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Internal Rotation of Tetraphenylethylene Dianion as Studied by H-1 and C-13 NMR

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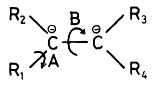
Synopsis. The line-shape analyses of the ^{1}H NMR spectra of the title anion have been made by means of a program of DNMR3. The thermodynamical parameters thus obtained are discussed in terms of counterions and other additives.

The ^{1}H NMR spectra of the title dianion has been reported previously.[1] A pictorial description of the dianion studied is shown in Scheme 1. As shown in the scheme, two internal rotations, A and B, exist in the carbanion. This study aims to obtain the thermodynamical parameters of these internal rotations. Our preliminary results have previously been reported.[2]



$R_1=R_2=R_3=R_4=C_6H_5$

Scheme 1.

Experimental

The strarting material (Tetraphenylethylene) was a commercial one and was used without further purification except for degassing by repetitive melting and freezing in a vacuum. The procedures for preparing the carbanion were the same as those previously reported.[1]

The H-1 and C-13 NMR measurements were carried out on a Hitachi R-20B spectrometer at 60 MHz and on a Hitachi R-900 FT spectrometer at 22.6 MHz. The sample concentration was about 1.0 mol dm^{-3} in the case of the potassium salt in THF-d_8. The H-1 and C-13 chemical shifts were evaluated with the high-field solvent peaks of THF-d_7 and -d_8 used as internal references. They were taken to be 1.75 and 25.2 ppm respectively with respect to TMS.

The temperature-dependent H-1 NMR spectra were analyzed by using the program of DNMR3 (QCPE No. 165).[3] In the original program, the maximum dimension of the B submatrices has been fixed at 48 and the maximum line number, at 136. For the analysis of the present material, it was necessary to expand them to 100 and 210 respectively. The calculations were carried out by a HITAC-8400 computer system installed in this Institute.

Results and Discussion

H-1 and C-13 NMR Spectra. The spectra of the title dianion have been observed at temperatures from 31.5 to −90 °C, with potassium as counterions in THF-d_8. The C_o signals in the temperature-dependent C-13 NMR spectra have decreased in height at −50 °C, been broadened at −60 °C, and clearly split into doublets at −74 °C. The H-1 NMR spectra of the carbanion were analyzed by the LAOCN3 program.[4] The coupling constants and the chemical shifts thus obtained are tabulated in Table 1. The H-1 and C-13 chemical-shift differences at low temperatures are about δ 1.35 and 0.07 for the H_o and H_m, and δ 2.3 and 1.2 for the C_o and C_m, respectively. The comparatively large difference in chemical shift between two H_o peaks can be explained by the ring-current effect of the phenyl groups.[5]

Line-shape Analyses. The temperature-dependent H-1 and C-13 NMR spectra were measured by using the same sample sealed in a 5-mm O.D. tube. Therefore, the C-13 NMR spectra were not suitable for the line-shape analyses because of their low signal-to-noise ratio. However, the proton-decoupled C-13 spectra were so simple that a rough estimate of the two-site exchange problem using a computer program, CLATUX[6] was possible, giving the activation energy of about 34 kJ mol^{-1}. The H-1 NMR line-shape analyses, however, could give a more exact activation energy. The rate constants for the two-site-five-spin exchange problem are given in Table 2 for various temperatures. The calculated and corresponding observed spectra are given in Fig. 1 for three typical temperatures. From the values in Table 2, the thermodynamical parameters tabulated in Table 3 are obtained. The values are compared with those

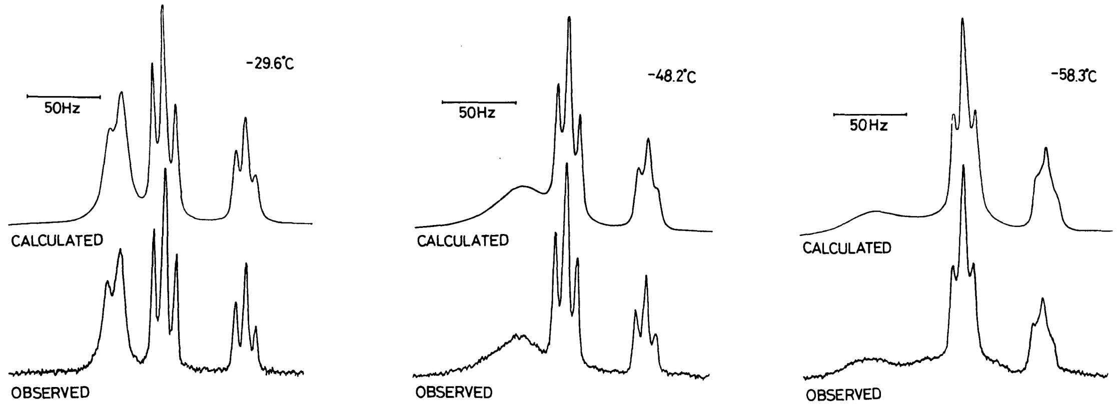
Table 1. H-1 and C-13 NMR data of tetraphenylethylene dianion potassium salt in THF-d_8

	H-1 Data at 31.5 °C[a)]	H-1 Data for DNMR3		C-13 Data at −74 °C
H_o:	418.83 Hz	459.4 Hz 378.2	C_o:	118.11 ppm 115.86
H_m:	387.72	389.7 385.7	C_m:	129.03 127.86
H_p:	334.62	334.6	C_p:	106.38
J_{om}:	8.58	8.6	C_i:	147.77
J_{op}:	1.12	1.2	C_α:	95.95
J_{mp}:	6.69	6.7		

a) The values are obtained with an RMS error of 0.18 Hz and with standard errors of 0.03 Hz.

Table 2. Rate constants (k) of the phenyl rotation in tetraphenylethylene dianion potassium salt in THF-d_8

Temp/K	k/s^{-1}
254.8	3460±70
243.6	1840±40
232.7	800±30
230.4	680±30
225.0	320±10
214.9	118± 5
204.7	40± 2



(a) (b) (c)

Fig. 1. Calculated (upper) and Observed (lower) H-1 NMR spectra of tetrapehnylethylene dianion potassium salt in THF-d_8 at 60 MHz; (a) at −29.6 °C; (b) at −48.2 °C; (c) at −58.3 °C.

Table 3. Thermodynamical parameters for the hindered rotation of the phenyl groups of tetraphenylethylene dianion potassium salt in THF-d_8

E_a/kJ mol^{-1}	ln A	ΔH^*/kJ mol^{-1}	ΔS^*/J K^{-1} mol^{-1}
39.8±1.5	27.1±0.8	37.9±1.5	−25.7±6.6

reported for the phenylmethanide and diphenylmethanide ions.[7-12] The activation energy observed in this study is the smallest value reported thus far. This may be attributed to the fact that the carbanion is sterically inhibited from having the planar structure rather than to its resonance stabilization in the ground state.

Effects of Counterions and Other Additives. The coalescence temperatures of the H_o in the carbanion are affected by the counterions. Several attempts were made to obtain the exact thermodynamical parameters. However, the solubilities of the lithium and sodium salts are too small for us to obtain good line-shaped spectra in THF at low temperatures. Therefore, the line-shaped analyses described above are possible only for the potassium salt. The coalescence temperatures are estimated to be about −40, −55, and −60 °C for the K^+, Na^+, and Li^+ counterions respectively. The temperatures decrease with a decrease in the metal radius and with an increasing proximity of the metal to the active carbon site. The coalescence temperatures can be used to estimate the changes in the free energy of activation for the rotation A in the carbanions using the following equation:

$$\Delta G_c^{\ddagger} = aT_c[9.972+\log(T_c/\Delta\nu_{ab})],$$

where T_c, $\Delta\nu_{ab}$, and a are the coalescence temperature, the chemical-shift difference of two exchanging sites, and a constant of 19.14 J mol^{-1} respectively.[13] In the case of the sodium salt, the $\Delta G_c^{\ddagger}$ value is 43.7 kJ mol^{-1} when the values of T_c and $\Delta\nu_{ab}$ are adopted as *ca.* 218 K and 67 Hz. This value is reasonable as compared with that obtained for the potassium salt (43.9 kJ mol^{-1} at 233.2 K). Hexamethylphosphoric triamide (HMPA) was used to check the effect of other additives, because it has a high dielectric constant. The effect of HMPA caused a rise in the coalescence temperature by about 5 K in the potassium and sodium salts. Therefore, the effect appears as an increase in the activation energy of the rotation A. This is consistent with that observed for diphenylmethanide ions by Olah and Watkins.[12]

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