Redistribution of Dimethylberyllium with Beryllium Bromide in Diethyl Ether

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REDISTRIBUTION of this type shown in equation (1) is known to occur for systems of the Group II metals, Mg, Zn, Cd, Hg.

$$(1)\quad R_2M + MX_2 \underset{}{\overset{Et_2O}{\rightleftharpoons}} 2RMX$$

where R = alkyl, X = halogen

Only in the case of M = Be is this redistribution reported not to take place. Radioactive tracer studies,[1] using labelled beryllium, show that the beryllium system does not undergo redistribution in diethyl ether, when R = phenyl and X = bromide.

Further study of the anomalous behaviour of beryllium provides evidence that redistribution does occur in the system Me_2Be–$BeBr_2$ in diethyl ether. The evidence results from (i) low temperature n.m.r. spectra, (ii) ebullioscopic molecular association data and (iii) selective precipitation experiments using 1,4-dioxan as the precipitating agent.

All operations were carried out under conditions involving rigorous exclusion of moisture and oxygen. Me_2Be was prepared *via* the reaction of electrorefined (99·99% pure) beryllium flake and Me_2Hg at 110°. Traces of residual Me_2Hg were removed by heating at reduced pressure, and the product was purified by vacuum sublimation. $BeBr_2$ was synthesized by treating hot beryllium flake with bromine vapour. The white, fluffy crystalline product was purified by sublimation and dissolved in cold Et_2O. Gas chromatographic analysis of the $BeBr_2$–Et_2O solution showed that the ether was not cleaved or halogenated on standing. Me_2Be and $BeBr_2$ solutions were combined volumetrically to give stable, clear, colourless solutions, markedly less reactive than ethereal Me_2Be.

Ebullioscopic molecular association measurements for a (1 : 1) mixture of Me_2Be and $BeBr_2$ in diethyl ether over a concentration range of 0·05—0·10 molal in Be gave *i*-values of 1·0—1·1, based on MeBeBr. Similarly, Me_2Be was monomeric in ether over the same range.

The addition of 1,4-dioxan to a (1 : 1, 0·1M solution) Me_2Be and $BeBr_2$ in ether resulted in the precipitation of a fine white solid which on analysis established a Be : Br ratio of 1 : 1. This was observed when dioxan was in great molar excess, in exact molar equivalence, or in molar excess of Be. When $Me_2Be/BeBr_2 > 1$, the excess Me_2Be,n-dioxan is easily washed from the (1 : 1) precipitate.

N.m.r. spectra (60 Mc./sec.) were observed over a temperature range of +35° to −75° for Me_2Be in ether, (1 : 1) mixture of Me_2Be and $BeBr_2$ in ether, and (2 : 1) mixtures of Me_2Be and $BeBr_2$, respectively, in ether. Comparison of the spectra, with internal and external Me_4Si as reference standard, showed identical spectra, and the values quoted here are in c./sec. upfield from the internal Me_4Si singlet. Concentration of beryllium in the mixtures was 0·1 molar. For Me_2Be in ether, a sharp singlet was observed which shifted with temperature from 70·5 at 35° to 78 c./sec. at −75°. Similarly the (1 : 1) mixture displayed a singlet which moved from 71 at 35° to 75 c./sec. at −75°. The (2 : 1) mixture, however, was markedly different, for a singlet was observed at 71 c./sec. at 35°, which shifted upfield with decreasing temperature and split into a doublet of equal peak height at −75°, the low field peak being at 75 and the high field peak at 79 c./sec.

The monomeric nature of the (1 : 1) mixture of Me_2Be and $BeBr_2$ in ether and the stoicheiometry of the dioxan-precipitation product, leads us to conclude that redistribution does occur in this system according to equation (1). We suggest that the n.m.r. spectra of the (2 : 1) mixture is indicative of the Me_2Be species, mixed with the redistribution product MeBeBr. The downfield shift of the Me resonance singlet expected for electron withdrawal by Br in the species MeBeBr is small but definite. In the −75° spectrum of the 2 : 1 mixture, the signal at 78 c./sec. is attributed to the excess of Me_2Be and the signal at 75 c./sec. is attributed to MeBeBr.

Further work on this system with R = Ph is being performed.

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[1] R. E. Dessy, *J. Amer. Chem. Soc.*, 1960, **82**, 1580.