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THE MOLECULAR STRUCTURE OF THE COMPLEX TRIMETHYLALUMINIUM DIMETHYL ETHER, $(CH_3)_3AlO(CH_3)_2$, DETERMINED BY GAS PHASE ELECTRON DIFFRACTION

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Summary

The molecular structure of $(CH_3)_3AlO(CH_3)_2$ has been determined by gas phase electron diffraction. The main molecular parameters are Al—C = 1.973(11), Al—O = 2.014(14), O—C = 1.436(3) Å, O—Al—C = 98.7(1.5), Al—O—C = 122.6 (0.5) and C—O—C = 114.5(1.7)°. The O—C bond distance and the C—O—C valence angle are significantly larger than those in free dimethyl ether. The three valencies of the oxygen atom appear to lie in one plane. It is suggested that the planarity of the oxygen atom is due to across-angle repulsion Al···C(O).

Introduction

Trimethylaluminium, Me_3Al, forms stable complexes with amines, ethers and phosphines [1]. The enthalpy of formation of the gaseous complexes from the gaseous components

$$Me_3Al\ (g) + D\ (g) = Me_3AlD\ (g)$$

is $H_f = -30.69 \pm 0.29$ kcal mol^{-1} when D = NMe_3 [2,3] and $H_f = -21.92 \pm 0.18$ kcal mol^{-1} when D = OMe_2 [2]. The molecular structure of the complex Me_3AlNMe_3 has been determined by gas phase electron diffraction [3] and compared with the structure of free monomeric Me_3Al [4] and NMe_3 [5]. It was found that the Al—C bond distance in the complex is significantly longer than in the free acceptor, and while the free acceptor has a planar AlC_3 skeleton, the N—Al—C valence angle in the complex is 102.3(0.3)° [3]. These differences can be rationalized in terms of the VSEPR model [6]. It was further found that the N—C bond distance in the complex is significantly longer than in the free donor, while the C—N—C valence angle remains essentially unchanged. The elongation of the N—C bond on formation of the complex cannot be rationalized in terms of the VSEPR model, and it has been suggested that it is due to increased repulsion between the substituents on the N atom [7].

In the hope of learning more about the changes in structure of donor and acceptor on complex formation, we have now determined the molecular structure of the somewhat weaker complex Me_3AlOMe_2. A study of Me_3AlPMe_3 has also been initiated.

The conformation of the O atom in Me_3AlOMe_2 is also of interest: The three valencies of the O-atoms in siloxy- and alkoxy-bridged species like $(Me_2AlOSiMe_3)_2$ [8], $(Br_2AlOSiMe_3)_2$ [9], $(Me_2AlOMe)_3$ [10] and $(Me_2AlOCMe_3)_2$ [11] tend to lie in one plane. This planarity might be attributed to dative $p\pi$—$d\pi$ bonding between O and Al or to repulsion between the large substituents surrounding the O atom [7]. The latter view receives support from the results of recent ab initio molecular orbital calculations on the model compound $(H_2AlOH)_2$ [12]. The O atom in these species is surrounded by two Al and one Si or C atom. The O atom in Me_3AlOMe_3 is surrounded by one Al and two C atoms and should therefore be less crowded, and the conformation about the O atom might consequently be nonplanar.

Experimental and structure analysis

Me_3AlOMe_2 was synthesized by direct combination of Al_2Me_6 and OMe_2 at about —30°C [1] and purified by distillation at 80°C. The electron scattering pattern was recorded on the Oslo electron diffraction unit [13] with a recervoir temperature of about 50°C (corresponding to a vapor pressure of about 15 Torr [1]) and a nozzle temperature of about 60°C. Vapor pressure measurements show that the complex is not measurably dissociated at 40 Torr and 150°C [1]. Exposures were made with nozzle-to-photographic plate distances of about 48 and 25 cm. The optical densities of three plates from the first set and five plates from the second were processed using the programs described by Andersen et al. [14]. The resulting modified molecular intensity points are shown in Fig. 1.

A molecular model of Me_3AlOMe_2 is shown in Fig. 2. It was assumed that: (*i*) Me_3AlOMe_2 has C_s symmetry with the OC_2 plane of the ether perpendicular to the symmetry plane [12]. (*ii*) The Me_3AlO fragment has C_{3v} symmetry. The angle of rotation of the Me groups about the Al—C bonds is such that the H atoms are staggered with respect to the bonds radiating from the Al atom. (*iii*) The angle of rotation of the Me groups about the C—O bonds is such that one C—H bond is anti to the Al—O bond. (*iv*) All C—H bond distances are equal. (*v*) All Me groups have C_{3v} symmetry with the threefold axes coinciding with the C—Al or C—O bonds.

The molecular structure is then determined by nine independent parameters, e.g. the C—H (mean), Al—C, Al—O, and O—C bond distances and the Al—C—H, O—Al—C, Al—O—C, C—O—C and O—C—H valence angles.

The molecular structure was refined by least-squares calculations on the intensity data under the constraints of a geometrically consistent r_a structure using a program written by Seip [15]. The final refinements were carried out to take into account an estimated uncertainty of 0.1% in the electron wavelength.

Modified molecular intensity curves calculated for the best model are shown in Fig. 1. An experimental radial distribution curve and the difference between this curve and one calculated for the best model is shown in Fig. 3.

Discussion

The value obtained for the Al—C bond distance in Me_3AlOMe_2 is intermediate between the Al—C bond distances in free Me_3Al [4] and those in the stronger complex Me_3AlNMe_3 [3], but the combined uncertainties are too large to allow us to draw any conclusions. The valence angle D—Al—C (D = donor atom) in Me_3AlOMe_2, 98.7(1.5)°, is smaller than in Me_3AlNMe_3, 102.3(0.3)°. The difference is of marginal statistical significance.

The O—C bond distance in Me_3AlOMe_2, 1.436(3) Å, however, is significantly longer than the O—C bond distance in free OMe_2, 1.416 ± 0.003 Å, also by gas phase electron diffraction [16]. As in the case of Me_3AlNMe_3 the elongation of the D—C bond can be rationalized as the result of repulsion between the Al atom and the C atoms bonded to the donor atom, Al---C(D). The C—O—C valence angle is significantly wider in the complex, 114.5(0.7)°, than in the free ether, 111.5 ± 1.5°. This was unexpected: If the elongation of the O—C bond and the planarity of the O atom (see below) are due to Al---C(O) repulsion, one would expect C—O—C to be smaller in the complex than in the free ether. It is however possible that C(O)---C(O) repulsion is significantly larger in the complex since the Me(O) groups would carry a greater net positive charge than in the ether. In this connection one may note that the H—O—H valence angle in the oxonium ion, H_3O^+, tends to be greater than in water [17].

The sum of the three valence angles around the O atom in Me_3AlOMe_2 is 359.7° and the angle between the Al—O bond and the OC_2 plane of the ether is 5.1(4.3)°. The deviation from planarity cannot be regarded as significant, particularly since shrinkage corrections have been neglected during the refinement.

The main structure parameters of Me_3AlOMe_2 and the 2 : 1 complex of Me_3Al with dioxane, $Me_3AlOC_4H_8OAlMe_3$, which has been studied by X-ray diffraction [18], are listed for comparison in Table 2. The latter complex con-

TABLE 2

STRUCTURE PARAMETERS OF Me_3AlOMe_2 AND $(Me_3Al)_2$ · DIOXANE [18]. (Bond lengths in Å and angles in degrees.)

	Me_3AlOMe_2	$(Me_3Al)_2$ · dioxane	
Al—C	1.973(11)	1.96 (1)	2 ×
		1.98(2)	1 ×
Al—O	2.014(14)	2.02(2)	
Al—C(O)	3.04(2)	3.06(4)	
O—Al—C	98.7(1.5)	99.6(0.4)	2 ×
		101.9(0.6)	1 ×
Al—O—C	122.6(0.5)	122.3(0.5)	
C—O—C	114.5(0.7)	108.2(0.9)	
ϕ [a]	5.1(4.3)	24.4(2.9)	

[a] ϕ is the angle between the Al—O bond and the OC_2 plane of the ether.

tains non-planar O atoms, the angle between the Al—O bonds and the OC_2 planes of the ether being $\phi = 24.4(2.9)°$. This value is intermediate between that expected for a planar ($\phi = 0°$) and tetrahedral ($\phi = 55°$) O atom. Ab initio molecular orbital calculations on the model compound H_3AlOH_2 yielded a value of 27° for the angle between the Al—O bond and the OH_2 plane [12]. The energy of a planar configuration was however found to be only 0.19 kcal mol^{-1} higher than the equilibrium conformation and it was suggested that the conformation actually adopted by analogous alkyl derivatives $R_3AlOR'_2$ is determined by repulsions of the type Al---R′ and R---R′.

The planarity of the O atom in Me_3AlOMe_2 indicates that the conformation is determined by Al---C(O) repulsions: If C(Al)---C(O) repulsions were important, the distances C_1—C_4 and C_2—C_4 would tend to be equal. In fact C_1---C_4 = 3.29(3) Å and C_2···C_4 = 3.81(5) Å.

Since the O atoms in the 2 : 1 complex of Me_3Al with dioxane are non-planar the Al—C(O) distance, 3.06(4) Å and the Al—O—C valence angle, 122.3(0.5)°, may be regarded as optimal. In fact the Al---C(O) distances and Al—O—C angles in the two complexes are indistinguishable. The reason why the O atom in Me_3AlOMe_2 is planar while the O atoms in the dioxane complex are not, is that the C—O—C angle in the dimethylether complex, 114.5(0.7)°, is considerably larger than the C—O—C angle in the cyclic dioxane donor, 108.2(0.9)°. In the former case the three valence angles around O add up to 360°, in the latter they do not.

Bartell has shown that the valence angles X—Y—Z in a number of organic molecules can be rationalized in terms of across-angle repulsions X---Z and has assigned values to the corresponding "intramolecular van der Waals radii" of C, N, O, F, Cl and H [19]. More recently Glidewell has surveyed a large number of molecules containing O or N bonded to one, two or three second row atoms like Si or P and shown how the wide valence angles often found in such molecules can be rationalized in a similar way, i.e. without the need to invoke dative $p\pi$—$d\pi$ bonding between the first and second row element [20,21]. Glidewell also assigned an intramolecular van der Waals radius to Al, 1.85 Å, equal to half the Al---Al distance in the Cl-bridged ion $Al_2Cl_7^-$ [22].

Accepting Bartell's value for the across angle repulsion radius of C, $R_{\angle}(C)$ = 1.25 Å, we calculate an across angle repulsion radius of Al, $R_{\angle}(Al)$ = 1.81 Å, from the Al—C(O) distance in the dioxane complex discussed above. In the crystalline complexes $Cl_3AlOC(Cl)R$ (R = C_2H_5 [23], *o*-, *m*-, and *p*-C_6H_4Me [24]) the Al—O—C valence angles range from 138.3 to 146.2° and the Al---C(O) distances from 2.87 to 2.93 Å. Subtraction of $R_{\angle}(C)$ yields values of $R_{\angle}(Al)$ ranging from 1.62 to 1.68 Å. Clearly it is more hazardous to assign a definite value to the across angle repulsion radius of a large, diffuse, polarizable atom like Al than to the more compact atoms further to the right in the periodic table.

If $R_{\angle}(Al)$ = 1.74 Å is selected as a compromise value, combination with $R_{\angle}(C)$, = 1.25 and $R_{\angle}(Si)$ = 1.55 Å [19] leads to calculated optimal Al---Al, Al---Si and Al---C distances that are larger than those found in $(Br_2AlOSiMe_3)_2$ [9], $(Me_2AlOMe)_3$ [10], and $(Me_2AlOCMe_3)_2$ [11] in agreement with the view that the planarity of the O atoms in these molecules is due to repulsion between the substituents.

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