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REACTIONS OF NAPHTHALENE AND CHLORO-SUBSTITUTED NAPHTHALENES WITH LITHIUM METAL*

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INTRODUCTION

The formation of anion-radical by reaction of alkali metals with aromatic hydrocarbons in the presence of solvents such as 1,2-dimethoxyethane and tetrahydrofuran has been known for some time[2-4]. The chemistry and electronic structure of these mono-negative ions of aromatic hydrocarbons have been a field of active investigation[5]. The same reaction may also lead to divalent negative ions[4,6,7,8]. This report deals with the formation of dianions of naphthalene with lithium metal and with elucidation of the reaction mechanism and the electronic structure of the intermediate.

Another objective of this research is the study of reactions of lithium metal and chloro-substituted naphthalenes.

EXPERIMENTAL

Reagents

1-Chloronaphthalene and dichloronaphthalene were purchased from Eastman Kodak Company. They were technical grade and used as received. The monochloro-substituted compound contained about 0.6% naphthalene and trace amounts of dichloro-substituted naphthalenes according to gas chromatographic analysis. The dichloro-substituted compound is a mixture of isomers which contains some naphthalene and monochloronaphthalenes. Lithium metals in wire form were obtained from Lithium Corporation of America, Inc. The "low-sodium" grade lithium, containing less than 0.005% sodium, was used in most of the experiments. In a few instances, lithium containing 1% sodium was employed. Anhydrous ethyl ether (Eastman Kodak) was the solvent.

Reactions

All the experiments were carried out in 7-oz. or 12-oz. beverage bottles. Measured amounts of ethyl ether, naphthalenes and lithium metal were added to the bottles. The metal in wire form was cut into very small pieces prior to the experiment. The bottles were sealed with toluene-extracted, rubber gaskets under perforated metal caps. They were evacuated and repressured with argon through a hypodermic needle three times. Final argon pressure in the bottles was 25 psi. The bottles were then tumbled in constant temperature baths.

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* Some of the data has been presented in ref. 1.

Total alkalinity was determined by removing a 2-ml aliquot of solution by means of a syringe and hypodermic needle. It was hydrolyzed and titrated with standard acid using phenolphthalein as indicator.

Gas-chromatographic (GLC) analyses of hydrolyzed products

The reaction mixtures were separated from excess lithium metal and hydrolyzed. The solutions of the hydrolyzed products were washed with deionized water in a separatory funnel and then evaporated to dryness. They were analyzed by heating samples to liquid phase and diluting 1 to 100 with benzene. The solutions (1 μl) were injected into a Perkin–Elmer Model 226 gas chromatography with a microliter syringe. The samples were split at a ratio of 1000 to 1.

The instrument was operated isothermally at 150° for 9 min then programmed to 220° at 4°/min and was held at 220° for 5 min. The column used was $200' \times 0.02''$ capillary Apiezon L column. It was run at 10 psig helium pressure. The method of calculation was area % X factor = weight %. The factor used was 1.26 for monochloronaphthalene and 1.00 for dihydronaphthalene and naphthalene. These values were determined using a prepared synthetic blend.

Mass spectrographic analyses of deuterated products

The reaction mixtures were separated from excess lithium metal and a slight excess of D_2O (99.8%) was added. The solutions were washed with deionized water and dried. Samples were admitted through a gallium orifice into the heated inlet system. Spectrum was taken and the pertinent peaks were examined. The instrument used was a 21–103C mass spectrometer manufactured by Consolidated Electrodynamics Corporation.

Electron spin resonance (ESR) spectroscopic analyses

Samples of lithium-naphthalene in ethyl ether or tetrahydrofuran were transferred by syringe to 4 mm O. D. quartz ESR sample tubes which had been sealed with rubber caps. The concentration of all samples used in this investigation was approximately 0.06 molar.

The ESR measurements were made in the variable temperature apparatus at room temperature (26°) and at selected temperatures down to −100°. The instrument was Model V4502 made by Varian Associates.

Tuning difficulties were encountered with the ESR spectrometer when the solutions were observed at −70° and −100°. These difficulties were apparently due to increased dielectric loss or increased electrical conduction or both at these temperatures.

RESULTS AND DISCUSSION

Lithium-naphthalene reactions

Aromatic hydrocarbons react with alkali metals in suitable solvents forming ion-radicals or dianions[2,3,4,6,7]. For example, sodium metal reacts with naphthalene in 1,2-dimethoxyethane yielding colored, soluble complexes containing one sodium atom for each naphthalene molecule. Their structure has been shown to be composed of aromatic anion-radicals and sodium cations[9]. This system is paramagnetic since there is an extra electron spin resonance (ESR) signal of 25 resolvable hyperfine lines. The origin of this ESR spectrum can be understood as follows: A sodium atom in dimethoxyethane contributes its single valence electron to the π^*-system of a naphthalene molecule, thus forming a negatively charged naphthalene ion and a positively charged sodium ion. The unpaired electron in the π^*-system of the naphthalene molecule is delocalized over the complete molecule. As a result of this electronic delocalization there is an interaction between the unpaired electron and the nuclear magnetic moments of the 8 hydrogen atoms attached to the naphthalene molecule. Because of the high symmetry of the naphthalene molecule, the 8 hydrogen atoms can be divided into two groups each containing 4 hydrogen atoms. The interaction between the unpaired electron and the 4 hydrogen atoms in the a-group result in 5 ESR hyperfine lines $[2I+1=2(4/2)+1=5]$. In addition, the interaction with the 4 hydrogen atoms in the *b*-group causes each of the above lines to split into 5 more lines for a total of 25 ESR hyperfine lines. Fig. 1 shows the theoretically calculated ESR spectrum from naphthalene anion-radical and the experimentally measured hyperfine coupling constants[10]. Hydrolysis of naphthalene anion-radical yields naphthalene and dihydronaphthalenes in about equal amounts (Table 1).

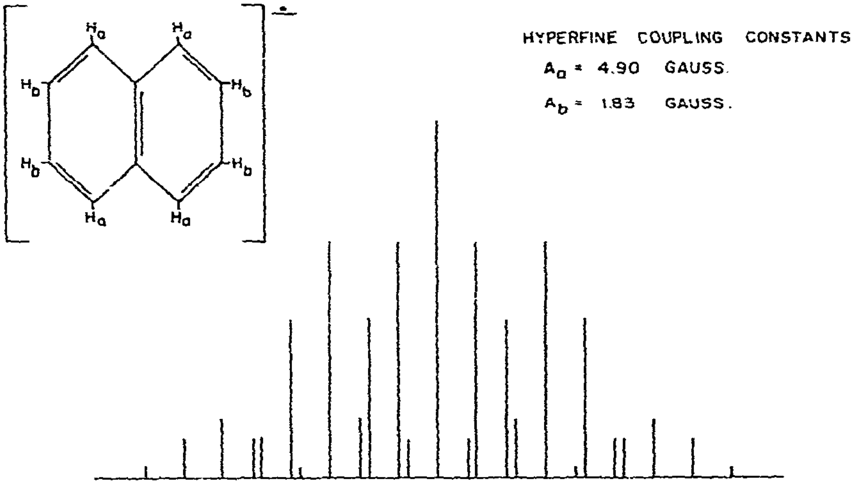


Fig. 1. Theoretical ESR spectrum of the naphthalene radical anion.

On the other hand we have found that lithium (in excess) reacts with naphthalene readily in tetrahydrofuran to form a dianion. This also was reported by Smid in a recent communication[8]. The dinegative ions, which may be represented as species having two coupled electrons in the π^*-orbital, are diamagnetic. Hydrolysis of this deep purple solution yielded almost exclusively dihydronaphthalenes (Table I).

Very little work has been reported on the reaction of alkali metal with polynuclear aromatic hydrocarbon in diethyl ether. It often is stated that this solvent is not suitable for this type of reaction. However, we observed that temperature had an unusual effect on the reaction between lithium metal and naphthalene in diethyl ether. The rate of reduction was much greater at −30° than it was at 0°. No reaction was observed at 50°. The solutions produced at lower temperatures had an intense purple color. The reaction products corresponded to 2 lithium atoms for each

TABLE 1

REACTION OF NAPHTHALENE WITH SODIUM AND LITHIUM IN TETRAHYDROFURAN

Naphthalene (mole)	0.34	0.34
Sodium (g-atom)	1.0	
Lithium (g-atom)		1.0
Tetrahydrofuran (ml)	1000	1000
Temperature (°C)	30	30
Reaction time (h)	*Total alkalinity (N)*	
0.25	0.23	0.45
1.0	0.33	0.70
2.0	0.35	0.70[b]
3.0	0.35	
5.0	0.38[a]	
Products from hydrolysis[c]		
Naphthalene	44	5
Dihydronaphthalene	56	95

[a] Na/Naphthalene = 1. [b] Li/Naphthalene = 2. [c] By GLC analysis.

naphthalene molecule. Hydrolysis of the lithium–naphthalene adduct resulted in mostly dihydronaphthalenes with about 6% naphthalene. The chemical evidence suggested the formation of dianions.

The ESR spectrum of lithium and naphthalene in diethyl ether, however, showed a paramagnetic species (Fig. 2). The experimental spectra contained many more than 25 hyperfine lines. Examination of the spectrum taken at −70° showed that it could be divided into groups of 4 lines and that these groups then reproduced

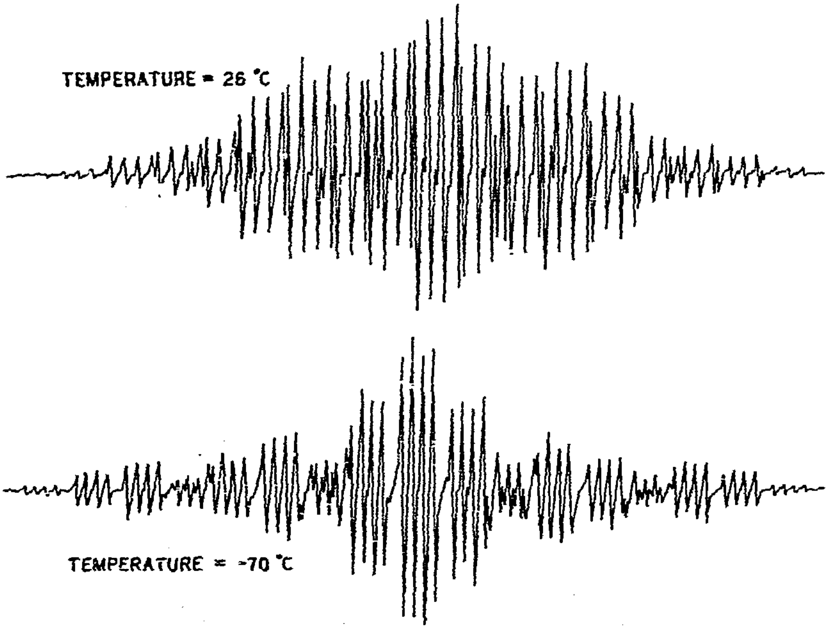


Fig. 2. ESR spectra of the lithium-naphthalene in diethyl ether.

the spectrum of the naphthalene anion-radical shown in Fig. 1. In the case of lithium metal and naphthalene in ethyl ether, the lithium atoms do not donate their valence electrons to naphthalene molecules but share them. Others have also observed the extra hyperfine lines in the fully resolved spectra of several ion-radicals[9,11]. It has been interpreted as being due to ion-pair association between the aromatic anions and the metal cations. Thus, the interaction of the unpaired electron with the naphthalene molecule produces a 25-line spectrum each of which is split into 4 lines by interaction with the nuclear magnetic moment of the lithium atom ($I=3/2$ so $2I+1=4$) for a total of 100 ESR hyperfine lines. The theoretical ESR spectrum calculated as described above and using the hyperfine coupling constants measured at −70° for the lithium-naphthalene solution is shown in Fig. 3.

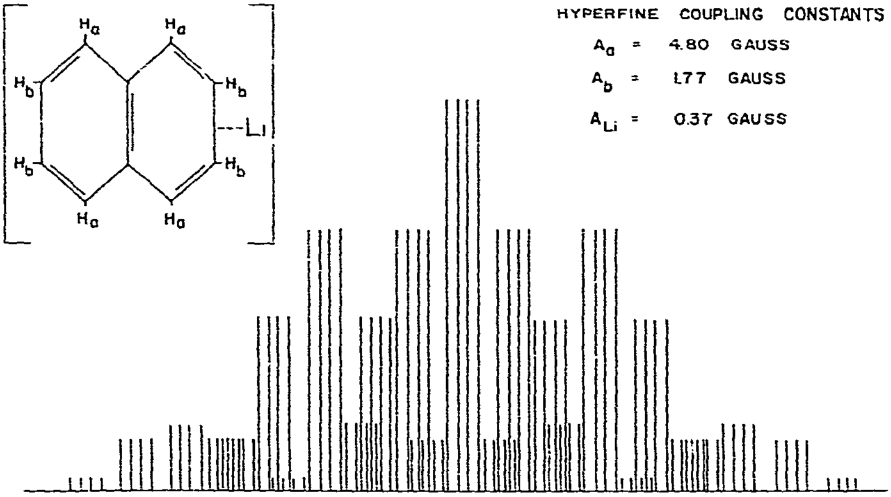


Fig. 3. Theoretical ESR spectrum of the lithium-naphthalene ion pair.

The three hyperfine coupling constants as a function of the temperature for the lithium-naphthalene solution are shown in Table 2.

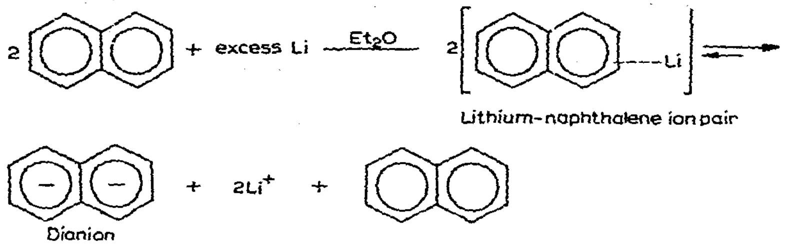
TABLE 2

LITHIUM-NAPHTHALENE IN DIETHYL ETHER

Sample temp. (°C)	*Hyperfine coupling constants*		
	α-Hydrogen (Gauss)	*β-Hydrogen (Gauss)*	*Lithium (Gauss)*
26	4.49	1.67	0.50
−30	4.77	1.77	0.44
−70	4.80	1.77	0.37
−100	4.84	1.81	0.30

The theoretically calculated spectrum and the experimentally measured spectra agree very well. Thus, the above description of the origin of the spectrum is considered to be valid.

The magnitude of the ESR signals was such that the paramagnetic lithium-naphthalene ion-pair concentration was estimated to correspond to only a very small fraction (< 2%) of the total products. We suspect that the lithium-naphthalene ion-pairs are in equilibrium with the dianions of naphthalene.



Thus, the majority of the naphthalene molecules are dianions in agreement with the chemical evidence.

Lithium-chloronaphthalene reactions

Chlorine-substituted naphthalenes can undergo both reduction and replacement of chlorine with lithium metal. Reactions between dichloronaphthalene and excess lithium metal were carried out in ethyl ether at different temperatures. The reactions were followed by determining the total alkalinity of the solutions at various times, and thus, the ratios of Li/hydrocarbon of the products. The results are shown in Fig. 4. Two very significant facts were evident. First, at 5°, 30°, and 50°, the final alkalinity approached that calculated for a tetralithium product. At −30° the shape of the curve suggested that the same product would result after a longer time. In fact, this was demonstrated to be the case. Second, at all four temperatures a change in reaction rate, whether it was from fast to slow or *vice versa*, occurred approximately at the alkalinity calculated for formation of a dilithium compound. It appears that two stages of reaction take place, each of which provides two lithium atoms to one hydrocarbon molecule. One is favored at low temperatures. The second is favored at high temperatures, but its starting material is the product of the first. In this regard, we found that the most effective way to carry out this reaction is that of starting at low temperatures (−30°), followed by high temperatures (30°).

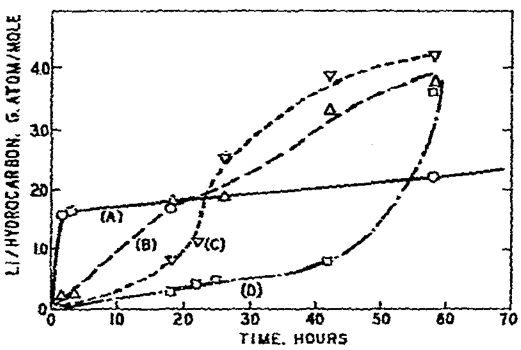


Fig. 4. Effect of temperature on the rate of reaction of lithium (excess) and dichloronaphthalene (0.05 mole) in ethyl ether (100 ml): (A) −30°, (B) 5°, (C) 30°, (D) 50°.

The same experiment was carried out with 1-chloronaphthalene. Again, the temperature effects were observed (Fig. 5). In addition, it revealed a very significant point. The change of rates in this experiment occurred at a Li/hydrocarbon ratio of about 1 to 1.

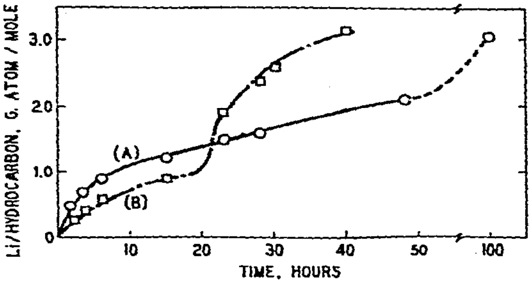
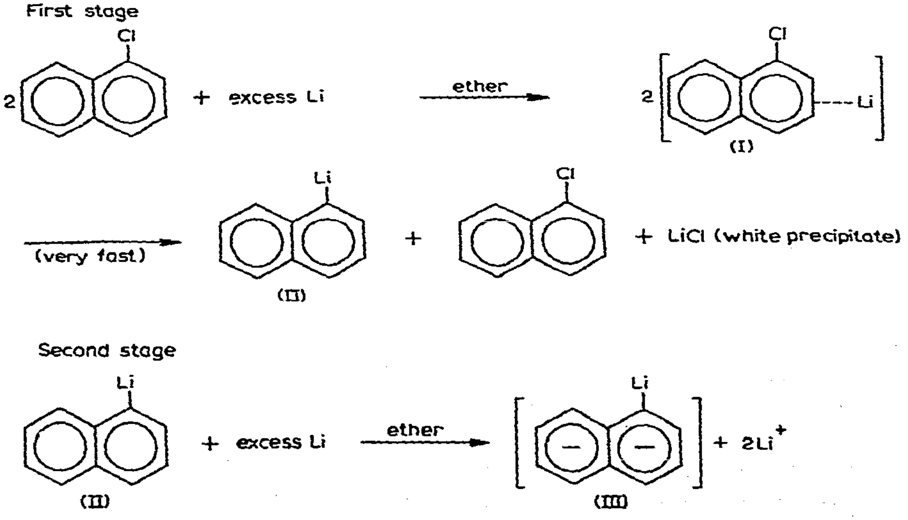


Fig. 5. Effect of temperature on the rate of reaction of lithium (excess) and 1-chloronaphthalene (0.06 mole) in diethyl ether (90 ml): (A) 5°, (B) 50°.

In both dichloronaphthalene and 1-chloronaphthalene experiments, at the very beginning of the reaction, regardless of temperature, one can observe the formation of reddish-brown spots on the lithium surface. Subsequently, the colorless solution becomes a light reddish-brown color. Meanwhile a white precipitate forms rapidly. Finally, the solution turns to a very dark purple color. It is speculated that three reactions actually occur. The first reaction is the reduction of chloro-substituted naphthalene with excess lithium metal to form an ion-pair (I). This reaction, like the lithium-naphthalene reaction, prefers low temperature. The very active lithium thus formed reacts with chlorine atoms immediately. Therefore, the second reaction is the replacement of chlorine with lithium. The products are monolithium- or dilithium-substituted naphthalenes (II) and lithium chloride (white precipitate). These two reactions occur almost simultaneously and could not be separated. They are followed by the reduction reaction of the compounds (II) to yield the major products (III). For simplicity, only the reactions of 1-chloronaphthalene are illustrated.



Positive evidence for this reaction sequence was obtained by chlorine analysis, gas chromatographic analysis of the hydrolyzed products and mass spectrographic analysis of the deuterated products. In Fig. 6 the results obtained from the hydrolysis experiments are shown. 1-Chloronaphthalene was treated with excess lithium metal in diethyl ether at 5°. The reaction mixtures were hydrolyzed at various Li/hydrocarbon ratios. The hydrolysis products were identified by means of gas chromatography. Chloronaphthalene disappeared and naphthalene formed rapidly at first. At Li/hydrocarbon ratios of around 1 to 1, the concentration of chloronaphthalene reached the minimum ($< 5\%$) and naphthalene reached the maximum ($\sim 95\%$) with only a trace of dihydronaphthalene. As the alkalinity of the solution increased, naphthalene concentration decreased and dihydronaphthalene increased.

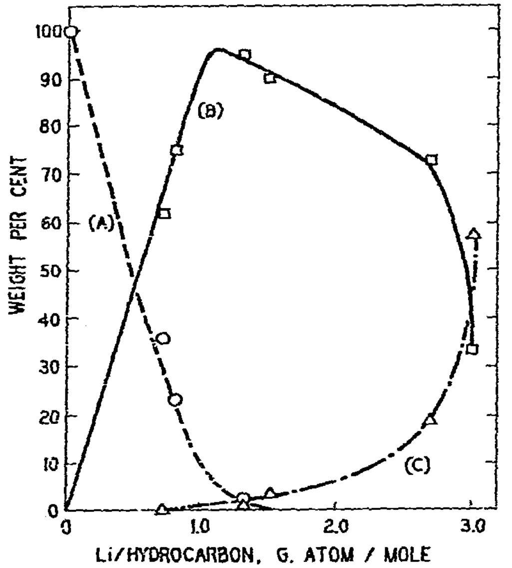


Fig. 6. Concentration of hydrolyzed products at various lithium to hydrocarbon (chloronaphthalene) ratios: (A) chloronaphthalene, (B) naphthalene, (C) dihydronaphthalene.

Chlorine analyses confirmed the GLC data that only a trace of the starting materials, *i.e.*, 1-chloronaphthalene and dichloronaphthalene, was present after passing the Li/hydrocarbon ratios of 1/1 and 2/1 respectively. By direct weighing, it was also shown that approximately 2 g atoms of lithium metal were consumed at Li/hydrocarbon ratio of 1/1 for each mole of chloronaphthalene and 4 g atoms of lithium metal were consumed at ratio of 2/1 for dichloronaphthalene.

The reaction products of 1-chloronaphthalene and lithium at Li/hydrocarbon ratios of about 1/1 and 3/1 were then treated with excess deuterium oxide. The products were isolated and examined by mass spectrography. At 1/1 ratio, over 85% of the naphthalene isolated was 1-deuteronaphthalene. There were only traces of dihydro-, dideutero- or 1-chloro-compounds. At a ratio close to 3/1, the mixture contained about 6% naphthalene, 29% 1-deuteronaphthalene, and about 5% dihydronaphthalene, with the remaining ($\sim 60\%$) consisting largely of mass numbers of 131, 132, and 133. The last three numbers correspond to 1-deuterodihydronaphthalenes, dideuteronaphthalenes, and 1-deuterodideuterionaphthalenes. The exact amounts of the three were not determined but the relative ratios of 131, 132, and 133 were estimated to be about 1 to 1.5 to 4. These independent experimental results are all in agreement with the proposed reaction sequence.

The ESR spectrum of lithium and chloronaphthalene in diethyl ether also showed a paramagnetic species. It was identical to the spectrum of lithium-naphthalene ion-pair in the same solvent (Fig. 2). The paramagnetic species represented only very small fraction of the total products. We did not observe any signal which could be attributed to lithium-1-substituted naphthalene ion-radical.

The overall rate of reaction is dependent on the surface area of lithium metal as shown in Table 3.

TABLE 3

EFFECT OF AMOUNT OF LITHIUM ON REACTION RATE (5°)

Dichloronaphthalene (mole)	0.10	0.10
Lithium (g-atom)	2.0	0.80
Diethyl ether (ml)	180	180
Theoretical concentration (M)	0.50	0.50
Reaction time (h)	*Total alkalinity (N)*	
18	1.0	
42	1.8	
56	2.0	1.3
104		1.7
120		2.1

It is also dependent on the concentration of chloro-substituted naphthalene. The result is shown in Table 4.

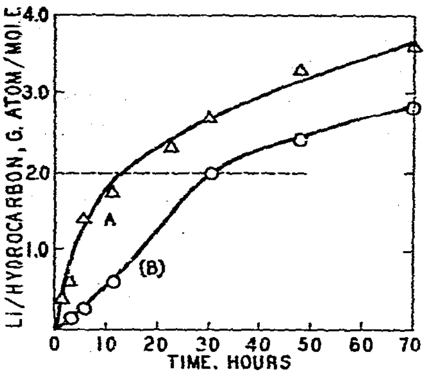
TABLE 4

EFFECT OF CONCENTRATION AT 5°

Dichloronaphthalene (mole)	0.05	0.10
Lithium (g-atom)	2.0	2.0
Diethyl ether (ml)	90	90
Theoretical concentration (M)	0.5	1.0
Reaction time (h)	*Total alkalinity (N)*	
48	2.0[a]	2.7
72		3.3
96		4.0[a]

[a] Li/hydrocarbon = 4.

The sodium content of the lithium metal has been shown to affect the ease of preparation of alkyllithium compounds by the metalorganic halide reaction[12-15] and by the metal–diene reaction[16]. We found that the rate of reaction of lithium metal and chloro-substituted naphthalenes is also dependent on this factor. The effect of lithium metal with different sodium content was most obvious in the first part of the reaction as shown in Figs. 7 and 8.



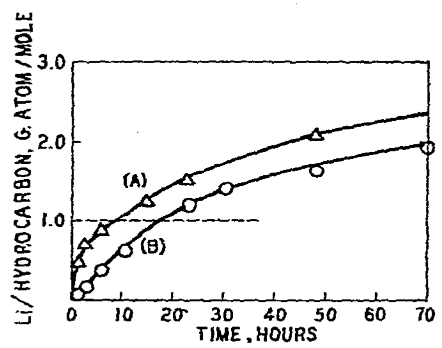


Fig. 7. Effect of sodium content in lithium on lithium-dichloronaphthalene reaction: (A) 1% Na, (B) < 0.005% Na.

Fig. 8. Effect of sodium content in lithium on lithium-1-chloronaphthalene reaction: (A) 1% Na, (B) < 0.005% Na.

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SUMMARY

Naphthalene reacts with lithium metal in diethyl ether at low temperatures to form a dianion. The solution also contains about 2% "ion-pair" which yields an ESR spectrum having 100 hyperfine lines.

Chloronaphthalene and dichloronaphthalene react with lithium in diethyl ether to form deep purple solutions which contain approximately three and four atoms of lithium, respectively, per mole of chloro- and dichloronaphthalenes.

The effect of reaction temperature, lithium surface area and sodium content of the lithium metal is discussed. A reaction sequence is proposed and evidence presented to support this mechanism.

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