OFFICE OF NAVAL RESEARCH

Contract Nonr 3364(00)

Task No. NR 055-427

TECHNICAL REPORT NO. 16

A Proton Magnetic Resonance Study of Boron Trihalide Complexes with Diethyl Ether

by

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Prepared for Publication

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December, 1967

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A room-temperature proton magnetic resonance ^1H n.m.r. spectrum of a solution of a boron trihalide in an organic base consists of one set of signals, displaced to lower field from their positions in the pure solvent spectrum.[1] The one set of signals results from a rapid exchange which averages the resonance peaks arising from bulk and complexed solvent molecules. In addition to complex formation, the positions of the signals in such a system are influenced by factors such as temperature and the extent of solvent-solvent interactions.

Our low-temperature ^1H n.m.r. studies of solutions of boron trihalides in diethyl ether (Et_2O) have revealed separate resonance signals for bulk and complexed ether molecules. A spectrum of a 1 : 5 molar ratio of BCl_3 to Et_2O, recorded at -45° in a Varian A60 Spectrometer, along with a recording of the electronic integration of all peaks, is shown in the Figure; the peaks corresponding to bulk (B) and complexed (C) Et_2O are identified. At this temperature, similar spectra are observed for solutions of BF_3 and BBr_3 in Et_2O. The integrations are rapid and result in co-ordination numbers of one, within 10%, for BF_3 and BCl_3 ether complexes. This rules out the existence of the dietherates in these systems. Some evidence for slight decomposition in the BBr_3 solution was apparent, but the chemical shifts of the bulk and complexed ether signals were easily discernible and accurately measured. An accurate co-ordination number measurement was not possible in this solution.

The separations between the bulk and complexed methylene proton signals are 54, 82, and 89 c./sec., respectively, for BF_3, BCl_3, and BBr_3 solutions. The methyl signal separations for the corresponding complexes are 15, 27, and 30 c./sec. The observed trend, BBr_3 BCl_3 BF_3, is opposite to what one would predict on the basis of electronegativities of the halogen atoms. Also, for these tetrahedral boron complexes, any

correlation between the observed chemical shift differences and Lewis acidities[2] of the reagent boron halides is to be regarded presently as merely coincidental. Another approach is to assess how the separations observed between bulk and complexed solvent molecules reflect all possible electronic changes in the solvent molecule. These changes could include the charge withdrawal and decreased shielding resulting from complex formation along with changes in any paramagnetic effect which may be operative at the oxygen atom. In addition, the possibility of a similar anisotropic effect in the B–X bond should be considered.

To permit more definitive statements regarding the cause of the observed chemical shifts, investigations of boron trihalide complexes with a wide variety of organic bases are under way, using low-temperature n.m.r. techniques. Temperature studies are also in progress to obtain kinetic data for the ligand-exchange processes occurring in these systems.

This work was supported in part by a grant from the National Institutes of Health (A.F.) and a grant from the Office of Naval Research (T.P.O.). The technical assistance of A. Morriss and O. R. Vanderstay is also acknowledged.

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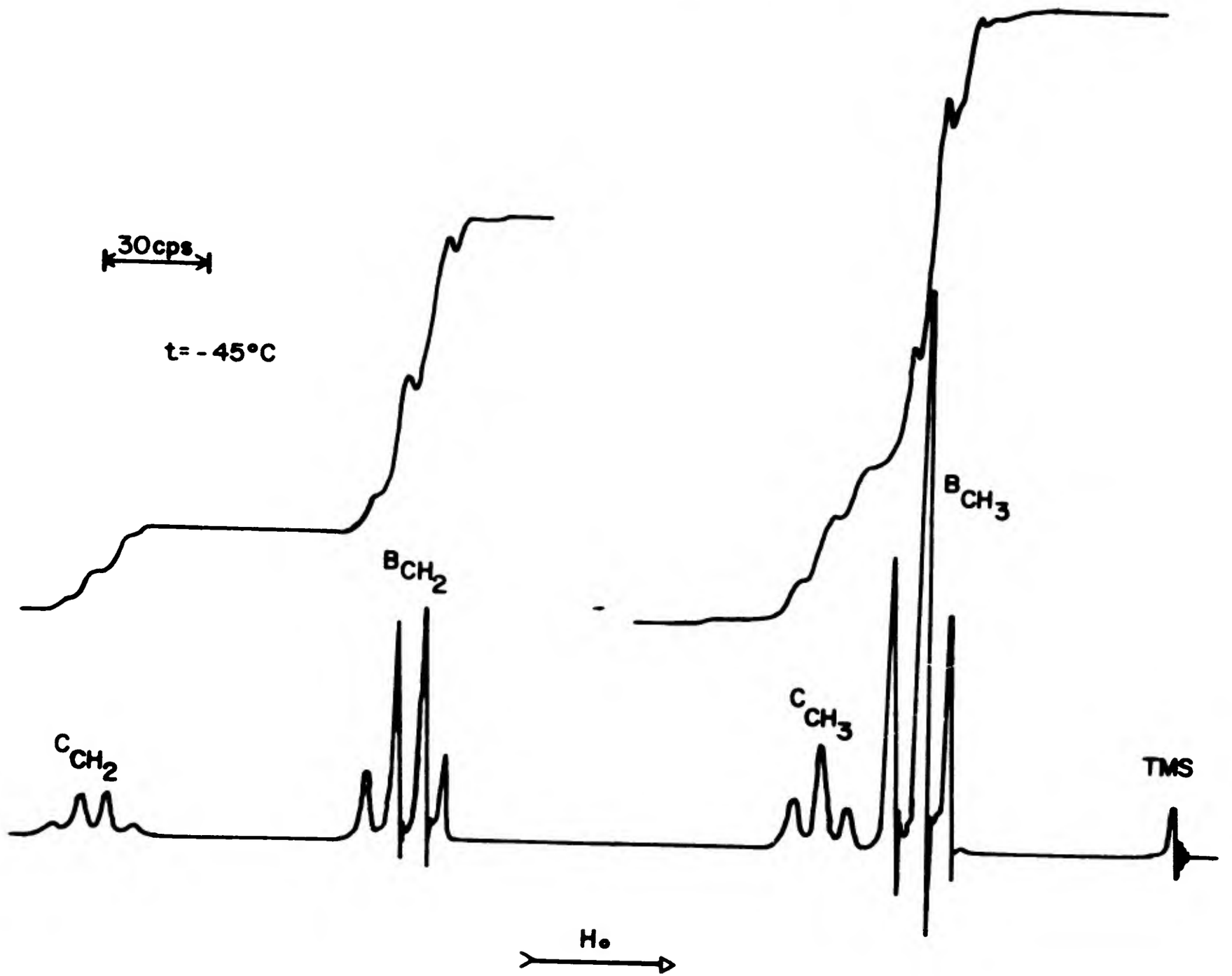
[1]T. D. Coyle and F. G. A. Stone, J. Amer. Chem. Soc., 1961, 83, 4138; J. M. Miller and M. Onyszchuk, Canad. J. Chem., 1964, 42, 1518; S. T. Kuhn and J. S. McIntyre, ibid., 1965, 43, 375; E. Gore and S. S. Danyluk, J. Phys. Chem., 1965, 69, 89; M. Okada, K. Suyama, and Y. Yamashita, Tetrahedron Letters, 1965, 2329; P. N. Gates, E. J. McLauchlan, and E. F. Mooney, Spectrochim. Acta, 1965, 21, 1445; A. G. Massey and A. J. Park, J. Organometallic Chem., 1966, 5, 218.

[2]L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 3rd edn. 1960, p. 317; H. C. Brown and R. R. Holmes, J. Amer. Chem. Soc., 1956, 78, 2173.

Figure Caption

Figure 1. The proton magnetic resonance spectrum of a 1:5 mole ratio solution of BCl_3 to diethyl ether, recorded at -45°C on a Varian A60 Spectrometer. The peaks are identified as bulk (B) or complexed (C) ether signals.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Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY (Corporate author)	2a REPORT SECURITY CLASSIFICATION
Los Angeles State College Foundation	Unclassified
	2b GROUP not applicable

3 REPORT TITLE

A PROTON MAGNETIC RESONANCE STUDY OF BORON TRIHALIDE COMPLEXES WITH DIETHYL ETHER

4 DESCRIPTIVE NOTES (Type of report and inclusive dates)

Interim

5 AUTHOR(S) (Last name, first name, initial)

L. Schuster, A. Fratiello and T. Onak

6 REPORT DATE	7a TOTAL NO. OF PAGES	7b. NO. OF REFS
December, 1967	4	9

8a CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
Nonr 3354(00)	Technical Report No. 16
b. PROJECT NO. NR 055-427	
c	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) None
d	

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11 SUPPLEMENTARY NOTES	12 SPONSORING MILITARY ACTIVITY
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13 ABSTRACT

At low temperatures, separate proton resonance signals are observed for bulk ether and ether molecules complexed with the boron halide. The methyl signal separations for the BF_3, BCl_3 and BBr_3 complexes show a trend which is opposite to what one would predict on the basis of electronegativities of the halogen atoms.

DD FORM 1 JAN 64 1473 0101-807-6800

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Nuclear magnetic resonance						
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