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Equilibria between Contact and Solvent-Separated Ion Pairs of 1,1-Diphenylethylene Dimer Dianion and Tetraphenylethylene Dianion

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Temperature-dependent ^{1}H NMR chemical shifts of the two title carbanions have been measured in three solvents and with three counter ions. The equilibria between two types of ion pairs of the carbanions have been discussed in terms of solvent, counter ion, and temperature.

The equilibria between two types of ion pairs (contact and solvent-separated ion-pairs, abbreviated as CIP and SSIP) have been studied extensively by UV, NMR spectroscopy, and conductance measurements. Hogen-Esch and Smid represented CIP and SSIP as R^-,M^+ and $R^-//M^+$, respectively, in their articles,$^{1)}$ where R^- is a carbanion and M^+ is a counter ion. Although ^{1}H, ^{13}C, and ^{7}Li NMR data have attracted attention for several carbanionic systems such as 9-fluorenyl, 1-indenyl, cyclopentadienyl, triphenylmethyl, 1,3-diphenylallyl, 1-phenylalkyl, and 1- and 2-naphthylmethyl, only a few data have been reported on the dianionic system.$^{2)}$ So we have studied the equilibria between CIP and SSIP for the two title dianionic systems by measuring the temperature-dependent ^{1}H NMR chemical shifts in three solvents and with three counter ions. The two title carbanions, **1** and **2**, are shown in Fig. 1. As seen in the figure, the carbanions have two active sites and the distance between the two active sites of **1** is about three times larger than that of **2**. This is one of the interesting points considered in the two dianionic systems.

Experimental

Methods of preparation of the carbanions are similar to those described previously.$^{3,4)}$ Tetrahydrofuran, 2-methyltetrahydrofuran, and 1,2-dimethoxyethane were used as solvents, and hereafter they are abbreviated as THF, MTHF, and DME, respectively. DME with two donor sites is stronger than THF in its solvation power. THF is more effective than MTHF due to its less hindered donor site. Lithium, sodium, and potassium were used as counter ions. The ^{1}H NMR spectra were measured at 60 MHz on a Hitachi R-20B spectrometer with a R-202VTC temperature controller. The temperature was calibrated with temperature-dependent chemical shifts of methanol (low-temperature range) or ethylene glycol (high-temperature range) using the standard equations.$^{5)}$ Chemical shifts of the carbanions are referred to an internal TMS signal and obtained with the first-order approximation, and sample concentrations are about 0.2 mol dm^{-3} or less based on starting materials used.

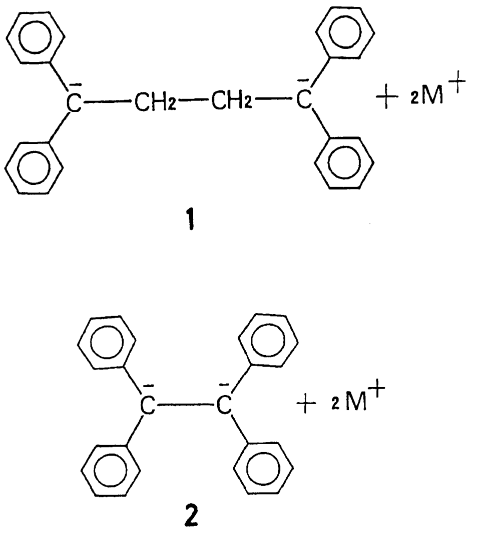

Fig. 1. Numberings of the carbanions studied.

Results and Discussion

Typical ^{1}H NMR spectra are shown in Fig. 2. As shown in Fig. 2, the peaks in the region of aromatic protons are well divided into three. The ^{1}H NMR chemical shifts of the two carbanions are given in Table 1 in three solvents and with three counter ions. The values are almost the same as those previously reported.$^{3,4)}$ Several typical temperature-dependent chemical shifts for the para protons in **1** and **2** are plotted in Figs. 3a and 3b, respectively. The para-proton chemical shift is selected as a good empirical measure of the equilibrium in ques-

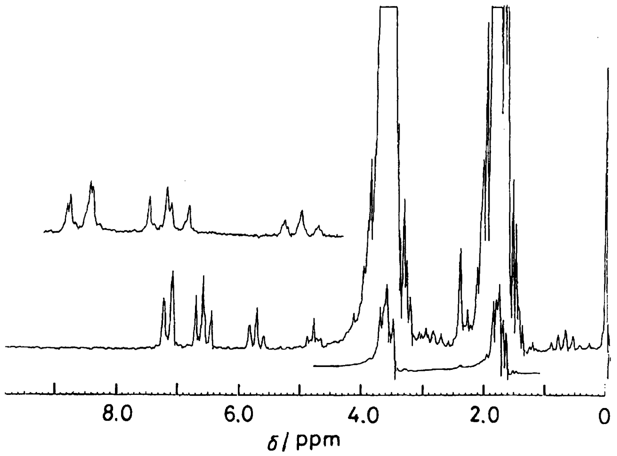

Fig. 2. ^{1}H NMR spectrum of **1** in THF with sodium as counter ions at 60 MHz and 31.6 °C.

Table 1. ^{1}H NMR Parameters of **1** and **2** at 31.6 °C and 60 MHz

Anion	Cation	Solvent	Chemical shift δ/ppm		
			H_p	H_m	H_o
1	K	MTHF	5.66	6.51	6.96
	Na	MTHF	5.74	6.59	7.18
	Li	MTHF	5.79	6.52	6.93
	K	THF	5.63	6.50	6.98
	Na	THF	5.73	6.60	7.18
	Li	THF	5.65	6.47	6.98
	K	DME	5.66	6.55	7.12
	Na	DME	5.58	6.48	6.83
	Li	DME	5.59	6.48	6.83
2	Na	MTHF	5.66	6.54	6.99
	Li	MTHF	5.65	6.45	6.95
	K	THF	5.56	6.44	6.99
	Na	THF	5.61	6.51	6.98
	Li	THF	5.59	6.42	6.92
	K	DME	5.58	6.46	7.00

tion, because the para proton is more distant from the carbanionic center than the meta or ortho proton. Several annoying factors contributing to the ^{1}H chemical shifts such as a ring-current effect and a metal-proximate effect etc, may be weakened at the para position. Another reason for the selection of the para-proton shift is that the line shapes of the ortho- or meta-proton signals are expected to be extremely temperature-dependent which would make difficult their analyses with lowering temperature, for example in the case of **2**.$^{6)}$ Hereafter chemical shifts are usually concerned with the para-proton shifts.

In Fig. 3a, very distinct temperature-dependent behavior for **1** is found for two solvents, THF and MTHF, with lithium as counter ions, while, with Na or Li as counter ions, the para-proton chemical shifts of **1** and **2** show two types of temperature dependency. For example, with Li as counter ions in THF, **1** gives temperature-variable chemical shifts, but the shift of **2** is temperature invariant. With Li as counter ions in MTHF, **1** gives a downfield shift below −20 °C, while **2** gives an upfield shift above 20 °C. Therefore **1** and **2** show a very distinct contrast.

General Consideration of Temperature-Dependent ^{1}H Chemical Shifts of the Carbanions. In general, the equilibrium between CIP and SSIP moves to the former at higher temperature and to the latter at lower temperature. For CIP, the cation strongly interacts with the active site in the carbanion. Then the excess negative charge in the carbanion moves to the active site. This causes a downfield shift of the para proton signal. Thus, the chemical shift of the para proton in the phenyl ring moves upfield at lower temperatures and downfield at higher temperatures. Therefore the H_p chemical shift becomes a measure of the equilibrium between CIP and SSIP. If one of the two ion pairs is dominant in the equilibrium, the shift does not change with temperature. Therefore in the temperature-variable experiment, two cases are considered. One is that the chemical shift shows a variation following with temperature. A typical case is given for **1** with Li as counter ions in THF or MTHF as shown in Fig. 3a. However another case is that the chemical shift does not show any variation with temperature. For example, **1** does not change its chemical shift with K as counter ions in THF.

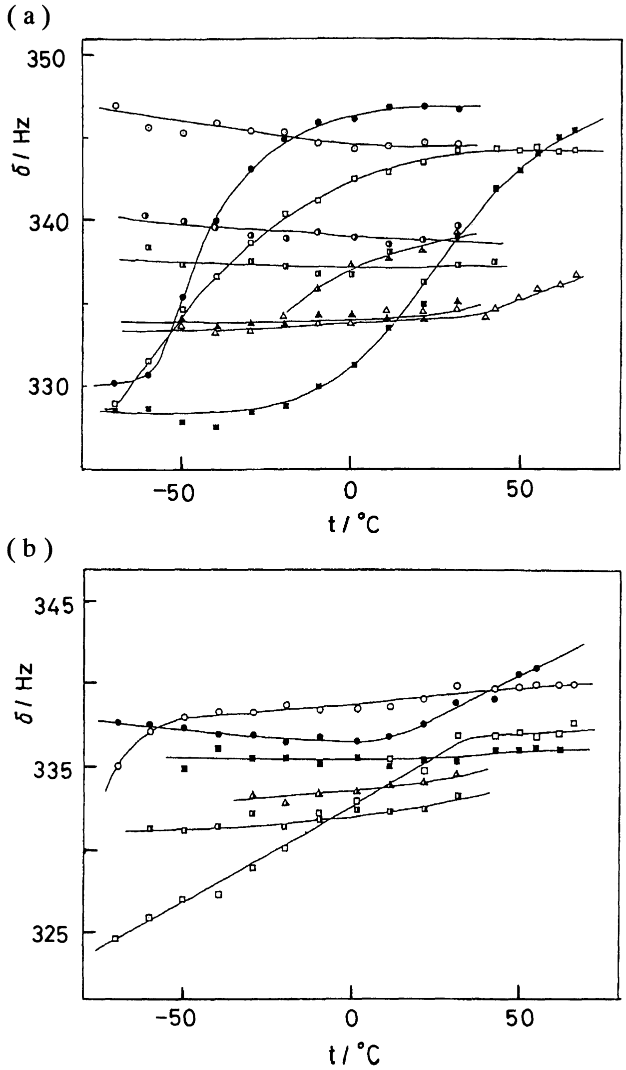

Fig. 3. Temperature-dependent chemical shifts of **1** (a) and **2** (b) in MTHF (◑, ○, and ●), THF (◨, □, and ■), and DME (◭, △, and ▲), respectively, with the order of K, Na, and Li as counter ions.

For the cases of **1** and **2** having K as counter ions, temperature-variable chemical shifts were only observed for **1** in DME at a narrow range. In other cases CIP is considered to be the major species for both **1** and **2**.

Apparent Analysis on Equilibrium between CIP and SSIP. There have been several reports concerning the equilibrium between CIP and SSIP.$^{7-10)}$

For **1** and **2** in this study, the H_p chemical shifts can become a good measure of the equilibrium. As shown in Fig. 3, the chemical shifts of **1** and **2** change with temperature for the next four cases; (1) **1** with Li in MTHF, (2) **1** with Li in THF, (3) **1** with Na in THF, (4) **2** with Na in THF. The other cases, the chemical shifts for **1** and **2** are almost constant with variation in temperature. In these cases, therefore, either one of the two species, CIP or SSIP, is considered to be dominant. In the case whose chemical shifts are temperature-dependent, the equilibrium constant, K, between CIP and SSIP can be calculated for each temperature using the observed chemical shifts. The constant K is defined as to be

$$K = (\delta_c - \delta_o)/(\delta_o - \delta_s), \qquad (1)$$

where δ_o is the observed chemical shift of a particular proton, and δ_c and δ_s are the limiting values of the chemical shifts for CIP and SSIP, respectively.[9] The enthalpy and entropy changes of the ion-pair interconversion can be calculated from K vs. T^{-1} data. For the evaluation of K, the values of both δ_c and δ_s must be measured and are assumed to be temperature invariant for each carbanion. They sometimes cannot be obtained directly and must be estimated. In many cases, either one of the two, δ_c or δ_s for each carbanion will be obtained directly. The other one must be estimated. For estimation of δ_c or δ_s, the linearity of the K vs. T^{-1} plot was computed for each combination of δ_c and δ_s.[9] The acceptable value for δ_c or δ_s was then selected on the basis of the least standard deviation of the data points from the correlated straight line, using a program named DSO (Direct Search of Optimization).[11] The values of δ_c and δ_s for **1** and **2** thus obtained are given in Table 2. An example of plotting the data in the van't Hoff relation is given in Fig. 4. Thermodynamic parameters obtained are given in Table 3. These values can be compared to those found for several monoionic anions,[9] and are explained in terms of equilibrium between two types of ion pairs, CIP and SSIP. All values are negative for both enthalpy and entropy changes.

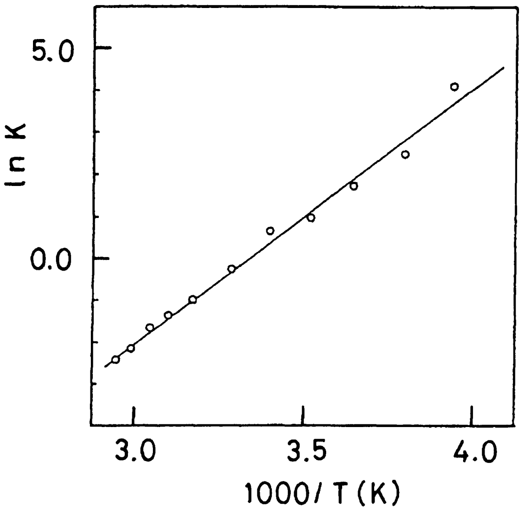

Fig. 4. Plots of ln K vs. T^{-1} for **2** with Na in THF.

Table 3. Thermodynamic Parameters for Equilibrium of Ion Pairs

Carbanion /Cation	Solvent	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
1/2Li$^+$	MTHF	−39.3	−171
1/2Li$^+$	THF	−50.6	−169
1/2Na$^+$	THF	−22.6	−100
2/2Na$^+$	THF	−32.2	−128

Table 4. The Para Proton Chemical Shifts of CIP in **1** and **2** in ppm at 60 MHz and 31.6 °C

Anion	Cation	Solvent		
		MTHF	THF	DME
1	K	5.66	5.63	5.66
	Na	5.74	5.73	—[b]
	Li	5.79	5.76(66)[a]	—
2	K	—	5.56	5.58
	Na	5.67(66)	5.63(66)	—
	Li	5.68(55)	5.60(62)	—

a) The value in parentheses is the temperature (°C) for observation. b) Not available.

Effects of Counter Ions and Solvent. As stated in many reports, when the size of the cations becomes larger, the H_p chemical shift moves upfield. The electron density on the active site of the carbanion decreases with increase of the size of the counter ion.[7,8] In Table 4, the para-proton shifts of CIP for **1** and **2** are tabulated. For **1** the values in Table 4 are arranged in a predictable order concerning the size of the cation. These are quite normal. For **2**, however, there is a little abnormal behavior about Li as counter ions in THF. The value is 5.60 ppm and smaller than that of Na as counter ions. The value in MTHF is about 5.62 ppm below 20 °C. Above 20 °C, it gives a further downfield shift, which reaches 5.68 ppm at 55 °C. If the latter value is that for the true CIP, the former one will be a little different from that of CIP. This behavior appeared in MTHF, which has the weakest solvation power among the three solvents. Therefore the true CIP will have a shift larger than 5.63 or 5.67 ppm in THF or MTHF. If it is so, we can expect normal behavior concerning the cation size. If the solvation power of the solvents is

Table 2. Estimated and Observed Chemical Shifts of CIP and SSIP of **1** and **2** in Hz at 60 MHz

Carbanion/Cation/Solvent	δ_c	δ_s
1/Li/MTHF	347.2[a]	328.6
1/Li/THF	346.9	328.5[a]
1/Na/THF	344.3[a]	324.3_5
2/Na/THF	337.1[a]	324.4

a) Experimentally observed.

strong, interaction between the cation and anion will be weakened. Then the H_p shift moves upfield. This phenomenon is observed in δ_c for **1** and **2** between THF and MTHF as shown in Table 4. Concerning δ_s, only a few data are experimentally available. In THF **1** with Li as counter ions gives δ_s 328.5 Hz (Table 2), while δ_s of **1** in DME is about 334 Hz (Fig. 3a). These values are difficult to understand as a situation caused from the solvent effect. This will be due to different structures of SSIP formed.

If the solvation power of solvents becomes stronger, conversion from CIP to SSIP becomes easier. For example, for **1** with Li as counter ions in MTHF it begins at −20 °C, while in THF it begins at 50 °C (Fig. 3a).

Characteristics of Dianionic Systems. In treatment of the dianionic system, the equilibrium between CIP and SSIP has a problem when compared with other monoanionic systems, because the dianionic system has two active sites. Therefore the equilibrium will be treated as a two-step equilibrium as follows,

$$\mathrm{C} \overset{K_1}{\rightleftarrows} \mathrm{M} \overset{K_2}{\rightleftarrows} \mathrm{S}. \tag{2}$$

In the case of the monoanionic system, the intermediate species M is not present. For the monoanionic system, $K = X_s/X_c$ where X_c and X_s are mol fractions of CIP and SSIP, respectively.

$$X_c + X_s = 1, \quad \text{and} \quad \delta_o = X_c\delta_c + X_s\delta_s. \tag{3}$$

However, for the two-step equilibrium, three species must be considered. Because they have two active sites which are expressed as combinations of CIP–CIP, CIP–SSIP, and SSIP–SSIP, and these are abbreviated as C, M, and S, respectively.

$$K_1 = X_m/X_c, \quad K_2 = X_s/X_m,$$
$$K = X_s/X_c = (\delta_c - \delta_o)/(\delta_o - \delta_s) = K_1K_2, \tag{4}$$

$$\Delta G_1 = -RT \ln K_1 \quad \text{etc}, \tag{5}$$

$$\delta_o = X_c\delta_c + X_m\delta_m + X_s\delta_s, \text{ and } X_c + X_m + X_s = 1. \tag{6}$$

If one among three (X_c, X_m, and X_s) is evaluated, the equilibrium constant is obtained from δ_o.

For the two-step equilibrium, the limiting chemical shifts of three species will become δ_c, $(\delta_c + \delta_s)/2$, and δ_s, respectively, because the species is symmetric. For these cases,

$$K = (2X_s + X_m)/(2X_c + X_m). \tag{7}$$

$$\text{If } K_1 \gg K_2, \quad K = X_m/(2X_c + X_m). \tag{8}$$

$$\text{If } K_1 \ll K_2, \quad K = X_s/X_c. \tag{9}$$

Therefore in the two-step equilibrium, the equilibrium constant will be obtained in the two next cases. A) Two-step change can be treated separately and independently at the two sites. B) The intermediate species is minor in concentration. For other cases, it is difficult to obtain the equilibrium constant between ion pairs by means of the NMR technique.

For the case of **1**, CIP is dominant at room temperature, therefore, the latter case (B) is considered as follows,

$$\mathrm{C} \rightleftarrows \mathrm{S}. \tag{10}$$

As seen in Fig. 3a, the temperature-dependent chemical shifts of **1** were expressed with two remarkable sigmoidal curves which imply changes in the ion-pair equilibria with temperature in the two solvents, MTHF and THF, having lithium as counter ions. The thermodynamic parameters thus obtained are given in Table 3 which are for ΔH to be −39.3 and −50.6 kJ mol^{-1} in MTHF and THF, respectively. Takaki et al. studied a similar two-step equilibrium for 9,9′-dilithio-9,9′-polymethylenedifluorene in toluene.[12] In this example the ratio of K_1/K_2 was 0.3 for a case connected with $(CH_2)_2$ and this is an example mentioned as B and is followed with the conditions of Eq. 9.

Structure of **1** is considered to be a combination of two diphenylmethanide ions. Concerning the diphenylmethanide ion (**3**), O'Brien et al. reported that ΔH or ΔS is −7.1 kcal mol^{-1} or −23 cal K^{-1} mol^{-1} with Li as counter ions. Our obtained value for **1** is about twice of that for **3**, respectively, as given in Table 3. ΔH in THF for **1** is absolutely larger than that in MTHF, but ΔS in THF is similar to that in MTHF. ΔH is dependent on the solvation power of the solvent. The power of THF will be stronger than that of MTHF, while ΔS will depend on the freezing out of solvent molecules around cations. Solvent molecules are similarly frozen out in the two solvents.

In Fig. 3b, the temperature-dependent chemical shifts for **2** were observed in the two next cases, one with Na in THF and the other with Li in MTHF. In the former case, ΔH and ΔS were −32.2 kJ mol^{-1} and −130 J K^{-1} mol^{-1}. The structure of **2** is also considered to be a combination of **3**. Concerning the CIP–SSIP equilibrium of **3**, O'Brien et al. reported that ΔH and ΔS are −7.6 kcal mol^{-1} and −31 eu in THF with Na as counterions.[7,8] These values are quite similar to those of ours for **2**. But **2** is a dianionic system, which has to active sites. If two metal cations of **2** are concerned with the equilibrium between CIP and SSIP, the thermodynamic parameters of **2** must be twice of those for **3**, as mentioned earlier. But the values for **2** are nearly equal to those for **3**. Therefore it is understood that the temperature-dependent chemical shift of **2** is only concerned with one CIP–SSIP change at one active site. The process of the equilibrium in **2** is, therefore, concerned with one carbanionic center, which is expressed with Eq. 11, as follows. Our ΔH value for Eq. 11 is also consistent with that obtained by a conductance measurement in which ΔH is −30 kJ mol^{-1}.[13]

$$\mathrm{C} \rightleftarrows \mathrm{M}. \tag{11}$$

Conclusion

In this article, behavior of two dianionic systems was studied by measuring the temperature-dependent chemical shifts. Cation size and solvents are affected ordinarily for **1** but not for **2**. The equilibrium between CIP and SSIP has been discussed in terms of thermodynamic parameters compared with other systems. Dianionic systems are necessary to be treated with different ideas from those for the monoanionic systems.

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