



Nitryl Fluoride: A New Method of Preparation, Nuclear Magnetic Spectrum and Structure

Richard A. Ogg Jr. and James D. Ray

Citation: The Journal of Chemical Physics **25**, 797 (1956); doi: 10.1063/1.1743081 View online: http://dx.doi.org/10.1063/1.1743081 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/25/4?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in

New method for calculation of nuclear cluster structure of nuclei AIP Conf. Proc. **768**, 395 (2005); 10.1063/1.1932977

Rotational spectrum, structure, and chlorine nuclear quadrupole tensor of the vinyl fluoride–HCl dimer J. Chem. Phys. **93**, 3054 (1990); 10.1063/1.458839

Microwave Spectrum and Structure of Perrhenyl Fluoride J. Chem. Phys. **31**, 633 (1959); 10.1063/1.1730439

Microwave Spectrum and Structure of Sulfuryl Fluoride J. Chem. Phys. **26**, 734 (1957); 10.1063/1.1743394

Vibrational Spectrum and Structure of Nitryl Chloride J. Chem. Phys. **22**, 2000 (1954); 10.1063/1.1739981



These intensities are inversely proportional to the absolute temperature, that is, the numbers of unpaired spins remain constant. Very likely therefore, these absorptions are due to free radicals and not to triplet state.1

A more detailed description of this work will be published elsewhere.

We wish to present our sincere thanks to Professor K. Higasi for his kind interest and to Professor Y. Nagai and his collaborators, University of Tokyo for the gift of perylene which was specially prepared for the present experiment.

¹ Hirshon, Gardner, and Fraenkel, J. Am. Chem. Soc. **75**, 4115 (1953), ² J. E. Wertz and J. L. Vivo, J. Chem. Phys. **23**, 2193 (1955). * We refer "the free radicals" only to the ground state of $S = \frac{1}{2}$.

Spectroscopic Observations on Pentaborane-Air Flames and Explosions*

W. G. BERL, E. L. GAYHART, AND H. L. OLSEN, Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland AND

H. P. BROIDA AND K. E. SHULER, National Bureau of Standards, Washington 25, D. C. (Received July 19, 1956)

NO spectroscopic studies have been reported previously for the combustion of boron hydrides. These compounds are of particular interest owing to their unusually high flame speeds in their reactions with oxygen. This letter describes some recent work on pentaborane (B_5H_9) diffusion flames in air and on premixed pentaborane-air explosions at atmospheric pressure.

Gaseous pentaborane¹ was diluted with nitrogen in a storage tank. The resulting mixture was burned as a diffusion flame above a porous metal disk in air. For high nitrogen dilution the blue reaction zone was surrounded by a white mantle. Thermocouple traverses showed that the maximum temperature of these diffusion flames is about 500°K.

Oxygen was added to the nitrogen-diluted B5H9 in a flow system to prepare pentaborane-air mixtures. These mixtures were ignited by an electric spark giving rise to a rapidly expanding flame kernel. The duration of such explosions is of the order of a millisecond.

Spectra were taken with a F/4 Hilger spectrograph giving a resolution of about 4 A at 5200 A (glass) and 0.8 A at 2600 A (quartz). Eastman 103a-O, 1N, and 1F plates were used, permitting a survey of the spectral region from 2200 to 8500 A.

Figure 1(a) shows the spectrum obtained from the inner cone of a diffusion flame in air of pentaborane diluted with nitrogen in the ratio of 1 to 69.5. The main spectral feature observed were the α bands of BO between 3370 and 6200 A due to the transition from the $A^2\pi_i$ state to the $X^2\Sigma^+$ ground state. In addition, a weak system of diffuse bands was observed in the same region and found to be identical with the so-called "boric acid fluctuation band."2 No emission was observed at wavelengths shorter than 3350 A or longer than 6400 A. These spectra were obtained under conditions in which the white mantle covered the entire inner cone. In the absence of this mantle the exposure time had to be increased by a factor of six to obtain spectra of comparable intensity.

Figure 1(b) shows the spectrum obtained from 12 consecutive explosions of a lean pentaborane-air mixture (equivalence ratio =0.78). The only spectral feature observed were the diffuse "boric acid fluctuation bands" in the spectral region from 3850 to 6350 A. In agreement with Singh² we find that some of the bands have heads and are degraded to longer wavelengths. In addition, there is a band with a head near 4080 A which is degraded to the violet. The α bands of BO observed in the diffusion flame were not found in the explosion spectra.

Singh³ expressed the opinion that the diffuse bands in the region from 3850 to 6350 A are due to a transition of BO with the upper state about 64 000 cm⁻¹ above the $X^2\Sigma^+$ ground state. There is now, however, quite conclusive evidence that the emitter of the "boric acid fluctuation bands" is B₂O₃ and not BO.⁴ This was



FIG. 1. (a) Spectrum of a pentaborane-nitrogen diffusion flame $(B_8H_9/N_2 = 1/69.5)$. Eastman 1F Plate, 18 minute exposure, F/4 glass spectrograph. The Hg comparison spectrum is at the center. (b) Spectrum of pentaborane, air explosions. Equivalence ratio =0.78, Eastman 1F Plate, 12 explosions. F/4 glass spectrograph.

established by a photometric study of the vapor over liquid B2O3 which showed that the spectral intensity of these bands varied with temperature in the same manner as the equilibrium vapor pressure of B₂O₃. It is interesting to note that a penta-atomic species such as B₂O₃ is stable at the high temperature reached in the pentaborane-air explosions ($\sim 2500^{\circ}$ K).

No bands of BH, BN, or OH were observed in either the diffusion flame or the explosions. Furthermore, no BO bands were observed in the explosions and only the α system of BO was found in the diffusion flames. It is possible that the observed emission from the high-temperature explosions is thermal. However, the appearance of BO $-\alpha$ bands and B₂O₃ bands in the low-temperature (~500°K) diffusion flame strongly indicates a chemiluminescent origin of the radiation in this flame.

* This work was supported by the Bureau of Ordnance, Department of the Navy under Contract NOrd-7386 and by the U.S. Air Force through the Office of Scientific Research of the Air Research and Development Command,

Command.
¹ The pentaborane was obtained through the courtesy of the Olin Mathieson Company.
² N. L. Singh, Proc. Indian Acad. Sci. 29A, 424 (1949).
³ N. L. Singh, J. Sci. Research Banaras Hindu Univ. 2, 147 (1951).
⁴ Soulen, Sthapitanonda, and Margrave, J. Phys. Chem. 59, 132 (1955).

Nitryl Fluoride: A New Method of Preparation, Nuclear Magnetic Spectrum and Structure

RICHARD A. OGG, JR., AND JAMES D. RAY Department of Chemistry, Stanford University, Stanford, California (Received August 8, 1956)

HE nitryl halides present an important example of the type of error incumbent in choice of molecular structure based on classical methods of chemical reactivity. Thus in the case of nitryl chloride, Schmeisser's1 data lead to the conclusion that the chlorine atom is attached to oxygen. Yet, the conclusion of Ryason and Wilson² based on the infrared spectrum of nitryl chloride as confirmed by the microwave spectrum observed by Smith and Magnuson,³ and the completely parallel infrared spectrum of nitryl fluoride of Dodd, Rolfe, and Woodward⁴ is that the halogen atoms are attached to nitrogen.

This paper gives nuclear magnetic resonance data which corroborates existing spectral data in a completely unambiguous fashion.

Nitryl fluoride was prepared by a new method not dependent on the use of elemental fluorine. Equation (1) represents the stoichiometry of the new reaction.

$$NaF + N_2O_5 = NaNO_3 + FNO_2.$$
(1)

The reaction was carried out in the apparatus of Fig. 1, which was attached to a vacuum system equipped with a glass Bourdon gauge. All joints and stopcocks were lubricated with Halocarbon grease.

Nitrogen pentoxide was prepared by the reaction of dry ozone with dry nitrogen dioxide.

Sodium fluoride was placed in the bottom of tube B and a small amount at D. While the system was open to a high vacuum pump,

the sodium fluoride was heated with a yellow flame to remove all water. Nitrogen pentoxide was condensed on the sodium fluoride in tube B in molar amount corresponding to the gas volume of the system. Stopcock A was closed and a water bath at 35° used to warm the nitrogen pentoxide. Warming and condensation by liquid nitrogen with intermediate evacuating of the oxygen byproduct of the simultaneous spontaneous decomposition of the nitrogen pentoxide was repeated several times. Trap B was allowed



FIG. 1. Apparatus for preparation of nitryl fluoride.

to warm to about -110° while a liquid nitrogen bath was used to condense the nitryl fluoride product in tip E. The constriction at the top of sample bulb C was sealed off so that the sample could be moved to the nuclear magnetic resonance spectrometer.

A further small quantity of nitryl fluoride was transferred to an evacuated Pyrex infrared cell equipped with silver chloride windows. The gas displayed a spectrum identical with that of a sample of nitryl fluoride which had been prepared by the reaction of elemental fluorine with nitrogen dioxide at a previous time.

The nitryl fluoride sample was condensed in tip E of the sample tube of Fig. 1 by means of liquid nitrogen. The tip was inserted in



the probe of the nuclear magnetic resonance spectrometer. On warming to just above the melting point of the nitryl fluoride, the F¹⁹ spectrum shown in Fig. 2 was obtained. The instrument employed was the 30-megacycle high-resolution nuclear magnetic resonance spectrometer at the research and development laboratories of Varian Associates. The 225-cycle separation between outside peaks is of such large magnitude as to preclude any possibility that this splitting caused by the N¹⁴ nucleus could be transferred through an intermediate oxygen atom. The splitting is similar to that observed with nitrogen trifluoride.

The authors wish to express their appreciation to Dr. James Shoolery of Varian Associates for his assistance in the magnetic resonance study, and to Professor Anton B. Burg who supplied the sample of nitrogen trifluoride.

Infrared Flow Dichroism*

GEORGE R. BIRD, † Children's Cancer Research Foundation, Children's Medical Center, Boston 15, Massachusetts AND

ELKAN R. BLOUT, Chemical Research Laboratory, Polaroid Corporation, Cambridge 39, Massachusetts (Received August 15, 1956)

BSERVATION of the visible birefringence of flowing polymer solutions has become an accepted method for securing information on the shape and molecular weight of macromolecules.1 Such compounds have also been studied as oriented solid films by infrared spectroscopy, using polarized radiation.^{2,3} It is difficult to prepare such films with uniform



FIG. 1. Flow dichroism in the infrared spectrum of poly- γ -benzyl-L-glutamate.

	107 000
Weight average molecular weight:	195 000
Concentration:	10.0 g/100 ml of solution
Solvent:	U.S.P. chloroform plus 0.5% forma-
	mide by volume
Cell thickness:	0.00382 cm
Upper solid line:	Solvent
Lower solid line:	Solution at rest
Dotted line:	Flowing solution with maximum gra-
	dient of 4630 sec ⁻¹ . Direction of flow
	is parallel to the radiation electric

The band at 1655 cm⁻¹ shows strong parallel dichroism, while the band at 1550 cm⁻¹ shows strong perpendicular dichroism. The band at 1730 cm⁻¹ has weak but significant parallel dichroism.

thickness and orientation, but the film technique has yielded valuable information on the orientation of certain chemical groups within macromolecules in the solid state. However, it is desirable to examine the optical absorption of macromolecules oriented in

¹ M. Schmeisser and E. Gregor-Haschke, Z. anorg. u. allgem. Chem. 225,

 ¹ M. Schneisser and D. Gregor Haddina, D. Muor, et al. (1947).
 ² R. Ryason and M. Kent Wilson, J. Chem. Phys. 22, 2000 (1954).
 ³ D. F. Smith and D. W. Magnuson, Phys. Rev. 87, 226 (1952).
 ⁴ Dodd, Rolfe, and Woodward, Trans. Faraday Soc. 52, 145 (1956).