zero field conversion rates, $k_0$, are discussed first. The ratios $k_0/\mu^2$ show a random fluctuation of about 50% above and below the average value 1.1. No influence of the lanthanide contraction is observed. This agreement is better than could have been expected in view of the large probable errors in the specific surface determinations and also of uncertainties, as pointed out by Ashmead *et al.* (*7*), in our knowledge of the fraction of the BET surface actually participating in catalytic action. The constancy of $k_0/\mu^2$ compares favorably with that obtained by Farkas and Sachsse (*15*) many years ago on rare earth ions in solution. But the constancy is poorer than that found by Ashmead *et al.* (*11*) over five of the rare earths reported here. A better constancy was also reported by Buyanov (*16*) for studies on the rare earth hydroxides.

It appears from all these results that $\mu^2$ does indeed play an important part in determining the rate of the magnetic conversion. Furthermore, the ratio for $Gd_2O_3$ is definitely not larger than the average for all rare earths. Yet if $Gd^{3+}$ in the oxide surface has the long spin-lattice relaxation time shown by magnetically dilute $Gd^{3+}$ systems, and if this is rate-determining, then the conversion rate shown by $Gd_2O_3$ should be greater than for the other rare earths. In view of the results obtained, and especially for those over $Gd_2O_3$, it seems unlikely that the spin-lattice relaxation time can be rate-determining for the conversion. It may be questioned whether arguments based on properties shown by ions in a crystal lattice have any meaning as applied to surface reactions. But it has to be pointed out that development of the spin-lattice theory (*10*) was itself based on the validity of exactly this argument, although with reference to magnetically dilute systems.

The moderately low value over $Yb_2O_3$ suggests the possibility of partial surface reduction to $Yb^{2+}$. Divalent ytterbium is more readily prepared than is divalent neodymium and Barrett and Barry (*17*) have reported surface reduction of $Nd_2O_3$ under experimental conditions only moderately more severe than those described above. Divalent ytterbium is isoelectronic with trivalent lutetium and hence would exhibit no magnetic conversion activity. But pretreatment of $Yb_2O_3$ with hydrogen at 600° produced no further loss of activity of $Yb_2O_3$ as compared with that treated at 550°. Also, the more easily reduced $Eu_2O_3$ showed no abnormal activity as it might be expected to show if, under the conditions used, the europium ion became isoelectronic with $Gd^{3+}$.

One further comment in connection with the $k_0$ values is related to the rather low values of catalytic activity shown by the rare earths as a group compared with oxides of the first transition series elements. Thus, $\alpha$-$Cr_2O_3$ after treatment in hydrogen at 500° has a much larger specific activity for the magnetic parahydrogen conversion (*18*) than does $Dy_2O_3$, although the effective moment in the latter is larger by a factor of 2.7. This phenomenon has been observed and commented upon by several authors, including Buyanov (*16*) and Wakao *et al.* (*19*).

Inasmuch as the dependence of $k_0$ on $\mu^2$ is strongly supported by the work of Ashmead *et al.* (*11*) and by the results shown in Table 2, it is less probable that any solution to the extrinsic field effect in paramagnetics will be based on spin-lattice relaxation times. Actually, the ratios $(k_{18} - k_0)/k_0$ shown in Table 2 are fairly constant from samarium to erbium. Neodymium and thulium give moderately higher values, while ytterbium gives a very high value. There is no indication that even or odd numbers of unpaired electrons in the paramagnetic ion have any effect on the conversion rates in an extrinsic field.

A possible explanation for the extrinsic field effect over paramagnetics may be found in the local field gradients generated at the surface of any body of matter having a susceptibility different from zero. That such gradients exist at the surfaces of paramagnetics has been shown by Drain (*20*) and studied by Zamir and Cotts (*21*) in connection with NMR line broadening for protons at or near the surfaces of powder particles. It is not clear if there is any independent evidence that the field gradients so produced are sufficient to decouple the protons in molecular hydrogen. A simple calculation shows that the increase in field intensity entering a particle of, say, $Dy_2O_3$, is several hundred gauss at room temperature in an extrinsic field of 18 kOe, but the gradient over the length of a hydrogen molecule must be quite small.

Some of the data reported in this paper and in earlier papers from this laboratory, point to the possibility mentioned in the preceding paragraph. Such an effect, if it exists, would be most readily detected, as an extrinsic field change of conversion rate, if the catalyst surface were composed of paramagnetic ions of relatively low moment but supported on a solid of high susceptibility. But the extrinsic field rate change would be expected to be minimized for a paramagnetic surface species supported on a diamagnetic solid, as actually occurs for many catalyst preparations such as the familiar chromia supported on alumina.

Of the oxides shown in Table 1 all fall in the category of fairly low ($Sm^{3+}$) to very high ($Dy^{3+}$) atomic moments at the surfaces of solids of fairly low ($Sm_2O_3$) to very high ($Dy_2O_3$) bulk susceptibilities. It may be surmised that in all these cases the extrinsic field gradient at the surface is added to that provided by the intrinsic field in such a manner as to provide a fractional increase in the volume at the surface accessible to molecular hydrogen and providing the minimum field gradient necessary to decouple the proton spins.

Support for this view is to be found in the absence of any measurable extrinsic high field effect for $Tb_2O_3$ supported at low surface concentration on high-area (diamagnetic) alumina, and this in spite of the fact that this system shows a large value of $k_0$. Other examples, previously published, are the moderate values of $(k_{18} - k_0)/k_0$ found for $Cr_2O_3$ supported at low surface concentrations on $\alpha$-$Al_2O_3$ and also for a 1 atom % $Cr_2O_3$ solid solution (ruby) in $\alpha$-$Al_2O_3$ (*1*). It must be noted that paramagnetic oxides supported on diamagnetic solids must be at quite low surface concentration if aggregation into particles, as of $Cr_2O_3$, on the surface is to be avoided. Such aggregates, while contributing less per ion to $k_0$ would themselves provide extrinsic field gradients, and other complications due to increasing antiferromagnetic interaction. In these studies no attempt has been made to consider the additional complexities that arise below the Néel temperature over antiferromagnetics such as $\alpha$-$Cr_2O_3$, as previously described (*1*).

In summary it may be said that neither the zero field parahydrogen conversion rates, nor the extrinsic field rate increases, offer any support for the idea that the spin-lattice relaxation time may be rate-determining, as these processes occur at the surfaces of the rare earths.

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