The Crystal Structure of Ethylzinc *t*-Butoxide

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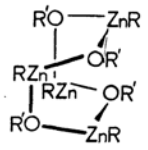
For several years one of the present authors has been sudying $ZnEt_2$ or its derivatives as catalysts for the polymerization of alkylene oxides; in these studies it has been assumed that RZnOR' plays an important role in $ZnEt_2$-alcohol-Al_2O_3 or RZnOR'-Al_2O_3 catalyst systems.[1]

Recently, Coates et al.[2] speculated about the structure of RZnOR' (I). This has prompted us to report our results, obtained through X-ray



(I)

analysis which had been carried out in this laboratory. Since there seems to be some discrepancy between their results and ours, we want to publish a short account of our results now.

Ethylzinc *t*-butoxide was prepared by mixing *t*-butanol and $ZnEt_2$ (molar ratio: 1/1) in dry hexane under nitrogen; single crystals, as colorless prisms, were thus obtained.

The unit cell is monoclinic, with parameters of $a=16.96$ Å, $b=11.02$ Å, $c=10.06$ Å, and $\beta=119°$. The assumption of $(C_6H_{14}OZn)_8$ in a unit cell leads to a reasonable calculated density of 1.35 gcm^{-3}. Systematic extinctions of F_{obs} (h, k, l) when $h+k$ is odd, lead to a *C*-centered lattice, that is, *C*2, *Cm* or *C*2/*m*. A total of 740 independent reflections was recorded photographically with a Weissenberg camera; from these reflections the three-dimensional Patterson function was computed. The results show that a molecule consists of four $EtZnOBu^t$ and that it is in a form resembling a cube, its eight corners being occupied by four zinc and four oxygen atoms.

There are various cubic models that have a different arrangement of atoms. The analysis of the Patterson function alone is not enough to determine the true structure among them. Calculation was carried out by the least-squares method on the assumption of various arrangements of zinc and oxygen atoms in the molecule. However, the temperature factors of the atoms, which were assumed to be oxygen, came to have minus values. Thus, oxygen atoms should not be fixed at any four of the eight corners of the model. The reflection data can be explained most clearly on the hypothesis that the electron density at the eight corners is similar; i. e., the *R*-value reaches a minimum (23%) when such is the case. The structure could not be explained without a consideration of some kind of disorder. In this case, the most possible space group would be *C*2/*m* (*pseudo* symmetry) and the molecules would occupy the special position of 2/*m* in the unit cell. The bond distances and bond angles in this molecule are illustrated in Fig. 1.

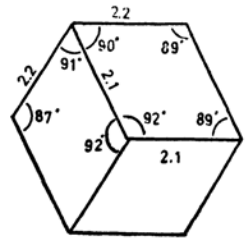
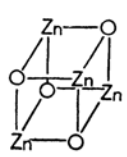


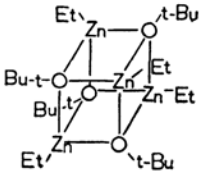
Fig. 1.

A disordered structure consisting of II and III is most probable, because bond distances between metals are usually above 2.5 Å, and the value of 2.15 Å obtained by our calculation is appropriate for Zn-O. In the disordered sturcture, it may be difficult to clarify the configuration of substituents. However, IV could presumably be assumed to be the structure of this molecule. At present, analysis is still under progress by means of the (F_o-F_c) synthesis to determine the configuration of ethyl and *t*-butoxyl groups.

(II)



(III)



(IV)

Coates has estimated that six probable forms of I would interconvert rapidly, in which case the time-average structure would be cubic. However, it has been shown from the present study that the molecule takes a form resembling a cube, consisting of not three-, but of four-coordinated zinc and oxygen atoms. There is thus no necessity for assuming the time-average structure of I.

1) Y. Matsui, T. Saegusa and J. Furukawa, *J. Chem. Soc. Japan. Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), in press.
2) G. E. Coates and D. Ridley, *J. Chem. Soc.*, **1965**, 1870.