

PRELIMINARY COMMUNICATION

METHYL GROUP EXCHANGE IN THE $\text{CH}_3\text{Li}-(\text{CH}_3)_2\text{Hg}$ SYSTEM IN ETHER AND TETRAHYDROFURAN

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We wish to report proton NMR results which indicate that methyllithium facilitates methyl group exchange between molecules of dimethylmercury in diethyl ether and tetrahydrofuran (THF). Ordinarily, exchange of alkyl groups where an organomercury species is involved is very slow^{1, 2}. For example, Dessy *et al.*¹ observed slight or no exchange between $(\text{CH}_3)_2\text{M}$ (M = Zn, Cd, and Hg) and $(\text{CD}_3)_2\text{Hg}$ after eight days in tetrahydrofuran at 28°. Also, McCoy and Allred², using NMR observed no exchange in the $(\text{CH}_3)_2\text{M}-(\text{CH}_3)_2\text{Hg}$ (M = Zn and Cd) systems.

Consequently, a proton spectrum of dimethylmercury in THF or ether consists of three sharp lines at +36°; one intense line due to methyl groups bonded to mercury isotopes of spin zero and two satellite lines due to methyl groups bonded to mercury-199 of spin 1/2 (16.92% natural abundance). The two satellites are separated by 103 Hz in both ether and THF.

Proton spectra* (Fig.1) of ether solutions containing dimethylmercury and methyllithium show two broad resonances at +36°, a result of methyl group exchange between these two compounds. When the temperature is lowered to about +6°, the methyllithium resonance becomes very sharp with the line width being essentially the same as that for methyllithium alone in ether indicating that exchange between methyllithium and dimethylmercury has become slow on the NMR time scale. At this same temperature, however, the dimethylmercury resonance remains broad and it is not until about -60° is reached that the satellite lines approach the sharpness observed for dimethylmercury alone at +36°. Thus, a rather facile exchange of methyl groups between molecules of dimethylmercury is apparent.

The same general pattern of temperature dependence is observed with THF solutions, but it appears that the exchange reactions are faster in THF than in ether. At -60° in THF (Fig.1), the dimethylmercury resonance is still broad and the satellite lines cannot be seen; the spectrum appears similar to that for ether solutions at about -10°. Clearly, therefore, solvent plays an important role in determining the rate of these exchange reac-

*Proton spectra were recorded using a Varian Associates A-60 spectrometer equipped with the standard low temperature accessories.

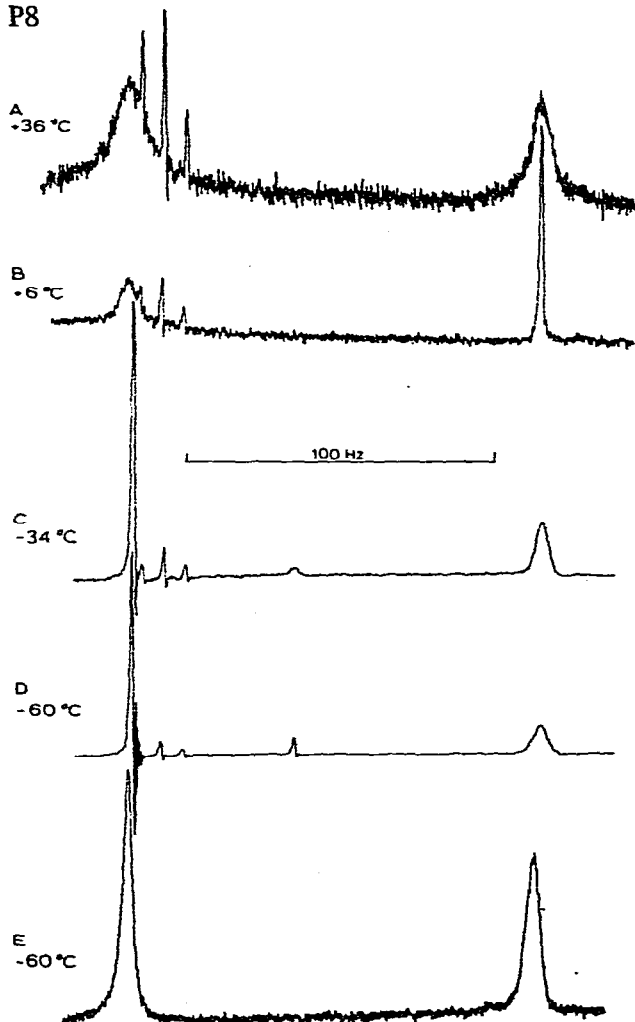
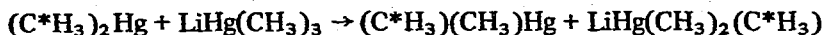


Fig. 1. Proton spectra of $\text{CH}_3\text{Li}-(\text{CH}_3)_2\text{Hg}$ in ether (A, B, C, and D; $\text{Li}/\text{Hg} = 1.2$) and tetrahydrofuran (E; $\text{Li}/\text{Hg} = 2.0$). The dimethylmercury resonance is at low field. In the ether solution spectra, the triplet just upfield from dimethylmercury is a ^{13}C -H satellite from the ether triplet. The low field ^{199}Hg -H satellite from dimethylmercury is obscured by the ether triplet

tions. Toppet *et al.*³ observed an acceleration of the exchange reaction between ethyllithium and diethylmercury when minute amounts of THF are added to benzene solutions.

In contrast to the corresponding cadmium⁴, zinc⁵, magnesium⁵, and beryllium^{6*} systems, no mixed complex is observed in the NMR spectra of the $\text{CH}_3\text{Li}-(\text{CH}_3)_2\text{Hg}$ system. However, we believe that a minute amount of complex, possibly $\text{LiHg}(\text{CH}_3)_3$, is present which serves to facilitate the dimethylmercury self-exchange. The exchange could occur through a reaction of the type:



Similar exchanges in the magnesium, zinc, and cadmium systems are known to be very

* A study of the $\text{CH}_3\text{Li}-(\text{CH}_3)_2\text{Be}$ system in ether and THF is in progress.

rapid. It is notable that ordinary Lewis bases, such as ethers, amines and other basic solvents, do not bring about rapid dimethylmercury self-exchange whereas the apparent formation of an "ate" complex does. There is also the possibility that the presumed complex, $\text{LiHg}(\text{CH}_3)_3$, aids in the exchange between methyl lithium and dimethylmercury.

Detailed spectral analyses, by the use of complete line shape calculations, are in progress to obtain quantitative rate data for dimethylmercury self-exchange and methyl lithium-dimethylmercury exchange. These results, and information relating to solvent effects and exchange mechanisms, will be reported in a later publication.

ACKNOWLEDGMENT

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