The following full text is a publisher's version.

For additional information about this publication click this link.
http://hdl.handle.net/2066/28496

Please be advised that this information was generated on 2020-01-12 and may be subject to change.
Identification of a Silver Hydroxymethyl Radical in Ag-NaA Zeolite Using Electron Spin Echo Envelope Modulation Spectroscopy

André van der Pol, Jacek Michalik, Eduard Reijerse,* and Engbert de Boer

Laboratory of Molecular Spectroscopy, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands, and Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland

Received: July 31, 1995; In Final Form: November 13, 1995

In Ag-loaded NaA zeolite the silver hydroxymethyl radical (Ag'CH$_2$OD) was stabilized and studied with electron spin echo envelope modulation (ESEEM) spectroscopy. Careful control of the CH$_2$OD concentration enabled the measurement of ESEEM spectra from which the hyperfine and quadrupole parameters of the intramolecular hydroxyl deuteron nucleus could be estimated. The isotropic hyperfine splitting constant, $A_{iso}$, is equal to $+2.9$ MHz, the electron–deuteron dipolar coupling parameter $T$ ($T = g_e g_d / (4h)$) is equal to $-1.4$ MHz, and the quadrupole parameter $P$ ($P = e^2 q Q / (4h)$) is equal to $±0.12$ MHz. These data are compared to listed data for the CH$_2$OH radical. The differences can be interpreted in terms of electronic, electrostatic, and matrix effects.

Introduction

For some years the Ag-NaA zeolite has been attracting attention because NaA zeolite is a highly symmetric system and Ag is a transition metal with potential catalytic and photographic properties.

Van Beeckel et al. introduced the Ag-NaA zeolite as a promoter for $\beta$-glycosidic bond formation, and Whitfield et al. revealed stereoselectivity in this reaction. Zhang et al. showed that silver-loaded zeolites can be used as NOI adsorbents for flue gases. Beer et al. introduced the Ag-NaA zeolite as a possible coupler between the oxidative and reductive parts of a photochemical energy storage system. In addition the NaA zeolite can trap transient species, a property that is useful in the study of reaction mechanisms. The formation of silver clusters is especially attracting much interest. In dehydrated NaA zeolites with organic adsorbate molecules, in particular methanol, were observed but now with smaller splittings in the range 269–303 MHz. The reduction of the silver hyperfine coupling was attributed to matrix effects. Again, the loss of signals due to CH$_2$OH correlated well with the growth of the doublet signal of the silver–methanol adduct. Although high silver concentrations immediately lead to the adduct signal, low concentrations require annealing to 180 K. This proves that the second reactant is Ag$^+$. Since methanol and methanol radicals are present in the $\alpha$-cages and for low silver concentrations Ag$^+$ is present only in the $\beta$-cages, annealing is necessary because Ag$^+$ has to migrate to the $\alpha$-cage in order to react with the hydroxymethyl radical. For high silver concentrations Ag$^+$ also resides in the $\alpha$-cages so that the silver adduct can be formed without annealing.

Michalik et al. using three-pulse ESEEM spectroscopy, studied the organosilver adduct in Ag-SAPO-42 and Ag-NaA zeolite using deuterium-labeled methanol. The time domain traces showed modulations due to two distant methanol molecules. Although the exact methanol concentration was not known, we assume that the Ag-NaA zeolite was saturated with methanol because Dikanov et al. carrying out primary echo experiments on CH$_2$OH in NaA zeolites with methanol adsorbates, also found modulations due to two distant methanol molecules but only for the case of complete saturation.

Definite identification would require detection of hyperfine couplings to intramolecular deuteron nuclei. Michalik et al. stated that such interactions are ESEEM invisible because they are too large. Here, we would like to consider the alternative possibility that the modulations due to the abundant distant nuclei simply mask the modulations due to the intramolecular deuterons. Therefore we decided to study nonsaturated samples and analyze the ESEEM spectra in the frequency domain.

Experimental Section

Linde NaA (4A) zeolite was washed with 0.1 M sodium acetate and then ion-exchanged at room temperature in the dark...
Silver Hydroxymethyl Radical in Ag-NaA Zeolite

The Ag-NaA sample was placed in a Suprasil quartz tube (inner diameter of 3 mm) and connected to a vacuum line (0.001 mm Hg) for dehydration. During the dehydration, the temperature was raised to 140 °C at a speed of 1 degree per min or slower. Then the sample was exposed to methanol for 24 h with a solution of 0.4 mM AgNO₃. The sample was dried in the dark at atmospheric pressure and subsequently analyzed with atomic absorption spectrometry. The silver concentration was one Ag⁺ per unit cell of zeolite (Ag-NaA).

The CW-EPR and ESEEM spectra were measured with a Bruker ESP-300 X-band spectrometer. For the ESEEM spectra the stimulated echo sequence (three-pulse) π/2-τ-π/2-τ-π/2-τ and the primary echo sequence (two-pulse) π/2-τ-π-τ-echo and the stimulated echo sequence (three-pulse) π/2-τ-π/2-τ-π/2-τ-π/2-τ were used. The microwave π/2 pulses were 16 and 24 ns long for the two- and three-pulse measurements, respectively. The ESEEM time domain traces were corrected for exponential decay. Thereupon, a sine bell and a Hamming window function were applied followed by zero filling and finally fast fourier transformation. All spectra were presented in the amplitude mode. ESEEM simulations were carried out using the spin Hamiltonian program MAGIXE.¹⁰

Results and Discussion

Figure 1 shows the EPR spectrum of Ag-NaA with CH₃OH adsorbate, irradiated and annealed at 180 K. Clearly visible is the isotropic doublet signal with a splitting of 317 MHz, a line width of 64 MHz, and a g-value of 2.003. The triplet signal in the center of the spectrum is due to the CH₃OH radical with $A_{\text{iso}} = 50$ MHz.

Figure 2 shows two-pulse ESEEM spectra for various deuterated methanol molecules, taken with the magnetic field at the position of the high-field line of the doublet. If CH₃OH is used as an adsorbate only, isotropic lines at once and twice the aluminum Larmor frequency are observed. The lines are due to distant aluminum nuclei of the zeolite matrix and are indicated in Figure 2a with $v_{\text{Al}}$ and 2$v_{\text{Al}}$. An unidentified line below 1 MHz might be caused by distortion due to the filtering procedure. Upon the use of CD₃OH as an adsorbate, two new lines are observed, indicated in Figure 2b with $v_{\text{D}}$ and 2$v_{\text{D}}$. These lines are due to distant deuterium nuclei of solvent CD₃OH molecules. No lines due to intramolecular deuterium nuclei are observed despite the use of various methanol concentrations. The spectrum for the case of the CH₃OD adsorbate is shown in Figure 2c. Besides the lines due to distant aluminum and deuterium nuclei a new strong line is observed at 1.41 MHz, indicated in Figure 2c by an asterisk. This line can only be due to a deuterium nucleus. Its position is significantly shifted from the deuterium Larmor frequency, indicating that the hyperfine interaction is fairly large and that it is due to an intramolecular deuterium nucleus. In order to obtain a spectrum with such a pronounced line, due to the close hydroxyl deuterium nucleus, it is necessary to optimize the methanol concentration inside the zeolite. We varied the concentration by changing the contact time period to methanol. For low concentrations the signal intensity of the electron spin echo is too low to measure ESEEM traces with sufficient signal-to-noise ratios; for high methanol concentrations the lines at the deuterium Larmor frequencies due to solvent molecules obscure the lines due to close deuterium nuclei.

Figure 2. Two-pulse ESEEM spectra of the silver hydroxymethyl: (a) ($\text{Ag}^+\text{CH}_3\text{OH}$), $B = 350.1$ mT; (b) ($\text{Ag}^+\text{CD}_3\text{OH}$), $B = 350.1$ mT; (c) ($\text{Ag}^+\text{CH}_3\text{OD}$), $B = 352.1$ mT.
The dipolar point approximation is justified because the distance \( r \) is about 2 Å (vide infra). For \( T = +1.4 \text{ MHz} \) the best result was obtained. In the figure we labeled the lines at the primary frequencies due to the \( \alpha \)- and \( \beta \)-electron spin manifolds with \( \nu_\alpha \) and \( \nu_\beta \), respectively. Combination harmonic lines were identified using the equation derived by Tyryshkin et al.,\(^{11}\) and are indicated in the figure as well. No quadrupolar interaction and no distant deuterium and aluminum nuclei were taken into account. The simulation of Figure 4 is the result of optimizing both \( A_{\text{iso}} \) and \( T \). The best fit was obtained with \( A_{\text{iso}} = +2.9 \text{ MHz} \) and \( T = +1.4 \text{ MHz} \). The striking differences from the previous simulations are that the \( \nu_\alpha \) and \( \nu_\beta \) lines correspond better to the experimental lines and that the higher order combination harmonic line labeled \( 2\nu_\alpha + \nu_\beta \) increased in intensity. Finally, we took into account the quadrupolar interaction, with principal components \(-P, -P, +2P \) \( (P = e^2q(\mu_0/4\pi)) \), and the relative orientation of its unique axis with respect to the unique axis of the dipolar coupling tensor of \( \beta \) degrees. Generally, as shown by Tyryshkin et al.,\(^{11}\) the effect of a small quadrupolar interaction on the primary frequencies is small. However, the combination line \( 2\nu_\alpha + \nu_\beta \) is split. This splitting is dependent on angle \( \beta \) and reaches its maximum value of \( 3 \times P \) for \( \beta \approx 30^\circ \). For \( P = \pm 0.12 \text{ MHz} \) and \( \beta = 30^\circ \) we were able to reproduce the experimental splitting of about 0.36 MHz (see Figure 5). Note that the introduction of a quadrupole interaction increases the line width of all resonance peaks.

It is still unsatisfactory that the \( \nu_\beta \) line cannot be observed directly; it is hidden under the strong \( \nu_\alpha \) line. Therefore, we carried out a three-pulse experiment in which we suppressed the \( \nu_\alpha \) line by choosing the appropriate \( r \) value of 264 ns (3.8 MHz). The result of the experiment is shown in Figure 6. The \( \nu_\alpha \) line is completely absent, and the \( \nu_\beta \) line now becomes visible.

The three-pulse spectrum was simulated using the spin Hamiltonian parameters for the close deuterium nucleus cited above. In addition a number of distant deuterium nuclei at different distances were taken into account. It was necessary to include deuterium nuclei at different distances in order to reproduce a line at the double Zeeman frequency (2\( \nu_\alpha \)) of sufficient intensity. The agreement between the results of the experiment and simulation is good. In particular we draw attention to the \( r \)-suppression effect on the \( \nu_\beta \) line. In the two-pulse spectra the \( \nu_\alpha \) line has a higher intensity than the \( \nu_\beta \) line. The opposite behavior is found in the three-pulse spectrum. Since the \( r \)-suppression frequency is close to \( \nu_\beta \) (3.8 MHz), the corresponding line in the \( \alpha \)-manifold (\( \nu_\alpha \)) is suppressed. This effect is beautifully reproduced in the simulation, which is strong support for the interpretation.
can be seen in parts a and h of Figure 2, We were able, seems reasonable. Thus, apart from lines due to distant deuterium nuclei are ESEEM invisible because they are too large. For the very close α-deuterium nuclei this assumption is confirmed by our experiments, as expected by Dikanov et al. Furthermore, they took into account the quadrupolar interaction and found a value of 0.05 MHz. We found for the (Ag(CH$_2$OD)$_2$)$^+ \text{ radical} P \approx \pm 0.12 MHz. Electrostatic fields present in the zeolite matrix cannot explain the difference entirely since $P$ values for deuterium nuclei in many organic molecules do not differ much in organic and zeolitic matrices. A more plausible explanation may arise from the charge present in the (Ag(CH$_2$OD)$_2$)$^+$ radical. This charge may give rise to large electrostatic fields. Moreover, because of the charge, the (Ag(CH$_2$OD)$_2$)$^+$ radical can be located closer to the negatively charged zeolite framework than the neutral CH$_2$OD radical.

Finally, we remark that it might be worthwhile to carry out external nuclear double resonance (ENDOR) experiments to detect the coupling constants to the α-protons of the silver-hydroxy methyl radical. An overall picture of the spin density distribution in the silver radical could then be obtained, enabling a comparison to the spin distribution in the CH$_2$OH radical.

Concluding Remarks

Michalik et al.\(^{8}\) stated that interactions with intramolecular deuterium nuclei are ESEEM invisible because they are too large. For the very close α-deuterium nuclei this assumption seems reasonable. Thus, apart from lines due to distant deuterium nuclei of solvent methanol molecules, we expect the (Ag($\text{CH}_2$OD)$_2$)$^+$ radical to the parameters obtained by Dikanov et al.\(^{12}\) for the CH$_2$OD radical in frozen CH$_2$OD. For the CH$_2$OD radical they found $A_{\text{iso}} = \pm 1.1$ MHz and $T = \pm 1.5$ MHz; we found for the (Ag($\text{CH}_2$OD)$_2$)$^+$ radical $A_{\text{iso}} = +2.9$ MHz and $T = \pm 1.4$ MHz. A quadrupolar interaction was not taken into account by Dikanov et al.\(^{12}\). If we compare the $A_{\text{iso}}$ values for the two radicals, it can be concluded that the spin density on the deuterium nucleus in the (Ag($\text{CH}_2$OD)$_2$)$^+$ radical is larger than in the CH$_2$OD radical. The reason is that CH$_2$OD is a nearly flat radical in which the unpaired electron is localized in a $p_c$ orbital centered at the carbon nucleus. (Ag($\text{CH}_2$OD)$_2$)$^+$, however, has a pyramidal configuration at the carbon nucleus and is a $\pi$-radical. Therefore, the unpaired electron can be delocalized via $\pi$-bonds over the –OD fragment of the radical. The dipolar coupling parameter $T$ corresponds to an average distance of the unpaired electron to the deuterium nucleus of 1.99 Å for the $\text{CH}_2$OD radical. For the (Ag($\text{CH}_2$OD)$_2$)$^+$ radical this distance is 2.05 Å. Apparently in the (Ag($\text{CH}_2$OD)$_2$)$^+$ radical the average position of the electron is somewhere in between the positions of the carbon and the silver nucleus.

Iwasaki and Toriyama\(^{13}\) also studied the CH$_2$OD radical but trapped in frozen CH$_3$OH. For $A_{\text{iso}}$ and $T$ they found values comparable to the values of Dikanov et al.\(^{12}\). Moreover, they found a hyperfine interaction of an intramolecular (deuterium) nucleus of solvent methanol molecules, we expect a larger $A_{\text{iso}}$. For the very close α-deuterium nuclei this assumption seems reasonable. Thus, apart from lines due to distant deuterium nuclei of solvent methanol molecules, we expect the (Ag($\text{CH}_2$OD)$_2$)$^+$ radical to the parameters obtained by Dikanov et al.\(^{12}\) for the CH$_2$OD radical in frozen CH$_2$OD. For the CH$_2$OD radical they found $A_{\text{iso}} = \pm 1.1$ MHz and $T = \pm 1.5$ MHz; we found for the (Ag($\text{CH}_2$OD)$_2$)$^+$ radical $A_{\text{iso}} = +2.9$ MHz and $T = \pm 1.4$ MHz. A quadrupolar interaction was not taken into account by Dikanov et al.\(^{12}\). If we compare the $A_{\text{iso}}$ values for the two radicals, it can be concluded that the spin density on the deuterium nucleus in the (Ag($\text{CH}_2$OD)$_2$)$^+$ radical is larger than in the CH$_2$OD radical. The reason is that CH$_2$OD is a nearly flat radical in which the unpaired electron is localized in a $p_c$ orbital centered at the carbon nucleus. (Ag($\text{CH}_2$OD)$_2$)$^+$, however, has a pyramidal configuration at the carbon nucleus and is a $\pi$-radical. Therefore, the unpaired electron can be delocalized via $\pi$-bonds over the –OD fragment of the radical. The dipolar coupling parameter $T$ corresponds to an average distance of the unpaired electron to the deuterium nucleus of 1.99 Å for the $\text{CH}_2$OD radical. For the (Ag($\text{CH}_2$OD)$_2$)$^+$ radical this distance is 2.05 Å. Apparently in the (Ag($\text{CH}_2$OD)$_2$)$^+$ radical the average position of the electron is somewhere in between the positions of the carbon and the silver nucleus.

Iwasaki and Toriyama\(^{13}\) also studied the CH$_2$OD radical but trapped in frozen CH$_3$OH. For $A_{\text{iso}}$ and $T$ they found values comparable to the values of Dikanov et al.\(^{12}\). Moreover, they took into account the quadrupolar interaction and found $P = 0.05$ MHz. We found for the (Ag($\text{CH}_2$OD)$_2$)$^+$ radical $P \approx \pm 0.12$ MHz. Electrostatic fields present in the zeolite matrix cannot explain the difference entirely since $P$ values for deuterium nuclei in many organic molecules do not differ much in organic and zeolitic matrices. A more plausible explanation may arise from the charge present in the (Ag($\text{CH}_2$OD)$_2$)$^+$ radical. This charge may give rise to large electrostatic fields. Moreover, because of the charge, the (Ag($\text{CH}_2$OD)$_2$)$^+$ radical can be located closer to the negatively charged zeolite framework than the neutral CH$_2$OD radical.

Finally, we remark that it might be worthwhile to carry out external nuclear double resonance (ENDOR) experiments to detect the coupling constants to the α-protons of the silver-hydroxy methyl radical. An overall picture of the spin density distribution in the silver radical could then be obtained, enabling a comparison to the spin distribution in the CH$_2$OH radical.

References and Notes


JP952177Z.