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Chemical Shift Anisotropy Relaxation in ^{103}Rh NMR

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Chemical shift anisotropy (CSA) has been shown to be an important contributor to spin-lattice relaxation in a number of heavier spin 1/2 nuclei [1]. Variable field measurements have previously confirmed the CSA contribution for ^{205}Tl [1], ^{195}Pt [2], ^{207}Pb [3] and ^{57}Fe [4]. Recently, Cocivera and coworkers suggested that the shorter T_1's in ^{103}Rh NMR of five-coordinate complexes compared to symmetric four-coordinate rhodium complexes are due to CSA [5]. Measurement of the T_1 of ^{103}Rh of one of the compounds reported by Cocivera *et al.*, *i.e.*, Rh(COD)(Bpz$_4$), (Bpz$_4$ = tetrakis(1-pyrazole)borate) at three different magnetic fields verifies their suggestion.

The contribution of CSA to spin-lattice relaxation is given by eqn. (1), where $\Delta\sigma$ is an anisotropy term, B_o is the applied field and τ_c is the

$$T_1^{-1}(\mathrm{CSA}) = 2/15\gamma^2 B_o^2 \Delta\sigma^2 \tau_c \qquad (1)$$

correlation time. It is seen from Fig. 1 that the relaxation rate ($1/T_1$) varies linearly with the square of the applied field which verifies that CSA does indeed contribute to the spin-lattice relaxation of ^{103}Rh. Since the field dependence of T_1^{-1} results entirely from $(T_1)^{-1}$ CSA, eqn. (2) can be written to determine the proportion of the total relaxation due to CSA [3].

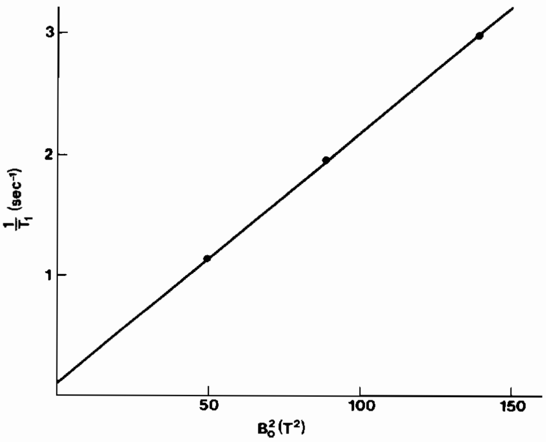

Fig. 1. ^{103}Rh spin-lattice relaxation rate in Rh(COD)(Bpz$_4$) *vs.* the square of the applied field.

$$(T_1)^{-1}{}_{\mathrm{CSA}}(B_o) = [(T_1)^{-1}{}_{\mathrm{obs}}(B_o) - (T_1)^{-1}{}_{\mathrm{obs}}(B_o')]\,[1-(B_o'/B_o)^2]^{-1} \qquad (2)$$

Using eqn. (2), it is found that the CSA contribution to the total relaxation is 92 and 97% at 7.05 and 11.75 *T*, respectively.

If it is assumed that dipolar relaxation with bound hydrogens dominates the spin-lattice relaxation of ^{13}C, an estimation of the molecular correlation time can be estimated from eqn. (3), where N is the number of hydrogens bound to a carbon atom [6].

$$T_1^{-1}(^{13}\mathrm{C}) = \frac{\gamma_C^2 \gamma_H^2 \tau_C N}{r_{C-H}^6} \qquad (3)$$

Assuming a C–H distance of 1.09 Å, a measurement of T_1 of the olefinic carbons of 0.95 s yields a correlation time of 5.2×10^{-11} s. Substituting the T^{-1} (CSA) value of ^{103}Rh calculated from the data obtained at 11.75 *T* (2.89 s^{-1}) into eqn. (1) yields a value of 6,500 ppm for the CSA of Rh(COD)(Bpz$_4$). The only other reported example of CSA being estimated for ^{103}Rh NMR is 524 ppm in the slower relaxing Rh(η^5-C$_5$H$_5$)(COD) [7].

TABLE I. Rhodium-103 T_1 Relaxation Times in Rh(COD)(Bpz$_4$) as a Function of Applied Field Strength^a.

B_o (*T*)	T_1 (s)	B_o^2 (*T*^{2})	$1/T_1$ (s^{-1})
7.05	0.886(21)	49.70	1.13(3)
9.39^b	0.510(5)	88.17	1.96(2)
11.75	0.334(5)	139.06	2.99(4)

^{a}Measured in CDCl$_3$ at 298 K. ^{b}Data from reference 5.

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