NMR Measurement of Hydrogen Diffusion in β-Palladium Hydride*

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The pulsed–field-gradient spin-echo method has been applied to measure the self-diffusion coefficient, D, for hydrogen in β-PdH$_{0.70}$. For 296 K $< T <$ 413 K, $D = 9.0 \times 10^{-4} \times \exp[-(0.228 \pm 0.006\ \text{eV})/k_B T]$ cm^2/sec with an uncertainty in D of ±8% at 413 K. These results, together with proton spin-lattice relaxation-time measurements in the same specimen, are consistent with diffusion by a random walk on octahedral interstitial sites.

For some years there has been disagreement regarding the value of the self-diffusion coefficient of hydrogen in palladium measured by different techniques. Permeation and internal-friction techniques have been applied mainly to the α phase, and a satisfactory representation of much of such data was found by Birnbaum and Wert[1] to be $D = D_0 \exp(-E_a/k_B T) = 4.5 \times 10^{-3} \exp[-(0.248\ \text{eV})/k_B T]$ cm^2/sec. Proton spin-lattice relaxation time measurements, T_1, of Cornell and Seymour[2] indicated Arrhenius behavior with $E_a = 0.228 \pm 0.010$ eV for β-PdH$_{0.70}$,[3] and a 300-K value of D three times smaller than that from Birnbaum and Wert; other workers find similar results by this method. Quasielastic neutron-scattering experiments[4] yielded $E_a = 0.147$ eV for β-PdH, and D(300 K) ten times larger than given by Birnbaum and Wert. A genuine difference between nuclear magnetic dipolar relaxation and neutron-scattering values would be particularly interesting because the two methods measure closely related correlation functions of the fluctuations accompanying diffusional motion.

Using a microscopic model of the diffusion process, magnetic dipolar relaxation times yield a model-dependent mean jump time τ_D, from which $D = \langle l^2 \rangle / 6\tau_D$, where $\langle l^2 \rangle$ is the model mean squared jump distance. In order to provide a model-independent check on the diffusion coefficient we have applied the pulsed magnetic field gradient spin-echo technique[5] to measure D for β-PdH$_{0.70}$. By measuring both D and T_1 for the protons in the same specimen, we have the opportunity, at least in principle, to identify the detailed diffusion mechanism. (The spin-spin relaxation time T_2 could be used instead of T_1 but it is difficult to obtain reliable T_2 values when rapid diffusion is occurring.[6])

The pulsed-gradient technique measures the decrease in the amplitude of the echo following a 90°-τ-180° rf pulse sequence, produced by a pair of matched field-gradient pulses, amplitude G and duration δ and with axis along the steady field, following the 90° and 180° pulses, respectively. In the absence of diffusion the dephasing of spins in the plane perpendicular to the steady field caused by the first gradient pulse is exactly nullified by the second and the gradient has no effect on the spin-echo amplitude, $M_0(2\tau)$. However, complete rephasing is not achieved if spins diffuse in the time between gradient pulses to regions of different magnetic field and the echo amplitude is reduced to

$$M(2\tau) = M_0(2\tau) \exp[-\gamma^2 G^2 D \delta^2 (\tau - \delta/3 + \epsilon)], \quad (1)$$

where γ is the nuclear gyromagnetic ratio, $\epsilon = A(2\tau/\delta - 1)$ is a small correction for finite gradient-pulse rise and fall times, and A is the difference between those times.

The sample was a cylindrical roll of 25-μm foil interleaved with 50-μm Teflon and oriented with its axis parallel to the rf magnetic field. The palladium, of 99.98% purity, was vacuum annealed at 850°C for 1 h, loaded with hydrogen from the gas phase to yield β-PdH$_{0.70}$, and sealed in a close-fitting thick-walled glass capsule. Measurements were made at 18.5 MHz where the rf skin depth at 300–400 K is about 55 μm. Most observations were made with $\tau = 10.0$ msec, $\delta = 2.48$ msec, and $G = 60$–150 G/cm; the largest gradient gave rise to values of $M(2\tau)$ of about $\frac{1}{4}$ at the upper end of the temperature range, which was limited by insensitivity at the lower end and by hydrogen pressure in the capsule at the upper end. Results are shown in Fig. 1. The diffusion length in 10 msec is about 1 μm at most so that no bounded-medium correction[7] was required. Allowance for background field gradients arising from bulk magnetism of the sample is sometimes necessary.[8] In this case, since β-PdH$_{0.70}$ is diamagnetic and since foils were used rather than powders, the effect is expected to be small and the correction can be deduced approximately from measurements of proton T_1 and T_2: Diffu-

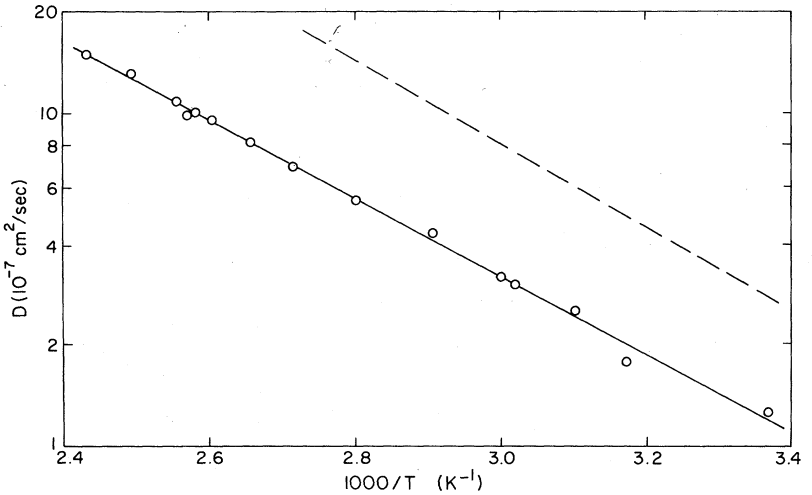

FIG. 1. Self-diffusion coefficient, D, of hydrogen in β-PdH$_{0.70}$. ○, experimental results of the pulsed gradient method. — —, conflation of permeation and internal friction results from Ref. 1.

sion in the background gradients causes T_2 measured, for instance, by a Carr-Purcell-Meiboom-Gill (CPMG) technique to be less than T_1 under circumstances where they would otherwise be equal. The required correction to D, deduced from the variation of T_2(CPMG) with pulse spacing, is a maximum of $+3\frac{1}{2}\%$ at the highest temperature and has been incorporated in plotting the experimental points in the figure. The results can be expressed as

$$D = 9.0\times 10^{-4} \exp[-(0.228\pm 0.006 \text{ eV})/k_BT] \text{ cm}^2/\text{sec}, \quad (2)$$

(296 K$<T<$413 K), with an uncertainty in D of ± 8% at the highest temperature and rather more at lower temperatures, arising approximately equally from scatter among repeated observations of $M(2\tau)$ and from possible calibration errors.

Measurements of T_1 for the protons were made using a 180°-(90°, 180°, echo) technique. Our measurements were entirely consistent with the more extensive data of Cornell and Seymour[2] on a powder sample of β-PdH$_{0.70}$ and will not be reproduced here in full, therefore. The present measurements do, however, extend the temperature range of their data from 315 to 413 K to match that of our D measurements. Over this range T_1 at 18.5 MHz increases from 70 to 145 msec. Above 340 K the relaxation rate begins to be dominated by the conduction-electron contribution, $T_{1e}T = 68\pm 2$ sec K.[2] The remaining rate, T_{1D}^{-1}, may be attributed to proton-proton dipolar interactions; dipolar interaction with palladium nuclei is negligibly small. To interpret the results we use the theoretical formulation of Torrey[9] as evaluated by Sholl.[10]

There is strong evidence from neutron diffraction[11] that hydrogen atoms in fcc β-PdH$_x$ occupy octahedral (O) interstitial sites. Since in our sample only 70% of the sites are occupied it is likely that diffusion occurs by a random walk with jump length equal to the distance between nearest-neighbor O sites (2.85 Å). Correlations between successive jumps which occur when the fraction of vacancies is small need not be considered. Such a model accounts quantitatively[2] for the minima of T_{1D} observed at different resonance frequencies (Table I). Furthermore, the whole of the $T_{1D}(T)$ data can be used to deduce $\tau_D(T)$ and hence $D(T)$. The resulting values of D can be fitted by the values of D_0 and E_a in Table II; they are in excellent agreement with the parameters deduced from the pulsed gradient experiment.

TABLE I. Minimum values of $T_1(T)$. Numbers in parentheses indicate uncertainties in the least significant digit.

Frequency (MHz)	Minimum T_1 (msec) Expt[a]	O-O model	T-T model
7	11.9(4)	10.5(6)	9.2(6)
11	19.4(8)	16.6(9)	14.5(9)
47	77(6)	71(4)	62(4)

[a] Ref. 2.

TABLE II. Hydrogen diffusion parameters in β-$PdH_{0.70}$.

D_0 (10^{-3} cm^2/sec)	E_a (eV)	
0.9(3)	0.228(6)	Pulsed gradient
0.7(3)	0.228(10)	T_1[a]
0.5(3)	0.231(10)	T_1[b]

[a] Assuming octahedral-octahedral jumps.
[b] Assuming tetrahedral-tetrahedral jumps.

In order to investigate the ability of a comparison of the two types of NMR data to distinguish between different diffusion mechanisms, we have also calculated $\tau_D(T)$ assuming a random walk between nearest-neighbor tetrahedral interstitial sites. Such sites form a simple cubic lattice with $l = 2.02$ Å. The shape of the predicted T_{1D}-T curve is not significantly different from that for the O-O model, but the magnitude of τ_D (and also of D) for a given T_{1D} is somewhat changed. The results are included in Tables I and II; this model does not reproduce the T_{1D} minima as well as the O-O model nor does it yield a D_0 value as close to that obtained from the pulsed gradient experiment.

The NMR results are thus internally consistent with a random-walk, nearest-neighbor O-O diffusion process and a diffusion coefficient given by Eq. (2), although if these were the only relevant data available a tetrahedral-tetrahedral jump process could not be entirely ruled out. The values of D are about $2\frac{1}{2}$ times smaller than those (Fig. 1) given by the Birnbaum and Wert compilation. Although some[12] of the sets of data included by them individually indicate an E_a value agreeing with the NMR value, none yields absolute D values as small as ours. Those data refer, however, to small hydrogen concentrations and one could perhaps expect a simple $1-x$ concentration dependence of D arising from blocking of O sites already occupied by protons. There is some indication of this from T_1 observations[2] as well as in β-phase permeation experiments.[13] Indeed, the latter yield a value of D, including the factor $1-x$, for 25°C and $x = 0.74$, which is within 35% of our value. The discrepancy between the neutron scattering results[4] and other data remains to be explained. Further neutron scattering measurements with the better instrumental resolution now available[14] may resolve this problem.

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