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Structure and Properties of the Condensed Phosphates. XIII. Refractometry

BY EDWARD J. GRIFFITH

RECEIVED JULY 26, 1956

The refractive indices, n^{25}_{D}, of aqueous solutions of condensed sodium phosphates have been measured as a function of concentration and the number average chain length of the phosphates. The concentration contribution of end groups and middle groups to refractive index was determined. The apparent molar refractions of several sodium phosphates were determined as a function of concentration and interpreted in terms of the polarizability of the phosphate anions. An expression was developed for the dependence of the density at 25.0° of aqueous solutions of sodium phosphates as a function of concentration and Na_2O/P_2O_5 ratio. A new, very rapid method of determining the number average chain length of condensed phosphates by end-group titrations is described.

Introduction

Many of the physical properties of condensed phosphates have been studied in recent years, but the optical methods have received very little attention. In particular, the refractive indices of solutions of phosphates have not been investigated although the refractive indices of the solid crystals and glassy phosphates have been studied.

It is the purpose of this study to correlate the refractive properties of aqueous solutions of sodium phosphates with modern theories[1] of their structures. Also, many useful applications of the refractometer are demonstrated which greatly reduce the work and time required to characterize condensed phosphate glasses.

Several methods exist for characterizing condensed phosphates, but probably the most simple and reliable method is by end-group titrations of aqueous solution of the phosphates.[1-3] Van Wazer has shown that the intrinsic viscosity of polyphosphates is a linear function of their average chain lengths.[4] Light scattering[5] as well as ultracentrifuge methods have also been employed.[6,7]

The work reported in this article has been based upon the end-group titration methods, and all values of average chain lengths were measured in this manner. A new method of determining the average chain lengths of short-chain glass ($2 \leqslant \bar{n} < 100$) by end-group titration which eliminates the hydrolysis procedure was developed and will be discussed.

Experimental

The chemicals used throughout this work were either reagent grade or were prepared and purified by the more or less standard practices employed in the chemistry of phosphates.

The refractometer employed was a Bausch and Lomb Precision instrument which has been shown to have a precision of about ± 0.00003 unit under ideal conditions.[8] The temperature of the refractometer was controlled at $25.00 \pm 0.05°$ with a water-bath purchased from the Precision Scientific Company.

Several light sources were employed with the refractometer. A sodium vapor lamp was used for most of the measurements, but the 546 mμ and 486 lines of mercury were also used with the aid of filters and a mercury vapor lamp.

The solutions used in the work were prepared by weighing a quantity of phosphate into a volumetric flask, diluting the flask to the mark at room temperature, and diluting aliquots of the original solution to prepare the other samples used in a series.

The density measurements were made with a jacketed pycnometer of the overflow type. The solutions were thermostated to 25.0° until just prior to their measurement. Then they were transferred to the pycnometer and weighed. The same solutions were used to make the density measurements that were used in the refractive index measurements.

Ion-exchange Neutralization.—Treat the weak cation-exchange resin, Amberlite IRC-50, with excess sodium hydroxide solution for one day. Then filter the resin from the

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[1] J. R. Van Wazer, THIS JOURNAL, **72**, 647 (1950).

[2] J. R. Van Wazer, E. J. Griffith and J. F. McCullough, *Anal. Chem.*, **26**, 1755 (1954).

[3] E. J. Griffith, *ibid.*, **28**, 525 (1956).

[4] J. R. Van Wazer, THIS JOURNAL, **72**, 906 (1950).

[5] U. P. Strauss, E. H. Smith and P. L. Wineman, *ibid.*, **75**, 3935 (1953).

[6] O. Lamm, *Arkiv Kemi. Mineral. Geol.*, **25**, 1 (1949).

[7] C. F. Callis, J. R. Van Wazer and P. G. Arvan, *Chem. Revs.*, **54**, 777 (1954).

[8] A. Weissberger, "Physical Methods of Organic Chemistry," 2nd ed., Interscience Publishers, New York, N. Y., 1949.

basic solution and wash it with about four volumes of water for each volume of resin. Air-dry the resin until it is free-flowing and then bottle it until used.

Place one gram of the resin in a 50-ml. beaker, and add 10 ml. of the phosphate solution containing 5 g. of phosphate per 100 ml. to the beaker and stir it with a magnetic stirrer for 15 minutes. Measure the refractive index of the solution. Figure 1 is a typical curve obtained from the above procedure. With refractometers capable of reading refractive indices to only four decimals the concentration of phosphate glass and resin should be doubled in this procedure. The resin completely replaces the hydrogen ions of the glassy phosphates with sodium ions, and no interfering reagents are required. Small variations may occur as new batches of resins are employed, but since two pounds of resin are sufficient for about one thousand determinations, this presents no serious problem.

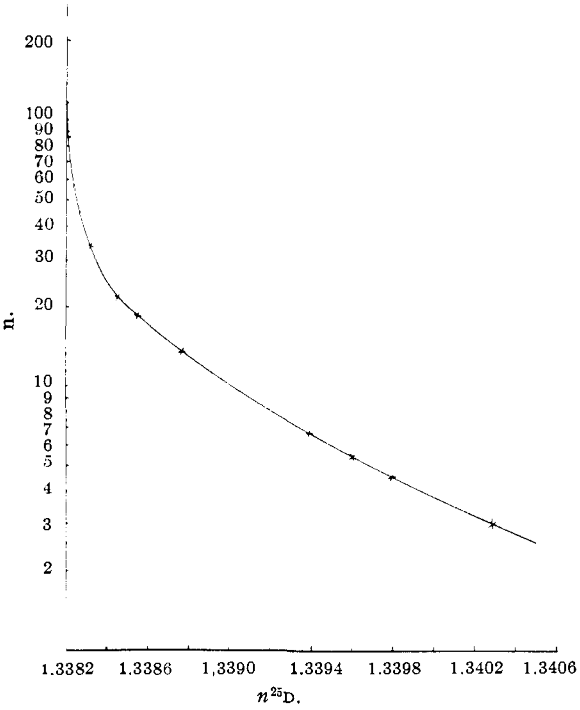


Fig. 1.—The change of refractive index of sodium polyphosphate solutions as the average chain length of the phosphate is changed.

End-group Titration.—Accurately weigh about 2 to 5 g. of sodium phosphate glass into a 250-ml. beaker, and add 50 to 100 ml. of water. Titrate the sample from its natural *p*H to the end-point near *p*H 8.5. This determines the hydrogen ions associated with the glass and will be referred to as titration A. Then add enough hydrochloric acid (6 *N*) to the solution to bring the *p*H of the solution to about *p*H 4. Retitrate the sample from the end-point near *p*H 4 to the end-point near 8.5. This is a measure of the end group constituent of the glass and will be referred to as titration B. The following relationships exist for sodium phosphates.

$$Y = \frac{W + (N\cdot\text{ml}_A)(0.0220) - (N\cdot\text{ml}_B)(0.1330)}{0.1020} \quad (1)$$

where

W = weight of phosphate in g.
N = normality of base employed
ml_A and ml_B = ml. of base used in titrations A and B, respectively
Y = meq. of middle groups in the sample
(0.0220) = meq. wt. of sodium minus the meq. wt. of hydrogen
(0.1330) = meq. wt. of a sodium phosphate end group
(0.1020) = meq. wt. of a middle group

$$X = N\cdot\text{ml}_B \quad (2)$$

X = the meq. of end groups in the sample

thus

$$\bar{n} = \frac{2Y}{X} + 2 \quad (3)$$

Discussion and Results

Refractive Index *versus* Chain Length and Concentrations.—It generally has been found that a graph of refractive index, *n*, of a sodium phosphate *versus* the concentration of the phosphate yields a straight line. It is, therefore, convenient to give the relationships in terms of the slope of a straight line. Table I is a compilation of the slope coefficients for use with the phosphates studied in this work. For convenience, the units in Table I are expressed as gram formula-weights of phosphorus per l. of solution. The units may be easily converted to other systems as desired (*e.g.*, as g./l. or mole/l., etc.) by multiplying the units by the appropriate factor.

A relationship exists between the average chain length of a sodium phosphate glass and the refractive index of a solution of the glass. Since the refractive index of a solution is also concentration dependent, the concentration of phosphate glass used to calibrate a curve of *n versus* n̄ must be at some fixed value of concentration. The curve shown in Fig. 1 was obtained by dissolving 5.000 g. of sodium phosphate in enough water to yield 100.0 ml. of solution adjusting the *p*H of the solution, and then determining the refractive index at 25°.

TABLE I

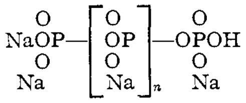
THE REFRACTIVE INDEX, n^{25}, OF SODIUM AND POTASSIUM PHOSPHATE AS A FUNCTION OF CONCENTRATION AND LIGHT SOURCE[a]

$$n^{25}_{\text{D}} = AC + n'^{25}_{\text{D}}$$
$$n^{25}_{\lambda=546} = AC + n''^{25}_{\lambda=546}$$

Phosphate	*A* To obtain formula wt. P/l. × 10²	To obtain g./100 ml. × 10³
NaH_2PO_4	1.380	1.150
Na_2HPO_4	2.266	1.594
$Na_4P_2O_7$	2.209	1.658
$Na_5P_3O_{10}$	1.778	1.450
$Na_3P_3O_9$	1.034	1.016
$Na_4P_4O_{12}$	1.128	1.106
Glassy sodium phosphate, n̄ = 5.4	1.496	1.319
Glassy sodium phosphate, n̄ = 18	1.206	1.144
Glassy sodium phosphate, n̄ = 87	1.099	1.070
KH_2PO_4	1.841	1.056
K_2HPO_4	2.369	1.360
$K_4P_2O_7$	2.272	1.376

[a] A = the constant for each phosphate when C is expressed in the appropriate concentration units. n' and n'' = the refractive indices of the water used to prepare the solutions measured at λ = 589 mμ and λ = 546 mμ, respectively.

Unless a phosphate glass is heated for a long time or otherwise treated to remove the final traces of the water of composition, at least half of the end groups of the glass may contain hydrogen ions rather than sodium ions as the cation. Example



$$\mathrm{NaO}\overset{\mathrm{O}}{\underset{\mathrm{\underset{Na}{O}}}{\mathrm{P}}}-\left[\mathrm{O}\overset{\mathrm{O}}{\underset{\mathrm{\underset{Na}{O}}}{\mathrm{P}}}\right]_n-\mathrm{O}\overset{\mathrm{O}}{\underset{\mathrm{\underset{Na}{O}}}{\mathrm{P}}}\mathrm{OH}$$

The hydrogen contributes very little to the refractive index of the solution and, consequently, an appreciable error is introduced.

One solution to the above problem would be to adjust the *p*H of each solution to some fixed value (*e.g.*, *p*H 8.5), but this is awkward since *p*H and concentration must be held constant and no additional buffering reagents may be added without causing errors. The problem was solved by treating the sample with a small quantity of the sodium form of the weak cation-exchange resin, Amberlite IRC-50. For details of the procedure, see Ion-exchange Neutralization in the Experimental section.

The ion-exchange technique was employed only as a practical method for determination of $\bar{n}$ of glassy phosphates with the refractometer. In all other instances, the *p*H of the solutions was adjusted with NaOH to neutralize completely the phosphates if the phosphate was not already neutralized.

From Table I it is seen that the disodium ortho- and tetrasodium pyrophosphates each have almost the same refractive index at the same concentration based on formula-weights of phosphorus, *i.e.*, both ortho- and pyrophosphates are composed entirely of end groups.[9]

Sodium trimetaphosphate is composed of middle groups only and contributes to the refractive index as though it were very long chains. This clearly illustrates that the refractive index of a sodium phosphate depends almost entirely upon the concentration of the phosphate and the Na_2O/P_2O_5 ratio of the phosphate and not upon the molecular complexity of the phosphate anions. With the exception of sodium tetrametaphosphate, the complexity of the phosphate structure does not influence the refractive index of the solution. As a result of this fact, one can assign a concentration–refractive index, dependence upon end and middle groups.

The equation developed for the concentration dependence of the refractive index of end and middle groups is

$$\begin{aligned} n^{25}\mathrm{D} &= A(C_{\mathrm{ends}}) + B(C_{\mathrm{mids}}) + n(\mathrm{water}) \\ &= 0.0216_8(C_{\mathrm{ends}}) + 0.0102_9(C_{\mathrm{mids}}) + n(\mathrm{water}) \end{aligned} \tag{4}$$

C is the concentration of end or middle groups expressed in moles/l.

Equation 4 is merely another way of expressing the Na_2O/P_2O_5 of the dissolved phosphates. An interesting example of the contribution of sodium ions to the refractive index occurs in the orthophosphate system. As the Na_2O/P_2O_5 ratio is increased, a family of straight-line curves is obtained when the refractive index is plotted as a function of concentration of the orthophosphate. As the Na_2O/P_2O_5 ratio of the salt increases, the slope of the lines increase in the graph mentioned above.

End-group Titration.—A new method of determining $\bar{n}$ by the end-group titration method was developed to characterize the glassy phosphates used in this work. The older methods were very time-consuming when a large number of short-chain-length sodium phosphates were to be characterized.[2,3] The hydrolysis step in the determination was the most time-consuming, and this step was eliminated. It has never been necessary to hydrolyze polyphosphates with average chain lengths greater than about 75 because the phosphate formula could be considered to be $(NaPO_3)_n$, and the strong acid function (middle groups) could be calculated from the weight of the sample without causing serious errors. The new method is based on the fact that the weight of a phosphate may be considered to be the sum of the weights of end groups and middle groups. The end groups may be determined by a single titration of a known quantity of phosphate. This allows the middle groups to be calculated from the weight and titration data. The hydrogen associated with a chain phosphate which has not been completely neutralized during the polymerization synthesis must be determined by a second titration on the sample to correct the weight of the sample to the sodium saturated condition.

The time required for characterizing a glass by the new method is about 5 min. as compared to one hour by the most rapid of the older methods. Table II is a comparison of the value of $\bar{n}$ determined by the old method and the new method of calculating $\bar{n}$. Any polyphosphate may be characterized by the method, but the method loses its significance when the chain length of the phosphate exceeds about 75 phosphorus atoms per average chain. For the details of this method see End-group Titration in the Experimental section.

Density.—Before molar refractions could be determined for the phosphates, it was necessary to determine the density of the phosphate solutions. It has been shown[10] previously that the density of an aqueous solution of a sodium phosphate glass is not a linear function when the concentration is very great (above *ca.* 25% phosphate), but in the concentration range below 25% phosphate, a nearly linear relationship exists. At concentrations up to 10% sodium phosphate, the experimental error in this work was greater than the deviation from a straight line. Therefore, the densities of "dilute" phosphate solutions may be calculated for a specific phosphate from the slope of the curves, density *versus* concentration.

TABLE II

THE TITRATION VALUES OF THREE SODIUM PHOSPHATE GLASSES DETERMINED BY THE NEW METHOD AND COMPARED TO THE HYDROLYSIS METHOD

$\bar{n}$, old method		$\bar{n}$, new method	
5.3_8	5.3_1	5.4_5	5.3_6
13.9	13.8	13.9	14.0
17.9	17.9	17.9	17.9

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[9] For a complete discussion of phosphate structures see J. R. Van Wazer and E. J. Griffith, THIS JOURNAL, **77**, 6140 (1955).

[10] J. R. Van Wazer, *Ind. Eng. Chem.*, **41**, 189 (1949).

Table III is a compilation of coefficients, B, for the calculation of densities.

It was found empirically that a graph of $\sqrt{B}$ *vs.* the P/Na ratio of a sodium phosphate glass was also a straight line, thus allowing the calculation of density of any "dilute" sodium polyphosphate glass solution. The error of several calculated values was no greater than ±0.0003 g./ml. from the measured values. Figure 2 shows a graph of these data.

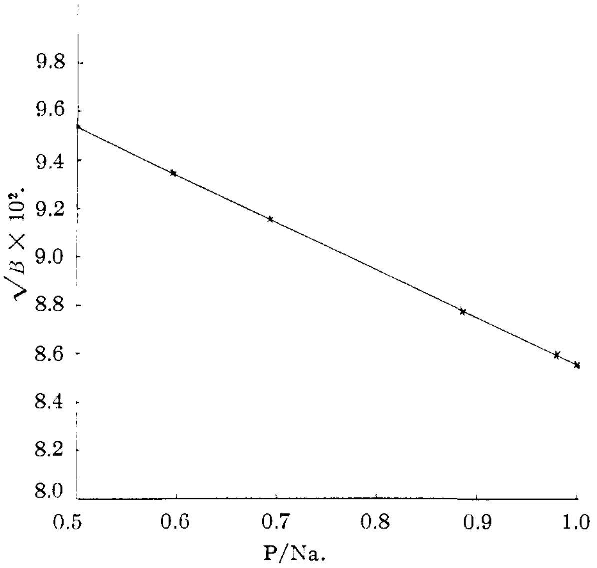

Fig. 2.—The change of the square root of the density coefficient of aqueous solutions of sodium polyphosphates with changes in the P/Na ratio of the phosphate.

The apparent molar refractions,[8] [R$_{\text{app}}$], were measured for the phosphate series by the use of eq. 5.

$$[\mathrm{R_{app}}] = \frac{n^2 - 1}{n^2 + 2} \frac{M_1 + W_0}{d} - r_0 W_0 \qquad (5)$$

where

n = refractive index
M_1 = molecular weight of solute
W_0 = weight of solvent
d = density of solution
r_0 = specific refraction of the solvent

It was found that the molar refraction of phosphates in aqueous solution vary with the concentration of the phosphate at a fixed wave length of radiation. This also has been observed with other electrolytes dissolved in aqueous and non-aqueous solvents.[11]

As shown in Tables IV and V, all of the phosphates increased in molar refraction as the solution was diluted. Under comparable conditions the metaphosphates exhibit a greater change with concentration than the polyphosphates. Following the reasoning of Fajans and Johnson, this may be interpreted to mean that the metaphosphate molecule is more polarizable than the other phosphates studied.

TABLE III

THE DENSITY OF AQUEOUS SOLUTIONS OF SODIUM PHOSPHATES AS A FUNCTION OF CONCENTRATION AT 25°[a]

$d_{25} = BC + d'_{25}$

Phosphate	$B \times 10^3$	$\sqrt{B} \times 10^2$
Na_2HPO_4[b]	8.42	9.18
$Na_4P_2O_7$	9.20	9.59
$Na_5P_3O_{10}$	8.77	9.36
$Na_3P_3O_9$	7.32	8.56
$Na_4P_4O_{12}$	7.53	8.68
Phosphate glass, $\bar{n}$ = 4.6	8.40	9.17
Phosphate glass, $\bar{n}$ = 16	7.61	8.78
Phosphate glass, $\bar{n}$ = 87	7.40	8.61

[a] d_{25} = density of the phosphate solution; B = a constant for each phosphate; C = concentration of phosphate expressed in g./100 ml.; d'_{25} = density of water at 25°. [b] Disodium orthophosphate does not behave as the other members of the series and is not included in Fig. 2.

TABLE IV

THE APPARENT MOLAR REFRACTION OF SODIUM PHOSPHATES

$(n = n_{\mathrm{D}}^{25})$

Phosphate	Concn., g./l.	[R$_{\text{app}}$]	[R$_{\text{app}}$]/$\bar{n}$
Na_2HPO_4	50.0	28.26	28.26
	100.0	27.36	27.36
$Na_4P_2O_7$	50.0	53.05	26.52
	100.0[a]	52.52	25.76
$Na_5P_3O_{10}$	50.0	73.55	24.52
	100.0	71.49	23.83
Sodium phosphate glass, $\bar{n}$ = 5.4	50.0	123.0	22.78
	100.0	119.9	22.20
Sodium phosphate glass, $\bar{n}$ = 18	50.0	381.9	21.22
	100.0	373.4	20.74
Sodium phosphate glass, $\bar{n}$ = 87	50.0	1800	20.69
	100.0	1762	20.25
$Na_4P_4O_{12}$ (ring phosphate)	50.0	81.72	20.43
	100.0	79.62	19.91
$Na_3P_3O_9$ (ring phosphate)	50.0	61.19	20.40
	100.0	59.47	19.82

[a] $Na_4P_2O_7$ is not soluble to the extent of 100.0 g./l. at 25°, and the value given was obtained by extrapolation.

TABLE V

THE CHANGE OF MOLAR REFRACTION WITH CONCENTRATION AND MOLECULAR COMPLEXITY

$\Delta[\mathrm{R_{app}}]$ = [R$_{\text{app}}$] at 100.0 g./l. − [R$_{\text{app}}$] at 50.0 g./l.

Phosphate	$\Delta[\mathrm{R_{app}}]$	$\frac{\Delta[\mathrm{R_{app}}]}{\bar{n}}$	$\frac{\Delta[\mathrm{R_{app}}]}{\bar{n}} / \mathrm{Na_2O/P_2O_5}$
Na_2HPO_4	−0.90	−0.90	−0.45
$Na_4P_2O_7$	−1.6	− .80	− .40
$Na_5P_3O_{10}$	−2.06	− .69	− .41
Glassy phosphate, $\bar{n}$ = 5.4	−3.1	− .57	− .42
Glassy phosphate, $\bar{n}$ = 18	−8.5	− .47	− .42
Glassy phosphate, $\bar{n}$ = 87	−38	− .44	− .43
$Na_3P_3O_9$	−1.72	− .57	− .57
$Na_4P_4O_{12}$	−2.10	− .52	− .52

Table V relates the change in [R$_{\text{app}}$] with concentration to the molecular complexity of the phosphate. The polarizability of the phosphate per phosphorus atom in the molecule is expressed as

$$\frac{\Delta[\mathrm{R_{app}}]}{\bar{n} \text{ atoms per molecule}}$$

($\bar{n}$ refers to the average number of phosphorus atoms per chain or ring molecule-ion.) This value decreases as the average chain length $\bar{n}$ increases; but as the $\bar{n}$ increases, the concentration of sodium ions relative to phosphorus atoms decreases. The atmosphere of sodium ions is, therefore, greater

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(11) K. Fajans and O. Johnson, *Trans. Electrochem. Soc.*, **82**, 273 (1942).

for the shorter-chain-length phosphates. If the value, $\Delta[R_{app}]/\bar{n}$, is divided by the Na_2O/P_2O_5 ratio of the phosphate, the results are more nearly comparable. The members of the sodium polyphosphate system exhibit a nearly constant change of $\Delta[R_{app}]$ per $\bar{n}$ atoms per molecule per sodium ion per P atom. This is interpreted to mean that the sodium ions of a solution will cause about the same polarization in a phosphate group, irrespective of the size of the molecule-ion in which the phosphate group is found.

The orthophosphates and sodium tetrametaphosphate do not conform to the patterns exhibited by the other phosphates in this work. In Table I, disodium orthophosphate contributes slightly more to the refractive index of its solutions than tetrasodium pyrophosphate does when the salts are compared at concentrations of equal formula-weights of phosphorus.

Tetrametaphosphate contributes more to the refractive index of its solutions than does trimetaphosphate at the same concentration. The trimetaphosphate behaves normally (*i.e.*, as though it were very long chains). It may be seen from the data of Table IV that the contribution to molar refraction of each formula-weight of phosphorus in trimetaphosphate is smaller than any of the other phosphates studied.

Those compounds exhibiting high refractive properties also show high density-concentration relationships. In neither case are the differences large, but they are well beyond the limits of experimental error.

DAYTON, OHIO

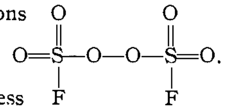
[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AT THE UNIVERSITY OF WASHINGTON, AND THE UNIVERSITY OF NEW ENGLAND]

Peroxydisulfuryl Difluoride

BY F. B. DUDLEY[1] AND G. H. CADY

RECEIVED APRIL 27, 1956

The high temperature reaction between fluorine and sulfur trioxide, the latter being kept in excess, results in the formation of a substance having the empirical formula $S_2O_6F_2$.[1a] The evidence obtained from its chemical reactions and its infrared and nuclear magnetic resonance spectra suggests that it has the structure shown. Strong infrared absorption bands occur at 755, 848, 1246 and 1495 cm.$^{-1}$. The substance is a colorless liquid at room temperature. It melts at −55.4° and boils at 67.1°.



$$\mathrm{O{=}\underset{F}{\overset{O}{\overset{\|}{S}}}{-}O{-}O{-}\underset{F}{\overset{O}{\overset{\|}{S}}}{=}O}$$

During the preparation of some fluorine fluorosulfonate,[2] b.p. −31.3° by the action of fluorine on sulfur trioxide, a small amount of a reactive by-product, liquid at room temperature, was obtained. The object of this investigation was to vary the reaction conditions in an effort to obtain this new compound in sufficient quantity to permit identification. A decrease in temperature was found to decrease the yield of fluorine fluorosulfonate but to increase the yield of the higher boiling material.

Experimental

(a) Streams of sulfur trioxide and fluorine, each diluted with nitrogen, were allowed to mix in a silver difluoride catalytic reactor[3] heated to 100°. The fluorine was present in excess and the gases, after reaction, were led through two traps cooled with Dry Ice and liquid air, respectively. Practically the entire product was condensed in the Dry Ice trap, and was very largely a new compound with the empirical formula $S_2O_6F_2$. No fluorine fluorosulfonate was obtained at this temperature.

The reactants were then allowed to mix at successively higher temperatures, and it was not till a temperature of 170° was reached that fluorine fluorosulfonate was readily detected in the reaction products. At 190°, the amount of fluorine fluorosulfonate in the mixture of reaction products had increased to over 90%, the remainder being essentially $S_2O_6F_2$. At temperatures from 220 to 280° the amount of $S_2O_6F_2$ was negligible, the product being essentially fluorine fluorosulfonate whilst fluorine was present in excess.

On two occasions, although the rate of flow of fluorine was unchanged, combustion of the metal packing apparently occurred, for no fluorine could be detected in the exit gases. Under these circumstances the product obtained was essentially $S_2O_6F_2$. The production of peroxydisulfuryl difluoride at high temperature thus appears to require an excess of sulfur trioxide.

(b) A mixture of nitrogen, fluorine and sulfur trioxide vapor was passed into a one inch diameter nickel tube 18 inches long and heated to 250°. The products, collected as before, consisted of a mixture of SO_3F_2 and $S_2O_6F_2$ in approximately equal amounts. The crude materials obtained by methods (a) and (b) were distilled to obtain $S_2O_6F_2$ of moderate purity.

(c) Sulfur trioxide and fluorine fluorosulfonate, the former in small excess, were mixed in a 500-cc. glass bulb, the total pressure in the bulb being about two thirds of an atmosphere. No reaction occurred at room temperature, but after holding the bulb at about 300° for a minute a substance, liquid at room temperature, was separated from the reaction products. Its boiling point, melting point and infrared spectrum showed that it was the same compound as that obtained by methods (a) and (b).

Analyses.—A weighed sample of the compound was caused to react with an excess of sodium hydroxide solution and the solution was then heated overnight on a steam-bath to ensure the complete hydrolysis of any fluorosulfonate ions formed initially. Separate aliquots of this solution were used in the analyses for sulfur and fluorine. The sulfur was determined gravimetrically as barium sulfate and the fluorine by titration with thorium nitrate using sodium alizarin sulfonate as indicator.[4] Prior to titration the fluoride was separated from interfering sulfate ions by steam distillation of SiF_4 from a perchloric acid solution.

Anal. Calcd. for $S_2O_6F_2$: S, 32.42; F, 19.2. Found: S, 32.15, 31.93; F, 18.5, 18.9.

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(1) The University of New England, Armidale, N.S.W., Australia.

(1a) U. Wannagat and G. Mennicken (*J. anorg. allgem. Chem.*, **278**, 310 (1955)) have produced a peroxy-compound probably having the empirical formula $S_2O_6F_2$. It differs considerably in properties from peroxydisulfuryl difluoride. The two do not appear to be identical compounds

(2) F. B. Dudley, G. H. Cady and D. F. Eggers, Jr., THIS JOURNAL, **78**, 290 (1956).

(3) K. B. Kellogg and G. H. Cady, *ibid.*, **70**, 3986 (1948).

(4) R. H. Kimball and L. E. Tufts, *Ind. Eng. Chem.*, *Anal. Ed.*, **19**, 150 (1947).