CONTRIBUTION FROM THE DEPARTMENT OF INORGANIC CHEMISTRY,
UNIVERSITY OF MELBOURNE, VICTORIA, AUSTRALIA

Reactivity of Transition Metal Fluorides. III. Higher Fluorides of Vanadium, Niobium, and Tantalum

BY J. H. CANTERFORD AND T. A. O'DONNELL

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A series of oxidation–reduction and halogen-exchange reactions has been used to compare the chemical reactivities of the pentafluorides of vanadium, niobium, and tantalum. Vanadium pentafluoride is extremely reactive and its reaction pattern with many reagents is extremely complex, depending largely on relative proportions of reagents and other experimental conditions. The pentafluorides of niobium and tantalum are very much less reactive than that of vanadium and are similar to each other. There is some evidence that of the two, the niobium compound is slightly more reactive. The reactivities of these three pentafluorides are discussed in terms of their physical properties and in relation to the higher fluorides of neighboring transition elements.

Introduction

The comment was made in the first paper of this series[1] that little is known of the chemical reactivities of the fluorides of transition metals in higher oxidation states. As a group, vanadium, niobium, and tantalum pentafluorides are probably the three most widely studied of the higher fluorides, considering both physical and chemical properties.[2–4] However, no attempt has been made to systematize the observed chemical reactions or to relate them with the physical properties of these pentafluorides.

Previously some reactions of the subgroup V pentafluorides have been reported with an unrelated series of chemical compounds but no systematic study of their reactivity has been carried out. As part of a general project on the comparative reactivity of transition metal fluorides, a study of the chemical reactivities of the subgroup V pentafluorides was undertaken, and the results so far obtained are described and related to their physical properties. The general approach was similar to that adopted in the study of the fluorides of subgroup VI reported separately,[1,5] *i.e.*, the reactions carried out are of two types, first oxidation–reduction reaction with lower fluorides and, second, halogen-exchange reactions.

Experimental Section

Apparatus.—Generally, the reactions were studied using the type of apparatus and techniques described in the first paper of this series, except that reactions of niobium and tantalum pentafluorides with solid compounds were carried out in sealed thick-walled Pyrex tubes. All manipulations involving niobium and tantalum pentafluorides were performed in a nitrogen-filled drybox.

Vanadium pentafluoride has been reported to attack Kel-F,[6] and this observation was confirmed in the present study. It was found that as vanadium pentafluoride, which had been trapped into a Kel-F tube, melted and ran down the walls of the tube, it changed to a brownish color from pale yellow. The intensity of the brown color increased with time and the compound tended to solidify on the walls. After standing for several days at room temperature, white crystals were observed to be growing from the dark brown spots on the walls of the tube. This Kel-F attack is believed to involve the extraction of the chlorine from the polymer, although this could not be confirmed either by infrared or mass spectral investigation.

Because of the possibility of contamination from Kel-F attack, it was necessary to carry out the reactions of vanadium pentafluoride using a vast excess of the second reactant. Study of reactions using excess vanadium pentafluoride is being carried out in silica apparatus and will be reported later.

Reagents.—Niobium and tantalum pentafluorides were prepared by direct fluorination of the respective metals and were purified by sublimation. Vanadium pentafluoride was also prepared from the metal, and after trap-to-trap distillation was stored over sodium fluoride. Arsenic tribromide and tin tetrabromide were purified by vacuum sublimation after bromination of the respective metals. Carbon tetraiodide was prepared by shaking a mixture of carbon tetrachloride, ethyl iodide, and aluminum chloride, filtering, washing, and drying the product under vacuum.[7] Passage of a 1:1 mixture of fluorine and nitrogen over selenium powder at 0° produced selenium tetrafluoride.[8] Sulfur monofluoride was prepared by heating a mixture of silver(I) fluoride and sulfur at 165° for 40 min.[9] Commercial cylinder sulfur tetrafluoride, containing about 15% thionyl fluoride, was purified by preparing the sulfur tetrafluoride–boron trifluoride adduct, distilling Grignard ether onto the adduct, and trapping the pure sulfur tetrafluoride so released.[10] Laboratory reagent sulfur monochloride was vacuum distilled before use. All other reagents used were obtained as previously described.[1,11]

Results

Tables I and II summarize the reactions of vanadium pentafluoride that have been fully worked out to date and all those of the pentafluorides of niobium and tantalum that have been studied in this project. A large number of the reactions of vanadium pentafluoride that have been investigated have proved to be very complex, and further work must be done before their reaction patterns are completely elucidated.

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[1] T. A. O'Donnell and D. F. Stewart, *Inorg. Chem.*, **5**, 1434 (1966).

[2] H. C. Clark and H. J. Emeléus, *J. Chem. Soc.*, 190 (1958).

[3] F. Fairbrother, K. H. Grundy, and A. Thompson, *ibid.*, 761, 765 (1965).

[4] R. G. Cavell and H. C. Clark, *J. Inorg. Nucl. Chem.*, **17**, 257 (1961).

[5] T. A. O'Donnell, D. F. Stewart, and P. Wilson, *Inorg. Chem.*, **5**, 1438 (1966).

[6] L. E. Trevorrow, J. Fischer, and R. K. Steunenberg, *J. Am. Chem. Soc.*, **79**, 5167 (1957).

[7] R. E. McArthur and J. H. Simons, *Inorg. Syn.*, **3**, 37 (1950).

[8] E. E. Aynsley, R. D. Peacock, and P. L. Robinson, *J. Chem. Soc.*, 1231 (1952).

[9] O. Glemser, W. D. Heussner, and A. Haas, *Naturwissenschaften*, **50**, 402 (1963).

[10] N. Bartlett and P. L. Robinson, *J. Chem. Soc.*, 3417 (1961).

[11] T. A. O'Donnell and D. F. Stewart, *J. Inorg. Nucl. Chem.*, **24**, 309 (1962).

TABLE I

REACTIONS OF VANADIUM PENTAFLUORIDE

Reagent	Reaction products
BCl_3[a]	VCl_4, BF_3, Cl_2
CS_2[a]	VF_3, SF_4, $(CF_3)_2S_2$, $(CF_3)_2S_3$
$BiCl_3$[b]	VCl_4, BiF_3, Cl_2
BiF_3	No reaction
SeF_4	$SeF_4 \cdot VF_5$[c]
S_2F_2[d]	VF_4, SF_4
SF_4	No reaction

[a] Reaction occurred as VF_5 was condensed onto excess reactant at liquid nitrogen temperature. [b] Slow at room temperature. [c] Very pale pink solid, only slightly soluble in excess SeF_4. [d] Reacts below room temperature.

TABLE II

REACTIONS OF NIOBIUM AND TANTALUM PENTAFLOURIDES

Reagent[a]	NbF_5	TaF_5
PF_3,[b] AsF_3, SbF_3,[c] BiF_3[c]	No reaction	No reaction
PF_3 + anhydrous HF[d]	No reaction	No reaction
PCl_3[e]	$NbCl_5$, PF_3	$TaCl_5$, PF_3
PBr_3	$NbBr_5$, PF_3	$TaBr_5$, PF_3[f]
$AsCl_3$, $SbCl_3$,[c] $BiCl_3$,[c] $AsBr_3$[c]	No reaction	No reaction
BCl_3[e]	$NbCl_5$, BF_3	$TaCl_5$, BF_3
CCl_4, $SiCl_4$, $SnCl_4$	No reaction	No reaction
$TiCl_4$	$NbCl_5$, TiF_4[g]	$TaCl_5$, TiF_4[g]
CBr_4,[c] CI_4,[c] $SnBr_4$[c]	No reaction	No reaction
S_2Cl_2, CS_2	No reaction	No reaction

[a] Each of the reagents listed in this table (BiF_3 excepted) reacts readily with vanadium pentafluoride. [b] No reaction occurred even when the pentafluorides were in the molten state. [c] Heated to 145° for 2–6 days. [d] It has been shown that the reduction of tungsten hexafluoride to the tetrafluoride is accelerated in liquid hydrogen fluoride.[1] [e] In these reactions, niobium pentafluoride reacted slightly more rapidly than tantalum pentafluoride, as shown by changes in pressure. [f] Virtually no reaction was observed with tantalum pentafluoride at room temperature. However, on heating to 60° for 30 min, reaction took place rapidly. [g] These reaction products were not identified by analysis as very little separation was obtained when the products were vacuum sublimed in a glass tube. Since a large excess of titanium tetrachloride was used, the formation of mixed halides of Nb (Ta) or Ti was considered to be unlikely.

The reasons for this complexity and the preliminary results will be discussed later. However, a sufficient number of reactions of vanadium pentafluoride have been worked out thoroughly to allow a comparison of the reactivity of vanadium pentafluoride with the reactivities of the pentafluorides of niobium and tantalum.

The reactions of niobium and tantalum pentafluorides with volatile compounds were studied by distilling an excess of the volatile compound onto the pentafluoride at −196° and allowing apparent equilibrium to be attained at room temperature. Involatile compounds were mixed with the pentafluorides in a drybox and sealed under vacuum in thick-walled Pyrex tubes and heated in a muffle furnace. The vanadium pentafluoride in all reactions was distilled onto a vast excess of the second reactant at −196° so that Kel-F attack was kept to a minimum. The violent reactions that then took place in the majority of the cases were controlled by judicious cooling with liquid nitrogen.

Preliminary investigation of many other reactions of vanadium pentafluoride, namely with phosphorus, arsenic, and antimony trifluorides and trichlorides, with tin, titanium, and silicon tetrachlorides, and with sulfur monochloride, indicates that these reactions are extremely complicated, involving a number of intermediate and possibly competing steps.

With the group V trifluorides (except bismuth trifluoride), reduction of the vanadium to the tetravalent state occurs with oxidation to the group V pentafluoride. However, the group V fluoride is not free as the pentafluoride in the case of arsenic or antimony but is in the form of the hexafluoro anion. In the phosphorus trifluoride reaction, there is evidence for both the pentafluoride and the hexafluorophosphate anion from separate reactions. These facts can be accounted for on the basis of the relative strengths of the group V pentafluorides as Lewis acids, *i.e.*, as fluoride ion acceptors. Qualitative work carried out by Clifford, *et al.*,[12] indicates that the relative strengths of the three pentafluorides is as follows: $SbF_5 > AsF_5 > PF_5$. Some preliminary quantitative work supports this.[13] Thus a possible scheme for these reactions would involve initially an oxidation–reduction one, for example

$$2VF_5 + MF_3 \longrightarrow 2VF_4 + MF_5$$

This would be followed by complex formation, *e.g.*, of the type

$$VF_4 + MF_5 \longrightarrow VF_4 \cdot MF_5 \text{ (ideally } VF_3{}^+ \cdot MF_6{}^-\text{)}$$

this only occurring with phosphorus pentafluoride under certain conditions, as yet not defined.

Reactions between vanadium pentafluoride and the group V trichlorides (except bismuth trichloride) and with the other chlorides listed above are extremely violent. All except those with arsenic and antimony trichlorides occur immediately when the vanadium pentafluoride is trapped onto the excess chloride at −196°. The initial product in all cases was a brown-green solid, presumably vanadium tetrachloride, further violent reaction taking place as the reacting chloride melted. The vanadium was reduced to an oxidation state of either 3 or 4. With phosphorus trichloride, phosphorus tri- and pentafluorides were observed. With silicon tetrachloride, silicon tetrafluoride was produced, and with sulfur monochloride, sulfur tetrafluoride resulted. Chlorine was not observed as a separate product in any of the tetrachloride or sulfur monochloride reactions. This is consistent with its high solubility in all these reagents. The involatile products of the silicon tetrachloride and sulfur monochloride reactions contained no silicon or sulfur, respectively.

Quantitative analysis of the chlorine-exchange reaction products, which contained both chloride and fluoride, indicated that these products were not pure compounds, the analytical percentages varying from one reaction to the next as duplication was attempted.

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(12) A. L. Clifford, H. C. Beachell, and W. M. Jack, *J. Inorg. Nucl. Chem.*, **5**, 57 (1957).

(13) H. H. Hyman, T. J. Lane, and T. A. O'Donnell, Abstracts, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept 1963, p. 63T.

Discussion

Systematics of Reactions.—It would be difficult to formulate at this stage a detailed scheme of reactions for vanadium pentafluoride because of the complications outlined above. However, work is proceeding and will be reported later.

With niobium and tantalum pentafluorides, the observed reactions are relatively simple, involving halide exchange without any change in oxidation state. Generally, a simple metathetical reaction occurs of the type

$$3NbF_5 + 5PCl_3 \longrightarrow 3NbCl_5 + 5PF_3$$

Interesting features of the reactions carried out were that both niobium and tantalum pentafluorides exchanged chloride much more readily than bromide and that there were indications that halogen exchange occurred somewhat more readily for niobium pentafluoride than for the tantalum compound.

Relative Reactivities of the Pentafluorides of Vanadium, Niobium, and Tantalum.—From the above tables and notes it is obvious that vanadium pentafluoride is both a violent oxidizing and fluorinating agent while niobium and tantalum pentafluorides are very weak fluorinating agents, niobium being slightly more reactive than tantalum.

The extreme reactivity of vanadium pentafluoride is in good agreement with the work of Clark and Emeléus,[2,14] who found it to be an effective fluorinating agent. Its reactivity may seem somewhat enhanced in the present work because it reacts in the monomeric form in the vapor[6] as it is trapped onto the other reagent. Its reactivity as the polymeric solid[15] may be somewhat reduced.

The relative chemical inertness of niobium and tantalum pentafluorides is in good agreement with the observations of several other workers. For example, Fairbrother, *et al.*,[3] prepared stable 1:1 adducts with dimethyl and diethyl ethers, dimethyl and diethyl sulfides, and tetrahydrothiophene, while Clark, *et al.*,[2,4] have found that niobium pentafluoride forms stable 1:2 adducts with ammonia and pyridine and a solvated 1:1 adduct with ethylenediamine. Only the 1:2 tantalum pentafluoride–pyridine adduct has been reported. However, in all cases the niobium and tantalum are present in the pentavalent state. On the other hand, vanadium pentafluoride reacts with ammonia, pyridine, and ethylenediamine forming tetravalent vanadium adducts. Niobium and tantalum pentafluorides form adducts with xenon difluoride,[16] but vanadium pentafluoride does not react.[17]

Many reactions of niobium and tantalum pentafluorides were carried out by Ruff and Schiller.[18] Considering the experimental difficulties encountered in that work, their results are in general agreement with ours. They stated, however, that "niobium pentafluoride proved to be substantially more reactive than tantalum pentafluoride." This statement appears to be based mainly on differences in solubilities, in colors obtained on heating the various reaction mixtures, and in behavior in hydrofluoric acid solutions containing potassium fluoride. These observations, however, represent only a small part of the work. In the present study, niobium pentafluoride was found to be slightly more reactive than tantalum pentafluoride. The evidence for this was based mainly on the rate of formation of volatile products. Because it was felt that the different rates of reaction might be due to different amounts of surface hydrolysis of the pentafluorides, the work was repeated and similar, but not quite identical, results were obtained. The subdivision and solubility of reactants would have affected rates of reaction.

The similarity in reactivity of niobium and tantalum pentafluorides can be described in terms of the lanthanide contraction. The vast difference in reactivity between the pentafluoride of vanadium and those of niobium and tantalum can be accounted for in terms of stabilities of valence states and in trends in physical properties.

Edwards has recently shown[19] that solid niobium and tantalum pentafluorides are isostructural with molybdenum pentafluoride; that is, they have a basic tetrameric unit. It now appears that vanadium pentafluoride also has a polymeric structure.[15] When the pentafluorides are melted, there is partial breakdown of the polymer, the liquids still being associated but undergoing some self-ionization as indicated by conductivity, viscosity, and other measurements.[3] Vapor density measurements[6] indicate that vanadium pentafluoride is monomeric in the vapor phase. The infrared spectrum of gaseous vanadium pentafluoride, however, does not clearly indicate whether it has a trigonal bipyramidal or square pyramidal structure.[20]

Table III lists some of the physical properties of the subgroup V pentafluorides. These values reflect the similarity in physical properties of niobium pentafluoride and tantalum pentafluoride, and their differences from the properties of vanadium pentafluoride. This trend is found, as expected, in the chemical reactivities.

The property that would best illustrate the trend in reactivity found is the bond energy, since reactivity will depend in large part on this energy. Unfortunately, very few data are available, either from spectroscopic or thermochemical measurements, but experimental heats of formation allow a mean metal-to-fluorine bond dissociation energy to be calculated. Values of this energy are 114 and 142 kcal/mole for vanadium and niobium pentafluorides, respectively.[21] No experimental heat of formation is available as yet for tantalum pentafluoride, and the use of calculated

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(14) H. C. Clark and H. J. Emeléus, *J. Chem. Soc.*, 2119 (1957).

(15) R. D. Peacock, private communication.

(16) A. J. Edwards, J. H. Holloway, and R. D. Peacock, *Proc. Chem. Soc.*, 275 (1963).

(17) A. J. Edwards, private communication.

(18) O. Ruff and E. Schiller, *Z. Anorg. Chem.*, **72**, 329 (1911).

(19) A. J. Edwards, *J. Chem. Soc.*, 3714 (1964).

(20) R. G. Cavell and H. C. Clark, *Inorg. Chem.*, **3**, 1789 (1964).

(21) R. G. Cavell and H. C. Clark, *Trans. Faraday Soc.*, **59**, 2706 (1963).

TABLE III

PHYSICAL PROPERTIES OF THE SUBGROUP V PENTAFLUORIDES[3]

	VF_5	NbF_5	TaF_5
Mp, °C	19.5	80.0	95.1
Bp, °C	48.3	235	229
V_m, cc mole^{-1} [a]	58.33 (25°)	69.71	71.10
η, cp[a]	124	91.41	70.31
$10^5\kappa$, ohm^{-1} cm^{-1} [a]	24	1.63	1.56
ΔH_{vap}, kcal mole^{-1}	10.64	12.9	13.0
Trouton constant	33.1	25.4	25.9

[a] At the melting point unless stated otherwise.

data, such as those of Glassner,[22] is not recommended, as recent experimental values differ greatly from the calculated values for many transition metal halides. However, the difference in the dissociation energies for vanadium and niobium pentafluorides is consistent with the differences in chemical reactivity. The differences in energy and reactivity of these pentafluorides are much greater than the differences for the hexafluorides of molybdenum, tungsten, and uranium. Here the M–F dissociation energies of 105, 121, and 108 kcal/mole, respectively, are consistent with a less marked trend in reactivity,[1,5] as observed. Vanadium pentafluoride has been found to be more reactive than these three hexafluorides, since qualitative experiments show that it will oxidize the lower fluorides to the appropriate hexafluoride for each of these elements. Vanadium tetrafluoride is found as the other product.

Although, as pointed out above, the trend in reactivities follows trends in physical properties, and since the three pentafluorides are thermally stable, the greatest factor influencing the relative reactivities of the three pentafluorides must be one of the stability of the valence state involved. The known subgroup V fluorides are listed in Table IV. Although niobium[23] and tantalum[24] trifluorides have been reported and their crystal structures determined,[23,25] it is now believed[26] that the compounds prepared were in actual fact oxide fluorides, since the substitution of oxygen for fluorine does not vary lattice dimensions to any great extent and, on thermodynamic grounds, stable lower tantalum fluorides should not exist.

TABLE IV

SUBGROUP V FLUORIDES

VF_5	NbF_5	TaF_5
VF_4	NbF_4[a]	
VF_3	$NbF_{2.5}$[a]	

[a] H. Schafer and H. G. Schnering, *Angew. Chem.*, **76**, 833 (1964).

For vanadium, the pentafluoride is the only pentavalent halide known, while for niobium and tantalum, the pentavalent state is the most stable state, all eight possible pentahalides being known. Preparation of lower niobium and tantalum halides is far more difficult than that of the appropriate pentahalide and normally involves reduction of the pentahalide. Thus we can see that passing from tantalum through to vanadium, there is a decrease in the stability of the pentavalent state, particularly with the fluorides, this being consistent with the marked trend in reactivity observed.

It is interesting to compare the differences in chemical behavior between the second and third row transition metal fluorides as we pass from subgroup IV across the periodic table. Although most modern textbooks indicate that the second and third row transition metals are quite close in their chemistry, we now find with the fluorides at least that there are quite systematic differences in reactivity. Also, reactivity of higher fluorides increases across the periodic table for both second and third row transition elements.

In general, knowledge of zirconium and hafnium tetrafluorides is limited to their physical properties and the fact that they form hydrates and complexes. Very little is known of their chemistry, but enough is known to indicate that they are virtually identical in their chemical behavior, an effect of the lanthanide contraction. With niobium and tantalum, we have shown in the present study that there is a slight difference in the reactivities, niobium being the more reactive. The difference between the second and third row transition metal fluorides increases as we pass to molybdenum and tungsten hexafluorides, again the second row element being the more reactive.[1] For example, molybdenum hexafluoride is readily reduced by phosphorus trifluoride, whereas reduction occurs very slowly with tungsten hexafluoride. Similarly, molybdenum hexafluoride reacts readily with phosphorus trichloride, but tungsten hexafluoride is immiscible, no reaction occurring even on heating to 150° in a sealed tube. This marked difference in reactivity is in direct contrast to the statement, which appears in the majority of inorganic chemistry textbooks, that molybdenum and tungsten hexafluorides are identical in chemical properties as well as being similar in physical properties.

Although very little is known about the chemistry of the two technetium fluorides that have been reported, there is evidence that the hexafluoride is more easily reduced than the corresponding rhenium compound[27] and thus would be expected to be more reactive. The lack of a technetium heptafluoride is also good evidence that higher fluorides of technetium are more reactive than those of rhenium. Reactivity and thermal stability are obviously linked.

By comparison with technetium and rhenium, even less is known about the chemistry of the higher fluorides as we pass further across the periodic table. However, it appears that the difference in reactivity between the second and third row transition metal fluorides increases, at least as far as palladium and platinum. Evidence for the horizontal and vertical trends in reactivity for the subgroup VIII hexafluorides comes

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(22) A. Glassner, U. S. Atomic Anergy Commission Report ANL-5750.

(23) P. Ehrlich, F. Ploger, and G. Pietzka, *Z. Anorg. Allgem. Chem.*, **282**, 19 (1955).

(24) H. J. Emeléus and V. Gutmann, *J. Chem. Soc.*, 2115 (1950).

(25) V. Gutmann and K. H. Jack, *Acta Cryst.*, **4**, 244 (1951).

(26) H. Schafer and H. G. Schnering, *Angew. Chem.*, **76**, 833 (1964).

(27) A. J. Edwards, D. Hugill, and R. D. Peacock, *Nature*, **200**, 672 (1963).

from both thermal stabilities and the closely related oxidative strengths. The thermal stabilities of these hexafluorides are in the following order

$RuF_6 > RhF_6 > (PdF_6$[28]$)$

$OsF_6 > IrF_6 > PtF_6$

$OsF_6 > RuF_6, IrF_6 > RhF_6$

The oxidizing power of these hexafluorides is of course in the reverse order as the following reactions show. Selenium tetrafluoride reduces platinum hexafluoride to the tetrafluoride, while osmium and iridium hexafluorides are reduced only to the pentavalent state.[29] Also ruthenium, rhodium, and platinum hexafluorides will oxidize xenon whereas osmium and iridium hexafluorides do not react.[30]

Further evidence for the increase in reactivity as we go across the periodic table comes from the reactions of osmium, iridium, and platinum pentafluorides with both selenium tetrafluoride and bromine trifluoride. The platinum compound is reduced to the tetravalent state while osmium and iridium form 1:1 adducts. Similarly, the reactions of the third row transition metal hexafluorides with nitric oxide support this systematic trend. Tungsten hexafluoride does not react,[31] osmium forms $NO^+OsF_6^-$,[32] but iridium and platinum form $(NO)_2IrF_6$[33] and $(NO)_2PtF_6$,[32] respectively.

Although there are relatively few chemical reactions that can be adduced as evidence, there is an obvious generalization that for higher fluorides thermal stability decreases and chemical reactivity increases with increase in atomic number for transition elements in the second and third rows. Also, it is easy to support the systematization that for subgroups of transition elements thermal stability of higher fluorides increases and chemical reactivity decreases as atomic number increases. It is not generally realized that for second and third row transition elements these differences become progressively greater in moving from a consideration of zirconium and hafnium, through niobium and tantalum, and on through molybdenum and tungsten to the elements of subgroups VII and VIII. It can be predicted confidently that these systematics can be made more rigorous as more work is done on the chemical reactivity of a wide range of transition metal fluorides.

(28) No fluoride above PdF_4 is thermally stable.

(29) N. Bartlett and D. H. Lohman, *J. Chem. Soc.*, 619 (1964).

(30) J. G. Malm, H. Selig, J. Jortner, and S. A. Rice, *Chem. Rev.*, **65**, 209 (1965).

(31) J. R. Geichman, E. A. Smith, S. S. Trond, and P. R. Ogle, *Inorg. Chem.*, **1**, 661 (1962).

(32) N. Bartlett, *Chem. Can.*, **15**, 33 (Aug 1963).

(33) P. L. Robinson and C. J. Westland, *J. Chem. Soc.*, 4481 (1956).

Contribution from the Department of Chemistry,
Cornell University, Ithaca, New York

Mass Spectrometric Study of Intermediates in the Oxidation of B_5H_9, B_4H_{10}, and BH_3CO[1]

By LAWRENCE BARTON, C. PERRIN, and RICHARD F. PORTER

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A mass spectrometric technique was used to follow the stoichiometry of oxidation of B_5H_9, B_4H_{10}, and BH_3CO as O_2 is slowly added to a borane sample at pressures between 5 and 20 mm. In the B_5H_9–O_2 reaction boroxine ($H_3B_3O_3$) is formed initially and further oxidation yields $H_2B_2O_3$(g). Boroxine formed when B_5H_9 reacts with $^{16}O_2$–$^{18}O_2$ mixtures contains oxygen atoms in a statistical distribution while the oxidized product, $H_2B_2O_3$, contains oxygen in a nonstatistical distribution. Boroxine is not produced in the initial stage of oxidation of B_4H_{10} and BH_3CO, but $H_2B_2O_3$ produced with $^{16}O_2$–$^{18}O_2$ mixtures contains oxygen atoms in a nonstatistical distribution. Results of these isotope distribution experiments indicate that the precursor to $H_3B_3O_3$ (and $H_2B_2O_3$) in the B_5H_9–O_2 reaction is probably HBO or H_2BOH. In the B_4H_{10}–O_2 and BH_3CO–O_2 reactions the precursor to $H_2B_2O_3$ is probably H_3BO_2 (borane peroxide). Solids produced in the reaction of B_5H_9 and O_2 act as a catalyst to accelerate the decomposition of $H_3B_3O_3$(g).

Introduction

Studies of the reaction of pentaborane-9 and oxygen have shown that the mechanism of oxidation is complex and is dependent on a number of factors including the order in which the reactants are mixed and the nature of the surface of the reaction vessel. Bauer and Wiberley[2] made an extensive investigation of the conditions of this system which lead to an explosive reaction. If O_2 is slowly added to gaseous B_5H_9 in Pyrex vessels, the reaction is nonexplosive at ordinary temperatures. Products of this reaction[3] include diborane, hydrogen, $H_2B_2O_3$(g), and solid boron oxide. Complete oxidation is not realized under these condi-

(1) Work supported by the Army Research Office, Durham, and the Advanced Research Projects Agency.

(2) (a) W. H. Bauer and S. E. Wiberley, Advances in Chemistry Series, No. 32, American Chemical Society, Washington, D. C., 1961, p 115; (b) G. H. Lee, W. H. Bauer, and S. E. Wiberley, *J. Phys. Chem.*, **67**, 1742 (1963).

(3) J. F. Ditter and I. Shapiro, *J. Am. Chem. Soc.*, **81**, 1022 (1959).