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Mobility of Hydrogen in Hydrogen Tungsten Bronze

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In order to understand the slow stages of the catalytic reduction of WO_3 to hydrogen tungsten bronzes H_xWO_3, the mobility of hydrogen in the latter has been studied by NMR spectroscopy between −50 and −195°C. Values of the spin-lattice relaxation time T_1 plotted vs. the inverse temperature show a minimum indicating one main relaxation process, namely that due to diffusion. The corresponding calculated diffusion coefficient of H in H_xWO_3 is very high. Thus transport of H in H_xWO_3 cannot be the rate determining step in the catalytic reduction of WO_3. Rather, that step is suggested to be the penetration of the reducing species below the surface of WO_3 into the lattice.

INTRODUCTION

In recent years, several examples have been given of a phenomenon of special importance in adsorption and catalysis with supported metals. This phenomenon, which has been termed *spillover* and has been reviewed lately (*1*), consists in the dissociative adsorption of hydrogen on the metal under conditions which are inadequate for sizeable direct adsorption of hydrogen on the support. Hydrogen atoms can then diffuse across the metal-support interface and participate in reduction and catalytic steps on the support.

The most striking example of spillover thus far is that studied by one of us (*2*) in which a mechanical mixture of tungsten oxide WO_3 and platinum black was found to take up enough hydrogen at room temperature to reduce WO_3 to a hydrogen tungsten bronze H_xWO_3 with $x = 0.35$. The catalytic reduction of WO_3 to H_xWO_3 at room temperature necessitates hydrogen atoms spilled over from platinum and also adsorbed water which apparently helps in the transport of atomic adsorbed hydrogen from the metal to the oxide.

In previous work (*1*, *2*), it has been established that water took part chemically in the transport of H atoms presumably by formation of H_3O intermediates and that the large internal surface area of the WO_3 particles was invaded in the first couple of minutes with enough atoms to cover these particles with a monolayer of dissociated hydrogen. The initial fast uptake was then followed by a slower process with a time constant of the order of ten minutes so that at the end of about thirty minutes the reduction process was over and the reduction product, blue H_xWO_3 was obtained. The present work was undertaken to understand the nature of this slow process and to measure the mobility of hydrogen in the interesting hydrogen tungsten bronzes.

Nuclear magnetic resonance studies of hydrogen dissolved in metals (*3–6*) have allowed the calculation of diffusion coefficients for hydrogen nuclei in these solid systems. It was hoped that the application of NMR to hydrogen tungsten-bronze would yield similar information. Infrared studies were also attempted to define the nature of the bonding of hydrogen with oxygen in the WO_3 lattice. Sienko and

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Oesterreicher (*7*) found no evidence for the formation of the OH radical in H_xWO_3 with $0.1 \leq x \leq 0.5$. The preparation procedure used by these authors being different from that used in this work, we reexamined the infrared transmission spectra of a WO_3 wafer in the course of the reduction process.

EXPERIMENTAL

The materials and the procedure used in the preparation of hydrogen tungsten bronze H_xWO_3 were the same as those described in Ref. (*2*). A mechanical mixture of WO_3 and 0.25 wt % Pt black was reduced at room temperature in hydrogen. After 1 hr reduction, hydrogen was flowed through the sample as the temperature was raised to approximately 130°C and kept at that temperature for 2 hr. This procedure appears sufficient to remove adsorbed water since no hydrogen NMR signal was observed on an unreduced sample of Pt/WO_3 which had been evacuated 2 hr at 130°C following previous exposure to water vapor as in the regular preparation. The Pyrex sample tubes were then sealed under a hydrogen atmosphere of 100 Torr.

For wideline proton magnetic resonance spectra, a Varian DP 60 instrument with a 14 Kgauss magnet was used. The correction to the second moment for the intensity of the modulation field was less than 0.5 gauss^2. The longitudinal T_1 and transverse T_2 relaxation times were obtained in the range from —50 to —195°C using a Brücker B. K. R. 302 Pulse Spectrograph operating at $\omega = 60$ Mc and coupled to the Varian 14 Kgauss magnet. The probe used in this work was designed by W. Stone (*8*). The temperature was adjusted by varying the flow rate of liquid air or liquid nitrogen around the sample tube. A thermocouple placed next to the sample tube recorded the temperature. T_2 was obtained from the exponential decay of the magnetization after a pulse while T_1 was calculated from 90° pulse sequences. Under the experimental conditions adopted in this work, T_1 was obtained within $\pm 10^{-2}$ sec, and T_2 was reproducible within $\pm 10^{-5}$ sec.

For the infrared studies, a Beckman IR-4 spectrophotometer was employed. The Pt/WO_3 wafers were made by supporting the powder on a fine mesh platinum screen and compressing at 100 Kg/cm^2. This film was then placed in the IR cell and reduced *in situ* prior to the recording of the IR spectra in a way similar to that used in the NMR work.

RESULTS AND DISCUSSION OF THE SPECTROSCOPIC WORK

By extending the general theory of Bloembergen, Purcell, and Pound (*9*), Torrey (*10–12*) has found that the longitudinal relaxation time T_1 for translational isotropic diffusion in fcc and bcc lattices is related to the lattice and motion parameters as follows:

$$T_1^{-1} = (8\pi/5)\gamma^4(h/2\pi)^2 I(I+1) \times (n/k^3 l^3 \omega)\psi(k,y) \quad (1)$$

where γ is the proton gyromagnetic ratio, h is Planck's constant, n is the number of protons per cm^3, k is a normalization constant, l is the jump distance, and $\psi(k, y)$ results from the transformation of the spectral densities of the random time function of positions of neighboring spins. $\psi(k, y)$ has been tabulated with respect to $y = 1/2\ \omega\tau$ where τ is the diffusional correlation time.

Experimental values of T_1 as a function of inverse temperature are shown in Fig. 1. The presence of a minimum is expected from Torrey's theory and substantiates the assumption that *there is only one main relaxation process occurring, i.e., that of diffusion.* T_2 values were between 16 and 32 μsec and showed no defined trend with temperature. This may be accounted for by the relative experimental error in this range. To calculate τ values in Eq. (1), a lattice must be chosen for the hydrogen in H_xWO_3. Unreduced WO_3 possesses a distorted ReO_3 structure, but the limiting structure with x values near 0.5 is that of perovskite with WO_3 possessing a cubic lattice as shown in Fig. 2. As a first approximation, the hydrogen tungsten bronze may be regarded as a solution of hydrogen in the cubic WO_3 matrix. However, it has not been established whether the hydrogen

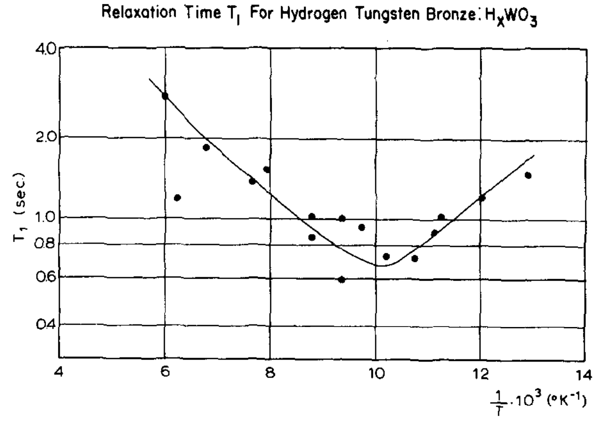

FIG. 1. Experimental values of T_1.

is preferentially located in the center or at the face of a unit cell. Dickens and Hurditch (*13*) attempted to define the position of hydrogen nuclei in tungsten bronzes with composition $H_{0.23}WO_3$. With respect to a tetragonal distorted unit cell, the coordinates of the two sites available to hydrogen are 000 and 1/21/20. If the nuclei jump from face to face, the jump distance is 2.68 Å and k^3_{fcc} in Eq. (1) is applicable. But if the nuclei move from center to center, the jump distance is the lattice constant, 3.82 Å and $k^3_{bcc}/2$ is appropriate. k^3_{bcc} is divided by 2 since only ½ the sites are available to hydrogen.

The latter model was chosen for this study. This was supported by a point-charge electrostatic field calculation for a proton in a WO_3 lattice which revealed that the path of lowest potential lay along one of the three axes of 4-fold symmetry. However, the choice of either the bcc or fcc structure does not seriously alter τ values, and, in fact, the calculation of the activation energy E_a is independent of the lattice since k^3 affects only the preexponential factor of τ.

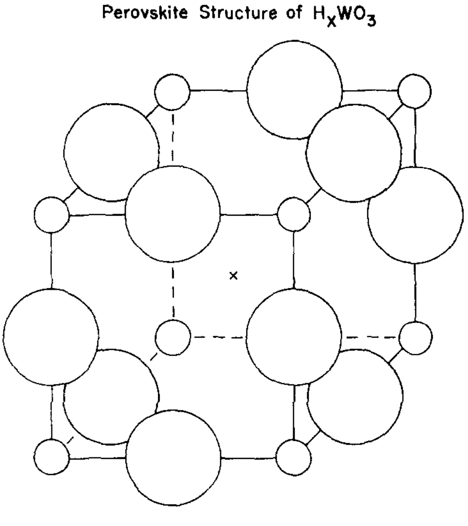

FIG. 2. Perovskite structure of H_xWO_3.

The jump frequency may be deduced from the correlation time as shown in Eq. (2):

$$v = \tau^{-1} = v_o \exp(-E_a/RT). \qquad (2)$$

For diffusion in a three-dimensional lattice, the diffusion coefficient is then $D = \nu l^2/6$. From Fig. 3, the value of E_a is 1.3 kcal/mole and agrees favorably with that found in the H/Pd system for $T < 220°K$ where $E_a = 1.84$ kcal/mole (*4*). The value of v_o is 2.7×10^{11} sec^{-1} using a bcc lattice. This gives an extrapolated value for D of 7×10^{-6} cm^2/sec at 298°K.

Complementary NMR broad-line measurements were also made. The NMR first derivative signal was measured at room temperature and at −150°C. The values obtained for the second moments of the constructed absorption curves were 0.1 and 0.4 gauss^2 at 20 and −150°C, respectively. Assuming a cubic structure and using Van Vleck's (*15*) equation for a powder sample, we calculated a rigid lattice second moment of the order of 1 gauss^2 (*16*). This value is not too far removed from that mea-

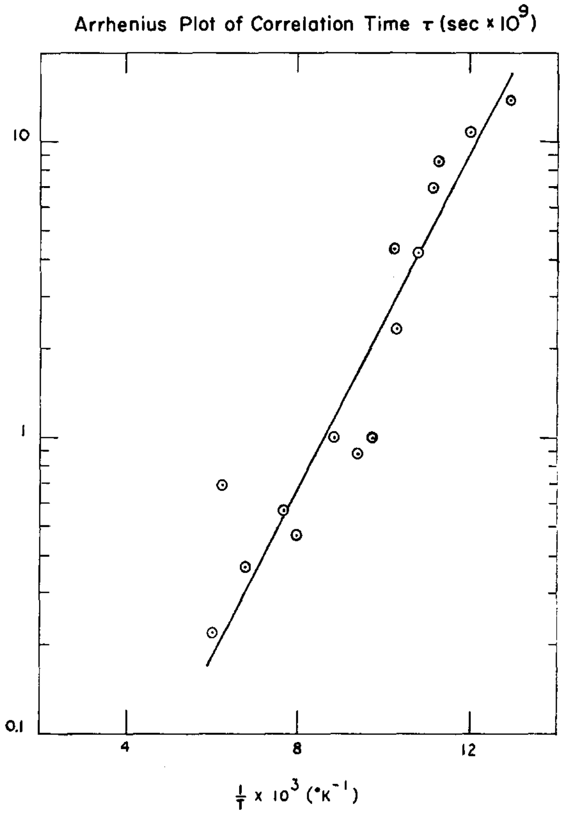

FIG. 3. Arrhenius Plot of Correlation Time τ[sec $\times$ 10^9].

sured at $-150°C$. This can be explained if the nuclei are assumed to be paired on nearest-neighbor sites. If the diffusion process involves exchange between pairs of nuclei, the statistical distribution of nearest neighbor pairs will not vary greatly from the rigid lattice approximation. The proton pairing and the coherence of their motions seems to be the most obvious hypothesis to reconcile the high protonic mobility suggested by the longitudinal relaxation rate and the proximity of the rigid second moment value and the experimental mean square width of the absorption spectrum at low temperature.

From the line width of the absorption curves, a T_2 value at $-150°C$ of 60 μsec was obtained which agreed within a factor of 2 with those measured by the pulse technique. This agreement was felt to be satisfactory considering the non-Lorentzian shape of the absorption curves.

A large difference between T_1 and T_2 has been observed before for protons in boehmite (*14*). This difference of nearly 5 orders of magnitude indicates the transverse and longitudinal relaxation rates are governed by different processes. Although it is quite clear that diffusion is the mechanism ruling the longitudinal relaxation time T_1, the mechanism governing the transverse relaxation time T_2 is not so obvious. Spark analysis of WO_3 showed paramagnetic impurities to be below detection limits, with Fe, Ni, Co < 5 ppm and Cr < 10 ppm. Such low concentrations cannot thus be invoked in order to explain the large T_1/T_2 ratio. The behavior attributable to conduction electrons, a linear increase as T is lowered, is not observed in the data. Also,

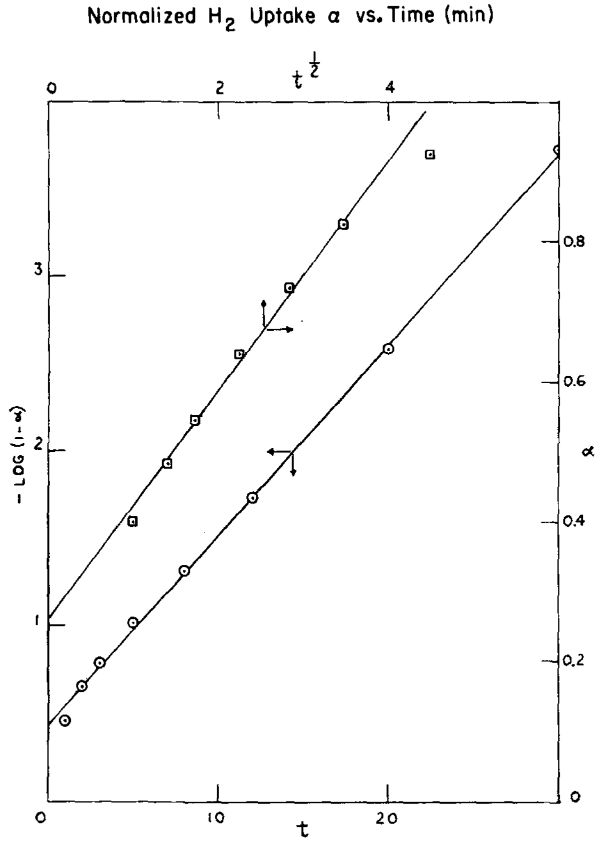

FIG. 4. Normalized Hydrogen Uptake α versus time (minutes) ⊡ corresponding to diffusional process ⊙ following Eq. (3) Data from run shown in Fig. 3, Ref. *2*.

no nuclei with quadrupoles exist in WO_3. Therefore, these three relaxation processes cannot explain the large difference between T_1 and T_2 values. However, the pairing of hydrogen nuclei mentioned earlier may explain the rapid spin-spin relaxation process.

Infrared spectra on a WO_3 sample equilibrated with the atmosphere showed absorption bands at 6.1 and 2.9 μ, characteristic of the bending and stretching modes, respectively, of water. These bands disappeared after a 2 hr evacuation at 110°C. The transmission of the IR beam through the sample was completely suppressed for the tungsten blue, either at 20 or —170°C, due to an extremely high extinction coefficient. This same effect has been reported for other tungsten bronzes (*17*) although Sienko and Oesterreicher (*7*) have reported absorption bands for the hydrogen-reduced WO_3. Upon reoxidation, it was again possible to obtain the IR beam transmission.

DISCUSSION OF THE RATE OF CATALYTIC REDUCTION

In view of the very large mobility of H in H_xWO_3 as expressed by its measured diffusion coefficient, we have reexamined the kinetic information available for this system. Uptakes published previously (*1*) were plotted as $\alpha = U_t/U_\infty$ vs. $t^{1/2}$ where U_t is the uptake at time t and U_∞ is the uptake at infinite time (Fig. 4). The linear relationship allows us to calculate an apparent diffusion coefficient D_a for the overall reduction process. If the WO_3 particle radius is taken to be 400 Å, an average of the values obtained by surface area and X-ray line broadening, a value of $D_a \simeq 10^{-15}$ cm^2/sec is calculated for the macroscopic diffusion process.

This value of D_a is 7 to 8 orders of magnitude smaller than the diffusion coefficients of various species the transport of which might be controlling (Table 1). It must be concluded that the transport of these species cannot explain the slow stage of reduction.

TABLE 1

Diffusion Coefficients for Various Species

System	D(cm²/sec)
Molecular H_2 in H_2O	3.4×10^{-5} (*18*)
Atomic H in H_2O	7×10^{-5} (*19*)
Protons in a H_2O monolayer	10^{-8} (*20*)
Hydrated electrons in H_2O	4.8×10^{-5} (*21*)
Hydrogen in WO_3	7×10^{-6} (This work)

In the overall reduction process, we propose the following five steps to occur in series:

(1) Transport of molecular hydrogen to the platinum surface;
(2) Dissociation of hydrogen on the platinum;
(3) Diffusion of atomic hydrogen through the water monolayer to the WO_3 surface;
(4) Transfer across the water-WO_3 interface;
(5) Diffusion of hydrogen through WO_3.

The large values of the diffusion coefficients in Table 1 preclude steps 1, 3, and 5 from being rate-determining. Besides, the rate of uptake is known to be independent of the number of platinum particles (*2*), thus also precluding step 2. An activation barrier might exist at the WO_3-H_2O interface, thus making step 4 the slow step in striking analogy with the slow step in the hydrogen-palladium system studied by Brodowsky and Wicke (*22*).

If the net rate of transport of hydrogen species across this interface represents the experimentally measured uptake, the rate is the difference between the forward $\overrightarrow{r}$ and reverse $\overleftarrow{r}$ rates across the interface.

The simplest kinetic behavior is that of a first order rate limited by equilibrium. Let U_t be the uptake of hydrogen at time t and U_∞ the uptake at infinite time. Then we simply write:

$$\frac{dU_t}{dt} = k(U_\infty - U_t)$$

where k will have the simple meaning of the inverse of a relaxation time for the observed phenomenon. With $(U_t/U_\infty) = \alpha$, the integrated rate expression is:

$$\alpha = 1 - e^{-kt} \tag{3}$$

if it is assumed that for the interfacial process considered here $U_t = 0$ at $t = 0$.

As can be seen on Fig. 4, a plot of $\ln(1-\alpha)$ vs. t is linear at least over the range of α and t values which pertain to the process as pictured, i.e., after the hydrogen atoms have invaded the internal surface of the WO_3 particles. The value of k is 0.11 min^{-1}, corresponding to a time constant of about 10 min. Further interpretation of the kinetics awaits additional information on the nature (H_3O?) of the hydrogen species in the water layer at the surface of WO_3.

Conclusion

In establishing the high mobility of H in H_xWO_3, nuclear magnetic resonance has proved to be very useful in furthering our understanding of the kinetics of catalytic reduction of WO_3. The present study, together with previous information, strongly suggests that the rate determining step in the reduction is the penetration of the reducing species below the surface of the WO_3 particles. This is followed by fast motion of H through the WO_3 lattice as shown by the study of T_1.

Besides, the high value obtained for the proton jump frequency in WO_3 as well as the similarity between the observed second moment and the corresponding rigid lattice value suggest a remarkable protonic behavior in the hydrogen tungsten bronze. This behavior may well be related to the failure of IR spectroscopy to provide useful additional information. Further work on H_xWO_3 single crystals ought to yield valuable, much needed information on the properties of hydrogen in this solid.

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REFERENCES

1. BOUDART, M., VANNICE, M. A., AND BENSON, J. E., *Z. Phys. Chem. N. F.* **64**, 171 (1969).
2. BENSON, J. E., KOHN, H. W., AND BOUDART, M., *J. Catal.* **5**, 307 (1966).
3. NORBERG, R. E., *Phys. Rev.* **86**, 745 (1952).
4. TORREY, H. C., Sup. A., Vol. IX, Ser. X, Del Nuovo Cimento, No. 1, 3rd Trimestre, 96 (1958).
5. BURGER, J. P., PAULIS, N. J., AND HASS, W. P. A., *Physica* **27**, 514 (1961).
6. STALINSKI, B., COOGAN, C. K., AND GUTOWSKY, H. S., *J. Chem. Phys.* **34**, 1191 (1961).
7. SIENKO, M. J., AND OESTERREICHER, H., *J. Amer. Chem. Soc.* **90**, 6568 (1968).
8. STONE, W., Unpublished results.
9. BLOEMBERGEN, N., PURCELL, E. M., AND POUND, R. V., *Phys. Rev.* **73**, 679 (1948).
10. TORREY, H. C., *Phys. Rev.* **92**, 962 (1953).
11. TORREY, H. C., *Phys. Rev.* **96**, 690 (1954).
12. RESING, H. A., AND TORREY, H. C., *Phys. Rev.* **131**, 1102 (1963).
13. DICKENS, P. G., AND HURDITCH, R. J., *Nature* **215**, 1266 (1967).
14. FRIPIAT, J. J., AND TOUILLAUX, R., *Trans. Faraday Soc.* **65**, 1236 (1969).
15. VAN VLECK, J. H., *Phys. Rev.* **74**, 1168 (1948).
16. ABRAGAM, A., "Les Principles du Magnétisme Nucléaire," Presses Universitaires de France (1958).
17. DICKENS, P. G., AND WHITTINGHAM, M. S., *Quart. Rev.* **22**, 30 (1968).
18. Perry's Chemical Engineers' Handbook, 4th ed., 1963.
19. SCHWARZ, H. A., *J. Phys. Chem.* **73**, 1928 (1969).
20. TOUILLAUX, R., SALVADOR, P., VAN MEERSCHE, C., AND FRIPIAT, J. J., *Israel J. Chem.* **6**, 337 (1968).
21. SCHMIDT, K. N., AND BUCK, W. L., *Science* **151**, 70 (1966).
22. BRODOWSKY, H., AND WICKE, E., Engelhard Industries, Inc. Technical Bulletin **7**, 41 (1966).