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Inorganic Coordination Polymers. IX. Titanium(IV) Phosphinate Polymers[1]

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The following titanium(IV) phosphinates have been prepared, mainly by metathesis: (i) $Ti(OR'')_2(OPRR'O)_2$ with R, R′, and R″, respectively, CH_3, CH_3, and CH_3 or C_4H_9; CH_3, C_6H_5, and C_2H_5; or C_6H_5, C_6H_5, and C_2H_5 or i-C_3H_7; (ii) $TiCl_2[OP(C_6H_5)_2O]_2$; (iii) $TiO(OPRR'O)_2$ with R and R′ both CH_3, both C_6H_5, or one CH_3 and one C_6H_5; (iv) $Ti[OP(C_6H_5)_2O]_4$; and (v) $Ti(BB)(OPRR'O)_2$ with BB, R, and R′, respectively, $C_6H_4O_2$, CH_3 or C_6H_5, and C_6H_5; $C_6H_4(O)COO$, CH_3, and C_6H_5; $(CH_3)_2C(O-)CH_2CH(O-)CH_3$, C_6H_5, and C_6H_5; OC_3H_6O, CH_3 or C_6H_5, and C_6H_5; or $C_6H_5P(O)_2CH_2P(O)_2C_6H_5$, CH_3, and C_6H_5. $TiCl_2[OP(C_6H_5)_2O]_2$ was prepared by the thermal decomposition of $TiCl_4[OP(C_6H_5)_2OC_2H_5]_2$. Molecular weight data show that all of the titanium(IV) phosphinates made are at least trimers and that some have degrees of polymerization exceeding 20. Their infrared spectra are consistent with phosphinate bridging, and it is probable that double phosphinate bridges are present in most of the polymers. Infrared data also are in accord with Ti(O) rather than Ti–O–Ti bonding in the titanyl phosphinates. Thermogravimetric analysis shows that weight loss starts at temperatures as high as 450° in nitrogen for some of the polymers prepared.

Introduction

Our success in making poly(metal phosphinates) based on bivalent[2] and tervalent[3] metallic ions led us to undertake the study of the phosphinates of a typical hexacoordinate, quadrivalent element, titanium. Two general classes of compounds which can be formulated as $Ti(b)_2X_2$ and $Ti(BB)X_2$ offer the possibility for a double-bridged linear polymeric structure. In these formulas b represents a uninegative, unidentate ligand, X a phosphinate group, and BB a binegative chelating group. As we were completing our work, some reports relating particularly to the first class appeared. Andrianov and Kuznetsova[4] in an attempt to make a phosphorus-containing titanium siloxane used $Ti(OC_4H_9)_2[OP(CH_3)_2O]_2$ as an intermediate and isolated $TiO[OP(CH_3)_2O]_2$ from reactions designed to yield silicon-containing products. They also reported the isolation of $Ti_2[OP(CH_3)_2O]_6O$ and $Ti[OP(CH_3)_2O]_4$ and subsequently the controlled hydrolysis of the dibutoxy compound to a series of oligomers.[5] Recent patents disclose the synthesis and hydrolysis of $Ti(OC_4H_9)_2[OP(C_6H_5)_2O]_2$[6] and the synthesis of $Ti[OP(C_6H_5)_2O]_4$.[7] Feld has isolated 1:1 and 1:2 products from the reaction of titanium(IV) alkoxides with $C_6H_5(H)P(O)OH$ and a 1:2 product from the reaction of $TiCl_4$ with the same acid.[8] Although part of our experimental work overlaps results already reported, we do not agree with some of the postulated structures.

Experimental Section

All chemicals and solvents were reagent grade or better and were used without further purification unless otherwise indicated.

Starting Materials.—Diphenylphosphinic acid, $(C_6H_5)_2P(O)OH$, methylphenylphosphinic acid, $CH_3(C_6H_5)P(O)OH$, and dimethylphosphinic acid, $(CH_3)_2P(O)OH$, were prepared by previously described procedures.[9] The ethyl esters of diphenyl- and methylphenylphosphinic acid were prepared by alcoholysis of $(C_6H_5)_2P(O)Cl$ and $CH_3(C_6H_5)P(O)Cl$, respectively, in the presence of triethylamine. The crude products were fractionally distilled, and fractions boiling at 190° at 3 torr and 150° at 8 torr, respectively, were collected. Ethyl diphenylphosphinate solidified to a crystalline mass melting at 41–43°. The melting point of 165° reported for this compound appears to be in error.[10]

Anal. Calcd for $C_{14}H_{15}O_2P$: C, 68.29; H, 6.14. Found: C, 67.92; H, 6.21. Calcd for $C_9H_{13}O_2P$: C, 58.69; H, 7.11; P, 16.82. Found: C, 59.07; H, 7.12; P, 16.95.

Tetraisopropyl titanate was obtained commercially (E. I. du Pont de Nemours and Co.), whereas $Ti(OC_2H_5)_4$ and $Ti(OCH_3)_4$ were prepared by a published procedure.[11] Prior to use, the alkoxides were purified by distillation under nitrogen. Solvents

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[1] Part VIII: S. H. Rose and B. P. Block, *J. Polymer Sci. Suppl. A-1*, **4**, 573 (1966).

[2] B. P. Block, S. H. Rose, C. W. Schaumann, E. S. Roth, and J. Simkin, *J. Am. Chem. Soc.*, **84**, 3200 (1962).

[3] A. J. Saraceno and B. P. Block, *ibid.*, **85**, 2018 (1963).

[4] K. A. Andrianov and I. K. Kuznetsova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 651 (1964)

[5] K. A. Andrianov and I. K. Kuznetsova, *ibid.*, 945 (1965).

[6] R. A. Sutton, British Patent 975,460 (1964).

[7] R. A. Sutton and J. Wood, British Patent 1,018,456 (1966).

[8] R. Feld, *J. Chem. Soc.*, 3963 (1964).

[9] A. J. Saraceno and B. P. Block, *Inorg. Chem.*, **3**, 1699 (1964).

[10] A. Michaelis and H. Götter, *Ber.*, **11**, 885 (1878). *Cf.* G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p 361.

[11] W. Wardlaw, D. C. Hancock, and D. C. Bradley, *J. Chem. Soc.*, 2773 (1952).

TABLE I

ANALYTICAL DATA FOR $Ti(OR'')_2(OPRR'O)_2$

			Analyses, %									
			C		H		P		Ti		Mol wt[a]	
R	R'	R''	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
CH_3	CH_3	CH_3	24.34	24.09	6.13	6.19	20.92	20.70	16.18	16.50	296	943
CH_3	CH_3	n-C_4H_9[b]	37.91	37.13	7.95	7.93	16.29	18.18	12.60	12.95	380	1735[b]
												1850[d]
CH_3	C_6H_5	C_2H_5	48.23	47.97	5.85	5.86	13.82	13.86	10.69	11.0	448	...
C_6H_5	C_6H_5	C_2H_5	58.76	58.53	5.28	5.14	10.82	10.98	8.37	8.7	572	...
C_6H_5	C_6H_5	i-C_3H_7	60.01	59.22	5.71	5.65	10.32	10.84	7.98	8.14	600	1706[c]
												1840[d]

[a] Calculated molecular weight is for monomer. [b] *Cf.* ref 4. [c] In C_6H_6. [d] In $CHCl_3$.

TABLE II

ANALYTICAL DATA FOR $TiO(OPRR'O)_2$

		Analyses, %									
		C		H		P		Ti		Mol wt[a]	
R	R'	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
CH_3	CH_3	19.22	20.00	4.84	4.93	24.78	23.56	19.16	19.09	250	...[b]
CH_3	C_6H_5	44.95	44.58	4.31	4.56	16.56	15.85	12.80	13.00	374	4300
			44.18		4.63		16.22		13.10[c]		...
C_6H_5	C_6H_5	57.85	57.83	4.05	4.36	12.43	11.86	9.61	9.80	498	7400 to >10,000
			57.03		4.28		11.67		9.51[c]		...

[a] Calculated value is for monomer. [b] Insoluble. [c] Prepared from $TiCl_2(OPRR'O)_2$.

were dried, usually by distillation from sodium. The petroleum ether used had a boiling range of 60–110°. Whenever there was hydrolytic instability of starting materials and intermediates, reactions were carried out under nitrogen. For syntheses in which polymers were expected to be formed, the weights of reagents were measured to three significant figures in order to achieve exact stoichiometry. Extractions were made in a Soxhlet extractor.

$Ti(OR'')_2(OPRR'O)_2$.—The various alkoxytitanium phosphinates were prepared by the same basic procedure, both in the presence and absence of a solvent. Two typical preparations are described.

$Ti(OC_2H_5)_2[OP(CH_3)(C_6H_5)O]_2$.—To a solution of 5.18 g (0.023 mole) of $Ti(OC_2H_5)_4$ in toluene was added with stirring over a period of 40 min 7.09 g (0.045 mole) of $CH_3(C_6H_5)P(O)OH$. The clear solution was refluxed for 1 hr, and the solvent was next removed by distillation. The yellow-brown residue after extraction with petroleum ether softened at 138°. Visual decomposition occurred above 230°; yield, 76%.

$Ti(OC_2H_5)_2[OP(C_6H_5)_2O_3]_2$.—A mixture of 4.35 g (0.019 mole) of $Ti(OC_2H_5)_4$ and 8.32 g (0.038 mole) of $(C_6H_5)_2P(O)OH$ was heated at 130° for 20 min and finally at 170–180° *in vacuo* for 15 hr. A near-theoretical amount of ethanol was collected in a cold trap. The product was extracted first with petroleum ether and then briefly with ethanol. Visual decomposition occurred above 270°; yield, 55%.

Analytical results for the $Ti(OR'')_2(OPRR'O)_2$ prepared are summarized in Table I.

$TiO(OPRR'O)_2$.—These phosphinates were prepared by addition of an excess of water to a suspension of the corresponding alkoxytitanium phosphinate in alcohol or a chloroform–acetone mixture. The reaction mixture was heated to boiling with rapid stirring. After the organic solvent had boiled off, heating was continued for an additional hour. The solid was then filtered off and dried to constant weight at 100°, redissolved in chloroform, filtered from any insolubles present, usually only a small amount, and recovered by evaporation of the solvent on the steam bath. The products obtained were pale yellow to yellow-brown solids which did not appear to melt. The methylphenyl and diphenyl products were soluble in chloroform and benzene. Analytical results are summarized in Table II. Intrinsic viscosities in chloroform were in the range 0.06–0.14 dl/g. Thermogravimetric analysis indicated that in nitrogen weight loss started at 450° for the diphenyl and dimethyl compounds and at 435° for the methylphenyl derivative.

$TiCl_4[OP(C_6H_5)_2OC_2H_5]_2$.—A solution of 17.20 g (0.0907 mole) of freshly distilled $TiCl_4$ in 150 ml of benzene was added to a stirred solution of 44.74 g (0.182 mole) of $(C_6H_5)_2P(O)OC_2H_5$ in 200 ml of benzene. A precipitate began to appear after about half of the $TiCl_4$ had been added. After the suspension had been stirred overnight, the yellow adduct was filtered off, washed with benzene, and dried *in vacuo* at 65–70°. The yellow product, mp 158–159°, is soluble in chloroform and acetone but insoluble in petroleum ether and cyclohexane; yield, 68%. *Anal.* Calcd for $C_{28}H_{30}Cl_4O_4P_2Ti$: C, 49.30; H, 4.43; Cl, 20.79; P, 9.08; Ti, 7.02. Found: C, 49.56; H, 4.47; Cl, 20.72; P, 8.85; Ti, 7.18. Calculated formula wt, 682; mol wt found in chloroform, 660.

$TiCl_2[OP(C_6H_5)_2O]_2$.—A sample of $TiCl_4[OP(C_6H_5)_2OC_2H_5]_2$ was heated with agitation to 160–175°, a temperature at which the evolution of ethyl chloride proceeded quite readily. Heating was continued *in vacuo* for *ca.* 20 hr at 180° to complete the reaction. The pale yellow product is readily soluble in chloroform and benzene and does not melt below 300°. *Anal.* Calcd for $C_{24}H_{20}Cl_2O_4P_2Ti$: C, 52.11; H, 3.64; Cl, 12.82; P, 11.20; Ti, 8.66. Found: C, 52.40; H, 3.98; Cl, 12.70; P, 11.18; Ti, 8.9. Calculated formula wt, 553; mol wt in chloroform >10,000; intrinsic viscosity in chloroform, 0.03 dl/g. Thermogravimetric analysis indicates initial weight loss under nitrogen at 370°.

Although this reaction did not occur in refluxing toluene, it could also be carried out in inert solvents at higher temperatures.

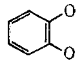
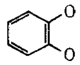
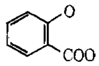
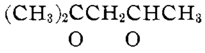
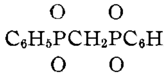
Hydrolysis of $TiCl_2[OP(C_6H_5)_2O]_2$.—Approximately 6.41 g of $TiCl_2[OP(C_6H_5)_2O]_2$ was treated by suspending it repeatedly in boiling water until no further liberation of chloride ions could be detected. Extraction with 95% ethanol, drying, and recovery from chloroform gave 4.51 g (78.5% yield) of light brown product. The analytical data are in Table II.

$TiO[OP(CH_3)(C_6H_5)O]_2$ from $TiCl_4$.—A solution of 16.49 g (0.09 mole) of $TiCl_4$ in 75 ml of benzene was added gradually to 30.28 g (0.12 mole) of $CH_3(C_6H_5)P(O)OC_2H_5$ in 75 ml of benzene. Removal of solvent by distillation from the dark orange solution resulted in a viscous residue which rapidly evolved ethyl chloride upon heating to 165°. After the evolution of ethyl chloride was completed, there remained a brown-yellow solid which was hydrolyzed in boiling water until a chloride test was negative. Analytical data for the dried, light yellow product are given in Table II.

$Ti[OP(C_6H_5)_2O]_4$.—To a suspension of 9.573 g (0.0438 mole) of $(C_6H_5)_2P(O)OH$ in 200 ml of toluene was added 2.502 g (0.01095 mole) of $Ti(OC_2H_5)_4$. The reaction mixture was refluxed for 20

TABLE III

ANALYTICAL DATA FOR Ti(BB)(OPRR'O)$_2$

BB	R	R'	% yield		Analysis, % C	H	P	Ti	Mol wt[a]
	CH_3	C_6H_5		Calcd	51.52	4.32	13.29	10.27	466
			87	Found	51.86	4.81	13.59	10.4	3400
			98[b]		51.22	4.53	13.42	10.5	1100
	C_6H_5	C_6H_5		Calcd	61.04	4.10	10.49	8.11	590
			96	Found	60.94	4.38	10.57	7.7	. . .[c]
	CH_3	C_6H_5		Calcd	51.03	4.08	12.53	9.69	494
			. . .[d]	Found	51.53	4.28	. . .[d]	10.7	2700
 $\underset{O}{(CH_3)_2C}CH_2\underset{O}{CH}CH_3$	C_6H_5	C_6H_5		Calcd	60.21	5.39	10.35	8.00	598
			20	Found	60.39	5.31	10.55	8.53	1680
OC_3H_6O	CH_3	C_6H_5		Calcd	47.24	5.13	14.33	11.08	432
			99	Found	48.50	5.61	. . .[d]	11.06	. . .[d]
OC_3H_6O	C_6H_5	C_6H_5		Calcd	58.29	4.71	11.13	8.61	556
			66	Found	59.29	5.03	12.43	8.8	. . .[c]
 $C_6H_5\overset{O}{\underset{O}{P}}CH_2\overset{O}{\underset{O}{P}}C_6H_5$	CH_3	C_6H_5		Calcd	49.72	4.33	18.99	7.34	652
			56	Found	49.78	5.28	19.25	7.26	1175

[a] Calculated value is for monomer. [b] Prepared from Ti($C_5H_7O_2$)$_2$($C_6H_4O_2$). [c] Insoluble. [d] Not determined.

hr, and then the volatiles were distilled from the yellow solution. The residue was extracted with petroleum ether and dried *in vacuo* at 80°; it softened at 135° and became liquid at 180°. Prolonged heating at these temperatures caused visual decomposition, and thermogravimetric analysis showed initial weight loss at 200° under nitrogen. *Anal.* Calcd for $C_{48}H_{40}O_8P_4Ti$: C, 62.90; H, 4.40; P, 13.52; Ti, 5.2. Found: C, 62.52; H, 4.79; P, 13.02; Ti, 5.3. Calculated formula wt, 917; mol wt found by ebulliometry in chloroform, 3000.

Chelated Titanium(IV) Phosphinates.—Details for the preparation of the dialkoxytitanium(IV) chelates used in the following reactions have been reported earlier.[12]

Ti($C_6H_4O_2$)(OPRR'O)$_2$.—To the dark red solution of 3.215 g (0.0117 mole) of Ti(O-*i*-C_3H_7)$_2$($C_6H_4O_2$) in benzene was added with stirring 5.117 g (0.0235 mole) of (C_6H_5)$_2$P(O)OH. After the reaction mixture had been stirred overnight, volatiles were removed by distillation. The purple product, Ti($C_6H_4O_2$)[OP(C_6H_5)$_2$O]$_2$, does not melt below 300°, is practically insoluble in chloroform and benzene, and shows no solubility in dioxane, acetonitrile, dimethyl sulfoxide, or acetic acid. Ti($C_6H_4O_2$)[OP(CH_3)(C_6H_5)O]$_2$, which was prepared in analogous fashion, is also a purple solid which does not melt up to 300°. Although it appears to decompose in air at this temperature, thermogravimetric analysis showed initial weight loss at 440° in nitrogen. It is readily soluble in chloroform and benzene. Alternatively, the latter was prepared from a mixture of 3.01 g (0.01 mole) of Ti($CH_3COCHCOCH_3$)$_2$($C_6H_4O_2$)[12] and 2.63 g (0.02 mole) of CH_3(C_6H_5)P(O)OH. The intimate mixture was heated in a tubular reaction flask under reduced pressure to 135–155° for 1.5 hr to displace 2,4-pentanedione. The brown-black product was kept under high vacuum at 125–135° for an additional 4 hr.

Ti($C_7H_4O_3$)[OP(CH_3)(C_6H_5)O]$_2$.—This compound was prepared by the reaction of Ti(O-*i*-C_3H_7)$_2C_6H_4$(O)COO with CH_3(C_6H_5)P(O)OH in benzene. It was recovered as an orange-yellow solid which was washed with petroleum ether. It starts to melt at 230° but turns dark red in air at 180° and undergoes gradual weight loss beginning at *ca.* 150° under nitrogen in thermogravimetric analysis.

Ti[(CH_3)$_2$C(O)CH_2CH(O)CH_3][OP(C_6H_5)$_2$O]$_2$.—To a solution of 9.514 g (0.034 mole) of Ti(O-*i*-C_3H_7)$_4$ in 200 ml of benzene was added 3.957 g (0.034 mole) of 2-methylpentane-2,4-diol. The liberated alcohol was azeotroped off, and 14.60 g (0.0668 mole) of (C_6H_5)$_2$P(O)OH was added. The reaction mixture was refluxed in *ca.* 350 ml of benzene for 8 hr. The insoluble reaction product was filtered off and subsequently extracted with benzene for 16 hr. An estimated 20–25% of the product proved to be extractable as a pale yellow solid which did not melt below 300°. Decomposition appeared to occur above 200° in a capillary tube.

Ti($C_3H_6O_2$)(OPRR'O)$_2$.—Since Ti(OR)$_2$($OCH_2CH_2CH_2O$) cannot be conveniently isolated,[12] Ti($C_3H_6O_2$)[OP(C_6H_5)$_2$O]$_2$ and Ti($C_3H_6O_2$)[OP(CH_3)(C_6H_5)O]$_2$ were prepared by the procedure described for the previous compound. The diphenyl product was insoluble in benzene and was extracted with 2-propanol to remove unreacted acid. The methylphenyl product was isolated from benzene solution and obtained as a slightly yellow powder upon washing with petroleum ether.

Ti[($C_6H_5PO_2$)$_2CH_2$][OP(CH_3)(C_6H_5)O]$_2$.—This compound was prepared from Ti(O-*i*-C_3H_7)$_2$($C_6H_5PO_2CH_2PO_2C_6H_5$) and CH_3(C_6H_5)P(O)OH by reaction in benzene in a fashion similar to the procedure for Ti($C_6H_4O_2$)[OP(C_6H_5)$_2$O]$_2$. The white product softened beginning at 170°.

Analytical results for the chelated titanium(IV) phosphinates are given in Table III.

Molecular Weight Measurement.—The ebullioscopic molecular weight measurements were made with equipment similar to that described by Dimbat and Stross.[13] A Mechrolab thermoelectric molecular weight apparatus was used in some cases. The molecular weights were calculated from data obtained in the 0.2–1.5% concentration range in chloroform or benzene. Comparative slope methods were employed, and in general good straight lines passing through or reasonably near the origin were obtained.

Intrinsic Viscosity Measurements.—Apparent intrinsic viscosities were determined in chloroform at 30.0 ± 0.1° with a Cannon-Ubbelohde dilution viscometer. Values of η_{sp}/c were plotted as a function of concentration, *c*, to obtain the intrinsic viscosity, $[\eta]$, at the ordinate intercept (*i.e.*, infinite dilution) in units of deciliters per gram.

Infrared Spectra.—Infrared spectra were measured in the 5000–650-cm^{-1} region with a Perkin-Elmer Model 221 instrument equipped with a sodium chloride prism or in the 4000–400-cm^{-1} region with an Infracord Model 337 grating instrument.

Thermal Stability.—Thermal stability was investigated by

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[12] G. H. Dahl and B. P. Block, *Inorg. Chem.*, **5**, 1394 (1966).

[13] M. Dimbat and F. H. Stross, *Anal. Chem.*, **29**, 1517 (1957).

visual observation and by our usual thermogravimetric analysis procedure with a heating rate of 5°/min.[14]

Discussion

A variety of titanium(IV) phosphinates of the types we sought have been prepared and in most cases have proved to be polymers with relatively low degrees of polymerization. The alkoxy phosphinates $[Ti(OR'')_2(OPRR'O)_2]_n$ for which we have determined molecular weights are all oligomers with values of n in the range 3–5. This is in marked contrast to earlier workers, who considered $Ti(OC_4H_9)_2[OP(CH_3)_2O]_2$[4] and $Ti(OC_4H_9)_2[OP(C_6H_5)_2O]_2$[6] to be monomeric. We also prepared the former and found it to have a molecular weight corresponding to a degree of polymerization of 4.6 in benzene and 4.9 in chloroform, not to a monomer. Perhaps the discrepancy between our molecular weight results and those of Andrianov and Kuznetsova[4] is due to a difference in solvents, for how they determined their value is not reported. Although Sutton called the latter monomeric, he presented no supporting evidence. We did not prepare his exact compound, but its isopropyl analog has a molecular weight corresponding to a degree of polymerization of 2.8 in benzene and 3.1 in chloroform. In view of the well-known tendency for titanium(IV) to exhibit a coordination number of six,[15] especially as exemplified by the tendency for titanium(IV) alkoxides to associate,[16,17] some degree of association is to be expected in these compounds. Furthermore the rather high degrees of polymerization of other poly(metal phosphinates)[9,18,19] makes it surprising that the degree of polymerization of the dialkoxytitanium(IV) phosphinates is so low. Possibly the presence of unoccupied d orbitals in the titanium permits depolymerization and equilibration in solution to the degrees of polymerization observed. It is interesting to note that some samples prepared at 150–190° only dissolved in chloroform after 1–2 hr, but that, once recovered from chloroform, they readily dissolved. Solvolytic attack on a cross-linked structure could explain this observation.

The other representative of the $Ti(b)_2X_2$ class that we prepared, $(TiCl_2[OP(C_6H_5)_2O]_2)_n$, was found to have a substantially higher degree of polymerization, n being greater than 18. This is perhaps related to the synthetic procedure employed, for it was possible to prepare the intermediate $TiCl_4[OP(C_6H_5)_2OC_2H_5]_2$ in very pure form prior to the elimination of C_2H_5Cl. As a result, there was apparently nothing present in sufficient amount to stop chain growth. The reaction in question

$$nTiCl_4[OP(C_6H_5)_2OC_2H_5]_2 \xrightarrow{\Delta} (TiCl_2[OP(C_6H_5)_2O]_2)_n + 2nC_2H_5Cl$$

is, in effect, an example of the type of polymerization that we have termed "elimination–addition"[20] and apparently results in the formation of a polymer so that titanium(IV) can maintain its coordination number of six. That titanium(IV) does have a coordination number of six in this environment is indicated by the monomeric nature of the phosphinate ester adduct of $TiCl_4$ in solution; *i.e.*, the adduct is not dissociated.

When either the dialkoxy- or dichlorotitanium(IV) phosphinates are hydrolyzed, titanyl phosphinates $[TiO(OPRR'O)_2]_n$ are produced. Hydrolysis does not appear to proceed beyond the removal of alkoxy or chloro groups, but aqueous bases readily decompose the titanyl phosphinates. We find degrees of polymerization from about 11 to greater than 20 for the soluble polymers of this type in agreement with the earlier statements that titanyl phosphinates are polymeric.

The reaction of $Ti(OC_2H_5)_4$ with $(C_6H_5)_2P(O)OH$ in 1:4 molar ratio produced samples analyzing well for $Ti[OP(C_6H_5)_2O]_4$. This phosphinate started to soften at 135°, was completely liquid at 180°, and was not stable to prolonged heating at these temperatures. It, too, was associated in solution, exhibiting a degree of polymerization of a little over 3; *cf.* ref 7.

The soluble chelated titanium(IV) phosphinates exhibit degrees of polymerization of about 2–7, so in no case can a high polymer be considered to have formed. There appears to be a correlation between the degree of polymerization and the bulk of the ligand—the higher values being found for the less bulky ligands. As expected, the salicylate and pyrocatecholate ligands lead to colored products, orange-yellow and purple, respectively.

Perhaps the most interesting question about these polymers concerns which groups serve as bridges. The earlier workers either assumed a coordination number of four for titanium with unidentate phosphinate ligands and oxygen bridges in the titanyl phosphinates[4,6] or a coordination number of six with bidentate or bridge phosphinate ligands and oxygen bridges.[21] The tetrakisphosphinates of titanium(IV) have been considered to be monomeric[4] and polymeric with both bridging and unidentate phosphinates.[7] Our evidence indicates that all of the kinds of phosphinates we have made are polymeric. This suggests that the only group common to them all, the phosphinate group, is the likely bridging group unless different groups act as bridges in the different types of phosphinates. In the tetrakisphosphinates and chelated phosphinates phosphinate bridging appears the most reasonable possibility.

Infrared spectra of the various polymers have been examined in an attempt to find some evidence for their structures. The major absorption bands in the 1300–800-cm^{-1} region are given in Table IV. This region covers the 1200–1000-cm^{-1} range characteristic for the appearance of PO absorption. The intensity of

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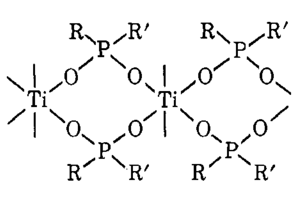
TABLE IV

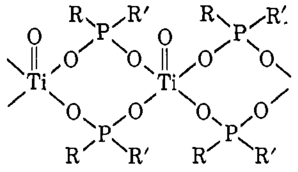
MAJOR ABSORPTION BANDS IN THE 1300–800-CM^{-1} REGION FOR NUJOL MULLS

Composition	Absorption bands, cm^{-1}
$Ti(OCH_3)_2[OP(CH_3)_2O]_2$	1300 s, 1220 m, 1150 s, 1090 s, 1035 s, 930 w, 867 s, 812 w
$Ti(O\text{-}i\text{-}C_3H_7)_2[OP(C_6H_5)_2O]_2$	1238 w, 1188 m, 1155 s, sh, 1130 s, 1117 s, 1068 m, sh, 1041 s, 1020 s, 995 s, 930 m, sh, 848 w
$TiO[OP(CH_3)_2O]_2$	1299 s, 1210 w, sh, 1109 s, 1078 s, 1052–1032 s, 928 m, 882 s, 870 s, 813 s
$TiO[OP(CH_3)(C_6H_5)O]_2$	1293 w, 1183 m, sh, 1130 s, 1121 s, sh, 1080 m, sh, 1063 m, sh, 1037 s, 1020 s, 996 m, 962 w, sh, 885–881 m, 807–800 w
$TiO[OP(C_6H_5)_2O]_2$	1204 w, 1185 w, 1131 vs, 1088 m, 1066 s, sh, 1051–1042 s, 1020–1013 s, 995 s, 927–922 w, 847 w
$Ti[OP(C_6H_5)_2O]_4$	1220 m, 1180 m, sh, 1130 s, 1099 s, sh, 1065 s, sh, 1036 s, 1012 s, 990 s, 840 w

the bands in the vicinity of 1200 cm^{-1} is rather low, whereas a very strong band or group of bands occurs at 1100–1130 cm^{-1}. This frequency range suggests that they are due to the presence of PO coordinated with metal centers. A similar shift of the asymmetric PO vibration bands has been reported by Mayants and Matrosov for polymeric metal hypophosphites.[22] In their study they found that PO frequencies calculated for a covalent chain model in which all of the PO bonds are equivalent agree well with the experimentally observed frequencies. The absence of significant PO absorption at higher frequencies in the titanium phosphinates suggests that equivalent PO bonds are also present in them and that the bands at 1060–1030 cm^{-1} are due to symmetrical PO vibrations. Consequently, we conclude that the phosphinate groups act as bridges between titanium atoms and that the polymers probably contain double phosphinate bridges, similar to the double bridges present in $Mn(CH_3COOC_2H_5)_2(OPCl_2O)_2$,[23] *i.e.*



The titanyl phosphinates present another problem in that there are not sufficient groups present to furnish six donor atoms for each titanium atom unless the oxygen is also a bridging group or the phosphinates are bonded to three titanium atoms. It has been suggested that Ti(O) gives a band at about 1090 cm^{-1}, whereas the Ti–O–Ti absorption is found in the region of 900–800 cm^{-1}.[24] Comparison of the infrared spectra of the alkoxytitanium(IV) phosphinates with those of the corresponding titanyl phosphinates clearly shows a band at 1080–1090 cm^{-1} in the latter not present in the former. In the spectrum of $TiO[OP(CH_3)_2O]_2$ there is also a band at 814 cm^{-1} which is much stronger than the one at about the same frequency in the spectrum of $Ti(OCH_3)_2[OP(CH_3)_2O]_2$ although such a band is not present in the spectra of $TiO[OP(C_6H_5)_2O]_2$ and $TiO[OP(CH_3)(C_6H_5)O]_2$. On the whole then the infrared spectra of the titanyl phosphinates are in agreement with Ti(O) rather than Ti–O–Ti bonding, and these polymers are probably to be formulated



with five-coordinate titanium(IV). Structural studies have demonstrated that titanium(IV) can have a five-coordinate, trigonal-bipyramid structure as in $[TiCl_2(OC_6H_5)_2]_2$,[25] so that such a structure is reasonable.

The thermal stability of the various classes of titanium(IV)–phosphinate polymers prepared, although substantial, particularly in the case of the titanyl phosphinates, did not prove outstanding, ranging up to about 450° for initial weight loss by our thermogravimetric procedure. Softening points varied from 135° to infusible. The dialkoxytitanium(IV) and titanyl phosphinates are recovered from solution as resinous materials, and the latter can be cast from chloroform as rather brittle films. With a plasticizer such as Aroclor 1248, however, flexible films are formed.

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