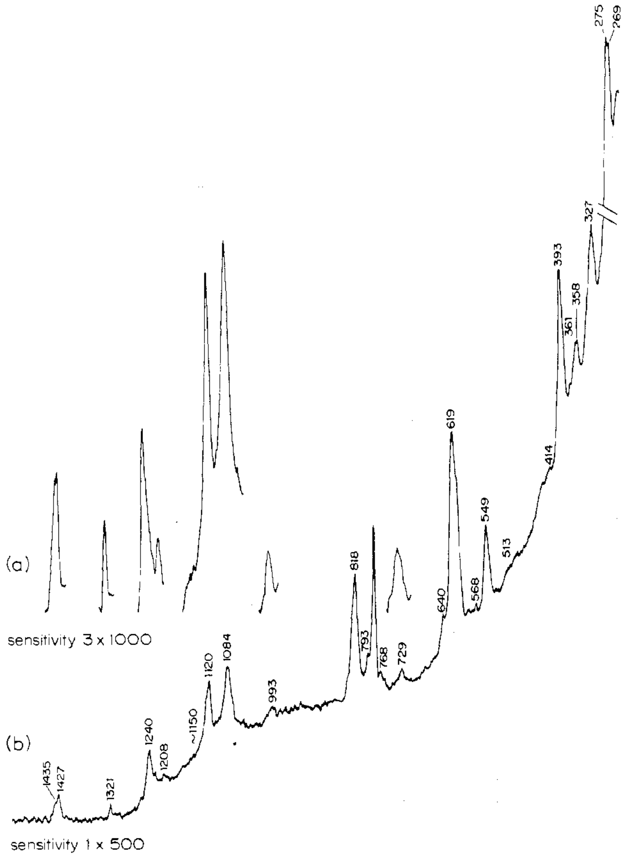

Figure 1. Raman spectrum of $I(OSO_2CF_3)_3$.

due to CF_3 stretching modes. No definite assignment of IO stretching modes is possible since almost all observed bands in the region of 430-380 cm^{-1} are found to be ir and Raman active, which in turn may be due to distortions of a possible square-planar IO_4 group by nonequivalent SO_3CF_3 groups.

The infrared spectrum of $IOSO_2CF_3$, the observed frequencies are listed in the Experimental Section, is distinctly different from the ones obtained for $I(OSO_2CF_3)_3$ and $[I(OSO_2CF_3)_4]^-$ and also for the $SO_3CF_3^-$ ion. This implies that $IOSO_2CF_3$ cannot be considered merely as a stoichiometric mixture of I_2 and $I(OSO_2CF_3)_3$ and that the structural formulations such as $I_3[I(OSO_2CF_3)_4]$ or the very unlikely ionic $I^+SO_3CF_3^-$ must be ruled out as well. A polymeric structure with a polydentate SO_3CF_3 group appears to be most likely, but a more detailed discussion of the infrared spectrum appears to be rather hazardous.

(D) Summary and Conclusion

Even though in both $I(OSO_2F)_3$[9] and in $I(OSO_2CF_3)_3$ monodentate and bridging bidentate sulfonate groups are evident from the respective vibrational spectra, the observed differences in thermal stability, reactivity, and solubility in the parent acids are best explained by assuming a different degree of polymerization. In addition to dimers, perhaps reminiscent of I_2Cl_6,[33] higher chain type polymers are feasible. It is this structural difference which allowed the isolation of pure $I(OSO_2CF_3)_3$ in the first place.

Iodine(I) trifluoromethanesulfonate, produced by the reduction of $I(OSO_2CF_3)_3$ with stoichiometric amounts of I_2, can be useful as a precursor for polyiodine cations in HSO_3CF_3. The oxidation by halogens to form interhalogen trifluoromethanesulfonates of the type $IX_2OSO_2CF_3$, with X = Cl, Br, and I, is currently being studied.

Acknowledgments. We thank the National Research Council of Canada for financial support and Mrs. B. Krizsan for technical assistance.

Registry No. I_2, 7553-56-2; $S_2O_6F_2$, 13709-32-5; $I(OSO_2CF_3)_3$, 41524-03-2; KI, 7681-11-0; $K[I(OSO_2CF_3)_4]$, 41523-89-1; $Rb[I(OSO_2CF_3)_4]$, 41523-90-4; $CsSO_3CF_3$, 41524-04-3; $Cs[I(OSO_2CF_3)_4]$, 41523-91-5; $IOSO_2CF_3$, 41524-06-5; HSO_3CF_3, 1493-13-6; $(CH_3)_3GeOSO_2CF_3$, 41524-05-4.

(33) K. H. Boswijk and E. H. Wibenga, *Acta Crystallogr.*, 7, 417 (1954).

Contribution from the Department of Inorganic Chemistry,
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Condensed Methyl Phosphates. Separation by Molecular Distillation[1]

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Pentamethyl triphosphate and hexamethyl tetraphosphate were isolated with small amounts of analogous polymers as byproducts. It was found that the triphosphate reorganized to form the tetraphosphate and diphosphate esters with an apparent second-order reaction rate having an approximate half-life of 1.00 × 10^7 sec.

Introduction

The preparation of hexaethyl tetraphosphate has been described before[2] but was subsequently shown to consist of a mixture of condensed polyphosphates with differing chain lengths.[3] Similar mixtures have been shown to form when differing amounts of phosphorus pentoxide and trimethyl phosphate are brought to equilibrium.[4] Separation of the diphosphate from these mixtures has been described.[3,5] The technique of gas-liquid chromatography failed to separate[6] all the constituents of these mixtures at 150°.

It has been reported[7] that although ester interchange in the

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(1) This subject is discussed in the D.Sc. Thesis of R. A. Schep, University of Pretoria.

(2) G. Schrader, German Patent 720,577 (1948).

(3) S. A. Hall and M. Jacobson, *Ind. Eng. Chem.*, **40**, 694 (1942).

(4) J. R. Van Wazer and S. Norval, *J. Amer. Chem. Soc.*, **88**, 4415 (1966).

(5) S. Norval, D.Sc. Thesis, University of Pretoria, 1967.

(6) R. A. Schep and K. de Clerk, *J. Gas Chromatogr.*, 10, 530 (1972).

orthophosphate is very slow, it is to be presumed that at least P-O-P linkages will make and break rather rapidly in the esters of the condensed phosphoric acids at temperatures of 150°. The separation of the polymer mixture using the technique of molecular distillation, which can take place at temperatures considerably below 150°, and the availability of well-designed, "careful treatment" all-glass stills makes this process feasible.

Experimental Section

Phosphorus Pentoxide. Fresh bottles of Merck reagent grade product were the initial source of phosphorus pentoxide. Further purification took place by subliming the oxide in a steel pipe heated by gas flames through which nitrogen gas was flowing, after being passed through a U-tube containing phosphorus pentoxide. The oxide was sublimed directly into the reaction vessel.

Trimethyl Phosphate. A ^{1}H nmr spectrum showed the Merck reagent grade trimethyl phosphate to consist solely of a doublet, and the compound was used without any further purification. Had any hydrolysis taken place, a POH group resonance would have appeared at about 10 ppm from the TMS peak.

Preparation of Polymer Mixture. Considerable effort was required to avoid moisture pickup by the phosphorus pentoxide.

Directly after the phosphorus pentoxide was sublimed, and while the flask was full of nitrogen, it was stoppered. Trimethyl phosphate was added to the flask under dry nitrogen atmosphere and the flask was topped with a drying tube containing 1:1 parts by weight of anhydrous calcium chloride and phosphorus pentoxide. The mixture was prepared so that the molar ratio R of methoxy groups to phosphorus equalled 1.45.

The flask was heated in a mantle at 50°, and 24 hr later, with intermittent shaking, all pentoxide had dissolved.

Molecular Distillation Apparatus. A micro-type, molecular distillation apparatus, Reference No. 24 833 00 manufactured by Schott, Mainz, of Duran 50 was used.

The charge was dropped onto the top of the spiral at the rate of 6 drops per minute or approximately 0.003 l. hr^{-1}. The vacuum was brought up to 0.5 mm of pressure with a rotary vacuum pump and increased to a maximum of 1×10^{-5} mm with an oil vapor jet pump. The pressure was measured in the atmospheric pressure to 5×10^{-3} mm range with a Balzers TPR 010 pirani gauge and in the 5×10^{-3}-1×10^{-5} mm range with a Balzers IKR 010 cold cathode gauge.

Distillations took place at temperatures from 30 to 119°, and the pressure varied from 10^{-3} to 10^{-5} mm, depending on the temperature and vapor pressure of the charge. The temperature of the condensing surface, regulated by ambient temperature waterflow, varied from 17 to 18°. The spiral rotation speed was 0.5 rps.

^{1}H Nmr Measurements. The 100-Mc spectra were obtained with a Varian HA-100 nmr spectrometer on the 100-Hz scale with a sweep rate of 2 Hz sec^{-1}; 60-Mc spectra were obtained with a Varian A-60A nmr spectrometer, sweep rate 0.4 Hz sec^{-1}. The areas of overlapping peaks can be evaluated quantitavely using a computer program as developed and described by Coetzee and Norval.[8]

Other Measurements. Refractive index measurements were made with an Abbe refractometer and densities by weighing in a micropipet.

Results and Discussion

In this work, polymers and structural units will be given in terms as symbols[9] where neso represents trimethyl phosphate, e represents an end [-(O)P(OMe)$_2$] structural unit, and m represents a middle [-(O)P(OMe)-] unit. When the ^{1}H nmr resonance of a methoxy group attached to a particular structural unit is referred to, the symbol of that structural unit will be printed in italics; for example, in the molecule e*m*me, the methoxy resonance attached to a middle structural unit is being referred to. For brevity, ee will represent tetramethyl diphosphate, eme pentamethyl triphosphate, emme hexamethyl tetraphosphate, and emmme heptamethyl pentaphosphate.

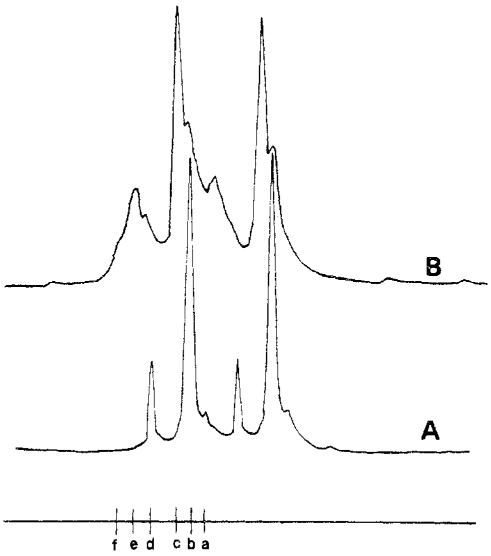

Figure 1. ^{1}H 60-Mc nmr spectra. A is a spectrum of the isolated eme, while B is a spectrum of 90% pure emme, both directly after distillation. The assignments are as follows: a, ee; b, *e*me; c, *e*mme; d, e*mm*e, f, m*m*m.

Pentamethyl Triphosphate. The separation of 97% pure pentamethyl triphosphate took place with three successive distillations, the first where trimethyl phosphate was distilled off the mixture at 30° at a pressure of 1×10^{-4} mm. Most of eme and ee was distilled off at 80°, where a pressure of 8×10^{-5} mm was maintained. The ee in the distillate was then distilled off at a temperature of 58° and a pressure of 3.5×10^{-4} mm, leaving a residue consisting of 97% pure eme which contained 2% ee and 1% neso as impurities. The distillate showed to be reasonably pure ee with n^{17}D 1.4185 compared to a value of n^{25}D 1.4170 given elsewhere.[7] In the ^{1}H nmr spectrum of the eme, relative areas of 1 and 4 are expected for the e*m*e and *e*me resonances, respectively, while the values 1 and 4.05 were found. The *HCOP* coupling constants of these two pairs of doublets are in reasonable agreement with the values given by Van Wazer and Norval[4] for these resonances occurring in mixtures (see spectrum A, Figure 1).

Reorganization Reaction Rate of Pentamethyl Triphosphate. The change in concentration at 20° of the building units of eme were measured by obtaining spectra at intervals of days. The growth of the ee ($J = 11.85$ Hz) and mm ($J = 12.64$ Hz) resonances, while maintaining their ratio of 2:1, indicate the following reaction

$$2\text{eme} \rightleftharpoons \text{emme} + \text{ee} \tag{1}$$

An interesting observation is that the neso resonance only showed a noticeable increase after 40 days, when a considerable amount of eme and ee had formed.

Second-order rate constants were calculated according to the special case where the concentration of the reagents is equal.[10] The values in Table I indicate that the reaction has a second-order rate constant with a half-life of $1.00 \pm 0.18 \times 10^7$ sec, which is in accordance with reaction 1.

Reorganization is expected to take place until the concentration of these structural units conforms to the equilibrium

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(7) J. R. Parks and J. R. Van Wazer, *J. Amer. Chem. Soc.*, 79, 4890 (1957).

(8) J. H. J. Coetzee and S. Norval, *J. S. Afr. Chem. Inst.*, 25, 94 (1972).

(9) J. R. Van Wazer, "Principles of Phosphorus Chemistry," Vol. 1, Interscience, New York, N. Y., 1958, p 724.

(10) W. J. Moore, "Physical Chemistry," 4th ed, Longmans, Green and Co., London, 1963, p 263.

Table I. Second-Order Reorganization Rate Constant of Pentamethyl Triphosphate

Time, days	Moles reacted, %	$k_2 \times 10^9$ $\text{mol}^{-1}\ \text{sec}^{-1}$	Half-life, $T \times 10^{-6}$ sec
10.9	8.4	10.3	10.0
18.9	16.1	12.5	8.2
41.0	22.2	8.6	11.9

Table II. Refractive Indexes and Densities of Polyphosphate Esters

	Compound			
	neso	ee	eme	emme
	This Work			
Temperature	25	17	17	23
Refractive index $n^T\text{D}$	1.3950	1.4185	1.4215	1.4302
Temperature T			18	23
Density			1.4215	1.5848
	References			
Temperature	25	25		
Refractive index $n^T\text{D}$	1.3950[a]	1.4170[b]		
Temperature T	25	25		
Density	1.197[a]	1.181[b]		

[a] Reference 9. [b] Reference 3.

constant $K = [\text{ee}][\text{mm}]/[\text{em}]^2$ measured[3] as having a value of 0.1.

Separation of Hexamethyl Tetraphosphate. A polymeric mixture (70 g) with an R value of OMe/P = 1.45 was first distilled at 58° and 1×10^{-2} mm of pressure to remove small amounts of neso and most of the ee which should be present in the mixture. The residue was redistilled at 83° and 1×10^{-4} mm of pressure to remove as much eme as possible. The residue was then distilled at 116° to remove any remaining eme and as much emme as possible. As the first drops of residue fell on the hot still, the pressure suddenly increased from 1.5×10^{-4} to 1×10^{-3} mm, indicating that a substance with a high vapor pressure had formed. Distillate (8 g) was collected, and an nmr spectrum showed the distillate to consist of 14% of emme, the rest being eme, ee, and neso. As all neso and ee had been removed during the distillations at 58 and 83°, this indicated that these volatiles had formed through reorganization during the distillation. A ^{1}H nmr analysis of the residue showed no neso to be present, and the ee and eme resonances were very small. The spectrum consisted mostly of emm and mmm resonances. To confirm reorganization, this residue was redistilled at 119°. Again neso, ee, and eme resonances were present in the spectrum of the distillate.

The remaining residue is an extremely viscous amber liquid, which solidifies at −10°.

The distillates of several distillations at 118° were added together to obtain 44 g of charge with estimated composition of 24% by weight emme, 66% eme, 9% ee, and 1% neso. By distilling off the less volatile compounds at 80°, emme could now be purified.

As many distillations had to be carried out, and nmr spectra were not always available immediately after the distillation, distillation curves were set up to predict the results of the distillation. Where all distillation curves are normally set up from the distillate compositions, it was found that a curve was just as effective when set up from residue compositions. In Figure 2 the mole fraction of eme with respect to emme (other components small enough to be ignored) in the charge was found on the x axis. The mole fraction of the residue was found on the y axis. The curve was estimated using the results of two distillations at 80° and 5×10^{-4} mm of pressure, where 73% pure emme was obtained. The curve predicted that a residue with an eme mole fraction of 0.04 would be obtained after two further distillations, and an experimental value of 0.043 was obtained when this was carried out. An interpretation of the ^{1}H nmr spectrum, which, in addition to the expected resonances, showed a m*m*m resonance, gave the following molar composition of the residue: 90% emme, 6% emmme, and 4% eme.

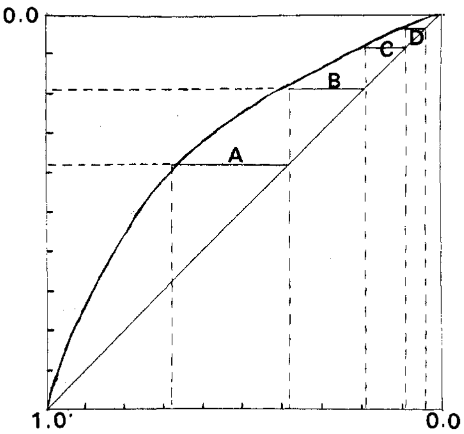

Figure 2. Distillation curve allowing the prediction of results of molecular distillations. The mole fraction of the more volatile component (eme) of the charge forms the abscissa while this same mole fraction for the residue forms the ordinate. The known results of two distillations supply coordinates at A and B for a curve, and a horizontal line to the diagonal predicts the results of the distillation. The results of distillations C and D can then be predicted using the extrapolated curve.

The relative areas of the *e*mme and emm*e* resonances, expected to be 1.0 and 2.0, respectively, were found to be 1.0 and 2.03. The residue thus appears to be 90% pure emme. The molar ratio R = OMe/P from the spectrum gave a value of 1.502 whereas 1.500 was expected. It appears that little could be gained by further distillation as one of the main impurities (emmme) will not be removed by additional distillation. The appearance of this compound is attributed to two sources, namely, that a small amount could have codistilled with the eme at 118° and more could have formed through reorganization during the many successive distillations at 83°.

The *HCOP* coupling constants of all structural units were found to be in reasonable agreement with those given by Norval[5] (Table II).

Acknowledgment. The writers thank Dr. K. G. R. Pachler and his staff of the Council for Scientific and Industrial Research, South Africa, for supplying the nmr spectra required for this study.

Registry No. neso, 512-56-1; ee, 690-49-3; eme, 41524-08-7; emme, 41524-09-8.