



Soviet-era science, translated into English

Chemistry

1957

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Abstract

Full Text

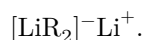
Chemistry

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On the Association of Aliphatic Organolithium Compounds in Hydrocarbon Solutions

(Presented by Academician A. N. Nesmeyanov, 10 IV 1957)

In determining the molecular weight of lithium phenyl and lithium benzyl in ether solutions by the ebullioscopic method, Wittig, Meyer, and Lange ⁽¹⁾ found that the indicated compounds form “auto-complexes” of the general formula:



We set ourselves the task of determining whether aliphatic organolithium compounds are capable of similar complex formation in hydrocarbon solutions. For this purpose, the molecular weight of lithium ethyl and lithium butyl was determined by the cryoscopic method. Benzene and cyclohexane of a degree of purity suitable for these solvents in cryoscopic measurements were used as solvents. Lithium ethyl and lithium butyl were synthesized in these same solvents by the known method, based on the interaction of the corresponding chloro derivative with metallic lithium ⁽²⁾.

After the synthesis had been carried out, the solutions of lithium ethyl and lithium butyl, under a stream of nitrogen free of oxygen, were transferred into Schlenk vessels equipped with a graduated burette (with a division value of 0.1 ml) and stopcocks. The concentration of the organolithium compounds in solution was determined by double titration ⁽³⁾. Special determinations established that, in benzene solutions of lithium ethyl and lithium butyl, lithium chloride was practically absent, and its content did not exceed 0.1-0.5 wt.% calculated as organolithium compound.

Solutions having, for lithium ethyl, a normality of ~0.6 and, for lithium butyl, 0.6-0.8 were used in the work. Taking into account the great sensitivity of organolithium compounds to moisture and oxygen, we carried out all cryoscopic determinations in a special cryoscope that excluded contact of the working solutions with the external atmosphere. The cryoscope had a ground-glass test tube with a Beckmann thermometer (division value 0.01°) and was equipped with two stopcocks, which made it possible to introduce solutions of organolithium compounds under a stream of nitrogen. The cryoscope was placed in an air glass jacket, and the entire apparatus during measurements was in a Dewar vessel in which a temperature of +1° was maintained. The solution was stirred by an

electromagnetic stirrer. Before the determinations were begun, the cryoscope was subjected to thorough preliminary treatment to remove gases and vapors occluded by the glass. This was achieved by prolonged conditioning of the apparatus under vacuum while heating, followed by purging with nitrogen purified from oxygen and moisture.

To determine the molecular weight, 30 ml of solvent (to an accuracy of 0.1 ml) was introduced into the cryoscope prepared in this way from a Schlenk vessel, in which the carefully purified solvent was stored over metallic sodium wire.

After determining the freezing temperature of the pure solvent, a solution of the organolithium compound (in the same solvent) was introduced into the cryoscope from the Schlenk vessel under a stream of nitrogen in amounts ensuring

Table 1

Data on the determination of the molecular weight of ethyllithium in benzene

Amount of benzene, ml	Amount of introduced LiC_2H_5 , mol	Concentration of LiC_2H_5 , mol per 1000 g benzene		Experiment 1: M found for LiC_2H_5		Experiment 2: M found for LiC_2H_5
		Experiment 1: depression, $^{\circ}\text{C}$	Experiment 2: depression, $^{\circ}\text{C}$	Experiment 1: M found for LiC_2H_5	Experiment 2: depression, $^{\circ}\text{C}$	Experiment 2: M found for LiC_2H_5
31.9	0.001178	0.042	0.11	68.4	0.10	77.0
32.9	0.001698	0.059	0.17	63.3	0.15	71.8
34.4	0.002728	0.091	0.24	68.9	0.22	76.9
36.5	0.004030	0.126	0.34	67.7	0.33	70.0
40.2	0.006324	0.180	0.50	65.6	0.49	65.3
47.5	0.010850	0.261	0.72	66.2	0.70	68.7
55.0	0.015500	0.313	0.87	67.6	0.87	67.6
69	0.024180	0.401	0.96	76.1	1.01	70.9
75	0.027900	0.425	0.99	78.3	—	—

the specified concentration of the organolithium compound for the determination of molecular weight.

After completion, the freezing temperature of the solution of the organolithium compound of the given concentration was determined, the cryoscope was removed from the Dewar vessel, and an additional amount of lithium alkyl solution was introduced into it. Thus, during the course of the experiment the total amount of solvent was continuously increased, which was taken into account in calculating the molecular weight. At the end of the experiment, the amount of organolithium compounds was determined⁽³⁾, which in all cases amounted to 99–99.5% of that introduced during the determination. The molecular weight was calculated according to the generally accepted formula:

$$M = \frac{E \cdot c \cdot 1000}{L \cdot d \cdot \Delta}.$$

The cryoscopic constant for benzene was taken, according to literature data, as 5.07, and for cyclohexane as 20.2. The specific gravity of benzene and cyclohexane was determined for the samples used and was, respectively, 0.875 and 0.777. Data on the determination of the molecular weights of ethyllithium in benzene solution and of butyllithium in benzene and cyclohexane solution are given in Tables 1-3.

Table 2

Data on the determination of the molecular weight of butyllithium in benzene

Amount of benzene, ml	Amount of intro- duced LiC ₄ H ₉ , mol	Concentration of LiC ₄ H ₉ , mol per 1000 g benzene		Experiment 1: <i>M</i> found for LiC ₄ H ₉		Experiment 2: <i>M</i> found for LiC ₄ H ₉	
		Experiment 1: de- pression, °C	Experiment 2: de- pression, °C	Experiment 1: <i>M</i> found for LiC ₄ H ₉	Experiment 2: de- pression, °C	Experiment 2: <i>M</i> found for LiC ₄ H ₉	
31.0	0.00088	0.032	0.08	131.7	0.08	131.7	
32.5	0.00220	0.077	0.19	132.2	0.20	125.6	
34.0	0.00352	0.118	0.26	147.7	0.28	137.0	
36.0	0.00528	0.168	0.37	147.1	0.40	136.1	
39.0	0.00792	0.227	0.51	147.8	0.53	142.2	
42.0	0.01056	0.287	0.63	148.4	0.66	141.3	
45.0	0.01320	0.335	0.73	149.1	0.75	142.5	
48.0	0.01584	0.377	0.83	147.5	0.87	140.9	
58.0	0.02464	0.486	1.07	147.3	1.08	146.3	
68.0	0.03344	0.562	1.22	149.3	1.23	149.0	

As can be seen from the data given in the tables, ethyllithium in benzene solution is in an associated state in the concentration range 0.04-0.4 mole per 1000 g of solvent. In this case the experimentally found molecular weight practically corresponds to twice the calculated molecular weight. Butyllithium in benzene solutions (in the range

Table 3

Data for the determination of the molecular weight of butyllithium in cyclohexane

Amount of benzene, ml	Amount of intro- duced LiC ₄ H ₉ , mol	Concentration of LiC ₄ H ₉ , mol per 1000 g of cyclohex- ane		Experiment 1: <i>M</i> found for LiC ₄ H ₉		Experiment 2: <i>M</i> found for LiC ₄ H ₉	
		Experiment 1: de- pression, °C		Experiment 1: de- pression, °C		Experiment 2: de- pression, °C	
31.0	0.00081	0.032	0.26	167.4	0.29	150.1	
32.5	0.00203	0.080	0.59	175.2	0.62	167.1	
34.0	0.00324	0.123	0.93	170.6	0.90	176.4	
36.0	0.00486	0.174	1.32	170.3	1.28	175.6	
39.0	0.00729	0.241	1.81	172.0	1.80	173.0	
42.0	0.00972	0.298	2.24	172.0	2.19	176.0	
45.0	0.01215	0.348	2.66	169.1	2.63	171.0	

of concentrations from 0.03 to 0.55 mole per 1000 g of solvent) and cyclohexane (in the concentration range from 0.03 to 0.35 mole per 100 g of solvent) is also in an associated state, but the experimentally found molecular weight of butyllithium somewhat exceeds twice the calculated molecular weight.

Thus, the work carried out has shown that organolithium compounds of the aliphatic series in hydrocarbon solutions are in an associated state, which corresponds to the dimeric form.

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of Synthetic Rubber
named after S. V. Lebedev

Received
10 IV 1957

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