[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

The Preparation and Properties of Crystalline Lithium Alkyls

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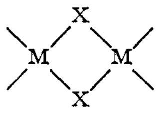
Pure, crystalline ethyllithium has been prepared by a modification of the method of Talalaeva and Kocheshkov. Methyllithium of about 95% purity has been prepared by reaction of ethyllithium with methyl iodide in benzene at 5–10°. The infrared spectra of solid methyl- and ethyllithium and of benzene solutions of ethyllithium are reported. Freezing point depression measurements show ethyllithium to be associated about sixfold in benzene solution. From the infrared data the thermochemical bond energy of the Li–C bond is estimated to be about 57 kcal./mole.

Introduction

Although the alkyl compounds of the metals of groups IA, IIA and IIIA are of particular interest in the theory of valence, and their physical properties are quite unusual,[2] they have not been extensively studied. The crystal structures of trimethylaluminum and dimethylberyllium, determined by X-ray diffraction,[3,4] have been important in revealing some of the principles governing the bonding in this class of substances. Rundle and co-workers have shown that the configurations assumed by these so-called electron-deficient compounds are largely determined by the tendency of the metal atom to utilize all its orbitals in bonding. The resulting structures may be described in terms of three-center bonds involving the overlap of two metal orbitals with a single hybrid orbital on carbon, producing four-membered rings (I). The metal–metal distances are short enough so that appreciable fractional bond order is indicated by application of Pauling's rule,[5] and it seems likely that overlap of the metal orbitals is also of importance in some of these compounds. The lithium alkyls are important members of this class of substances and information concerning their properties should help in the development of the theory of electron-deficient bonding. They closely resemble the corresponding beryllium and magnesium compounds in their physical properties; the bonding must be additionally complicated, however, by the fact that the lithium atoms have an extra orbital which is initially unfilled.



I

The lithium alkyls were first prepared by Schlenk, who noted that although methyl- and ethyllithium are solid at room temperature, the higher homologs are liquids.[6] The compounds are notably reactive, inflaming spontaneously in air. The older method of preparing the compounds involved the reaction of the appropriate dialkyl mercury with lithium metal, using benzene as solvent. An improved preparation of ethyllithium involved the reaction of ethyl halide with lithium metal in a hydrocarbon solvent, with subsequent crystallization of the ethyllithium.[7,8] Methyllithium has been prepared by the reaction of dimethylmercury with ethyllithium in benzene[6]

$$(CH_3)_2Hg + 2LiC_2H_5 \longrightarrow (C_2H_5)_2Hg + 2LiCH_3$$

The insoluble methyllithium is recovered as a precipitate but the use of mercury dialkyls is objectionable because of their toxicity.

The present article describes the preparation of pure crystalline ethyllithium by a modification of the method reported by Talalaeva and Kocheshkov,[8] and a new preparation of methyllithium which involves the reaction of ethyllithium with methyl iodide in benzene

$$LiC_2H_5 + CH_3I \longrightarrow LiCH_3 + C_2H_5I$$

Freezing point depression measurements on ethyllithium solutions in benzene are reported and the infrared spectra of solutions of various concentrations described. The infrared spectra of solid methyl- and ethyllithium are also presented and discussed. Electric moment measurements on the solutions and X-ray diffraction data on the solids are reported elsewhere.[9]

Experimental

Preparation of Ethyllithium.—Ethyllithium was prepared by a modification of the method of Talalaeva and Kocheshkov.[8] The benzene solution of ethyllithium was concentrated until solid precipitated, by distillation at reduced pressure, in order to avoid the use of higher temperatures. The ethyllithium was purified by recrystallization from benzene. Before filtering ethyllithium from the solutions it is desirable to chill it, since the temperature coefficient of solubility is high.

The material was analyzed for purity by dissolving it in benzene and treating aliquot samples with water or benzyl chloride reagent[10] to analyze for total and net base, respectively. The solutions were free of any impurities as determined by this test, and were also free of halide ion. Dried crystalline ethyllithium which had been exposed to the dry-box atmosphere for 5–10 minutes appeared to have undergone about 2–5% decomposition as determined by the above method of analysis.

Preparation of Methyllithium.—About 100 ml. of 0.1 *N* solution of purified ethyllithium in benzene and 2 g. of methyl iodide in about 25 ml. of benzene were used. Both solutions were cooled in the dry-box to about 5–10°, and then mixed together while stirring. A fine white precipitate formed after a few seconds. The solution was then filtered under suction and the precipitate on the filter washed twice with benzene, then with pentane.

Since methyllithium did not appear to have been made by this method previously, it was also prepared by the use of dimethylmercury, as mentioned in the Introduction. Di-

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[2] G. E. Coates, *Quart. Rev.* (*London*), **4**, 217 (1950).

[3] P. H. Lewis and R. E. Rundle, *J. Chem. Phys.*, **21**, 985 (1953).

[4] I. A. Snow and R. E. Rundle, *Acta Cryst.*, **4**, 348 (1950).

[5] L. C. Pauling, THIS JOURNAL, **69**, 542 (1947).

[6] W. Schlenk and J. Holtz, *Ber.*, **50**, 262 (1917).

[7] K. Ziegler and H-G. Gellert, *Ann.*, **567**, 179 (1950).

[8] T. V. Talalaeva and K. A. Kocheshkov, *J. Gen. Chem. U.S.S.R.*, English Translation, **23**, 399 (1953).

[9] M. T. Rogers and T. L. Brown, *J. Phys. Chem.*, **60**, 366 (1957); and unpublished results.

[10] H. Gilman, THIS JOURNAL, **66**, 1515 (1944).

methylmercury was prepared by the method of Marvel and Gould.[11]

The methyllithium obtained in the first instance was tested for the presence of iodide by dissolving in a small amount of ether, decomposing with water and then titrating with standard acetic acid. Upon acidification the iodide was analyzed for by titration with standard silver nitrate using eosin indicator. The mole percentage of iodide in the samples was around 5%. Comparison of the X-ray powder patterns and infrared spectra of methyllithium prepared by the two methods showed that they were identical in all respects.

All of the operations carried out on crystalline methyl- and ethyllithium were done in a dry-box, unless otherwise stated. The benzene solutions of ethyllithium were made up from recrystallized ethyllithium and manipulated in the dry-box whenever possible. The dry-box was prepared for use by thorough flushing with pre-purified nitrogen, followed by extensive drying with phosphorus pentoxide for at least 24 hours, while a positive pressure was maintained within the box.

Infrared Spectra.—Nujol and perfluorokerosene were used as mulling agents. The solids were freed from solvent by application of reduced pressure, using a vacuum pump, over a period of 1–2 hours. The dried solids were then covered with the mulling agent immediately, so that there was no contamination of the samples from the dry-box atmosphere. The solids were ground together with the mulling agents in an agate mortar until a fine cream was obtained, which was then placed between salt plates. The mulling agents were prepared for use by warming to about 100° for an extended period while bubbling through pre-purified nitrogen. There was no evidence of reaction of the solids with either mulling agent. It is worth noting that an attempt was made to use Fluorolube oil, a medium-length polymer of chlorotrifluoroethylene, as a mulling agent for ethyllithium. On mixing the two together, however, a vigorous reaction occurs, leaving a black residue.

Spectra of benzene solutions of ethyllithium were obtained by use of a conventional solution cell of 0.5 mm. thickness, with matching solvent cell. The spectra were obtained on a Perkin–Elmer model 21 infrared spectrometer with sodium chloride optics.

Freezing Point Measurements.—The freezing point depression of benzene solutions of ethyllithium was measured for solutions of various concentrations. Two cells were used for each measurement, one containing the solution, the other pure benzene. The cells were tubes about 20 cm. in length and 4 cm. in diameter, fitted with a female standard-taper connection. The top was a male standard-taper connection with a thermocouple well 6 mm. in diameter which extended to nearly the bottom of the cell through a neck in the top. A rubber sleeve at this neck was used to make the cells as air-tight as possible but still allowed enough freedom to use the wells for stirring. The cells were filled in the dry-box and then removed for measurement of the freezing point. The benzene in the pure solvent cell was half frozen and the cell immersed in a slush of frozen benzene in a Dewar flask. This cell was found to maintain a constant temperature to within about 0.005° over a 10–15 minute period, and was used as the reference cell. Copper–constantan thermocouples connected in series opposition were used for measuring the temperature difference. The thermocouple output was amplified and displayed on a recorder. The temperature difference could be read to about 0.005°. The solution cell was cooled at a convenient rate while stirring vigorously with the thermocouple well, the freezing point difference being obtained in the usual way by extrapolation of the time-temperature curve back to the initial cooling line.

Materials.—Thiophene-free C.P. benzene was fractionally crystallized once, distilled from calcium hydride in an efficient column packed with glass helices, and stored over sodium wire (d^{25}_4 0.87356 g./cm.^{3}). n-Pentane of the 99% purity grade was dried with calcium chloride prior to use as a solvent; the pentane used for washing methyllithium and for recrystallizations was dried and carefully fractionated prior to use. The alkyl halides were dried with phosphorus pentoxide and distilled before use. Sodium-free lithium used in the preparations of the lithium alkyls was obtained from Lithium Corporation of America, Minneapolis, Minn.

Results and Discussion

In Tables I, II and III are listed the frequencies and relative intensities of the bands present in the spectra of methyl- and ethyllithium. It will be noted that there are in all cases one or more relatively strong bands in the region 2800–2500 cm.$^{-1}$, These are due undoubtedly to carbon–hydrogen vibrations, but their frequencies are unusually low. No C–H frequencies in this region are observed for the methyl groups in the methyl derivatives of Sn, Hg, Zn or Cd.[12] Although the possibility exists

TABLE I

LIST OF FREQUENCY MAXIMA FOR METHYLLITHIUM SPECTRA

Nujol mull		Perfluorokerosene mull	
Frequency (cm.$^{-1}$)	Intensity	Frequency (cm.$^{-1}$)	Intensity
..	..	2925	6
2830	10	2826	10
2718 (s)[a]	3	2718 (s)[a]	3
2596	3	2590	1
1612	3	1612	3
..	..	1442	3
..	..	1380	3
1168	1	..	..
1150	1	..	..
1105	4	1105	2
1056	8	1056	5
..	..	980	2
967	1	967 (s)[a]	1
930	1	..	..
897	4	..	..
883	5	880	2
672	6	..	..

[a] The symbol (s) applies to bands which appear as a shoulder on the side of a more intense bond.

TABLE II

LIST OF FREQUENCY MAXIMA FOR ETHYLLITHIUM SPECTRA

Nujol mull		Perfluorokerosene mull	
Frequency (cm.$^{-1}$)	Intensity	Frequency (cm.$^{-1}$)	Intensity
..	..	2925	6
..	..	2810	10
2745	6	2745	8
..	..	1478	2
..	..	1450	3
..	..	1437 (s)[a]	2
..	..	1386	2
1230	1	..	..
1099	2	1104	3
1052	3	1062	4
948	3	948	6
918	1	904 (s)[a]	5
878	5	878	8
672	10	..	..

[a] See Table I.

TABLE III

LIST OF FREQUENCY MAXIMA FOR INFRARED SPECTRUM OF ETHYLLITHIUM IN BENZENE SOLUTION

Frequency, cm.$^{-1}$	Intensity	Frequency, cm.$^{-1}$	Intensity
2762[a]	10	1239	1
2730	8	1098	2
1448	3	920	9
1416	2	877[a]	2–0
1374	2		

[a] See Table I.

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(11) C. S. Marvel and V. L. Gould, THIS JOURNAL, **44**, 153 (1922).

(12) Landolt-Börnstein, "Physikalisch-chemischen Tabellen," Vol. VII, J. Springer, Berlin, 1951.

that the low frequencies are the result of electron-deficient bonding involving the carbon–hydrogen bond, it seems more likely that they are characteristic of the presence of ring structures similar in nature to I. Examination of the spectra of small-ring compounds as well as those of other cyclic structures such as dioxane and tetrahydrofuran shows a consistent absorption in this region by compounds of this type.[12,13] However, any assumptions made concerning the nature of the bonds in the polymer are necessarily quite tentative, since the structures of the lithium alkyls are at present unknown.

The strong absorption in the vicinity of 880 cm.$^{-1}$ is probably due to the carbon–metal stretch vibration. This absorption will be discussed later in connection with other results. The absorption at 672 cm.$^{-1}$ is completely absent from the spectra of benzene solutions of ethyllithium. It may be merely shifted to lower wave lengths inaccessible with the instrument used, or the band may be due to a configuration in the solid which is not present in the solution.

The results of the freezing point lowering measurements are shown in Table IV. The average degree of association, $\bar{n}$, was calculated by use of 5.12 as the molal freezing point constant for benzene. Although the use of a constant here is an approximation, the precision of the experiment does not appear to warrant a more exact treatment. Although the uncertainty in the values of $\bar{n}$ is large it is quite clear that ethyllithium is highly associated in benzene, the most probable degree of association being around six. Examination of the infrared spectra of ethyllithium in benzene solution reveals that although the strong absorption presumably due to metal–carbon stretching occurs at 920 cm.$^{-1}$, there is a band present in dilute solutions at 877 cm.$^{-1}$ which grows relatively more intense as concentration decreases. It appears probable that the lower frequency band is due to unassociated ethyllithium and the higher frequency band to the associated material. The relatively large frequency difference in the two bands may be indicative of a strong association bond. It is interesting to note that the bands are both quite narrow; formation of bonds of a single value of energy rather than the type of association exemplified by the alcohols is indicated.

TABLE IV

DATA FROM FREEZING POINT LOWERING EXPERIMENTS ON BENZENE SOLUTIONS OF ETHYLLITHIUM

Concn. (*m*)	$-\Delta T$(°C.)	$\bar{n}$
0.303	0.280	5.32
.392	.350	5.71
.347	.270	6.65
.0779	.065	6.09
.249	.185	6.94

Since no thermochemical information is available regarding the carbon–metal bond energy in lithium alkyls it seems worthwhile to attempt a rough evaluation by use of the infrared data. If the band at 878 cm.$^{-1}$ is assumed to be due to the metal–carbon stretch vibration in monomeric ethyllithium, and the harmonic oscillator approximation is used, a force constant for the vibration of about 2.6 × 10^5 dynes/cm. is obtained. In Table V are listed the force constants calculated for some bonds of various elements to methyl groups. In each case the harmonic oscillator approximation was used for the symmetric stretching frequency; in the case of the methyl halides the values so obtained are close to those given by Linnett for these bonds.[14] These values of force constant are plotted in Fig. 1 *vs.* thermochemical bond energy[15]; a reasonably smooth curve is obtained. If the value of *k* for the Li–C bond is inserted on this curve a bond energy of 57 kcal./mole is obtained. This value is of about the magnitude which is to be expected in view of the fact that cross-metallation reactions occur easily between alkyl lithium and alkyl chloride compounds.[16] Since the method used here has some theoretical justification it is felt that the value found for the bond energy is fairly good.[15]

TABLE V

VALUES OF FORCE CONSTANT CALCULATED FOR SOME BONDS TO CARBON IN METHYL COMPOUNDS

Bond	Force constant × 10^5, dynes/cm.	Bond	Force constant × 10^5, dynes/cm.
C–Cl	3.33	C–Zn	1.87
C–Br	2.77	C–Cd	1.71
C–I	2.19	C–Hg	2.20
C–Sn	2.09		

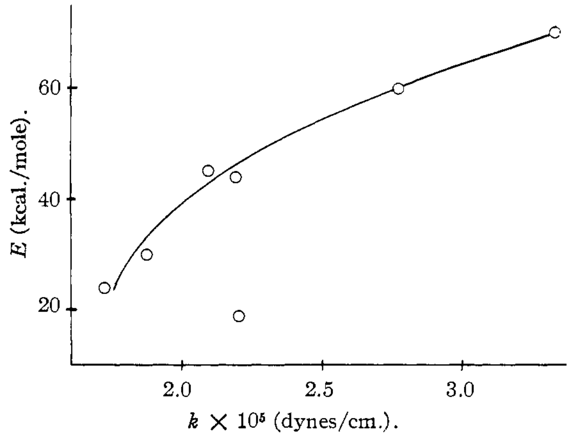

Fig. 1.—Force constant *vs.* bond energy for bonds to carbon in methyl compounds.

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(13) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London, 1954.

(14) J. W. Linnett, *Quart. Rev.* (*London*), **1**, 73 (1947).

(15) T. L. Cottrell, "The Strengths of Chemical Bonds," Academic Press, New York, N. Y., 1954.

(16) E. A. Braude, "Progress in Organic Chemistry," Vol. III, Academic Press, New York, N. Y., 1955.