Journal of Organometallic Chemistry, 219 (1981) 139—143
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

NMR STUDY OF THE COMPLEXATION OF SECONDARY-BUTYLLITHIUM BY *N,N,N',N'*-TETRAMETHYLETHYLENEDIAMINE

J.M. CATALA, G. CLOUET and J. BROSSAS

Centre de Recherches sur les Macromolécules, 6 rue Boussingault, 67083 Strasbourg Cedex (France)

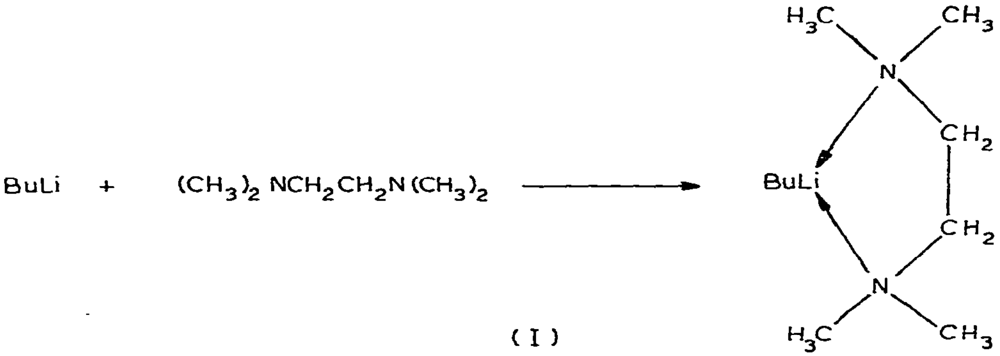
(Received May 20th, 1981)

Summary

Complexation of secondary-butyllithium (sec-BuLi) by *N,N,N',N'*-tetramethylethylenediamine (TMEDA) has been examined by NMR spectroscopy at various temperatures. The upfield chemical shift of the α-methine proton of the sec-BuLi has been determined as a function of the ratio R = TMEDA/sec-BuLi. The reversible variation of the chemical shift from —50°C to —20°C is explained in terms of an endothermic disproportionation of the 1 : 1 complex (1 sec-BuLi : 1 TMEDA) to the 1 : 2 complex (1 sec-BuLi : 2 TMEDA).

Introduction

The enhancement of the reactivity of carbanions by addition of a polyamine such as TMEDA was first employed by Langer [1] for the anionic polymerization of ethylene. To determine the structure of the complex, he studied the chemical shift of the α-proton of n-BuLi in the presence of the diamine and concluded that a 1 : 1 complex (I) was formed. Similar conclusions have been



(I)

0022-328X/81/0000—0000/$02.75

obtained from a cryometric study [2], the kinetics of ethylene polymerization [3], and the kinetics of the polymerization of aromatic compounds [4]. However, for different carbanions, different complexes have been proposed: it has been suggested that butadienyllithium forms a 1 : 2 complex [2]. For butadiene, Sgonnik [5] observed a propagation rate maximum at a ratio R = TMEDA/BuLi = 4. A similar observation was made by Erussalimsky [6] for isoprene propagation. Our recent kinetic study of the metallation of aromatic compounds [7] by the associated secondary-butyllithium-TMEDA suggested that the complexation of sec-BuLi is quite different from that of n-BuLi. To confirm that view we have tried to characterize the type of complexation by NMR studies.

Experimental

All reactions were carried out under argon.

Heptane was purified by refluxing over and distillation from sodium wire, and was distilled from living carbanion immediately before use. Sec-butyllithium was prepared in heptane by Gilman's method [8]. *N,N,N',N'*-Tetramethylethylenediamine was passed over molecular sieves and distilled under vacuum from butyllithium.

Preparation of tubes

To 100 ml of heptane in a round bottom flask was added 3.5×10^{-3} mol of sec-BuLi. The solution was cooled to −70°C, and 0.5 ml of it was placed in an NMR tube through a manifold holding six NMR tubes. The first tube was sealed under vacuum after the solution had been frozen. 1.75×10^{-3} mol of TMEDA was then added to the solution in the flask and another tube was prepared as previously described, and so on.

NMR spectra were measured with a Cameca spectrometer at 250 MHz.

Results and discussion

The spectra were run at low concentrations of sec-BuLi (3.5×10^{-2} *M*), and in order to enhance the signal of the α-methine proton of the sec-BuLi, it was necessary to accumulate several hundred scans. To avoid the broadening of the heptane peaks due to the scanning, the CH_2 and the CH_3 protons were irradiated. Thus the α-methine proton, whether complexed or not by the TMEDA, gave a singlet (a in Fig. 1), the chemical shifts of which were determined by reference to that of the methylene proton of the solvent (b in Fig. 1) and are shown in Table 1. The chemical shifts observed at −50°C are shown in Table 1 alongside the values of the ratio R = TMEDA/sec-BuLi.

The upfield chemical shift of the α-methine proton of the butyllithium is attributed to the increase of the negative charge on the carbanion due to the complexation of the lithium by the diamine. There is only one peak for the α-methine proton of sec-BuLi even when $R \leqslant 1$, which proves that a fast exchange exists between free sec-BuLi and complexed sec-BuLi. As R is increased from 0 to 1 the chemical shift rises. No further change occurs above $R = 1$, indicating that all the butyllithium is complexed by the TMEDA. Thus

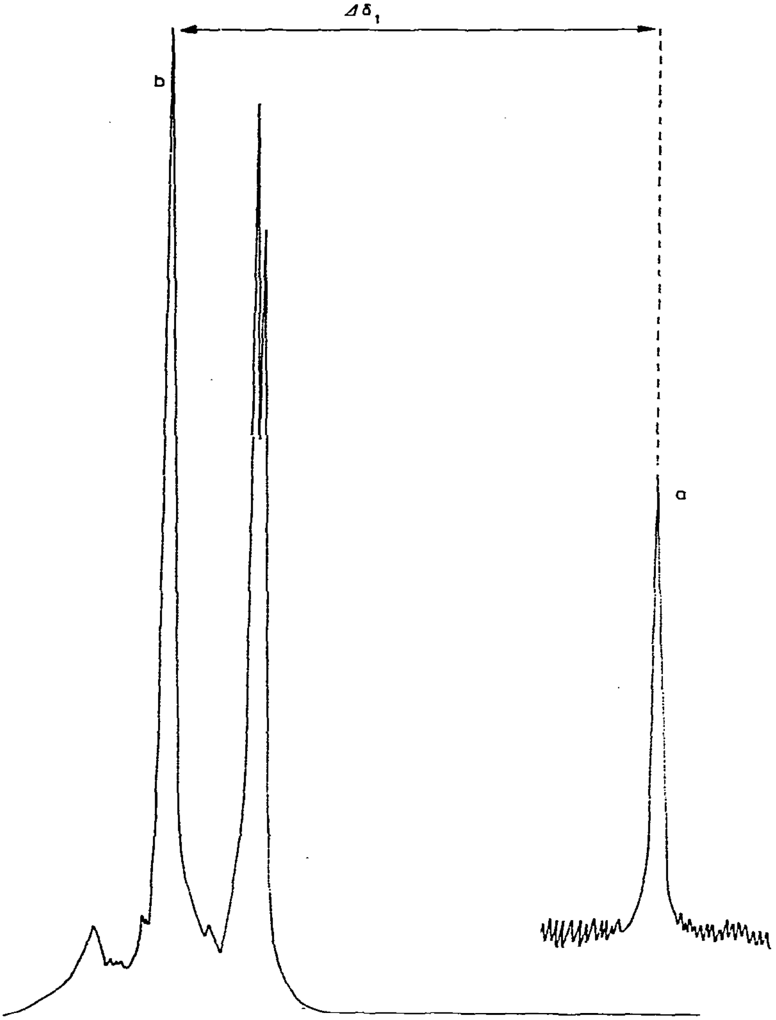


Fig. 1. ^{1}H NMR spectrum of the α-methine proton of the sec-BuLi in heptane, with irradiation of the CH_2 and CH_3 protons. a) α-methine proton of sec-BuLi; b) CH_2 of the heptane.

TABLE 1

^{1}H NMR UPFIELD CHEMICAL SHIFTS FOR α-METHINE PROTON OF sec-BuLi AS A FUNCTION OF THE RATIO R = TMEDA/sec-BuLi IN HEPTANE AT −50°C. [sec-BuLi] = 3.5×10^{-2} M

Exp.	δ (ppm)	R =					
		0	0.5	1	2	4	6
1	$\Delta\delta_1$ [a]	2.25	2.53	2.66	2.66	2.65	2.64
	$\Delta\delta_2$ [b]	—	0.28	0.41	0.41	0.40	0.39
2	$\Delta\delta_1$	2.24	2.52	2.64	2.64	2.64	2.64
	$\Delta\delta_2$	—	0.28	0.40	0.40	0.40	0.40
Average values	$\Delta\delta_2$	0	0.28	0.40	0.40	0.40	0.39

[a] From the methylene proton of heptane. [b] $\Delta\delta_2 = \Delta\delta_1(R) - \Delta\delta_1(R = 0)$.

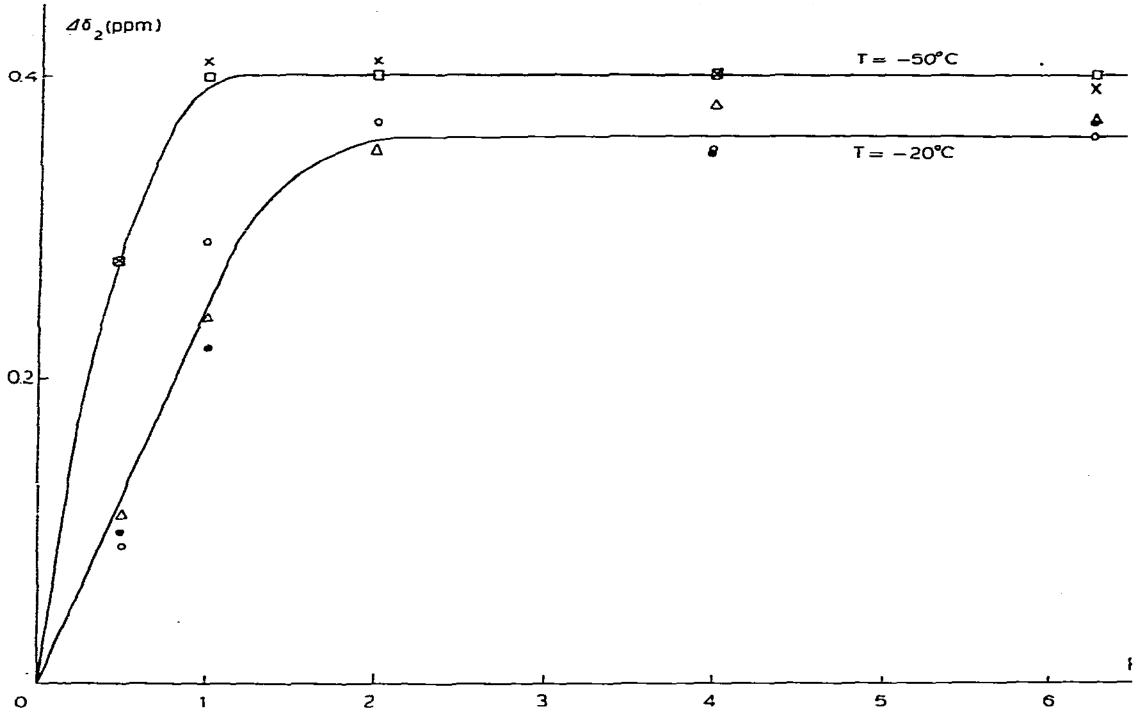


Fig. 2. A plot of the chemical shift of the α-methine proton of the sec-BuLi against R = TMEDA/sec-BuLi ratio at —50°C and at —20°C.

we can conclude that at —50°C the sec-BuLi and the TMEDA form a 1 : 1 complex (Fig. 2).

When the temperature is raised from —50°C to —20°C (Table 2, Fig. 2) a plateau is reached at R = 2. The maximum negative charge on the carbanion at —20°C is obtained for the complexation of 1 sec-BuLi by 2 TMEDA molecules.

TABLE 2

^{1}H NMR UPFIELD CHEMICAL SHIFTS OF THE α-METHINE PROTON OF THE sec-BuLi VERSUS THE RATIO R = RMEDA/sec-BuLi IN HEPTANE AT —20°C. [sec-BuLi] = 3.5 X 10^{-2} M

Exp.	δ (ppm)	R =					
		0	0.5	1	2	4	6
3	$\Delta\delta_1$ [a]	2.24	2.34	2.46	2.59	2.59	2.60
	$\Delta\delta_2$ [b]	—	0.10	0.22	0.35	0.35	0.36
4	$\Delta\delta_1$	2.28	2.37	2.57	2.65	2.63	2.67
	$\Delta\delta_2$	—	0.09	0.29	0.37	0.35	0.37
5	$\Delta\delta_1$	2.26	2.37	2.50	2.61	2.64	2.63
	$\Delta\delta_2$	—	0.11	0.24	0.35	0.38	0.37
Average values	$\Delta\delta_2$	0	0.10	0.25	0.35	0.36	0.36

[a] From the methylene proton of heptane. [b] $\Delta\delta_2 = \Delta\delta_1(R) - \Delta\delta_1(R = 0)$.

On the other hand, this table also shows that at −20°C the chemical shifts of the α-methine proton for $R = 0.5$ and $R = 1$ are lower than the corresponding values observed at −50°C. Moreover, at −20°C the chemical shift for $R = 1$ is close to that measured for $R = 0.5$ at −50°C. In other words, we are measuring an average chemical shift between one mole of 2 : 1 complex and one mole of uncomplexed sec-BuLi. At −20°C for $R = 0.5$ the data agree with an averaging between 1 mol of 2 : 1 complex and 3 mol of uncomplexed sec-BuLi. Therefore we must conclude that a 2 TMEDA : 1 sec-BuLi complex is formed. The values for the plateau in this last case are lower than those observed at −50°C (Fig. 2). The deshielding of the proton on the carbanion can be explained only in terms of steric hindrance. Thus, to allow a second molecule of TMEDA to come close to the lithium atom, the overlap between the lone pairs of the nitrogen atoms and the lithium orbitals must be reduced, and the overlap of the orbitals of the carbanion and the lithium is correspondingly increased. This causes a reduction in the negative charge on the carbanion.

All the observed phenomena are reversible with temperature. In other words, for a given temperature, only one type of complex is formed. The chemical shifts are not changed by running the spectra at −50°C, then at −20°C, then at −50°C again, and so on. Thus, we have an endothermic disproportionation of the 1 : 1 complex to the 2 : 1 complex:

$$\underset{(-50^\circ\mathrm{C})}{2\,[\text{sec-BuLi-TMEDA}]_n} \overset{\text{decreasing temperature}}{\rightleftharpoons} \underset{(-20^\circ\mathrm{C})}{[\text{sec-BuLi-(TMEDA)}_2]_n} + \frac{n}{x}\,(\text{sec-BuLi})_x$$

where n is the degree of aggregation of the complex in heptane and x that of sec-BuLi in the same solvent.

Conclusion

The ^{1}H NMR study has shown that in the complexes formed by sec-BuLi and TMEDA the lithium ion can be complexed by either one or by two molecules of TMEDA, depending upon the temperature. There is a disproportionation involving a finite enthalpy change between the two complexes.

Acknowledgment

The authors wish to thank Dr. Michael Szwarc for his fruitful help in this work.

References

1 A.W. Langer, Adv. Chem. Ser., Amer. Chem. Soc., Washington DC, 1974, 130.
2 J.N. Hay, J.F. McCabe and J.C. Robbe, J. Chem. Soc. Faraday I, 68 (1972) 1.
3 H. Magnin, F. Rodriguez, M. Abadie and F. Schue, J. Polym. Sci. Polym. Chem. Ed., 15 (1977) 875.
4 G. Helary and M. Fontanille, Europ. Polym. J., 14 (1978) 345.
5 L.V. Vinograda, N.I. Nikolayev and V.N. Sgonnik, Polym. Sci. USSR, 18 (1976) 2008.
6 A. Davidjan, N. Nikolayev, V.N. Sgonnik, B. Belenkii, V. Nesterow and B. Erussalimsky, Makromol. Chem., 177 (1976) 2469.
7 J.M. Catala, G. Clouet and J. Brossas, New Developments in Ionic Polymerization, First European Discussion Meeting on Polymer Science, Strasbourg, 1978.
8 H. Gilman, F.W. Moore and O. Baine, J. Amer. Chem. Soc., 63 (1941) 2479.