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Observation of Silicon-29 Lanthanoid-Induced Shifts and Its Use for Estimates of Equilibrium Constants for the Complex of an Organosilane with a Lanthanoid Shift Reagent

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On the successive addition of Pr(fod)$_3$(L) to a 0.53 M $CDCl_3$ solution of diethoxydimethylsilane(S) at 25 °C, the large lanthanoid-induced ^{29}Si shifts were observed and analyzed in terms of the least squares fits to one step equilibrium between L and S to estimate the intrinsic shift of the 1:1 complex and the equilibrium constant.

It has been demonstrated in our laboratory that the paramagnetic shifts of ^{59}Co,$^{1)}$ ^{27}Al,$^{2)}$ and ^{195}Pt$^{3)}$ nuclei induced by lanthanoid shift reagents(LSR's) can be successfully observed for non-charged (β-diketonato)metal complexes in a nonpolar solvent at an ambient probe temperature. On the other hand, a lanthanoid-induced shift(LIS) of ^{29}Si nucleus has not been observed so far to our knowledge. We now report the LIS detected at the ^{29}Si nucleus for silicon compounds containing donor oxygens bound directly to silicon.

On the successive addition of Pr(fod)$_3$(L)$^{4)}$ to a 0.53 M $CDCl_3$ solution of diethoxydimethylsilane(S) with 0.57 M TMS as an internal standard and 0.01 M Cr(acac)$_3$(R) as a relaxation agent, a large ^{29}Si shift of this silane toward higher-field was observed at an ambient probe temperature (25 °C). It has been confirmed that a small amount (0.01 M) of Cr(acac)$_3$ permits sufficient relaxation of the ^{29}Si nucleus and yet introduces no observable shift of the free form of S. It might possibly be considered that Cr(acac)$_3$ coordinates with the LSR via its three bridging oxygens,$^{5)}$ however since the concentration of R is much smaller than that of S, a possible equilibrium $L + R \rightleftharpoons LR$ may be neglected in the present discussion. The ^{29}Si shifts (δ_{obsd}) relative to TMS are plotted vs. the concentration ratios of L to S in Fig. 1. This implies that S rapidly exchanges on the NMR time scale between its free form and its coordination complex with L in solution. It has been known that bifunctional organic molecules incorporating two donor oxygens contiguous with each other are liable to act as bidentate ligands toward LSR.$^{6)}$ From this view, the 1:1 complex is expected to be formed via bidentate interaction. Then, an equilibrium $L + S \rightleftharpoons LS$ is given, where the equilibrium constant is denoted as K, and the calculated LIS can be described as $\delta_{calcd} = [LS]/[S_0]\cdot\Delta_{LS}$, where Δ_{LS} and $[S_0]$ are the intrinsic shift of the 1:1 complex and total concentration of S, respectively. The data analyses by the least squares fits of observed shifts (the number of data points is 21) to this equilibrium were

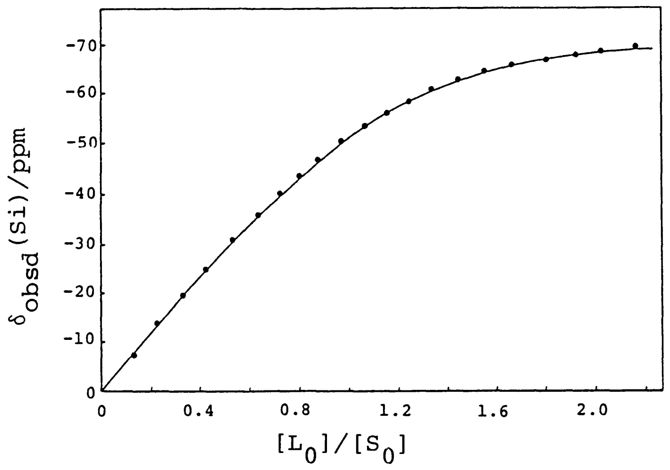

Fig. 1. Pr(fod)$_3$-induced ^{29}Si shifts vs. $[L_0]/[S_0]$ plots for a 0.53 M $CDCl_3$ solution of diethoxydimethylsilane at 25 °C on the successive addition of Pr(fod)$_3$. Negative signs denote high-field shifts. ^{29}Si NMR spectra were recorded on a Varian CFT-20 spectrometer equipped with a broad band accessory at 15.801 MHz using the deuterium internal-lock system. The acquisition time was taken as 1.023 s for the spectra width of 4000 Hz, the number of data points being 8192. The number of transients was ≈2000.

carried out using a computer iteration method. K and Δ_{LS} were consequently estimated to 7.2 M^{-1} and -84.2 ppm, respectively, with a satisfactory agreement (the standard deviation is 0.87 ppm). Addition of self-association mechanism $L + L \rightleftharpoons L_2$ to the equilibrium system resulted in rather poor agreement with the experimental data.

This K-value is almost consistent with that (15 ± 2 M^{-1}, averaged value) obtained from ^{1}H LIS for the same system$^{7)}$ within experimental errors but is fairly smaller than that (60 ± 10 M^{-1}, averaged value) observed for the corresponding compound having a carbon instead of a silicon.$^{7)}$ This might be attributed to the decrease in coordinating ability of lone pair electrons of donor oxygens due to $(d-p)_\pi$ bonding formed possibly between silicon and oxygens.

The magnitude of Δ_{LS} estimated above cannot strictly be separated into contact and pseudo-contact contributions to date. However, this may be expected to incorporate a large contact shift(cs) contribution, from the comparisons of roughly estimated pseudo-contact shift(pcs) ratios and observed LIS's for ^{1}H and ^{29}Si nuclei of this complex. The amount of cs of ^{29}Si may be largely affected by the magnitude of possible $(d-p)_\pi$ bonding in the pathway of electron spin from the lanthanoid ion into an s-orbital of silicon. Consequently, such a cs contribution of the ^{29}Si LIS is expected to be used for demonstrating the occurrence of $(d-p)_\pi$ interaction interested theoretically. In the near future, the complete sets of ^{1}H, ^{13}C, and ^{29}Si LIS data with a series of Ln(fod)$_3$ for related silanes will be observed and treated for the separation into cs and pcs.

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