Zinc 2,2,2-Trichloroethoxide. A Soluble Zinc Alcoholate

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In our previous studies,[1-3] aluminum 2,2,2-trichloroethoxide (I) was prepared and its properties were compared with those of such usual aluminum alcoholates as aluminum isopropoxide and *t*-butoxide. I is distinguished from usual aluminum alcoholates by the following properties: i) I dissociates to a monomer in donor solvents, whereas usual aluminum alcoholates are in associated form even in donor solvents. ii) I is a strong

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[1] T. Saegusa and T. Ueshima, *Inorg. Chem.*, **6**, 1679 (1967).

[2] T. Saegusa and T. Ueshima, to be published in This Bulletin.

[3] T. Saegusa, S. Tomita and T. Ueshima, *J. Organometal. Chem.*, **10**, 360 (1967).

Lewis acid and causes the cationic polymerization of vinyl monomers and cyclic ethers. iii) The insertion reaction of methylene into the Al–OR linkage in the reaction with diazomethane is observed in I, but not in usual aluminum alcoholates. The present study deals with the preparation and the properties of zinc 2,2,2-trichloroethoxide (II).

Experimental

Synthesis of II. Under a nitrogen atmosphere, 0.1 mol of diethylzinc in 20 m*l* of ethyl ether was added slowly with vigorous stirring into a mixture of CCl_3CH_2OH (0.2 mol) and ethyl ether (50 m*l*) at −50—−20°C. Then the reaction system was allowed to warm to room temperature and finally heated to reflux for 2 hr. A white precipitate separated from the solution; this was washed repeatedly with tetrahydrofuran to remove $C_2H_5Zn\text{-}OCH_2CCl_3$[4] and the starting materials. Reprecipitation was performed by the solvent-precipitant combination of pyridine and *n*-heptane. The yield was about 75%. Found: Zn, 18.08%. Calcd for $C_4H_4Cl_6O_2Zn$: Zn, 18.02%. The trichloroethoxy group was quantitatively determined by the v. p. c. analysis of trichloroethanol in the acid hydrolysis mixture. The CCl_3CH_2OH/Zn ratio was 1.94 (Calcd 2.00). II was decomposed without subliming under reduced pressure (0.08 mmHg) at *ca.* 120°C.

Results and Discussion

Zinc dialcoholates of unsubstituted alcohols, such as methanol and ethanol are known to be insoluble in organic solvents as a result of the strong tendency of the association through the oxygen atom of an alkoxy group.[5] The II prepared in the present study, however, was found to be soluble in the systems containing strong donor solvents, such as pyridine, quinoline, dimethylaniline, morpholine, piperidine, *N*-ethylpiperidine, and dimethyl sulfoxide. Ethers, ketones, esters, and trialkylamines were not effective in solubilizing II. In the present study, reference experiments showed that $Zn(OEt)_2$ was not soluble in any solvents which solubilized II. The specific solubility character of II may be due to the three chlorine atoms of the Cl_3CCH_2O-group, which have an electron-withdrawing effect to decrease the nucleophilicity of the oxygen of the Cl_3CCH_2O-group. The coordination of a donor molecule of a solvent onto zinc prevails over that of the oxygen of the Cl_3CCH_2O-group of another molecule of II. Thus, the coordination of a donor to zinc breaks the association through the oxygen-zinc bond and, hence, solubilizes II. On the contrary, the oxygen atom in usual zinc dialcoholates has a stronger nucleophilicity and a donor molecule does not break the association.

This explanation has been supported by the IR spectrum study. Three bands, at 1605, 1580, and 1572 cm^{-1} of the IR spectrum of the II-pyridine system (in Nujol), were due to the stretching vibration ($\nu_{C=N}$ or $\nu_{C=C}$) of pyridine. The first band, at 1605 cm^{-1}, can reasonably be ascribed to the pyridine which is coordinating onto the zinc atom,[1,6] whereas the latter two bands are due to free pyridine. On the other hand, the IR spectrum of the $Zn(OCH_2CH_3)_2$-pyridine system (in Nujol) showed only the two bands of free pyridine. Thus, the IR study has indicated that pyridine coordinates onto the zinc of II, but not onto the zinc of $Zn(OCH_2CH_3)_2$.

The coordination of pyridine to II, however, was not so strong that the pyridine-II complex could not be isolated. The recrystallization and evaporation of the excess pyridine-II mixture was attempted to isolate the pyridine-II complex. Pyridine was easily removed from the complex, and II was always left in these trials. A rather weak coordination of pyridine to II was further indicated by the finding that more than 10 mol of pyridine were required in order to dissolve 1 mol of II in a large amount of benzene. The IR spectrum indicated that a large portion of pyridine existed in a free, non-coordinating form.

The NMR spectrum of the solution of II in the benzene-pyridine mixture showed a sharp singlet at 4.70 ppm (δ) at temperatures from −30 to 23°C. This observation is taken to indicate that II is in a monomeric form in the solvent system containing pyridine. The effect of the CCl_3 group in II corresponds to that in $Al(OCH_2CCl_3)_3$.[1] These two haloalcoholates differ from each other in acid strength. The shift of the $\nu_{C=N(\text{or } C=C)}$ of pyridine by coordination was 30 cm^{-1} in the pyridine-$Al(OCH_2CCl_3)_3$ complex; this shift was larger than that of 25 cm^{-1} in the pyridine-II complex (not isolated). In addition, the 1 : 1 complex of $Al(OCH_2CCl_3)_3$ with pyridine was isolated,[1] whereas no complex of II was isolated.

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[4] T. Saegusa and T. Ueshima, *ibid.*, **13**, 249 (1968).

[5] G. E. Coates and D. Ridley, *J. Chem. Soc.*, **1965**, 1870.

[6] M. R. Basila, T. R. Kanter and K. H. Rhee, *J. Phys. Chem.*, **68**, 3197 (1967).