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A Stable Free Radical formed by Oxidation of Lithium Decachlorodecaborate (2–) ($Li_2B_{10}Cl_{10}$) with Thionyl Chloride

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Introduction

The report by Wong, Gatter and Kabbani [1] of the isolation of $B_{10}Cl_{10}^{\overline{\cdot}}$ radical prompts us to report an alternative way in which this radical is produced, namely oxidation by $SOCl_2$. The chemistry of the $Li_2B_{10}Cl_{10}$–$SOCl_2$ system is of current interest because of its use as an electrolyte in lithium/$SOCl_2$ batteries [2]. Use of this electrolyte is believed to alleviate the 'voltage delay', a problem with these batteries [3]. A white crystalline material has been reported [4] to precipitate from a solution of $Li_2B_{10}Cl_{10}$ in thionyl chloride. It has been suggested [4] that this precipitate was lithium chloride.

Experimental

Preparation of $Li_2B_{10}Cl_{10}$

Bistriethylammonium decahydrodecaborate (2–) ($(NH(C_2H_5)_3)_2B_{10}H_{10}$) was synthesized from decaborane [5]. The sodium salt was formed by reaction with sodium hydroxide in water. The triethylamine formed in this reaction was extracted with toluene for safety reasons [6] and the sodium salt was chlorinated *in situ* [6]. $B_{10}Cl_{10}^{2-}$ was isolated by precipitation as the triethylammonium salt. Reaction of this salt with lithium hydroxide formed $Li_2B_{10}Cl_{10}$. The $Li_2B_{10}Cl_{10}$ was purified by an azeotropic distillation of a tetrahydrofuran–water mixture [8] as described in a patent [2]. The salt was heated to 160 °C under vacuum to remove water and tetrahydrofuran. This recrystallization procedure [2] is not ideal, but the purity of the $Li_2B_{10}Cl_{10}$ does not appear to be critical for studying its reaction with thionyl chloride. A preferable procedure would be to recrystallize the triethylammonium salt of $B_{10}Cl_{10}^{2-}$ as previously described [6] and then make the lithium salt analytically as described elsewhere [8].

Reaction of $Li_2B_{10}Cl_{10}$ with $SOCl_2$, Isolation of LiCl

1.3497 g (2.83 mmol) of $Li_2B_{10}Cl_{10}$ was gently refluxed with 30 ml of $SOCl_2$ (supplied by MC/B) for 15 hours and permitted to stand for five days. The deep purple solution was filterered through a glass frit. The precipitate in the reaction bulb and on the frit was washed with $SOCl_2$. The weight of the white solid on the frit (0.0829 g, 1.96 mmol as LiCl) agreed with a total cation ion exchange analysis for lithium (1.93 mmol) and a Mohr titration for chloride (1.94 mmol). Analysis of the white solid still in the reaction bulb gave a total cation analysis in both samples of 2.35 mmol of an 83% yield of LiCl. No attempt was made to isolate the still dissolved free radical from the possible solid reduction product of sulfur [9] from the $SOCl_2$.

In a separate experiment $Li_2B_{10}Cl_{10}$ was permitted to react with $SOCl_2$ for two weeks at room temperature in vacuum. LiCl analyzed as described above was isolated from this experiment also.

EPR spectra were recorded with a Varian E-9 X-band spectrometer with a variable temperature accessory. Temperatures were measured with a copper–constantan thermocouple. Magnetic field measurements were performed with an AEG proton NMR field probe. Visible spectra were taken with a Cary-17 spectrometer.

Results

Upon mixing of $Li_2B_{10}Cl_{10}$ with $SOCl_2$, the resulting solution gradually turns dark purple and simultaneously develops a broad single line EPR signal. A 10^{-2} *M* solution maintained at room temperature developed a maximum signal in about one week. A comparison of the signal intensity of this probe with that of a Cu(II)-α-picolinate reference sample shows that the final radical concentration is of the order of 10^{-2} *M*. The margin of error in this concentration measurement is appreciable due to the extremely large linewidth of the signal. As a consequence, it is not possible to state that there is a one-to-one relationship between moles of $Li_2B_{10}Cl_{10}$ starting material and moles of radical product.

The g-value of the paramagnetic species (determined using DPPH as a reference) is 2.00 ± 0.01. The large uncertainty stems again from the large linewidth of the EPR signal under the conditions of the measurement (590 gauss at –85 °C). The

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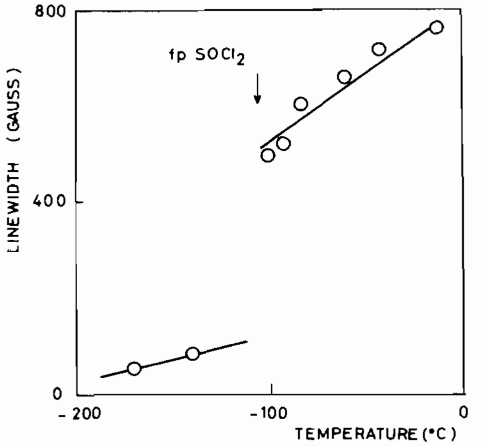

Fig. 1. Linewidth (peak to peak in first derivative spectrum) *vs.* temperature of EPR spectrum of 10^{-2} *M* solution of $Li_2B_{10}Cl_{10}/SOCl_2$.

linewidth of the resonance peak shows a strong dependence on temperature. As Fig. 1 shows, the width goes from 765 gauss at -12 °C to 545 gauss at -100 °C (measured from peak to peak in the first distinctive spectrum). Below the freezing point of $SOCl_2$ the linewidth is reduced sharply going from 83 gauss at -140 °C to 56 gauss at -170 °C. At no temperature does the signal show any indication of unresolved structure. Dilution of the sample does not affect the linewidth and a similar broad resonance is obtained when the $SOCl_2$ is distilled off and acetonitrile is added to the dark purple solid. The EPR signal cannot be saturated with microwave power levels up to 200 mW. Temperature variations do not appear to affect the radical concentration in solution.

The visible spectrum of the blue $SOCl_2$ solution, which is the same spectrum as that already reported in CH_2Cl_2 [1], has two absorption peaks, one at 575 nm and the other at 425 nm. Since the reaction may not have been complete we did not verify that Beer's Law Holds. However, we estimate that the molar absorptivity of the 575 nm peak is about 6×10^3 l mol^{-1} cm^{-1} and of the 425 nm peak about 3×10^3 l mol^{-1} cm^{-1}.

It has been reported [4] previously that when $(NH(C_2H_5)_3)_2B_{10}Cl_{10}$ is dissolved in thionyl chloride no blue color is observed. This observation was confirmed. However when lithium ion (as $LiAlCl_4$) dissolved in thionyl chloride is added to this solution, a blue color begins to develop immediately.

Discussion

It was reported [3] that $B_{10}Cl_{10}^{2-}$ anion is isolated unchanged from hydrolyzed solutions of $Li_2B_{10}Cl_{10}$ in $SOCl_2$. It was concluded [3] on this basis that no change occurs in the anion. Isolation of unchanged $B_{10}Cl_{10}^{2-}$ can be explained by the hydrolysis of $SOCl_2$ (present in excess) producing SO_2, a strong reducing agent in water, which could reduce a possible $B_{10}Cl_{10}^{\cdot-}$ species back to $B_{10}Cl_{10}^{2-}$. The fact that $B_{10}Cl_{10}^{2-}$ can be recovered under these conditions with the B_{10} cage intact gives further support to the conclusion that the radical we have observed is $B_{10}Cl_{10}^{\cdot-}$. Unfortunately, we have no explanation for the large linewidth and temperature dependence of the EPR spectrum.

The fact that $Li_2B_{10}Cl_{10}$ reacts with thionyl chloride has important implications regarding its use as an electrolyte in lithium/thionyl chloride batteries. Sulfur dioxide is a known product of the reduction of thionyl chloride in batteries [10] (*i.e.*, electrochemical reduction). It is also a product of the chemical reduction [9] of thionyl chloride. We have noticed the development of pressure when we have run the reaction reported on here in closed systems whether in vacuum or stoppered in air. It is likely that sulfur dioxide is one of the reaction products. Unfortunately it would be extremely difficult to determine SO_2 as a minor constituent of a $SOCl_2$ solution as SO_2 is a product of hydrolysis, oxidation (from decomposition of SO_2Cl_2), and reduction of thionyl chloride. The presence of sulfur dioxide in thionyl chloride based electrolytes is also reported [11] to alleviate 'voltage delay'. The reported beneficial effects of the use of $Li_2B_{10}Cl_{10}$ either as an electrolyte in lithium/thionyl chloride batteries [2, 4, 12] or as an additive to the electrolyte [13] in these batteries may be caused by sulfur dioxide formed in the reduction of thionyl chloride by $Li_2B_{10}Cl_{10}$.

It has been reported that reduction of benzene in liquid ammonia by lithium or in the presence of lithium bromide is faster than by other alkali metals alone [14]. The concentration of sodium either as dissolved metal or as sodium chloride, appeared in the rate law determined for the reduction of dimethylformamide and dimethylacetamide in liquid ammonia [15]. The observation that the free radical is formed in the presence of lithium ion but not in the presence of triethylammonium ion suggests that in a similar manner, reduction of thionyl chloride may be facilitated by a strongly polarizing ion such as lithium possibly through an ion pairing mechanism [15].

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References

1 E. H. Wong, M. G. Gatter and R. M. Kabbiani, *Inorg. Chim. Acta, 57,* 25 (1982).

2 C. R. Schlaikjer, *U.S. Patent,* 4,020,240.

3 N. Marincic, A. Lombardi and C. Schlaikjer, *Proc. Power Sources Symp., 27,* 37 (1976).

4 C. R. Schlaikjer, *Proc. Power Sources Symp., 28,* 241 (1978).

5 M. F. Hawthorne and R. L. Pilling, *Inorg. Synth , 9,* 16 (1967).

6 W. J. Knoth, H. C. Miller, J. C. Sauer, J. H. Balthis, Y. T. Chia and E. L. Muetterties, *Inorg. Chem , 3,* 159 (1964).

7 L. H. Horsley, *Adv. Chem. Ser., 116,* 21 (1973).

8 H. C. Miller and E. L. Muetterties, *Inorg. Synth., 10,* 81 (1967).

9 L. B. Pearce, M. H. Feingold, F. K. Cerny and J.-P. Anselme, *J. Org. Chem., 44,* 1881 (1979);
M. A. Englin and M. D. Vorob'ev, *J. Gen. Chem. USSR , 42 ,* 141 (1972) (*Zh Obshch. Khim , 42,* 146 (1972));
R. Maroca, O. T. Beachley, Jr. and A. W. Laubengayer, *Inorg. Chem , 6,* 575 (1967).

10 J. R. Driscoll, G. L. Hollech and D. E. Toland, *Proc. Power Source Symp , 27,* 28 (1976).

11 D. L. Chua, W. C. Merz and W. S. Bishop, *Proc Power Sources Symp , 27,* 33 (1976).

12 A. N. Dey and J. Miller, *J. Electrochem. Soc., 126,* 1445 (1979).

13 A. N. Dey, *U.S Patent,* 4,071,664.

14 A. P. Krapcho and A. A. Bothner-by, *J Am. Chem. Soc., 81,* 3658 (1959).

15 C. A. Young and R. R. Dewald, *J Am. Chem. Soc , 101,* 2884 (1979).