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Analysis of the NMR Line Shape Dually Modulated by the Chemical Exchange and by the Scalar Coupling Relaxation. ^{13}C NMR Spectrum of the Trimethylaluminum Dimer

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Synopsis. ^{13}C methyl signals of the trimethylaluminum dimer, broadened by the chemical exchange and the scalar coupling interaction with ^{27}Al, were analyzed in order to obtain the rates of the bridge-terminal exchange of the methyl groups. The exchange rates were compared with those obtained from the ^1H resonance, and a good agreement was obtained. A brief discussion is given of some advantages and difficulties of the analysis.

It is well known that the alkyl groups of the trialkylaluminum dimer undergo a rapid exchange between the bridge and the terminal positions at ambient temperature. This exchange in the trialkylaluminum dimer has been studied extensively by ^1H and ^{13}C NMR spectroscopies, and the Arrhenius parameters for the exchange have been calculated.[1,2] In a previous paper[3] we have shown that, even within the slow-exchange limits, the ^{13}C signals of the methyl groups in the trimethylaluminum (TMA) dimer are broadened by the scalar coupling between the ^{13}C and ^{27}Al nuclei, which is modulated by the rapid quadrupole relaxation of the Al nucleus. By analyzing the line shape of the ^{13}C signals and using the relaxation time of ^{27}Al, we were able to obtain the scalar coupling constant between ^{13}C and ^{27}Al (J_{C-Al}) within the slow-exchange limits. In this exchanging system, under the rapid and intermidiate exchange conditions, the signals of the ^{13}C nuclei directly bonded to Al are dually modulated by two time-dependent effects, *i.e.*, the chemical exchange and the scalar coupling with ^{27}Al, in which situation the analysis of the NMR line shape is rather complicated. However, if one of the effects of the interactions on the line shape could be accurately known, we would have the possiblity of obtaining information on the other interaction by analyzing the line shape. In the present note, as an example of the line-shape analysis under such circumstances, the methyl carbon signal of TMA is studied to obtain exchange rates at various temperatures, with the ^{27}Al relaxation rates and J_{C-Al} known, and the exchange rates thus obtained are compared with those obtained from the ^1H resonance.

The ^1H and ^{13}C spectra were recorded on a NEVA NV-14 spectrometer at 60 and 15.1 MHz respectively. The sample concentration is *ca.* 10% of TMA in cyclopentane-d_{10}. The other experimental details are the same as those reported in a previous paper.[3]

The expressions for the NMR intensities at the frequency of ω under the influence of the chemical exchange and the scalar coupling relaxation have the same form,[4] both given by

$$I(\omega) = Re[\mathbf{W}\cdot\mathbf{A}^{-1}\cdot\mathbf{1}], \tag{1}$$

where the vector **W** has components proportional to the populations, **1** is a unit column vector, and *Re* means the real part. For the methyl signals of TMA undergoing the bridge-terminal exchange, **A** has the form:

$$\mathbf{A} = i(\mathbf{\Omega}-\omega\mathbf{E}) + \mathbf{Q} + \mathbf{K}, \tag{2}$$

in which $\mathbf{\Omega}$ is the diagonal matrix whose elements are the chemical shifts of each site, and **E**, the unit matrix. **Q** and **K** are the matrices representing the effects of the scalar coupling relaxation and the chemical exchange respectively, and are further decomposed as

$$\mathbf{Q} + \mathbf{K} = \begin{pmatrix} \mathbf{Q}^b+\mathbf{K}_1{}^b & \mathbf{K}_2{}^b \\ \mathbf{K}_2{}^t & \mathbf{Q}^t+\mathbf{K}_1{}^t \end{pmatrix}, \tag{3}$$

where the superscripts b and t refer to the bridge and the terminal positions respectively. $\mathbf{Q}^b$, $\mathbf{K}_1{}^b$, *etc.* are also matrices whose components are referred to the ^{13}C lines which would be split by ^{27}Al if the scalar relaxation mechanism were absent. The detailed expressions for $\mathbf{Q}^b$, $\mathbf{Q}^t$ and **W** of TMA were presented in the previous paper.[3] **Q** contains information about the J_{C-Al} and ^{27}Al relaxation times, conversely, if the two quantities are known, the line shape of ^{13}C under the influence of the scalar relaxation can be calculated.

$\mathbf{K}_1{}^b$ and $\mathbf{K}_1{}^t$ are simple diagonal matrices whose diagonal elements are $-1/\tau_b$ and $-1/\tau_t$ respectively. τ_b and τ_t are the life-time of the methyl group at the bridge and the terminal positions respectively, and $2\tau_b=\tau_t$, since the population at the bridge position is one-half of that of the terminal. $\mathbf{K}_2{}^b$ and $\mathbf{K}_2{}^t$ correspond to the off-diagonal parts of the kinetic transfer matrix, **A**, in the usual expression for the exchanging system. In constructing $\mathbf{K}_2{}^b$ and $\mathbf{K}_2{}^t$, we assume that the exchange process is "intramolecular"[2] and one bridge bond is broken during the exchange. Thus, the methyl carbon at the terminal position which sees the ^{27}Al spin state of, say, $\left|\frac{5}{2}\right>$ goes to the bridge position at which the methyl carbon coupled with two Al nuclei, and sees one of the six composite ^{27}Al spin states; $\left|\frac{5}{2}\right>\left|\frac{5}{2}\right>$, $\left|\frac{5}{2}\right>\left|\frac{3}{2}\right>$,…… $\left|\frac{5}{2}\right>\left|-\frac{5}{2}\right>$. Thus, the elements of the corresponding column in the corresponding row of $\mathbf{K}_2{}^t$ have the values of $1/6\tau_t$, and the other elements of the row are 0. The bridge carbon, after exchange, goes to a site which corresponds to one of the spin states of ^{27}Al with which the bridge carbon couples before exchange. (For example, from the site of $\left|\frac{5}{2}\right>\left|\frac{3}{2}\right>$ to either $\left|\frac{5}{2}\right>$ or $\left|\frac{3}{2}\right>$ but from the site of $\left|\frac{5}{2}\right>\left|\frac{5}{2}\right>$ only to the site of $\left|\frac{5}{2}\right>$.) Consequently, $\mathbf{K}_2{}^b$

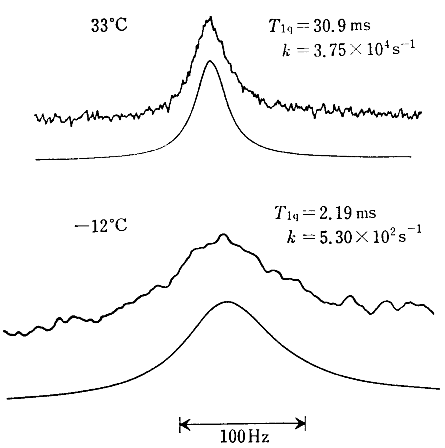

Fig. 1. Observed and calculated ^{13}C spectra of TMA at various temperature. The chemical shift difference between the bridge and the terminal carbons is 60 Hz at 15.1 MHz.

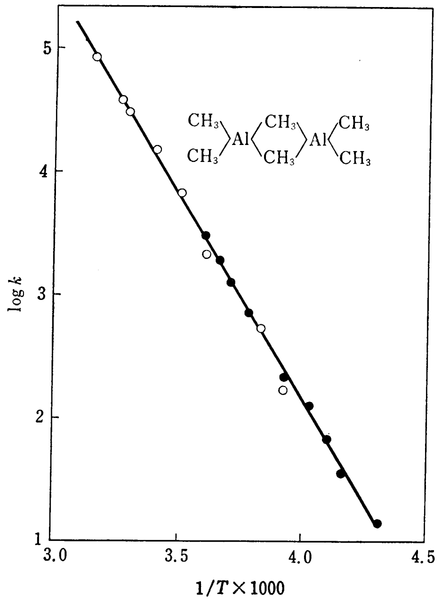

Fig. 2. Arrhenius plot of the exchange rates in TMA. ● from the ^1H resonance and ○ from the ^{13}C resonance. The straight line was obtained by the least squares fit of only the ^1H resonance data. The Arrhenius parametrs obtained from both ^1H and ^{13}C data are $E_a=15.2\pm0.8$, $\Delta H^*=14.6\pm0.8$, $\Delta G^*=11.6\pm0.1$ kcal /mol, and $\Delta S^*=10.0\pm2.0$ e.u. at 25 °C. These are in good agreement with literature valaues.[1,2)]

has the elements $1/\tau_t$, $1/2\tau_t$ or 0. In this way, the matrices $\mathbf{K}_2{}^b$ and $\mathbf{K}_2{}^t$ can be easily constructed.

The rate constant for the exchange $k=1/\tau_b$ can be calculated from Eq. 1 by a visual fitting of the observed spectra with the calulated ones in a try-and-error method if the coupling constant, J_{C-Al}, and the ^{27}Al relaxation time, T_{1q}, are known. The J_{C-Al}'s in TMA were found to be 19 and 110 Hz for the bridge and the terminal carbons respectively, and the ^{27}Al relaxation time, T_{1q}, were obtained from the line-widths of the ^{27}Al resonance lines.[3)]

The results obtained are shown in Figs. 1 and 2. The exchange rates were also obtained from the ^1H resonance, for which the usual line-shape analyses were carried out. It can be seen from Fig. 2 that the exchange rates obtained from the ^{13}C resonance fit well with the straight line which is obtained from the ^1H resonance, particularly in the higher temperature range. Thus, the procedure presented here, though complicated in its calculation, can be successfully used to obtain the exchange rates with an accuracy comparable with that of the usual line-shape analysis when the latter method cannot be employed. The results obtained in this work also provide a cross-check on the validity of the method and the accuracy in the values of the J_{C-Al}'s in TMA reported in the previous paper.[3)]

A difficulty in the line-shape analysis mentioned above arises from the different NOE-enhancement factors for the bridge and the terminal carbons in the ^1H decoupled ^{13}C spectra. The intensity ratio of the terminal to the bridge carbons is about 1.8 at −70 °C (at the slow-exchange limit). This indicates that the NOE factor for the bridge carbon is larger than that of the terminal. Since the J_{C-Al} is smaller in the bridge than in the terminal carbon, the contribution of the scalar coupling mechanism to the relaxation rate of ^{13}C is smaller, and thus that of the dipole-dipole interaction is larger, in the bridge carbon than in the terminal, which leads to the larger NOE factor in the bridge carbon. Therefore, the spectra calculated without taking account of the difference in the NOE factor will not agree with the observed one.

Indeed, this is the case for the spectra with intermediate and slow exchange rates (below *ca.* −30 °C). However, the difference in the NOE factor can be assumed to be negligible provided that the exchange rate is much faster than the ^{13}C relaxation rates, because the redistribution of the spin population among the various energy levels, which causes the NOE factors to be different, does not occur during the short life-time at each site. Thus, Eq. 1 can be safely employed in the high-temperature range.

Note that, in the ^1H resonance, the line-widths at temperatures of 10 °C or higher are too narrow to obtain accurate values of the exchange rates. In the ^{13}C resonance, however, the line-widths are sufficiently wide at room temperature because of the scalar coupling interaction, and accurate values are obtained in the high-temperature range, in which the ^1H resonance cannot be applied for the TMA system. This is another advantage of the present method.

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