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γ Irradiation of Alumina Catalysts

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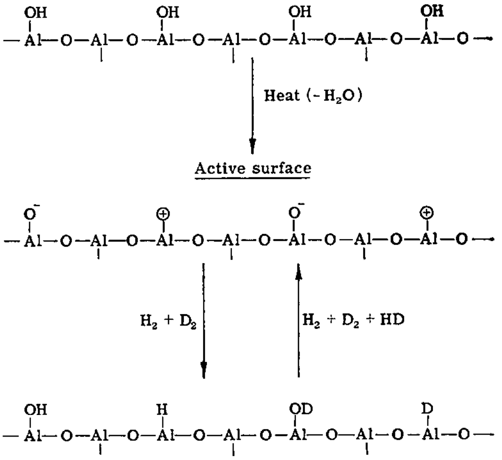
Thermal activation of α-alumina *in vacuo* creates active centers in the surface which catalyze the parahydrogen conversion (examined over 77° to 823°K) and the H_2D_2 equilibration (193° to 823°K). The conversion mechanism is mainly paramagnetic at low temperatures, changing to mainly chemical at high temperatures, while the equilibration can only involve the chemical mechanism. The apparent activation energy E of the conversion is 290 cal $mole^{-1}$ over 77° to 383°K, and above 383°K, where the rate is a maximum, $E = -490$ cal $mole^{-1}$. The activation energy for the H_2D_2 equilibration is 1400 cal $mole^{-1}$, the rate being nearly equal to that of the conversion at 823°K. These active centers, which probably arise in a dehydrated surface possessing mechanical strain, are thermally stable, and show a negligible ESR signal. Irradiation of the thermally activated catalyst *in vacuo* at 77°K with γ rays from Co^{60} gives an ESR signal with an absorption line 40 gauss wide, which is stable up to 193°K but anneals out at 273°K. There is a proportional increase in activity of irradiated catalysts for the parahydrogen conversion, but no increase in the rate of H_2D_2 equilibration. These new thermolabile active centers give a purely paramagnetic conversion. The ratio of observed rate to that calculated using the Wigner transition probability is 4030 at 77°K, and in line with data for rare earth oxides and transition metals.

INTRODUCTION

Aluminum oxide has been extensively studied by Pines and Haag (*1*) and shown to possess intrinsic acidity. The strength of these acidic sites depends upon the method of preparation, and affects the catalytic activity of the oxide for a number of reactions, such as alkene isomerization (*2*), dehydrogenation of alcohols (*3*), and hydrogen–deuterium equilibration (*4*). Hydrogen–deuterium equilibration has also been studied by Holm and Blue (*5*) and by Weller and Hindin (*6*). Catalytic activity was found to increase with outgassing temperature, reaching a maximum at 550°C (*5*, *6*). It was concluded that removal of water leaves the alumina surface in a strained condition and gives rise to the catalytic activity. Adsorption of oxygen has no effect on the catalytic activity, which would appear to exclude an oxygen-deficient structure as responsible for the catalytic activity. Water vapor, on the other hand, acts as a catalyst poison (*5*). According to electrical measurements, alumina is essentially an insulator, with an activation energy for conduction of 2.38 to 2.50 ev (*7*). The production of the active surface and its mode of action was visualized as follows (*8*):



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* British Council Scholar, University of Seville, 1962–63.

Alternatively the active sites may be viewed as paired by oxygen bridges.

On the other hand Hauffe (*9*) has associated catalytic activity in γ-alumina with electrical conductivity, probably in a quasi-isolated surface.

Kohn and Taylor (*10*) have investigated the effect of γ irradiation on the catalytic properties of γ-alumina for the hydrogen–deuterium equilibration. Gamma irradiation enhanced the catalytic activity to an extent which depended on the surface. The activity of the "pure" surface after extensive evacuation was not affected by γ irradiation. Kohn and Taylor (*11*) have also studied γ-irradiated silica gel.

In the present work we have studied the detailed kinetics of both para–ortho hydrogen conversion and hydrogen–deuterium equilibration on α-alumina before and after γ irradiation. The first reaction studied at 77°K leads to definite information about the presence of unpaired electrons acting as paramagnetic surface sites. In addition we have examined the catalysts by ESR absorption spectroscopy. A connection between paramagnetic conversion, ESR absorption, and hydrogen–deuterium equilibration has already been established for dextrose chars (*12*, *13*). It is hoped that information about these sites will assist in interpreting the conversion and equilibration reactions occurring by chemical mechanisms at the higher temperatures.

EXPERIMENTAL METHOD

The apparatus was essentially that used in earlier work in our laboratory (*14*). A cylindrical vessel containing the α alumina was connected via a liquid nitrogen trap and mercury cutoff to the usual vacuum line and gas storage bulbs. The reaction system could be pumped to 10^{-6} mm Hg or better. The parahydrogen, and hydrogen–deuterium–hydrogen deuteride mixtures were analyzed by a micro-Pirani gauge (*15*).

The ESR X-band spectrometer employed a reflection cavity operating in the H_{012} mode. It was designed and constructed by Mr. W. E. Porter, Chief Electronics Technician. The samples of α alumina for examination were sealed off in silica tubes, OD 3 mm, after degassing at 550°C for 60 hr *in vacuo*. Measurements could be carried out at 77°K by placing the sample tube in a small quartz dewar containing liquid nitrogen, which was inserted into the cavity of the ESR spectrometer.

Gamma irradiations were carried out in a 400 curie Co^{60} source, positioning the sample accurately so as to give a reproducible dose rate, not accurately measured but estimated as 10^{18} ev g^{-1} hr^{-1}. Doses were varied by changing the time of irradiation.

The aluminum oxide was supplied by Johnson & Matthey, Ltd., with stated impurities Na 2 ppm and Cu, 1 ppm. An X-ray powder pattern by Mr. M. A. Zammitt established the sample described in this paper (J. M. 345, Lab. No. 16371B) as α alumina (although a second specimen from the same manufacturers, Lab. No. 35352 is, in fact, γ alumina).

An X-ray diffraction study showed that γ irradiation caused no change in structure of the α-Al_2O_3 samples used in this study.

RESULTS

Activation of α-Al_2O_3. The effect of time of degassing at 550°C on the para-hydrogen conversion activity at 273°K and 77°K is shown in Fig. 1. The two activities run parallel and quickly reach a maximum. A pretreatment for 60 hr at 550°C in a vacuum better than 10^{-6} mm Hg was taken as standard in this work The surface area of a sample activated in this way was found to be 9.2 m^2 g^{-1}, by the BET method (*16*) using krypton at 77°K.

Kinetics of conversion and equilibration. The time course in all cases followed the usual first order law

$$k_e = (1/t) \ln (C_0/C_t) \text{ min}^{-1}$$

where C_0 (C_t) is the excess concentration of species at time zero (t) over the equilibrium concentration at the experimental temperature.

The absolute rate constant was calculated as

$$k_m = k_e pV/60AkT \text{ molecules cm}^{-2} \text{ sec}^{-1}$$

where p is the gas pressure, V the reaction volume at temperature T, A the area of the catalyst, and k Boltzmann's constant.

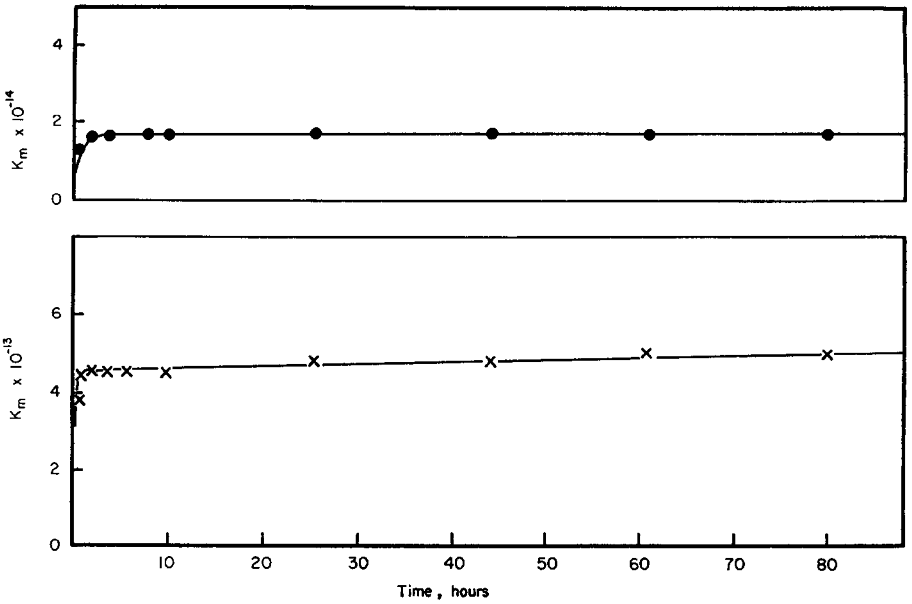


FIG. 1. Specific activity of α alumina for the parahydrogen conversion, after heating *in vacuo* for *t* hours at 550°C, measured at 273°K (●) and 77°K (×).

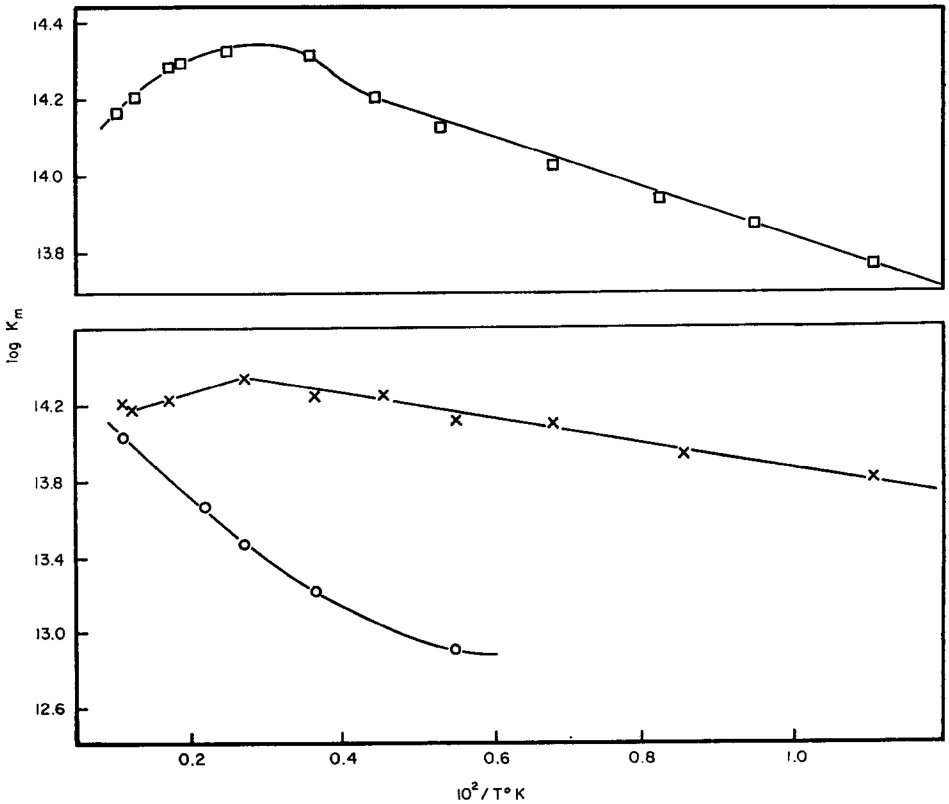


FIG. 2. Temperature coefficient of the parahydrogen conversion (×) and hydrogen-deuterium equilibration (○) at 5 mm pressure on α alumina. A repeat parahydrogen run as a second sample at 3.4 mm pressure is shown, □.

Apparent activation energies. The effect of temperature on the two reactions, from 77°K to 823°K, and at 5 mm pressure, is shown in Fig. 2. Between 77° and 383°K the conversion gives a straight line for $\log k_m$ vs T^{-1}, and an apparent activation energy of 290 cal mole^{-1}. The rate k_m reaches a maximum at 383°K and then decreases, with $E \simeq -490$ cal mole^{-1}. A very similar graph, with $E = 240$ cal mole^{-1} from 77° to 200°K, was obtained for a second series of reactions, carried out at 3.4 mm pressure.

Using the micro-Pirani technique, hydrogen–deuterium equilibration could only be measured above 193°K, (because of buildup of parahydrogen below these temperatures). The straight part of the log k_m vs T^{-1} graph between 273 and 823°K gives an activation energy for H_2D_2 equilibration of 1480 cal mole^{-1}.

Effect of pressure. The pressure dependencies change with temperature and are different for the conversion and equilibration reactions, as shown in Figs. 3 and 4, respectively. Expressing the absolute rate as a power law, $k_m = kp^n$, then n clearly changes with pressure in some instances. The results are summarized in Table 1.

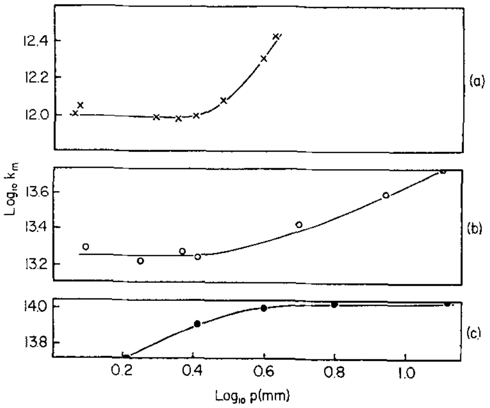


FIG. 4. Pressure dependencies of the hydrogen–deuterium conversion at (a) 193°K, (b) 273°K, and (c) 823°K, carried out on the same catalyst after the experiments of Fig. 3.

Effect of adsorbed or absorbed hydrogen on the conversion. Absolute activities k_m were studied as the temperature was in-

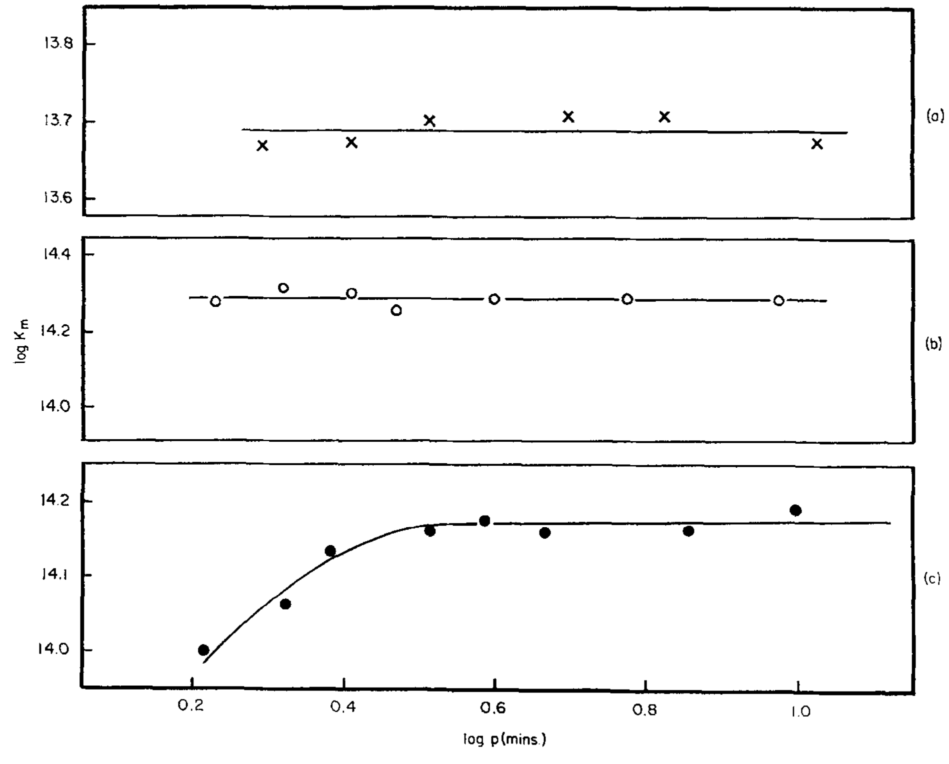


FIG. 3. Pressure dependencies of the parahydrogen conversion at (a) 77°K, (b) 273°K, and (c) 823°K.

TABLE 1
PRESSURE EXPONENT OF RATE n

T (°K)	Parahydrogen conversion[a]	Equilibration[a]
77	0	—
193	—	$0 \rightarrow 1$
273	0	$0 \rightarrow 1$
823	$1 \rightarrow 0$	$1 \rightarrow 0$

[a] The arrow denotes change in order as pressure is increased.

creased from 77° to 823°K and then again on the way down. Figure 5 shows that the results between 823° and 180°K are identical for increasing and decreasing temperature, but below 180°K the velocity constants observed are lower than those originally obtained for the initial stage of increasing temperature.

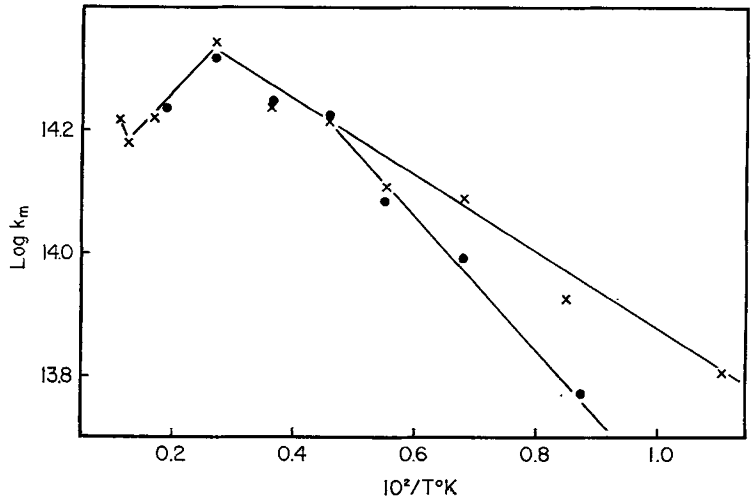


FIG. 5. Temperature cycling in hydrogen and the activation energy of the parahydrogen conversion; ×, increasing temperature followed by, ●, decreasing temperature.

Further experiments established that if hydrogen were admitted to the catalyst at 823°K and then pumped out to 10^{-6} mm for 5 min, the conversion rate (at 77°K) was decreased by about 17%. Pumping for 40 hr at 823°K completely restored the original conversion rate at 77°K. If hydrogen were admitted at temperatures up to 573°K, and pumped for 5 min *at the same* temperature, there was no effect on the rate at 77°K. This established the reversible character of the hydrogen adsorption at all temperatures below 573°K.

The effect of adsorbing hydrogen at a temperature A followed by pumping the catalyst at a lower temperature B, was to give a definite poisoning effect on the conversion at 77°K, as shown in Table 2.

TABLE 2
HYDROGEN POISONING EFFECTS

T (°K)		k_e, before admission of H_2 (min^{-1})	k_e, after pumping (min^{-1})
A	B		
823	273	1.12×10^{-1}	0.835×10^{-1}
273	193	0.835×10^{-2}	0.745×10^{-2}
193	77	0.745×10^{-2}	0.620×10^{-2}
823	77	1.00×10^{-1}	0.88×10^{-2}

The effect of absorbed (or chemisorbed) hydrogen is only to reduce the catalyst activity by less than 20%.

ESR absorption of alumina. The original sample of α alumina, sealed off *in vacuo* in the silica tube after pumping at 550°C and 10^{-6} mm for 60 hr, usually showed no ESR signal at room temperature. In one or two cases, a very small signal corresponding with a peak/peak line width of 2.7 gauss at room temperature was detected, but the effect was not reproducible. Irradiation for different periods of time at 77°K gave rise to a clearly marked, broad free-electron signal at 77°K. Figure 6 shows the *derivative* ESR absorption line resulting from 13 hr irradiation at 77°K. The g value and line width were not determined for this particular experiment, but in a continuation of the study, Mr. M. A. Zammitt finds for a similar signal a g value of 2.006 and a peak/peak line width of approximately 40 gauss. The number of free spins per gram was calculated by a comparison of peak area (minus that due to the silica tube) with peak area of a suitable carbon standard previously calibrated against DPPH. The free spin concentration per square centimeter could then be derived assuming all the measured free spins were accessible to the surface.

The narrow signal superimposed on the broad signal in Fig. 6 was due to the silica tube, and the free electron concentration in the α alumina, corresponding to the broad signal, is 3.0×10^{17} g^{-1}.

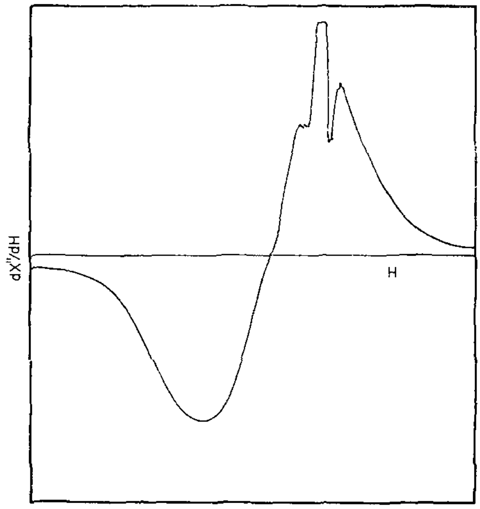


FIG. 6. Derivative of the ESR absorption line at 77°K, for a specimen irradiated for 13 hr at 77°K.

With continued irradiation at 77°K the free electron concentration increased, reaching a saturation value after some 12 hr irradiation, as in Fig. 7. If the sample after irradiation was maintained at 77° or 193°K the free electron concentration remained unchanged after 2 days, but it decreased nearly to zero in this period at 293°K, as shown in Fig. 8.

Free spins and parahydrogen conversion. Two samples of alumina were taken and irradiated for different periods of time at

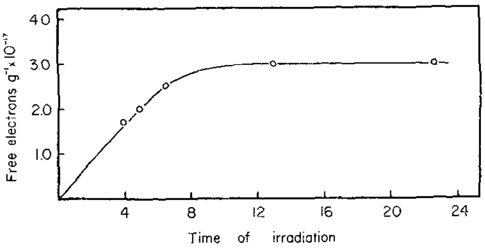


FIG. 7. The increase in free electron concentration at 77°K with time of irradiation at 77°K.

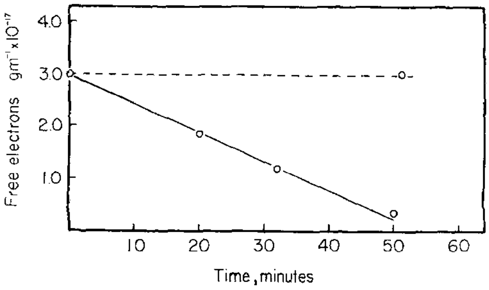


FIG. 8. The decrease in free electron concentration with time, post-irradiation, *in vacuo,* and at temperatures of 77°, 193° (dotted line), and 273°K (full line).

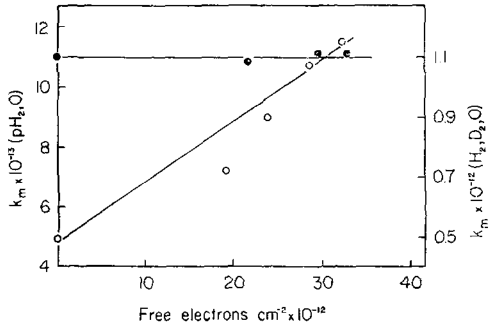


FIG. 9. Increase in ortho–para conversion activity at 77°K with free electron concentration for two samples irradiated at 77°K *in vacuo* for various times (○). Consistency of H_2D_2 equilibration activity, at 2.5 mm and 193°K, with free electron concentration for two samples irradiated at 77°K *in vacuo* for various times (●).

77°K and a series of measurements of ortho–para conversion were made at 4 mm pressure at 77°K on the first sample. On the second sample parallel measurements were made of free electron concentration. In Fig. 9 the relation between activity and free electron concentration is shown. There is a definite increase which may be linear or follow a shallow curve. Further work is required to decide between the two possibilities.

It was further found that a sample after irradiation at 77°K retained its ortho–para activity virtually unchanged *in vacuo* over 44 hr at 77°K (Table 3) and over 46 hr at 193°K (Table 4).

TABLE 3
CONVERSION ACTIVITY VS TIME AT 77°K AFTER IRRADIATION[a]

t (hr)	p (mm)	k_e (min^{-1})	k_m (molecules cm^{-2} sec^{-1})
0.5	3.9	0.395	11.7×10^{13}
26.0	3.9	0.395	11.7×10^{13}
44.0	3.6	0.403	11.0×10^{13}

[a] 0.0232 g α-Al_2O_3, irradiated 23 hr. Reaction volume 296 cm^3. Sample held post-irraidation for t hours *in vacuo* at 77°K.

TABLE 4
CONVERSION ACTIVITY VS TIME AT 193°K AFTER IRRADIATION[a]

t (hr)	p (mm)	k_e (min^{-1})	k_m (molecules cm^{-2} sec^{-1})
0.5	4.6	0.474	2.00×10^{14}
3.0	4.7	0.451	1.95×10^{14}
4.0	4.7	0.451	1.95×10^{14}
46.0	4.3	0.301	1.30×10^{14}

[a] 0.0209 g α-Al_2O_3, irradiated 8 hr. Reaction volume 320 cm^3. Sample held post-irradiation for t hours *in vacuo* at 193°K.

Irradiation and H_2D_2 equilibration. As before two samples were irradiated *in vacuo* at 77°K, one examined for catalytic activity (at 193°K) and the other for free electron concentration (at 77°K). Figure 9 shows that the catalytic activity for H_2D_2 equilibration remained constant, independent of the free electron concentration, in contrast to the result for the ortho–para conversion.

The activity of a catalyst was studied as a function of time *in vacuo* at 193°K, after irradiation of the catalyst *in vacuo* at 77°K. The results are shown in Table 5.

TABLE 5
HYDROGEN–DEUTERIUM EQUILIBRATION[a]

Sample	t (hr)	p (mm)	k_e (min^{-1})	k_m (molecules cm^{-2} sec^{-1})
a	1.75	2.2	9.5×10^{-3}	1.06×10^{12}
a	2.75	3.0	7.7×10^{-3}	1.17×10^{12}
b	4.5	2.2	9.0×10^{-3}	1.05×10^{12}
b	8.5	2.2	8.5×10^{-3}	9.2×10^{11}
a	24.0	2.7	5.8×10^{-3}	7.7×10^{11}
a	26.0	3.0	5.0×10^{-3}	7.5×10^{11}
b	27.0	2.1	6.5×10^{-3}	6.7×10^{11}

[a] a, 0.0213 g α-Al_2O_3 irradiated 5 hr. Reaction volume 179 cm^3. b, 0.0208 g α-Al_2O_3 irradiated 8 hr. Reaction volume 174 cm^3. Sample held post-irradiation for t hours *in vacuo* at 193°K.

A sample of α-Al_2O_3 was "activated" by heating *in vacuo* at 200°C instead of the 550°C otherwise used throughout this work. This sample showed no appreciable catalytic activity for H_2D_2 equilibration. However, subsequent irradiation caused the sample to reach the same specific activity as when activated *in vacuo* at 550°C, as shown below.

Sample activated at 550°C	k_m (2.5 mm, 193°K) $= 1.06 \times 10^{12}$ molecules cm^{-2} sec^{-1}
Same sample activated at 200°C	$k_m = 0.00$
Sample activated at 200°C then irradiated for 5 hr	$k_m = 1.05 \times 10^{12}$ molecules cm^{-2} sec^{-1}.

DISCUSSION

On thermally activated α alumina, *before* irradiation, the ratio of the rates of the para-H_2 conversion to the H_2D_2 equilibration decreases with increase in temperature (Fig. 1), but at all times is less than the maximum ratio which might arise from the difference in zero point energy of hydrogen and deuterium, which is exp $1800/RT$. This is shown in Table 6.

For a given mechanism the whole difference in zero point energy of 1800 cal mole^{-1} would not necessarily impress itself on the

TABLE 6

Ratio of the Parahydrogen Conversion Rate to the H_2D_2 Rate

T(°K)	823	623	423	193
k para-H_2/k, HD	1.5	2.4	5.0	17
exp 1800/RT	3.0	4.3	8.5	108.8

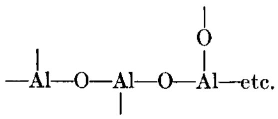
activation energies of the reactions. The observed difference in activation energies of 1480 − 290 = 1190 cal mole^{-1} could therefore arise from a simple zero point energy effect, with both reactions following the same chemical mechanism. However, as we shall see later, the evidence points to a contribution of the paramagnetic mechanism to the conversion reaction, at temperatures below 423°K.

The basic reaction orders for both conversion and H_2D_2 equilibration are zero at 273°K, although above 4 mm pressure the order of the H_2D_2 reaction shows a definite increase. The simplest explanation is that both reactions proceed via a recombination of hydrogen atoms in a chemisorbed layer (Bonhoeffer-Farkas' mechanism cf. ref. *20*) which is saturated at 273°K. However, the para-H_2 conversion at 273°K may also contain a big component due to a paramagnetic conversion occurring on thermally stable paramagnetic sites or surface free valencies. The main component of the conversion at 77°K and at 193°K (and perhaps mainly responsible for the ratio of rates of the ortho–para-H_2 to equilibration of 17 at 193°K) is the paramagnetic mechanism which gives way to predominantly atom recombination for the conversion at temperatures above 423°K. The H_2D_2 reaction will then go through atom recombination at all temperatures, except that at higher pressure (>4 mm) and temperatures below 273°K, the onset of a first order reaction denotes a second mechanism, hydrogen molecules exchanging with chemisorbed hydrogen atoms (Eley-Rideal mechanism, cf. ref. *20*).

At the highest temperature, 823°K, the pressure dependencies (Fig. 4) denote a partially desorbed layer of H atoms, saturating at about 4 mm, and catalyzing the two reactions by the atom recombination mechanism. This decrease in surface coverage will lead to the observed decrease in rate for the conversion setting in around 383°K. A decreased rate of paramagnetic conversion will also set in due to a decreased adsorption of physically adsorbed hydrogen molecule above 273°K, and, therefore, the proposed mechanisms explain the observed maximum in the Arrhenius plot (Fig. 2) for the conversion on α alumina.

Since a paramagnetic conversion rate with zero true activation energy is proportional simply to the concentration of physically adsorbed molecules, this will decrease with increase of temperature. On the other hand, the atom recombination mechanism will usually increase with temperature.* The net activation energy of 290 cal mole^{-1} is not unreasonable. Even a dominant paramagnetic conversion may show a zero or small positive apparent activation energy due to the presence of a true activation energy to bring the hydrogen molecule to a difficult accessible paramagnetic site (*17*).

We suppose the surface of thermally activated α alumina to be the strained surface postulated to arise from loss of water during activation at 823°K. However, we are inclined to replace the concept of ionic active sites by one involving stable free radicals, which would give a paramagnetic conversion of para-H_2, and explain the observed kinetics.



$$-\overset{|}{\mathrm{Al}}-\mathrm{O}-\underset{|}{\mathrm{Al}}-\mathrm{O}-\overset{\overset{|}{\mathrm{O}}}{\overset{|}{\mathrm{Al}}}-\text{etc.}$$

However, it was usually impossible to detect an ESR signal for thermally activated α alumina, with our equipment with a sensitivity of about 10^{15} spins g^{-1} for a line width of about 2 gauss.

Irradiation of thermally activated aluminum oxide brought on a clear increase in activity for the parahydrogen conversion, proportional to the number of free spins per

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* It may be almost independent of temperature. A detailed discussion of this mechanism was given by D. D. Eley and D. R. Rossington *in* "Chemisorption" (W. E. Garner, ed.), p. 137. Butterworths, London, 1957.

square centimeter at 77°K. Here we assume all the spins are in the surface, and whether the relation is linear or an upward curve remains uncertain. Although stable at 77°K and 193°K the unpaired electrons responsible for this conversion clearly anneal out at 293°K (Fig. 8). These sites must, therefore, be distinct from the thermally activated sites which are stable at 823°K (and undetectable in ESR). The H_2D_2 reaction velocity at 193°K is independent of the number of free spins per square centimeter created during irradiation (Fig. 9). Therefore, the free spins arising from γ irradiation at 77°K are unable to dissociate the hydrogen molecule and bring about H_2D_2 equilibration. One possible explanation is that irradiation may create isolated free electrons, while groups of at least two adjacent free valencies are necessary for chemical dissociation of the hydrogen molecule. The conversion on the irradiated α alumina is most probably, therefore, predominantly paramagnetic, and this is supported below by a quantitative calculation of rates.

Assuming the conversion at 77°K on the irradiated α alumina is zero order,* as on the unirradiated specimen (Fig. 4), we are led to suppose that the reaction proceeds by hydrogen molecules physically adsorbed in holes in the surface over "buried" paramagnetic sites. There must be some difference between the heat stable paramagnetic sites, and those created by γ irradiation, which are thermolabile. The former can also catalyze the H_2D_2 equilibration, which does not occur over the thermolabile γ-ray sites. The situation is similar to that recently described by Ashmead *et al.* (*18*) for the rare earth oxides and we therefore use their expression to calculate the paramagnetic conversion rate. If the number of sites per square centimeter is n_0, fractional coverage of surface θ, then we put $n_0 = 3.3 \times 10^{12}$ spins cm^{-2} and $\theta = 1$. If the vibration frequency on the site is taken as $\nu = 4.5 \times 10^{11}$ sec^{-1} (*19*) and ϕ is the Wigner transition probability, as given explicitly in the earlier paper (*18*) then,

$$k_m \text{ (calc, 77°K)} = n_0\theta\phi\nu \text{ molecules cm}^{-2}\text{ sec}^{-1}$$

gives the absolute rate of the paramagnetic conversion. For 77°K, and a paramagnetic moment of the active site of 1.73 Bohr magnetons corresponding to one unpaired electron, and for a hydrogen molecule site distance, r_s of 2 Å, we calculate $\phi(77°\text{K}, r_s = 2\text{ Å}, \mu = 1.73 \text{ B.M.}) = 1.92 \times 10^{-14}$. Hence k_m (calc) $= 2.85 \times 10^{10}$ molecules cm^{-2} sec^{-1}.

From Fig. 9 we have k_m (obs) for this number of free spins as 11.5×10^{13} molecules cm^{-2} sec^{-1}. This leads to the ratio

$$k_m(\text{obs})/k_m(\text{calc}) = 4.03 \times 10^3$$

This ratio may be compared with the ratio found for rare earth oxides of about 100 (*18*) and for the transition metals of the first period, 7.9×10^3 to 4.5×10^4 (*20*). Because such widely different catalyst surfaces give the same type of discrepancy, this may well arise from a common feature, such as an underestimate of ϕ or ν or both; this is a subject for later consideration.

It is a matter of interest that catalysts heated to only 200°C *in vacuo* and therefore catalytically inactive, on γ irradiation at room temperature are brought up to the level of activity produced otherwise by thermal activation at 550°C. The effect of irradiation at room temperature has presumably paralleled heating at 550°C in removal of water and produced a strained surface containing thermally stable sites, probably paramagnetic but undetectable with our present ESR spectrometer.

ACKNOWLEDGMENTS

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* Mr. M. A. Zammitt in our laboratory has now found this to be so experimentally.

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