CHEMISTRY LETTERS, pp. 1497-1500, 1982.

^{109}Ag NMR SPECTRA OF AQUEOUS SILVER IONS COORDINATED WITH NITROXIDE RADICAL. SILVER-TANOL COMPLEX AND TANOL AS A DOPING AGENT

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The effects of TANOL radical have been examined on chemical shifts and relaxation rates of ^{109}Ag nmr in aqueous solution of silver salts. The silver ion in aqueous solution is found to coordinate with TANOL radical. A small amount of TANOL is added as a doping agent(0.020M), since ^{109}Ag signals are obtained for (1.0M) silver ion within 30 minutes. The ^{109}Ag chemical shifts of silver salt in aqueous solutions were found within the range of 0 to -1000 ppm relative to that of 1.0M $AgNO_3$.

Silver nuclei ^{107}Ag and ^{109}Ag are not facile and profitable to nmr investigations, because they resonate at a very low frequency and have very small sensitivity. Another difficulty with ^{109}Ag nmr measurements arises from the fact that this nucleus has an extremely long relaxation time. As a result of these experimental difficulties, there have been only a few papers[1-7] on nmr studies of silver nuclei.

We have observed that ^{109}Ag spectra of silver salt solutions(1.0M or less) can be obtained with a short repetition time(2-3 s), when a small amount of TANOL(2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl)[8] is added as a doping agent(0.020M). The ^{109}Ag chemical shifts of aqueous silver salt solutions lie in the range of 0 to -1000 ppm relative to that of 1.0M $AgNO_3$. We also indicated that silver ion forms the bimolecular coordinate bond with TANOL. We estimated the positive scalar hyperfine coupling constant for the ^{109}Ag nucleus and lifetime between the odd electron and silver nucleus in the complex consisting of silver ion and TANOL.

Natural abundance ^{109}Ag spectra were obtained at 4.11 MHz from samples in 10 mm tubes on a JEOL FX 90Q spectrometer in Fourier transform mode. The measurements were made at ambient temperature, ca. 30°C. 500-700 transients of 2-3 s were accumulated with pulse angles of 45°. The signals of silver salts

were very sharp. An external field frequency ^{2}D lock(D_2O) was used. All chemical shifts for ^{109}Ag are defined by the equation that $\Delta\delta_{sam} = (\nu_{ref} - \nu_{sam})/\nu_{ref}$, where ν_{sam} is the resonance frequency of the sample and ν_{ref} is the reference frequency. The lower the shielding, the more negative is the shift formulated in this manner. A 1.0M $AgNO_3$ solution is taken as the chemical shift reference for all ^{109}Ag measurements. When samples of 1.0M silver salt solutions contained 0.020M of TANOL as a doping agent, we corrected the chemical shifts as -10 ppm from Figure 1: $\Delta\delta \simeq$ (Const.)$\cdot$(N/No), where N,No are the concentrations of TANOL and $AgNO_3$, respectively. The bulk susceptibility corrections were made with ^{1}H water resonance within the error of $\pm$ 0.5 ppm. The T_1 was measured by $180^\circ - \tau - 90^\circ$ pulse sequence and T_2 evaluated from signal widths at half-height. The line shape of the ^{109}Ag spectra is assumed to be Lorentzian. All the compounds used here were commercially available. The solutions for the silver spectra in Table 1 were freshly made before use by completely dissolving a large amount of ligands(more than 2.0M), then dissolving the silver salts because some silver salts except silver nitrate are only sparingly soluble in water.

We investigated the radical effect on ^{109}Ag resonance positions and relaxation time in a 2.0M concentration of silver nitrate. The ^{109}Ag nmr signal of $AgNO_3$ in aqueous solution showed a downfield shift and a broadening with further addition of TANOL. The ^{109}Ag chemical shift was -24.5 ppm for $AgNO_3$/TANOL aqueous solution in which the molar ratio of $AgNO_3$ to TANOL is 20. The relaxation times are (83$\pm$0.5)ms for T_1 and (1.6$\pm$0.3)ms for T_2. As is shown in Figure 1, this downfield shift is proportional to the concentration of added TANOL. The shift is most likely caused by the Fermi contact interaction(theory of Bloembergen[9]) between a silver nucleus and a TANOL radical. This trend is also explained by the relaxation study. The T_1/T_2 ratio is 52, indicating the predominance of the Fermi contact term in the line width

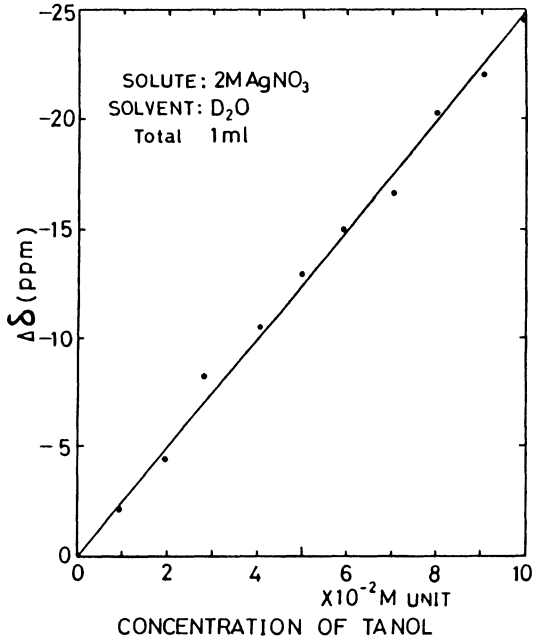

Figure 1. ^{109}Ag chemical shift at 30°C versus the concentration of added TANOL radical.

by using Solomon-Bloembergen(S-B) equations.[10] These results indicate that the silver ion forms a bimolecular coordinate bond (complex) with TANOL.

In the case of this bimolecular complex formation, we can estimate the scalar coupling constant for the ^{109}Ag nucleus and its lifetime in the Ag^+-TANOL complex. The relationship between the shift and the scalar coupling is approximated by Solomon's equation:

$$\Delta H/H = - \frac{\gamma_e A_{Ag} N n}{4 \gamma_{Ag} kTNo} \quad . \qquad (1)$$

where N,No are the numbers of radical and silver ion particles/cm^3, respectively; n is the number of silver ion molecules in the solvation sphere; γ_{Ag}, γ_e are the magnetogyric ratios of the silver and electron spin. We thus obtained a positive scalar hyperfine coupling constant(A_{Ag}) of 0.86 MHz. The rate of chemical exchange(τ_e) in the Ag^+-TANOL complex is estimated with the help of the S-B equations. The dipolar terms can be assumed to give nearly equal contributions to T_1 and T_2 and that $(\omega_s \tau_e)^2 \gg 1$, because the T_1/T_2 ratio is 52. Therefore, the simplified equation may be expressed as

$$(1/T_2)_{obsd} - (1/T_1)_{obsd} \simeq (A_{Ag}/2\pi)^2 \frac{N n \tau_e}{No} \quad . \qquad (2)$$

Using the notation of references,[10-12] we obtained $\tau_e \simeq 1.7 \times 10^{-9}$s. This value appears to correspond to those of the paramagnetic metal ion-water complexes obtained by nmr experiments[13] ($\tau_e \simeq 10^{-9}$s).

Table 1 presents the chemical shift data for a number of ^{109}Ag resonances in solutions containing TANOL as a doping agent. The chemical shifts

Table 1. ^{109}Ag chemical shifts for various silver salts in aqueous solution.

solution(in H_2O) silver salt	addend	chemical shift(ppm)*
$AgNO_3$(1.0M)/	$N(CH_2CH_2OH)_3$(4.0M)	-232
$AgNO_3$(1.0M)/	$HN(CH_2CH_2OH)_2$(4.0M)	-306
$AgNO_3$(1.0M)/	$H_2NCH_2CH_2OH$(4.0M)	-363
AgBr(0.072M)/	NaBr(4.0M)	-623+
AgI(1.0M)/	NaI(4.0M)	-739
AgCl(1.0M)/	$Na_2S_2O_3$(4.0M)	-826
$AgNO_3$(1.0M)/	KSCN(6.0M)	-951

*More negative values refer to lower shielding.

+ 27500 transients of 5s were collected for ^{109}Ag spectrum of the aqueous solution of 0.072M AgBr in 4.0M NaBr.

span a range of -1000 ppm. Such large variations in shielding are attributed to domination of the shielding constant by local paramagetic contributions.[14)]

We express our appreciation to Professor Tetsuo Yano, Messers. Shogo Ebato and Eiji Kanada for their interest and encouragement in this study.

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(Received July 8, 1982)