Quantitative Molecular Dynamics for Solid Cs_2WO_4 and $KMnO_4$ from ^{17}O VT MAS NMR

H.J. Jakobsen, H. Bildsoe (Aarhus U., Denmark, Chemistry); M. Brorson (Haldor Topsoe, Denmark); Z. Gan, I. Hung (NHMFL)

Introduction

Recent 21.15 T ^{17}O VT MAS NMR studies of Cs_2WO_4 [1], $KMnO_4$ [2], $KReO_4$ and NH_4ReO_4 [3] show that the ^{17}O MAS NMR spectra of the XO_4 anions for these salts change dramatically at low temperatures compared to the spectra at RT. This is caused by rapid reorientations of the tetraoxoanions in the solid-state, which make the four oxygens interchange positions, a phenomenon that is easily detected by solid-state ^{17}O MAS NMR spectroscopy. We here report determination of quantitative dynamic data for Cs_2WO_4 and $KMnO_4$ from a ^{17}O VT MAS NMR study. These data include exchange times, $\tau_{exch}(^{17}O)$, and activation energies, E_a, for the rotational dynamics of the WO_4^{2-} and MnO_4^- anion in Cs_2WO_4 and $KMnO_4$, respectively, obtained using the standard Arrhenius equation $k\tau_{exch} = 1/\tau_{exch} = A*\exp(-E_a/RT)$, where A is the so-called *frequency factor* (Hz) for a first-order reaction.

Experimental

^{17}O VT MAS NMR spectra of ^{17}O-enriched (~42%) Cs_2WO_4 and (~10%) $KMnO_4$ were recorded at 21.15 T (121.50 MHz) using the NHMFL 900 MHz ultra-widebore magnet and a 3.2 mm transmission-line VT MAS probe designed and constructed at the NHMFL. ^{17}O VT 1D/2D EXSY experiments were performed from –11 to –135 ºC.

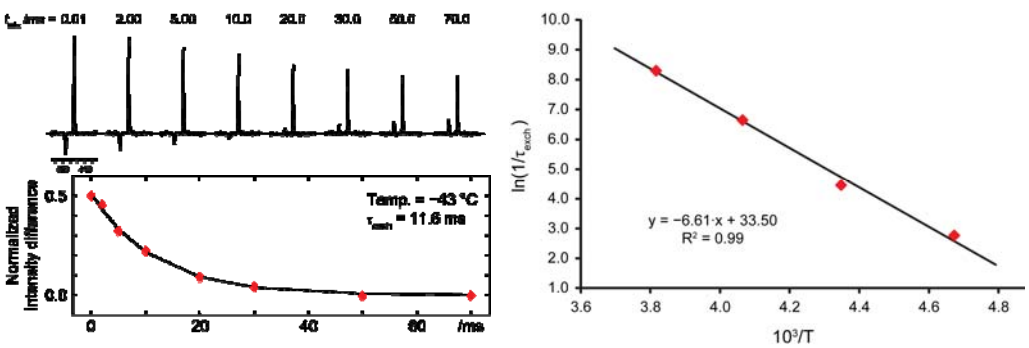

Figure. Left (upper): ^{17}O EXSY 1D MAS NMR spectra for the two 1:3 intensities for the CTs in Cs_2WO_4 at -43 °C. Left (lower): Optimum fit to the above intensities at -43 °C giving $\tau_{exch}(^{17}O)$ = 11.6 ms. Right: Linear fit of $\ln(1/\tau_{exch})$ versus $10^3/T$ for four different temperatures (–59, –43, –27, and –11 °C) . Thus, E_a = 55±2 kJ/mole is obtained for the dynamics of WO_4^{2-} in Cs_2WO_4.

Results and Discussion

Approximately similar 1D ^{17}O VT MAS NMR spectra to those presented above for Cs_2WO_4 have been observed in our recent ^{17}O VT MAS NMR study on the MnO_4^- anion of $KMnO_4$ as communicated in the NHMFL 2012 MagLab Research Report and our poster presented at EUROMAR 2013, Creete, Greece and at the SEMRC 2013, Tallahassee, Florida [2]. However, the ^{17}O VT MAS NMR spectrum for $KMnO_4$ requires much lower temperatures for the rotationally averaged singlet spectrum observed at RT to split into two equally intense groups of resonances, each representing two O-atoms and separated by ~56 ppm. This indicates a much lower E_a value compared to that determined above for Cs_2WO_4. ^{17}O VT EXSY MAS experiments on $KMnO_4$ from –85 to –135 ºC give $\tau_{exch}(^{17}O)$ values in the range 20 to101 ms, which result in an activation energy E_a = 6.8±0.4 kJ/mole for the MnO_4^- anion. Determination of the corresponding frequency factors A (Hz) from the respective linear plots for Cs_2WO_4 (see Figure) and $KMnO_4$ give $A = 3.5*10^{14}$ and $3.64*10^3$ Hz for the WO_4^{2-} and MnO_4^- anions, respectively. In conclusion, ^{17}O VT 1D/2D EXSY MAS NMR experiments have allowed determination of precise values for the rotational activation energies E_a = 55±2 and E_a = 6.8±0.4 kJ/mole for the XO_4 anions in Cs_2WO_4 and $KMnO_4$, respectively.

Acknowledgements

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References

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