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Spin Echo Double Resonance Detection of Deuterium Quadrupole Resonance Transitions in $DMn(CO)_5$[1]

Sir:

Hydride compounds of the transition metals form an important class of substances.[2] Aside from the intrinsic interest which attaches to an understanding of the nature of the metal-hydrogen bond, the fact that many transition metal hydrides are important in catalysis provides an additional incentive for their study. The number of physical studies which shed light on metal-hydrogen bonding is rather limited. Although bond distance data have become more abundant in recent years,[2-4] information on the electronic structural characteristics of the bond is not plentiful. We report here a direct determination of the quadrupole coupling constant at deuterium in solid $DMn(CO)_5$ by use of the nuclear spin echo double resonance (SEDOR) technique. The experiment provides not only the quadrupole coupling constant at deuterium but in addition gives a direct measure of the Mn-D bond distance with an accuracy comparable to that obtainable from a diffraction experiment.

The pure nuclear quadrupole resonance (NQR) transitions at 77°K for ^{55}Mn ($I = 5/2$) in $DMn(CO)_5$ occur at 13.683 MHz ($\pm 3/2 \rightarrow \pm 5/2$) and 6.890 MHz ($\pm 1/2 \rightarrow \pm 3/2$).[5] From these results we calculate a quadrupole coupling constant of 45.66 MHz, and asymmetry parameter η of 0.07. Employing a pulse spectrometer at zero magnetic field, nuclear spin echo signals resulting from these transitions are readily observable following a 90–180° pulse sequence. The deuterium pure quadrupole transitions are excited by application of a 180° pulse via a B channel, low frequency transmitter, using a second orthogonal coil. The double resonance experiment is carried out by monitoring the ^{55}Mn spin echo amplitude, while sweeping the B channel in frequency. When the B channel transmitter passes through the low frequency D quadrupole resonances, the altered dipolar coupling is observed as a change in ^{55}Mn spin echo amplitude. Figure 1 shows the double resonance spectra obtained from the change in spin echo amplitude for both (a) upper and (b) lower Mn transitions.

The centers of the doublet occur at 51.05 kHz in both transitions. The splitting observed is ascribable entirely to dipolar coupling, so there is a single deuterium transition; i.e., the asymmetry parameter η is approximately zero. The frequency of the observed transition corresponds to a quadrupole coupling constant of 68.07 kHz. This is by far the lowest deuterium quadrupole coupling constant ever observed in a direct, zero magnetic field experiment.[6]

The crystal structure of $HMn(CO)_5$ has been determined by both X-ray and neutron diffraction techniques.[3,4] The packing of molecules in the structure is such that the dipolar interaction between the Mn and D pair within a given molecule is much greater than that of either nucleus with any other nucleus on an adjacent molecule. It is thus permissible to treat the Mn-D spin systems as isolated pairs.

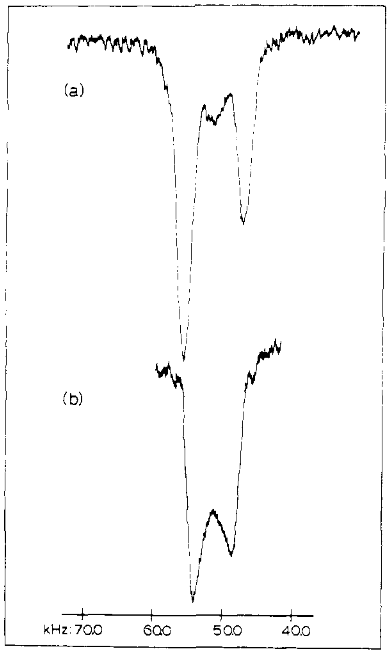

Figure 1. SEDOR spectrum of ^2D in $DMn(CO)_5$: (a) $\pm 3/2 \rightarrow \pm 5/2$ ^{55}Mn transition; (b) $\pm 1/2 \rightarrow \pm 3/2$ ^{55}Mn transition.

Application of the 90–180° pulse sequence at a radiofrequency corresponding to the higher ^{55}Mn quadrupole transition causes a mixing of the 5/2 and 3/2 spin states of the same sign. Since spin-lattice relaxation is slow ($T_1 \sim 0.3$ sec) on the time scale in which the spin echo is observed, the dipolar coupling between D and ^{55}Mn following the 90° pulse (the 180° pulse does not change the magnitudes of mixing coefficients, only their signs) corresponds to the average value of the ^{55}Mn–D couplings appropriate to Mn in the 5/2 and 3/2 spin states, i.e.

$$E_{\mathrm{dd}}{}^{\mathrm{mk}} = \langle \psi_{\mathrm{Mn}}\psi_{\mathrm{D}} | \mathcal{H}_{\mathrm{dd}} | \psi_{\mathrm{Mn}}\psi_{\mathrm{D}} \rangle$$

where

$$\begin{aligned} \psi_{\mathrm{Mn}} &= \frac{1}{\sqrt{2}}(\phi_{\pm m} + i\phi_{\pm(m-1)}),\ m = 5/2,\ 3/2 \\ \psi_{\mathrm{D}} &= \phi_k,\ k = \pm 1,\ 0 \\ \mathcal{H}_{\mathrm{dd}} &= \frac{-\gamma_{\mathrm{Mn}}\gamma_{\mathrm{D}}\hbar^2}{r^3}(3\cos^2\theta - 1)I_{z,\mathrm{Mn}}I_{z,\mathrm{D}} \end{aligned} \qquad (1)$$

The label dd refers to the dipolar interaction, and m and k refer to the spin states of the Mn and D nuclei, respectively. The angle θ is that between the principal field gradient axes of Mn and D, and $\mathcal{H}_{\mathrm{dd}}$ is the portion of the complete dipolar coupling Hamiltonian appropriate for heteronuclear coupling.[10]

Application of the 90–180° pulse sequence at the frequency of the lower transition similarly mixes the 1/2 and 3/2 spin states of like sign. The dipolar splitting in the deuterium spectrum using the lower frequency Mn transition is calculated to be one-half that obtained using the higher frequency ^{55}Mn transition, in agreement with the results shown in Figure 1.

The only prior determinations of quadrupole coupling constants for deuterium bound to transition metals have been made by Wei and Fung,[11] who observed the broadline NMR spectrum of D in high field for $(C_5H_5)_2MoD_2$ and $(C_5H_5)_2WD_2$. From the line shape it is possible to deduce the quadrupole coupling contant, but the experiment is not very precise, especially if η is much different from 0. The low values for e^2qQ/h reported for the two deuterides studied are reasonably consistent with the present results.

Using the magnitude of the splitting observed in the upper spectrum of Figure 1, 8.8 kHz, in eq 1, it is possible to calculate the Mn–D distance. We assume that the field gradient tensors on Mn and D are colinear. Since this is necessarily the case in the isolated molecule, and since there is very little distortion in the crystals, it appears a very safe assumption. The fact that the asymmetry parameter is approximately zero for D, and very nearly so for ^{55}Mn is additional indication that the field gradient tensors are aligned along the Mn–D axis. The calculated value for the Mn–D distance from the observed splitting is 1.61 Å with an uncertainty of about 0.01 Å, in excellent agreement with the diffraction result.[4]

The SEDOR experiment, first performed at zero or very low magnetic field by Emshwiller, Hahn, and Kaplan,[12] has received little attention. Ragle and coworkers have employed it in essentially the same manner we have to obtain several D quadrupole coupling constant data, using ^{35}Cl spin echoes as the indicator nuclear channel.[13-15] The present results, however, are the only ones of which we are aware in which a clearly defined dipolar splitting has been seen. It is apparent from this example, that application of the SEDOR technique to other hydride complexes of the transition metals has the potential for yielding interesting information about M–D bonds. In addition to observing terminal M–D bonding in species such as $DRe(CO)_5$, $DCr(CO)_5^-$, $DCo(CO)_4$, and $HCo[P(C_6H_5)_3]_3N_2$, the technique may be very useful in more precisely defining the nature of bridge bonding situations, as in $H_3Mn_3(CO)_{12}$, $H_3Re_3(CO)_{13}$, $HRe_3(CO)_{14}$, and many others.

References and Notes

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(5) These results are complicated to a slight extent by the fact that $DMn(CO)_5$ is capable of crystallizing in more than one form.[4] The details, none of which affect the conclusions presented here, will be discussed elsewhere.

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A Chiral Electrode

Sir:

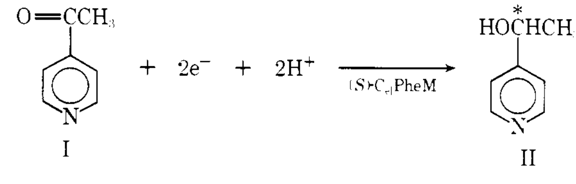
Although electrode surfaces can be altered by adsorption it would be of interest to more drastically and permanently modify the surface by covalently binding molecules to it. If a method for securely anchoring such molecules could be found, advantage could be taken of the molecular structure to build surfaces with unique and widely varying properties. Indeed, the attached molecules could be used in the sense of chemical reagents to perform reactions in tandem with the electron transfer processes characteristic of chemically inert electrodes. In the present case a chiral electrode surface was synthesized and used to perform an asymmetric reduction.

Heating graphite in air produces acidic surface oxides, some of which have been chemically characterized as carboxylic acids.[1] Our initial approach was to bind optically active amino acids to these sites via amide bonds, thereby providing a stable, chiral interfacial region for electrochemical reactions.

Spectroscopic grade graphite rods (4 in × 0.25 in., density = 0.65 g/cm^3) were baked in air at 160° for 36 hr. This introduced acidic groups which could be titrated with base.[1,2] Modification of these oxidized electrodes was accomplished by first treating them with thionyl chloride in dry benzene for 24 hr. This was followed by reaction with 1 g of (*S*)-(−)-phenylalanine methyl ester ((*S*)-(−)-PheM) in 50 ml of methylene chloride. Crystals of phenylalanine methyl ester hydrochloride formed in the solution indicating that reaction between the amino acid and acid chloride was successful. After 24 hr the electrodes were removed, and then soaked in 100 ml of 0.5 *M* acetate buffer for 4 hr. These modified electrodes, (*S*)-C_{el}PheM, were indistinguishable by eye or sweep voltammetry (−0.5 to −1.5 V, acetate buffer, sweep rate 5 mV/sec) from the unmodified version.

The reduction of 4-acetylpyridine was chosen for initial study. This ketone reduces at relatively positive potentials[3] and the expected product, alcohol(II), has been characterized.[4] All reductions were performed under N_2 at −1.05 V vs. SCE in a three-compartment cell, and the catholyte was 100 ml of 0.5 *M* acetate buffer, 100 ml ethanol. When the (*S*)-C_{el}PheM was used as a cathode, addition of I (0.5 ml, 4.5 mmol) caused an increase in current from 8 to 32.5 mA. The current decayed to 19 mA after a period of 320 min (1.10 faraday/mol). The catholyte was then reduced to 40 ml volume on a rotary evaporator. This was made basic (pH 10) with solid Na_2CO_3 and extracted with three 50-ml portions of ether. The combined extracts were washed with saturated NaCl solution and dried over anhydrous calcium sulfate. The solution was filtered and evaporated to give a clear, water white oil. The oil (0.5 g) was analyzed by NMR and showed only I and II in the ratio 48:52. GLC collection of the product at 107° from an SE-30 column resulted in a colorless oil (45 mg) identified by comparison with an authentic sample of II. The electrolysis product had $\alpha_{OBS} = -0.325$, $[\alpha]^{20}D$ −7.22 (c = 3, $CHCl_3$). Reinjection on the GLC gave only one peak. Recollection gave an identical specific rotation.

Reduction of I to II on an electrode treated with $SOCl_2$ in benzene followed by buffer acetate soaking proceeded very similarly. The yields of II were again high, but it was optically inactive.



The absolute configuration and specific rotation of II have been reported.[4] However, both we and others[5] have