

NMR SPECTRA OF CO-ORDINATION COMPOUNDS OF TRIALKYL ALUMINUMS
WITH DONORS

Koichi Hatada and Heimei Yuki
Department of Chemistry, Faculty of Engineering Science,
Osaka University,
Toyonaka, Osaka, Japan

(Received in Japan 28 August 1967)

High resolution proton magnetic resonance spectra of alkyl metal compounds, especially of ethyl derivatives, have been studied in recent years. In trying to evaluate the electronegativity of the metal with the chemical shifts in the spectra, Dailey (1) first proposed a relationship between the separation of methyl and methylene proton resonances of an ethyl group and the electronegativity of the metal. Later the relationship was modified by Shoolery (2,3) through altering the empirical constants of the equation. The modified form of the relation is:

$$\text{Electronegativity} = 0.62\delta + 2.07 \quad (1)$$

where δ is the difference between the methyl and methylene proton shifts in p.p.m. According to this equation, the internal chemical shift of ethyl group increases as the electronegativity of the metal increases. In the case of aluminum alkyls, the electronegativity of aluminum is less than the constant 2.07, so δ becomes negative, that is, the methyl protons are less shielded than the methylene protons.

The measurement of this internal chemical shift δ would also be useful in studying the change in the electronegativity of metal in a ethyl metal compound upon co-ordination with donor compounds. Brownstein (4) has reported that the internal chemical shift of triethyl aluminum decreased upon co-ordination with diethyl ether and this indicated the electronegativity of aluminum being decreased by the donation of electrons from the oxygen. However, contrary to expectation, he has found that the δ value of diethyl ether also decreased upon co-ordination.

Now we investigated the NMR spectra of co-ordination compounds of triethyl aluminum or trimethyl aluminum with various donors. It was found that the apparent electronegativity of aluminum in the trialkyl aluminums decreased upon co-ordination with donor compound and the magnitude of the decrease depends on the donating power of the co-ordinating compound. We also found that the apparent electronegativity of the oxygen in n-alkyl ether generally increased with co-ordination to triethyl aluminum. This result is different from Brownstein's one.

The NMR spectra were obtained at 21.0°C with a JNM-4H-100 Spectrometer (Japan Electron Optics Laboratory Co. Ltd.,) at 100 Mc/sec by using a solution in toluene. It has been reported (5) that toluene shows some dilution effects on the signals of trialkyl aluminums. The effects were also observed in this investigation, so the concentration of the sample solution was kept to be constant (0.5 mole/l) in all measurements. Chemical shifts were referred to the methyl signal of solvent toluene. Trialkyl aluminum-donor complex was prepared by adding a donor to an equimolar amount of trialkyl aluminum in toluene.

The NMR spectra of various triethyl aluminum-donor complexes are shown in Table 1. The internal chemical shift δ of triethyl aluminum decreases upon co-ordination with donor and the stronger the donor was co-ordinated, the larger the decrease was obtained. The magnitude of decrease in δ changes in parallel with the logarithm of the basicity constant (6) of donor compound. These results indicate that the relative strength of donor can be generally determined by measuring the internal chemical shift δ in the triethyl aluminum-donor complex.

In the case of Et_3Al -pyridine complex the δ value was rather larger despite of the strong donating power of pyridine. This suggests that pyridine co-ordinated to the triethyl aluminum at the nitrogen atom and the induced ring current in the nuclei deshielded the methylene proton of ethyl group in triethyl aluminum.

On the other hand, the internal chemical shift δ of diethyl ether increased when the ether complexed to triethyl aluminum. If we understand

TABLE 1
NMR Spectra of Triethyl Aluminum-Donor Complexes at 21°C in Toluene

Donor	Chemical Shift of		δ (p.p.m.)	$\log K_D^*$
	C_2H_5-Al (p.p.m.)			
	CH_3-	$-CH_2-$		
$(C_2H_5)_3N$	-0.75	-2.00	-1.25	10.74
Pyridine	-0.76	-1.79	-1.03	5.17
THF	-0.80	-2.01	-1.21	—
Dioxane	-0.88	-2.09	-1.21	-3.67
$(C_2H_5)_2O$	-0.80	-2.01	-1.21	-0.27
$(n-C_3H_7)_2O$	-0.78	-1.99	-1.21	-1.63
$(n-C_4H_9)_2O$	-0.77	-1.96	-1.19	-2.32
$(n-C_6H_{13})_2O$	-0.80	-1.99	-1.19	—
$(n-C_8H_{17})_2O$	-0.82	-1.99	-1.17	—
$C_6H_5OCH_3$	-0.86	-2.00	-1.14	-6.40
$(C_6H_5)_2O$	-0.96	-1.88	-0.92	-9.79
None	-1.03	-1.81	-0.78	—

* Logarithms of the basicity constants, which are the ionization constants of the bases for water solution divided by the ion product constant of water (K_w) according to Gordy (6).

the δ as the difference between the ω -methyl and α -methylene proton shifts in higher n-alkyl groups, the δ values of n-alkyl ethers also increased with complexing to triethyl aluminum (Table 2). The difference between the δ of complexing ether and that of free one decreased as the alkyl group of ether became higher. These results show that the measurements of δ values in free and complexing ether may be used as a practical mean of estimating the relative change in the electronegativity of oxygen in ether upon co-ordination.

The relation between the chemical shift of methyl proton in trimethyl

TABLE 2
 NMR Spectra of Triethyl Aluminum-n-Alkyl Ether Complexes
 at 21°C in Toluene

Ether	δ of Alkyl Proton in Ether (p.p.m.) [*]		$\delta_c - \delta_f$
	Free Ether (δ_f)	Complexed Ether (δ_c)	
(C ₂ H ₅) ₂ O	2.16	2.55	0.39
(n-C ₃ H ₇) ₂ O	2.33	2.67	0.34
(n-C ₄ H ₉) ₂ O	2.39	2.68	0.29
(n-C ₆ H ₁₃) ₂ O	2.42	2.66	0.24
(n-C ₈ H ₁₇) ₂ O	2.43	2.66	0.23

^{*} $\delta = (\text{Chem. Shift of } \omega\text{-CH}_3) - (\text{Chem. Shift of } \alpha\text{-CH}_2)$

aluminum-donor complex and the donor character of the complexing compound was also studied with NMR spectroscopy. The signal of methyl proton in trimethyl aluminum showed higher shift upon co-ordination with donor compound, and the magnitude of the shift toward the higher field was closely related to the donor character of the co-ordinating compound as shown in Table 3. These results show that the co-ordination of the donor to trimethyl aluminum increased the electron density about the aluminum atom to shield the methyl proton more strongly. The anomaly in methyl proton shift of the pyridine complex may be caused by the induced ring current in pyridine nuclei as appeared in pyridine-triethyl aluminum complex. The values of δ in n-alkyl ethers showed similar behavior upon co-ordination as in the triethyl aluminum-ether complexes.

The authors wish to express their thanks to Mr. Yoshio Terawaki for the measurements of NMR spectra.

TABLE 3
 NMR Spectra of Trimethyl Aluminum-Donor Complexes
 at 21°C in Toluene

Donor	Chem. Shift of CH ₃ -Al (p.p.m.)	δ of Alkyl Proton in Ether (p.p.m.)		δ _c - δ _f
		Free(δ _f)	Complexed(δ _c)	
(C ₂ H ₅) ₃ N	-2.67	—	—	—
Pyridine	-2.56	—	—	—
THF	-2.65	—	—	—
Dioxane	-2.71	—	—	—
(C ₂ H ₅) ₂ O	-2.67	2.16	2.56	0.40
(n-C ₃ H ₇) ₂ O	-2.64	2.33	2.79	0.46
(n-C ₄ H ₉) ₂ O	-2.62	2.39	2.72	0.33
(n-C ₆ H ₁₃) ₂ O	-2.61	2.42	2.65	0.23
(n-C ₈ H ₁₇) ₂ O	-2.61	2.43	2.61	0.18
C ₆ H ₅ OCH ₃	-2.65	—	—	—
(C ₆ H ₅) ₂ O	-2.46	—	—	—
None	-2.46	—	—	—

References

- (1) B. P. Dailey and J. N. Shoolery, J. Am. Chem. Soc., 77, 3977 (1955)
- (2) J. N. Shoolery, Lecture Notes, Varian Associates Conference (1957)
- (3) P. T. Narasimhan and M. T. Rogers, J. Am. Chem. Soc., 82, 5983 (1960)
- (4) S. Brownstein, B. C. Smith, G. Ehrlich and A. W. Laubengayer, J. Am. Chem. Soc., 81, 3826 (1959)
- (5) O. Yamamoto and T. Suzuki, Presented at the 18th Annual Meeting of the Japan Chemical Society (1965)
- (6) W. Gordy, J. Chem. Phys. 9, 204, 215 (1941)