Raman and infra-red spectra of ethylzinc iodide

As with the Grignard reagents, a number of different species may be present in solutions of the alkylzinc halides, for example $ZnR_2 + ZnX_2$, $ZnR_2 \cdot ZnX_2$ or $(RZnX)_2$ and RZnX. Very recently, Abraham and Rolfe[1] have concluded, from chemical and ebullioscopic experiments, that ethylzinc iodide is largely, if not entirely, present as the monomeric form C_2H_5ZnI in ether and tetrahydrofuran solutions. We have obtained Raman and infra-red evidence which supports and extends this conclusion.

An ethereal solution of diethylzinc shows an intense polarized Raman band at 470 cm^{-1} ($\rho \leqslant 0.1$), which is clearly the symmetric zinc–ethyl stretching frequency. Pai[2] reports an analogous band at 476 cm^{-1} for pure liquid diethylzinc. The Raman spectrum of an ethereal solution of ethylzinc iodide shows only a very slight shoulder at 473 cm^{-1}, and an intense polarised band at 511 ± 2 cm^{-1} ($\rho \sim 0.5$), which can be assigned to the zinc–ethyl stretch in C_2H_5ZnI. Using the (uncomplexed) ether bands as an internal intensity standard, the concentration of free or weakly complexed diethylzinc in the ethylzinc iodide solution is found to be $\leqslant 2\%$ of the total zinc species present. These results do not, by themselves, definitely eliminate $(C_2H_5ZnI)_2$, with bridging iodines, as the main species, since it is possible that the asymmetric zinc–ethyl stretch in such a structure would be very weak in the Raman, or have approximately the same frequency as the symmetric zinc–ethyl stretch. However, further evidence for the C_2H_5ZnI structure is provided by the infra-red spectrum of an ethereal solution of ethylzinc iodide, which in the region 420–600 cm^{-1} shows only a single strong band at 510 ± 1 cm^{-1}. The earlier conclusion[3] that ethylzinc iodide should be formulated as $(C_2H_5)_2Zn \cdot ZnI_2$, which was based on the similarity in the proton resonance spectra of ethereal solutions of ethylzinc iodide and of diethylzinc, thus appears to be incorrect.

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