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A Study of the Redistribution Reaction of Tetramethyltin with Dimethyltin Dichloride in Several Aprotic Solvents

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The redistribution reaction of tetramethyltin with dimethyltin dichloride was studied in eight aprotic solvents by using the ^{1}H NMR technique. The second-order rate constant of the reaction ($\ln k_2$) is proportional to the dielectric constant of the solvent. There is a weak relation between the rate constants ($\ln k_2$) and the values of ^2J(Sn–H) of Me_2SnCl_2 in several solvents, which are considered to be related to the coordination ability of the solvents. The rate constants are also related to Kosower's Z values of the solvents. The activation entropies of the reaction in four typical solvents have large negative values. This predicts that the reaction proceeds *via* a four-center transition state.

There have thus far been many reports concerning redistribution reactions (or radical exchange reactions) of organometallic compounds.[1–5)]

The redistribution reaction, shown in Scheme 1, reported by Dessy *et al.*, was interpreted to proceed *via* a four-center transition state.[6)] This four-center

$$R_2Hg + HgX_2 \xrightarrow{\text{solvent}} 2RHgX$$

Scheme 1.

transition state is not yet decisive in interpreting the mechanism of similar kinds of reactions, but one piece of evidence is considered to be that the reaction has a large negative activation entropy. Another typical example of the reactions is shown in Scheme 2. This

$$Me_4Sn + Me_2SnCl_2 \xrightarrow{\text{solvent}} 2Me_3SnCl$$

Scheme 2.

is the reaction between tetramethyltin and dimethyltin dichloride which forms trimethyltin chloride. The equilibrium constant between the left- and right-hand systems has been reported to be 330.[5)] Plazzogna *et al.* reported the reaction in methanol and showed it to be a second-order reaction.[7)]

During the course of studying the ^{1}H and ^{119}Sn NMR spectra of some organotin compounds, our attention was drawn to the large solvent effects on the NMR parameters of many organotin compounds.[8)] Therefore, we have examined the reaction in Scheme 2 in several aprotic solvents and found that the reaction rates are largely dependent upon the solvents. The results have been analyzed as a second-order reaction and discussed in terms of dielectric constants, coordination ability, and Kosower's Z values of the solvents.

Experimental

The materials, the reactants, and the solvents were commercial ones and were used without further purification except for chloroform and acetone-d_6. Acetone-d_6 was dried by keeping it on a molecular sieve, while chloroform was purified by the conventional manner to remove traces of the stabilizer (ethanol). The reactants were weighed into an NMR sample tube, and then a solvent was added. The ^{1}H NMR measurement was carried out by means of a Hitachi R-20B spectrometer at 60 MHz with a variable-temperature controller. The reaction was followed by taking the methyl proton spectrum of the reaction mixture at intervals. The chemical shifts are referred to the signal of tetramethylsilane in a sealed Pyrex capillary inserted into each sample tube. The sweep width and time were 120 Hz and 200 s. The peak area of each methyl proton was measured by cutting and weighing the area under the peak on the chart, which was adjusted to have no wiggle. The temperature was measured by both a thermometer inserted into the probe and the chemical-shift difference of the two signals of ethylene glycol. The temperatures measured by the two methods were consistent within an error of ±0.5 °C.

Results and Discussion

Table 1 summarizes the equimolar second-order rate constants of the reaction as observed in eight solvents. The initial concentration of each reactant was

TABLE 1. SECOND-ORDER RATE CONSTANTS FOR THE REDISTRIBUTION REACTIONS OF TETRAMETHYLTIN WITH DIMETHYLTIN DICHLORIDE IN VARIOUS SOLVENTS[a)]

Solvent	$D^{b)}$	$Z^{c)}$	T/K	$k_2^{d)}$/l mol^{-1} s^{-1}
Acetonitrile	35.95	71.3	305.5	1.0×10^{-4}
			312.2	1.9×10^{-4}
			319.2	3.1×10^{-4}
Acetone-d_6	19.8	65.7	305.5	4.5×10^{-6}
			312.5	6.0×10^{-6}
			318.3	9.5×10^{-6}
			320.5	1.1×10^{-5}
1,2-Dichloroethane	10.13	63.3	305.5	1.1×10^{-6}
			323.2	3.3×10^{-6}
			333.4	6.6×10^{-6}
			343.2	9.9×10^{-6}
Nitrobenzene	34.82	—	305.5	4.5×10^{-5}
Benzonitrile	25.20	—	305.5	1.1×10^{-5}
Chloroform	4.806	63.1	305.5	5.8×10^{-7}
Bromobenzene	5.397	59.3	305.5	3.6×10^{-7}
Benzene	2.28	54	305.5	2.0×10^{-7}
			321.0	5.0×10^{-7}
			332.4	9.2×10^{-7}
			334.2	9.4×10^{-7}
			336.2	1.4×10^{-6}

a) The initial concentration of each reactant is about 0.5 mol l^{-1}. b) Dielectric constant. c) The values are cited from Ref. 14. d) The accuracy is about 10%.

taken to be 0.5 mol l^{-1}. One example of the rate analysis is given in Fig. 1. The second-order rate constant(k_2) increases with an increase in the dielectric constant(D) of the solvent. A linear relationship between $\ln k_2$ and D has been shown in Fig. 2 at the temperature of 305.5 K. Similar relationships between the rate constants and the dielectric constants have also been reported in other organotin compounds.[9–11]

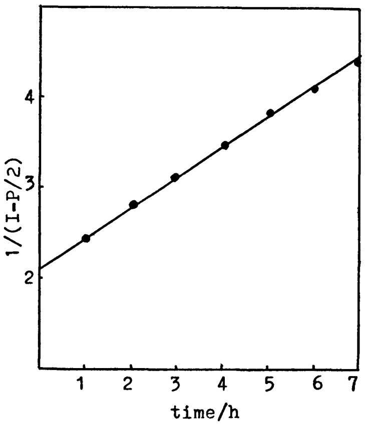


Fig. 1. An example of the concentration change of the reactant (ordinate; $1/(I—P/2)$) against time (abscissa) obtained for the reaction studied in acetonitrile at 305.5 K where I is the initial concentration of the reactant (*ca.* 0.5 mol/l) and P is the concentration of the product.

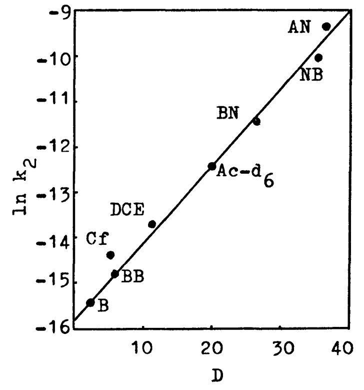


Fig. 2. Correlation between $\ln k_2$ and D for the eight solvents studied whose kinds are shown in the figure with abbreviated letters.

As is shown in Table 1, the rate observed in acetonitrile is 500 times faster than the slowest one observed in benzene. The observed thermodynamic data of the reaction are summarized in Table 2. The activation energy in acetonitrile is the largest one, but the other three values are similar in magnitude. The activation entropy change in acetonitrile is different from the other three in magnitude, although these values are negative and large, suggesting that the reaction proceeds *via* a four-center transition state, as has been suggested by Weingarten and Van Wazer.[2] The solvent used in the reaction significantly affects the activation entropy more than the activation energy.

The ${}^2J$(H–Sn) values of the related compounds are tabulated in Table 3 as determined in several solvents. The change is small for tetramethytin, but large for dimethyltin dichloride. Similar changes in the coupling constants have been reported.[12,13] The change is interpreted by the coordination of the solvent to the tin atom and by the hybridization change. Therefore, the coupling constant change observed largely manifests the coordination power of the solvent. The value in acetone-d_6 is larger than that in acetonitrile. This tendency is consistent with that observed for trimethyltin chloride, as reported by Bolles and Drago.[12] Therefore, acetone has a larger coordination power than acetonitrile for the tin compounds in question.

As has been stated before, the activation entropies of the reaction change with the kinds of solvents with large negative values. Therefore, the transition state of the reaction may be considered to be a rather ordered state. The entropy of the reaction system is considered to be dependent upon the coordination power of the solvent used. Therefore, it is suggested

TABLE 2. ARRHENIUS AND EYRING PARAMETERS FOR THE REDISTRIBUTION REACTIONS OF TETRAMETHYLTIN WITH DIMETHYLTIN DICHLORIDE IN VARIOUS SOLVENTS

Solvent	A	E_a	$\Delta H^{\#}$	$\Delta S^{\#}$
	l mol^{-1} s^{-1}	kJ mol^{-1}	kJ mol^{-1}	J K^{-1} mol^{-1}
Acetonitrile	1.1×10^7	64	62	−28
Acetone-d_6	2.0×10^3	51	48	−45
1,2-Dichloroethane	1.1×10^3	53	50	−47
Benzene	7.5×10	50	48	−52

TABLE 3. COUPLING CONSTANTS BETWEEN TIN AND PROTONS OF TETRAMETHYLTIN AND DIMETHYLTIN DICHLORIDE IN VARIOUS SOLVENTS IN Hz[a)]

Solvent	Me_2SnCl_2		Me_4Sn	
	${}^2J({}^1H-{}^{117}Sn)$	${}^2J({}^1H-{}^{119}Sn)$	${}^2J({}^1H-{}^{117}Sn)$	${}^2J({}^1H-{}^{119}Sn)$
Acetonitrile	79.4	82.8	52.8	54.9
Acetone-d_6	80.8	84.2	52.7	54.9
1,2-Dichloroethane	67.3	70.7	52.3	54.5
Nitrobenzene	71.2	74.6	52.4	54.6
Benzonitrile	75.4	78.8	52.2	54.8
Bromobenzene	66.6	69.4	51.6	54.0
Benzene	66.4	69.4	52.2	53.9

a) The accuracy is about 0.2 Hz.

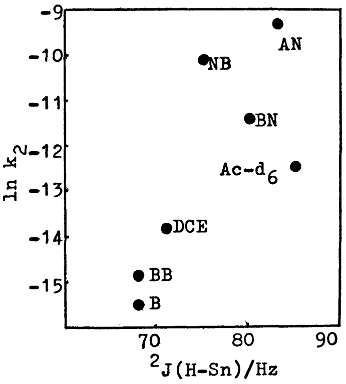


Fig. 3. Plotting of ln K_2 against the ^2J(Sn–H) of Me_2SnCl_2 (the values are given in Tables 1 and 3).

Table 4. ^{1}H chemical shifts of Me_2SnCl_2, Me_3SnCl, and Me_4Sn in various solvents in ppm[a)]

Solvent	Me_2SnCl_2	Me_3SnCl	Me_4Sn
1,2-Dichloroethane	1.79	1.21	0.64
Acetonitrile	1.37	0.78	0.24
Benzonitrile	1.36	0.70	0.04
Acetone-d_6	1.12	0.52	−0.04
Bromobenzene	1.12	0.74	0.34
Benzene	0.44	0.24	0.03

a) The values are referred to the external tetramethylsilane.

that the rate will be parallel to the coordination ability of the solvent. As is plotted in Fig. 3, there is a weak relation between the rate and ^2J(Sn–H), which is a measure of the coordination ability. The correlation coefficient of the points in Fig. 3 is 0.72; this is smaller than that calculated for Fig. 2 (0.99).

The ^{1}H chemical shifts are tabulated in Table 4. The chemical shifts change in a reasonable order with the successive substitution of an electronegative chlorine atom in the molecule. Chlorination causes a downfield shift of about 0.6 ppm per chlorine atom in four solvents from the top of the table. However, benzene shows a different behaviour. The observed chemical shift values may reflect the form of coordination. In this sense, the coordination may be supposed to be different for benzene and other four solvents. Bromobenzene is intermediate between the two.

There are many parameters which express the nature of the solvent. Figure 4 shows the relation between the ln k_2 value and Kosower's Z values of the solvents.[14)] Four points fall on a straight line, but not those of benzene and bromobenzene. Such exceptions of benzenes have previously been reported in the Menschtkin reaction.[15)] The rates become larger with larger Z values of the solvents.

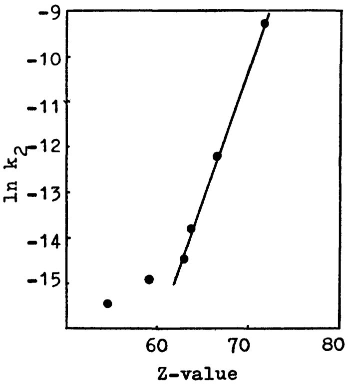
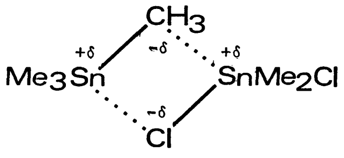


Fig. 4. Plotting of ln k_2 against the Z-values.

The reaction was also studied in the methanol solution by Plazzogna *et al.*[7)] They reported that tetramethyltin suffered an electrophilic attack by the Me_2Sn^{2+} species which is formed by the dissociation of Me_2SnCl_2. However, the ion, Me_2Sn^{2+}, is difficult to produce in acetone or acetonitrile. Therefore, they also stated that the reaction is very slow in acetone or acetonitrile. The rate observed by them in methanol is much greater than ours in Table 1, although the systems are different. The rate in methanol deviates greatly from the line plotted in Fig. 2. Therefore, it is reasonable to consider that the reaction mechanism in the aprotic solvents is different from that in the protic solvents.

We propose here a mechanism of the reaction which is dependent upon the dielectric constants of the solvents. The polarization of the reactants is important. Although one of the reactants, tetramethyltin, is nonpolar, the local polarization of the molecule occurs in the bond between the carbon and the tin atoms because of the different electronegativities of the atoms. The electrostatic attractive force leads to the four-center transition state shown in Scheme 3, which is supported by the negative activation entropies described above. The polarization of the reactants becomes larger in the polar solvents. The larger the dielectric constant of the solvent, the faster the reaction rate.



Scheme 3.

Conclusion

The redistribution reaction between tetramethyltin and dimethyltin dichloride has been studied in eight aprotic solvents. The logarithm of the rate of the reaction in the equimolar solutions is proportional to the dielectric constants of the solvents, and falls on a straight line. A weak relation is also observed between the rates and the ^2J(Sn–H) values, which are supposed to be measures of the coordination power of the solvents. The rate is almost parallel to Kosower's Z values of the solvents. The reaction has a large negative activation entropy. This is considered to be evidence of a reaction which proceeds *via* the four-center transition state.

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