2795 (1974); B. B. Wayland and M. E. Abd-Elmageed, *ibid.*, **96**, 4809 (1974).
(5) R. Samuels, R. Shuttleworth, and T. S. Stevens, *J. Chem. Soc. C*, 145 (1968).
(6) The following abbreviations are used: TPP, tetraphenylporphinate dianion; *i*-PrTPP, tetrakis(*p*-isopropylphenyl)porphinate dianion; CF_3TPP, tetrakis(*p*-trifluoromethylphenyl)porphinate dianion; OEP, octaethylporphinate dianion; *t*-Bu(py), 4-*tert*-butylpyridine.
(7) G. R. Eaton and S. S. Eaton, to be submitted for publication.
(8) J. J. Bonnet, S. S. Eaton, G. R. Eaton, R. H. Holm, and J. A. Ibers, *J. Amer. Chem. Soc.*, **95**, 2141 (1973).
(9) G. W. Sovocool, F. R. Hopf, and D. G. Whitten, *J. Amer. Chem. Soc.*, **94**, 4350 (1972); G. M. Brown, F. R. Hopf, J. A. Ferguson, T. J. Meyer, and D. G. Whitten, *ibid.*, **95**, 5939 (1973).
(10) Satisfactory elemental analyses were obtained for all stable new compounds.
(11) B. C. Chow and I. A. Cohen, *Bioinorg. Chem.* **1**, 57 (1971).
(12) M. Tsutsui, D. Ostfeld, and L. M. Hoffman, *J. Amer. Chem. Soc.* **93**, 1820 (1971); M. Tsutsui, D. Ostfeld, J. N. Francis, and L. M. Hoffman, *J. Coord. Chem.*, **1**, 115 (1971).
(13) S. S. Eaton, G. R. Eaton, and R. H. Holm, *J. Organometal. Chem.*, **39**, 179 (1972).
(14) D. Cullen, E. Meyer, Jr., T. S. Srivastava, and M. Tsutsui, *J. Chem. Soc., Chem. Commun.*, 584 (1972).
(15) F. A. Walker and G. L. Avery, *Tetrahedron Lett.*, 4959 (1971).
(16) J. E. Maskasky, Ph.D. Thesis, Case Western Reserve University, 1972.
(17) G. N. LaMar, *J. Amer. Chem. Soc.*, **95**, 1662 (1972).
(18) W. Bhatti, M. Bhatti, S. S. Eaton, and G. R. Eaton, *J. Pharm. Sci.*, **62**, 1574 (1973).
(19) S. S. Eaton and G. R. Eaton, *J. Chem. Soc., Chem. Commun.*, 576 (1974).

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Received September 30, 1974

No Susceptibility Effects on Transverse Relaxation of Water-Glass Granule Dispersion

Sir:

Glasel and Lee[1] have recently suggested that the nmr line widths and transverse relaxation times of the deuterium in D_2O-glass bead dispersion can be dominated by the effects of magnetic field inhomogeneities caused by magnetic susceptibility differences between the D_2O and the glass beads. In view of the importance of nmr measurements in investigating heterogeneous systems, we have tested their proposal by measuring the frequency dependence of the continuous wave (CW) line width and the transverse relaxation rate in a related system.

Three samples were prepared. Two contained H_2O in a dispersion of porous glass granules (BDH, type CPG-10, mesh size (U.S.) 120–200, pore diameter 66 Å, prepared according to Glasel and Lee's[1] prescription). The third sample was prepared in the same way with the exception that the water consisted of 79.7% D_2O and 20.3% H_2O by weight.

The line widths at half height, $\Delta\nu_{1/2}$, were measured using a JEOL 100-MHz and a Varian A-60A 60-MHz high-resolution spectrometer. The transverse relaxations were measured using a Bruker Physik B-Kr-322s pulsed spectrometer and a Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence[2] with the time between successive Π pulses, t_{cp} = 1 msec. The behavior of the transverse relaxations was independent of t_{cp} for $0.1 \leq t_{cp} \leq 20$ msec. The length of a $\Pi/2$ pulse was 2.5 μsec at 61 MHz and 7 μsec at 13.82 MHz. The maximum errors in the T_2 measurements due to rf field inhomogeneities[3] were determined from T_1 (longitudinal relaxation) measurements and found to be less than 1% at 61 MHz and less than 2% at 13.82 MHz.

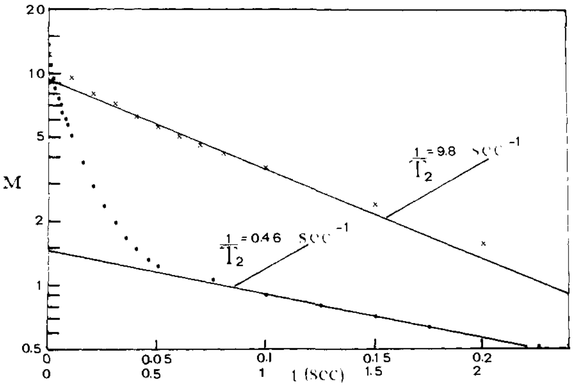

Figure 1. A semilog plot of the transverse magnetization (M) of the protons in a H_2O–glass bead dispersion as a function of time. The measurement was performed using a CPMG sequence at 61 MHz and 300°K with t_{cp} = 1 msec. The crosses (x) correspond to the upper time scale and the points (●) to the lower. The upper curve (x) was calculated by subtracting the lower line (long time relaxation) from the total magnetization.

Figure 1 shows the transverse relaxation of the 100% H_2O sample at 300°K and 61 MHz. All of the samples showed a similar behavior for the transverse relaxation with the long time decay corresponding to approximately 10% of the total signal.

One approach to the analysis of these data would be to assume that the water molecules are free to diffuse isotropically within the bulk water. Once a water molecule reaches the surface of a glass bead, however, its transverse magnetization relaxes to zero in a time short compared to the measurement time, *i.e.*, <0.1 msec. Assuming a Gaussian distribution[4] for the displacement of the water molecules with time and a relaxation time of T_2 for the bulk water, the magnetization at time t would be

$$M(t) = M(0)\exp(-t/T_2)(2/\Pi)^{1/2}\int_0^a \exp(-y^2/2)dy \quad (1)$$

where the integral represents the fraction of water molecules that have not reached a glass bead at time t and $a = x/(2Dt)^{1/2}$ where x is the distance a molecule must diffuse before reaching the surface of a glass bead, and D is the diffusion constant for the bulk water.

Equation 1 qualitatively reproduces the behavior of the

Table I. NMR Measurements on Glass Granule Dispersions

Sample	Nuc	Freq, MHz	Temp, °K	T_2^{-1} (short), sec^{-1}	T_2^{-1} (long), sec^{-1}	$\Delta\nu_{1/2}$, Hz
100% H_2O	^1H	100.00	301			50 ± 2
sample 1		60.00	301			29.5 ± 2
100% H_2O	^1H	61.00	300	9.8	0.46	
sample 2		13.82	300	10.3	0.43	
79.7% D_2O–	^1H	61.00	300	9.00	~0.3	
20.3% H_2O		13.82	300	8.85	~0.27	
sample 3		61.00	330	13.7	~0.21	
	^2H	13.82	300	13.4	1.9	
		13.82	330	17.9	1.1	

transverse decay with a single value of x ($\sim$10 μm); however, a quantitative fit would require a distribution of values for x. Consequently, in order to minimize the number of adjustable parameters, we have chosen an alternate approach.

We will assume that the water exists in three sites: (1) the bulk water (site A), (2) the "layered water" around the glass beads (site B) which is in rapid exchange with (3) the surface of the glass beads (site C). If the T_2 for the water in site C is much less than the lifetime at site C which is much less than the T_2 for site B, then sites B and C taken together relax with a single time constant[5] τ_{BC}, the lifetime for a molecule at site B to exchange to site C. Consequently, sites B and C, taken together, form a pseudo-site with relaxation time τ_{BC}. If τ_{BC} is much less than the relaxation time for the bulk water, T_{2A}, then the total magnetization relaxes[6] with two time constants, $1/\tau_B$ and $1/T_{2A} + 1/\tau_A$, where τ_i is the lifetime at site i ($1/\tau_B = 1/\tau_{BC} + 1/\tau_{BA}$).

An analysis of the data in terms of two rate constants, T_2^{-1}(short) and T_2^{-1}(long), is shown in Table I. Figure 1 shows that this analysis adequately describes the gross features of the relaxation; however, a more extensive analysis would probably require a description of the type given in eq 1.

The temperature dependence of T_2(short) shows that it behaves like an exchange time, as it should in terms of the above analysis. The temperature dependence of T_2(long), however, indicates that $\tau_A > T_{2A}$. Assuming a Gaussian distribution[4] for the displacement of the water molecules and a diffusion constant $D = 2.5 \times 10^{-5}$ cm^2/sec, then, after 2.5 sec, 10% of the molecules will have traveled less than 15 μm. In view of the diameter of the glass beads ($\sim$100 μm), then τ_A being larger than T_{2A} does not necessarily imply any restriction of the diffusion of the bulk water to the surface of the glass beads.

As indicated by Glasel and Lee,[1] one would expect effects arising from magnetic susceptibility differences in the two phases to be proportional to at least the first power of the frequency of the measurements. It can be seen from Table I that the line widths are proportional to the frequency. Also in agreement with Glasel and Lee,[1] it was found that spinning the sample reduced the line width by a factor of 2 (for a spinning rate of 50 Hz).

On the other hand, both T_2^{-1}(short) and T_2^{-1}(long) are independent of the frequency in the range studied within the experimental error of 10% for the short time component and considerably more for the long time component (due to the low amplitude of the latter). Consequently, it is clear that the transverse relaxation measured with a CPMG sequence is not dominated by magnetic susceptibility effects.

Irrespective of the analysis of the details of the transverse relaxation, the major conclusion of this work is that the transverse relaxation measured with a CPMG sequence is not dominated by effects resulting from field gradients produced by the difference in the magnetic susceptibilities of the beads and the bulk water. On the other hand, the line widths are dominated by these effects.

References and Notes

(1) J. A. Glasel and K. N. Lee, *J. Amer. Chem. Soc.*, **96**, 970 (1974).
(2) S. Meiboom and D. Gill, *Rev. Sci. Instrum.*, **29**, 688 (1958).
(3) T. E. Bull, *Rev. Sci. Instrum.*, **62**, 232 (1974).
(4) D. C. Douglass and D. W. McCall, *J. Phys. Chem.*, **62**, 1102 (1958).
(5) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).
(6) D. E. Woessner, *J. Chem. Phys.*, **35**, 41 (1961).

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Received June 13, 1974

Catalytic Hydrogenation of Arenes. II.[1] Arene Selectivity over Olefin and Reaction Mechanism for the Hydrogenation Reaction

Sir:

Recently, we reported[1] catalysis of arene hydrogenation at 25° by a discrete, soluble coordination complex, η^3-$C_3H_5Co[P(OCH_3)_3]_3$. We have now found that this catalyst exhibits a unique selectivity toward arenes over olefins. This finding of selectivity, buttressed with other new experimental results, provides considerable insight to the reaction mechanism in arene hydrogenations with this catalyst.

Competitive experiments[2] have demonstrated that the allyl-cobalt(I) complex catalyzes hydrogenation of benzene to cyclohexane at a rate three–four times that of cyclohexene to the alkane. Similar experiments with 1-hexene and with 2-hexene show analogous substrate selection with the rate of benzene hydrogenation at least twice that of the hexenes (isomerization of the hexenes does not proceed under these conditions). This remarkable, but not very large, selection for arenes raises the possibility of design of a practical, selective catalyst for arene hydrogenation. Additionally, the selection for the arene resolves unequivocally a mechanistic feature of arene hydrogenation with this cobalt catalyst.

Cyclohexene is not a detectable product in the catalytic hydrogenation of benzene.[3] The ring once partially hydrogenated must only rarely dissociate from the metal center (or separate from a solvent cage) as cyclohexene; cyclohexene cannot be an intermediate in the reaction because $k_{C_6H_6} > k_{C_6H_{10}}$. A similar argument applies to cyclohexadiene dissociation since the rate of cyclohexadiene to cyclohexane conversion by this cobalt catalyst is only about 1.3 times that for benzene hydrogenation (competitive experiments). Thus we can confidently visualize the hydrogenation sequence to proceed with transfer of hydrogen to ring without separation of reduced arene from the metal center until a cyclohexyl form is attained.

The above results, and ancillary experiments cited below, delineate some of the steps in the catalytic hydrogenation. The first step (eq 1) is postulated to be a $\pi \rightleftharpoons \sigma$ interconversion[4] for which there is convincing precedent;[5] this postulate is supported by experimental observations in ligand exchange reactions.[1,6] Arenes do not detectably[7] interact with the allyl complex but hydrogen does (eq 2) as shown initially[1] by tensimetric experiments.

$$\eta^3 - C_3H_5Co[P(OCH_3)_3]_3 \rightleftharpoons \eta^1 - C_3H_5Co[P(OCH_3)_3]_3 \quad (1)$$

$$\eta^1 - C_3H_5Co[P(OCH_3)_3]_3 + H_2 \rightleftharpoons \eta^1 - C_3H_5CoH_2[P(OCH_3)_3]_3(\alpha) \quad (2)$$

Formation of a hydride (α) has been confirmed through low temperature ^{1}H nmr studies of the allyl complex and hydrogen in cyclohexane. In addition to the ^{1}H resonances for η^3-$C_3H_5Co[P(OCH_3)_3]_3$, there is a weak, complex metal hydride resonance. Three stereoisomers are possible in an octahedral form of (α). There is no evidence of the isomer with the hydrogen ligands at trans positions. Thus, cis hydrogen addition prevails, and one of the two or both cis isomers of the dihydride (α) is present.[8]

Cis elimination of propylene (eq 3) does not occur to any significant extent in the dihydride provided that an arene is

$$\eta^1 - C_3H_5CoH_2[P(OCH_3)_3]_3 \rightleftharpoons C_3H_6 + HCo[P(OCH_3)_3]_3 \quad (3)$$