# The Rate of the Hexa-aquaruthenium(II)/(III) Self Exchange Reaction: $^{17}O$ and $^{99}Ru$ N.m.r. Spectroscopic Studies

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The self exchange rate for the $Ru(H_2O)_6{}^{2+/3+}$ couple determined by $^{17}O$ and $^{99}Ru$ n.m.r. spectroscopic studies is 44 ± 5 $dm^3\,mol^{-1}\,s^{-1}$ at 25 °C.

The $Ru(H_2O)_6{}^{2+/3+}$ couple merits special attention as the only known low-spin $d^6$–$d^5$ pair among transition metal aqua ions. Approximate values of $k$ for the self exchange reaction [reaction (1)] have been estimated by applying the Marcus cross relation to a series of redox reactions[1] and by using the results deduced from structural and spectroscopic studies of the solid hexa-aquaruthenium salts.[2] Both sets of calculations led to a value of *ca.* 60 $dm^3\,mol^{-1}\,s^{-1}$ for $k$. Here we report the first direct determination of the rate for the outer sphere electron transfer reaction (1) by $^{17}O$ and $^{99}Ru$ n.m.r. spectroscopy at 4.7 T. The outer sphere path for this reaction is confirmed by the rate of $(1.44 \pm 0.02) \times 10^{-2}\,s^{-1}$ (24.5 °C) for the water exchange measured by monitoring the $^{17}O$ n.m.r. signal for co-ordinated water at $\delta$ 198 p.p.m. (high field) relative to free $H_2{}^{17}O$ of a $Ru(H_2O)_6{}^{2+}$ salt quickly dissolved in water 10% enriched in $^{17}O$ (Figure 1). The linewidth of the $^{17}O$ resonance in the diamagnetic $Ru(H_2O)_6{}^{2+}$ is therefore determined only by the quadrupole

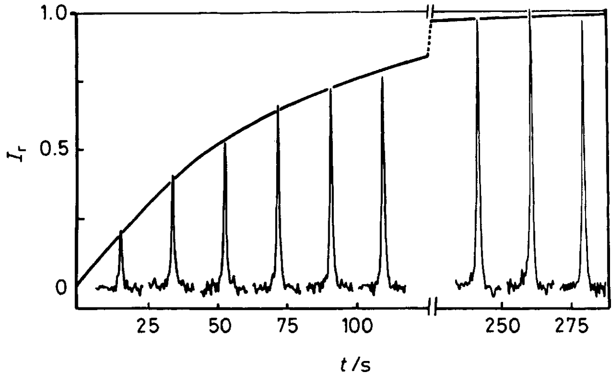

**Figure 1.** Relative intensity ($I_r = I_t/I_\infty$) *vs.* time ($t$) for the $^{17}O$ n.m.r. signal for co-ordinated $H_2{}^{17}O$ of $Ru(H_2O)_6{}^{2+}$ added to $^{17}O$ enriched water (10% $H_2{}^{17}O$).

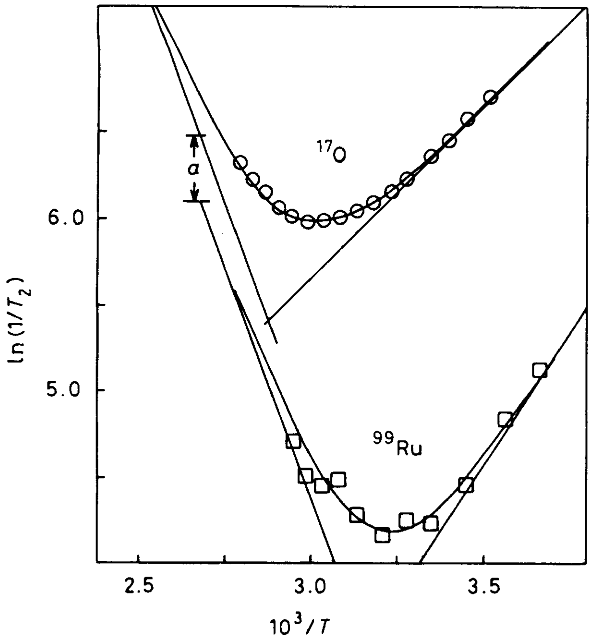

**Figure 2.** Temperature dependence of the relaxation rate for $^{17}O$ (○) and $^{99}Ru$ (□). The vertical displacement $a$ is determined by the different $Ru(H_2O)_6{}^{3+}$ concentrations (0.40 and 0.28 M, respectively): $a = \ln(0.40/0.28)$.

relaxation of $^{17}O$ and not by ligand exchange. For $Ru(H_2O)_6{}^{3+}$ the water exchange is even slower by a factor of 3000.[3] For $Ru(H_2O)_6{}^{2+}$, in the presence of $Ru(H_2O)_6{}^{3+}$, the electron transfer process provides an additional relaxation mechanism with an opposite temperature dependence. Since the temperature dependence of the diamagnetic shift is negligible, the observed relaxation rate is given by equation (2) where $1/T_2$ is related to the linewidth by $1/T_2 = \pi\cdot\Delta\nu_{\frac{1}{2}}$. $1/T_{2q}$ is the quadrupolar relaxation rate, $k$ the electron transfer rate of reaction (1), $k = (k_BT/h)\exp(\Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT)$. In a plot of $\ln(1/T_2)$ *vs.* $1/T$, two limiting straight lines are expected, one for each mechanism. Our study comprised solutions with $[Ru(H_2O)_6{}^{2+}]$ between 0.15 and 0.2 M, $[Ru(H_2O)_6{}^{3+}]$ between 0.2 and 0.7 M, and $[H^+]$ between 2.0 and 4.0 M, the counterion being trifluoromethanesulphonate. Figure 2 (upper curve) shows the plot for the $^{17}O$ signal of $Ru(H_2O)_6{}^{2+}$ in the range 0—90 °C for a solution 0.15 M in $Ru(H_2O)_6{}^{2+}$, 0.4 M in $Ru(H_2O)_6{}^{3+}$, and 3.8 M in $H^+$.

$$^*Ru(H_2O)_6{}^{2+} + Ru(H_2O)_6{}^{3+} \overset{k}{\rightleftharpoons} {}^*Ru(H_2O)_6{}^{3+} + Ru(H_2O)_6{}^{2+} \qquad (1)$$

$$1/T_2 = 1/T_{2q} + k[Ru(H_2O)_6{}^{3+}] \qquad (2)$$

Since we succeeded in detecting the $^{99}Ru$ n.m.r. signal of $Ru(H_2O)_6{}^{2+}$ at δ 16050 p.p.m. (low field) compared to the recently reported $^{99}Ru(CN)_6{}^{4-}$ resonance,[4] we used the linewidth of this signal as an additional independent probe to investigate the kinetics of reaction (1). Equation (2) is valid also for $^{99}Ru$, the small temperature dependence of the diamagnetic shift being neglected. The corresponding temperature dependence is represented by the lower curve in Figure 2 for a solution 0.3 M in $Ru(H_2O)_6{}^{2+}$, 0.28 M in $Ru(H_2O)_6{}^{3+}$, and 3.8 M in $H^+$. We notice the same behaviour for the two independent data sets.

The electron transfer process is the dominant relaxation mechanism only above 60 °C for which reason the precision of $k$ is affected by the extrapolation to 25 °C. The expansion of the temperature range is thus expected to improve the significance of our result. The simultaneous evaluation of the $^{17}O$ and $^{99}Ru$ n.m.r. spectroscopic experiments yields $k = 44 \pm 5\,dm^3\,mol^{-1}\,s^{-1}$, $\Delta H^{\ddagger} = 42.4 \pm 1.8\,kJ\,mol^{-1}$, and $\Delta S^{\ddagger} = -71.8 \pm 5.1\,J\,K^{-1}\,mol^{-1}$ for the $Ru(H_2O)_6{}^{2+/3+}$ self exchange reaction at 25 °C.

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