

the observed $\Delta\sigma$ but it is hardly the main cause.²² Another possibility is the expansion of the phosphorus radial wave function by an amount proportional to the paired-electron density in the phosphorus bonding orbitals. This effect would be greatest for the least ionic P-X bonds, and thus it would tend to decrease $\langle 1/r^3 \rangle_P$ and $\sigma^{(2)}$ for PH_3 and $\text{P}(\text{CH}_3)_3$ as compared to the trihalides, which is in the direction required. The magnitude of the effect is uncertain, but there is some e.s.r. evidence for its existence.²³

A noteworthy feature of the calculations of $\sigma^{(2)}$ and of the experimental shifts for the trihalides is the "reversal" of the trends in the case of PI_3 ; that is, the ordering is PF_3 , PI_3 , PCl_3 , and PBr_3 . This is a consequence of the fact that although the bond parameters such as ionicity and bond hybridization change monotonically in the usual sequence F, Cl, Br, and I, their ef-

(22) Of course one would expect π -bond contributions to be more appreciable in the tetravalent compounds X_3PO and X_3PS .

(23) K. DeArmond, B. B. Garrett, and H. S. Gutowsky, *J. Chem. Phys.*, **42**, 1019 (1965).

fects upon $\sigma^{(2)}$ are nonlinear and, in some instances opposed, so that $\sigma^{(2)}$ goes through a minimum for PBr_3 . The existence of the minimum is evident also in the ^{31}P shifts found in the series of compounds PCl_3 , PBrCl_2 , PBr_2Cl , and PBr_3 . In observations at 16.2 Mc./sec., their shifts²⁴ were found to be 10.5, 4.3, and 0.6 p.p.m. upfield with respect to PBr_3 . Thus, the change produced in σ by substitution of a Br for a Cl is 6.2, 3.7, and 0.6 p.p.m. for the first, second, and third Br, respectively, which follow the general pattern for the unmixed trihalides themselves.

The formulation given here is applicable in principle to ^{14}N or ^{15}N shifts in trivalent nitrogen compounds. However, few experimental data are available on nitrogen shifts. It would be particularly relevant to the present work if nitrogen shifts could be measured in NH_3 as well as in some of the nitrogen trihalides, to establish whether ammonia has a large upfield shift such as that found for ^{31}P in phosphine.

(24) E. Fluck, J. R. Van Wazer, and L. C. D. Groenweghe, *J. Am. Chem. Soc.*, **81**, 6363 (1959).

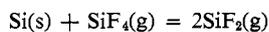
Silicon-Fluorine Chemistry. II. Silicon-Boron Fluorides^{1a}

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Received March 16, 1965*

Gaseous SiF_2 and BF_3 are observed to react when condensed together in a trap at liquid nitrogen temperature. Several silicon-boron fluorides have been identified mass spectrometrically, including Si_2BF_7 , Si_3BF_9 , and $\text{Si}_4\text{BF}_{11}$. From n.m.r., infrared, and mass spectral data, one concludes that these molecules are members of the homologous series $\text{SiF}_3-(\text{SiF}_2)_n-\text{BF}_2$. The silicon-boron fluorides are thermally stable to at least 200° as vapors but ignite spontaneously in air. A similar family of mixed fluoro-chloro compounds is obtained by treating BCl_3 with SiF_2 .

It was shown by Pease² that silicon difluoride gas, SiF_2 , can be conveniently prepared from silicon and silicon tetrafluoride at low pressures and temperatures above 1050° .



Studies in this laboratory have shown³ that silicon difluoride is a surprisingly stable gaseous species, although it can be made to react with a wide variety of compounds.

(1) (a) Presented in part before the 148th National Meeting of the American Society, Chicago, Ill., Sept. 1964; (b) Rice University; (c) National Bureau of Standards.

(2) D. C. Pease, U. S. Patents 2,840,588 (June 24, 1958) and 3,032,173 (March 20, 1962) assigned to the Du Pont Co., Wilmington, Del.

(3) (a) P. L. Timms, R. A. Kent, T. C. Ehlert, and J. L. Margrave, *Nature*, in press; (b) part I: *J. Am. Chem. Soc.*, **87**, 2824 (1965).

The molecule SiF_2 might act either as an electron donor or acceptor. This would be true if the molecule were in either the triplet or singlet state, since, by analogy with difluorocarbene,⁴ these states are likely to be separated by only a small energy barrier. Thus, it was thought that silicon difluoride should be capable of forming adducts of the type $\text{SiF}_2\text{-Y}$ where Y is a strong Lewis acid like boron trifluoride. Difluorocarbene has not been observed to act in this way, probably because the inductive effect of the fluorine limits the availability of the electron pair, but with silicon ($p \rightarrow d$) π -bonding could in part compensate for this.

In addition to being a possible acid-base reaction, the combination of silicon difluoride and boron trifluoride was of interest for two other reasons. First, the B-F and Si-F bond energies are rather similar so that a compound of type $\text{SiF}_2 \cdot \text{BF}_3$ might readily rearrange to SiF_3BF_2 ; and second, it was hoped that this reaction would provide a convenient route to forming simple compounds containing silicon-boron bonds, only a few of which have previously been described (the most recent being SiBCl_5 by Massey⁵).

Experimental

Silicon difluoride was prepared from silicon and silicon tetrafluoride at 0.1-0.2 mm. pressure and a temperature of 1150° as described elsewhere.³ Boron

(4) F. W. Dalby, *J. Chem. Phys.*, **41**, 2297 (1964).

(5) A. G. Massey and D. S. Urch, *Proc. Chem. Soc.*, 284 (1964).

Table I. N.m.r. Spectra of the Silicon-Boron Fluorides

Compound	Assignment	Chemical shift, p.p.m.	$J_{\text{Si-F}}$, Hz.	J_{FSiSiF} , Hz.	$J_{\text{B-F}}$, Hz.	Remarks
A. ^{19}F Spectra (reference $\text{CCl}_3\text{F} = 0$)						
Si_2BF_7	BF_2	47.4 ± 0.4 ^a	Broad quartet
	SiF_3	126.6 ± 0.6	351 ± 5	Unresolved triplet (?)
Si_3BF_9	SiF_2	143.5 ± 0.7	Broad singlet
	BF_2	46.6 ± 0.5	Broad doublet
	SiF_3	126.8 ± 0.6	355 ± 5	10.0 ± 0.3	...	Triplet
	$\beta\text{-SiF}_2$	141.8 ± 0.6	...	9.5 ± 0.3	...	Sextet
	$\alpha\text{-SiF}_2$	145.3 ± 0.6	Broad singlet
B. ^{11}B Spectra (reference $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2 = 0$)						
Si_2BF_7		-23.4 ± 0.3			122 ± 2	Broad triplet
Si_3BF_9		-24.5 ± 0.8			...	Broad singlet

^a Spacing between the two inner lines is 139 Hz.; spacing between the two outer lines is 351 Hz. Indicated error limits are standard deviations.

trifluoride (nominally 99.5% pure from the Matheson Co. and used without further purification) was introduced through a needle valve into the stream of silicon difluoride and unreacted silicon tetrafluoride emerging from the furnace. The pressure in this region was maintained at 0.2–0.3 mm., and the mole ratio of $\text{BF}_3:\text{SiF}_2$ was at least 2:1. The gases were condensed together in a trap cooled in liquid nitrogen. After 10–15 g. of this mixture had been condensed over a period of about 2 hr., silicon tetrafluoride and boron trifluoride were pumped away at -90° . The solid residue was then warmed to room temperature with pumping to take out the fraction containing volatile silicon-boron compounds. A creamy white, porous polymer mass was left in the trap; both this and the volatile fraction were exceedingly inflammable in air.

The yield of volatiles was 10–20% based on the silicon difluoride, with the highest yields being obtained when care was taken to condense the boron trifluoride and silicon difluoride at identical levels in the trap so that they were well mixed.

Two alternative methods for forming silicon-boron compounds were also tried. Either silicon tetrafluoride was treated with boron, or boron trifluoride with silicon. In each case the gas was passed over the solid contained in an inductively heated graphite tube. The graphite tube was enclosed by an evacuated quartz envelope and the gases emerging from the tube were pumped through a cold trap. A mixture of polymer and volatiles similar to those obtained directly from silicon difluoride and boron trifluoride was formed from both systems, but the yields of volatiles were rather poor.

The silicon-boron-containing volatiles were handled in a conventional high-vacuum line fitted with greaseless stopcocks (made by Springhams of Harlow, Essex, England). Temporary ground joints in the system were lubricated with Kel-F grease although Apiezon N was also fairly satisfactory. Silicone greases reacted rapidly with the boron-silicon compounds, methylfluorosilanes being among the compounds formed. The most volatile silicon-boron fraction was trapped in the range -48 to -59° , and another at -18 to -28° . A small amount of a less volatile fraction was collected at -10 to $+5^\circ$ but this was clearly inhomogeneous. The relative amounts of the three fractions were roughly 3:1:0.2.

The mass spectrum of the -48 to -59° fraction showed it to be essentially a single substance containing only silicon, boron, and fluorine. The heaviest ion observed, mass 181, clearly contained silicon and boron from the characteristic isotope ratios and was assigned to Si_2BF_6^+ . This was not the parent molecular ion, since the vapor density of the fraction indicated 201 ± 2 g. mole $^{-1}$ and thus the molecular formula of the compound was taken to be Si_2BF_7 .

The -18 to -28° fraction was also mainly a single substance containing Si-B-F. Its mass spectrum showed a molecular ion of mass 266 together with fragments indicative of the molecule Si_3BF_9 .

The least volatile fraction showed a complex mass spectrum suggesting the presence of at least $\text{Si}_4\text{BF}_{11}$ and $\text{Si}_5\text{BF}_{13}$, and perhaps higher compounds in this series. No compound of formula SiBF_5 , corresponding to SiF_3BF_2 or $\text{SiF}_2 \cdot \text{BF}_3$, was detected.

The polymer formed by condensing silicon difluoride with boron trifluoride and pumping off the volatiles contained only a few per cent of boron. It was a brittle, white solid which could be handled only in a dry nitrogen atmosphere. On heating to 150° under vacuum the polymer first lost some volatile silicon-boron-fluorine compounds, species up to $\text{Si}_6\text{BF}_{15}^+$ being detected mass spectrometrically, but on further heating to 250° it behaved more like a silicon difluoride polymer evolving only perfluorosilanes from SiF_4 to at least $\text{Si}_{13}\text{F}_{28}$.³

Mass spectra were taken with a Bendix Model 14-206A time-of-flight mass spectrometer (Bendix Corp., Cincinnati, Ohio). The inlet systems used for monitoring gas streams and studying polymers are described elsewhere.³

The infrared spectrum of Si_2BF_7 was recorded with a Beckman IR-9 instrument in a 10-cm. gas cell with KBr windows. The pressure of Si_2BF_7 in the evacuated cell was controlled by a cold trap connected directly to the cell.

N.m.r. spectra were obtained with a Varian HR-60 spectrometer operating at 19.25 (^{11}B) and 56.4 Hz. (^{19}F). Chemical shifts and multiplet line separations were measured from the recorded traces calibrated by the usual side-band techniques. Reference substances for chemical shift measurements, CCl_3F for ^{19}F and $(\text{C}_2\text{H}_5)_2\text{OBF}_3$ for ^{11}B , were contained in separate tubes

which were substituted for the sample tubes during the sweep to permit recording of sample and reference lines on the same spectrum.

The Structures of Si_2BF_7 and Si_3BF_9

The structures of Si_2BF_7 and Si_3BF_9 were conveniently determined by measurement of their ^{19}F and ^{11}B nuclear magnetic resonance spectra, the results of which are shown in Table I.

The boron chemical shifts in both compounds were in the region of the shifts in B_2F_4 (-23 p.p.m.)^{6a} and HBF_2 (-22 p.p.m.),^{6b} strongly suggesting that the boron was three-coordinate. The boron resonance in Si_2BF_7 was a broad 1:2:1 triplet, separation *ca.* 122 Hz., indicating two directly bonded fluorine atoms and thus the presence of a $-\text{BF}_2$ group. The broadness of the boron resonance is due to ^{11}B quadrupole relaxation. In Si_3BF_9 this relaxation almost completely obliterated the expected triplet structure, and the boron resonance appeared as a broad line with barely discernible shoulders.

The low-field multiplet (δ 47.4 p.p.m.) in the fluorine spectrum of Si_2BF_7 was a broad quartet of the type typically found in unsymmetrical fluoroboranes and was assigned to the $-\text{BF}_2$ group as seen in the ^{11}B spectrum. In the absence of quadrupole effects the spectrum would be expected to consist of four equally spaced lines of equal intensity with separation equal to $J_{\text{B-F}}$. Quadrupole relaxation of the ^{11}B nucleus could produce a partial collapse of the multiplet in such a way that the separation between the outer pairs of lines becomes smaller than the separation between the inner lines^{6b,7} as was observed. In the corresponding multiplet of Si_3BF_9 (δ 46.6 p.p.m.), the quadrupole collapse was more complete, and the resonance appeared as a broad doublet. The extent to which these lines in the fluorine spectra of the two compounds were broadened parallels the broadening observed in the boron spectra. The chemical shifts of the boron-bonded fluorine atoms are somewhat lower than in most X-BF_2 compounds,⁸ but, rather interestingly, are very close to the shift in B_2F_4 (52 p.p.m.).^{6a}

The remaining lines in the spectrum of Si_2BF_7 , at 126.6 and 143.5 p.p.m., were assigned respectively to a $-\text{SiF}_3$ and a $-\text{SiF}_2$ group on the basis of intensities and comparison of the chemical shift values with perfluorotrisilane, Si_3F_8 .³ These lines were broad envelopes with a suggestion of triplet structure in the $-\text{SiF}_3$ peak, most probably caused by coupling with the adjacent $-\text{SiF}_2$ fluorine atoms. The broadening observed may be due to a combination of coupling of the fluorine with the boron and the quadrupole relaxation of the boron. A similar effect has been observed in perfluorovinylboron compounds.⁹

These results strongly suggest that the structure of Si_2BF_7 is $\text{SiF}_3\text{SiF}_2\text{BF}_2$, perfluorodisilanylboron difluoride (alternatively named perfluoroborodisilane).

(6) (a) J. J. Ritter, T. C. Farrar, and T. D. Coyle, unpublished observations; (b) T. C. Farrar and T. D. Coyle, *J. Chem. Phys.*, **41**, 2612 (1964).

(7) J. Bacon, R. J. Gillespie, and J. W. Quail, *Can. J. Chem.*, **41**, 3063 (1963).

(8) T. D. Coyle, S. L. Stafford, and F. G. A. Stone, *J. Chem. Soc.*, 3103 (1961).

(9) T. D. Coyle, S. L. Stafford, and F. G. A. Stone, *Spectrochim. Acta*, **17**, 968 (1961).

The gradation of physical properties between Si_2BF_7 and Si_3BF_9 indicated that the compounds differed only by a $-\text{SiF}_2$ group in a straight Si-Si chain. This observation was confirmed by the fluorine n.m.r. spectrum of Si_3BF_9 , which showed three resonances of similar intensities and in similar positions to those observed for Si_2BF_7 , together with a fourth resonance at 141.8 p.p.m. This last was assigned to a $-\text{SiF}_2$ group adjacent to a $-\text{SiF}_3$ group as in the structure $\text{SiF}_3\text{-SiF}_2\text{SiF}_2\text{BF}_2$. The resonance was a sextet with intensities approximately in the ratio 1:5:10:10:5:1. This may have arisen from accidental overlap of lines arising from the coupling of the fluorine atoms of this group with those of the adjacent $-\text{SiF}_3$ and $-\text{SiF}_2$ groups. If these two coupling constants were almost equal, the expected quartet of triplets would overlap to give the observed spectrum. Spectra taken under "high magnification" suggested that this overlap is not perfect, supporting the above conclusions. The resonance at 126.6 p.p.m., assigned to a $-\text{SiF}_3$ group, was a triplet due to coupling with the adjacent $-\text{SiF}_2$ group; J_{FSiSiF} was about 10 Hz., close to the value found in Si_3F_8 .³ Thus, Si_3BF_9 is very probably $\text{SiF}_3\text{SiF}_2\text{SiF}_2\text{BF}_2$, perfluorotrisilanylboron difluoride (alternatively named perfluoro-1-borotrisilane).

The infrared spectrum of Si_2BF_7 agrees with the assigned structure of $\text{SiF}_3\text{SiF}_2\text{BF}_2$. The principal bands are given in Table II. The group of bands in the 840-900- and 970-1030-cm.⁻¹ regions are characteristic of the perfluorosilanes,³ and the bands in the 1200-1500-cm.⁻¹ region are found in other compounds containing BF_2 groups like B_2F_4 ¹⁰ and BrBF_2 .¹¹

Table II. The Infrared Spectrum of Si_2BF_7 ^a

Absorption, cm. ⁻¹	Intensity	Absorption, cm. ⁻¹	Intensity
422	s	974	vs
639	w	1005	m
694	w	1031	m
722	w	1249	s
844	s	1287	m
847	s	1383	s
896	m	1449	m
945	m	1461	m
		1502	w
		1512	w

^a 10-cm. gas cell, KBr windows, 0.1-2.0 cm. pressure.

The mass spectra of Si_2BF_7 and Si_3BF_9 shown in Table III are complex and do not help much in the detailed interpretation of structure. No parent ion was observed from Si_2BF_7 , the ions with lowest appearance potentials being at *m/e* 132 and 115 corresponding to Si_2F_4^+ and SiBF_4^+ . These may have been formed by processes such as



A parent ion was observed for Si_3BF_9 , the main fragment ions being Si_3F_6^+ , Si_2F_4^+ , and SiBF_3^+ . As in Si_2BF_7 , cleavage of the Si-B bond to form an ion of type $\text{Si}_n\text{F}_{2n+1}^+$ was not favored. Ions of this type are,

(10) J. N. Gayles and J. Self, *J. Chem. Phys.*, **40**, 3530 (1964).

(11) L. P. Lindeman and M. K. Wilson, *ibid.*, **24**, 242 (1956).

Table III. Mass Spectra of Si₂BF₇ and Si₃BF₉

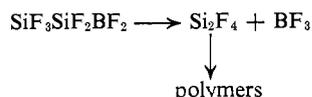
m/e	Probable identity	Relative ion abundances (Si ₂ F ₄ ⁺ = 100)			
		Si ₂ BF ₇		Si ₃ BF ₉	
		70 e.v.	17 e.v.	70 e.v.	17 e.v.
96	SiBF ₃ ⁺	8.0	11.0	114	95
115	SiBF ₄ ⁺	144	71	86	18.0
132	Si ₂ F ₄ ⁺	100	100	100	100
151	Si ₂ F ₅ ⁺	22.0	3.0	40	45
162	Si ₂ BF ₆ ⁺	<1.0	...	6.6	7.0
181	Si ₂ BF ₆ ⁺	59	<1.0	28.5	12.1
198	Si ₃ F ₆ ⁺	14.5	24.0
200	Si ₂ BF ₇ ⁺
217	Si ₃ F ₇ ⁺	2.2	<0.1
247	Si ₃ BF ₈ ⁺	23.8	6.2
266	Si ₃ BF ₉ ⁺	<1.0	4.7

however, commonly formed from the perfluorosilanes by breaking either a Si-F or a Si-Si bond.³

Properties of Si₂BF₇ and Si₃BF₉

Both compounds are colorless liquids at room temperature (Si₂BF₇: m.p. 0°, b.p. 42°; Si₃BF₉: m.p. 11–12°, b.p. 85°). They ignite spontaneously in air, burning with a bright green flame. They are rapidly but incompletely hydrolyzed by water, forming a white mass which will evolve some silanes on treatment with aqueous HF.³

The compounds are thermally stable to at least 200° in the vapor state. At higher temperatures slow decomposition to oily polymers takes place. When a sample of Si₂BF₇ was passed through a tube packed with quartz wool at 500° in a fast stream of helium, most of the compound was decomposed. Boron trifluoride was the main gaseous product and crystalline polymers were deposited along the Pyrex tubing beyond the hot zone. Some silicon was deposited on the quartz wool. Since no perfluorosilanes were formed, the first stage in decomposition may be the transfer of fluorine from silicon to boron, followed by polymerization of the resulting Si₂F₄ moiety



At 700° rapid and complete decomposition of Si₂BF₇ to silicon, silicon tetrafluoride, and boron trifluoride occurred.

The reaction of Si₂BF₇ with iodine is slow and complex. With excess iodine at elevated temperatures, BI₃, BF₃, SiI₄, and SiF₄ were the end products. With less iodine, Si₂F₆ was also isolated in good yield, suggesting that the primary attack of the iodine is on the Si-B bond rather than the Si-Si bond.

Triethylamine reacts smoothly at low temperatures with Si₂BF₇ to form a liquid complex Si₂BF₇·N(C₂H₅)₃. This is rather involatile, but its identity was first established mass spectrometrically from the presence of the ions SiBF₄N(C₂H₅)₃⁺ (mass 216), Si₂BF₇⁺ (mass 200), and other smaller fragments. No molecular ion was observed. On standing for a few hours the liquid complex became dark brown in color and very viscous, but it has remained in this form without further decomposition for many months at room temperature.

An explosion occurred on condensing liquid carbon monoxide onto solid Si₂BF₇. However, the reaction in

the vapor state is slow even at elevated temperatures and results in a very complicated mixture of compounds including some perfluorosilanes and one compound of molecular formula Si₂BF₅CO.

There was no reaction between tetrafluoroethylene and Si₂BF₇ in the gas phase at temperatures up to 130°.

Mechanism of the Reaction of Boron Trifluoride and Silicon Difluoride

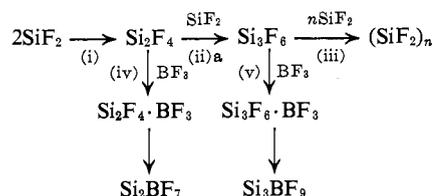
There are three interesting facts about the reaction of silicon difluoride and boron trifluoride which give clues to a possible mechanism.

(1) Gaseous boron trifluoride has not been observed to react with silicon difluoride. The rate of decay of SiF₂ gas at room temperature in the presence of boron trifluoride is only slightly faster than in the presence of an equal pressure of nitrogen. In addition, a mixture of equal amounts of SiF₂ gas and BF₃ passed through a cooled tube at a total pressure of 0.2 mm. did not react together until the dew point of the BF₃ was reached (ca. -160°), although the SiF₂ gas was fully condensed below -70°.

(2) The formation of silicon-boron compounds is dependent on boron trifluoride being present at the moment silicon difluoride condenses. For example, when boron trifluoride was condensed on a layer of silicon difluoride which had been condensed a few seconds previously at -196°, no silicon-boron compounds were formed. Yet silicon difluoride condensed on a layer of boron trifluoride at -196° formed detectable amounts of Si₂BF₇ and its homologs.

(3) No SiBF₅ is formed. The simplest compound which is made, Si₂BF₇, contains a Si-Si bond.

A possible explanation of these observations is that the first step in the reaction is the dimerization of the SiF₂ to form a diradical or unsaturated species, Si₂F₄. This species adds on additional SiF₂ groups rapidly to form Si₃F₆, Si₄F₈, ... (SiF₂)_n, where *n* may be as great as 20. Boron trifluoride may add on to these "unsaturated" compounds to form intermediates like Si₂F₄·BF₃ which could rearrange to Si₂BF₇.



If reactions ii and iii are very rapid compared with iv and v, only at low temperatures in the presence of condensed BF₃ will much Si₂BF₇ and Si₃BF₉ be formed. Yields fall off rapidly along the series Si₂BF₇, Si₃BF₉, Si₄BF₁₁, Si₅BF₁₃, which is as expected since reaction iv should be faster than v and so on. Preliminary argon matrix isolation infrared experiments have shown that SiF₂ begins to polymerize in the temperature range 20–40°K. It is hoped that this technique will enable the reaction with BF₃ to be followed over this same temperature range.

The System Si-B-F-Cl

When boron trichloride was used in place of boron trifluoride in the reaction with silicon difluoride, condensation of the gas mixture at -196° gave a bright

blue deposit. On warming this to room temperature excess silicon tetrafluoride was pumped away and a number of other volatile liquid fractions were obtained, together with a residue of a white spontaneously inflammable polymer. Mass spectrometric investigation of the liquid fractions showed that extensive exchange of fluorine and chlorine between the silicon and boron had occurred. No ion containing boron was observed except BF_2^+ . However the predominance at low electron voltages of ions of the type $\text{Si}_n\text{F}_{2n-z}\text{Cl}_z^+$ suggests that compounds of the type $\text{Si}_n\text{F}_{2n+1-z}\text{Cl}_z\text{BF}_{2-x}\text{Cl}_x$ (where $x = 2$ to 0 and z was observed to be 3 to 0) were present in

the mixture, as both Si_2BF_7 and Si_3BF_9 readily give Si_2F_4^+ and Si_3F_6^+ , respectively, on electron impact.

Acknowledgments. We gratefully acknowledge the support of this work at Rice University by the Advanced Research Projects Agency, under a contract administered by the Army Research Office at Durham. We thank Dr. S. Slaymaker of the Shell Refinery, Houston, Texas, for helping initiate the n.m.r. studies of the compounds, Dr. K. Sathianandan for helpful comments on the infrared spectra, and Mr. Dechard Stump for assistance in preparing and purifying many of the samples studied.

Kinetics of the Decomposition of Tetraperoxychromate(V) Ion in Basic Solution

Denis Quane and Joseph E. Earley

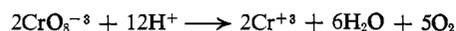
Contribution from the Department of Chemistry, Georgetown University, Washington, D. C. Received April 15, 1965

The rate of decomposition of tetraperoxychromate ion in basic 3 M NaClO₄ follows the rate law $R = k_1[H^+][\text{CrO}_8^{-3}]_{\text{total}}/[H^+] + k''$, where $k_1 = 1.04 \text{ min.}^{-1}$ and $k'' = 6.9 \times 10^{-8} \text{ M}$ at 30°; at 40° $k_1 = 1.4 \text{ min.}^{-1}$, $k'' = 4.0 \times 10^{-8} \text{ M}$; at 50° $k_1 = 1.9 \text{ min.}^{-1}$, $k'' = 2.5 \times 10^{-8} \text{ M}$. The presence of NH_4^+ , CO_3^{-2} , EDTA, O_2 , or H_2O_2 causes little or no change in the rate. A mechanism involving unimolecular decomposition of a protonated peroxychromate(V) ion is proposed.

Hydrogen peroxide reacts with chromates in basic solution to give brown crystals of tetraperoxides, M_3CrO_8 . These compounds decompose in basic solution according to the equation¹



The structure of the tetraperoxychromate(V) ion has been well established and the presence of chromium in the +5 oxidation state confirmed.² The kinetics of the decomposition is not as well known. Bogdanov³ has studied the kinetics of this reaction by following the rate of oxygen evolution. In basic solution the rate is first order in $[\text{CrO}_8^{-3}]$. The reaction in acid solution is said to be more complex, there being two modes of decomposition: by means of the equation above, and also by the equation



The mechanism of the first-order decomposition in basic solution has not been established. The reaction lends itself readily to study spectrophotometrically and titrimetrically (using a pH-Stat); these methods should yield results of greater accuracy than can be obtained from oxygen evolution.

(1) E. H. Riesenfeld, H. E. Wohlers, and W. A. Kutsch, *Ber. deut. chem. Ges.*, **38**, 1885 (1905).

(2) J. A. Connor and E. A. V. Ebsworth, *Advan. Inorg. Chem. Radiochem.*, **6**, 301 (1964).

(3) G. A. Bogdanov, *Zh. Fiz. Khim.*, **25**, 61 (1951); *Chem. Abstr.*, **45**, 6028f (1951); *Tech. Trans.*, **11**, 1176 (1964), OTS 63-23208.

Experimental

Potassium peroxychromate(V) was prepared by the reaction of hydrogen peroxide with chromium trioxide⁴ in the presence of KOH. Samples were analyzed for potassium by ion exchange and for chromate spectrophotometrically at 370 μ after decomposition. *Anal.* Calcd. for K_3CrO_8 : K, 39.46; Cr, 17.49. Found: K, 38.49; Cr, 17.82. All other reagents were prepared and purified by standard methods.

Reactions were followed on a Sargent pH-Stat, a Cary Model 14 spectrophotometer at 370 μ , and a Warburg apparatus. On the pH-Stat, solid K_3CrO_8 was dissolved in water having a concentration of NaClO_4 calculated to bring the total, nominal ionic strength to 3 M and sufficient NaOH to give the desired pH. The rate of decomposition of the sample was followed from the point at which dissolution was complete. For reactions followed on the Cary spectrophotometer and the Warburg apparatus, aliquots of a stock solution of K_3CrO_8 in 0.1 M NaOH were mixed with solutions containing sufficient NaClO_4 and buffer to make the final solutions 0.1 M in buffer with 3 M total, nominal ionic strength. pH measurements of reactions followed using the pH-Stat were made on the instrument itself. The pH of all other solutions was measured using a Beckman Model G pH meter. Reaction mixtures were thermostated to $\pm 0.1^\circ$.

First-order rate constants were calculated using an IBM 1620 computer, programed to find the values of D_∞ and k giving the best straight-line fit to the equation

$$\ln(D_\infty - D) = \ln(D_\infty - D_0) + kt$$

by least-squares analysis where D represents volume of acid added to maintain pH for reactions followed on the pH-Stat. When points taken over two half-times were used, values of D_∞ so computed agreed well with

(4) G. Brauer, "Handbuch der Preparativen Anorganischen Chemie," Vol. 2, Georg Thieme Verlag, Stuttgart, 1962, p. 1216.