

THE ELECTRONEGATIVITIES OF ALUMINUM IN ETHYL AND  
ISOBUTYL ALUMINUMS AND THEIR COMPLEXES BY NMR

by T. Takeshita and W. E. Frankle\*  
E. I. du Pont de Nemours and Company, Inc.  
Elastomer Chemicals Department  
Experimental Station  
Wilmington, Delaware 19898

Contribution No. 193

(Received in USA 11 July 1968; received in UK for publication 24 October 1968)

An empirical relationship between the electronegativity  $\chi$  of a central metal atom of a compound  $\text{CH}_3\text{-CH}_2\text{M}$  and its internal chemical shift  $\Delta_{\text{CH}_2\text{-CH}_3}$ , a difference in proton chemical shifts of  $\text{CH}_2$  and  $\text{CH}_3$ , has been useful in comparing properties of organometallics. (1,2) The usual form for this relationship is given by the modified Dailey-Shoolery equation (1,3):  $\chi = 0.62\Delta + 2.07$  (1), which has been applied to triethylaluminums and ethyl aluminum halides. (4,5,6,7,8) Although changes in magnetic shielding are caused not only by a difference in inductive effect, but also by magnetic effects such as anisotropy, the D-S equation (1) offers a simple means for identifying Lewis acid strength of alkyl aluminums and their complexes with bases. The present authors wish to report on the application of the rule to ethyl aluminum and its extension to isobutyl aluminums and their complexes.

The PMR spectra were run at an ambient temperature unless noted otherwise, on a Varian HA-100 spectrometer using a 10 mole % benzene

---

\*A summer employee June-August 1967. Present address:  
Department of Chemistry, Princeton University.

solution. The chemical shift of benzene was taken as 7.37 ppm from tetramethylsilane. The 1:1 complex with a Lewis base was prepared by mixing equimolar amounts of the reagents.

Table I summarizes the internal shifts  $\Delta_{\text{CH}_2-\text{CH}_3}$  of alkyl aluminums and their complexes, which allow us to calculate the electronegativities of Al in the Et series using eq. (1). (See the Et series in Table II.) For an obvious reason the same equation is not applicable for the estimations of  $\chi_{\text{Al}}$  in the isobutyl series, which are developed later in this communication. It is clear that the greater the  $\Delta$  value is (i.e. less negative), the greater is the electronegativity of the aluminum and the smaller is the electron density around Al. Replacement of Et with Cl results in increasing the electronegativity of the central metal, as observed in the series  $\text{Si}(\text{C}_2\text{H}_5)_4-\text{SiCl}_2(\text{C}_2\text{H}_5)_2$  (3), or the Lewis acid strength, while the complex formation with bases causes its decrease. Table I also lists downfield shifts of internal shift  $\Delta_{\alpha\text{CH}_m-\beta\text{CH}_n}$  of bases upon complex formation with  $\text{R}_n\text{AlCl}_{3-n}$ . The decrease in the electronegativity of the Al monitored by  $\text{CH}_2-\text{CH}_3$  protons means in a simplified picture an increase in the electron density on Al, which finds its counterpart in terms of the increased electronegativity of oxygen of bases on complex formation. (9) For example, as the internal shift of  $\text{O}-(\text{CH}_2-\text{CH}_3)_2$  increases from 2.17 to 2.68, the increase in the electronegativity corresponding to an  $\chi_{\text{O}}$  3.42 $\rightarrow$ 3.74, on complex formation with  $\text{Et}_2\text{AlCl}$ , the  $\chi_{\text{Al}}$  of  $\text{Et}_2\text{AlCl}$  decreases from 1.52 to 1.37 (Table II). Since the complete thermochemical data are not available, the decrease in a C-O stretching frequency upon complex formation may be substituted for the strength of the complex, where the shift  $\nu_{\text{C-O}}^{\text{Free}} - \nu_{\text{C-O}}^{\text{Complex}}$  will be greater, the stronger the complex, hence with the stronger aluminum species. Evidently Fig. 1 shows such a relationship, where  $\chi_{\text{O}}$  calculated from eq. (1) increases in proportion to the  $\nu_{\text{C-O}}$  shift or the Lewis acid strength of the Al species, which also proportionally changes the  $\chi_{\text{Al}}$ 's. Therefore, the internal shifts of oxygen bases seem to give a good indication of the strength of the complex with the Lewis acid  $\text{R}_n\text{AlCl}_{3-n}$  since the acids are similar in structure and no large anisotropy differences are anticipated. They are useful common grounds on which to compare ethyl

TABLE I

Internal Shifts  $\Delta_{\text{CH}_2-\text{CH}_3}$  of Ethyl and Isobutyl Aluminums,  
and  $\Delta_{\alpha\text{CH}_m-\beta\text{CH}_n}$  of the Base Resonances

Concn.: 10 mole % in Benzene  
Complex: 1:1

Bases	$\text{Et}_3\text{Al}$	$\text{Et}_2\text{AlCl}$	$\text{EtAlCl}_2$	$\text{iBu}_3\text{Al}$	$\text{iBu}_2\text{AlCl}$	$\text{iBuAlCl}_2$	None
None	-0.79 (-1.12)*	-0.88	-0.74	-0.72	-0.57	-0.51	
$\text{Ph}_2\text{O}$	-0.94	-0.89	-0.82	-0.78	-0.58	-0.69	
$\text{PhOCH}_3$	-1.16	-1.05	-0.91	-0.98	-0.91	-0.86	
THF	-1.22 (2.29)**	-1.11 (2.36)	-0.98 (2.46)	-1.05 (2.28)	-0.96 (2.36)	-0.83 (2.48)	(1.94)
$\text{Et}_2\text{O}$	-1.22 (2.59)	-1.13 (2.68)	-0.99 (2.76)	-1.05 (2.48)	-0.98 (2.68)	-0.85 (2.79)	(2.17)
$(\text{i-Pr})_2\text{O}$	-1.19 (3.07)	-1.08 (3.23)	-1.00 (3.34)	-0.98 (3.07)	-0.93 (3.18)	-0.84 (3.33)	(2.41)
Pyr.	-1.05	-0.93	-0.80	-0.81	-0.74	-0.62	

\* Terminal ethyl groups at  $-70^\circ\text{C}$ . Lit. value, -1.11 [O. Yamamoto (10)].

\*\* Figures ( ) indicate internal shifts of base resonances ( $\Delta_{\alpha\text{CH}_m-\beta\text{CH}_n}$ ).

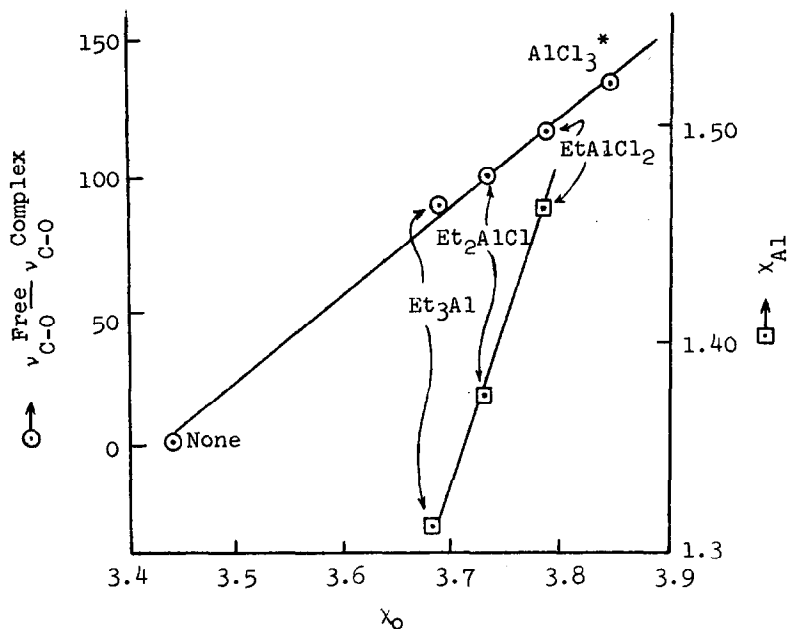
with isobutyl aluminum series. One may now say that the Al electronegativities of both series are equal if the base resonances with complexes of two series show identical internal shifts, whether THF,  $\text{Et}_2\text{O}$  or  $(\text{i-Pr})_2\text{O}$  is used. (Table I) A plot of the  $\chi_{\text{Al}}$  in the isobutyl series against  $\Delta_{\text{CH}_2-\text{CH}_3}$  using eight such data gives the following isobutyl equation analogous to the ethyl eq. (1).

$$\chi_{\text{iBu}_n\text{Al}_{3-n}} = 0.73\delta + 2.08; \Delta(\text{CH}_2-\text{CH}_3) \quad (2)*$$

\*correl. coeff.  $r = 0.976$ , standard deviation  $S_\chi = 0.014$

Fig. 1

Correlation between  $\chi_O$  and  $\chi_{Al}$  in Complexes  
 $Et_2O-Et_nAlCl_{3-n}$  and  $\nu_{C-O}^{Free} - \nu_{C-O}^{Complex}^{**}$



\* Taken from ref. (10), corrected for the difference in values of free  $Et_2O$ .

\*\* Ref. (11).

It is of interest to note that the equation has the same intercept as the equation (1) with a somewhat greater slope. This is reasonable since when  $M=H$ , i.e.  $\Delta=0$ ,  $\chi$  calc. should become the electronegativity of H, 2.07, which should be, and indeed is identical in both series. A greater slope simply shows a better insulation in transmission of electronic effects by an extra carbon. Equation (2) now allows us to calculate and compare electronegativities of both complexed and noncomplexed isobutyl series in one place as given in Table II together with the Et series already obtained from eq. (1). The fact that  $\chi_{Al-iBu} > \chi_{Al-Et}$  in the noncomplexed

TABLE II

 $\chi_{Al}$  of Ethyl and Isobutyl Aluminums and Their Complexes

Base	$Et_3Al$	$Et_2AlCl$	$EtAlCl_2$	$iBu_3Al$	$iBu_2AlCl$	$iBuAlCl_2$
None	1.37*	1.52	1.61	1.55	1.66	1.71
$Ph_2O$	1.49	1.52	1.56	1.51	1.66	1.58
$PhOCH_3$	1.35	1.42	1.51	1.36	1.42	1.45
THF	1.31	1.38	1.47	1.31	1.38	1.47
$Et_2O$	1.31	1.37	1.46	1.31	1.36	1.46
$(1-Pr)_2O$	1.33	1.40	1.45	1.36	1.40	1.47
Pyridine	(1.42)**	(1.49)	(1.57)	(1.49)	(1.54)	(1.63)

\* Calculated from terminal ethyl groups ( $-70^\circ C.$ ).

\*\* These may not reflect true values. For details, see the text.

cases is not known, but a steric factor may be involved. However, among the complexes the  $\chi$ 's were generally in the following order (or the relative Lewis acid strength order) regardless of the alkyl groups:

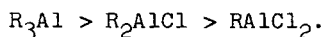


Table II indicates also that such a weak base as diphenyl ether does not form a complex with  $R_2AlCl$  as revealed by no change in  $\chi$ . Since  $R_2AlCl$  usually exists as a dimer, diphenyl ether is not strong enough to cleave the dimer for the complex formation. However, much strong acid of the type  $RAlCl_2$  forms a complex. Since  $iBu_3Al$  is a monomer at room temperature requiring no reorganization energy, diphenyl ether can form a complex with it. This is in contrast to  $Et_3Al$ , most of which exists as a dimer (12,13), and only a portion in a complex form, where a rapid exchange in an NMR time scale produces an averaged shift.

The apparently weaker basicity of pyridine which was also previously noted by others (8,9) may be due to a positive charge developed in the pyridine ring where the ring current may result in an abnormal deshielding of the methylene protons yielding an erroneously high Al electronegativity for the complex.

References

1. B. P. Dailey and J. N. Shoolery, J. Am. Chem. Soc. 77, 3977 (1955).
2. cf. J. W. Emsley, J. Feeney and L. H. Sutcliffe, High Resolution Nuclear Magnetic Resonance Spectroscopy, Vol. 2, p. 670, Pergamon Press, London (1966).
3. P. T. Narasimhan and M. T. Rogers, J. Am. Chem. Soc. 82, 5983 (1960).
4. E. G. Hoffmann and G. Schomburg, Adv. in Molecular Spectroscopy, Vol. 2, p. 804, Pergamon Press, Oxford (1962); Proc. IVth Inter. Meeting on Mole. Spectroscopy.
5. S. Brownstein, B. C. Smith, G. Ehrlich and A. W. Laubengayer, J. Am. Chem. Soc. 81, 3826 (1959).
6. O. Yamamoto, Bull. Chem. Soc. Jap. 36, 1463 (1963).
7. C. A. Smith and M. G. H. Wallbridge, J. Chem. Soc. 1966A 7.
8. Y. Takashi, Bull. Chem. Soc. Jap. 40, 612 (1967).
9. Similar to an independent observation recently reported. K. Hatada and H. Yuki, Tetrahedron Letters; 213 (1968).
10. R. L. Richards and A. Thompson, J. Chem. Soc. (A) 1245 (1967).
11. S. Takeda and R. Tarao, Bull. Chem. Soc. Jap. 38, 1567 (1965).
12. O. Yamamoto, Bull. Chem. Soc. Jap. 37, 1125 (1964).
13. N. Muller and D. E. Pritchard, J. Am. Chem. Soc. 82, 248 (1960).

Acknowledgment

Authors are indebted to the Elastomer Chemicals Department for the permission to publish and encouragement received. We also thank Dr. E. G. Brame for reading the manuscript and valuable suggestions.