Ethylzinc Iodide

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CONFLICTING results have been reported[1-3] on the interaction of diethylzinc and zinc halides, and on the species obtaining in solutions of ethylzinc halides. In particular, it has been suggested that ethylzinc iodide in solvent ether exists as Et_2Zn,ZnI_2,[4] and as EtZnI.[5] This latter formulation has also been coupled[1,2] with the implication that equilibrium (1), (X = I), lies well to the right, although work by Dessy and Coe[6] indicates that (1), (X = Cl), lies to the left, in solvents ether and tetrahydrofuran (THF).

$$Et_2Zn + ZnX_2 \rightleftharpoons 2\ EtZnX \qquad (1)$$

In view of the known existence of alkylmagnesium halides, as monomeric RMgX,[7] we have thought it of interest to study ethylzinc iodide, prepared by the action of ethyl iodide on a Zn–Cu couple.

Addition of *NNN'N'*-tetramethylethylenediamine (TMED) to solutions of ethylzinc iodide in solvents ether and THF, precipitates complexes which analyse for EtZnI,TMED;* these complexes are obtained both from freshly prepared solutions of ethylzinc iodide and from solutions kept for several days. Addition of TMED to an equimolar mixture of diethylzinc and zinc iodide, in solvent THF, two hours after preparation of the mixture, gave the complex of zinc iodide, ZnI_2,TMED,* but if the TMED was added to the mixture after the latter had been kept for seven days at 25°, the complex EtZnI,TMED* was once again obtained. Hence it is clear that equilibrium (1), (X = I), lies well to the right in solvent THF, and that in THF and also in ether, ethylzinc iodide cannot be represented as a mixture of Et_2Zn plus ZnI_2, nor as Et_2Zn,ZnI_2; the latter is also excluded by our ebullioscopic measurements.

It is possible that ethylzinc iodide exists as dimers, $(EtZnI)_2$, rather than as monomers, EtZnI; however ebullioscopic measurements gave an association constant for EtZnI of about 1·2, over a range of concentrations in solvents ether (at 35°) and THF (at 66°). It is known[8] that

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* Satisfactory analyses were obtained for these compounds.

[1] G. Jander and L. Fischer, *Z. Elektrochem.*, 1958, **62**, 971.

[2] N. I. Sheverdina, L. V. Abramova, and K. A. Kocheshkov, *Doklady Akad. Nauk S.S.S.R.*, 1959, **124**, 602; *Proc. Acad. Sci.* (*U.S.S.R.*), 1959, **124**, 65.

[3] A. B. Garrett, A. Sweet, W. L. Marshall, D. Riley, and A. Touma, *Rec. Chem. Progr.*, 1952, **13**, 155.

[4] D. F. Evans and J. P. Maher, *J. Chem. Soc.*, 1962, 5125.

[5] K. A. Kocheshkov, N. I. Sheverdina, and J. E. Paleeva, *Bull. Soc. chim. France*, 1963, 1472.

[6] R. E. Dessy and G. R. Coe, *J. Org. Chem.*, 1963, **28**, 3592.

[7] A. D. Vreugdenhil and C. Blomberg, *Rec. Trav. chim.*, 1963, **82**, 453, 461; E. C. Ashby and W. E. Becker, *J. Amer. Chem. Soc.*, 1963, **85**, 118; E. C. Ashby and M. B. Smith, *ibid.*, 1964, **86**, 4363.

[8] N. Muller and A. L. Otermat, *Inorg. Chem.*, 1965, **4**, 296; A. D. Vreugdenhil and C. Blomberg, *Rec. Trav. chim.*, 1965, **84**, 39.

traces of air and moisture result in an increase in the observed molecular weights of alkylmagnesium halides and trialkylgalliums, and we suggest that ethylzinc iodide must be largely, if not exclusively, in the monomeric form, EtZnI, in the above solutions.

From p.m.r. studies on THF solutions of ethylzinc iodide and of diethylzinc, we have found that the spectrum of the ethylzinc group is very similar in the two cases. In view of our other results, this suggests not that the same species is present (as concluded by Evans and Maher[4] from similar p.m.r. spectra in solvent ether) but that p.m.r. cannot distinguish between the two systems.

(*Received, May 25th,* 1965.)