Oxygen Isotope Effect on ^{55}Mn Nuclear Magnetic Shielding in Permanganate

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By Fourier transform NMR spectroscopy the ^{55}Mn resonance lines of the different permanganate species

$$^{55}\mathrm{Mn}^{16}\mathrm{O}_{4-n}{}^{18}\mathrm{O}_n^- \; (n=0, 1, 2, 3, 4)$$

have been resolved in aqueous solutions of potassium permanganate. An isotope effect on the Larmor frequency of ^{55}Mn of (0.599 ± 0.015) ppm to lower frequency was found for the substitution of an ^{16}O atom by an ^{18}O atom in the permanganate ion. An oxygen exchange rate in the permanganate-water system is given.

Introduction

Isotopic substitution is the minimal modification of a molecule. This may result in a change of the nuclear magnetic shielding. The study of such an effect is therefore important for elucidating the origin of chemical shift.

Intramolecular isotopic effects on the Larmor-frequency induced by the replacement of protons by deuterons are well known for many nuclei [1–4]. The order of magnitude of this effect comes up to 1 ppm in some molecules. An isotope effect induced by heavier nuclei has been found as far as we know only in a few favourable cases in the NMR spectra of ^{13}C (Ref. [5]), ^{19}F (Ref. [6–8]) and ^{59}Co (Ref. [9, 10]). A further example is the ^{55}Mn nucleus in the permanganate ion since the linewidth in this ion is small [11] and further large chemical shifts have been found for manganese compounds [12].

Experimental

^{55}Mn FT NMR spectra have been measured at 22.31 MHz with a multinuclei Bruker spectrometer [13] at (299 ± 2) K. A rotating spherical sample of 10 mm diameter was used. Potassium permanganate of natural abundance (^{55}Mn: 100%, ^{16}O: 99.76%, ^{17}O: 0.037%, ^{18}O: 0.204%) was dissolved in $H_2{}^{18}O$ (99% enriched in ^{18}O). The concentration was 0.27 molal.

The ^{55}Mn NMR spectra have been measured as a function of time after preparation of the sample since the exchange between the water oxygen atoms and the oxygen atoms in the permanganate is very slow at room temperature.

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Results

In Fig. 1 three of the ^{55}Mn spectra of the mentioned sample at different times after preparation are given. Due to the slow exchange of the oxygen atoms the five permanganate species

$$^{55}\mathrm{Mn}^{16}\mathrm{O}_{4-n}{}^{18}\mathrm{O}_n^- \; (n=0, 1, 2, 3, 4)$$

have highly different abundances as a function of time. Shortly after preparation only the $^{55}\mathrm{Mn}^{16}\mathrm{O}_4^-$-ion of the solute is present in the solution and as a result only the usual narrow single line [11] is observable. The substitution of one ^{16}O-atom by an ^{18}O-atom gives a further ^{55}Mn resonance line the intensity of which is proportional to the occurence

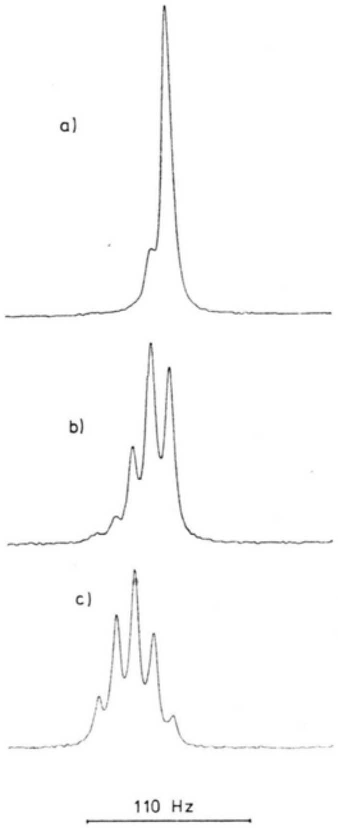

Fig. 1. ^{55}Mn spectra of a 0.27 molal solution of natural abundant $KMnO_4$ in $H_2{}^{18}O$ (99% enriched in ^{18}O) as a function of time: a) 4 hours, b) 5 days, c) 34 days after preparation. The frequency increases from the left to the right. Experimental parameters: Larmor frequency 22.311341 MHz; experimental spectrum width: 1 kHz; plotted spectrum width: 222 Hz; pulse repetition frequency: 1.67 Hz; number of pulses: 100; measuring time: 1 min; rotating spherical sample with 10 mm outer diameter; 1 K data points were accumulated followed by 7 K of zero-filling before Fourier transformation.

of the species $^{55}\mathrm{Mn}^{16}\mathrm{O}_3{}^{18}\mathrm{O}^-$. With running time all five possible species are present in the solution with characteristic abundances which can be calculated assuming a time constant T for the exchange process. At the end of the oxygen substitution the $^{55}\mathrm{Mn}^{18}\mathrm{O}_4{}^-$-ion is present with overwhelming concentration. At a time of $20 \cdot T$ about 97% of the permanganate ions are in this species with $n = 4$.

All five lines which are due to the five species are well resolved in the spectra at different times (see Figure 1). The substitution of an ^{16}O atom by an ^{18}O atom ($n = 0$ to $n = 1$) results in a change of the Larmor frequency of (12.48 ± 0.33) Hz to lower frequency, which is an isotopic effect of $-(0.559 \pm 0.015)$ ppm. The evaluation of the spectra yields an isotopic effect of $-(2.245 \pm 0.032)$ ppm for the two species $^{55}\mathrm{Mn}^{16}\mathrm{O}_4{}^-$ and $^{55}\mathrm{Mn}^{18}\mathrm{O}_4{}^-$, this is $-(0.281 \pm 0.004)$ ppm per mass unit. It should be noted, that the lines are equidistant within the limits of error.

For comparison, in the ^{59}Co-spectrum of the $\mathrm{Co(CN)}_6{}^{3-}$-ion an isotopic effect of (0.914 ± 0.004) ppm for the isotopic pair ^{12}C, ^{13}C and of (0.197 ± 0.007) ppm for the isotopic pair ^{14}N, ^{15}N has been found [9], which are of the same order of magnitude and also to lower frequency [10].

The evaluation of the intensities of the five lines as a function of time yields the time constant for the oxygen exchange in the water-permanganate system. A preliminary value for the time constant in the given sample is $T \approx 7$ days at room temperature.

Using these values, the very complicated ^{55}Mn pattern of a ^{17}O enriched permanganate sample, which contains also ^{18}O and ^{16}O, used in Ref. [13] for evaluating the scalar spin-spin coupling between ^{55}Mn and ^{17}O can be explained. A detailed investigation of these isotopic effect phenomena is running.

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