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On the Formation of Radicals during the Reaction of Sodium Tetrahydroborate with Alcohols

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In continuation of our studies on the application of the spin-trapping technique to photoreactions of inorganic and coordination compounds [1], we were interested in the reaction of sodium tetrahydroborate with alcohols. Although reactions of the tetrahydroborate ion with alcohols have been investigated by several workers [2], to date there has not been reported any evidence for the formation of free radicals in these reactions. Therefore, it was rather surprising for us to detect some radicals in the reaction between tetrahydroborate ion and alcohols. Thus, using nitrosodurene as a spin-trap, the ESR spectrum of methyl spin adducts *1* (a_N = 1.440 ± 0.015 mT; a_H = 1.289 ± 0.015 mT (3H) [3]) could be easily detected in the reaction of $NaBH_4$ with methanol at room temperature, whereas in higher alcohols (ethanol, propan-1-01, propan-2-01, butan-1-01, butan-2-01, 2-methylpropan-1-01) a rather complex spectrum was obtained (Fig. 1). No nitroxides were formed under the action of $NaBH_4$ (as a complex with 18-crown-6) on nitrosodurene in benzene solution in the absence of any alcohol.

The spectrum represented in Fig. 1 can be explained by assuming an interaction of the unpaired electron with the nuclear spins of one ^{14}N (I = 1), one ^{11}B (I = 3/2) and two ^{1}H (I = 1/2), respectively. The g value (g_0 = 2.0058 ± 0.0005) is typical for nitroxide radicals. Therefore, the radical observed has been attributed to the $^{\bullet}BH_2$ spin adduct to nitrosodurene *2*.

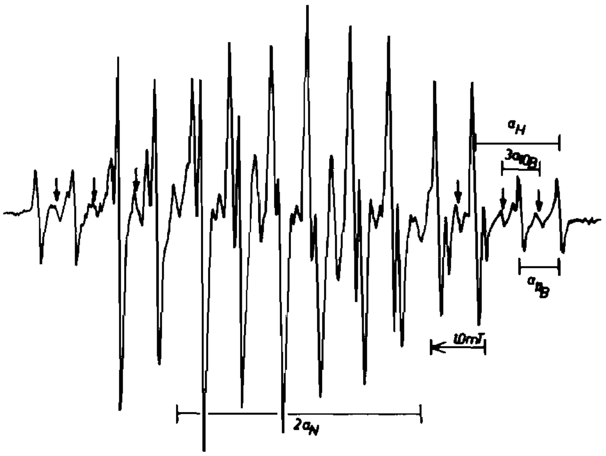
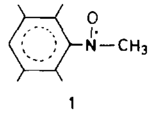
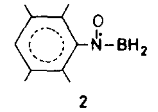


Fig. 1. ESR spectrum of boryl duryl nitroxide *2* in ethanol recorded at room temperature (some of the lines corresponding to the ^{10}B isotope are indicated by arrows).


1


2

As far as we are aware, this is the first boron containing nitroxide reported until now. The following coupling constants could be extracted from the ESR spectrum: a_N = 2.267 ± 0.015 mT, $a_{^{11}B}$ = 0.708 ± 0.005 mT, a_H = 1.563 ± 0.010 mT (2H). Furthermore, the spectrum given in Fig. 1 exhibits some additional lines corresponding to the ^{10}B containing nitroxide. The complete spectrum agrees well with the calculated one obtained by consideration of different magnetogyric ratio ($\gamma(^{10}B) \cong 1/3\ \gamma(^{11}B)$; $a_{^{10}B}$ = 0.235 ± 0.005 mT), nuclear spin ($I(^{10}B) = 3$), and the abundance of the ^{10}B isotope (18%), respectively. Unfortunately, oxygen centered radicals do not give stable spin adducts with nitrosodurene and, therefore, cannot be proved.

Attempts to detect any oxygen centered radicals using phenyl N-tert-butyl nitrone (*PBN*), which is known to be a good spin trap for those radicals [4], were unsuccessful since *PBN* gives rise to thermal reactions with $NaBH_4$. However, considering the results outlined in the literature [5] the following reaction pathways seem to be very likely:

$$BH_4^- + 2ROH \longrightarrow ROBH_2 + 2H_2 + RO^- \qquad (1)$$

$$ROBH_2 \xrightarrow[\Delta]{h\nu} \begin{cases} ^{\bullet}OBH_2 + {^{\bullet}R}\ (R = CH_3) & (2a) \\ ^{\bullet}BH_2 + {^{\bullet}OR}\ (R > CH_3) & (2b) \end{cases}$$

$$ROBH_2 + 2ROH \longrightarrow B(OR)_3 + 2H_2 \qquad (2c)$$

No evidence was found for the formation of nitrosodurene anion radicals which are known to be stable enough for ESR detection under our reaction conditions [1]. In addition, the reaction of $LiAlH_4$ with alcohols did not give any radicals to be trapped by nitrosodurene. Therefore, any reactions in which radicals are formed by synproportionation steps of ionic intermediates seem to be irrelevant in explaining the formation of radicals observed. The suggestion that homolytic bond fission occurs is further supported by the fact that irradiation of the samples causes higher yields of methyl and boryl nitroxides, respectively. However, it should be noted that the radical reactions (2a, 2b) discussed here amount to only less than one percent compared with reaction (2c) and, probably, in the absence of any scavenger completely vanish, as follows from our mass spectroscopic investigations.

References

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