Because of this systematic weakness, it is very difficult to decide what, if any, are the systematic absences of the true cell. Indices of the type $hh2\bar{h}l$ appear to be absent for l odd and this, if it is a true absence, fixes the space group as $P6_3mc$, $P\bar{6}2c$, or $P6_3mmc$.

Because of the method of preparation of the sample, the quantity available was too small to attempt a density determination by a bulk method, and sufficiently dense liquids were not available to attempt a sink-or-float determination. Ford, *et al.*,[6] give $d = 4.70$; using this value $Z = 17.8$ (or 18) for the true unit cell. $Z = 18$ is compatible with any of the possible space groups.

The lines in the α-$CaCr_2O_4$ powder pattern index equally well on the tetragonal cell proposed by Ford, *et al.*,[6] or on the true hexagonal cell. Unit cells deduced from powder data alone are not reliable except in very simple cases.

The value of the a axis of the pseudo-cell ($\sim$2.9 Å.) suggests that the structure contains sheets of approximately close-packed oxygen atoms perpendicular to c. The pseudo-cell then would contain one oxygen of each layer, and the true cell sixteen, affording a plausible explanation of the systematic weakness. From the length of the c-axis, it also is apparent that the layers are not entirely close packed in the c-direction. The number of atoms in the true cell is too great for any attempt to be made at guessing a structure. It seems likely, however, that α-$CaCr_2O_4$ represents a new hexagonal structure type unrelated either to the stuffed-silica-like $BaAl_2O_4$ or to the spinel structure.

CONTRIBUTION NO. 47 FROM THE EXPLORATORY RESEARCH
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Vapor Phase Pyrolysis of the Lower Alkyl Orthoborates

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Received July 28, 1961

The thermal decomposition of the higher alkyl orthoborates has received some attention. Thus, tri-n-hexyl, n-octyl, n-decyl,[1] n-dodecyl,[2] and 1-menthyl[3] orthoborates have been shown to give the corresponding olefins in good yield. By contrast, virtually no information is available on the pyrolysis of the lower esters. Makishima, Yoneda, and Tajima[4] found trimethyl orthoborate vapor stable up to 470°, the highest temperature attainable with their Pyrex glass apparatus. Washburn, *et al.*,[5] observed very slight decomposition on refluxing tri-n-butyl orthoborate for one hour at atmospheric pressure (b.p. 230.0–231.0°[6]), but did not analyze the products.

We have made a preliminary study of the vapor phase pyrolysis of the methyl, ethyl, n-propyl, isopropyl, and n-butyl esters, with emphasis on the temperature of decomposition and the identity of the products. The results are summarized in Tables I and II, in which are listed the temperature range of each experiment and the composition of the volatile products at various times during the decompositions. Some trace components are not included. The lower temperature quoted for each ester is the temperature at which decomposition first became measurable. The pyrolyses of methyl and ethyl borates were carried almost to completion and the solid residues found to consist of hydrated diboron trioxide plus, in the case of methyl borate, a material which might be an organic polymer.

Of the esters studied, only isopropyl borate decomposed cleanly, giving substantially pure propylene at the beginning of the pyrolysis.

Experimental

General Procedure.—The esters, supplied by the U.S. Borax and Chemical Corp., Pacific Coast Borax Company

TABLE I

PRODUCT COMPOSITION IN MOLE %

R in $B(OR)_3$	CH_3			C_2H_5		
Decompn. temp., °C.	530–555			415–460		
Reaction time, hr.	1	4.5	10.5	2	10	11
H_2	48.4	58.5	80	16.9	20.3	18.9
CO	28.0	29.8	16	2.8	21.4	22.0
CH_4	23.6	11.7	4	4.4	25.4	25.7
C_2H_4				73.8	23.9	19.4
C_2H_6				2.1	9.0	12.5

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(1) D. M. Young and C. D. Anderson, *J. Org. Chem.*, **26**, 2158 (1961).

(2) T. Asahara and K. Kanabu, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **55**, 589 (1952).

(3) G. L. O'Connor and H. R. Nace, *J. Am. Chem. Soc.*, **77**, 1578 (1955).

(4) S. Makishima, Y. Yoneda, and T. Tajima, *J. Phys. Chem.*, **61**, 1618 (1957).

(5) R. M. Washburn, E. Levens, C. F. Albright, and F. A. Billig, "Metal-Organic Compounds," Advances in Chemistry Series No. 23, American Chemical Society, Washington, D. C., 1959, p. 144.

(6) A. Scattergood, W. H. Miller, and J. Gammon, Jr., *J. Am. Chem. Soc.*, **67**, 2150 (1945).

TABLE II

PRODUCT COMPOSITION IN MOLE %

R in $B(OR)_3$	n-C_3H_7			i-C_3H_7			n-C_4H_9		
Decompn. temp., °C.	350–450			350–400			385–420		
Reaction time, hr.	4	8	11	6	13	15	1.42	2.70	10.90
H_2	*a*	2.6	1.8	2.0	9.3	18.3	4.4	3.6	3.8
CO	*a*	12.4	16.2	...	1.1	0.4	...	...	...
CO_2	*a*	...	...	...	...	...	2.2	2.0	1.1
CH_4	9.8[a]	29.0	32.7	1.3	3.6	4.2	2.8	7.1	10.8
C_2H_2	0.4[a]	...	1.3	...	...	...	4.7	1.8	1.6
C_2H_4	9.8[a]	7.1	2.6	...	0.7	0.4	...	1.9	6.4
C_2H_6	3.6[a]	3.6	5.2	...	0.3	...	11.3	11.2	12.7
C_3H_6	69.2[a]	43.4	33.4	95.8	78.7	66.3	6.5	7.7	12.6
C_3H_8	0.8[a]	0.9	3.9	0.6	...	...	6.3	4.1	6.4
1-C_4H_8	6.1[a]	[b]	1.5	...	...	...	47.1	51.7	31.3
2-C_4H_8				...	...	...	10.0	5.5	10.5
C_4H_{10}	0.1[a]	0.7[c]	0.9	...	...	...	3.4	2.1	0.3
$(CH_3)_2CO$	...	...	...	0.1	2.4	5.7	...	...	...
Mass 44[d]	...	...	...	...	2.3	3.3	...	...	...

[a] Fraction volatile at −78° but not at −195°. [b] These components would not have been detected with the column used. [c] Identified as isobutane. [d] Probably acetaldehyde.

Division, were fractionally distilled over sodium to remove the parent alcohol. Final purification was effected by treatment, in the vacuum system, with vacuum distilled sodium or with liquid sodium–potassium alloy. Several bulb-to-bulb distillations served to remove dissolved gases. The butyl ester was too involatile to be distilled from bulb to bulb. Accordingly, a 30-ml. sample, freshly distilled over sodium, was injected into the flask of the pyrolysis apparatus with a hypodermic syringe through a serum cap attached to a glass side arm, which then was sealed off under vacuum, and any dissolved gases were removed by prolonged pumping.

The pyrolysis apparatus is shown diagrammatically in Fig. 1. The purified ester (25 ml.) was heated in a 50-ml. round bottom flask. The vapor was passed through a 2.5-cm. diameter Vycor tube heated by a 30.5-cm. tube furnace. The pyrolyzate was led through a water-cooled Liebig condenser and a dewar-type condenser cooled with Freon 12 (methyl, ethyl) or crushed ice (propyl, butyl). Condensate was returned to the round bottom flask *via* a separate 5-mm. o.d. tube fitted with a U-trap to prevent vapor from by-passing the pyrolysis tube. The dewar-type condenser facilitated the distillation of the ester into the pyrolysis apparatus at the start of each experiment and also permitted rough fractionation of the products. The mercury pot manometer indicated the extent of reaction and served as a safety device. The temperature was measured by an iron–constantan thermocouple, the junction of which was strapped firmly to the outside of the Vycor tube with asbestos cord.

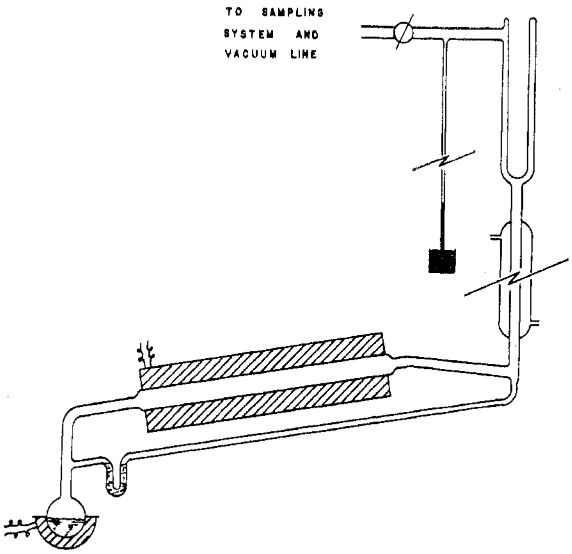

Fig. 1.—Pyrolysis apparatus.

Gas samples were collected as soon as enough gas had been generated and at various times during the reaction. Collection was effected by cooling the flask and the dewar trap with liquid air, Dry Ice–acetone, or crushed ice, in order to free the gas samples from ester and to effect a rough fractionation. The gas samples were analyzed by a mass spectrometer and, in a few cases, by gas chromatography.

No carbon deposits were observed in the pyrolysis tube except after 16 hr. pyrolysis of the ethyl ester.

Analysis of Residues. (1) Trimethyl Orthoborate.—The liquid residues from two pyrolysis experiments were combined (total volume 25 ml.) and distilled under reduced pressure. Methyl borate (5–10 ml.) was removed at 50 mm. pressure. The pressure was reduced to 15 mm. and the pot temperature raised to 140°, but no other fractions were obtained. On reducing the pressure to 3 mm. and increasing the pot temperature to 250°, the residue, formerly glassy, expanded to fill the neck of the flask.

This expanded material was a light, fluffy solid, similar in color and texture to expanded mica. A melting point determination (sealed tube) revealed slow charring at 119° followed by gradual melting and further charring at higher temperatures. At 290° the entire sample became black. The material was slightly soluble in carbon tetrachloride, more so in water; evaporating the water extract to dryness yielded only boric acid. The solid gave on analysis C = 11.29, H = 4.22, B = 22.68%. These are average values, the agreement between duplicate analyses being poor. They correspond to the very approximate empirical formula $CH_{4.5}B_2O_4$, which might well represent a mixture of, substantially, metaboric acid (HBO_2) and polymethylene $(CH_2)_n$. The X-ray diffraction pattern indicated a mixture of orthoboric acid and an additional phase which could not be identified, but the orthoboric acid must have been formed by inadvertent exposure of the X-ray sample to moisture; orthoboric acid is unstable under the conditions used in the vacuum distillation and would have been dehydrated to metaboric acid.[7]

(2) **Triethyl Orthoborate.**—At the end of the pyrolysis, the flask and dewar trap were cooled to −78° and all gases volatile at that temperature removed by pumping. The flask and trap were warmed to room temperature and the apparatus pumped again, any material volatile at room temperature being caught in a U-trap cooled to −78°. This trap then was sealed off and removed. It contained a few ml. of a colorless liquid and some white solid, presumably diboron trioxide. Several sections of the pyrolysis system also were coated with this white solid. The liquid was examined by infrared spectroscopy and found to contain ethanol, acetal, and a small amount (∽10%) of ethyl borate. The pot residue consisted of a dark gummy solid, 99.4% of which was volatile in methanol and presumed to be metaboric acid.

Acknowledgments.—The authors are indebted to J. Starr for gas chromatography analyses and to E. O. Camehl, of the Dow Chemical Company Analytical Laboratories, Midland, Michigan, for mass spectrometer analyses.

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(7) "Gmelins Handbuch der Anorganischen Chemie," Supplement, **13**, 148 (1954).

CONTRIBUTION FROM ROHM AND HAAS COMPANY,
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The Infrared Spectrum of NF_2

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Received December 1, 1961

The dissociation of tetrafluorohydrazine (N_2F_4) to difluoramino radicals (NF_2) has been demonstrated recently.[1,2] The results of our investigation of the infrared spectrum of the difluoramino free radical are given below.

When equilibrium mixtures of N_2F_4 and NF_2 are heated in a conventional infrared cell to increase the proportion of NF_2, profound changes in the infrared spectrum are observed. The 1010 cm.$^{-1}$ band of N_2F_4 is found to decrease drastically while smaller decreases are found at 960 and 740 cm.$^{-1}$. A large increase is found between 940 and 910, with smaller increases at 990–970 and 735–730 cm.$^{-1}$. It is not possible to distinguish the bands, however, because of severe overlapping by N_2F_4 bands at 1010, 960, and 735 cm.$^{-1}$.

To increase the resolution of the NF_2 spectrum, a compensating technique was used to cancel the N_2F_4 spectrum. A short cell (2-cm.) was filled to a high pressure of N_2F_4 and placed in the reference beam of a Perkin–Elmer Model 21 with a rock salt prism. A long cell (1 or 10-m.) was placed in the sample beam and a much lower pressure (where the relative concentration of NF_2 is large) admitted to just cancel the N_2F_4 peaks. In Fig. 1b, the long cell pressure was about 0.2 mm. at 25°. The short cell pressure was adjusted until the characteristic N_2F_4 maximum at 960 cm.$^{-1}$ was indistinct in the difference spectrum. The 10-m. cell then was heated to 110°; from equilibrium data[2] the N_2F_4 was 70% dissociated, hence there were about 5 NF_2 molecules per N_2F_4 in the long cell. In some instances N_2 or He was admitted to the long cell to reduce pressure broadening effects, but little difference was noted.

Under the above conditions the observed spectrum should be that due to NF_2 alone. Strong bands were found at 920, 980, and 730 cm.$^{-1}$ with a weak, rather broad peak at 1100 cm.$^{-1}$. These peaks were observed to increase with increasing temperature and decrease again on cooling.

The observed spectrum is similar to that of OF_2,[3] which has its three infrared active fundamentals at 929 (ν_1), 826 (ν_3), and 461 (ν_2). The ν_2 "scissors" of NF_2 appears to be surprisingly high in frequency, particularly in view of the values[4,5] of 666 and 650 cm.$^{-1}$ for ν_2 of CF_2. Limitations in cell optics prevented study below 650 cm.$^{-1}$. In view of the lack of detail in the absorptions observed insufficient data were available to calculate meaningful force constants.

Our results are in partial agreement with those of Schoen, Lide, and Mann,[6,7] who observed two regions of absorption at 1075 and 940 cm.$^{-1}$ by

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(1) C. B. Colburn and F. A. Johnson, *J. Chem. Phys.*, **33**, 1869 (1960).

(2) F. A. Johnson and C. B. Colburn, *J. Am. Chem. Soc.*, **83**, 3043 (1961).

(3) H. T. Bernstein and J. Powling, *J. Chem. Phys.*, **18**, 685 (1950).

(4) P. Venkateswarlu, *Phys. Rev.*, **77**, 676 (1950).

(5) D. E. Mann and B. A. Thrush, *J. Chem. Phys.*, **33**, 1732 (1960).

(6) L. J. Schoen, D. R. Lide, Jr., and D. E. Mann, National Bureau of Standards Report No. 7129, April, 1961.

(7) M. D. Harmony, R. J. Myers, L. J. Schoen, D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, **35**, 1129 (1961).