A Study of the Interaction of Diethylcadmium with Lewis Bases as Solvents

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The infrared spectra of diethylcadmium($CdEt_2$) in a variety of different solvents were measured. The affinity of $CdEt_2$ toward oxygen and sulfur bases was studied by infrared frequency shifts of $CdEt_2$. Linear relationships were observed for the plots of the two frequency shifts $\Delta\nu_a$(C–Cd–C) of $CdEt_2$ *vs.* $\Delta\nu_a$(C–Zn–C) of $ZnEt_2$ and $\Delta\nu_a$(C–Cd–C) *vs.* $\Delta\nu$(O–D) of CH_3OD. The deviation of the plots for the systems of $CdEt_2$ with cyclic sulfides from the linear behavior was interpreted in terms of dative back-bonding from $CdEt_2$ to sulfides. The enhanced reactivity of the Cd–S compound toward propylene oxide compared to that of the Cd–O compound was considered to result from a harder acid character of the Cd atom in the Cd–S compound caused by its back-bonding nature.

Several studies of organozinc compounds as catalysts for propylene oxide polymerization have been reported.[1-3] The polymerization proceeds by a coordinate anionic mechanism, in which the coordination of the monomer molecule to the zinc atom is considered to be important in the activation of the monomer and of the catalyst, and also for the high stereoregulation observed in this polymerization.

The binary system of diethylzinc with water[2,4] or alcohol[1,5] has an excellent activity for propylene oxide polymerization. In contrast, the corresponding binary system of diethylcadmium with water or alcohol has little or no activity for the ring-opening reaction of propylene oxide.[6] It was recently found, however, that systems of $CdEt_2$ with thiocarboxylic acid[6] and of $CdEt_2$ with mercaptan[7] have favorable catalyst activities for the ring-opening reactions of propylene oxide; especially, $CdEt_2$–RCOSH systems gave high-molecular-weight polymers in satisfactory yield. A marked difference in catalyst activity between Cd-S and Cd-O compounds has been noted.

In order to elucidate the factors influencing the catalytic activities of Group IIb organometallic compounds, the mode of the interaction of $CdEt_2$ with an oxygen base and a sulfur base was studied in terms of the magnitude of the infrared frequency shifts of $CdEt_2$ and was compared with those of $ZnEt_2$ and methanol-*d*. It was previously reported that cadmium metal ions are classified into "soft"[8] or "class b"[9] acids, whereas zinc ions are "borderline" acids. The bonding natures of Group IIb organometallic compounds with oxygen (hard) and sulfur (soft) bases are of considerable interest.

Results and Discussion

Infrared Spectrum of Diethylcadmium. The infrared spectrum of $CdEt_2$ in the region of 4000 to 200 cm^{-1} was measured. The spectrum in the range of 4000 to 650 cm^{-1} is approximately identical to the data reported by Kaesz and Stone.[10] However, the bands[10] at 1186 (assigned to the CH_2 rocking vibration), 670, and 663 cm^{-1} ($C–CH_3$ rocking) were not observed in our spectrum. These bands may be due to the contamination of diethylmercury (*cf.* the spectrum in Ref. 10), which could itself be formed by the reaction of $CdEt_2$ with mercury metal.[11]

Three bands for $CdEt_2$ at 614, 494, and 441 cm^{-1} were observed in the region of 700 to 200 cm^{-1}. To obtain a reasonable assignment for the infrared frequencies, it is necessary to consider its plausible symmetry form. It was previously reported that methyl derivatives of Group IIb metals, $Cd(CH_3)_2$, $Zn(CH_3)_2$, and $Hg(CH_3)_2$, have linear C–M–C chains (M=Cd, Zn and Hg).[12] We interpreted the bands of $CdEt_2$ on the basis of the reasonable assumption that the C–Cd–C skeleton is linear in a similar way to $ZnEt_2$.[1] From the general similarity of the spectra between $CdEt_2$ and $ZnEt_2$ shown in Table 1, the bands at 614, 494, and 441 cm^{-1} were assigned to the CH_2 rocking $\gamma_r(CH_2–(Cd))$, C–Cd–C antisymmetric ν_a(C–Cd–C), and C–Cd–C symmetric ν_s(C–Cd–C) vibrations, respectively. Although the C–Cd–C skeleton is considered to be linear, a very weak band of ν_s(C–Cd–C) was observed similarly to the ν_s(C–Zn–C) of $ZnEt_2$;[3] this indicates some deviation of the above C–Cd–C symmetric vibration from the ideal one, probably due to the interaction of $CdEt_2$ with another $CdEt_2$ or solvent molecule and/or the free internal rotation of the ethyl groups of the $CdEt_2$ molecule itself. The deformation frequency of the C–Cd–C chain is expected to lie beyond the range of our measurement.

Table 1. INFRARED FREQUENCIES OF DIETHYLCADMIUM IN KBr REGION[a]

$CdEt_2$	Ref. $ZnEt_2$[3]	Assignment
614(s)	617(s)	$\gamma_r(CH_2–(M))$
494(s)	561(s)	ν_a(C–M–C)
441(w)	479(w)	ν_s(C–M–C)

a) Measured without solvent. cm^{-1}. (s): strong; (w): weak

The reliability of the above assignment for $CdEt_2$ was roughly checked for the spectra of reaction products between $CdEt_2$ and CH_3OH. The frequencies of $EtCdOCH_3$ and $Cd(OCH_3)_2$ in the region of 700 to 200 cm^{-1} are shown in Table 2. Tentative assignments for the frequencies of $EtCdOCH_3$ and $Cd(OCH_3)_2$ were made on the assumption of bending structures of the C–Cd–O and O–Cd–O chains, with reference to the corresponding zinc systems.[1,3] The bands of $CdEt_2$ at 494 and 441 cm^{-1} ascribed respectively to the ν_a(C–Cd–C) and ν_s(C–Cd–C) vibration disappeared completely in the spectra of $EtCdOCH_3$ and $Cd(OCH_3)_2$. The CH_2 rocking vibration of $EtCdOCH_3$ was observed at 608 cm^{-1}, a frequency somewhat lower than that of $CdEt_2$; no sign of the corresponding band was observed in the spectrum of

TABLE 2. INFRARED FREQUENCIES (cm^{-1}) OF $Cd(C_2H_5)_2$-CH_3OH SYSTEM[a]

	$\gamma_r(CH_2)$	ν(OCdO)	ν_a(CCdC)	ν_a(CCdO)	ν_s(CCdC)	ν_s(CCdO)	ν(OCdO)
$CdEt_2$	614(s)	—	494(s)	—	441(w)	—	—
EtCdOMe	608(s)	—	—	461(s)	—	345(s)	—
$Cd(OMe)_2$	—	550(m)	—	—	—	—	245(s)

a) cm^{-1}. (s): strong; (w): weak; (m): medium

TABLE 3. INFRARED FREQUENCY SHIFTS OF DIETHYLCADMIUM IN SOLVENTS[a]

No.	Solvent	Et_2Cd $\gamma_r(CH_2)$ (s)	Et_2Cd ν_a(C-Cd-C) (s)	Et_2Cd ν_s(C-Cd-C) (w)	Et_2Cd $\Delta\nu_a$(C-Cd-C)	Et_2Zn[b] $\Delta\nu_a$(C-Zn-C)	CH_3OD[b] $\Delta\nu$(O-D)
1	*n*-Heptane	617.5	497	441	0	0	—
2	Benzene	620	495.5	440	1.5	2.0	29
3	Toluene	620	495.5	—	1.5	2.0	26
4	Diethyl ether	613.5	491	—	6.0	10.5	96
5	Propylene oxide	612.5	489.5	—	7.5	14.0	99
6	Styrene oxide	617	491	—	6.0	11.0	85
7	Epichlorohydrin	614.5	491.5	—	5.5	9.5	80
8	Dioxane	—	488	435	9.0	17.0	111
9	Tetrahydrofuran	611.5	487.5	433	9.5	{19.0 {30.0	117
10	Diethyl sulfide	613	489	434	8.0	14.5	106
11	Propylene sulfide	—	487	433	10.0	15.5	99
12	Tetrahydrothiophene	610	485	429	12.0	20.0	117

a) An instrument of EPI-G3 was used. See "Experimental" section. (−): not observed due to the bands of solvents. b) ν_a(C-Zn-C) of $ZnEt_2$[3] and ν(O-D) of CH_3OD[15] for the solvents (No. 1—9) were previously reported. Differences between the values in this paper and those in the previous ones were ± 1 cm^{-1}.

$Cd(OCH_3)_2$. The two strong bands at 461 and 345 cm^{-1} in the spectrum of $EtCdOCH_3$ were assigned to the pseudoantisymmetric and pseudosymmetric ν(C–Cd–O) vibrations, respectively. The bands at 550(m) and 245(s) cm^{-1} in $Cd(OCH_3)_2$ could be assigned to the skeletal vibrations of the O–Cd–O chain, ν(O–Cd–O), from the spectral similarity between $Cd(OCH_3)_2$ and $Zn(OCH_3)_2$.[1]

In the light of these spectral changes, the above-mentioned assignments for the frequencies of $CdEt_2$ are considered to be reasonable.

Interaction between $CdEt_2$ and Lewis Bases. The infrared spectra of $CdEt_2$ in a variety of different solvents were measured in the KBr region. The frequencies of $CdEt_2$, $\gamma_r(CH_2)$, ν_a(C–Cd–C), and ν_s(C–Cd–C) in a series of Lewis base solvents are summarized in Table 3, together with three frequency shifts, $\Delta\nu_a$(C–Cd–C) of $CdEt_2$, $\Delta\nu_a$(C–Zn–C) of $ZnEt_2$, and ν(O–D) of CH_3OD. The frequency shifts of $CdEt_2$ and $ZnEt_2$ were calculated by reference to each frequency in *n*-heptane solvents. The shifts of methanol-d were calculated on the basis of the value in carbon tetrachloride.

Since the frequency shifts in donor solvents are due to the formation of donor-acceptor complexes between Lewis acids and bases, the magnitudes of the frequency shifts are considered to reflect the strength of the bondings of these complexes. For instance, some enthalpy data for hydrogen bondings have been reported to generate linear relationships with the infrared OH frequency shifts.[13]

The $\Delta\nu_a$(C–Cd–C) shifts of $CdEt_2$ are plotted against the corresponding shifts, $\Delta\nu_a$(C–Zn–C), of $ZnEt_2$, in Fig. 1. The $\Delta\nu_a$(C–Zn–C) *vs.* $\Delta\nu_a$(C–Cd–C) plots lie on a straight line for most of the Lewis base solvents examined.

In tetrahydrofuran solution, the ν_a(C–Zn–C) of $ZnEt_2$ showed a doublet band at 543 and 532 cm^{-1}; it was assigned to the vibrations of the $ZnEt_2$·THF and $ZnEt_2$·2THF complexes, respectively.[3] On the other hand, the spectrum of $CdEt_2$ in the same solvent showed a singlet band of ν_a(C–Cd–C). The plot for $CdEt_2$ in tetrahydrofuran (No. 9) against the one-to-one complex of $ZnEt_2$·THF lies on the straight line of $\Delta\nu_a$(C–Zn–C) *vs.* $\Delta\nu_a$(C–Cd–C) in Fig. 1, indicating the presence of $CdEt_2$·THF as the sole complex in the tetrahydrofuran solution of $CdEt_2$. The difference in affinity with tetrahydrofuran between $CdEt_2$ and $ZnEt_2$ indicates the difference between their Lewis acidities toward ether-oxygen. The weaker Lewis acidity of $CdEt_2$ than that of $ZnEt_2$ is also suggested by the slope of the plots in Fig. 1, which is much smaller than unity. It was previously reported by Bellamy, Hallam and Williams (BHW)[14] that a linear relationship held between the relative frequency shifts of the common characteristic bands of two different solutes in a variety of different solvents; the $\Delta\nu/\nu$ (O–D) of CH_3OD, for example, has a linear relationship with the $\Delta\nu/\nu$ (N–H) of $C_6H_5NH_2$ or the $\Delta\nu/\nu$ (S–H) of H_2S. It has been suggested that the slopes of the plots for solutes against a standard acid are a measure of their Lewis acidities. The BHW plots between $\Delta\nu/\nu$(C–Cd–C) and $\Delta\nu/\nu$(C–Zn–C) gave a linear relationship, the slope of

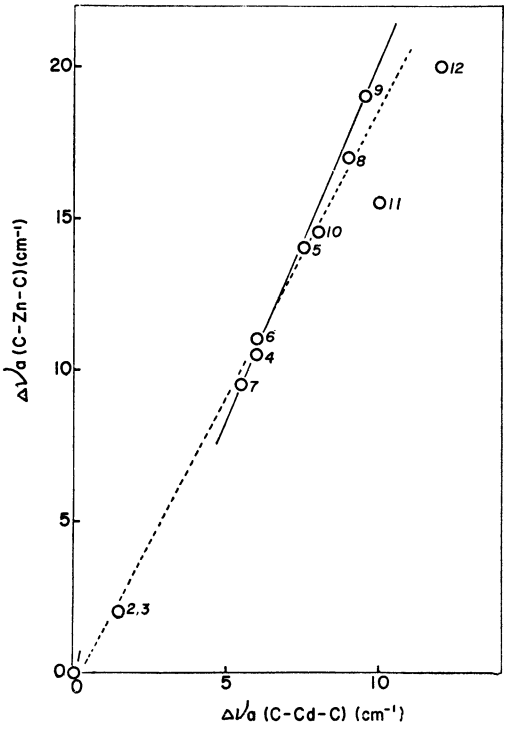

Fig. 1. Frequency shifts of $\Delta\nu_a$(C-Zn-C) of $ZnEt_2$ *vs.* frequency shifts of $\Delta\nu_a$(C-Cd-C) for a series of Lewis base solvents.
1: *n*-heptane, 2: benzene, 3: toluene, 4: diethyl ether, 5: propylene oxide, 6: styrene oxide, 7: epichlorohydrin, 8: dioxane, 9: tetrahydrofuran, 10: diethyl sulfide, 11: propylene sulfide, 12: tetrahydrothiophene.

Table 4. Frequency shifts of ν(C-O) of dioxane

Organometal. compd.	ν(C-O) (cm^{-1})	$\Delta\nu$ (cm^{-1})
None	873	0
$CdEt_2$	832	41
$ZnEt_2$	830	43
$InEt_3$	831	42
$AlEt_3$	823	50

which again suggested a weaker acidity for $CdEt_2$. Then the relative Lewis acidity of $CdEt_2$ toward ether-oxygen was precisely examined by measuring the magnitude of the infrared band shift of ν(C-O) of dioxane[2] at 873 cm^{-1} due to the coordination of oxygen to metal. The results are shown in Table 4, toegther with those for $AlEt_3$ and $InEt_3$ as references. The Lewis acidity toward ether-oxygen increases in the order: $CdEt_2 < InEt_3 < ZnEt_2 < AlEt_3$.

The most remarkable point about the $\Delta\nu_a$(C-Zn-C) *vs.* $\Delta\nu_a$(C-Cd-C) relationship in Fig. 1 is the anomaly of the plots for propylene sulfide and tetrahydrothiophene (No. 11 and 12) from the linear behavior. Namely, the relative affinity of $CdEt_2$ with the sulfur base compared with that with oxygen bases is different from that of $ZnEt_2$. The greater affinity of $CdEt_2$ toward soft bases of sulfide than that of $ZnEt_2$ is coincident with the "softer"[8] nature of the cadmium ion.

The rocking vibration of the CH_2 group of $CdEt_2$ in π-bases of benzene and toluene (No. 2 and 3) was observed at higher frequencies than that for *n*-heptane, similarly to the case of $ZnEt_2$.[3] Another type of interaction, *i. e.*, that of the π-complex of $CdEt_2$ with benzene rings, is suggested by the deviation of the plots for benzene, toluene, and styrene oxide (No. 6) from the linear relationship of $\Delta\gamma_r CH_2$ (calculated from the value in *n*-heptane) *vs.* $\Delta\nu_a$(C-Cd-C), as is shown in Fig. 2.

In order to examine in detail the above difference

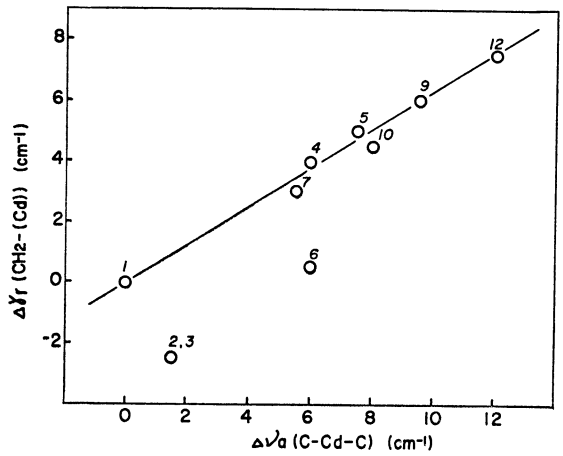

Fig. 2. Frequency shifts of $\Delta\gamma_r(CH_2\text{-}(Cd))$ *vs.* frequency shifts $\Delta\nu_a$(C-Cd-C) of $CdEt_2$ for a series of Lewis base solvents. Numbers for solvents as in Fig. 1.

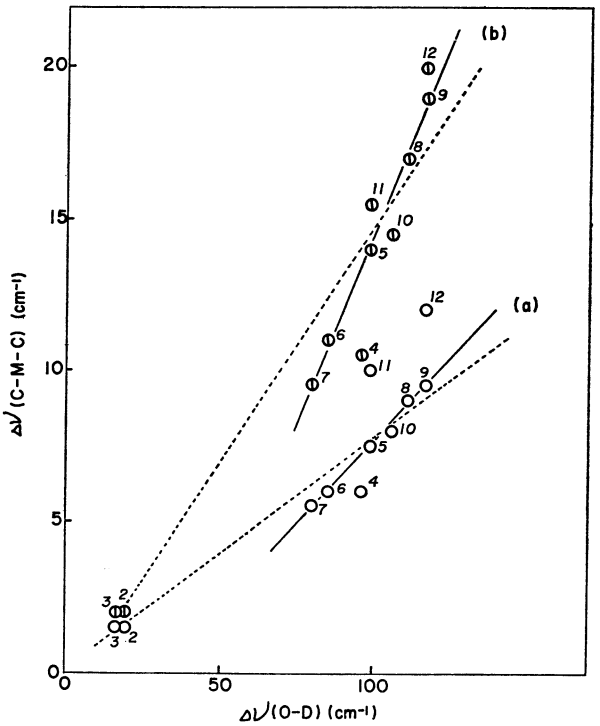

Fig. 3. Frequency shifts of $\Delta\nu_a$(C-M-C) of $CdEt_2$ and $ZnEt_2$ *vs.* frequency shifts of $\Delta\nu$(OD) of CH_3OD for a series of Lewis base solvents. Numbers for solvents as in Fig. 1.
(a): $CdEt_2$, (b): $ZnEt_2$

Table 5. Interactions of $Cd(C_2H_5)_2$ and $Zn(C_2H_5)_2$ with cyclic sulfides and ethers[a]

Lewis base	$CdEt_2$		$ZnEt_2$		CH_3OD
	$\Delta\nu_a$(C-Cd-C) (cm^{-1})	$\Delta\nu/\nu$ ($\times 10^3$)	$\Delta\nu_a$(C-Zn-C) (cm^{-1})	$\Delta\nu/\nu$ ($\times 10^3$)	$\Delta\nu$(OD) (cm^{-1})
Propylene sulfide	10.0	20	15.5	27	100
Propylene oxide	7.5	15	14.0	25	99
Tetrahydrothiophene	12.0	24	20.0	35	116
Tetrahydrofuran	9.5	19	19.0 30.0	34 53	117
Diethyl sulfide	8.0	16	14.5	26	106
Diethyl ether	6.0	12	10.5	19	96

a) The frequencies ν of $\Delta\nu/\nu$ for $CdEt_2$ and $ZnEt_2$ are each value in *n*-heptane solvents.

between $CdEt_2$ and $ZnEt_2$, the frequency shifts of $CdEt_2$ and $ZnEt_2$ for a series of Lewis base solvents are plotted against the $\Delta\nu$(O–D) of methanol-*d* in Fig. 3. The steric requirement of a hard acid of CH_3CD is small, and its frequency shift, $\Delta\nu$(O–D), is known as a scale of the basicity in the usual sense.[15]

The plots of $\Delta\nu_a$(C–Cd–C) *vs.* $\Delta\nu$(O–D) in Fig. 3(a) indicate again a special interaction of $CdEt_2$ with such cyclic sulfides as propylene sulfide and tetrahydrothiophene. In contrast, such a special interaction is considerably weak in the systems of $ZnEt_2$ with cyclic sulfur bases, as is shown by the $\Delta\nu_a$(C–Zn–C) *vs.* $\Delta\nu$(O–D) plots in Fig. 3(b). This phenomenon is more clearly shown by the relative frequency shifts of $CdEt_2$, $ZnEt_2$, and CH_3OD with cyclic sulfides and ethers, as are listed in Table 5. The shifts of $CdEt_2$ with cyclic sulfides are much greater than those with the corresponding ethers. Namely, the "soft" characters of the above Lewis acids are in this order: $CdEt_2 > ZnEt_2 \gtrsim CH_3OD$.

However, the plot for $CdEt_2$ with diethyl sulfide (No. 10) falls onto a straight line in Fig. 3. The apparent lack of any special interaction for this system is considered to be caused by the steric hindrance between ethyl groups of $CdEt_2$ and those of diethylsulfide. The marked deviation of the plots for diethyl ether with $CdEt_2$ and $ZnEt_2$ from the linear behavior in the direction of the methanol-*d* side (No. 4 in Fig. 3) can also be explained in terms of the above steric hindrance.

The special interaction of $CdEt_2$ with sulfide can be interpreted in terms of dative back bonding[9,16] from the occupied 4d orbital of the cadmium atom of $CdEt_2$ to the 3d vacant orbital of the sulfur atom of sulfide.

It was described in the "Introduction" section that Cd–S compounds are much more reactive toward propylene oxide than the Cd–O compounds. This fact can be interpreted as follows; Cd atoms in Cd–S compounds are "harder" than those of Cd–O compounds because of their back-bonding nature which increases the positive charge of Cd atoms by a process of electron transfer from Cd to S; accordingly, they are much more reactive toward a hard oxygen base of propylene oxide.

Experimental

All the experiments concerned with organometallic compounds were carried out under purified nitrogen atmosphere.

Reagents. Diethylcadmium[17] and triethylindium[18] were prepared by the methods which involve the reactions of metal halides with Grignard reagents. Organometallic compounds ($CdEt_2$, $ZnEt_2$, $AlEt_3$ and $InEt_3$) were purified by fractional distillation under reduced pressure. Methanol-*d* was used after distillation.

Propylene sulfide was prepared by the reaction between propylene oxide and potassium thiocyanate.[19] Solvents (hydrocarbons, ethers, and sulfides) were purified by the standard methods[20] and were fractionally distilled.

Infrared Measurements. A Hitachi EPI-G3 and a JASCO DS-402G grating infrared spectrometers were used to collect the infrared data. The spectrum of diethylcadmium was measured as a liquid film. The spectra of diethylcadmium, diethylzinc, and methanol-*d* in solvents were measured using liquid cells with KBr windows at the concentration of 1.0 mol/l. Ethylcadmium methoxide and cadmium dimethoxide were measured as mulls in dry liquid paraffin. Expanded frequency scales were used to obtain accurate values of the shifts, $\Delta\nu$. The frequencies in the KBr region were corrected by reference to the band of CO_2 at 667 cm^{-1}. The data in Tables 1 and 2 were recorded with a DS-402G instrument, while the data in Tables 3, 4 and 5 were recorded with an EPI-G3 instrument. A slight difference in frequency for any sample, but especially for γ_r (CH_2), was observed when it was measured with the above two instruments, however, the magnitude of the frequency shifts ($\Delta\gamma_r$) was approximately the same (± 1 cm^{-1}).

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