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Boronitroxides.
II. On the Reaction of Sodium Borohydride with Nitroso Compounds in Alcohols

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Since the discovery of sodium borohydride [1], little attention has been devoted to the study of paramagnetic intermediates which in some instances are formed in the reactions of this reducing agent [2].

In continuation of our studies on electron-transfer reductions [3], we recently described [4] ESR spectral data of boronitroxides $RN(O^{\bullet})\overline{BH_3}M^{+}$ 1, formed in the reaction of Na or K borohydride with various nitroso compounds. The formation of 1 occurs in aprotic solvents as well as in benzene in the presence of dicyclohexyl-18-crown-6.

While our manuscript [4] had been submitted, a paper appeared in this journal [5] on the formation of radicals during the reaction of sodium borohydride with alcohols and their characterization using the spin-trapping technique. Since most of the results reported in this paper are in disagreement with ours, we believe that some points of the work need further comments.

When methanol is reacted with $NaBH_4$ in the presence of nitrosodurene, a weak ESR spectrum of the methyl radical spin adduct to the scavenger is observed (a_H = 12.7 G (3H), a_N = 13.7 G) in agreement with the Rehorek's claim.

When ethanol or isopropanol is used in the same reaction a complex spectrum (total width L = 96.5 G) is observed which closely resembles the spectrum shown in the Rehorek's paper. The computer simulation (Fig. 1B) of this spectrum shows that the following set of hyperfine splitting constants (hfscs): a_N = 15.34, G, a_H = 15.10 G (3H), a_{11B} = 6.90 G and a_{10B} = 2.30 G, gives a very good fit between the experimental and calculated curves. The spectrum calculated with the following hfscs: a_N = 22.80 G, a_H = 15.10 G (2H), and the same boron hfscs which corresponds to the Rehorek's assignment reproduces the general pattern of the experimental curve but the intensity ratio of the lines does not fit with the experimental one.

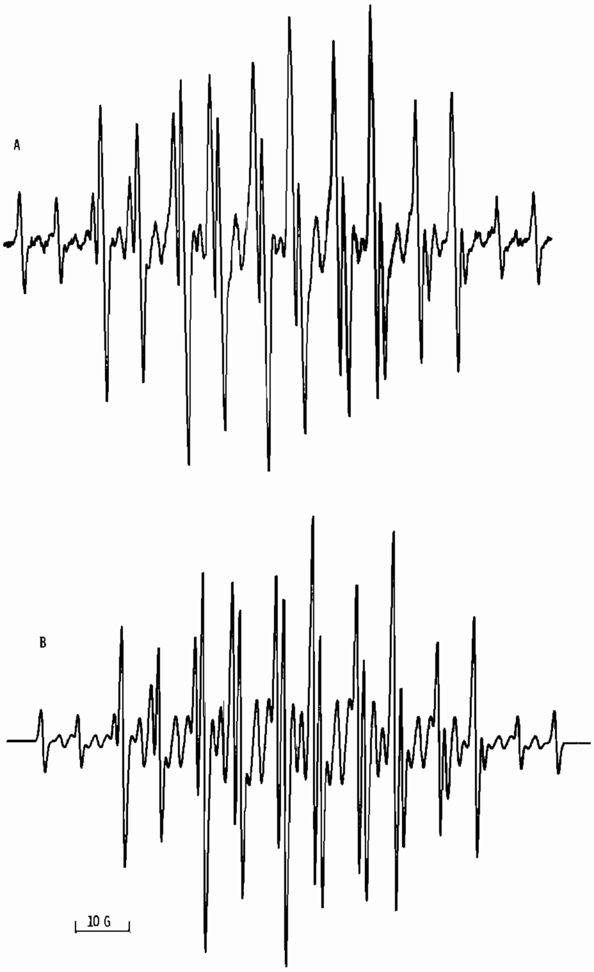


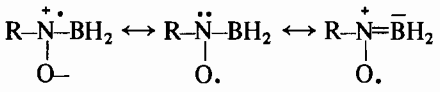
Fig. 1. (A) ESR experimental spectrum obtained from a mixture of nitrosodurene and $NaBH_4$ in ethanol at 25 °C. (B) Derivative curve computer simulated by the use of the hyperfine splitting constants: a_N = 15.345 G, a_H = 15.104 G (3H), a_{11B} = 6.900 G and a_{10B} = 2.300 G; line-shape Lorentzian; line-width of ^{11}B and ^{10}B spectra 0.860 G and 0.980 G; weight of ^{11}B and ^{10}B spectra 80.42% and 19.58%.

If $NaBD_4$ is reacted with ethanol in the presence of nitrosodurene, we observed a complex spectrum, the total width of which (L = 64.25 G) is that expected for the substitution of three equivalent protons by three equivalent deuterons.

When $NaBH_4$ is reacted with nitrosodurene in DMF the same kind of spectrum (a_N = 13.4 G, a_H = 12.6 G (3H), a_{11B} = 5.9 G and a_{10B} = 1.97 G) is observed and has been unambiguously assigned [4] to the following structure $DurN(O^{\bullet})\overline{BH_3}Na^{+}$ (Dur = duryl).

The above discussion clearly demonstrates that the spectrum observed in ethanol must be assigned to the boronitroxide $DurN(O^\bullet)BH_3^-Na^+$ 1 and not to $DurN(O^\bullet)BH_2$ 2 as proposed by Rehorek *et al.*

The increase of hfscs a_N and $a_H(BH_3)$, when the boronitroxide 1 is observed in ethanol is a well-known effect of hydrogen-bonding on the hfscs of nitroxides [6]. On the other hand in the case of structure 2, the contribution of the canonical form (C) would be expected to decrease the a_N value relative to that of a dialkylnitroxide (a_N = 15 G).



$$R{-}\overset{+\,\bullet}{\underset{\underset{O^-}{|}}{N}}{-}BH_2 \longleftrightarrow R{-}\overset{\bullet\bullet}{\underset{\underset{O^\bullet}{|}}{N}}{-}BH_2 \longleftrightarrow R{-}\overset{+}{\underset{\underset{O^\bullet}{|}}{N}}{=}\overset{-}{B}H_2$$

(A) (B) (C)

The formation of boronitroxides in the reaction of sodium borohydride with nitroso compounds in alcohol is not general and for instance the corresponding hydronitroxides are observed with 2-methyl-2-nitrosopropane or 2,4,6-tri-tert-butyl-3,5-dideuterionitrosobenzene.

Finally we would like to point out that using a freshly prepared 18-crown-6- benzene solution, $NaBH_4$ reacts instantaneously with nitrosodurene to form the boronitroxide 1. However the 18-crown-6 benzene solution loses in value with age and this might explain the lack of ESR signals reported by Rehorek *et al.* in the same experiments.

Our results lead to the conclusion that the reaction pathway proposed by Rehorek *et al.* to explain the paramagnetic species formed from the reaction of $NaBH_4$ with ethanol in the presence of nitrosodurene is not the major pathway.

The formation of boronitroxides 1 could be tentatively explained by two different reactions (eqns. 1 and 2), the paramagnetic species resulting from electron-transfer reactions:

$$RNO^{-\bullet}M^+ + BH_3 \rightarrow RN(O^\bullet)BH_3^-M^+ \qquad (1)$$

$$RNO + BH_3^{-\bullet} \rightarrow RN(O^\bullet)BH_3^-M^+ \qquad (2)$$

If some results [4] agree with the borane radical anion $BH_3^{-\bullet}$ as an intermediate and its subsequent trapping on nitroso compound, further work is in progress to give details on the mechanism of formation and chemical reactivity of these new nitroxides.

Acknowledgments

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