TABLE II

INFRARED AND RAMAN FREQUENCIES IN VARIOUS NITRONIUM SALTS AND SOLID CARBON DIOXIDE (CM.$^{-1}$)

NO_2ClO_4		NO_2NO_3		NO_2BF_4		$CO_2(s)$		
Infrared	Raman	Infrared[a]	Raman[b]	Infrared[c]	Raman[c]	Infrared[d]	Raman[e]	
570[f]	571	538	. . .	590 605	. . .	653 660	. . .	ν_2, bending mode
. . .	1396	. . .	1400	. . .	1399	. . .	1388	ν_1, symmetric str. mode
2360	. . .	2375	. . .	2380	. . .	2344	. . .	ν_3, antisymmetric str. mode

[a] Ref. 8. [b] Ref. 9. [c] Ref. 11. [d] W. E. Osberg and D. F. Hornig, *J. Chem. Phys.*, **20**, 1345 (1952). [e] J. C. McLannan and H. D. Smith, *Can. J. Res.*, **7**, 551 (1932). [f] Ref. 2a.

available for nitronium nitrate (infrared,[8] Raman,[9] and structure by X-ray[10]) and nitronium fluoroborate (Raman and infrared[11]). The fundamental frequencies of the nitronium ions and carbon dioxide are presented in Table II. While the stretching frequencies are very nearly identical in all cases, the only NO_2^+ bending mode closely equal to that of carbon dioxide is that of nitronium fluoroborate (doublet centered at 598 cm.$^{-1}$). In nitronium perchlorate and nitronium nitrate, the bending modes are shifted to lower frequencies (570 and 538 cm.$^{-1}$, respectively). These shifts clearly indicate decreased resistance to bending. This transformation is accomplished with little effect on nitrogen–oxygen bonding energies, as the stretching frequencies are almost identical for all four cases.

It can be inferred from the above comparisons that NO_2^+ bending frequencies are a measure of the extent of interaction, in crystals, between the nitronium cation and companion anion. In nitronium fluoroborate little cation–anion interaction is indicated, and one predicts a linear NO_2^+ ion. On this basis, NO_2^+ in nitronium fluoroborate is deemed to be more completely ionic than in nitronium perchlorate and nitronium nitrate. The cation of nitronium nitrate is by the same reasoning the least ionic; this conclusion is supported by the ease with which this compound volatilizes and reverts to appropriate covalent species.

Walsh[12] has shown that addition of an electron to NO_2^+ should theoretically be accompanied by the observed change in angle from 180 to 143°. The small change in angle observed in nitronium perchlorate can therefore be considered to result from a partial transfer of charge from perchlorate ion to nitronium ion. The transferred charge would be concentrated on the nitrogen atom and would not be expected to contribute significantly to the nitrogen–oxygen bond energy. Thus, the stretching frequencies should remain unchanged. On the other hand, the additional charge on the nitrogen atom would significantly affect the bending frequency. In nitronium nitrate, linearity is enforced by crystal symmetry, and the excess charge is evidenced only by a lowering of the bending frequency.

The proposed partial charge transfer can be treated as a resonance phenomenon, which implies a contribution of neutral NO_2 and neutral ClO_4 species to the overall wave function of the crystal. This minor contribution is exclusive of those for the individual NO_2^+ cations and ClO_4^- anions. From a molecular orbital point of view, the model implies a small overlap between orbitals of the nitronium and perchlorate ions. The overlap would be much too small to interpret as covalency. Our interpretation presents a picture of the observed interactions which is consistent with the concept that ionic crystals are inadequately described by purely electrostatic forces.

Acknowledgment.—Support of this research by the Office of Naval Research is gratefully acknowledged.

(8) R. Teranishi and J. C. Decius, *J. Chem. Phys.*, **22**, 896 (1954).
(9) J. Chedin, *Compt. rend.*, **201**, 552 (1935).
(10) E. Grison, K. Eriks, and J. L. deVries, *Acta Cryst.*, **3**, 290 (1950).
(11) J. C. Evans, H. W. Rinn, S. J. Kuhn, and G. A. Olah, *Inorg. Chem.*, **3**, 857 (1964).
(12) A. D. Walsh, *J. Chem. Soc.*, 2266 (1953).

CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY,
UNIVERSITY OF MELBOURNE, MELBOURNE, AUSTRALIA

The Preparation and Thermal Stability of Trichloroboroxine

BY D. J. KNOWLES AND A. S. BUCHANAN

Received June 10, 1965

The preparation of trichloroboroxine as a low-temperature photoinitiated reaction of boron trichloride and oxygen has been investigated. Trichloroboroxine was shown to be relatively stable as a gas-phase species at normal temperatures but to undergo decomposition when condensed on glass surfaces. A suggested reaction mechanism involves the initial photolysis of boron trichloride followed by reaction with oxygen to yield boron monochloride.

Introduction

The present work had its origin in a study of the photochemistry of volatile boron compounds. In the case of BCl_3 it seemed likely that the continuous absorption of radiation beginning at about 2200 Å. and extending into the vacuum ultraviolet would give rise to photodecomposition. Photolysis of BCl_3 alone yielded little decomposition, possibly due to reversal of the photolysis reaction, but in the presence of oxygen reaction was rapid and relatively extensive. Chlorine was found to be a major product and in addition at least one other species of relatively short life. Further experiment indicated that this product was probably trichloroboroxine $(BOCl)_3$, and the method proved convenient for the preparation of this compound.

Experimental

Purified BCl_3 was mixed in the required ratio with dry oxygen (usually 1:1) and the mixture (250 mm. total pressure) admitted to a silica reaction vessel. Two medium-pressure 120-watt mercury arcs supplied continuous radiation in the region of absorption by BCl_3. After irradiation for the required period the reaction mixture was transferred to a Ward–LeRoy low-temperature fractionating column for separation of products. At a later stage in the work this step was eliminated and the reaction mixture transferred directly to an infrared cell so that products of relatively short lifetime could be detected and their behavior observed by repeated scanning at short intervals.

Although low-temperature fractionation introduced difficulties with products of short life, some useful information was obtained. One product produced in relatively small yield and removed from the column in the temperature range −165 to −135° yielded a consistent molecular weight as measured with a micro gas density balance incorporated in the vacuum line. Chemical analysis of this product was partially successful. Chloride was determined on the hydrolyzed material using a potentiometric method, but boron analysis proved unsatisfactory, partly because of the small amounts of material and the difficulty of hydrolyzing to boric acid without introducing unacceptably high and variable blank values.

Hoke metal valves were used where necessary in the vacuum line to eliminate reaction of products with stopcock grease. Pressure measurements were made with the aid of a metal bellows gauge operating with a sensitivity of 2 mm./mm. of pressure on the optical scale. Mercury was thereby eliminated from the reaction section of the vacuum line.

Results

Photolysis of the BCl_3–O_2 mixture always produced a small pressure decrease usually in the range 10–20%. Cl_2 was invariably a product.

The volatile product obtained from the fractionating column in the range −165 to −135° yielded a molecular weight of 60.1 (mean of four values), which is within experimental error of the molecular weight (62.3) of the only likely species, BOCl. Chloride analysis on this compound gave a mean value of 55.9% compared with the theoretical value of 57% for BOCl. The presumed BOCl proved quite unstable. When condensed in contact with glass at liquid air temperature a white involatile solid and molecular chlorine resulted. The instability and small yields of BOCl resulted in failure of attempts to record the infrared spectrum of the compound.

When the spectrum of the nonfractionated reaction mixture was recorded immediately on termination of photolysis it was clear that a new molecular species was present. A strong absorption was present at about 1380 $cm.^{-1}$ with weaker absorption at 1470 and 1205 $cm.^{-1}$. These peaks overlap BCl_3 absorptions (1203 m, 1376 s, 1395 s, 1420 s, and 1464 m $cm.^{-1}$) but are distinguishable even in the presence of residual BCl_3.

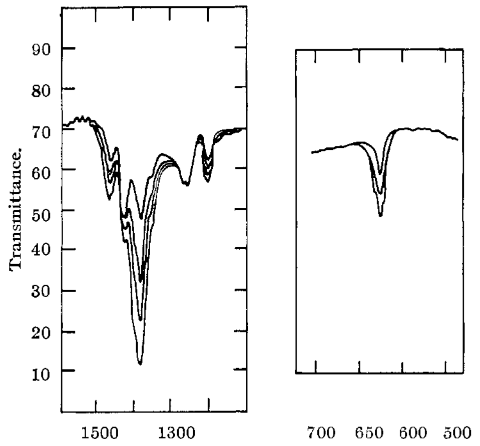

Figure 1.—Infrared spectrum of the photolysis products of 250 mm. pressure of a mixture of BCl_3 and O_2 (2:1). Photolysis time 30 min. Spectrum recorded at increasing intervals after termination of photolysis.

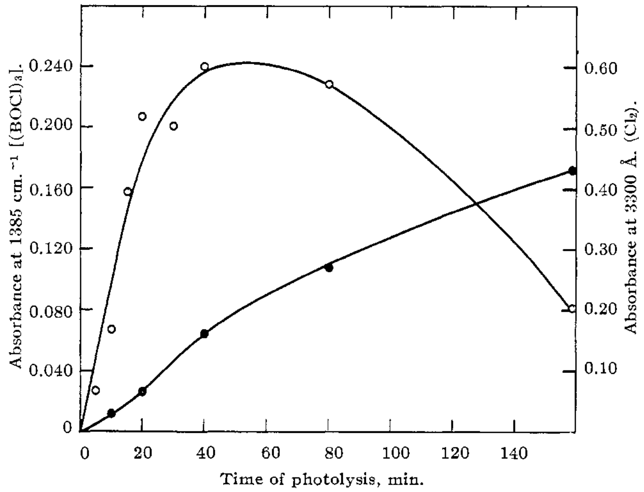

Figure 2.—Variation of the yields of $(BOCl)_3$ (○) and Cl_2 (●) with time of photolysis. In all cases reaction involved 250 mm. pressure of a 2:1 BCl_3–O_2 mixture.

The new compound proved unstable at room temperature and the infrared absorptions diminished to virtually zero over a period of 90–120 min. (Figure 1a). A further absorption (possibly multiple) occurred at 620 $cm.^{-1}$ and this also diminished rapidly with time (Figure 1b).

The strong absorption at 1385 $cm.^{-1}$ proved convenient in monitoring the buildup and decay of the new compound. Since the molecule concerned decays rapidly it is likely that its concentration will reach a maximum during the course of the photolysis and thereafter diminish as the rate of decay matches and eventually exceeds the rate of formation since the latter will fall away following depletion of the reactants BCl_3 and O_2. This expectation is realized and, in the conditions of the current experiments the maximum yield was found after about 40 min. photolysis (Figure 2).

The increase in concentration of the product Cl_2 during the course of the photoreaction is also shown in

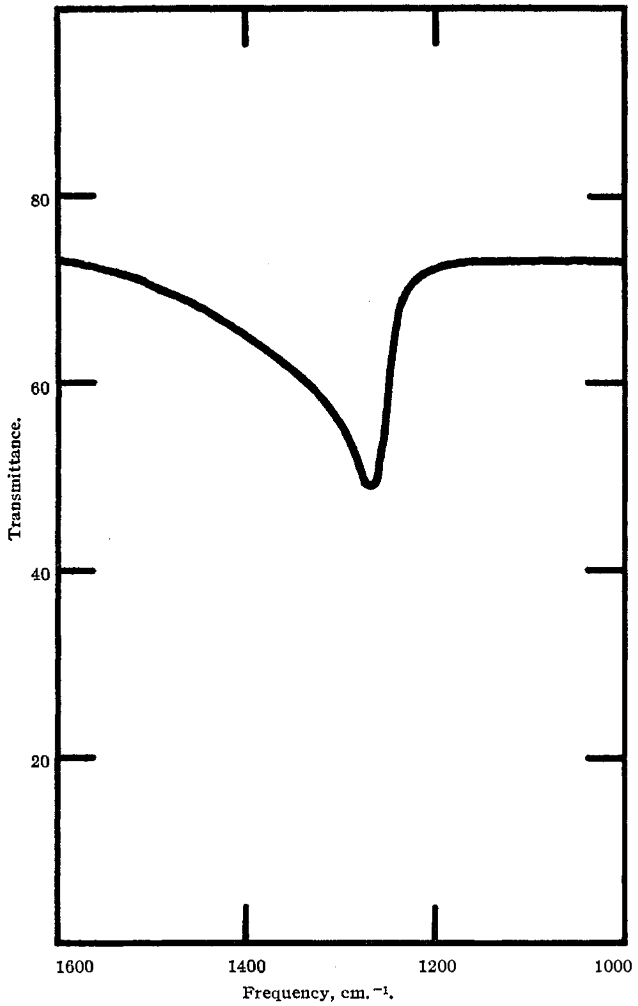

Figure 3.—Infrared spectrum of the oxide product deposited on the cell windows during the decay of the BCl_3–O_2 photolysis product (chiefly $(BOCl)_3$).

Figure 2. Approximate measurements indicated that one molecule of Cl_2 was produced for each BCl_3 lost.

During decay of the new product in the infrared cell a white solid deposit appeared on the cell windows. The spectrum of the deposit is shown in Figure 3. It corresponds reasonably well to the spectrum of B_2O_3 at 1260 cm.$^{-1}$. The broad nature of the band indicates a variety of bond types. On hydrolysis the substance was shown to contain chlorine and is probably a polymer of boron and oxygen with some residual chlorine.

Discussion

In the light of the evidence of this study it is probable that the major products of the photoinduced reaction of BCl_3 and O_2 are Cl_2 and $(BOCl)_3$. Identification of the trichloroboroxine rests chiefly on the similarity of its infrared spectrum to those of boroxine, trifluoroboroxine, and trimethylboroxine (Table I) and also on the evidence quoted above relating to the monomer BOCl.

Fisher, Lehmann, and Shapiro[1] on the basis of comparison of the spectrum of BF_3 and $F_3B_3O_3$ suggest that the asymmetric B–F stretching frequency decreases by about 500 cm.$^{-1}$ in the latter as compared with the former molecule. An analogous decrease of about 240 cm.$^{-1}$ occurs with $(CH_3)_3B_3O_3$. It is therefore reasonable to seek the asymmetric B–Cl stretching frequency of $Cl_3B_3O_3$ at frequencies significantly lower than that for BCl_3 (956 cm.$^{-1}$ for the B^{11} molecule). The absorption at about 620 cm.$^{-1}$ (Figure 1b) seems a logical choice.

TABLE I

INFRARED SPECTRA OF $F_3B_3O_3$,[a] $H_3B_3O_3$,[b] $(CH_3)_3B_3O_3$,[a] AND $Cl_3B_3O_3$

Assignment	Frequency, cm.$^{-1}$ $F_3B_3O_3$	$H_3B_3O_3$	$(CH_3)_3$-B_3O_3	$Cl_3B_3O_3$
Ring puckering (out-of-plane)	714		784	
B–X stretching (asymmetric)	966	2620	918	620
Ring stretching	1381	1213	1227	1385
Ring stretching	1450	1384 1394	1384	1430 1470
Out-of-plane B–X bend		918		
Unassigned	1233			1210
	1280			(doublet)

[a] H. D. Fisher, W. J. Lehmann, and I. Shapiro, *J. Phys. Chem.*, **65**, 1166 (1961). [b] S. K. Wason and R. F. Porter, *ibid.*, **68**, 1443 (1964).

Irrespective of the validity of the assignments of Table I (which are not based on vibrational analyses) the general similarities of the infrared spectra provide a reasonably sound basis for identification of $Cl_3B_3O_3$. On the assumption that trichloroboroxine is a major gaseous product of the photoinduced reaction of BCl_3 and O_2, the following tentative mechanism is suggested for the reaction.

$$BCl_3 \xrightarrow{h\nu} BCl + Cl_2 \qquad (1)$$

or

$$BCl_3 \xrightarrow{h\nu} BCl_2 + Cl \qquad (2)$$

$$BCl + O_2 \longrightarrow BClO_2 \qquad (3)$$

$$BClO_2 + BCl \longrightarrow 2BOCl \qquad (4)$$

$$3BOCl \longrightarrow (BOCl)_3 \qquad (5)$$

In this scheme reaction 1 is to be preferred to reaction 2 as the initiation step on several counts. BCl and not BCl_2 has been detected as a product of the flash photolysis of BCl_3 and B_2Cl_4.[2] BCl is stated to have a relatively long life and may not have unpaired electrons. If Cl atoms were produced in reaction 2 it seems certain that oxides of chlorine would appear in the stable products. No evidence for the oxides could ever be found. Reaction 1 satisfactorily accounts for the experimental observation that one molecule of chlorine is produced for each molecule of boron trichloride consumed.

Reactions 3, 4, and 5 follow logically and are analogous to processes suggested by Holliday and Massey[3] in the oxidation of B_2Cl_4.

The over-all stoichiometry of the photoinduced reaction can be written

$$6BCl_3 + 3O_2 \longrightarrow 2(ClBO)_3 + 6Cl_2 \qquad (6)$$

---

(1) Footnote *a* of Table I.

(2) A. G. Massey and J. J. Zwolenik, *J. Chem. Soc.*, 5354 (1963).

(3) A. K. Holliday and A. G. Massey, *J. Inorg. Nucl. Chem.*, **18**, 108 (1961).

which will give a pressure decrease of about 11% if the species on the right are the chief products. This decrease is in accord with the order of magnitude observed experimentally.

Observations on the thermal stability of $(BOCl)_3$ in this and other published work[4,5] might appear to be inconsistent at first sight. In the present study decay of the trimer is found to be quite rapid at room temperature (Figures 1 and 2), while in the studies at elevated temperature the compound is formed and presumably has significant stability at 1400°K. However, the high-temperature observations indicate that the reaction

$$BCl_3(g) + B_2O_3(l) = (BOCl)_3(g) \qquad (7)$$

is endothermic and is favored thermodynamically as the temperature is increased. The existence of the trimer as a transient species at low temperature is then evidence of a sufficiently slow rate of reversion to the equilibrium state to permit observation of some of its properties. Gaseous boroxine ($B_3O_3H_3$) appears to behave in a similar fashion.[6,7]

The low-temperature decay of the trimer appears to involve a wall reaction yielding a solid product with an infrared spectrum (Figure 3) corresponding approximately to B_2O_3 but analysis shows that this deposit still contains chlorine. Molecular chlorine is also a significant decay product of the trimer. BCl_3 may also be produced but this is not easy to establish satisfactorily in the presence of excess BCl_3 from the preparative stage. In the light of these comments it is clear that the reverse of reaction 7 is not the only operative mode of thermal decomposition of $(BOCl)_3$ at low temperatures.

(4) J. Blauer and M. Farber, *J. Chem. Phys.*, **39**, 158 (1963).

(5) J. Blauer and M. Farber, *Trans. Faraday Soc.*, **60**, 301 (1964).

(6) G. H. Lee, W. H. Bauer, and S. E. Wiberley, *J. Phys. Chem.*, **67**, 1742 (1963).

(7) R. F. Porter and S. K. Gupta, *ibid.*, **68**, 280 (1964).

CONTRIBUTION FROM THE CHEMICAL TECHNOLOGY DIVISION,
U. S. NAVAL RADIOLOGICAL DEFENSE LABORATORY, SAN FRANCISCO, CALIFORNIA

Liquid-Liquid Extraction in the Sodium Oxide-Boron Oxide-Sodium Chloride System[1]

BY MONTE H. ROWELL

Received August 4, 1965

Liquid-liquid extraction has been accomplished in molten salt media by the use of molten borates as the extracting phase. Radioactive tracers were used to measure the distribution of micro quantities of Cs, Rb, Ba, Sr, Nd, Eu, and Ag between the two conjugate liquid phases throughout the immiscibility region in the system $Na_2O-B_2O_3-NaCl$ at 830°. Borate/salt distribution coefficients are extremely sensitive both to phase compositions and to the nature of the solute ion. Cations of the alkali metal, alkaline earth, and rare earth groups show good separation factors and an order of selectivity dependent upon field strength. Selectivity appears to be based largely upon cation-exchange properties of the borate phase. The distribution behavior of silver is compatible with that which might be expected of a highly charged chloro anion.

Introduction

Efforts to apply analytical tools such as liquid-liquid extraction and ion exchange to the study of chemistry in molten salts have been hampered by the scarcity of immiscible liquid pairs and ion-exchange materials which are both effective for the separation of solutes and stable at the high temperatures involved. Molten alkali borates are generally immiscible with molten electrolytes and they show excellent selectivity between various ionic species in the latter phase. Molten boron oxide is generally thought of as a nonionic, covalently bonded, high polymer, in contrast to most molten salts which are ionic fluids. As would be expected, the two liquids are usually quite immiscible. As alkali oxide is added to a molten system of salt and boron oxide, the phases gradually become mutually soluble, but before complete miscibility occurs there is normally an extensive immiscibility region. Within this region solute ions are distributed between the two conjugate phases in a ratio strongly dependent upon both the phase compositions and the nature of the solute ion. For the investigation of this behavior, the solvent system studied in this work was that of $Na_2O-B_2O_3-NaCl$ at 830°. Distribution of solute ions from the alkali metal, alkaline earth, and rare earth groups was measured to determine the effect of size and charge of cations which are expected to show a minimum of complex ion formation. Distribution of silver was measured to observe the behavior of an element suspected of complex anion formation.

Experimental

Preparation of Borate Glasses.—Reagent grade boron oxide (B_2O_3), anhydrous borax ($Na_2O \cdot 2B_2O_3$), and mixtures of borax and sodium metaborate ($Na_2O \cdot B_2O_3$) were melted and heated at 900° until bubbling stopped, which removed all but a small amount of residual water. The glasses were then cooled, coarsely crushed, and stored in desiccators. From these glasses of known

(1) This work was supported by the U. S. Atomic Energy Commission under Contract No. AT-(49-2)-1167.