Substituent Effects. VIII. Correlation of Aluminum-27 Chemical Shifts of Tetrahaloaluminate Ions by Pairwise Interactions

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Received February 28, 1969

Abstract: ^{27}Al shifts of the tetrahaloaluminate ions are found to be pairwise additive. This fact lends further credence to the theoretical work of Malinowski and Vladimiroff.

Kidd and Traux[1] recently measured ^{27}Al chemical shifts of a series of tetrahaloaluminate ions. They observed "that each halogen does not contribute a fixed increment to the aluminum shielding, but rather the contribution of each halogen is dependent upon the other substituents bonded to aluminum." No further statements concerning the nature of this dependency are ventured. The purpose of the present note is to point out that the ^{27}Al shifts of the tetrahaloaluminate ions are pairwise additive.

Table I contains a list of six pairwise parameters which are required to reproduce the experimental data shown in Table II. All 15 values obtained from pairwise additivity agree with the experimental values well within the experimental error, ± 0.02 to ± 0.05 ppm.

The assignment of approximately -79 ppm to $AlCl_2BrI^-$ by Kidd and Traux[1] is based on the observation that the resonance line of $AlBr_4^-$, which appears at -79.6 ppm, is somewhat wider than expected. The shift of $AlCl_2BrI^-$ is thus assigned on the belief that the two lines overlap. The value, -78.5 ppm, obtained from pairwise additivity (see Table II) indeed confirms this assignment and illustrates the utility of the rule.

Table I. Pairwise Parameters for ^{27}Al Shifts of Some Tetrahaloaluminate Ions

Substituents i,j	Pairwise parameters, ppm η_{ij}
I,I	+4.5
Br,I	−6.8
Cl,I	−11.6
Br,Br	−13.3
Cl,Br	−15.7
Cl,Cl	−17.1

(1) R. G. Kidd and D. R. Traux, *J. Am. Chem. Soc.*, **90**, 6867 (1968).

Table II. Comparison between Calculated and Observed ^{27}Al Shifts of Some Tetrahaloaluminate Ions

Anion	Pairwise additivity		Observed[a]
AlI_4^-	$6\eta_{I,I}$	+27.0	+27.0
AlI_3Cl^-	$3\eta_{I,I} + 3\eta_{Cl,I}$	−21.3	−21.7
$AlI_2Cl_2^-$	$\eta_{I,I} + 4\eta_{Cl,I} + \eta_{Cl,Cl}$	−59.0	−59.4
$AlICl_3^-$	$3\eta_{Cl,I} + 3\eta_{Cl,Cl}$	−86.1	−86.2
$AlCl_4^-$	$6\eta_{Cl,Cl}$	−102.6	−102.4
$AlBr_4^-$	$6\eta_{Br,Br}$	−79.8	−79.6
$AlBr_3I^-$	$3\eta_{Br,Br} + 3\eta_{Br,I}$	−60.3	−60.6
$AlBr_2I_2^-$	$\eta_{Br,Br} + \eta_{I,I} + 4\eta_{Br,I}$	−36.0	−36[b]
$AlBrI_3^-$	$3\eta_{Br,I} + 3\eta_{I,I}$	− 6.9	−7[b]
$AlCl_3Br^-$	$3\eta_{Cl,Cl} + 3\eta_{Cl,Br}$	−98.4	−99[b]
$AlCl_2Br_2^-$	$\eta_{Cl,Cl} + \eta_{Br,Br} + 4\eta_{Cl,Br}$	−93.2	−94[b]
$AlClBr_3^-$	$3\eta_{Cl,Br} + 3\eta_{Br,Br}$	−87.0	−87.2
$AlClBrI_2^-$	$\eta_{Cl,Br} + 2\eta_{Cl,I} + 2\eta_{Br,I} + \eta_{I,I}$	−48.0	−47.7
$AlClBr_2I^-$	$2\eta_{Cl,Br} + \eta_{Cl,I} + 2\eta_{Br,I} + \eta_{Br,Br}$	−69.9	−69.3
$AlCl_2BrI^-$	$2\eta_{Cl,Br} + 2\eta_{Cl,I} + \eta_{Br,I} + \eta_{Cl,Cl}$	−78.5	~−79

[a] Data taken from R. G. Kidd and D. R. Traux, *J. Am. Chem. Soc.*, **90**, 6867 (1968). [b] These shifts were taken directly from the graphs published because values were not presented elsewhere.

Interestingly, the shifts of carbon-13,[2] fluorine-19,[3] boron-11,[3] and proton-1[3] also have been shown to obey pairwise additivity. Theoretical justification of the pairwise additivity rule for chemical shifts can be found in the work of Vladimiroff and Malinowski.[3] Accordingly, pairwise contributions arise because the wave function of each substituent group suffers a linear correction due to the presence of each neighboring substituent group.

Acknowledgment. The author gratefully acknowledges the support of the U. S. Army Research Office (Durham), Contract No. DA-31-124-ARO(D)-90.

(2) E. R. Malinowski, T. Vladimiroff, and R. F. Tavares, *J. Phys. Chem.*, **70**, 2046 (1966).
(3) T. Vladimiroff and E. R. Malinowski, *J. Chem. Phys.*, **46**, 1830 (1967).